Selected Applications
for Surfactant Titration
Dear Reader

The analysis of surfactants in formulations, raw products, liquid detergents, cosmetic products, lubricants, cooling emulsions etc. is an important quality criterion in production.

Depending on the nature of the surfactant and sample matrix composition METTLER TOLEDO provides the right sensor to cope with the demanding analytical requirements:

- The DS800-TwoPhase sensor is a dedicated sensor for the titration of anionic as well as cationic surfactants using the two-phase titration technique according to the standards DIN EN14480, 14668 and 14669.
- The DS500 sensor has been optimized for the titration of anionic, cationic as well as non-ionic surfactants in aqueous solutions.
- The DP5 Phototrode™ is an excellent probe for photometric-indicated surfactant titrations involving the classical colorimetric two-phase titration according to Epton.

The application power of the METTLER-TOLEDO surfactant-specific sensors can be fully exploited with the Excellence titrators. The sensor inputs are optimized in terms of speed, signal-to-noise ratio and resolution, the available method parameters enable specific optimization for the individual titration task.

We are proud to present to you this unique application brochure that provides you essential know-how about surfactant titration and well-documented, field tested applications on real customer samples. Both shall serve as valuable information source for your method development and daily tasks.

We wish you great success and enjoyment in surfactant titration.

Hans-Joachim Muhr   Rolf Rohner
Market Support Manager   Marketing Manager
BA Titration   BA Titration
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</tr>
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</tr>
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</table>
Overview of the surfactant titration techniques

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.

Colorimetric two-phase titration

To determine the anionic (cationic) surfactant content in a water/chloroform two-phase medium [1-4], 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].

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].

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].

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.
# Turbidimetric Titrations

<table>
<thead>
<tr>
<th>Method</th>
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</tr>
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</tr>
</tbody>
</table>
Anionic Surfactant Content in Liquid Detergents by Turbidimetric Titration

The anionic surfactant content in liquid dish washers as SDS content (sodium dodecyl sulfate, or sodium lauryl sulfate) is determined by precipitation titration with Hyamine®1622, a cationic surfactant. The turbidity increase during titration is monitored by the DP5 Phototrode™.

Preparation and Procedures

1) The titer determination is performed by titrating 1 mL 0.01 mol/L SDS, which is diluted with 60 mL deionized water.

2) Sample titration:
   5 mL of an aqueous solution of liquid detergent is added into the titration beaker and diluted with 60 mL deionized water.

3) The concentration of the liquid detergent solution was chosen to get an approx. titrant consumption of 5 mL. Its value is stored as auxiliary value $H[\text{SDS}]$ in g/mL.

4) Preparation of the liquid detergent solution:
   Approx. 8 g liquid detergent is given into 1 L volumetric flask. The flask is filled up with deionized water (here: 8.5856 g liq. detergent, which gives a content of 0.0429 g/5 mL)

5) The sample series was analyzed using a sample changer. The conditioning time was set to 30 s (e.g. Rondolino settings: 4) to clean the sensor in water before starting the subsequent sample.

Remarks

1) After turning on the Phototrode™, wait 15-10 min before starting analysis to achieve a stable signal. Check the transmission signal in deion. water and set it to 1000 mV by turning the knob on the top.

2) Avoid the formation of air bubbles during titration since they disturb the photometric indication. Thus, select the appropriate stirring speed.

3) The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.

4) This method allows an automated analysis with a Rondolino sample changer. The method can be modified for manual operation. Select “Manual stand” in the method function "Titration stand".

Literature:
Application M549, see Titration Applications Brochure 18, "Standardisation of Titrants", ME-51724917.

| Sample | 5 mL liquid detergent solution, approx. 8 g/L |
| Compound | Sodium dodecyl sulfate, $\text{C}_{12}\text{H}_{25}\text{NaO}_4\text{S}$, $M = 288.38$ g/mol, $z = 1$ |
| Chemicals | 60 mL deionized water |
| Titrant | Hyamine®1622, $\text{C}_{27}\text{H}_{42}\text{ClNO}_2$, $c(\text{Hyamine}) = 0.004$ mol/L |
| Standard | SDS, 1 mL 0.01 mol/L, see M549 |
| Indication | DP5 Phototrode™, 550 nm |
| Chemistry | Simplified scheme: $\text{C}_{27}\text{H}_{42}\text{NO}_2^+ + \text{C}_{12}\text{H}_{25}\text{O}_4\text{S}^- = \text{C}_{27}\text{H}_{42}\text{NO}_2^-\text{C}_{12}\text{H}_{25}\text{O}_4\text{S}$ |
| Calculation | R1: SDS-Content (%) $R1 = Q*C/(m*H[\text{SDS}])$, $C = M/(10*z); z = 1$ $H[\text{SDS}] =$ concentration of liquid detergent stock solution (g/mL). |
| Waste disposal | Disposal as aqueous solution; a special treatment is not necessary |
| Author, Version | Cosimo De Caro, MSG Anachem, August 2006 |
**Instruments**
- Titration Excellence T50/T70/T90
- Rondolino Sample Changer

**Accessories**
- 10 mL DV1010 burette
- Titration beaker ME-101974
- XS205 Balance
- Olivetti Printer JobJet 210

**Results**

**All results**

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Content</th>
<th>R1 (Content) %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquid detergent solution (1/1)</td>
<td>13.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid detergent solution (1/2)</td>
<td>13.89</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid detergent solution (1/3)</td>
<td>13.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid detergent solution (1/4)</td>
<td>13.91</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid detergent solution (1/5)</td>
<td>13.90</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Liquid detergent solution (1/6)</td>
<td>13.83</td>
<td></td>
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</tbody>
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**Statistics**

<table>
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<td></td>
<td>Samples</td>
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<td></td>
<td>Mean</td>
<td>13.88   %</td>
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<tr>
<td></td>
<td>s</td>
<td>0.04    %</td>
</tr>
<tr>
<td></td>
<td>srel</td>
<td>0.275   %</td>
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</table>

**Titration curve**

![Titration curve graph](image)
### Table of measured values

<table>
<thead>
<tr>
<th>Consumption V / mL</th>
<th>Potential E / mV</th>
<th>Derivative dE/dV</th>
<th>Time / s</th>
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<td>NaN</td>
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<td>1010.3 NaN</td>
<td>NaN</td>
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<td>987.3 NaN</td>
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<td>747.3 -1662.57</td>
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<td></td>
</tr>
<tr>
<td>5.2</td>
<td>501.2 -1695.85</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>5.3</td>
<td>276.4 -1379.92</td>
<td>108.1</td>
<td></td>
</tr>
<tr>
<td>5.4</td>
<td>218.4 -823.4</td>
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<td></td>
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<td>5.5</td>
<td>212.4 -252.82</td>
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<tr>
<td>5.6</td>
<td>213.8 108.44</td>
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<td>218.6 NaN</td>
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</tr>
</tbody>
</table>

### Comments

--
**Method**

### 001 Title
- **Type:** General titration
- **Compatible with:** T50 / T70 / T90
- **ID:** M41
- **Title:** SDS content photometric
- **Author:** METTLER TOLEDO
- **Date/Time:** 02.08.2006 15:00:00
- **Modified by:** --
- **Protect:** No
- **SOP:** None

### 002 Sample
- **Number of IDs:** 1
- **ID 1:** Liquid detergent solution
- **Entry type:** Fixed volume
- **Volume:** 5.0 mL
- **Density:** 1.0 g/mL
- **Correction factor:** 1.0
- **Temperature:** 25.0°C

### 003 Titration stand (Rondolino TTL)
- **Type:** Rondolino TTL
- **Titration stand:** Rondolino TTL 1

### 004 Stir
- **Speed:** 35%
- **Duration:** 30s

### 005 Titration (EQP) [1]
- **Titrant:** Hyamine 1622
- **Concentration:** 0.004 mol/L
- **Sensor:** Phototrode
- **Sensor Type:** DP5
- **Unit:** mV
- **Temperature acquisition:** No
- **Stir:**
  - **Speed:** 35%
- **Predispense**
  - **Mode:** Volume
  - **Volume:** 4.5 mL
  - **Wait time:** 15 s
- **Control**
  - **Control:** User
  - **Titrant addition:** Incremental
  - **dV:** 0.1 mL
  - **dE:** 1.0 mV
  - **dr:** 1 s
  - **t(min):** 3 s
  - **t(max):** 10 s
- **Evaluation and recognition**
  - **Procedure:** Standard
  - **Threshold:** 200 mV/mL
  - **Tendency:** Negative
  - **Ranges:** 0
  - **Add. EQP criteria:** No
- **Termination**
  - **At Vmax:** 10 mL
  - **At potential:** No
  - **At slope:** No
  - **After number of recognized EQPs:** Yes
  - **Number of EQPs:** 1
  - **Combined termination criteria:** No

### 006 Calculation R1
- **Result:** Content
- **Result unit:** %
- **Formula:** R1=Q*C/(m*H[SDS])
- **Constant:** C/M/10^2
- **M:** H(sodium dodecyl sulfate)
- **z:** (Sodium dodecyl sulfate)
- **Decimal places:** 2
- **Result limits:** Yes
- **Record statistics:** Yes
- **Send to buffer:** No

### 007 Record
- **Results:** Per series
- **Raw results:** Per series
- **Table of meas. values:** Last titration function
- **Sample data:** Per series
- **Resource data:** No
- **E - V:** Last titration function
- **dE/dV - V:** Last titration function
- **log dE/dV - V:** No
- **dE/dV - V:** No
- **E - t:** No
- **V - t:** No
- **dV/dt - t:** No
- **T - t:** No
- **E - V & dE/dV - V:** No
- **V - t & dV/dt - t:** No
- **Calibration curve:** No
- **Method:** No
- **Series data:** No

### 008 End of sample
The anionic surfactant content in several liquid detergents, shower foams, washing powders and raw materials is determined by precipitation titration with Hyamine®1622, a cationic surfactant. The turbidity increase during titration is monitored by a photometric sensor at 550 nm.

### Preparation and Procedures

1. The titer determination is performed by titrating 10 mL 0.01 mol/L SDS, which is diluted with 50 mL deionized water.

2. Sample titration:
   - 10 mL of an aqueous solution of liquid detergent is added into the titration beaker and diluted with 50 mL deionized water.

3. Preparation of the liquid detergent solution:
   - Approx. 5 g liquid detergent is given into a 500 mL volumetric flask. The flask is filled up with deionized water (Liquid detergent 1: 5.0621 g).
   - A few ethanol (1-3 mL) allows to avoid the formation of foam before filling up to the mark.
   - Then the filling mark is reached with deionized water.

4. The concentration of the liquid detergent solution was chosen to get an approx. titrant consumption of 5 mL.

5. After each sample, the sensor, the titration tube and the stirrer are thoroughly cleaned with deionized water.

### Remarks

1. After turning on the Phototrode™, wait 15-10 min before starting analysis to achieve a stable signal. Check the transmission signal in deionized water and set it to 1000 mV by turning the knob on the top.

2. Avoid the formation of air bubbles during titration since they disturb the photometric indication. Thus, select the appropriate stirring speed.

3. The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.

4. A sample changer can be used for a fully automated analysis procedure. The method can be easily modified: enter “ST20A” as titration stand in the DL5x titration method.

### Literature

Application M549, see Titration Applications Brochure 18, "Standardisation of Titrants", ME-51 724 917.
Instruments
- DL58 Titrator
- AT261 Balance
This method can be run also with the following titrators: DL50, DL53, DL55, DL67, DL70ES, DL77, and G20, T50, T70, T90 – minor adaptations

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974
- Printer

Results

METTLER TOLEDO DL58 Titrator V2.0 Mettler-Toledo GmbH
Team OST: ms/dr Market Support Laboratory

Method 80042 Tenside/Anionics/DP550 01-Apr-1997 20:08
Measured 01-Apr-1997 20:28
User dr

ALL RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Spül. 1</td>
<td>5.0621 g R1 = 4.6145 mL Vbr. TM R2 = 17.238 % AT mittl. M.=387</td>
</tr>
<tr>
<td>2</td>
<td>Spül. 1</td>
<td>5.0621 g R1 = 4.6085 mL Vbr. TM R2 = 17.216 % AT mittl. M.=387</td>
</tr>
<tr>
<td>3</td>
<td>Spül. 1</td>
<td>5.0621 g R1 = 4.6152 mL Vbr. TM R2 = 17.241 % AT mittl. M.=387</td>
</tr>
<tr>
<td>4</td>
<td>Spül. 1</td>
<td>5.0621 g R1 = 4.6198 mL Vbr. TM R2 = 17.258 % AT mittl. M.=387</td>
</tr>
<tr>
<td>5</td>
<td>Spül. 1</td>
<td>5.0621 g R1 = 4.6135 mL Vbr. TM R2 = 17.234 % AT mittl. M.=387</td>
</tr>
</tbody>
</table>

STATISTICS

Number results R2 n = 5
Mean value x = 17.237 % AT mittl. M.=387
Standard deviation s = 0.01512 % AT mittl. M.=387
Rel. standard deviation srel = 0.088 %

Titration curve

Sample liquid detergent 1
In this application the total content of washing active matter is determined. According to the producer, the average molar mass used for the calculation of the total washing active matter is 387. The sample contains fatty alcohol ether sulfate and secondary alkyl sulfonate as anionic surfactants, as well as cocoamidopropyl betaine (amphoteric surfactant).

The sum of these components is defined as **total washing active matter**. Classical two-phase (2P) titration is the standard method performed by the producer. As a reference, the value of 17.1% is obtained with 2P-titration.

Generally, the pH value has to be adjusted to avoid interferences due to other surfactants present in the sample. In this case, it was not necessary to adjust the pH since the results obtained show an excellent agreement with the reference value of 17.1% (see comparison on page 62).

Formation of air bubbles during titration has to be avoided since they disturb the photometric indication. Thus, the stirring speed is not too high.

The transmission change at the equivalence point usually shows a pronounced curve profile. Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value.

The amount of surfactant used for the preparation of the solution is given as sample size m. The dilution is taken into account with the formula (m*10/500) in the calculation.

---

**Table of measured values**

<table>
<thead>
<tr>
<th>Volume</th>
<th>Increment</th>
<th>Signal</th>
<th>Change</th>
<th>1st deriv.</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL</td>
<td>mL</td>
<td>mL</td>
<td>mL</td>
<td>mL/mL</td>
<td>min</td>
</tr>
<tr>
<td>EPT</td>
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<td>0.0000</td>
<td>-3.1</td>
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<tr>
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<td>2.8000</td>
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<td>-2.9</td>
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<td>-2.7</td>
<td>-2.5</td>
</tr>
<tr>
<td></td>
<td>3.2000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-2.5</td>
<td>-2.4</td>
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<tr>
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<td>4.2000</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-1.6</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

**Comments**

- Liquid detergent 3

- In this application the total content of washing active matter is determined. According to the producer, the average molar mass used for the calculation of the total washing active matter is 387. The sample contains fatty alcohol ether sulfate and secondary alkyl sulfonate as anionic surfactants, as well as cocoamidopropyl betaine (amphoteric surfactant).

- The sum of these components is defined as **total washing active matter**. Classical two-phase (2P) titration is the standard method performed by the producer. As a reference, the value of 17.1% is obtained with 2P-titration.

- Generally, the pH value has to be adjusted to avoid interferences due to other surfactants present in the sample. In this case, it was not necessary to adjust the pH since the results obtained show an excellent agreement with the reference value of 17.1% (see comparison on page 62).

- Formation of air bubbles during titration has to be avoided since they disturb the photometric indication. Thus, the stirring speed is not too high.

- The transmission change at the equivalence point usually shows a pronounced curve profile. Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value.

- The amount of surfactant used for the preparation of the solution is given as sample size m. The dilution is taken into account with the formula (m*10/500) in the calculation.
## Additional results

<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>srel (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid detergent 1</td>
<td>Average molar mass: M = 387</td>
<td>18.0</td>
<td>17.1</td>
<td>5</td>
<td>17.24</td>
<td>0.09</td>
<td>No pH adjustment</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>10.0</td>
<td>pH 3</td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Secondary alkanesulfonate</td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>2.0</td>
<td></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</td>
<td>5</td>
<td>34.49</td>
<td>0.02</td>
<td>No pH adjustment</td>
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<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>11.0</td>
<td>pH 3</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Secondary alkanesulfonate</td>
<td>20.0</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>3.5</td>
<td></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>
<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>
<td></td>
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<tr>
<td></td>
<td>Anionics A, M=346</td>
<td>27.0</td>
<td></td>
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<tr>
<td></td>
<td>Anionics B, M=385</td>
<td>6.0</td>
<td></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</td>
<td>5</td>
<td>14.32</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lit.: 15-10</td>
<td></td>
<td>pH 1-2</td>
<td></td>
<td></td>
<td></td>
<td></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>
<td></td>
</tr>
<tr>
<td>Shower foam 1</td>
<td>Na-Laurylalkylsulfate, M=430</td>
<td>15.0</td>
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<td>7</td>
<td>15.01</td>
<td>0.63</td>
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<tr>
<td></td>
<td>Betaine, M=390</td>
<td>13.0</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
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<td></td>
<td></td>
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<tr>
<td>Na-Laurylalkylsulfate</td>
<td>Raw material, M=432</td>
<td>71.0</td>
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<td>7</td>
<td>76.85</td>
<td>0.23</td>
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<tr>
<td>Washing powder 1</td>
<td>Anionics as SDS, M=288.38</td>
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<td></td>
<td>6</td>
<td>7.28</td>
<td>2.22</td>
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<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>
<td>4.53</td>
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<td></td>
<td>Fatty acids FA, M=274</td>
<td>3-5</td>
<td></td>
<td></td>
<td>3.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nonionics, M=740</td>
<td>4-6</td>
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<td></td>
<td>pH 10</td>
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<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-4</td>
<td></td>
<td></td>
<td>Na-DBS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>FA</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Shampoo 1</td>
<td>Anionics as SDS, M=288.38</td>
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<td></td>
<td>5</td>
<td>19.88</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>Nonionics</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></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.

**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.

**Remarks:**
- No pH adjustment
- m = 15 g/500 mL
- INC = 0.1 mL
- EQU: dE/dt = 0.5/1 mV/s
- t = 3 – 20 s
- Threshold = 500

*(n): Sample dissolved in water without any pH adjustment value.*
General remarks to the titrated samples:

- 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:**
  1. 3 g washing powder was dissolved in 100-200 mL warm water and subsequently diluted to 500 mL in a volumetric flask.
  2. 20 mL aliquots have been titrated, and diluted to 50 mL with deionized water.

  **Titration:**
  1. First, the pH value was adjusted to pH 3 before starting the titration of sodium dodecyl benzene sulfate (Na-DBS) with Hyamine®1622 as a titrant.
  2. Subsequently, the pH was adjusted to pH 10 in order to titrate both fatty acids and Na-DBS with Hyamine®1622.
  3. 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.

- Washing powders:
  
  In general, washing powders contain solid particles which lead to a turbid solution. If necessary, filtrate the sample standard solution before titration in order to improve the transmission signal.

- 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.
Method

DL5x Titrator

Method 80042 Tenside/Anionics/DP550

Version 01-Apr-1997 20:08

Title
Method ID: 80042
Title: Tenside/Anionics/DP550
Date/time: 01-Apr-1997 20:08

Sample
Sample ID: Spülm. 1
Entry type: Weight
Lower limit [g]: 4.0
Upper limit [g]: 6.0
Molar mass M: 387
Equivalent number z: 1
Titration stand: Stand 1
Temperature sensor: Manual

Stir
Speed [%]: 40
Time [s]: 10

EQP titration
Titrant/Sensor
Titrant: Hyamine
Concentration [mol/L]: 0.01
Sensor: DP550
Unit of meas.: mV

Predispensing
Volume [mL]: 3
Wait time [s]: 20

Titrant addition
Incremental
dV [mL]: 0.1

Measure mode
Titled increment
dt [s]: 4.0

Recognition
Threshold: 500 mV/mL
Tendency: Negative

Termination
at maximum volume [mL]: 10.0
at potential: No
at slope: No
after number EQPs: Yes

Evaluation
Procedure: Standard
Potential: No
Stop for reevaluation: Yes

Calculation
Formula: R1=Q*C/(m*H[Anionics])
Constant: M[M[Anionics]]
z[z[Anionics]]

Record
Results: Yes

Tensile Excellence
Note: H[Anionics]: Conc. in g/mL of standard solution

001 Title
Type: General titration
Comaptible with: T50 / T70 / T90
ID: 80042
Title: Anionics content photometric
Author: METTLER TOLEDO
Date/Time: 01.01.2010 15:00:00
Modified: --
Modified by: --
SOP: None

002 Sample
Number of IDs: 1
ID 1: Liquid detergent
Entry type: Fixed volume
Volume: 0.01 mL
Density: 3.0 mL
Correction factor: 1.0
Temperature: 25.0°C

003 Titration stand (Manual stand)
Type: Manual stand

004 Stir
Speed: 35%
Duration: 10 s

005 Titration (EQP) [1]

Titrant
Type: Hyamine 1622
Concentration: 0.01 mol/L
Sensor
Type: Phototrode
Unit: mV

Predispensing
Mode: Volume
Volume: 3 mL
Wait time: 20 s

Control
User: Standard
Threshold: 5.00 mV/mL
Tendency: Negative
Ranges: 0
Add. EQP criteria: No

Termination
At Vmax: 10 mL
At potential: No
At slope: No
After number of recognized EQPs: Yes
Number of EQPs: 1
Combined termination criteria: No

006 Calculation R1

Result: Content

007 Record
Results: Yes
Extra statistical func.: No
Send to buffer: No

008 End of sample
Turbidimetric Titration of a Cocoamidopropylbetaine Solution

The content of an aqueous solution of the amphoteric surfactant cocoamidopropylbetaine F is determined by precipitation titration with sodium tetraphenylborate. The turbidity increase during titration is monitored by a photometric sensor at 550 nm.

<table>
<thead>
<tr>
<th>Sample</th>
<th>3 mL aliquot (5.0017 g of a 30% solution in 500 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Cocoamidopropylbetaine F Average M = 350; z = 1</td>
</tr>
</tbody>
</table>
| Chemicals | - 5 mL 0.1 mol/L HCl  
- 5 mL PVA-solution  
- 40 mL deionized water |
| Titrant | Sodium tetraphenylborate, NaTPB, Na(B(C₆H₅)₄)  
c(NaTPB) = 0.004 mol/L (Titrant sol. adjusted to pH 9-10) |
| Standard | Silver nitrate, AgNO₃ (AgNO₃-sol., pH adjusted to 4-5) |
| Indication | DP550 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (550 nm) |
| Chemistry | Simplified scheme:  
Betaine⁺ + B(C₆H₅)₄⁻ = Betaine-B(C₆H₅)₄ |
| Calculation | DL₅ₓ:  
- R₁ = VEQ (mL)  
- R₂ = Q*M/m (mg/mL)  
- R₃ = R₂*100/3.001 (%) |
| Waste disposal | Neutralization of the titrated sample; disposal as aqueous solution. |
| Author, Version | Cosimo De Caro/MSG Anachem, June1997 / Revised January 2010 |

Preparation and Procedures

1) The titer determination is performed by titrating e.g. 5 mL 0.004 mol/L AgNO₃, which is diluted with 50 mL deionized water and acidified to pH 4-5.

2) Sample titration:  
3 mL is added into the titration beaker, and diluted with 40 mL deionized water.  
5 mL 0.01 M HCl is added to acidify the sample, and 5 mL PVA solution is added to achieve a finely dispersed precipitate.

3) Polyvinyl alcohol (PVA) solution:  
Dissolve 3-4 g PVA in ca. 250 mL warm water, and allow the solution to cool down before addition.

4) After each sample, the sensor, the titration tube and the stirrer are thoroughly cleaned using a conditioning beaker with deionized water.

Remarks

1) To precipitate the betaine compound present in the sample solution, it is necessary to protonate the carboxylic group. This is achieved by adding HCl.

2) After turning on the Phototrode™, wait 15-10 min before starting analysis to achieve a stable signal. Check the transmission signal in deion. Water and set it to 1000 mV by turning the knob on the top.

3) Avoid the formation of air bubbles during titration since they disturb the photometric indication. Thus, select the appropriate stirring speed.

3) The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.
**Instruments**
- DL58 Titrator with ST20A Sample Changer
- AT261 Balance
This method can be run also with the following titrators: DL50, DL53, DL55, DL67, DL70ES, DL77, and G20, T50, T70, T90 --minor adaptations

**Accessories**
- 10 mL DV1010 burette
- Peristaltic pump
- Titration beaker ME-101974
- Printer

### Results

<table>
<thead>
<tr>
<th>METTLER TOLEDO DL58 Titrator V2.0 Mettler-Toledo GmbH 004 Market Support Laboratory</th>
</tr>
</thead>
<tbody>
<tr>
<td>Method</td>
</tr>
<tr>
<td>Measured</td>
</tr>
<tr>
<td>User</td>
</tr>
</tbody>
</table>

**ALL RESULTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.867 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.738 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td></td>
<td>R3 = 91.236 %</td>
<td>recovery</td>
</tr>
<tr>
<td>2</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.926 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.766 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td></td>
<td>R3 = 92.169 %</td>
<td>recovery</td>
</tr>
<tr>
<td>3</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.846 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.728 mg/mL</td>
<td>Betain F Con.</td>
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<tr>
<td></td>
<td>R3 = 90.903 %</td>
<td>recovery</td>
</tr>
<tr>
<td>4</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.893 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.750 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td></td>
<td>R3 = 91.636 %</td>
<td>recovery</td>
</tr>
<tr>
<td>5</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.912 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.759 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td></td>
<td>R3 = 91.936 %</td>
<td>recovery</td>
</tr>
<tr>
<td>6</td>
<td>Betain F</td>
<td>3.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.919 mL</td>
<td>Consumption</td>
</tr>
<tr>
<td></td>
<td>R2 = 2.762 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td></td>
<td>R3 = 92.034 %</td>
<td>recovery</td>
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</tbody>
</table>

**STATISTICS**

<table>
<thead>
<tr>
<th>Number results</th>
<th>R2</th>
<th>n = 6</th>
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</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x = 2.750 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s = 0.01474 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel = 0.536 %</td>
<td></td>
</tr>
</tbody>
</table>

**STATISTICS**

<table>
<thead>
<tr>
<th>Number results</th>
<th>R3</th>
<th>n = 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x = 91.682 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s = 0.49139 mg/mL</td>
<td>Betain F Con.</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel = 0.536 %</td>
<td></td>
</tr>
</tbody>
</table>
According to the producer, the concentration is 30.01% (see calculation R3). Stock solution: 5.0017 g of a 30.01% betaine solution are diluted with water in a 500 mL flask.

The recovery shows an average value of 91%. This is most probably due to incomplete precipitation. Cocoamidopropylbetaine has a distribution of different alkyl chain lengths, and chains shorter than C8 are hardly precipitated. Therefore, a calibration factor is needed when samples are measured.

If no transmission minimum can be found, e.g. the transmission signal does not increase again, use the evaluation procedure «Standard» and evaluate the titration curve obtained from the titer determination with the same procedure.

Formation of air bubbles during titration has to be avoided since they disturb the photometric indication. Thus, the stirring speed is not too high.
**Method**

**DL5x Titrator**

<table>
<thead>
<tr>
<th>Method</th>
<th>Bet</th>
<th>Betain content</th>
</tr>
</thead>
</table>

**Title**

- **Method ID**: Bet
- **Title**: Betain content
- **Date/time**: 27-Jun-1997 13:33

**Sample**

- **Sample ID**: Betain F
- **Entry type**: Fixed volume
- **Volume [mL]**: 3.0
- **Molar mass M**: 350
- **Equivalent number z**: 1

**Titration stand**

- **ST20A**
- **Pump**: Yes
- **Solvent**: H2O
- **Volume [mL]**: 50.0
- **Stir**: No
- **Pump**: No
- **Rinse**: No
- **Conditioning**: Yes
- **Time [s]**: 20
- **Interval**: 1
- **Stir**: No
- **Conditioning**: No
- **Temperature sensor**: Manual
- **Speed [%]**: 20
- **Duration**: 30 s

**EQP titration**

- **Titrant/Sensor**
  - **Titrant**: NaTPB
  - **Concentration [mol/L]**: 0.004
  - **Sensor**: Phototrode
  - **Unit**: mV
- **Temperature acquisition**: No
- **Stir**: No
- **Speed [%]**: 35%
- **Predispense**: Mode None
- **Wait time**: 0 s
- **Control**: User
- **Titrant addition**: Incremental
- **dV [mL]**: 0.15 mL
- **Measure mode**: Fixed time
- **dt [s]**: 5.0 s
- **Threshold**: Negative

**Evaluation and recognition**

- **Procedure**: Standard
- **Threshold**: 150 mV/mL
- **Tendency**: Negative
- **Ranges**: 0
- **Add. EQP criteria**: No
- **Termination**
  - **At Vmax**: 7 mL
  - **At potential**: No
  - **At slope**: No
  - **After number of recognized EQPs**: No
  - **Combined termination criteria**: No

**Calculation**

- **Result**: Recovery
- **Result unit**: %
- **Formula**: R=Q*C/m
- **Constant**: C=M*(100/3.001)
- **M**: M[None]
- **z**: z[None]
- **Decimal places**: 3
- **Result limits**: No
- **Record statistics**: Yes
- **Extra statistical func.**: No
- **Send to buffer**: No

**Record**

- **Results**
  - **Per series**: . . .
  - **E - V**: Last titration function
  - **dE/dV – V**: Last titration function

**Method Excellence**

- **Type**: General titration
- **Compatible with**: T50 / T70 / T90
- **Title**: Betain content
- **Author**: METTLER TOLEDO
- **Date/Time**: 01.01.2010 15:00:00
- **Modified by**: --
- **Protect**: No
- **SOP**: None

---

**Sample**

- **Number of IDs**: 1
- **ID 1**: Betain F
- **Entry type**: Fixed volume
- **Volume**: 3.0 mL
- **Density**: 1.0 g/mL
- **Correction factor**: 1.0
- **Temperature**: 25.0°C

---

**Titration stand (Manual stand)**

- **Type**: Rondo/Tower A
- **Rondo60/1A**

---

**Stir**

- **Speed [%]**: 20
- **Duration**: 30 s

---

**Calculation R2**

- **Result**: Recovery
- **Result unit**: %
- **Formula**: R2=Q*M/m
- **Constant**: M[None]
- **z [None]
- **Decimal places**: 3
- **Result limits**: No
- **Record statistics**: Yes
- **Extra statistical func.**: No
- **Send to buffer**: No

---

**Calculation R3**

- **Result**: Recovery
- **Result unit**: %
- **Formula**: R3=R2*100/3.001
- **Constant**: M[None]
- **z [None]
- **Decimal places**: 3
- **Result limits**: No
- **Record statistics**: Yes
- **Extra statistical func.**: No
- **Send to buffer**: No

--

**End of sample**
Turbidimetric Titration of Nonionic Surfactants

The recovery rate of an aqueous solution of the nonionic surfactant Triton N101 is determined by precipitation titration with sodium tetraphenylborate. The turbidity increase during titration is monitored by a photometric sensor at 550 nm.

**Sample**
- 5 mL aliquot (2-3 g in 1 L, c=2.55157 g/L)

**Compound**
- Triton N101
- Average M = 638.86; z = 1

**Chemicals**
- 10 mL BaCl₂ 0.1 mol/L
- 5 mL PVA-solution
- 40 mL deionized water

**Titrant**
- Sodium tetraphenylborate, NaTPB, Na(B(C₆H₅)₄)
- c(NaTPB) = 0.004 mol/L (Titrant sol. adjusted to pH 9-10)

**Standard**
- --

**Indication**
- DP550 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (550 nm)

**Chemistry**
- Simplified scheme:
  1. Activation:
     NIO + x Ba²⁺ = (Ba-NIO)⁺²ˣ⁻
  2. Titration:
     (Ba-NIO)⁺²ˣ⁻ + y B(C₆H₅)₄⁻ = (x Ba-NIO)⁻(B(C₆H₅)₄)y

**Calculation**
1) Factor determination (DL5x)
- \( R₁ = \frac{V_{\text{EQ}}}{C₂ \cdot R₁} \quad \text{(mg/mL)} \)
- \( C₂ = 2.55157 \text{ g/L} \)

2) Sample recovery (DL5x)
- \( R₁ = \frac{V_{\text{EQ}}}{C₂} \quad \text{(mL)} \)
- \( R₂ = \frac{H₂ \cdot R₁ \cdot 100}{(m \cdot C₂)} \quad \% \)

**Preparation and Procedures**
1) Since the titration reaction is not stoichiometric, the titration of nonionic surfactants is based on a **comparative titration** with a standard solution. This gives a calibration factor i.e. the titrant consumption per amount of sample in mg/mL. Subsequently this factor is used in the sample titration calculation.

2) Factor and sample titrations:
- 5 mL aliquot is added into the titration beaker, and diluted with 40 mL deionized water.
- 10 mL 0.1 M BaCl₂ is added to activate the sample, and 5 mL PVA solution is added to achieve a finely dispersed precipitate.

3) Polyvinyl alcohol (PVA) solution:
- Dissolve 3-4 g PVA in ca. 250 mL warm water, and allow the solution to cool down before addition.

4) After each sample, the sensor, the titration tube and the stirrer are thoroughly cleaned using a conditioning beaker with deionized water on the sample changer.

**Remarks**
1) To precipitate the nonionic surfactant, it is necessary to activate it by adding a barium chloride solution to it. Barium is complexed by the ethylene oxide units present in the molecule of Triton N101. A pseudo-cationic complex is formed which can be precipitated by tetraphenylborate.

2) After turning on the Phototrode™, wait 15-10 min before starting analysis to achieve a stable signal. Check the transmission signal in deion. Water and set it to 1000 mV by turning the knob on the top.

3) Avoid the formation of air bubbles during titration since they disturb the photometric indication. Thus, select the appropriate stirring speed.

3) The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.

**Waste disposal**
- Disposal as inorganic metal ion solutions.

**Author, Version**
- Cosimo De Caro/MSG Anachem
- September 1997/Revised January 2010
Instruments
- DL58 Titrator with ST20A Sample Changer
- AT261 Balance
This method can be run also with the following titrators:

Accessories
- 10 mL DV1010 burette
- Peristaltic pump
- Titration beaker ME-101974
- Printer

Results

**Method 32 f: Calibration factor f**

Method: 32 f  NIO/DP550/Factor  05-Sep-1997  17:12
Measured:  05-Sep-1997  17:55
User: Cosimo De Caro

<table>
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<th>results</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.091 mL Consumption</td>
<td>R2 = 1.799 mL Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.090 mL Consumption</td>
<td>R2 = 1.799 mL Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.085 mL Consumption</td>
<td>R2 = 1.801 mL Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.091 mL Consumption</td>
<td>R2 = 1.799 mL Factor</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 6.875 mL Consumption</td>
<td>R2 = 1.856 mL Factor</td>
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<tr>
<td>6</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 6.844 mL Consumption</td>
<td>R2 = 1.853 mL Factor</td>
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<td></td>
</tr>
</tbody>
</table>

**STATISTICS**
Number results: R2 n = 4
Mean value: x = 1.800 Factor
Standard deviation: s = 0.00076 Factor
Rel. standard deviation: srel = 0.042 %
Sample No. 5 deleted
Sample No. 6 deleted

**Method 32 g: recovery (%)**

Method: 32 g  NIO/DP550/Content  05-Sep-1997 18:25
Measured:  05-Sep-1997  19:09
User: Cosimo De Caro

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<td>5.0 mL</td>
<td>R1 = 6.889 mL Consumption</td>
<td>R2 = 97.192 % Content</td>
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<td></td>
</tr>
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<td>2</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.056 mL Consumption</td>
<td>R2 = 99.557 % Content</td>
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<td></td>
</tr>
<tr>
<td>3</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 7.055 mL Consumption</td>
<td>R2 = 99.535 % Content</td>
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<tr>
<td>4</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 6.711 mL Consumption</td>
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<tr>
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<tr>
<td>6</td>
<td>TritonN101</td>
<td>5.0 mL</td>
<td>R1 = 6.888 mL Consumption</td>
<td>R2 = 97.185 % Content</td>
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**STATISTICS**
Number results: R2 n = 5
Mean value: x = 98.061 % Content
Standard deviation: s = 1.36139 % Content
Rel. standard deviation: srel = 1.390 %
Sample No. 4 deleted
Tables of measured values

**Method 32 f (calibration factor)**

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<th>Change</th>
<th>1st deriv.</th>
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<td>mV</td>
<td>mV/mL</td>
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**Method 32 g (sample determination)**

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<td>mL</td>
<td>mV</td>
<td>mV/mL</td>
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</table>
Calibration factor (method 32 f):
- A standard solution of known concentration is titrated according to method 32 f. From the titrant consumption VEQ and the known concentration, a factor R2 (mg surfactant/mL titrant) is determined, stored as auxiliary value H2, and taken into account in the main titration (32 g). In this case, the factor is 2.55157 mg/mL.
- Since no transmission minimum was detected, the curve was evaluated by the "Standard" procedure. In this case, the same evaluation must be used for sample titration (32 g).

Sample titration (method 32 g):
- The second calculation R2 in sample method 32 g gives the content of nonionic surfactant in the sample. Since we have used the same nonionic surfactant solution for the standard as well as for the sample, method 32 g will give the recovery rate (%) of the standard solution.
- Calculation of recovery (R2):
  - multiply the titrant consumption by the calibration factor H2,
  - divide by the sample size m,
  - divide again by the concentration of the sample solution stored as C2 = 2.55157 mg/mL.
  - multiply by a factor of 100 to get %-values.

Structure of Triton N101:

Chemical reaction:
- Samples of unknown composition are measured and compared against a reference nonionic surfactant, for instance, nonylphenol ethoxylate with 10 EO (1 EO: CH2-CH2-O ) or a pure solution of the nonionic surfactant present in the sample.
- Nonionic surfactants form a complex with barium cations Ba^{2+}. The formed complex has a positive charge (pseudo-cationic surfactant). The sample can now be titrated with a bulky anion which is able to precipitate the pseudo-cationic surfactant. Tetraphenylborate (TPB, B (C6H5)4^-) is used to form an insoluble complex with the pseudo-cationic surfactant.
- The reaction is not stoichiometric, i.e., there is no well-defined ratio between the amount of substance of the two species. Thus, before titration of the sample a calibration titration with a standard solution of known concentration must be performed to get an indication of the titrant consumption. Its result, a calibration factor, is then used in the calculation of the sample titration.

Titration technique:
- Use the same surfactant concentration for both methods 32 f (factor) and 32 g (content).
- Choose the sample volume to get a titrant consumption of about 5 mL.

Unknown sample:
- First run a titration with termination at maximum volume to record the whole titration curve. In this way, the parameters and the evaluation procedure of the method can be easily optimized.
- In particular, from the profile of the titration curve you can select the most suitable evaluation procedure, i.e. “Standard” or “Minimum”.
Method

DL5x Titrator (calibration factor)

Method 32 f NIO/DPS50/Factor
Version 05-Sep-1997 17:12

Title
Method ID .......................... 32 f
Title .............................. NIO/DPS50/Factor
Date/time .......................... 05-Sep-1997 17:12

Sample
Sample ID .......................... TritonN101
Entry type ......................... Fixed volume
Volume [mL] .................... 5.0
Molar mass M ................. 638.86
Equivalent number s .......... 1

Titration stand
Pump ........................... Yes
Stir ........................... No
Rinse .......................... Yes
Volume [mL] ............... 30
Conditioning ................... Yes
Time [s] .................. 15
Interval .................. 1

Temperature sensor ......... Manual
Stir
Speed [%] .......................... 40
Time [s] ........................... 10

EQP titration
Titrant/Sensor
Titrant ......................... NaTPB
Concentration [mol/L] ...... 0.004
Sensor ............................ DPS50
Unit of meas. .................. mV
Predispensing ................. Yes
Titrant addition ............... Incremental
DV [mL] .................... 0.4
Measure mode ................. Timed increment
S [s] ...................... 15
Recognition
Threshold ......................... 150.0
Steepest jump only ........... Yes
Range .......... Negative
Temperature acquisition .... No
Stir
Speed ........................... 35%
Duration .................... 15 s

Measurement
Procedure ..................... Standard
Potential 1 ..................... No
Potential 2 ..................... No
Stop for reevaluation ....... Yes
Condition = .................... none

Calculation
Formula .......................... R=VEQ
Constant .........................
Result unit ...................... mL
Result name .................... Consumption
Statistics ....................... No

Calculation
Formula .......................... R2=C2*m/R1
Constant ......................... C2=2.55157
Decimal places ................. 3
Result unit ...................... mL
Result name .................... Factor
Statistics ....................... Yes

Auxiliary value
ID .......................... Factor mg/mL
Formula .......................... H2ex

Report
Output unit ..................... Printer
Results .......................... Yes
All results ..................... No
Raw results ..................... No
Table of measured values .... Yes
E - V curve ................. Yes

Titration Excellence (calibration factor)

001 Title
Type General titration
Compatible with T50 / T70 / T90
ID .......................... 32f
Title .......................... NIODPS50/Factor
Author ......................... METTLER TOLEDO
Date/Time .......................... 01.01.2010 15:00:00
Modified ................. No
Modified by ................. No
SOP .......................... None

002 Sample
Number of IDs ................. 1
ID .......................... TritonN101
Entry type ....................... Fixed volume
Volume ......................... 5.0 mL
Density ......................... 1.0 g/mL
Correction factor .......... 1.0
Temperature ..................... 25.0°C

003 Titration stand (Manual stand)
Type .......................... Rondo/Tower A
Volume ......................... 50.0 mL

004 Pump
Auxiliary reagent .............. Water
Volume ......................... 50.0 mL

005 Stir
Speed ........................... 40%
Duration .................... 10 s

006 Titration (EQP) [1]
Titrant
Titrant ......................... NaTPB
Concentration .................. 0.004 mol/L
Sensor ............................ Phototrode
Unit ....................... mV
Temperature acquisition .... No
Stir
Speed ........................... 35%
Duration .................... 15 s

Evaluation and recognition
Procedure ..................... Standard
Threshold ......................... 150 mV/mL
Tendency ..................... Negative
Ranges .............. Steepest jump
Steepest jumps ............ 1
Termination
At Vmax ......................... 10 mL
At potential .................... No
At slope ....................... No
After number of EQPs ........ No
Combined termination criteria .... No

007 Calculation R1
Result .................... Consumption
Result unit ...................... mL
Formula .......................... R1=VEQ
Constant ......................... C=1

008 Calculation R2
Result .................... Factor
Result unit ...................... mg/mL
Formula .......................... R2=C2*m/R1
Constant ......................... C2=2.55157

009 Auxiliary value
Name .......................... Factor
Formula ......................... Mean[R2]
Limits .......................... No

010 Record

011 Rinse
012 Conditioning
013 End of sample
**DL5x Titrator (Sample determination)**

**Method** 32 g NIO/DP50/Content  
**Version** 05-Sep-1997 18:25  

**Title**  
**Method ID** .................. 32 f  
**Title** ...................... NIO/DP50/Content  
**Date/time** .................. 05-Sep-1997 18:25  

**Sample**  
**Sample ID** .................. TritonN101  
**Entry type** .................. Fixed volume  
**Volume [mL]** ................ 5.0  
**Molar mass M** ................ 638.86  
**Equivalent number k** ........... 1  

**Titration stand** .......... ST20A  
**Pump** ....................... Yes  
**Solvent** ..................... H_2O  
**Stir** ....................... No  

**Rinse** ..................... Yes  
**Solvent** ..................... H_2O  
**Volume [mL]** ............... 10  
**Conditioning** .............. Yes  
**Time [s]** .................. 15  
**Interval** .................. 1  
**Rinse** ..................... No  

**Temperature sensor** ........ Manual  
**Speed [%]** .................. 40  
**Time [s]** .................. 10  

**EQP titration**  
**Titration/Sensor** ........... NaTPB  
**Concentration [mol/L]** .... 0.004  
**Sensor** ..................... DP550  
**Unit of meas.** ............... mV  

**Temperature acquisition** .......... No  
**Stir** ....................... Speed 35%  
**Predispense** ................. Mode None  
**Wait time** .................. 0 s  

**Control**  
**Control** ..................... User  
**Titrant addition** .......... Incremental  
**dV [mL]** ................... 0.4  
**Measure mode** .......... Fixed time  
**dt [s]** .................... 15 s  

**Evaluation and recognition** .......... No  
**Threshold** .................. 150.0 mV/mL  
**Tendency** ................... Negative  
**Range**  
**Stop for reevaluation** .......... Yes  
**Condition** ................. = neq 0  

**Calculation**  
**Formula** ................... R=V*EQ  
**Constant** ................... C=1  

**Statistics** .................. No  

**Report**  
**Output unit** ............... Printer  
**Result** ..................... No  
**All results** .................. Yes  
**Raw results** ................. No  
**Table of measured values** .......... Yes  
**E - V curve** .................. Yes  
**dV/dt - t curve** .......... No  

---

**Titration Excellence (Sample determination)**

001 Title  
**Type** General titration  
**Compatible with** T50 / T70 / T90  
**ID** 32g  
**Title** NIO/DP50/Content  
**Author** METTLER TOLEDO  
**Date/Time** 01.01.2010 15:00:00  
**Modified** --  
**Modified by** --  
**Protect** No  

002 Sample  
**Number of IDs** 1  
**ID 1** TritonN101  
**Entry type** Fixed volume  
**Volume [mL]** 5.0  
**Density [g/mL]** 1.0  
**Correction factor** 1.0  
**Temperature** 25.0°C  

003 Titration stand (Manual stand)  
**Type** Rondo/Tower A  
**Titrator** Rondo60/1A  

004 Pump  
**Auxiliary reagent** Water  
**Volume [mL]** 50.0  

005 Stir  
**Speed [%]** 40%  
**Duration** 10 s  

006 Titration (EQP) [1]  
**Titrant** NaTPB  
**Concentration [mol/L]** 0.004  
**Sensor** Phototrode  
**Unit** mV  

**Temperature acquisition** .......... No  
**Stir** ....................... Speed 35%  
**Predispense** ................. Mode None  
**Wait time** .................. 0 s  

**Control**  
**Control** ..................... User  
**Titrant addition** .......... Incremental  
**dV [mL]** ................... 0.4  
**Measure mode** .......... Fixed time  
**dt [s]** .................... 15 s  

**Evaluation and recognition** .......... No  
**Threshold** .................. 150.0 mV/mL  
**Tendency** ................... Negative  
**Range**  
**Stop for reevaluation** .......... Yes  
**Condition** ................. = neq 0  

007 Calculation R1  
**Result** Consumption  
**Result unit** mL  
**Formula** R1=V*EQ  
**Constant** C=1  

008 Calculation R2  
**Result** Content  
**Result unit** %  
**Formula** R2=H2*R1*100/(m*C2)  
**Constant** C2=2.55157  

010 Record  
**Rinse**  
**Auxiliary reagent** Water  
**Volume [mL]** 10  

012 Conditioning  
**Rinse**  

013 End of sample
## Colorimetric Two-Phase Titrations

<table>
<thead>
<tr>
<th>Method</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>M434</td>
<td>Anionic Surfactant Content in Liquid Detergents by Two-Phase Titration</td>
</tr>
<tr>
<td>M606</td>
<td>Standardization of Hyamine®1622 by Two-Phase Titration (DL58)</td>
</tr>
<tr>
<td>M607</td>
<td>Determination of Anionic Surfactants by Two-Phase Titration (DL58)</td>
</tr>
<tr>
<td>M608</td>
<td>Mixed Two-Phase Titration: Standardization of Hyamine®1622</td>
</tr>
<tr>
<td>M609</td>
<td>Mixed Two-Phase Titration: Anionic Surfactants in Liquid Detergents</td>
</tr>
<tr>
<td>M652</td>
<td>SPS Content of Drilling Emulsion by Epton Titration (DL58)</td>
</tr>
</tbody>
</table>
Anionic Surfactant Content in Liquid Detergents by Two-Phase Titration

The anionic surfactant content in liquid dish washers as SDS (sodium dodecyl sulfate) is determined by precipitation titration with Hyamine® 1622, a cationic surfactant. The content is determined by colorimetric two-phase titration with the DP5 Phototrode™ (automated Epton titration).

### Preparation and Procedures

**CAUTION:** Chloroform is toxic. Work in a fume hood.

1. Add 10 mL deion. water into the titration beaker.
2. Add 10 mL of mixed indicator solution.
3. Add 60 mL of chloroform. This step was performed with an additional dosing unit. It can be done manually with a pipette.
4. Add 5 mL of the liquid detergent sample solution.

**Liquid detergent solution:** The concentration was chosen to get a titrant consumption of 5 mL. Its value is stored as auxiliary value H[SDS] in g/mL.

**Sample preparation:** Dissolve ca. 8 g into a 1 L volumetric flask and fill up with deionised water (here: 8.5856 g liquid detergent, 0.0429 g/5 mL).

**DP5 Phototrode™:** After turning it on, wait for 10-15 min. before starting to get a stable light intensity. Check the transmission in deion. water and set it to 1000 mV by turning the knob on the top of it.

### Remarks

1. The method parameters have been optimized for this sample used. It may be necessary to slightly adapt the method to your specific sample.
2. Avoid bubbles formation during separation time since they disturb the photometric indication. Thus, select the appropriate stirring speed.
3. **Mixed indicator solution:** Dimidium bromide (DB): Weigh 0.2 g into a 100 mL flask and dissolve it with 10% (v/v) ethanol. If necessary, warm gently to achieve dissolution. After cooling, fill with 10% (v/v) ethanol to the mark. **CAUTION:** DB is toxic. Work under appropriate conditions e.g. wear gloves.

**Disulfine Blue VN:** Weigh 0.1 g into a 100 mL volumetric flask and dissolve the dye with 10% (v/v) ethanol. If necessary, warm gently. After cooling, fill with 10% (v/v) ethanol to the mark.

**Mixed indicator solution:** 10 mL dimidium bromide solution, 10 mL disulfine blue solution and 10 mL 2.5 mol/L (245 g/L) sulfuric acid solution (be careful: the solution becomes hot) are poured into a 250 mL volumetric flask. The solution is diluted to the mark with deionized water. Store it in the dark.

### Literature

See Applications M606 and M607.

---

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 mL liquid detergent solution, approx. 8 g/L</th>
</tr>
</thead>
</table>
| Compound | Sodium dodecylsulfate, SDS C_{12}H_{25}NaO_{4}S  
M = 288.38 g/mol, z = 1 |
| Chemicals | 10 mL deionised water  
10 mL mixed indicator*  
60 mL chloroform  
*see Remarks |
| Titrant | Hyamine®1622, C_{27}H_{42}ClNO_{2}  
c(Hyamine) = 0.004 mol/L |
| Standard | SDS, 1 mL 0.01 mol/L |
| Indication | DP5 Phototrode™, 520 nm |
| Chemistry | Simplified scheme:  
C_{27}H_{42}NO_{2}^{+} + C_{12}H_{25}O_{4}S^{-} =  
C_{27}H_{42}NO_{2}C_{12}H_{25}O_{4}S |
| Calculation | R1: SDS-Content (%)  
\[ R1 = \frac{Q\cdot C}{(m\cdot H[SDS])}, \]  
\[ C = \frac{M}{(10\cdot z)}; z = 1 \]  
\[ H[SDS] = \text{concentration of liquid detergent stock solution (g/mL)}. \] |
| Waste disposal | Separation of chloroform and final disposal as halogenated organic waste. Neutralization of the aqueous phase. |
| Author, Version | Cosimo De Caro, MSG Anachem, August 2006 |
**Instruments**
- Titration Excellence T50/T70/T90
- 1 additional dosing unit (for automatic dosing of chloroform with a 20 mL burette)

**Accessories**
- 10 mL DV1010 and 20 mL DV1020 burettes
- Two-phase titr. beaker ME-51107655
- XS205 Balance
- Olivetti Printer JobJet 210

**Results**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Liquid detergent solution</th>
<th>R1 (Content)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/1</td>
<td>13.59 %</td>
<td></td>
</tr>
<tr>
<td>1/2</td>
<td>13.53 %</td>
<td></td>
</tr>
<tr>
<td>1/3</td>
<td>13.45 %</td>
<td></td>
</tr>
<tr>
<td>1/4</td>
<td>13.59 %</td>
<td></td>
</tr>
<tr>
<td>1/5</td>
<td>13.60 %</td>
<td></td>
</tr>
<tr>
<td>1/6</td>
<td>13.57 %</td>
<td></td>
</tr>
</tbody>
</table>

**Statistics**

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>M434</th>
</tr>
</thead>
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<tr>
<td>R1 Content</td>
<td>13.56 %</td>
</tr>
<tr>
<td>Samples</td>
<td>6</td>
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<tr>
<td>Mean</td>
<td>13.56 %</td>
</tr>
<tr>
<td>s</td>
<td>0.06 %</td>
</tr>
<tr>
<td>srel</td>
<td>0.422 %</td>
</tr>
</tbody>
</table>

**Titration curve**

![Titration curve graph](image)
## Table of measured values

<table>
<thead>
<tr>
<th>Consumption V / mL</th>
<th>Potential E / mV</th>
<th>Derivative dE/dV</th>
<th>Time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>21.3</td>
<td>NaN</td>
<td>0</td>
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<tr>
<td>2.5</td>
<td>21.3</td>
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<td>2.65</td>
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<td>93.2</td>
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<td>2.8</td>
<td>21.2</td>
<td>NaN</td>
<td>138.6</td>
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<tr>
<td>2.95</td>
<td>21.5</td>
<td>NaN</td>
<td>183.9</td>
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<td>3.1</td>
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<td>4</td>
<td>60.2</td>
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<td>5.2</td>
<td>403.6</td>
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<td>64.12</td>
<td>909.2</td>
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<td>5.5</td>
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<td>437.7</td>
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<td>5.8</td>
<td>422.5</td>
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<td>1045.2</td>
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<td>401.1</td>
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<td>1090.5</td>
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<tr>
<td>6</td>
<td>438.4</td>
<td>NaN</td>
<td>1135.8</td>
</tr>
</tbody>
</table>

Sample 2

## Comments

- The mixed indicator solution is not stable for a long period of time.
- The solution must be protected against light.
- It is recommended to keep the mixed indicator solution in the refrigerator to improve stability.
Method

001 Title
Type General titration
Compatible with T50 / T70 / T90
ID M434
Title SDS content (2-phase)
Author METTLER TOLEDO
Date/Time 02.08.2006 15:00:00
Modified --
Modified by --
Protect No
SOP None

002 Sample
Number of IDs 1
ID 1 Liquid detergent solution
Entry type Fixed volume
Volume 5.0 mL
Density 1.0 g/mL
Correction factor 1.0
Temperature 25.0°C

003 Titration stand (Manual stand)
Type Manual stand
Titration stand Manual stand 1

004 Dispense (normal) [1]
Titrant Chloroform
Concentration 1
Volume 60 mL
Dosing rate 60.0 mL/min

005 Stir
Speed 60%
Duration 60 s

006 Titration (2-phase) [1]
Titrant Hyamine 1622
Concentration 0.004 mol/L
Sensor Type Phototrode
Sensor DP5
Unit mV
Temperature acquisition
Temperature acquisition No
Stir
Speed 60%

Predispense
Mode Volume
Volume 2.5 mL
Wait time 5 s

Control
Control User
Titrant addition Incremental
dV 0.15 mL
Meas. val. acquisition Fixed time
Mixed time 5 s
Separation time 40 s
Stir time (S. time) 20%

Evaluation and recognition
Procedure Standard
Threshold 8 mV/mL
Tendency Positive
Ranges 1
Lower limit 1 120 mV
Upper limit 1 500 mV
Add. EQP criteria No

Termination
At Vmax 6.0 mL
At potential No
At slope No
After number of recognized EQPs No
Combined termination criteria No

007 Calculation R1
Result Content
Result unit %
Formula R1=Q*C/(m*H[SDS])
Constant M M[Sodium dodecyl sulfate]
z z[Sodium dodecyl sulfate]
Decimal places 2
Result limits No
Record statistics Yes
Extra statistical func. No
Send to buffer No

008 Record
Results Per series
Raw results Per series
Table of meas. values Last titration function
Sample data Per series
Resource data No
E - V Last titration function
dE/dV - V Last titration function
log dE/dV - V No
dE/dV - V No
BETA - V No
E - t No
V - t No
dV/dt - t No
T - t No
E - V & dE/dV - V No
V - t & dV/dt - t No
Calibration curve No
Method No
Series data No

009 End of sample
The titer of the cationic surfactant Hyamine®1622 is determined by classical colorimetric two-phase titration using SDS as a primary standard. The color change is monitored by a photometric sensor.

### Preparation and Procedures

**CAUTION:** Chloroform is toxic. Work in a fume hood.

1) Add 10 mL deion. water into the titration beaker.
2) Add 10 mL of mixed indicator solution.
3) Add 50 mL of chloroform.
4) Add 5 mL of the SDS standard solution.

**DP5 Phototrode™:**

After turning it on, wait for 10-15 min. before starting to get a stable light intensity.

Check the transmission in deionized water and set it to 1000 mV by turning the knob on the top of it.

Note:

See also Applications M434 and M607 for more details on colorimetric two-phase titration.

### Remarks

**Mixed indicator solution:**

- **Dimidium bromide (DB):**
  Weigh 0.2 g into a 100 mL flask and dissolve it with 10% (v/v) ethanol. If necessary, warm gently to achieve dissolution. After cooling, fill with 10% (v/v) ethanol to the mark. **CAUTION:** DB is toxic. Work under appropriate conditions e.g. wear gloves.

- **Disulfine Blue VN:**
  Weigh 0.1 g into a 100 mL volumetric flask and dissolve the dye with 10% (v/v) ethanol. If necessary, warm gently. After cooling, fill with 10% (v/v) ethanol to the mark.

- **Mixed indicator solution:**
  10 mL dimidium bromide solution, 10 mL disulfine blue solution and 10 mL 2.5 mol/L (245 g/L) sulfuric acid solution (be careful: the solution becomes hot) are poured into a 250 mL volumetric flask. The solution is diluted to the mark with deionized water. Store it in the dark.

### Sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sodium dodecylsulfate, SDS C_{12}H_{25}NaO_4S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>c(SDS) = 0.004 mol/L Average M = 288.38; z = 1</td>
</tr>
</tbody>
</table>

### Chemicals

- 10 mL mixed indicator
- 50 mL chloroform
- 10 mL deionized water

### Titrant

Hyamine®1622, C_{27}H_{42}CINO_{2}  
c(Hyamine) = 0.004 mol/L

### Standard

--

### Indication

DP550 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (520 nm)

### Chemistry

Simplified scheme:  
C_{27}H_{42}NO_{2}^{+} + C_{12}H_{25}O_{4}S^{-} = C_{27}H_{42}NO_{2}C_{12}H_{25}O_{4}S

### Calculation

Titer (DL58)

- \( R_1 = m/(\text{VEQ} \cdot c \cdot C) \)
- \( C = 1/(H1 \cdot z) \)
- \( H1= \) concentration of SDS standard solution

### Waste disposal

Separation of chloroform and final disposal as halogenated organic waste. Neutralization of the aqueous phase.

### Author, Version

Dieter Rehwald/MSG Anachem, June 1997 / Revised January 2010
**Instruments**
- DL58 Titrator
- AT261 Balance

This method can also be run with the T50/T70/T90 Titration Excellence (minor adaptations in their method, see M434), and with the DL53+ and DL55+ instruments (extension dongle)

**Accessories**
- 10 mL DV1010 burette
- Two-phase titration beaker ME-51107655 (or glass beaker ME-101446 when used with sample changer and peristaltic pump for rinsing – see method).
- Printer

**Results**

Measured: 03-Jun-1997 13:06
User: rd

**ALL RESULTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>2</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>3</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>4</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>5</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>6</td>
<td>SDS</td>
<td>5.0 mL</td>
</tr>
</tbody>
</table>

**TITRANT**

- Titrant: Hyamine 0.004 mol/L
- New titer: \( t = 1.06608 \)

**STATISTICS**

<table>
<thead>
<tr>
<th>Number results</th>
<th>R1</th>
<th>( n = 6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>( x = 1.0661 )</td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>( s = 0.02235 )</td>
<td></td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>( s_{rel} = 2.097 % )</td>
<td></td>
</tr>
</tbody>
</table>

**Titration curves**

![Titration curve graph]
Table of measured values

Not available

Comments

- **CAUTION:**
  Chloroform is toxic. Work in a fume hood

- The Phototrode™ was dipped into chloroform (lower phase) when using the standard glass beaker.

- The appropriate stirring speed during separation time must be chosen to avoid formation of water bubbles in the measuring cell of the Phototrode™.

- If this is not possible, then use the special two-phase titration vessel ME-51107655. In this application it was still possible to work with standard glass titration beakers ME-101446 and a sample changer since water bubbles did not severely affect the transmission signal.

- After each sample the Phototrode™ is thoroughly rinsed with water to clean the mirror surface. If necessary, a conditioning step can be performed to ensure a complete cleaning of the sensor.

- H1 indicates the concentration of the SDS standard solution.
Method

DLP Titrator

Method 91003  Titer AT/SDS/Bpt. P./Chl PP
Version 03-Jun-1997 12:06

Title
Method ID .......................... 91003
Title .............................. Titer AT/SDS/Bpt. P./Chl PP
Date/time .......................... 03-Jun-1997 12:06

Sample
Sample ID .......................... SDS
Entry type ......................... Fixed volume
Volume [mL] .................... 5.0
Molar mass M ....................... 288.38
Equivalent number z ............. 1
Titrator stand .................... ST20A
Pump ........................... No
Pump ........................... No
Rinse .......................... Yes
Solvent ................... H2O
Volume [mL] ............... 30.0
Conditioning ................... No
Temperature sensor ................. Manual

Stir
Speed [%] .......................... 75
Time [s] ........................... 30

Two-phase titration
Titrant/Sensor
Titrant ............................ Hyamine
Concentration [mol/L] .......... 0.004
Sensor ......................... DP550
Unit of meas. .................. mV
Predispensing ...................... to volume
Volume [mL] .................... 3
Waiting time [s] ............... 15
Titrant addition
• V [mL] ........................ 0.15
Measure mode
Mixing time [s] ............... 20.0
Separation time [s] ............ 30
Stirrer speed (sep. time) [%] . 25
Recognition
Threshold ...................... 8.0
Range .......................... No
Tendency ........................ Positive
Termination
at maximum volume [mL] ......... 6.0
at potential ................... No
at slope ........................ No
after number EQPs ............. No
comb. Termination criteria .......
Evaluation
Procedure ...................... Standard
Potential 1 ...................... No
Potential 2 ...................... No
Stop for reevaluation ............ Yes
Condition = .............................. neq=0

Calculation
Formula ........................... R/m/(VEQ*c*C)
Decimals places ................. 4
Result name ........................ Titer Hyamine
Statistics ........................ Yes

Titer
Titrant ............................ Hyamine
Concentration [mol/L] .......... 0.004

Report
Output unit ...................... Printer
Results .......................... Yes
All results ........................ Yes
Raw results ...................... No
Table of measured values ....... Yes
Sample data ...................... No
K × V curve ...................... No
dK/dV – V curve ................. No
d2K/dV² – V curve .............. No
log dK/dV – V curve .......... No
K × t curve ....................... No
V – t curve ....................... No
dV/dt + t curve .................. No

Titration Excellence

001 Title
Type General titration
Compatible with TSS / T70 / T90
ID 91003
Title Titer Hyamine
Author METTLER TOLEDO
Date/Time 01.01.2010 15:00:00
Modified --
Modified by --
Protect No
SOP None

002 Sample (Titer)
Number of IDs 1
ID 1 SDS
Entry type Fixed volume
Volume 5.0 mL
Density 1.0 g/mL
Correction factor 1.0
Temperature 25.0°C

003 Titration stand (Manual stand)

004 Stir
Speed 75%
Duration 30 s

005 Titration (2-phase) [1]

006 Calculation R1
Result Titer
Result unit --
Formula R1=m/(VEQ*c*C)
Constant C=1/(cst*z)
M M[Sodium dodecyl sulfate]
z z[Sodium dodecyl sulfate]
Decimal places 4
Result limits No
Record statistics Yes
Extra statistical func. No
Send to buffer No

007 Titer
Titrant Hyamine 1622
Concentration [mol/L] .......... 0.004
TITRE= Mean[R1]
Limits No

008 Record

009 End of sample

M 606-2010
**Determination of Anionic Surfactants by Two-Phase Titration (DL58)**

The anionic surfactant content in liquid detergents is determined by titration with the cationic surfactant Hyamine®1622 by classical colorimetric two-phase titration. The color change is monitored by a photometric sensor.

### Sample
10 mL aliquot containing 0.1 g detergent.

### Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecylsulfate, SDS</td>
<td>c(SDS) = 0.02 mol/L, Average M = 288.38; z = 1</td>
</tr>
</tbody>
</table>

### Chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 mL mixed indicator, 50 mL chloroform, 10 mL deionized water.</td>
<td></td>
</tr>
</tbody>
</table>

### Titrant

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hyamine®1622, C_{27}H_{42}ClNO_{2}</td>
<td>c(Hyamine) = 0.02 mol/L</td>
</tr>
</tbody>
</table>

### Standard

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium dodecylsulfate, SDS</td>
<td>c(SDS) = 0.02 mol/L, 5 mL (see M606).</td>
</tr>
</tbody>
</table>

### Indication

<table>
<thead>
<tr>
<th>Indication</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP50 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (520 nm)</td>
<td></td>
</tr>
</tbody>
</table>

### Chemistry

**Simplified scheme:**

\[
\text{C}_{27}\text{H}_{42}\text{NO}_{2}^{+} + \text{C}_{12}\text{H}_{25}\text{O}_{4}\text{S}^{-} = \text{C}_{27}\text{H}_{42}\text{NO}_{2}\text{C}_{12}\text{H}_{25}\text{O}_{4}\text{S}
\]

### Calculation

- **Content determination (DL58):**
  - \( R1=Q^*C/m \) (\%)
  - \( C=M/(10^z) \)
  - \( R2=VEQ\times 5.7676)/m, \ mg/g \)
  - 1 mL 0.02 M Hyamine corresponds to 5.7676 mg SDS (see literature)

### Waste disposal

Separation of chloroform and final disposal as halogenated organic waste. Neutralization of the aqueous phase.

### Preparation and Procedures

**CAUTION:**
Chloroform is toxic. Work in a fume hood

1) Add 10 mL deion. water into the titration beaker.
2) Add 10 mL of mixed indicator solution.
3) Add 50 mL of chloroform.
4) Add 5 mL of the SDS standard solution.

**Photometric indication:**
- **DP5 immersed in chloroform phase:** Liquid detergents 1 and 2.
- **DP5 immersed in water phase:** Liq. det. 3 and 4

**DP5 Phototrode™:**
- After turning it on, wait for 10-15 min. before starting to get a stable light intensity.
- Check the transmission in deionized water and set it to 1000 mV by turning the knob on the top of it.

**Note:**
See also Application M434 for more details on colorimetric two-phase titration.

### Remarks

**Mixed indicator solution:**
- **Dimidium bromide (DB):**
  Weigh 0.2 g into a 100 mL flask and dissolve it with 10% (v/v) ethanol. If necessary, warm gently to achieve dissolution. After cooling, fill with 10% (v/v) ethanol to the mark. **CAUTION:** DB is toxic. Work under appropriate conditions e.g. wear gloves.
- **Disulfine Blue VN:**
  Weigh 0.1 g into a 100 mL volumetric flask and dissolve the dye with 10% (v/v) ethanol. If necessary, warm gently. After cooling, fill with 10% (v/v) ethanol to the mark.
- **Mixed indicator solution:**
  10 mL dimidium bromide solution, 10 mL disulfine blue solution and 10 mL 2.5 mol/L (245 g/L) sulfuric acid solution (be careful: the solution becomes hot) are poured into a 250 mL volumetric flask. The solution is diluted to the mark with deionized water. Store it in the dark.
Instruments
- DL58 Titrator
- AT261 Balance

This method can be also run with the T50, T70, T90 Titration Excellence (with minor adaptations in their method), and with the DL53+ and DL55+ instruments (extension dongle)

Accessories
- 10 mL DV1010 burette
- Two-phase titration beaker ME-51107655 (or glass beaker ME-101446 when used with sample changer, and peristaltic pump for rinsing).
- Printer

Results

Photometric detection in the aqueous phase:
Method 91004 2-Phasen-Titr./Epton 17-Mar-1997 21:06
Measured 17-Mar-1997 23:35
User rd

ALL RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liq. Det 4</td>
<td>0.1 g</td>
</tr>
<tr>
<td></td>
<td>R1 = 13.61%</td>
<td>Content</td>
</tr>
<tr>
<td></td>
<td>R2 = 139.6 mg/g</td>
<td>Content AT</td>
</tr>
<tr>
<td>2</td>
<td>Liq. Det 4</td>
<td>0.1 g</td>
</tr>
<tr>
<td></td>
<td>R1 = 13.57%</td>
<td>Content</td>
</tr>
<tr>
<td></td>
<td>R2 = 139.2 mg/g</td>
<td>Content AT</td>
</tr>
<tr>
<td>3</td>
<td>Liq. Det 4</td>
<td>0.1 g</td>
</tr>
<tr>
<td></td>
<td>R1 = 13.46%</td>
<td>Content</td>
</tr>
<tr>
<td></td>
<td>R2 = 138.1 mg/g</td>
<td>Content AT</td>
</tr>
<tr>
<td>4</td>
<td>Liq. Det 4</td>
<td>0.1 g</td>
</tr>
<tr>
<td></td>
<td>R1 = 13.35%</td>
<td>Content</td>
</tr>
<tr>
<td></td>
<td>R2 = 137.0 mg/g</td>
<td>Content AT</td>
</tr>
<tr>
<td>5</td>
<td>Liq. Det 4</td>
<td>0.1 g</td>
</tr>
<tr>
<td></td>
<td>R1 = 13.41%</td>
<td>Content</td>
</tr>
<tr>
<td></td>
<td>R2 = 137.6 mg/g</td>
<td>Content AT</td>
</tr>
</tbody>
</table>

STATISTICS
Number results R1 n = 5
Mean value x = 13.48% | Content
Standard deviation s = 0.10555% | Content
Rel. standard deviation srel = 0.783%

STATISTICS
Number results R2 n = 5
Mean value x = 138.3 mg/g | Content AT
Standard deviation s = 1.08265 mg/g | Content AT
Rel. standard deviation srel = 0.783%

Titration curves

Photometric detection in the aqueous phase
## Additional results

<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>srel (%)</th>
<th>Remarks</th>
</tr>
</thead>
</table>
| Liquid detergent 1 | Average molar mass: $M = 387$ | 18.0 | 17.1 | 6 | 17.84 | 3.43 | Stir time: 5 s, speed: 75%  
Separ. time: 30 s (30%)  
INC: 0.2 mL, $c(H_2A) = 0.01$ M  
Detection in chloroform  
2-phase titration beaker ME-51107655 |
|             | Fatty alcohol ether sulfate | 10.0 | 17.1 pH 3 |  | 17.84 pH 3 | | |
|             | Secondary alkanesulfonate | 6.0 | | | | | |
|             | Cocamidopropylbetaine | 2.0 | | | | | |

| Liquid detergent 2 | Average molar mass: $M = 362$ | 38.5 | 32.8 | 5 | 31.13 | 3.17 | Stir time: 5 s (Speed: 70%)  
Separ. time: 50 s (20%)  
INC: 0.15 mL, $c(H_2A) = 0.01$ M  
Detection in chloroform  
2-phase titration beaker ME-51107655 |
|             | Fatty alcohol ether sulfate | 11.0 | 32.8 pH 3 | | 31.13 pH 3 | | |
|             | Secondary alkanesulfonate | 20.0 | | | | | |
|             | Cocamidopropylbetaine | 3.5 | | | | | |
|             | Nonionics (7 EO, M=520) | 4.0 | | | | | |

| Liquid detergent 3 | Average $M = 353.09$ | 33.0 | 33.10 | 5 | 33.10 pH 1-2 | 0.5 | Stir time: 10 s, speed: 70%  
Separ. time: 4 s (10%)  
INC: 0.2 mL, $c(H_2A) = 0.01$ M  
Detection in water  
Glass titration beaker ME-101446 |
|             | Anionics A, $M=346$ | 27.0 | | 33.10 pH 1-2 | | | |
|             | Anionics B, $M=385$ | 6.0 | | | | | |

| Liquid detergent 4 | Anionics as SDS, $M=288.38$ | Lit.: 15-30 | 14.18 | 5 | 13.48 | 0.78 | See method in this application |
|             | | | pH 1-2 | | (n) 13.48 | | |

Nominal value: 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.

**Remarks**

- To avoid interferences by water bubbles during separation time, the signal can be also recorded in the water phase (liq. det. 3 and 4). In this case, the amount of chloroform is consistently reduced. The curve shows a lower light transmission due to emulsion which is formed during stirring.

- Predispensing is not used for the analyses of liquid detergents 3 and 4 since it affects the curve profile when monitoring the color change with the Phototrode™ in the water phase.

- Each sample must be tested to obtain the optimal method parameters for automatic titration.

- It is recommended to first perform a titration without termination after the first equivalence point to obtain the whole titration curve. In this way, the appropriate parameters (threshold, evaluation) can then be selected.
Comments

- **CAUTION:**
  Chloroform is toxic. Work in a fume hood.

- In this application, the photometric detection was achieved in two different ways:
  - in the **chloroform phase** with the two-phase beaker (classical detection).
    This setup has been used for the titration of samples “Liquid detergent 1” and “Liquid detergent 2”.
  - in the **aqueous phase** (standard titration beaker).
    This setup has been used for the titration of samples “Liquid detergent 3” and “Liquid detergent 4”.
    The signal was monitored in the water phase to avoid interference of water bubbles during the separation time. Since the color change is weaker than in the chloroform phase, the signal change at the EQP is also weaker.

- The appropriate stirring speed during separation time must be chosen to avoid formation of bubbles in the measuring cell of the Phototrode™.

- After each sample the Phototrode™ is thoroughly rinsed with water to clean the mirror surface. If necessary, a conditioning step can be performed to ensure a complete cleaning of the sensor.

- The anionic content AT in **unknown** samples can be expressed as sodium laurylsulphate (SDS) amount / Sample size.
  1 mL 0.02 mol/L Hyamine® 1622 corresponds to 5.7676 mg SDS (see literature). This is given in calculation R2.

Literature:

H. Block,
«Mikroprozessorgesteuerte Phototitration anionischer und kationischer Tenside in Wasch- und Reinigungsmitteln»,
Method

DLS8 Titrator
Method 91004 2-Phasen-Titr./Epton
Version 17-Mar-1997 21:06

Title
Method ID .................. 91004
Title .......................... 2-Phasen-Titr./Epton
Date/time .......................... 17-Mar-1997 21:06

Sample
Sample ID .......................... Liq. Det. 4
Entry type ......................... Weight
Lower limit [g] ................ 0.1
Upper limit [g] ................ 0.5
Molar mass M ....................... 288.38
Equivalent number z ................ 1
Titration stand ............... Stand 1
Temperature sensor .......... Manual

Stir
Speed [%] .......................... 65
Time [s] ........................... 10

Two-phase titration
Titrant/Sensor
Titrant .......................... Hyamine
Concentration [mol/L] .......... 0.02
Sensor ........................... DP5
Unit of meas. .................. mV
Predispensing ...................... No

Titrant addition
•V [mL] ........................ 0.1

Measure mode
Mixing time [s] .................. 10.0
Separation time [s] ............ 45
Stir speed (segm. time) [%] . 15

Recognition
Threshold ...................... 8.0
Steepest jump only ......... No
Range .......................... No
Tendency .................... Negative
Termination .......................... No
at maximum volume [mL] ...... 4.0
at potential ................. No
at slope ................. No
after number EQPs ........ Yes
n = ..................... 1

Stop for reevaluation ......... Yes
Condition = ..................... neq=0

Evaluation
Procedure ....................... Standard
Potential .......................... No
Potential 2 ......................... No
Stop for reevaluation ......... Yes

Calculation
Formula ........................... R=Q*C/m
Constant ......................... C=m/(10*z)
Decimal places .......................... 2
Result unit .......... mg/g
Result name .......................... Content
Statistics ......................... Yes

Calculation
Formula ........................... R2=(VEQ*t*5.7676)/m
Constant ......................... M[M(sodium dodecyl sulfate)]
z[M(sodium dodecyl sulfate)]
Decimal places .......................... 2
Result limits .............. No
Record statistics ........ Yes
Extra statistical func. .... No
Send to buffer .......... No

Report
Output unit ....................... Printer
Results .......................... Yes
All results ....................... Yes
Raw results ....................... No

Table of measured values .... Yes
Sample data ......................... Yes
X - V curve .......................... Yes
dV/dV - V curve .......... No
dV/dV - V curve .......... No
log dV/dV - V curve .......... No
X - t curve ......................... No
V - t curve ......................... No
dV/dt - t curve .................. No

Titration Excellence

001 Title
Type .................. General titration
Compatible with T50 / T70 / T90
ID .......................... 91004
Title .......................... 2-Phasen-Titr./Epton
Author ......................... METTLER TOLEDO
Date/Time .......................... 01.01.2010 19:00:00
Modified ................. No
Modified by .......... No
Protect ................. No
SOP .......................... None

002 Sample
Number of IDs .......................... 1
ID 1 .......................... Liq. Det. 4
Entry type ......................... Weight
Lower limit ................... 0.1 g
Upper limit ................ 0.5 g
Density ......................... 1.0 g/mL
Correction factor .......... 1.0
Temperature ..................... 25.0°C

003 Titration stand (Manual stand)
Type .......................... Manual stand
Titrination stand .......... Manual stand 1

004 Stir
Speed ......................... 65%
Duration ..................... 10 s

005 Titrant (2-phase) [1]
Titrant .......................... Hyamine 1622
Concentration ................... 0.02 mol/L
Sensor ........................... DP5
Unit of meas. .................. mV

Temperature acquisition
Temperature acquisition .......... No
Stir .......................... Yes
Speed ......................... 65%

Predispense
Mode ......................... None
Wait time .......... 0 s

Control
Control ......................... Yes
Titrant addition .......... Incremental
dV ......................... 0.1 mL
Meas. val. acquisition .......... Fixed time
Mixed time .......... 30 s
Separation time .......... 45 s
Stir time (S. time) .......... 15%

Evaluation and recognition
Procedure ....................... Standard
Threshold ................. 8 mV/mL
Tendency ............... Negative
Ranges .............. 0
Add. EQP criteria ......... No
Termination
At Vmax .......................... 4.0 mL
At potential .......... No
At slope ................. No
After number of recognized EQPs .... Yes
Number of EQPs .......... 1
Combined termination criteria ...... No

006 Calculation R1
Result .......................... Content
Result unit .......................... %
Formula ........................... R1=Q*C/m
Constant ......................... C=m/(10*z)
M .......................... M(sodium dodecyl sulfate)
z .......................... z(sodium dodecyl sulfate)
Decimal places .......................... 2
Result limits .............. No
Record statistics ........ Yes
Extra statistical func. .... No
Send to buffer .......... No

007 Record
Results .......................... Per series
Raw results ....................... Per series
Table of meas. values .......... Last titration function
Sample .............. Last titration function
dE - V .................. Last titration function
dE/dV - V .................. Last titration function

008 End of sample
Mixed Two-Phase Titration: Standardization of Hyamine®1622

The titer of the cationic surfactant Hyamine®1622 is determined by colorimetric two-phase titration under continuous stirring (mixed 2P titration) using SDS as a primary standard. The color change is monitored by a photometric sensor.

### Preparation and Procedures

**CAUTION:**
Chloroform is toxic. Work in a fume hood.

1) Add 40 mL deionized water into the titration beaker.
2) Add 10 mL of mixed indicator solution.
3) Add 10 mL of chloroform.
4) Add 5 mL of the SDS standard solution.

**DP5 Phototrode™:**
After turning it on, wait for 10-15 min. before starting to get a stable light intensity.

Check the transmission in deionized water and set it to 1000 mV by turning the knob on the top of it.

The transmission signal is monitored under continuous stirring i.e. there is no separation of the two phases water and chloroform before signal acquisition.

### Remarks

**Mixed indicator solution:**
- **Dimidium bromide (DB):**
  Weigh 0.2 g into a 100 mL flask and dissolve it with 10% (v/v) ethanol. If necessary, warm gently to achieve dissolution. After cooling, fill with 10% (v/v) ethanol to the mark. **CAUTION:** DB is toxic. Work under appropriate conditions e.g. wear gloves.
- **Disulfine Blue VN:**
  Weigh 0.1 g into a 100 mL volumetric flask and dissolve the dye with 10% (v/v) ethanol. If necessary, warm gently. After cooling, fill with 10% (v/v) ethanol to the mark.

**Mixed indicator solution:**
10 mL dimidium bromide solution, 10 mL disulfine blue solution and 10 mL 2.5 mol/L (245 g/L) sulfuric acid solution (be careful: the solution becomes hot) are poured into a 250 mL volumetric flask. The solution is diluted to the mark with deionized water. Store it in the dark.

**Literature:** see [1, 2] under Comments
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Sample Changer with pump.
- Glass beaker ME-10146.
- Printer

Results
Method       11    Titer Hya/Epton mixed  02-Jun-1997  18:39
Measured     03-Jun-1997  19:15
User         rd

ALL RESULTS

No.  ID           Sample size and results
  1  SDS       5.0 mL     R1 = 1.0422              Titer Hyamine
  2  SDS       5.0 mL     R1 = 1.0478              Titer Hyamine
  3  SDS       5.0 mL     R1 = 1.0435              Titer Hyamine
  4  SDS       5.0 mL     R1 = 1.0450              Titer Hyamine
  5  SDS       5.0 mL     R1 = 1.0421              Titer Hyamine
  6  SDS       5.0 mL     R1 = 1.4936              Titer Hyamine

STATISTICS
Number results       R1       n = 5
Mean value                    x = 1.0441        Titer Hyamine
Standard deviation            s = 0.00239       Titer Hyamine
Rel. standard deviation    srel = 0.229    %
Sample no. 6 deleted

TITER

Titrant       Hyamine  0.004 mol/L
New titer                     t = 1.11902

Titration curves

![Titration curve diagram]
Tables of measured values

Not available

Comments

- **CAUTION:**
  Chloroform is toxic. Work in a fume hood
- After each sample the Phototrode™ is thoroughly rinsed with water to clean the mirror surface. If necessary, a conditioning step can be performed to ensure a complete cleaning of the sensor.
- H1 indicates the concentration of the SDS standard solution.

General comments:

- The classical two-phase titration is automated by the «Two-phase titration» function. The sequence of the classical two-phase titration i.e.
  1. Addition of increment
  2. Mixing and extraction (strong stirring)
  3. Separation of the two phases (slow stirring)
  4. Signal acquisition
  is performed automatically by the titrator. Although the analysis can be automated, it still can take a long time since the separation of the two phases is the time-consuming step. To shorten the analysis time, the signal can be acquired while the titrator is stirring the sample solution at a high speed i.e. without phase separation. In this case, a conventional EQP-Titration function can be used [see 1, 2].

- A comparison between the mixed two-phase titration and the classical manual procedure has been presented in detail by H. Block in 1985 [1]. In particular, the content of anionics and cationics by two-phase titration in various commercially available products were compared. A determination of SDS by mixed two-phase titration shows an excellent agreement with results obtained by classical manual two-phase titration [2].

- The advantages of the mixed two-phase titration are:
  1. **Automation** (a sample changer can be easily used for this operation).
  2. Considerable **time-saving** with respect to the automated procedure including phase separation.
  3. Endpoint detection is operator-**independent** with respect to the manual procedure.
  4. The consumption of chloroform is consistently reduced.

- Since the signal acquisition is performed in a stirred, heterogeneous two-phase system, the solution is turbid and thus, the light transmission measured by the Phototrode™ is decreased considerably. Nevertheless, the color change of the mixed indicator can still be detected by the sensor. The author of the article H. Block describes the signal detection as it follows [1]: «Since during the whole titration a constant stirring speed is maintained, a clear and well-defined phase separation is not visible. The overall colour change is measured in the emulsion. At the beginning the color is milky-pink, it turns to grey-green at the equivalence point and after the equivalence point it becomes blue-turquoise.» [citation translated from the German text].
  In this way, a continuous, mixed colorimetric two-phase titration is achieved which does not require a phase separation for the evaluation of the endpoint.

- Note that the mixed colorimetric two-phase titration can be performed by means of a single equivalence point titration method function (EQP). Thus, it can be performed by any titrator which can run this method function.

Literature:

<table>
<thead>
<tr>
<th><strong>Method</strong></th>
<th>DL5x Titrator</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method 11</strong></td>
<td>Titer Hyamine/Epton mixed</td>
</tr>
<tr>
<td><strong>Version</strong></td>
<td>02-Jun-1997 18:39</td>
</tr>
<tr>
<td><strong>Title</strong></td>
<td>Method ID ... 11</td>
</tr>
<tr>
<td></td>
<td>Title ... Titer Hyamine/Epton mixed</td>
</tr>
<tr>
<td><strong>Sample</strong></td>
<td>Sample ID ... SDS</td>
</tr>
<tr>
<td></td>
<td>Entry type ... Fixed volume</td>
</tr>
<tr>
<td></td>
<td>Volume [mL] ... 5.0</td>
</tr>
<tr>
<td></td>
<td>Molar mass M ... 288.38</td>
</tr>
<tr>
<td></td>
<td>Equivalent number z ... 1</td>
</tr>
<tr>
<td><strong>Titration stand</strong></td>
<td>Pump ... Yes</td>
</tr>
<tr>
<td></td>
<td>Rinses ... No</td>
</tr>
<tr>
<td></td>
<td>Solvent ... H2O</td>
</tr>
<tr>
<td><strong>Pump</strong></td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td>H2O</td>
</tr>
<tr>
<td><strong>Volume [mL]</strong></td>
<td>30.0</td>
</tr>
<tr>
<td><strong>Conditioning</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>Temperature sensor</strong></td>
<td>Manual</td>
</tr>
<tr>
<td><strong>Stir</strong></td>
<td>Speed [%] ... 75</td>
</tr>
<tr>
<td></td>
<td>Time [s] ... 15</td>
</tr>
<tr>
<td><strong>EQP titration</strong></td>
<td>Volume [mL] ... 0.15</td>
</tr>
<tr>
<td><strong>Measure mode</strong></td>
<td>Equilibrium controlled</td>
</tr>
<tr>
<td><strong>Titrant/Sensor</strong></td>
<td>Titrant ... Hyamine 1622</td>
</tr>
<tr>
<td></td>
<td>Concentration [mol/L] ... 0.004</td>
</tr>
<tr>
<td></td>
<td>Sensor ... Phototrode</td>
</tr>
<tr>
<td></td>
<td>Unit ... mV</td>
</tr>
<tr>
<td><strong>Titrant addition</strong></td>
<td>dV ... 0.15 mL</td>
</tr>
<tr>
<td><strong>Threshold</strong></td>
<td>dE ... 0.5 mV</td>
</tr>
<tr>
<td><strong>Recognition</strong></td>
<td>dt ... 1.0 s</td>
</tr>
<tr>
<td><strong>Evaluation</strong></td>
<td>t(min) ... 6.0 s</td>
</tr>
<tr>
<td><strong>Procedure</strong></td>
<td>Standard</td>
</tr>
<tr>
<td><strong>Stop for reevaluation</strong></td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Condition</strong></td>
<td>neque</td>
</tr>
<tr>
<td><strong>Calculation</strong></td>
<td>R1 = m/(VEQ<em>c</em>C)</td>
</tr>
<tr>
<td><strong>Constant</strong></td>
<td>C = 1/(cst*z)</td>
</tr>
<tr>
<td><strong>Result name</strong></td>
<td>Titer Hyamine</td>
</tr>
<tr>
<td><strong>Titer</strong></td>
<td>Titrant ... Hyamine 1622</td>
</tr>
<tr>
<td></td>
<td>Concentration [mol/L] ... 0.004</td>
</tr>
<tr>
<td><strong>Report</strong></td>
<td>Output unit ... Printer</td>
</tr>
<tr>
<td></td>
<td>All results ... Yes</td>
</tr>
<tr>
<td></td>
<td>Table of measured values ... Yes</td>
</tr>
<tr>
<td><strong>Sample data</strong></td>
<td>Sample data ... No</td>
</tr>
<tr>
<td><strong>X - V curve</strong></td>
<td>Yes</td>
</tr>
<tr>
<td><strong>dV/dx - V curve</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>log dE/dV - V curve</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>K - t curve</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>Limit</strong></td>
<td>Titer Hyamine 1622</td>
</tr>
<tr>
<td><strong>Limit</strong></td>
<td>Concentration [mol/L] ... 0.004</td>
</tr>
</tbody>
</table>

**Example Calculation R1**

| **Titer** | Titrant ... Hyamine |
|           | Concentration [mol/L] ... 0.004 |
| **Result unit** | % |
| **Formula** | R1 = m/(VEQ*c*C) |
| **Constant** | C = 1/(cst*z) |
| **M** | [Sodium dodecyl sulfate] |
| **s** | [Sodium dodecyl sulfate] |
| **Decimals places** | 4 |
| **Result limits** | No |
| **Record statistics** | Yes |
| **Extra statistical func.** | No |
| **Send to buffer** | No |

**Method Excellence**

| **001 Title** | Type | General titration |
|               | ID | 11 |
| **002 Sample (Titer)** | Number of IDs | 1 |
|               | ID | SDS |
| **004 Stir** | Speed [%] ... 75 |
|               | Duration ... 15 s |
| **005 Titration EQP [1]** | Temperature acquisition | °C |
|               | Temperature acquisition | No |
|               | dE ... 0.5 mV |
|               | dt ... 1.0 s |
|               | t(max) ... 30.0 s |

**006 Calculation R1**

| **Result** | Titer Hyamine |
| **Limit** | Mean[R1] |

**008 Record**

**009 End of sample**
Mixed Two-Phase Titration: Anionic Surfactants in Liquid Detergents

The anionic surfactant content in various liquid detergents is determined by colorimetric two-phase titration under continuous stirring (mixed 2P titration) with Hyamine®1622 as a titrant. The color change is monitored by a photometric sensor.

### Preparation and Procedures

**CAUTION:** Chloroform is toxic. Work in a fume hood.

1. Add 40 mL deion. water into the titration beaker.
2. Add 10 mL of mixed indicator solution.
3. Add 10 mL of chloroform.
4. Add 10 mL of the liquid detergent solution.

**DP5 Phototrode™:**

After turning it on, wait for 10-15 min. before starting to get a stable light intensity.

Check the transmission in deionized water and set it to 1000 mV by turning the knob on the top of it.

The transmission signal is monitored under continuous stirring i.e. there is no separation of the two phases water and chloroform before signal acquisition.

### Remarks

**Mixed indicator solution:**

- **Dimidium bromide (DB):**
  Weigh 0.2 g into a 100 mL flask and dissolve it with 10% (v/v) ethanol. If necessary, warm gently to achieve dissolution. After cooling, fill with 10% (v/v) ethanol to the mark. **CAUTION:** DB is toxic. Work under appropriate conditions e.g. wear gloves.

- **Disulfine Blue VN:**
  Weigh 0.1 g into a 100 mL volumetric flask and dissolve the dye with 10% (v/v) ethanol. If necessary, warm gently. After cooling, fill with 10% (v/v) ethanol to the mark.

- **Mixed indicator solution:**
  10 mL dimidium bromide solution, 10 mL disulfine blue solution and 10 mL 2.5 mol/L (245 g/L) sulfuric acid solution (be careful: the solution becomes hot) are poured into a 250 mL volumetric flask. The solution is diluted to the mark with deionized water. Store it in the dark.

**Literature:** see M608, and [1, 2] in “Comments”.

### Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>Liquid detergents, 10 mL aliquot (standard solution: 5 g in 500 mL)</th>
</tr>
</thead>
</table>

### Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sodium dodecylsulfate, SDS C_{12}H_{25}NaO_{4}S</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Average M = 288.38; z = 1</td>
</tr>
</tbody>
</table>

### Chemicals

- 10 mL mixed indicator
- 10 mL chloroform
- 40 mL deionized water

### Titrant

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Hyamine®1622, C_{27}H_{42}CINO_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C(Hyamine) = 0.01 mol/L</td>
</tr>
</tbody>
</table>

### Standard

<table>
<thead>
<tr>
<th>Standard</th>
<th>5 mL 0.01 mol/L SDS</th>
</tr>
</thead>
</table>

### Indication

<table>
<thead>
<tr>
<th>Indication</th>
<th>DP550 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (520 nm)</th>
</tr>
</thead>
</table>

### Chemistry

<table>
<thead>
<tr>
<th>Chemistry</th>
<th>Simplified scheme: C_{27}H_{42}NO_{2} + C_{12}H_{25}O_{4}S^- = C_{27}H_{42}NO_{2}C_{12}H_{25}O_{4}S</th>
</tr>
</thead>
</table>

### Calculation

<table>
<thead>
<tr>
<th>Calculation</th>
<th>Content (DL5x)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>• R1 = (Q*^C)/(m*10/500)</td>
</tr>
<tr>
<td></td>
<td>• C = M/(10*z)</td>
</tr>
<tr>
<td></td>
<td>10/500: dilution factor of the liquid detergent amount m = 5 g in 500 mL vol. flask and the aliquot size (10 mL).</td>
</tr>
<tr>
<td></td>
<td>• R2 = (VEQ<em>t</em>2.8838)/(m/50) mg AT/g as SDS</td>
</tr>
</tbody>
</table>

### Waste disposal

| Waste disposal | Separation of chloroform and final disposal as halogenated organic waste. Neutralization of the aqueous phase. |

### Author, Version

<table>
<thead>
<tr>
<th>Author, Version</th>
<th>Dieter Rehwald/MSG Anachem, April 1997 / Revised January 2010</th>
</tr>
</thead>
</table>

METTLER TOLEDO Application M609-2010
Instruments
- DL58 Titrator
- AT261 Balance

This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Glass beaker ME-10146.
- Printer

Results

Method 71004 Eptontitration gerührt 04-Apr-1997 9:34
Measured 04-Apr-1997 10:53
User rd

ALL RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Liq. Det 1</td>
<td>5.0621 g R1 = 14.892 % Content R2 = 113.6 mg/g as SDS</td>
</tr>
<tr>
<td>2</td>
<td>Liq. Det 1</td>
<td>5.0621 g R1 = 14.929 % Content R2 = 113.8 mg/g as SDS</td>
</tr>
<tr>
<td>3</td>
<td>Liq. Det 1</td>
<td>5.0621 g R1 = 14.940 % Content R2 = 113.9 mg/g as SDS</td>
</tr>
<tr>
<td>4</td>
<td>Liq. Det 1</td>
<td>5.0621 g R1 = 14.644 % Content R2 = 111.6 mg/g as SDS</td>
</tr>
<tr>
<td>5</td>
<td>Liq. Det 1</td>
<td>5.0621 g R1 = 14.851 % Content R2 = 113.2 mg/g as SDS</td>
</tr>
</tbody>
</table>

STATISTICS

<table>
<thead>
<tr>
<th>Number results</th>
<th>R1</th>
<th>n = 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x</td>
<td>14.851 % AT Content</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s</td>
<td>0.814 %</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel</td>
<td>81.4 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Number results</th>
<th>R2</th>
<th>n = 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x</td>
<td>113.2 % AT/g as SDS</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s</td>
<td>0.814 %</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel</td>
<td>81.4 %</td>
</tr>
</tbody>
</table>

Titration curves

![Titration Curve Graph]
### Additional results

<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>srel (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid detergent 1</td>
<td>Average molar mass: $M = 387$</td>
<td>18.0</td>
<td>17.1</td>
<td>6</td>
<td>17.05</td>
<td>1.19</td>
<td>Method 71004</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>10.0</td>
<td></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>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>2.0</td>
<td></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</td>
<td>6</td>
<td>35.30</td>
<td>0.538</td>
<td>Method 71004</td>
</tr>
<tr>
<td></td>
<td>Fatty alcohol ether sulfate</td>
<td>11.0</td>
<td></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>
<td></td>
</tr>
<tr>
<td></td>
<td>Cocamidopropylbetaine</td>
<td>3.5</td>
<td></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>
<td></td>
</tr>
<tr>
<td>Liquid detergent 3</td>
<td>Average $M = 353.09$</td>
<td>33.0</td>
<td>-</td>
<td>5</td>
<td>32.12</td>
<td>0.019</td>
<td>INC = 0.15 mL, Additional components unknown</td>
</tr>
<tr>
<td></td>
<td>Anionics A, $M = 346$</td>
<td>27.0</td>
<td></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>
<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</td>
<td>5</td>
<td>14.15</td>
<td>0.784</td>
<td>Same se method 71004, unknown composition</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH 1-2</td>
<td>(n)</td>
<td></td>
<td></td>
<td></td>
<td></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.

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.

**Remarks**

- Predispensing is **not used** since it affects the curve profile and thus the detection of the largest signal change.

- The anionic content AT in **unknown** samples can be expressed as sodium laurylsulphate (SDS) / Sample size [1]. 1 mL 0.01 mol/L Hyamine corresponds to 2.8838 mg SDS (see calculation R2).

- Each sample must be tested to obtain the optimal method parameters. It is recommended to first perform a titration without termination after the first equivalence point to obtain the whole titration curve. In this way, the appropriate parameters (threshold, evaluation,...) can be selected.

- Liquid detergents 1 and 2:
  The producer gives reference values for the content of washing active matter, 17.1 % and 32.8 % respectively. The value was obtained by classical manual two-phase titration at pH 3.

- Liquid detergent 3:
  An average value for $M$ was calculated based on the content of the two anionic surfactants A and B, i.e. 27% and 6%. Additional components are not specified.

- Liquid detergent 4: The composition is unknown. The anionic content is expressed as SDS.

- In the case of **unknown sample** or of **formulated products**:
  a) first perform a calibration titration on a standard solution of known composition (reference value),
  b) then compare the reference value with the result obtained by titrating the sample.
Table of measured values

Not available

Comments

- **CAUTION:**
  Chloroform is toxic. Work in a fume hood

- After each sample the Phototrode™ is thoroughly rinsed with water to clean the mirror surface. If necessary, a conditioning step can be performed to ensure a complete cleaning of the sensor.

**General comments:**

- The classical two-phase titration is automated by the «Two-phase titration» function. The sequence of the classical two-phase titration i.e.
  1. Addition of increment
  2. Mixing and extraction (strong stirring)
  3. Separation of the two phases (slow stirring)
  4. Signal acquisition
   is performed automatically by the titrator. Although the analysis can be automated, it still can take a long time since the separation of the two phases is the time-consuming step. To shorten the analysis time, the signal can be acquired while the titrator is stirring the sample solution at a high speed i.e without phase separation. In this case, a conventional EQP-Titration function can be used [see 1, 2].

- A comparison between the mixed two-phase titration and the classical manual procedure has been presented in detail by H. Block in 1985 [1]. In particular, the content of anionics and cationics by 2P-titration in various commercially available products were compared. A determination of SDS by mixed two-phase titration shows an excellent agreement with results obtained by manual 2P-titration [2].

- The advantages of the mixed two-phase titration are:
  1. **Automation** (a sample changer can be easily used for this operation).
  2. Considerable **time-saving** with respect to the automated procedure including phase separation.
  3. Endpoint detection is operator-**independent** with respect to the manual procedure.
  4. The consumption of chloroform is consistently reduced.

- Since the signal acquisition is performed in a stirred, heterogeneous two-phase system, the solution is turbid and thus, the light transmission measured by the Phototrode™ is decreased considerably. Nevertheless, the color change of the mixed indicator can still be detected by the sensor.

The author of the article H. Block describes the signal detection as it follows [1]:
«Since during the whole titration a constant stirring speed is maintained, a clear and well-defined phase separation is not visible. The overall color change is measured in the emulsion. At the beginning the color is milky-pink, it turns to grey-green at the equivalence point and after the equivalence point it becomes blue-turquoise.» [citation translated from the German text].
In this way, a continuous, mixed colorimetric two-phase titration is achieved which does not require a phase separation for the evaluation of the endpoint.

- Note that the mixed colorimetric two-phase titration can be performed by means of a single equivalence point titration method function (EQP). Thus, it can be performed by any titrator which can run this method function.

**Literature:**

**Method**

**DL5x Titrator**

**Title**
- Method ID: 71004
- Title: Eptontitration gerührt

**Sample**
- Sample ID: Liq Det. 1
- Entry type: Weight
- Lower limit [g]: 4.0
- Upper limit [g]: 5.0
- Molar mass M: 387
- Equivalent number z: 1
- Titration stand: Stand 1
- Temperature sensor: Manual

**Stir**
- Speed [%]: 40
- Time [s]: 10

**EQP titration**

**Titrant/Sensor**
- Titrant: Hyamine
- Concentration [mol/L]: 0.01
- Sensor: DP5
- Unit of meas.: mV

**Predispensing**
- Mode: None
- Wait time: 0 s

**Titrant addition**
- Incremental
- dV: 0.1 mL
- Meas. val. acquisition: equilibrium controlled
- dE: 0.5 mV
- dt: 1.0 s
- t(min): 6.0 s
- t(max): 30.0 s

**Recognition**
- Threshold: 8.0 mV/mL
- Tendency: Negative

**Termination**
- at maximum volume [mL]: 12.0
- at potential: No
- at slope: No
- after number of EQPs: Yes
- n = 1
- comb. Termination criteria: No

**Calculation**

**Result Content**
- Formula: $R1 = \frac{(Q \times C)}{(m \times 10/500)}$
- Constant: $C = M / (10 \times z)$
- Decimal places: 3

**Statistics**
- Yes

**Report**
- Output unit: Printer

**Titration Excellence**

**001 Title**
- Type: General titration
- Compatible with: T50 / T70 / T90

**002 Sample (Titer)**
- Number of IDs: 1
- ID: Liq Det. 1
- Entry type: Weight
- Lower limit: 4.0 g
- Upper limit: 5.0 g
- Density: 1.0 g/mL
- Correction factor: 1.0
- Temperature: 25.0°C

**003 Titration stand (Manual stand)**
- Type: Manual stand

**004 Stir**
- Speed: 40%

**005 Titration (EQP) [1]**

**Titrant**
- Titrant: Hyamine 1622
- Concentration: 0.01 mol/L

**Sensor**
- Type: Phototrode
- Unit: mV

**Temperature acquisition**
- No

**Stir**
- Speed: 40%

**Predispensing**
- Mode: None
- Wait time: 0 s

**Control**
- Control: User
- Titrant addition: Incremental
- dV: 0.1 mL
- Meas. val. acquisition: equilibrium controlled
- dE: 0.5 mV
- dt: 1.0 s
- t(min): 6.0 s
- t(max): 30.0 s

**Evaluation and recognition**
- Procedure: Standard
- Threshold: 8 mV/mL
- Tendency: Negative
- Ranges: 0
- Add. EQP criteria: No

**Termination**
- At Vmax: 12.0 mL
- At potential: No
- At slope: No
- After number of recognized EQPs: No
- Combined termination criteria: No

**006 Calculation R1**

**Result Content**
- Formula: $R1 = \frac{(Q \times C)}{(m \times 10/500)}$
- Constant: $C = M / (10 \times z)$
- M: [AT Liq. Det. 1]
- z: [AT Liq. Det. 1]
- Decimal places: 3

**007 Calculation R2**

**Result**
- as SDS
- Formula: $R2 = \frac{(VEQ \times t \times 2.8838)}{(m/50)}$
- Constant: $C = 1$
- M: [SDS]
- z: [SDS]
- Decimal places: 1

**008 Record**

**009 End of sample**
**Determination of Anionic Surfactants by Two-Phase Titration (DL58)**

The anionic surfactant content in used drilling emulsions is determined by titration with the cationic surfactant Hyamine®1622 by classical colorimetric two-phase titration. The color change is monitored by a photometric sensor.

### Preparation and Procedures

**CAUTION:**
Chloroform is toxic. Work in a fume hood

1) Add 10 mL deion. water into the titration beaker.
2) Add 5 mL of mixed indicator solution.
3) Add 50 mL of chloroform.
4) Add 5 mL Na₂SO₄ acidic solution

**DP5 Phototrode™:**
- After turning it on, wait for 10-15 min. before starting to get a stable light intensity.
- Check the transmission in deionized water and set it to 1000 mV by turning the knob on the top of it.

**Note:**
See also Applications M434, M606 and M607 for more details on colorimetric two-phase titration.

### Remarks

**Mixed indicator solution:**
- **Thymol Blue (TB):**
  Weigh accurately 0.050 g thymol blue and dissolve it with 50 mL 20% (v/v) ethanol, then filter into a 500 mL volumetric flask and fill with distilled water to the mark.
- **Methylene Blue (MB):**
  Weigh accurately 0.036 g methylene blue into a 1000 mL volumetric flask, dissolve the dye with and fill up to the mark with distilled water.
- **Mixed indicator solution:**
  225 mL thymol blue solution and 30 mL methylene blue solution are poured into a 500 mL volumetric flask. The solution is diluted to the mark with distilled water. Store it in the dark.

**Acidic Na₂SO₄ solution:**
Weigh 100 g Na₂SO₄ and pipette 12.6 mL concentrated H₂SO₄ into a 1000 mL volumetric flask, then fill with distilled water up to the mark.

### Table: Preparation and Procedures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Used drilling emulsions, 0.2 g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Sodium petroleum sulfate, SPS</td>
</tr>
<tr>
<td>Average M = 420; z = 1</td>
<td></td>
</tr>
<tr>
<td>Chemicals</td>
<td>5 mL mixed indicator, 5 mL Na₂SO₄ acidic solution 10 mL deion. water 50 mL chloroform</td>
</tr>
<tr>
<td>Titrant</td>
<td>Hyamine®1622, C₂₇H₄₂ClNO₂ c(Hyamine) = 0.004 mol/L and Cetylpyridium chloride, CPC c(CPC) = 0.004 mol/L</td>
</tr>
<tr>
<td>Standard</td>
<td>Sodium dodecylsulfate, SDS c(SDS) = 0.004 mol/L, 5 mL (see M606).</td>
</tr>
<tr>
<td>Indication</td>
<td>DP5 Phototrode™ with DIN-LEMO adapter cable ME-89600 or: DP5 Phototrode™ (520 nm)</td>
</tr>
<tr>
<td>Chemistry</td>
<td>Simplified scheme: C₂₇H₄₂NO₂⁺ + SPS⁻ = C₂₇H₄₂NO₂⁻-SPS</td>
</tr>
<tr>
<td>Calculation</td>
<td>Content determination (DL58)</td>
</tr>
<tr>
<td></td>
<td>R₁ = Q<em>C/m (%), C = M/(10</em>z)</td>
</tr>
<tr>
<td></td>
<td>R₂ = Q<em>C₂/m (ppm), C₂ = M</em>1000/z</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>Separation of chloroform and final disposal as halogenated organic waste. Neutralization of the aqueous phase.</td>
</tr>
</tbody>
</table>
**Instruments**
- DL58 Titrator
- AT261 Balance
  This method can also run with the T50, T70, T90 Titration Excellence (with minor adaptations in their method), and with the DL53+ and DL55+ instruments (extension dongle)

**Accessories**
- 10 mL DV1010 burette
- Two-phase titration beaker ME-51107655 (or beaker ME-101974 when used with sample changer, and peristaltic pump for rinsing).
- Printer

**Results**

**Titer determination of 0.0001 and 0.004 M CPC**

<table>
<thead>
<tr>
<th>c(CPC) / mol/l</th>
<th>n</th>
<th>SDS / mmol</th>
<th>Titer</th>
<th>srel / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0001</td>
<td>6</td>
<td>0.0005</td>
<td>1.0982</td>
<td>6.96</td>
</tr>
<tr>
<td>0.004</td>
<td>3</td>
<td>0.02</td>
<td>0.9012</td>
<td>0.48</td>
</tr>
</tbody>
</table>

**Titer determination of 0.001 and 0.004 M Hyamine**

<table>
<thead>
<tr>
<th>c(Hyamine) / mol/l</th>
<th>n</th>
<th>SDS / mmol</th>
<th>Titer</th>
<th>srel / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.001</td>
<td>4</td>
<td>0.005</td>
<td>0.0848</td>
<td>5.16</td>
</tr>
<tr>
<td>0.004</td>
<td>5</td>
<td>0.02</td>
<td>1.0078</td>
<td>0.29</td>
</tr>
</tbody>
</table>

**SPS content determination with 0.004 M Hyamine**

<table>
<thead>
<tr>
<th>Sample size / g</th>
<th>n</th>
<th>SPS / mmol</th>
<th>SPS / mmol/g</th>
<th>srel / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.19587</td>
<td>6</td>
<td>0.0253</td>
<td>0.1292</td>
<td>0.46</td>
</tr>
<tr>
<td>0.14075</td>
<td>6</td>
<td>0.0182</td>
<td>0.1293</td>
<td>1.14</td>
</tr>
<tr>
<td>0.09383</td>
<td>8</td>
<td>0.0120</td>
<td>0.1279</td>
<td>3.01</td>
</tr>
<tr>
<td>0.03916</td>
<td>4</td>
<td>0.0057</td>
<td>0.1456</td>
<td>5.67</td>
</tr>
<tr>
<td>0.01959</td>
<td>6</td>
<td>0.0034</td>
<td>0.1703</td>
<td>7.56</td>
</tr>
</tbody>
</table>

**Comments:**
The determination limit is defined as the smallest amount of substance that can be treated with a good precision. In this case, a relative standard deviation of 3 % was chosen. Depending on the analysis and quality management requirements, other values can be defined.

In Epton two-phase titration, the smallest amount of SPS in the sample must be larger than 0.015 mmol to achieve a reproducibility of 3%.
The drilling emulsion contains a mixture of surfactants called sodium petroleum sulfonate (SPS) which has an average molecular mass of 420 g/mol. The main surfactant component is sodium dodecylbenzene sulfate (SDBS).

The appropriate stirring speed during separation time must be chosen to avoid formation of bubbles in the measuring cell of the Phototrode™.

After each sample the Phototrode™ is thoroughly rinsed with water to clean the mirror surface. If necessary, a conditioning step can be performed to ensure a complete cleaning of the sensor.

The titrant 0.0001 M CPC did not prove to be suitable since the color change was not sharp anymore.
Method

DL58 Titrator

Method 19 2-phase titration (SDSDS)


Title

Method ID ...................... 19
Title ............................ 2-phase titration (SDSDS)
Date/time .......................... 19-Mar-1997 21:06

Sample

Sample ID ...................... SDSDS
Entry type ......................... Weight
Lower limit [g] ................ 0.0
Upper limit [g] ................ 2.0
Molar mass M ................. 420
Equivalent number z .............. 1

Titrator stand .................... ST20A
Pump ........................... Yes
Solvent ......................... H2O
Volume [mL] .................... 10.0
Stir ........................... Yes
Pump ........................... No
Rinse ........................... Yes
Solvent ......................... H2O
Volume [mL] .................... 10.0
Conditioning .................... 1
Time [s] .......................... 60
Interval .......................... 1
Rinse ........................... Yes
Solvent ......................... H2O
Volume [mL] .................... 10.0
Temperature sensor ................. Manual
Stir

Speed [%] ...................... 80
Time [s] .......................... 15

Two-phase titration

Titrant/Sensor

Titrant ......................... Hyamine
Concentration [mol/L] .......... 0.004
Sensor ......................... DP550
Unit of meas. .................. mV
Predispensing ...................... No
Titrant addition

• V [mL] .................. 0.15

Measure mode

Mixing time [s] ................ 20.0
Separation time [s] .......... 50.0
Stirrer speed (sep. time) [%] . 5

Recognition

Threshold ...................... 200.0
Steepest jump only ........................ No
Range .......................... No
Tendency ........................ Positive
Termination

at maximum volume [mL] .......... 8.0
at potential ...................... No
at slope ........................ No
after number EQPs .................. Yes
n = ........................... 1
comb. Termination criteria .... No
Evaluation

Procedure ...................... Standard
Potential 1 ...................... No
Potential 2 ...................... No
Stop for reevaluation ............ Yes
Condition = ........................ neg0
Calculation

Formula ......................... R=Q*C/m
Constant ......................... C=m/(10*z)
Decimal places .................. 4
Result unit ....................... %
Result name ...................... Content
Statistics ........................ Yes

Calculation

Formula ......................... R2=Q*C2/m
Constant ......................... C2=M*(10*z)
Decimal places .................. 4
Result unit ....................... ppm
Result name ...................... ppm
Statistics ........................ Yes

Report

Output unit ...................... Printer
Results .......................... Yes

002 Sample

Number of IDs ........................ 1
ID 1 .................. SDSDS
Entry type ......................... Weight
Lower limit ........................ 0.0 g
Upper limit ...................... 2.0 g
Density ....................... 1.0 g/mL
Correction factor .................. 1.0
Temperature ...................... 25.0°C

004 Stir

Speed ...................... 80%
Duration ..................... 15 s

005 Titration stand (2-phase) [1]

Titrant

Titrant ......................... Hyamine 1622
Concentration ................. 0.004 mol/L
Sensor

Type ......................... Phototrode
Sensor ......................... DP5
Unit ....................... mV
Temperature acquisition ....... No

Stir

Speed ...................... 80%
Predispensing ...................... None
Wait time ..................... 0 s

Control

Control ......................... User
Titrant addition ................. Incremental
dV .................. 0.15 mL
Meas. val. acquisition .......... Fixed time
Mixed time .................. 20 s
Separation time ............. 50 s
Stir time (S. time) ................ 10%

Evaluation and recognition

Procedure ...................... Standard
Threshold ....................... 200 mV/mL
Tendency ........................ Positive
Ranges .......................... 0
Add. EQP criteria ................. No
Termination

At Vmax ................... 8.0 mL
At potential ..................... No
At slope ........................ No
After number of recognized EQPs .... Yes
Number of EQPs .................. 1
Combined termination criteria .... No

006 Calculation R1

Result .......................... Content
Result unit ....................... %
Formula ......................... R1=Q*C/m
Constant ......................... C=m/(10*z)
M ....................... M[SDSDS]
2 ....................... 2[SDSDS]
Decimal places .................. 4
Result limits ...................... No
Record statistics ................. Yes
Extra statistical func. ...... No
Send to buffer ...................... No

007 Record

Results .......................... Per series
Raw results ...................... Per series
Table of meas. values ............... Last titration function
....
E - V .......................... Last titration function
dE/dV – V .......................... Last titration function

008 End of sample
# Potentiometric Titrations in Aqueous Phase

<table>
<thead>
<tr>
<th>Method</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>M414</td>
<td>Anionic Surfactant Content in Liquid Detergents by Potentiometric Titration</td>
</tr>
<tr>
<td>M610</td>
<td>Titer of Hyamine®1622 0.004 mol/L by Potentiometric Titration</td>
</tr>
<tr>
<td>M611</td>
<td>Titer of SDS 0.004 mol/L by Potentiometric Titration</td>
</tr>
<tr>
<td>M612</td>
<td>Titer of Sodium Tetraphenylborate 0.004 mol/L by Potentiometric Titration</td>
</tr>
<tr>
<td>M613</td>
<td>Potentiometric Titration: Anionic Surfactants in Liquid Detergents</td>
</tr>
<tr>
<td>M614</td>
<td>Potentiometric Titration of Nonionic Surfactants in Raw Materials</td>
</tr>
<tr>
<td>M615</td>
<td>Potentiometric Titration of a Betaine in Shampoo</td>
</tr>
<tr>
<td>M654</td>
<td>SPS Content of Drilling Emulsion by Potentiometric Titration</td>
</tr>
</tbody>
</table>
The anionic surfactant content in liquid dish washers as SDS content (sodium dodecyl sulfate, sodium lauryl sulfate) is determined by precipitation titration with Hyamine® 1622, a cationic surfactant. The potential change during titration is monitored by the DS500 surfactant sensitive electrode.

### Preparation and Procedures

1) The titer is determined by titrating 1 mL 0.01 M SDS in 60 mL deionized water.

2) Sample titration: 5 mL of an aqueous solution of liquid detergent is added into the beaker and diluted with 60 mL deionized water.

3) The concentration of the liquid detergent solution was chosen to get an approx. titrant consumption of 5 mL. Its value is stored as auxiliary value $H[SDS]$ in g/mL.

4) Preparation of the liquid detergent solution: Approx. 8 g liquid detergent is given into 1 L volumetric flask. The flask is filled up with deionized water (here: 8.0482 g liq. detergent in 1 L).

5) The sample series was analyzed using a sample changer. The conditioning time was set to 30 s (e.g. Rondolino settings: 4) to clean the sensor in water before starting the subsequent sample.

6) Before starting it is recommended to condition the DS500 electrode by running a trial titration with SDS or the liquid detergent.

### Remarks

1) The method parameters have been developed and optimized for the sample used in this application. Thus, it may be necessary to slightly adapt the method to your specific sample.

2) DS500 surfactant sensitive electrode (SSE):
   - Fill the DS500-SSE and the electrode tip with the electrolyte.
   - Screw the electrode tip onto the shaft.
   - Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
   - Rinse it with deionized water.
   - Condition it in 0.01 mol/L SDS solution for 20-30 minutes.

3) This method allows an automated analysis with a Rondolino sample changer. The method can be modified for manual operation. Select "Manual stand" in the method function "Titration stand".
Instruments
- Titration Excellence T50/T70/T90
- Rondolino Sample Changer

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974
- XS205 Balance
- Olivetti Printer JobJet 210

Results
All results

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.10 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.14 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.16 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.23 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/5)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.20 %</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>Sample</th>
<th>Liquid detergent solution (1/6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1 (Content)</td>
<td>14.19 %</td>
<td></td>
</tr>
</tbody>
</table>

Statistics

<table>
<thead>
<tr>
<th>Method-ID</th>
<th>R1 Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Samples</td>
<td>6</td>
</tr>
<tr>
<td>Mean</td>
<td>14.17 %</td>
</tr>
<tr>
<td>s</td>
<td>0.05 %</td>
</tr>
<tr>
<td>srel</td>
<td>0.328 %</td>
</tr>
</tbody>
</table>

Titration curve

![Titration curve graph]
Table of measured values

<table>
<thead>
<tr>
<th>Consumption V / mL</th>
<th>Potential E / mV</th>
<th>Derivative dE/dV</th>
<th>Time / s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-80.4</td>
<td>NaN</td>
<td>0</td>
</tr>
<tr>
<td>1.143</td>
<td>-70.7</td>
<td>NaN</td>
<td>4.5</td>
</tr>
<tr>
<td>1.714</td>
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<td>NaN</td>
<td>9.6</td>
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<tr>
<td>2</td>
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<td>14.7</td>
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<tr>
<td>2.2</td>
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<td>NaN</td>
<td>35</td>
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<tr>
<td>2.4</td>
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<tr>
<td>2.6</td>
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<td>16.82</td>
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<td>3.2</td>
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<td>71.1</td>
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<td>3.8</td>
<td>-20.1</td>
<td>36.12</td>
<td>76.9</td>
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<td>4</td>
<td>-12.4</td>
<td>45.57</td>
<td>82.5</td>
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<td>4.2</td>
<td>-2.9</td>
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<td>88</td>
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<td>4.342</td>
<td>6</td>
<td>63.23</td>
<td>93.1</td>
</tr>
<tr>
<td>4.438</td>
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<td>67.55</td>
<td>99.5</td>
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<td>4.51</td>
<td>19.8</td>
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<td>105.3</td>
</tr>
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<td>4.613</td>
<td>26.2</td>
<td>69.41</td>
<td>110.3</td>
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<tr>
<td>4.78</td>
<td>37.1</td>
<td>64.46</td>
<td>116.8</td>
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<tr>
<td>4.896</td>
<td>44.3</td>
<td>59.75</td>
<td>121.9</td>
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<td>5.032</td>
<td>52.6</td>
<td>54.66</td>
<td>128.1</td>
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<tr>
<td>5.166</td>
<td>59.8</td>
<td>NaN</td>
<td>133.2</td>
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<tr>
<td>5.334</td>
<td>67.4</td>
<td>NaN</td>
<td>138.2</td>
</tr>
<tr>
<td>5.534</td>
<td>74.9</td>
<td>NaN</td>
<td>143.3</td>
</tr>
<tr>
<td>5.734</td>
<td>81.3</td>
<td>NaN</td>
<td>148.4</td>
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<tr>
<td>5.934</td>
<td>86.6</td>
<td>NaN</td>
<td>153.4</td>
</tr>
</tbody>
</table>

Comments

- Note that the DS500 Surfactant Sensitive Electrode has been developed for the titration of aqueous surfactant solutions.
- For this reason, the sample solution has to be free of organic solvents. Otherwise, the sensitive membrane will be damaged.
### Method

#### 001 Title
- **Type**: General titration
- **Compatible with**: T50 / T70 / T90
- **ID**: M411
- **Title**: SDS content potentiometric
- **Author**: METTLER TOLEDO
- **Date/Time**: 02.08.2006 15:00:00
- **Modified by**: --
- **Protect**: No
- **SOP**: None

#### 002 Sample
- **Number of IDs**: 1
- **ID 1**: Liquid detergent solution
- **Entry type**: Fixed volume
- **Volume**: 5.0 mL
- **Density**: 1.0 g/mL
- **Correction factor**: 1.0
- **Temperature**: 25.0°C

#### 003 Titration stand (Rondolino TTL)
- **Type**: Rondolino TTL
- **Titration stand**:
  - Rondolino TTL 1

#### 004 Stir
- **Speed**: 35%
- **Duration**: 60 s

#### 005 Titration (EQP) [1]
- **Titrant**: Hyamine 1622
- **Concentration**: 0.004 mol/L
- **Sensor**:
  - **Type**: mV
  - **Sensor**: DS500
  - **Unit**: mV
- **Temperature acquisition**:
  - **Temperature acquisition**: No
- **Stir**:
  - **Speed**: 35%
- **Predispense**:
  - **Mode**: Volume
  - **Volume**: 2 mL
  - **Wait time**: 15 s
- **Control**:
  - **Control**: User
  - **Titrant addition**: Dynamic
  - **dE(set value)**: 9.0 mV
  - **dV(min)**: 0.02 mL
  - **dV(max)**: 0.2 mL
- **Measure. Val. acquisition**:
  - **Equilibrium controlled**:
    - **dE**: 1.0 mV
    - **dt**: 2 s
    - **t(min)**: 5 s
    - **t(max)**: 30 s
  - **Evaluation and recognition**:
    - **Procedure**: Standard
    - **Threshold**: 50 mV/µL
    - **Tendency**: Positive
    - **Ranges**: 0
    - **Add. EQP criteria**: No
    - **Termination**:
      - **At Vmax**: 10 mL
      - **At potential**: No
      - **At slope**: No
      - **After number of recognized EQPs**: Yes
      - **Number of EQPs**: 1
      - **Combined termination criteria**: No

#### 006 Calculation R1
- **Result**: Content
- **Result unit**: %
- **Formula**: R1=Q*C/(m*H[SDS])
- **Constant**: C=5/[1(1+2)]
- **M**: M[Sodium dodecyl sulfate]
- **z**: z[Sodium dodecyl sulfate]
- **Decimal places**: 2
- **Result limits**: No
- **Record statistics**: Yes
- **Extra statistical func.**: No
- **Send to buffer**: No

#### 007 Record
- **Results**:
  - Per series
  - Last titration function
  - Last titration function
  - Last titration function
  - Last titration function
  - Last titration function
  - Last titration function
  - Last titration function
  - Last titration function
- **Table of meas. values**:
  - Per series
- **Sample data**:
  - Per series
- **Resource data**: No
- **E - V**:
  - No
- **dE/dV - V**:
  - No
- **log dE/dV - V**:
  - No
- **BETA - V**:
  - No
- **E - t**:
  - No
- **V - t**:
  - No
- **dV/dt - t**:
  - No
- **T - t**:
  - No
- **E - V & dE/dV - V**:
  - No
- **V - t & dV/dt - t**:
  - No
- **Calibration curve**: No
- **Method**: No
- **Series data**: No

#### 008 End of sample
## Titer of Hyamine® 1622 0.004 mol/L by Potentiometric Titration

The titer of the cationic surfactant Hyamine® 1622 is determined by potentiometric titration in aqueous solution using SDS as a primary standard. The potential change is monitored by a surfactant sensitive electrode SSE.

### Preparation and Procedures

- Add 50 mL deionized water into the titration beaker.
- Add 5 mL of the SDS standard solution.
- Before starting it is recommended to condition the DS500 electrode by running a trial titration with SDS and discard its result.

**DS500 surfactant sensitive electrode (SSE):**
- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in 0.01 mol/L SDS solution for 20-30 minutes.

**Automation:**
A sample changer is used in order to fully automate the procedure. In this way, the titration stand can be cleaned using a conditioning beaker.

### Remarks

- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.
- The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.
- After each titration the surfactant electrode and the reference electrode are dipped in a conditioning beaker on the sample changer with water to clean them thoroughly.
- Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value. In this way, incorrect evaluations can be avoided.
- The auxiliary value H1 gives the concentration of the standard solution for titer determination.

### Sample

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 mL SDS aliquot</th>
</tr>
</thead>
</table>

### Compound

<table>
<thead>
<tr>
<th>Compound</th>
<th>Sodium dodecylsulfate, SDS C_{12}H_{25}NaO_{4}S</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(SDS)</td>
<td>0.004 mol/L</td>
</tr>
<tr>
<td>M</td>
<td>288.38; z = 1</td>
</tr>
</tbody>
</table>

### Chemicals

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>50 mL deionized water</th>
</tr>
</thead>
</table>

### Titrant

<table>
<thead>
<tr>
<th>Titrant</th>
<th>Hyamine® 1622, C_{27}H_{42}ClNO_{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>c(Hyamine)</td>
<td>0.004 mol/L</td>
</tr>
</tbody>
</table>

### Standard

<table>
<thead>
<tr>
<th>Standard</th>
<th>--</th>
</tr>
</thead>
</table>

### Indication

- DS500 SSE
- InLab™ Mono ref. electrode (electrolyte: 3 mol/L KCl)

### Chemistry

**Simplified scheme:**

\[
\text{C}_{27}\text{H}_{42}\text{NO}_2^+ + \text{C}_{12}\text{H}_{25}\text{O}_4\text{S}^- = \text{C}_{27}\text{H}_{42}\text{NO}_2 \text{C}_{12}\text{H}_{25}\text{O}_4\text{S}
\]

### Calculation

**Titer (DL5x):**

\[
R_1 = \frac{m}{(\text{VEQ} \cdot c \cdot C)}
\]

\[
C = \frac{1}{(H1 \cdot z)}
\]

\[
H1 = \text{concentration of SDS standard solution}
\]

### Waste disposal

No special treatment

### Author, Version

Dieter Rehwald / MSG Anachem, June 1997 / Revised January 2010
Instruments
- DL58 Titrator
- AT261 Balance

This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Sample Changer with pump.
- Glass beaker ME-10146.
- Printer

Results

METTLER TOLEDO DL58 Titrator V2.0 Application Laboratory 002
Method 13 Titer Hyamine 0.004 mol/L 02-Jun-1997 15:29
Measured 02-Jun-1997 16:11
User rd

ALL RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SDS</td>
<td>5.0 mL R1 = 0.9876 Titer Hyamine</td>
</tr>
<tr>
<td>2</td>
<td>SDS</td>
<td>5.0 mL R1 = 0.9901 Titer Hyamine</td>
</tr>
<tr>
<td>3</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0000 Titer Hyamine</td>
</tr>
<tr>
<td>4</td>
<td>SDS</td>
<td>5.0 mL R1 = 0.9901 Titer Hyamine</td>
</tr>
<tr>
<td>5</td>
<td>SDS</td>
<td>5.0 mL R1 = 0.9954 Titer Hyamine</td>
</tr>
<tr>
<td>6</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0081 Titer Hyamine</td>
</tr>
</tbody>
</table>

STATISTICS

Number results R1 n = 5
Mean value x = 0.9967 Titer Hyamine
Standard deviation s = 0.00758 Titer Hyamine
Rel. standard deviation srel = 0.761 %
Sample No. 1 deleted

TITER

Titrant Hyamine 0.004 mol/L
New titer t = 0.99521

Titration curves

![Graph showing titration curves with E [mV] on the y-axis and V [mL] on the x-axis.]
### Table of measured values

Not available

### Comments

- Note that the DS500 Surfactant Sensitive Electrode has been developed for the titration of aqueous surfactant solutions only.
- For this reason, the sample solution has to be free of organic solvents. Otherwise, the sensitive membrane will be damaged.

### Principle:

- The potential of a solution containing surfactants is measured as a function of the titrant added. 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 potential is formed by interaction between the ion carrier in the membrane and the analyte in the sample solution. It can be measured against a reference electrode at zero current.
- The general composition of a typical SSE is: PVC, plasticizer, and ion carrier. 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 a specific activator prior to titration is necessary to form a complex between analyte and titrant. The activator is usually barium chloride, BaCl₂. The positively charged barium cation Ba²⁺ forms a complex with the uncharged nonionic surfactant. As a result, the surfactant-barium cation complex is positively charged - a pseudocationic complex - and therefore can be precipitated by titration with sodium tetraphenylborate (Na-TPB).

### Profile of the 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. If the curve shows a pronounced asymmetric profile, then the asymmetric evaluation can be used.

### Practical hints:

- SSEs are suitable for low concentrations (10⁻⁴ - 10⁻⁵ mol/L) in diluted solutions.
- Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible results.
- Choose the appropriate electrolyte to avoid interferences. For instance, replace KCl with 2 M NaNO₃ when using NaTPB for the titration of nonionic surfactant, since the potassium cation K⁺ forms a complex with TPB⁻ anions.
- Conditioning is sometimes needed for the reference electrode due to diffusion of the sample into the electrode through the ceramic diaphragm. If necessary, replace the electrolyte.
- Extreme pH-values, e.g. below pH 2, can damage the membrane of the surfactant sensitive electrode (operating working range of the DS500: pH 2-10).
Method

DL5x Titrator

Method ID 13

Sample

Sample ID SDS

Equivalent number x 1

Titrant/Sensor

Titrant Hyamine

Volume [mL] 5.0

Wait time [s] 3

Titrant addition Incremental

• E [mV] 1.0

Emin [mV] 4.0

Emax [mV] 20.0

Recognition Threshold 100.0

Steepest jump only No

Tendency Positive

Termination at maximum volume [mL] 6.0

at potential No

at slope No

after number EQPs No

comb. Termination criteria No

Evaluation Procedure Standard

Potential 1 No

Potential 2 No

Stop for reevaluation Yes

Condition = neq=0

Calculation

Formula R1=m/(VEQ*c*C)

Decimal places 4

Result unit %

Result name Titer Hyamine

Statistics Yes

Titer

Titrant Hyamine

Concentration [mol/L] 0.004

Formula t = x

Report

Output unit Printer

Results Yes

All results Yes

Raw results Yes

Table of measured values Yes

Sample data No

Sample

Sensor DS500

Unit mV

Volume 5.0 mL

Wait time 3 s

Control

Control User

Titrant addition Incremental

dV 0.05 mL

meas. val. acquisition equilibrium controlled

dE 1.0 mV

dt 2.0 s

t(min) 5.0 s

t(max) 20.0 s

Evaluation and recognition Procedure Standard

Threshold 100 mV/mL

Tendency Positive

Ranges 0

Add. EQP criteria No

Termination At Vmax 6.0 mL

At potential No

At slope No

After number of recognized EQPs No

Combined termination criteria No

006 Calculation R1

Result Titer Hyamine

Result unit %

Formula R1=m/(VEQ*c*C)

Constant C-1/(cst*z)

M M[Sodium dodecyl sulfate]

z z[Sodium dodecyl sulfate]

Decimal places 4

Result limits No

Record statistics Yes

Extra statistical func. No

Send to buffer No

007 Titer

Titrant Hyamine 1622

Concentration [mol/L] 0.004

TITREX Mean [R1]

Limits No

008 Record

--

009 End of sample

Titrator

Method 13 Titer Hyamine 0.004 mol/L

Version 02-Jun-1997 15:29

Title

Method ID 13

Titrant Hyamine 0.004 mol/L

Date/time 02-Jun-1997 15:29

Sample

Sample ID SDS

Equivalent number x 1

Titrant stand Manual stand 1

004 Stir

Speed 30%

Duration 90 s

005 Titrator (RQP) [1]

Titrator

Hyamine 1622

Concentration 0.004 mol/L

Sensor

Type mV

Sensor DS500

Unit mV

Temperature acquisition

Temperature acquisition No

Stir

Speed 30%

Predispensing

Mode Volume

Volume 4.0 mL

Wait time 3 s

Control

Control User

Titrant addition Incremental

dV 0.05 mL

meas. val. acquisition equilibrium controlled

dE 1.0 mV

dt 2.0 s

t(min) 5.0 s

t(max) 20.0 s

Evaluation and recognition Procedure Standard

Threshold 100 mV/mL

Tendency Positive

Ranges 0

Add. EQP criteria No

Termination

At Vmax 6.0 mL

At potential No

At slope No

After number of recognized EQPs No

Combined termination criteria No

006 Calculation R1

Result Titer Hyamine

Result unit %

Formula R1=m/(VEQ*c*C)

Constant C-1/(cst*z)

M M[Sodium dodecyl sulfate]

z z[Sodium dodecyl sulfate]

Decimal places 4

Result limits No

Record statistics Yes

Extra statistical func. No

Send to buffer No

007 Titer

Titrant Hyamine 1622

Concentration [mol/L] 0.004

TITREX Mean [R1]

Limits No

008 Record

--

009 End of sample

Titrator

Method 13 Titer Hyamine 0.004 mol/L

Version 02-Jun-1997 15:29

Title

Method ID 13

Titrant Hyamine 0.004 mol/L

Date/time 02-Jun-1997 15:29

Sample

Sample ID SDS

Equivalent number x 1

Titrant stand Manual stand 1

004 Stir

Speed 30%

Duration 90 s

005 Titrator (RQP) [1]

Titrator

Hyamine 1622

Concentration 0.004 mol/L

Sensor

Type mV

Sensor DS500

Unit mV

Temperature acquisition

Temperature acquisition No

Stir

Speed 30%

Predispensing

Mode Volume

Volume 4.0 mL

Wait time 3 s

Control

Control User

Titrant addition Incremental

dV 0.05 mL

meas. val. acquisition equilibrium controlled

dE 1.0 mV

dt 2.0 s

t(min) 5.0 s

t(max) 20.0 s

Evaluation and recognition Procedure Standard

Threshold 100 mV/mL

Tendency Positive

Ranges 0

Add. EQP criteria No

Termination

At Vmax 6.0 mL

At potential No

At slope No

After number of recognized EQPs No

Combined termination criteria No

006 Calculation R1

Result Titer Hyamine

Result unit %

Formula R1=m/(VEQ*c*C)

Constant C-1/(cst*z)

M M[Sodium dodecyl sulfate]

z z[Sodium dodecyl sulfate]

Decimal places 4

Result limits No

Record statistics Yes

Extra statistical func. No

Send to buffer No

007 Titer

Titrant Hyamine 1622

Concentration [mol/L] 0.004

TITREX Mean [R1]

Limits No

008 Record

--

009 End of sample
The titer of the anionic surfactant SDS (sodium dodecylsulfate) is determined by potentiometric titration in aqueous solution using CPC (Cetylpyridinium chloride) as a primary standard. The potential change is monitored by a surfactant sensitive electrode SSE.

### Preparation and Procedures

- Add 50 mL deionized water into the titration beaker.
- Add 5 mL of the CPC standard solution.
- Before starting it is recommended to condition the DS500 electrode by running a trial titration with CPC and discard its result.

### DS500 surfactant sensitive electrode (SSE):

- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in 0.01 mol/L CPC solution for 20-30 minutes.

### Automation:

A sample changer is used in order to fully automate the procedure. In this way, the titration stand can be cleaned using a conditioning beaker.

### Remarks

- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.
- The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.
- After each titration the surfactant electrode and the reference electrode are dipped in a conditioning beaker on the sample changer with water to clean them thoroughly.
- Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value. In this way, incorrect evaluations can be avoided.
- The auxiliary value H1 gives the concentration of the standard solution for titer determination.
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Sample Changer with pump.
- Glass beaker ME-10146.
- Printer

Results

METTLER TOLEDO DL58 Titrator V2.0 Application Laboratory 002

Method 23  Titer SDS 0.004 mol/L  06-Jun-1997 12:04
Measured 06-Jun-1997 15:17
User C. De Caro

RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0163 Titer SDS</td>
</tr>
<tr>
<td>2</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0152 Titer SDS</td>
</tr>
<tr>
<td>3</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0089 Titer SDS</td>
</tr>
<tr>
<td>4</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0057 Titer SDS</td>
</tr>
<tr>
<td>5</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0133 Titer SDS</td>
</tr>
<tr>
<td>6</td>
<td>SDS</td>
<td>5.0 mL R1 = 1.0173 Titer SDS</td>
</tr>
</tbody>
</table>

STATISTICS

<table>
<thead>
<tr>
<th>Number results</th>
<th>R1</th>
<th>n = 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x = 1.0128 Titer SDS</td>
<td></td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s = 0.00456 Titer SDS</td>
<td></td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel = 0.450 %</td>
<td></td>
</tr>
</tbody>
</table>

TITER

Titrant SDS 0.004 mol/L
New titer t = 1.0128

Titration curves
Table of measured values

<table>
<thead>
<tr>
<th>Volume Increment</th>
<th>Signal Change</th>
<th>1st deriv.</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL</td>
<td>mL</td>
<td>mV</td>
<td>mV/mL</td>
</tr>
<tr>
<td>ET1 0.0000</td>
<td>377.4</td>
<td>360.4</td>
<td>-17.1</td>
</tr>
<tr>
<td>2.0000</td>
<td>2.0000</td>
<td>348.5</td>
<td>-11.9</td>
</tr>
<tr>
<td>3.0000</td>
<td>1.0000</td>
<td>340.9</td>
<td>-7.6</td>
</tr>
<tr>
<td>3.5000</td>
<td>0.5000</td>
<td>336.9</td>
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</tr>
<tr>
<td>3.9000</td>
<td>0.2000</td>
<td>333.0</td>
<td>-3.9</td>
</tr>
<tr>
<td>4.1000</td>
<td>0.2000</td>
<td>327.9</td>
<td>-5.0</td>
</tr>
<tr>
<td>4.3000</td>
<td>0.2000</td>
<td>321.4</td>
<td>-6.6</td>
</tr>
<tr>
<td>4.4960</td>
<td>0.1960</td>
<td>313.9</td>
<td>-7.5</td>
</tr>
<tr>
<td>4.6790</td>
<td>0.1830</td>
<td>304.2</td>
<td>-9.6</td>
</tr>
<tr>
<td>4.7980</td>
<td>0.1190</td>
<td>294.9</td>
<td>-9.3</td>
</tr>
<tr>
<td>4.8750</td>
<td>0.0770</td>
<td>278.4</td>
<td>-16.5</td>
</tr>
<tr>
<td>4.8970</td>
<td>0.0220</td>
<td>265.3</td>
<td>-13.1</td>
</tr>
<tr>
<td>4.9170</td>
<td>0.0200</td>
<td>248.4</td>
<td>-16.9</td>
</tr>
<tr>
<td>EQP1 4.9370</td>
<td>0.0200</td>
<td>229.9</td>
<td>-18.5</td>
</tr>
<tr>
<td>4.9570</td>
<td>0.0200</td>
<td>212.3</td>
<td>-17.6</td>
</tr>
<tr>
<td>4.9770</td>
<td>0.0200</td>
<td>204.5</td>
<td>-7.9</td>
</tr>
<tr>
<td>4.9970</td>
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<td>197.2</td>
<td>-7.3</td>
</tr>
<tr>
<td>5.0200</td>
<td>0.0230</td>
<td>192.8</td>
<td>-4.4</td>
</tr>
<tr>
<td>5.0560</td>
<td>0.0450</td>
<td>184.9</td>
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<tr>
<td>5.1180</td>
<td>0.0520</td>
<td>178.2</td>
<td>-6.7</td>
</tr>
<tr>
<td>5.2090</td>
<td>0.0910</td>
<td>169.8</td>
<td>-8.3</td>
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<tr>
<td>5.3570</td>
<td>0.1480</td>
<td>160.5</td>
<td>-9.3</td>
</tr>
<tr>
<td>5.5570</td>
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<td>-8.4</td>
</tr>
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<td>5.7570</td>
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<td>-6.1</td>
</tr>
<tr>
<td>5.9570</td>
<td>0.2000</td>
<td>141.2</td>
<td>-4.8</td>
</tr>
<tr>
<td>6.0000</td>
<td>0.0430</td>
<td>140.4</td>
<td>-0.8</td>
</tr>
</tbody>
</table>

Comments

- The DS500 Surfactant Sensitive Electrode has been developed for the titration of aqueous surfactant solutions only.
- The potential of a solution containing surfactants is measured as a function of the titrant added. 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 a specific activator prior to titration is necessary to form a complex between analyte and titrant. The activator is usually barium chloride, BaCl2. The positively charged barium cation Ba2+ forms a complex with the uncharged nonionic surfactant. As a result, the surfactant-barium cation complex is positively charged -a pseudocationic complex- and therefore can be precipitated by titration with sodium tetraphenylborate (Na-TPB).
- 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. If the curve shows a pronounced asymmetric profile, then the asymmetric evaluation can be used.
- SSEs are suitable for low concentrations (10^-4 - 10^-5 mol/L) in diluted solutions.
- Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible 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 surfactant, since the potassium cation K+ forms a complex with TPB- anions.
- Conditioning is sometimes needed for the reference electrode due to diffusion of the sample into the electrode through the ceramic diaphragm. If necessary, replace the electrolyte.
- Extreme pH-values, e.g. below pH 2, can damage the membrane of the surfactant sensitive electrode (operating working range of the DS500: pH 2-10).
<table>
<thead>
<tr>
<th>Method</th>
<th>DL5x Titrator</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Method</strong></td>
<td>23 Titer SDS 0.004 mol/L</td>
</tr>
<tr>
<td><strong>Version</strong></td>
<td>06-Jun-1997 12:04</td>
</tr>
<tr>
<td><strong>Title</strong></td>
<td>Method ID: 23</td>
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<tr>
<td><strong>Sample</strong></td>
<td>Sample ID: CPC</td>
</tr>
<tr>
<td><strong>Sample ID</strong></td>
<td>CPC</td>
</tr>
<tr>
<td><strong>Entry type</strong></td>
<td>Fixed volume</td>
</tr>
<tr>
<td><strong>Volume [mL]</strong></td>
<td>5.0</td>
</tr>
<tr>
<td><strong>Molar mass M</strong></td>
<td>358.01</td>
</tr>
<tr>
<td><strong>Equivalent number z</strong></td>
<td>1</td>
</tr>
<tr>
<td><strong>Titration stand</strong></td>
<td>ST20A</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td>H2O</td>
</tr>
<tr>
<td><strong>Volume [mL]</strong></td>
<td>60.0</td>
</tr>
<tr>
<td><strong>Rinse</strong></td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Solvent</strong></td>
<td>H2O</td>
</tr>
<tr>
<td><strong>Volume [mL]</strong></td>
<td>20.0</td>
</tr>
<tr>
<td><strong>Conditioning</strong></td>
<td>No</td>
</tr>
<tr>
<td><strong>Temperature sensor</strong></td>
<td>Manual</td>
</tr>
<tr>
<td><strong>Stir Speed [%]</strong></td>
<td>30</td>
</tr>
<tr>
<td><strong>Stir Time [s]</strong></td>
<td>90</td>
</tr>
<tr>
<td><strong>EQP titration</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Titrant/Sensor</strong></td>
<td>Titrant SDS, Concentration 0.004 mol/L, Sensor Type: mV, Sensor DS500, Unit: mV</td>
</tr>
<tr>
<td><strong>Predispensing</strong></td>
<td>Mode: Volume, Volume 3.5 mL, Wait time 30 s</td>
</tr>
<tr>
<td><strong>Control</strong></td>
<td>Speed 30 %, Duration 90 s</td>
</tr>
<tr>
<td><strong>Titrant addition</strong></td>
<td>Dynamic, dE(set) 8 mV, dV(min) 0.02 mL, dV(max) 0.2 mL</td>
</tr>
<tr>
<td><strong>Measure mode</strong></td>
<td>Equilibrium controlled, dE</td>
</tr>
<tr>
<td><strong>Recognition</strong></td>
<td>Threshold 500.0 mV/mL, Steepest jump only: Yes, Range: Negative, Tendency: Negative</td>
</tr>
<tr>
<td><strong>Termination</strong></td>
<td>at maximum volume [mL]: 6.0, at potential: No, at slope: No, after number of EQPs: No</td>
</tr>
<tr>
<td><strong>Evaluation and recognition</strong></td>
<td>Procedure: Standard, Potential 1: No, Potential 2: No, Stop for reevaluation: Yes, Condition: neq=0</td>
</tr>
<tr>
<td><strong>Calculation</strong></td>
<td>Formula: ( R = \frac{m}{(V_{EQP} \cdot C)} ), Constant: ( C = 1/(\text{mL} \cdot z) ), Decimal places: 4, Result unit: Titer SDS, Result name: Titer SDS</td>
</tr>
<tr>
<td><strong>Report</strong></td>
<td>Output unit: Printer, Result: Yes, All results: Yes, Raw results: No, Table of measured values: Yes, Sample data: No, K - V curve: Yes</td>
</tr>
</tbody>
</table>

**Titration Excellence**

<table>
<thead>
<tr>
<th>001 Title</th>
<th>Titer SDS 0.004 mol/L</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample</strong></td>
<td>Number of IDs: 1, ID 1: CPC, Entry type: Fixed volume, Volume: 5.0 mL, Density: 1.0 g/mL, Correction factor: 1.0</td>
</tr>
<tr>
<td><strong>Temperature</strong></td>
<td>25.0°C</td>
</tr>
</tbody>
</table>

| 002 Sample (Titer) | Type: SDS, Concentration: 0.004 mol/L |

| 003 Titration stand (Manual stand) | Type: SDS, Concentration: 0.004 mol/L |

| 004 Stir | Speed: 30 %, Duration: 90 s |

| 005 Titration (EQP) | Titrant SDS, Concentration: 0.004 mol/L, Sensor: Type: mV, Sensor: DS500, Unit: mV |

| 006 Calculation | Result: Titer SDS, Formula: \( R = \frac{m}{(V_{EQP} \cdot C)} \), Constant: \( C = 1/(\text{mL} \cdot z) \), Decimal places: 4, Result unit: Titer SDS, Result name: Titer SDS |

| 007 Titer | Titrant SDS, Concentration: 0.004 mol/L, TITERS: Mean[R1], Limits: No |

| 008 Record | No |

| 009 End of sample | No |
The titer of sodium tetraphenylborate (Na-TPB) is determined by potentiometric titration in aqueous solution using silver nitrate as a primary standard. Silver tetraphenylborate is precipitated and the potential change is monitored by a surfactant sensitive electrode.

### Preparation and Procedures

- **Add 50 mL pH 4.75 acetate buffer into the titration beaker.**
- **Add 5 mL of the silver nitrate standard solution.**
- **Before starting it is recommended to condition the DS500 electrode by running a trial titration with silver nitrate and discard its result.**

**DS500 surfactant sensitive electrode (SSE):**
- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in Na-TPB solution for 20-30 min.

**Automation:**
A sample changer is used to fully automate the procedure. The titration stand can be cleaned using a conditioning beaker with acetate buffer.

**Acetate buffer 0.01 mol/L:**
- 1.0255 g sodium acetate is added to 125 mL 0.1 mol/L acetic acid in a 250 mL volum. flask.
- The buffer concentration is 0.1 mol/L. 50 mL of the 0.1 mol/L acetate buffer is diluted with deion. water in a 500 mL flask.

**Na-TPB Titrant:**
Adjust the pH to 9-10 with few drops of sodium hydroxide solution as a preservative.

### Remarks

- **After each titration the surfactant electrode and the reference electrode are dipped in a conditioning beaker on the sample changer with acetate buffer to clean them thoroughly.**
- **Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value.**
- **The auxiliary value H1 gives the concentration of the standard solution for titer determination.**

| Sample | 5 mL AgNO₃ aliquot  
c(AgNO₃) = 0.002 mol/L |
| Compound | Silver nitrate, AgNO₃  
M = 169.88;  z = 1 |
| Chemicals | 50 mL pH 4.75 acetate buffer solution |
| Titrant | Natrium tetraphenylborate, NaTPB  
NaB(C₆H₅)₄ , M = 342.22 g/mol  
c(NaTPB) = 0.004 mol/L adjusted to pH 9-10 |
| Standard | -- |
| Indication | DS500 SSE  
- InLab®Mono ref. electrode  
(electrolyte: 2 mol/L NaNO₃) |
| Chemistry | Ag⁺ + TPB⁻ = AgTPB |
| Calculation | Titer (DL5x)  
- R1 = m/(VEQ*c*C)  
- C = 1/(H1*z)  
- H1= concentration of AgNO₃ standard solution |
| Waste disposal | Filtration:  
The precipitate (AgTPB) has to be classified as special waste.  
The filtrate has to be neutralized with NaOH before final disposal. |
| Author, Version | P. Maurer/MSG Anachem,  
Nov 1997 / Revised Jan 2010 |
Instruments
- DL58 Titrator
- AT261 Balance

This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Sample Changer with pump.
- Titration beaker ME-101974.
- Printer

Results
Method  71007 Titer NaTPB 0.004mol/L  07-Nov-1997 16:14
Measured  08-Nov-1997  16:51
User  P. Maurer

ALL RESULTS

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgNO₃</td>
<td>R₁ = 0.90224 mL</td>
</tr>
<tr>
<td>2</td>
<td>AgNO₃</td>
<td>R₁ = 0.91740 mL</td>
</tr>
<tr>
<td>3</td>
<td>AgNO₃</td>
<td>R₁ = 0.90345 mL</td>
</tr>
<tr>
<td>4</td>
<td>AgNO₃</td>
<td>R₁ = 0.91734 mL</td>
</tr>
<tr>
<td>5</td>
<td>AgNO₃</td>
<td>R₁ = 0.90962 mL</td>
</tr>
<tr>
<td>6</td>
<td>AgNO₃</td>
<td>R₁ = 0.91361 mL</td>
</tr>
<tr>
<td>7</td>
<td>AgNO₃</td>
<td>R₁ = 0.91122 mL</td>
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<tr>
<td>8</td>
<td>AgNO₃</td>
<td>R₁ = 0.88365 mL</td>
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STATISTICS

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<tr>
<th>Number results</th>
<th>R₁</th>
<th>n = 7</th>
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<tbody>
<tr>
<td>Mean value</td>
<td>x = 0.91070 Titer NaTPB</td>
<td></td>
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<tr>
<td>Standard deviation</td>
<td>s = 0.00610 Titer NaTPB</td>
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<tr>
<td>Rel. standard deviation</td>
<td>s_rel = 0.669 %</td>
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</table>

Sample No. 8 deleted

TITRER

Titrant  NaTPB  0.004 mol/L
New titer  t = 0.90732

Titration curves
### Table of measured values

<table>
<thead>
<tr>
<th>Volume</th>
<th>Increment</th>
<th>Signal</th>
<th>Change</th>
<th>1st deriv.</th>
<th>Time</th>
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</thead>
<tbody>
<tr>
<td>mL</td>
<td>mL</td>
<td>mV</td>
<td>mV/mL</td>
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</tr>
<tr>
<td>ET1</td>
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<td>-32.3</td>
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<tr>
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<td>0.0200</td>
<td>0.0200</td>
<td>237.2</td>
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<td>0.0200</td>
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<tr>
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<td>0.0800</td>
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<tr>
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<td>-1.9</td>
<td>8:44</td>
</tr>
</tbody>
</table>

### Comments

- The DS500 Surfactant Sensitive Electrode has been developed for the titration of aqueous surfactant solutions only.
- Replace KCl with $2 \text{ M } \text{NaNO}_3$ when using NaTPB for the titration of nonionic surfactant, since the potassium cation $\text{K}^+$ forms a complex with TPB$^-\text{ anions}$.
- Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible results.
- The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.
- Conditioning is sometimes needed for the reference electrode due to diffusion of the sample into the electrode through the ceramic diaphragm. If necessary, replace the electrolyte.
- SSEs are suitable for low concentrations ($10^{-4} - 10^{-5} \text{ mol/L}$) in diluted solutions.
- Extreme pH-values, e.g. below pH 2, can damage the membrane of the surfactant sensitive electrode (operating working range of the DS500: pH 2-10).
- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.

### Principle:

- The potential of a solution containing surfactants is measured as a function of the titrant added.
- In the case of nonionic surfactants, addition of a specific activator prior to titration is necessary to form a complex between analyte and titrant. The activator is usually barium chloride, $\text{BaCl}_2$. The positively charged barium cation $\text{Ba}^{2+}$ forms a complex with the uncharged nonionic surfactant. As a result, the surfactant-barium cation complex is positively charged - a pseudocationic complex - and therefore can be precipitated by titration with sodium tetraphenylborate (Na-TPB).
Method

DL5x Titrator

Method 71007 Titer NaTPB 0.004 mol/L

Version 07-Nov-1997 16:14

Title

Method ID 71007

Title Titer NaTPB 0.004 mol/L

Date/time 07-Nov-1997 16:14

Sample

Sample ID AgNO3

Entry type Fixed volume

Volume [mL] 5.0

Molar mass M 169.88

Equivalent number z 1

Titration stand ST20A

Pump No

Rinse Yes

Solvent H2O

Volume [mL] 30.0

Conditioning Yes

Time [s] 90

Interval [s] 1

Rinse Yes

Solvent H2O

Volume [mL] 10.0

Temperature sensor Manual

Stir

Speed [%] 50

Time [s] 30

EQP titration

Titrant/Sensor

Titrant NaTPB

Concentration [mol/L] 0.004

Sensor SSE

Unit of meas. mV

Predispensing No

Titrant addition Dynamic

dE(set) [mV] 8.0

dV(min) [mL] 0.02

dV(max) [mL] 0.2

Measure mode Equilibrium controlled

x [mV] 0.5

t [s] 1.0

t(min) [s] 3.0

t(max) [s] 45.0

Equilibrium

Threshold 800.0

Steepest jump only Yes

Range No

Tendency Negative

Evaluation

Procedure Standard

Potential 1 No

Potential 2 No

Stop for reevaluation Yes

Condition = neq=0

Calculation

Formula R1=m/(VEQ*c*C)

Constant C=1/(cst*z)

Decimal places 5

Result unit mol/L

Result name Titer NaTPB

Statistics Yes

Titer Titrant NaTPB Concentration [mol/L] 0.004

Formula t = x

Report

Output unit Printer

Results Yes

All results Yes

Raw results No

Table of measured values Yes

Sample data No

K - V curve Yes

Titration Excellence

001 Title General titration

Compatible with T50 / T70 / T90

ID 71007

Title Titer NaTPB 0.004 mol/L

Author METTLER TOLEDO

Date/Time 01.01.2010 15:00:00

Modifed --

Modified by --

Protect No

SOP None

002 Sample (Titer)

Number of IDs 1

ID 1 AgNO3

Entry type Fixed volume

Volume 5.0 mL

Density 1.0 g/mL

Correction factor 1.0

Temperature 25.0°C

003 Titration stand (Manual stand)

Type Manual stand

004 Stir

Speed 30%

Duration 30 s

005 Titration (EQP) [1]

Titrant Titrant NaTPB

Concentration 0.004 mol/L

Sensor Type mV

Sensor DS500

Unit mV

Temperature acquisition No

Stir Speed 30%

Predispense Mode None

Wait time 0 s

Control

Control User

Titrant addition Dynamic

dE(set) 8 mV

dV(min) 0.02 mL

dV(max) 0.2 mL

Measure val. acquisition equilibrium controlled

dE 0.5 mV

dt 1.0 s

t(min) 3.0 s

t(max) 45.0 s

Evaluation and recognition

Procedure Standard

Threshold 800.0 mV/mL

Tendency Negative

Ranges 0

Add. EQP criteria No

Termination

At Vmax 4.0 mL

At potential No

At slope No

After number of recognized EQPs No

Combined termination criteria No

006 Calculation R1

Result Titer NaTPB

Result unit mol/L

Formula R1=m/(VEQ*c*C)

Constant C=1/(cst*z)

Decimal places 5

Result limits No

Record statistics Yes

Extra statistical func. No

Send to buffer No

007 Titer

Titrant NaTPB

Concentration [mol/L] 0.004

TITERS Mean[R1]

Limits No

008 Record No

009 End of sample
Potentiometric Titration: Anionic Surfactants in Liquid Detergents

The anionic surfactant content in various liquid detergents is determined by potentiometric titration in aqueous solution with Hyamine®1622 as a titrant. The potential change is monitored by a surfactant sensitive electrode.

### Preparation and Procedures

- Add 50 mL deionized water into the titration beaker.
- Add 10 mL of the liquid detergent solution.
- Before starting it is recommended to condition the DS500 electrode by running e.g. a trial titration with SDS or a sample, and discard its result.

**DS500 surfactant sensitive electrode (SSE):**
- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in e.g. 0.01 mol/L SDS solution for 20-30 minutes.

### Remarks

- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.
- The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.
- After each titration the surfactant electrode and the reference electrode are dipped in a beaker with water to clean them thoroughly.
- Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value. In this way, incorrect evaluations can be avoided.
- A sample changer can be used to fully automate the procedure. In this way, the sensors and the stirrer can be cleaned using a conditioning beaker.

### Literature

- See Application M610

### Sample

<table>
<thead>
<tr>
<th>Compound</th>
<th>Liquid detergents, 10 mL aliquot (stock solution: 5 g in 500 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemicals</td>
<td>50 mL deionized water</td>
</tr>
<tr>
<td>Titrant</td>
<td>Hyamine®1622, C_{27}H_{42}CINO_{2} c(Hyamine) = 0.01 mol/L</td>
</tr>
<tr>
<td>Standard</td>
<td>5 mL 0.01 mol/L SDS</td>
</tr>
</tbody>
</table>
| Indication | - DS500 SSE  
  - InLab®Mono ref. electrode (electrolyte: 3 mol/L KCl) |
| Chemistry | Simplified scheme:  
  C_{27}H_{42}NO_{2}^+ + C_{12}H_{25}O_{4}S^- =  
  C_{27}H_{42}NO_{2}-C_{12}H_{25}O_{4}S |
| Calculation | Content (DL5x)  
  - R1 = (Q*C)/(m*10/500)  
  - C = M/(10*z)  
  The factor 10/500 takes into account the dilution of the liquid detergent amount m = 5 g in 500 mL vol. flask and the aliquot size (10 mL). |
| Waste disposal | Special treatment is not necessary |
| Author, Version | D. Rehwald/C. De Caro/P. Maurer/MSG  
  April 1997 / Revised January 2010 |
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974.
- Printer

Results

Method  702  Tenside/Anionische  02-Apr-1997  8:50  
Measured  02-Apr-1997  9:20  
User  rd  

ALL RESULTS

No.  ID  Sample size and results

1  Liq. Det. 1  5.0621 g  
   R1 = 9.142 mmol/L  Tensid  
   R2 = 17.689 % AT  mittl.M=387  

2  Liq. Det. 1  5.0621 g  
   R1 = 8.967 mmol/L  Tensid  
   R2 = 17.350 % AT  mittl.M=387  

3  Liq. Det. 1  5.0621 g  
   R1 = 8.915 mmol/L  Tensid  
   R2 = 17.250 % AT  mittl.M=387  

4  Liq. Det. 1  5.0621 g  
   R1 = 9.046 mmol/L  Tensid  
   R2 = 17.504 % AT  mittl.M=387  

5  Liq. Det. 1  5.0621 g  
   R1 = 8.189 mmol/L  Tensid  
   R2 = 15.845 % AT  mittl.M=387  

STATISTICS

Number results  R1  n = 4  
Mean value  x = 9.017 mmol/L  Tensid  
Rel. standard deviation  srel = 1.096 %  
Sample No. 5 deleted  

STATISTICS

Number results  R2  n = 4  
Mean value  x = 17.448 %  AT  mittl.M=387  
Standard deviation  s = 0.19131 %  AT  mittl.M=387  
Rel. standard deviation  srel = 1.096 %  
Sample No. 5 deleted  

Titration curves

![Graph showing titration curves for liquid detergent 1]
### Nominal value
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.

### Remarks
- Stock solutions of the liquid detergents:
  - Addition of 20-50 mL methanol to the stock solution of the different liquid detergents (stock solution: 5 g in a 500 mL flask, diluted with water) decreases foaming of the solution.
  - Caution: Do not add more than 20-50 mL methanol to the stock solution since organic solvents damage the membrane of the surfactant electrode.

- The anionic content AT in unknown samples can be expressed as sodium laurylsulphate (SDS).

- Each sample must be tested to obtain the optimal method parameters. It is recommended to first perform a titration without termination after the first equivalence point to obtain the whole titration curve. In this way, the appropriate parameters (threshold, evaluation,...) can be selected.

- In the case of unknown sample or of formulated products:
  - a) first perform a calibration titration on a standard solution of known composition (reference value),
  - b) then compare the reference value with the result obtained by titrating the sample.

### Additional results

<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>srel (%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid detergent 1</td>
<td>Average molar mass: M = 387 Fatty alcohol ether sulfate Secondary alkanesulfonate Cocamidopropylbetaine</td>
<td>18.0</td>
<td>17.1 pH 3</td>
<td>6</td>
<td>17.27 pH 3</td>
<td>0.639</td>
<td>Method 702 INC: 0.1 mL Threshold: 100 mV/mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10.0</td>
<td></td>
<td></td>
<td>17.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td></td>
<td></td>
<td>17.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>2.0</td>
<td></td>
<td></td>
<td>17.27</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 2</td>
<td>Average molar mass: M = 362 Fatty alcohol ether sulfate Secondary alkanesulfonate Cocamidopropylbetaine Nonionics (7 EO, M=520)</td>
<td>38.5</td>
<td>32.8 pH 3</td>
<td>6</td>
<td>34.13 pH 3</td>
<td>0.401</td>
<td>Predispensing: 5 mL Wait time: 30 s DYN: 10 mV, 0.005-0.2 mL EQU: 0.5/1 mV/s, 5-30 s Threshold: 100 mV/mL Max. volume: 12 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11.0</td>
<td></td>
<td></td>
<td>34.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.0</td>
<td></td>
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<td>34.13</td>
<td></td>
<td></td>
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<td></td>
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<td>3.5</td>
<td></td>
<td></td>
<td>34.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.0</td>
<td></td>
<td></td>
<td>34.13</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 3</td>
<td>Average M=353.09 Anionics A, M=346 Anionics B, M=385</td>
<td>33.0</td>
<td></td>
<td>6</td>
<td>33.85 pH 1-2</td>
<td>1.23</td>
<td>Stir: 50%, 30 s c(CPC) = 0.004 mol/L INC: 0.25 mL, TFIX: 8 s Thres.: 60, max. vol.: 6 mL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid detergent 4</td>
<td>Anionics as SDS, M=288.38 Lit.: 15-30 Anionics A, M=346 Anionics B, M=385</td>
<td>14.18 pH 1-2</td>
<td>10</td>
<td>15.25 (n)</td>
<td>0.951</td>
<td>c(Hyamine) = 0.004 mol/L Stir: 50%, 30 s Predisposing: 5 mL, wait time: 30 s DYN: 6 mV, 0.1-0.5 mL EQU: 0.25/1 mV/s, 2-20 s Threshold: 50 mV/mL</td>
<td></td>
</tr>
</tbody>
</table>
### Table of measured values

Not available

### Additional samples

#### Recovery tests with standard solutions:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Number of samples</th>
<th>Concentration mol/L</th>
<th>Recovery %</th>
<th>srel %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard solution 1 CPC, c(CPC) = 0.004 mol/L</td>
<td>6</td>
<td>0.0040</td>
<td>100.62</td>
<td>0.728</td>
</tr>
<tr>
<td>Standard solution 2 SDS, c(SDS) = 0.004 mol/L</td>
<td>6</td>
<td>0.0040</td>
<td>99.95</td>
<td>0.746</td>
</tr>
<tr>
<td>Standard solution 3 SDS, c(SDS) = 0.01 mol/L</td>
<td>5</td>
<td>0.010</td>
<td>100.00</td>
<td>0.220</td>
</tr>
<tr>
<td>Standard solution 4 SDS, c(SDS) = 0.05 mol/L</td>
<td>5</td>
<td>0.052</td>
<td>104.00</td>
<td>3.541</td>
</tr>
</tbody>
</table>

**Comments:**

- Note that at higher concentrations, the recovery is increasing and the repeatability (expressed as relative standard deviation, srel) is worse. This is most probably due to the fact that we have exceeded the critical micelle concentration cmc of SDS in pure water (cmc(SDS) : 0.0082 mol/L, 25°C). Thus, micelle formation affects the precipitation reaction during titration.

**Literature:**

**Method**

**DLs5 Titrator**

**Method** 702  Tenside/Anionische

**Version** 02-Apr-1997 8:50

**Title**

Method ID .................................. 702

Title ...................................... Tenside/Anionische

**Date/time** 02-Apr-1997 8:50

**Sample**

Sample ID .................................. Liq Det. 1

Entry type ......................... Weight

Lower limit [g] ................ 4.0

Upper limit [g] ................ 6.0

Molar mass M ....................... 387

Equivalent number z ................ 1

**Titration stand** Stand 1

**Temperature sensor** Manual

**Stir**

Speed [%] .......................... 40

Time [s] ........................... 120

**EQP titration**

**Titrant/Sensor**

Titrant ........................ Hyamine

Concentration [mol/L] .......... 0.01

Sensor ......................... SSE

Unit of meas. .................. mV

Predispensing ...................... No

Titrant addition ................... DYN

\[E(\text{set})\] ........................ 6.0

\[V(\text{min})\] [mL] ............... 0.005

\[V(\text{max})\] [mL] ............... 0.1

Measure mode ................... Equilibrium controlled

\[t\] [s] .......................... 1.0

\[t(\text{min})\] [s] ............... 1.0

\[t(\text{max})\] [s] ............... 1.0

**Recognition**

Threshold ...................... 100.0 mV/mL

Steepest jump only ............. Yes

Range .......................... No

Tendency ....................... Positive

Termination at maximum volume [mL] .......................... 7.0

at potential ....................... No

at slope .......................... No

after number EQPs No

comb. Termination criteria .......

**Evaluation**

Procedure ......................... Standard

Potential 1 .......................... 0

Potential 2 .......................... 0

Stop for reevaluation Yes

Condition = .............. _=0

**Calculation**

Formula .......................... R1=Q*C/m

Constant .................. C=1000

Decimal places ............... 3

Result unit ....................... mmol/L

Result name ........................ Tensid

**Statistics** .......................... Yes

**Calculation**

Formula .......................... R2=(Q*C2)/(m*10/500)

Constant .................. C2=M/[10*z]

Decimal places ............... 3

Result unit ....................... % AT

Result name ........................ mittl.M=387

**Statistics** .......................... Yes

**Report**

Output unit .......................... Printer

Results .......................... Yes

All results ......................... Yes

Raw results ...................... Yes

Table of measured values ........ Yes

Sample data ......................... No

K - V curve ......................... Yes

\[dE/dV - V\] curve ............... No

\[dE/dV - V\] curve ............... No

log \[dE/dV - V\] curve ................. No

K - t curve .......................... No

V - t curve .......................... No

\[dV/dt - t\] curve ............... No

**Titration Excellence**

**001 Title**

Type ......................... General titration

Compatible with T50 / T70 / T90

ID .......................... 702

Title .......................... Tenside/Anionische

Author ......................... METTLER TOLEDO

Date/Time 01.01.2010 15:00:00

Modified --

Modified by --

Protect No

SOP None

**002 Sample (Titer)**

Number of IDs .......................... 1

ID .......................... Liq Det. 1

Entry type ......................... Weight

Lower limit [g] ................ 4.0 g

Upper limit [g] ................ 6.0 g

Density ....................... 1.0 g/mL

Correction factor 1.0

Temperature ....................... 25.0°C

**003 Titration stand (Manual stand)**

Type ......................... Manual stand

**004 Stir**

Speed [\%] .......................... 40\%

Duration ....................... 120 s

**005 Titration (EQP) [1]**

**Titrant**

Titrant ........................ Hyamine 1622

Concentration [mol/L] .......... 0.01

Sensor ......................... mV

Type ......................... SSE

Unit ....................... mV

Temperature acquisition .......

Stir ..........................

Speed .......................... 40\%

Predispensing .................

Mode .......................... None

Wait time .......................... 0 s

**Control**

Control .......................... User

Titrant addition ................... Dynamic

\[dE(\text{set})\] ............... 6.0 mV/mL

\[dV(\text{min})\] ............... 0.005 mL

\[dV(\text{max})\] ............... 0.1 mL

Meas. val. acquisition ...........

Temperature acquisition .......

**006 Calculation R1**

Result .......................... Tensid

Result unit ........................ mmol/L

Formula .......................... R1=Q*C/m

Constant .......................... C=1000

Dec. places ........................ 3

**007 Calculation R2**

Result .......................... Content AT

Result unit ........................ % AT

Formula .......................... R2=(Q*C2)/(m*10/500)

Constant .................. C2=M/[10*z]

Dec. places ........................ 3

**008 Record**

...
Potentiometric Titration of Nonionic Surfactants in Raw Materials

The content of nonionic surfactants in raw materials is determined by potentiometric titration in aqueous solution with sodium tetraphenylborate (Na-TPB). The potential change is monitored by a surfactant sensitive electrode.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 mL aliquot from raw material stock solution (10 in 1 L)</th>
</tr>
</thead>
</table>
| Compound | Ethoxylated nonionic surfactants, (fatty alcohol C10/C14 with 6 EO groups)  
EO: ethylene oxide unit, -(CH₂-CH₂-O)ₙ-  
EO: ethylene oxide unit, -(CH₂-CH₂-O)ₙ-  
EO: ethylene oxide unit, -(CH₂-CH₂-O)ₙ- |
| Chemicals | - 10 mL BaCl₂ 0.1 mol/L  
- 5 mL PVA solution  
- 40 mL deionized water  
- 40 mL deionized water  
- 40 mL deionized water |
| Titrant | Natrium tetraphenylborate, NaTPB  
NaB(C₆H₅)₄, M = 342.22 g/mol  
c(NaTPB) = 0.0203 mol/L adjusted to pH 9-10 |
| Standard | Triton N101  
C₉H₁₉-C₆H₄-(OCH₂CH₂)x-OH  
x= 9-10  
Average M: 636.86, z=1 |
| Indication | - DS500 SSE  
- InLab® Mono ref. electrode  
(electrolyte: 2 mol/L NaNO₃) |
| Chemistry | Simplified scheme:  
1. Activation:  
NIO + x Ba²⁺ = (Ba-NIO)₂⁺  
2. Titration:  
(Ba-NIO)₂⁺ + y B(C₆H₅)₄⁺ = (x Ba-NIO)⁻[(B(C₆H₅)₄)₀]y |
| Calculation | 1) Factor determination (DL5x)  
- \( R_1 = \frac{C_1 \times m}{R_1} \) (mg/mL)  
\( C_1 = 2.55157 \) g/L  
2) Sample recovery (DL5x)  
- \( R_1 = \text{VEQ} \) (mL)  
- \( R_2 = \frac{(H_3^+R_1^+100)}{50} \), (%) |
| Waste disposal | Disposal as inorganic metal ion solutions. |
| Author, Version | D. Rehwald, C. De Caro / MSG,  
June 1997 / Revised Jan 2010 |

Preparation and Procedures

- Since the titration reaction is not stoichiometric the titration of nonionic surfactants is based on a comparative titration with a standard solution. This gives a calibration factor \( f \) i.e. the titrant consumption per amount of sample in mg/mL. Subsequently this factor is used in the sample titration calculation.
- Factor and sample titrations:  
5 mL aliquot is added into the titration beaker, and diluted with 40 mL deionized water.  
10 mL 0.1 M BaCl₂ is added to activate the sample, and 5 mL PVA solution is added to achieve a finely dispersed precipitate.
- Before starting it is recommended to condition the DS500 electrode by running a trial titration with the sample and discard its result.
- After each sample, the sensor, the titration tube and the stirrer are thoroughly cleaned using a beaker with deionized water

DS500 surfactant sensitive electrode (SSE):
- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in Na-TPB solution for 20-30 min.

Polyvinyl alcohol (PVA) solution:
Dissolve 3-4 g PVA in ca. 250 mL warm water, and allow the solution to cool down before addition.

Na-TPB Titrant:
Adjust the pH to 9-10 with few drops of sodium hydroxide solution as a preservative.

Remarks

The method parameters have been optimized for the sample of this application. It may be necessary to adapt the method to your specific sample.
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974.
- Sample Changer with peristaltic pump
- Printer

Results

**Calibration factor, method 33 f / Calibration with Triton N101**

<table>
<thead>
<tr>
<th>Method</th>
<th>Factor NioT</th>
<th>Measured</th>
<th>User</th>
<th>rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 f</td>
<td></td>
<td>04-Jun-1997 12:10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33 f</td>
<td>Factor NioT</td>
<td>04-Jun-1997 12:10</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ALL RESULTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 8.48712  mg/mL Factor</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 8.47601  mg/mL Factor</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 8.78171  mg/mL Factor</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 8.97446  mg/mL Factor</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 9.00326  mg/mL Factor</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>TritonN101</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 8.86509  mg/mL Factor</td>
<td></td>
</tr>
</tbody>
</table>

**STATISTICS**

<table>
<thead>
<tr>
<th>Number results</th>
<th>R1</th>
<th>n = 6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x</td>
<td>8.79704</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s</td>
<td>0.19540</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel</td>
<td>2.221</td>
</tr>
</tbody>
</table>

**Auxiliary value**

| New value | H3 | 8.79704 | Factor NioT |

Content determination, Method 33 g / Titration of NIO Sample A

<table>
<thead>
<tr>
<th>Method</th>
<th>Content NioT</th>
<th>Measured</th>
<th>User</th>
<th>rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>33 g</td>
<td>Content NioT</td>
<td>05-Jun-1997 9:09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33 g</td>
<td>Content NioT</td>
<td>05-Jun-1997 9:09</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**ALL RESULTS**

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Nio Sample A</td>
<td>5.0 mL</td>
</tr>
<tr>
<td></td>
<td>R1 = 5.58600  mL Cons. TM</td>
<td></td>
</tr>
<tr>
<td></td>
<td>R2 = 100.040 % Content</td>
<td></td>
</tr>
</tbody>
</table>

**Statistics**

<table>
<thead>
<tr>
<th>Number results</th>
<th>R2</th>
<th>n = 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean value</td>
<td>x</td>
<td>96.852</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>s</td>
<td>0.84851</td>
</tr>
<tr>
<td>Rel. standard deviation</td>
<td>srel</td>
<td>0.876</td>
</tr>
</tbody>
</table>

Sample No. 1 deleted
Sample No. 5 deleted
### Titration curves

**Table of measured values**

**Calibration factor (Method 33 f)**

<table>
<thead>
<tr>
<th>Volume</th>
<th>Increment</th>
<th>Signal</th>
<th>Change</th>
<th>1st deriv.</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>mL</td>
<td>mL</td>
<td>mV</td>
<td>mV</td>
<td>mV/mL</td>
<td>min:s</td>
</tr>
<tr>
<td>ET1</td>
<td>0.0000</td>
<td>121.6</td>
<td>-0.1</td>
<td>-4.3</td>
<td>0:03</td>
</tr>
<tr>
<td></td>
<td>0.0150</td>
<td>0.0150</td>
<td>121.5</td>
<td>-0.1</td>
<td>0:06</td>
</tr>
<tr>
<td></td>
<td>0.0300</td>
<td>0.0150</td>
<td>121.4</td>
<td>-0.1</td>
<td>0:10</td>
</tr>
<tr>
<td></td>
<td>0.0600</td>
<td>0.0300</td>
<td>121.2</td>
<td>-0.2</td>
<td>0:13</td>
</tr>
<tr>
<td></td>
<td>0.1200</td>
<td>0.0600</td>
<td>121.0</td>
<td>-0.3</td>
<td>0:17</td>
</tr>
<tr>
<td></td>
<td>0.2400</td>
<td>0.1200</td>
<td>120.3</td>
<td>-0.7</td>
<td>0:20</td>
</tr>
<tr>
<td></td>
<td>0.3900</td>
<td>0.1500</td>
<td>119.1</td>
<td>-1.2</td>
<td>0:24</td>
</tr>
<tr>
<td></td>
<td>0.5400</td>
<td>0.1500</td>
<td>117.5</td>
<td>-1.6</td>
<td>0:28</td>
</tr>
<tr>
<td></td>
<td>0.6900</td>
<td>0.1500</td>
<td>114.3</td>
<td>-3.2</td>
<td>0:33</td>
</tr>
<tr>
<td></td>
<td>0.8400</td>
<td>0.1500</td>
<td>109.1</td>
<td>-5.2</td>
<td>0:41</td>
</tr>
<tr>
<td></td>
<td>0.9660</td>
<td>0.0300</td>
<td>104.7</td>
<td>-4.5</td>
<td>0:47</td>
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**Sample content (Method 33 g)**

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The DS500 Surfactant Sensitive Electrode has been developed for the titration of aqueous surfactant solutions only.

Replace KCl with 2 M NaNO₃ when using NaTPB for the titration of nonionic surfactant, since the potassium cation K⁺ forms a complex with TPB⁻ anions.

Conditioning of SSEs prior to titration is needed to achieve accurate and reproducible results.

The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.

Conditioning is sometimes needed for the reference electrode due to diffusion of the sample into the electrode through the ceramic diaphragm. If necessary, replace the electrolyte.

SSEs are suitable for low concentrations (10⁻⁴ - 10⁻⁵ mol/L) in diluted solutions.

Extreme pH-values, e.g. below pH 2, can damage the membrane of the surfactant sensitive electrode (operating working range of the DS500: pH 2-10).

The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.

Calibration factor (method 33 f):

An aliquot of a standard solution of known concentration C is titrated according to method 33 f. C is the concentration of the standard solution, in this case C=2.55157 g/L.

As a standard, the nonionic surfactant Triton N101 was selected.

From the titrant consumption VEQ and the known concentration, a factor f is determined and stored as auxiliary value H3. This is taken into account in the titration method 33 g for the sample content determination (see next page).

Content determination (method 33 g):

To obtain the content value in %, the titrant consumption must be:

1. multiplied by the calibration factor f stored as H3, and
2. subsequently divided by the sample size m.

R2 gives the nonionic surfactant content of the raw material of the sample expressed as Triton N101 (see method 33 f).

Titration technique:

Samples of unknown composition are measured and compared against a reference nonionic surfactant, e.g. Triton N101 or nonylphenol ethoxylate with 10 EO (1 EO: -CH₂-CH₂-O⁻).

Always take the same sample volume for both methods 33 f (factor) and 33 g (content). Choose the sample volume to get a titrant consumption of about 5 mL for a 10 mL burette.

First run a titration with termination at maximum volume to record the whole titration curve. In this way, the parameters and the evaluation procedure of the method can easily be optimized.

Principle of the precipitation titration:

In the case of nonionic surfactants, addition of a specific activator prior to titration is necessary to form a complex between analyte and titrant. The activator is usually barium chloride, BaCl₂.

The positively charged barium cation Ba²⁺ forms a complex with the uncharged nonionic surfactant. As a result, the surfactant-barium cation complex is positively charged -a pseudocationic complex- and therefore can be precipitated by titration with sodium tetraphenylborate (Na-TPB).
## Method

**DL5x Titrator**

### Title

- **Method** .......................... 33 f
- **Factor NioT**

### Sample

- **Sample ID** .......................... TritonN101
- **Entry type** .......................... Fixed volume
- **Volume [mL]** .................... 5.0
- **Molar mass M** ....................... 1
- **Equivalent number x** .................. 1

### Titration stand

- **Pump** ........................... No
- **Solvent** ................... Yes
  - **Volume [mL]** ............... 40.0
- **Rinse** .......................... No
- **Solvent** .................. H 2O
  - **Volume [mL]** ............... 10.0
- **Conditioning** ................. Yes
  - **Time [s]** .................. 60
  - **Interval [s]** .............. 1
- **Rinse** .......................... Yes
  - **Solvent** .................. H 2O
  - **Volume [mL]** ............... 10.0

### Stir

- **Speed [%]** .......................... 35
- **Time [s]** ........................... 90

### EQP titration

#### Titrant/Sensor

- **Titrant** .......................... NaTPB
- **Concentration [mol/L]** .......... 0.0203

#### Stir

- **Speed** ........................... 35%
- **Duration** ....................... 90 s

### Calculation

- **Result** .......................... Factor NioT
  - **Formula** ........................... R=C*m/VEQ
  - **Constant** ........................... C=2.55157
  - **Decimal places** .................. 5

### Auxiliary value

- **ID** ................................. Factor NioT
  - **Formula** ........................... H=x

### Report

- **Output unit** ....................... Printer
- **Results** .......................... Yes
- **All results** .......................... Yes
- **Raw results** .......................... No
- **Table of measured values** .......... Yes
- **Sample data** .......................... No
- **E - V curve** .......................... Yes

### Titration Excellence

#### 001 Title

- **Type** .......................... General titration
- **Compatible with** .................. T50 / T70 / T90
- **ID** .......................... 33 f
- **Title** .......................... Factor NioT
- **Author** .......................... METTLER TOLEDO
- **Date/Time** ....................... 01.01.2010  15:00:00
- **Modified** .......................... --
- **Modified by** .......................... --
- **Protect** .......................... No

#### 002 Sample (Titer)

- **Number of IDs** .................... 1
- **ID 1** .......................... TritonN101
- **Entry type** .......................... Fixed volume
- **Volume** .......................... 5.0 mL
- **Density** .......................... 1.0 g/mL
- **Correction factor** .................. 1.0
- **Temperature** ....................... 25.0°C

#### 003 Titration stand (Manual stand)

- **Type** .......................... Manual stand

#### 004 Stir

- **Speed** ........................... 35%
- **Duration** ....................... 90 s

#### 005 Titration (EQP) [1]

##### Titrant

- **Type** .......................... NaTPB
- **Sensor** ................... SSE
  - **Unit** .................. mV
- **Temperature acquisition** ........ No

##### Stir

- **Speed** ........................... 30%
- **Wait time** ....................... 0 s

##### Control

- **Mode** .......................... None
- **Predispense** .......................... None
- **Wait time** ....................... 0 s

##### Titrant addition

- **dE(set) [mV]** .................... 6.0
- **dV(min) [mL]** .................... 0.015
- **dV(max) [mL]** .................... 0.15
- **Meas. val. acquisition** .......... Equilibrium controlled

##### Evaluation and recognition

- **Threshold** ....................... 500 mV/mL
- **Tendency** ....................... Negative
- **Ranges** .......................... 0
- **Add. EQP criteria** ............... No

##### Termination

- **At Vmax** ....................... 5.0 mL
- **At potential** .......................... No
- **At slope** .......................... No
- **After number of recognized EQPs** .......... No
- **Combined termination criteria** ...... No

#### 006 Calculation R1

- **Result** .......................... Factor NioT
- **Result unit** ....................... mg/mL

#### 007 Auxiliary value

- **Name** .......................... Factor NioT
  - **Formula** ........................... H=Mean[R1]

#### 008 Record

- **Send to buffer** ....................... No

#### 009 End of sample
**Titration Application**

### Method Information

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### Stir Information

- **Speed [s]**: 35.0
- **Time [s]**: 90

### EQP Titration Information

- **Titrant/Sensor**: NaTPB
- **Concentration [mol/L]**: 0.0203
- **Sensor**: SSE
- **Unit of meas. [mV]**: No
- **Predispersing**: No
- **Titrant addition**: Dynamic
  - dV(set) [mL]: 6.0
  - dV(min) [mL]: 0.035
  - dV(max) [mL]: 0.15
- **Measure mode**: Equilibrium controlled
  - t [s]: 0.5
  - t(min) [s]: 4.0
  - t(max) [s]: 10.0
- **Threshold**: 45.0
- **Range**: No
- **Tendency**: Negative
- **Correction factor**: 1.0
- **Density**: 1.0 [g/mL]
- **Correction factor**: 1.0
- **Volume**: 5.0 [mL]
- **Entry type**: Fixed volume
- **ID**: 1
- **Sample ID**: Nio Sample A
- **Sample content**: 33 g
- **Date/Time**: 01.01.2010 15:00:00
- **Modified by**: --
- **Modified**: --
- **Protect**: No

### Calculation Information

- **Formula**: R2=(H3*R1*100)/50
- **Decimal places**: 5

### Report Information

- **Output unit**: Printer
- **Results**: Yes
- **All results**: Yes
- **Raw results**: Yes
- **Table of measured values**: Yes
- **Sample data**: No
- **E - V curve**: Yes

### Titration Excellence

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### Sample (Titration)

- **Number of IDs**: 1
  - **ID**: 1
  - **Sample ID**: Nio Sample A
  - **Volume [mL]**: 5.0
  - **Density [g/mL]**: 1.0
  - **Correction factor**: 1.0
  - **Temperature**: 25.0°C

### 003 Titration Stand (Manual stand)

- **Type**: Manual stand

### 004 Stir

- **Speed**: 35.0
- **Duration**: 90 s

### 005 Titration (EQP) [1]

- **Titrant**: NaTPB
- **Concentration [mol/L]**: 0.0203
- **Sensor**: wV
- **Unit**: wV

### Temperature acquisition

- **Temperature acquisition**: No

### Evaluation and recognition

- **Procedure**: Standard
- **Threshold**: 45 [mV/mL]
- **Tendency**: Negative
- **Ranges**: 0
- **Add. EQP criteria**: No
- **Termination**: At Vmax: 6.5 mL, At potential: No, At slope: No, After number of recognized EQPs: No, Combined termination criteria: No

### 006 Calculation R1

- **Result**: Cons. TM
- **Result unit**: mL
- **Formula**: R = R²
- **Constant**: 0.1
- **M [mol/L]**: M [None]
- **z [None]**: z [None]
- **Decimal places**: 5

### 007 Calculation R2

- **Result**: Content
- **Result unit**: %
- **Formula**: R2 = R2
- **Constant**: 0.1
- **M [mol/L]**: M [None]
- **z [None]**: z [None]
- **Decimal places**: 3

### 008 Record

- **...**

### 009 End of sample

---

**Page 6 of 6**

METTLER TOLEDO

Page 6 of 6

Titration Application M614-2010
Potentiometric Titration of a Betaine in Shampoo

The content of the amphoteric surfactant cocoamidopropylbetaine in shampoo is determined by potentiometric titration in nonaqueous solution with methanolic potassium hydroxide. The potential change is monitored by a combined pH glass electrode with nonaqueous electrolyte.

**Preparation and Procedures**
- Approx. 1 g shampoo is added into the titration beaker.
- 10 mL methanol is added to the sample beaker.
- 50 mL acetone/isopropanol 4:1 (v/v) is added to the beaker.
- The sample solution is acidified with 3 mL $0.5 \text{ mol/L HCl}$.

**Remarks**
- Betaines are protonated by adding an excess of HCl (Protonation of the carboxylic group, COOH). The protonated compound can be titrated with a strong base, in a similar way as an acid/base titration.
- Usually, formulated products and concentrated raw materials contain additional components which can not be distinguished and therefore they are titrated together.
- For this reason, a non-aqueous solvent is used to differentiate the different components. This titration leads to three equivalence points:
  1. EQP1: Neutralization of excess HCl
  2. EQP2: Titration of betaine ($Q_2$)
  3. EQP3: Titration of additional components
- Due to the quite low threshold value an appropriate threshold must be selected for different samples. Too low value leads to the recognition of fake equivalence points.

**Literature**:
- N. Buschmann, H. Wille «Titration of amphoteric surfactants - a comparison of methods», Atti delle 7$^{\text{a}}$ Giornate CID (Conference Proceedings), Comitato Italiano dei Derivati Tensioattivi, Genova, Italy, 22-24.10.97, and references therein:
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974.
- Sample Changer with peristaltic pump
- Printer

Results

METTLER TOLEDO DL58 Titrator V2.0 Application Laboratory 002

Method 61009 Betaine nonaq. solvent 27-Nov-1997 17:56
Measured 27-Nov-1997 19:05
User P. Maurer

RESULTS

No. ID Sample size and results
1 Cosmed 0.8688 g R1 = 4.027 % Content
2 Cosmed 0.9932 g R1 = 4.201 % Content
3 Cosmed 1.0078 g R1 = 4.287 % Content
4 Cosmed 0.8936 g R1 = 3.603 % Content
5 Cosmed 1.0348 g R1 = 4.236 % Content

STATISTICS

Number results R1 n = 4
Mean value x = 4.188 % Content
Standard deviation s = 0.11264
Rel. standard deviation srel = 2.690 %
Sample No. 4 deleted

Titration curves

1. EQP: Neutralization of excess HCl
2. EQP: Betaine
3. EQP: Neutralization of additional acid components
Table of measured values

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<tr>
<th>Volume</th>
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<th>Change</th>
<th>1st deriv.</th>
<th>Time</th>
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</tr>
<tr>
<td>. . . .</td>
<td>. . .</td>
<td>. . .</td>
<td>. . .</td>
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</tr>
<tr>
<td>16.6240</td>
<td>0.0360</td>
<td>106.1</td>
<td>-8.5</td>
<td>-235.1</td>
<td>5:59</td>
</tr>
<tr>
<td>16.6550</td>
<td>0.0310</td>
<td>98.8</td>
<td>-7.3</td>
<td>-235.6</td>
<td>6:06</td>
</tr>
<tr>
<td>EQP2</td>
<td>16.6880</td>
<td>0.0330</td>
<td>90.1</td>
<td>-8.7</td>
<td>-262.4</td>
</tr>
<tr>
<td>16.7180</td>
<td>0.0300</td>
<td>82.7</td>
<td>-7.4</td>
<td>-247.7</td>
<td>6:21</td>
</tr>
<tr>
<td>16.7520</td>
<td>0.0340</td>
<td>74.0</td>
<td>-8.7</td>
<td>-256.6</td>
<td>6:29</td>
</tr>
<tr>
<td>. . . .</td>
<td>. . .</td>
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<td>. . .</td>
<td>. . .</td>
<td>. . .</td>
</tr>
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<td>17.7090</td>
<td>0.0300</td>
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<td>-13.4</td>
<td>-448.0</td>
<td>9:44</td>
</tr>
<tr>
<td>17.7390</td>
<td>0.0300</td>
<td>-123.6</td>
<td>-14.5</td>
<td>-482.5</td>
<td>10:01</td>
</tr>
<tr>
<td>17.7690</td>
<td>0.0300</td>
<td>-148.5</td>
<td>-24.9</td>
<td>-831.5</td>
<td>10:25</td>
</tr>
<tr>
<td>EQP3</td>
<td>17.7990</td>
<td>0.0300</td>
<td>-199.3</td>
<td>-50.8</td>
<td>-1693.0</td>
</tr>
<tr>
<td>17.8290</td>
<td>0.0300</td>
<td>-244.5</td>
<td>-45.2</td>
<td>-1505.6</td>
<td>11:22</td>
</tr>
<tr>
<td>. . . .</td>
<td>. . .</td>
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<td>. . .</td>
<td>. . .</td>
<td>. . .</td>
</tr>
<tr>
<td>20.0000</td>
<td>0.1560</td>
<td>-359.7</td>
<td>-1.7</td>
<td>-11.2</td>
<td>13:14</td>
</tr>
</tbody>
</table>

Comments

- Conditioning of the combined pH glass electrode before titration is recommended in order to get accurate and precise results.
- The electrode can be conditioned in deionized water, and also by running a test sample titration. The result of the test titration is discarded.
- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.
**Method**

**DL5x Titrator**

**Method 61009**

Betaine nonaq. solvent

**Version**

27-Nov-1997 17:56

**Title**

Method ID .................. 61009

Title .............................. Betaine nonaq. solvent

**Date/time**

27-Nov-1997 17:56

**Sample**

Sample ID .................. Cosmed

Entry type ......................... Weight

Lower limit [g] ........ 0.8

Upper limit [g] ........ 1.2

Molar mass M ................... 372

Equivalent number n ................ 1

**Titration stand**

ST20A

Pump ........................... No

Rinse .......................... Yes

Solvent ................... H2O

Volume [mL] ............... 20.0

**Conditioning**

No

**Temperature sensor**

Manual

**Stir**

Speed [%] .......................... 50

Time [s] ........................... 30

**EQP titration**

Titrant/Sensor

Titrant .................. KOH in MeOH

Concentration [mol/L] .......... 0.1

Sensor ......................... DGi113

Unit mV

Predispensing ...................... to volume

Volume [mL] ............... 5

Molarity [m] .................. 1

Wait time [s] .................. 0

Control

Speed 30%

Predispense

Mode Volume

Volume 5 mL

Wait time 0 s

**Evaluation and recognition**

Procedure Standard

Threshold 70 mV/mL

Tendency Negative

Ranges 0

Stop for reevaluation Yes

Condition = neq=0

**Calculation**

Formula ...................... \( R=Q2 \times C/m \)

Constant ......................... \( C=M/(10 \times z) \)

Decimal places ................... 3

Result unit ......................... Printer

Result name ......................... Content

Statistics ......................... Yes

Report

Output unit ......................... Printer

Results ......................... Yes

All results ......................... Yes

Raw results ......................... No

Table of measured values ................ Yes

Sample data ......................... No

K - V curve ......................... Yes

dE/dV - V curve ......................... Yes

dV/dt - V curve ......................... No

K - t curve ......................... No

V - t curve ......................... No

**Titration Excellence**

001 Title

Type General titration

Compatible with T50 / T70 / T90

ID 61009

Title Betaine nonaq. solvent

**SOP**

None

**SOP**

None

**Sample (Titer)**

Number of IDs 1

ID 1 Cosmed

Entry type Weight

Lower limit 0.8 g

Upper limit 1.2 g

Density 1.0 g/mL

Correction factor 1.0

Temperature 25.0°C

**Titration stand (Manual stand)**

Type Manual stand

Manual stand 1

004 Stir

Speed 50%

Duration 30 s

005 Titration (EQP) [1]

Titrant

KOH in MeOH

Concentration 0.1 mol/L

Sensor

DGil13-SC

Unit mV

Temperature acquisition

Temperature acquisition No

Stir

Speed 30%

Predispense

Mode Volume

Volume 5 mL

Wait time 0 s

Control

Titrant addition Dynamic

dE(set) 8 mV

dV(min) 0.03 mL

dV(max) 0.3 mL

Meas. val. acquisition Equilibrium controlled

dE 0.5 mV

dt 1.0 s

t(min) 3.0 s

t(max) 30.0 s

Evaluation and recognition

Procedure Standard

Threshold 70 mV/mL

Tendency Negative

Ranges 0

Add. EQP criteria No

Termination

At Vmax 20.0 mL

At potential No

At slope No

After number of recognized EQPs No

Combined termination criteria No

006 Calculation R1

Result Content

Result unit %

Formula \( R=Q2 \times C/m \)

Constant \( C=M/(10 \times z) \)

M \( M[\text{Betaine}] \)

z \( z[\text{Betaine}] \)

Decimal places 3

Result limits No

Record statistics Yes

Extra statistical func. No

Send to buffer No

007 Record

...

008 End of sample
SPS Content of Drilling Emulsion by Potentiometric Titration

The anionic surfactant content in used drilling emulsions is determined by potentiometric titration in aqueous solution with the cationic surfactant Hyamine®1622 as a titrant. The potential change is monitored by a surfactant sensitive electrode.

**Preparation and Procedures**

- Add 0.2-8 g sample into the titration beaker.
- Add 5 mL methanol, 10 mL buffer, and 35 mL deionized water.
- Before starting it is recommended to condition the DS500 electrode by running e.g. a trial titration with SDS or a sample, and discard its result.

**DS500 surfactant sensitive electrode (SSE):**

- Fill the DS500 and its electrode tip with the DS500 electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the DS500 SSE 2-3 times to avoid the presence of air bubbles into the electrode tip.
- Rinse it with deionized water.
- Condition it in e.g. 0.01 mol/L SDS solution for 20-30 minutes.

**Remarks**

- The method parameters have been developed and optimized for this application. It may be necessary to adapt the method to your sample.
- The colloidal precipitate can cover the ceramic diaphragm of the reference electrode and thus, thorough cleaning is necessary.
- After each titration the surfactant electrode and the reference electrode are dipped in a conditioning beaker on the sample changer rack with water to clean them thoroughly.
- Problems arising from small irregularities of the titration curve, from air bubbles or other sources can be avoided by setting an appropriate threshold value. In this way, incorrect evaluations can be avoided.

**Sample**

- Used drilling emulsions, 0.2-8 g

**Compound**

- Sodium petroleum sulfate, SPS
  - Average M = 420; z = 1

**Chemicals**

- 5 mL methanol
- 10 mL pH 3.6 buffer solution (acetate buffer)
- 35 mL deion. water

**Titrant**

- Hyamine®1622, C<sub>27</sub>H<sub>42</sub>ClNO<sub>2</sub>
  - c(Hyamine) = 0.004 mol/L

**Standard**

- Sodium dodecylsulfate, SDS
  - C<sub>12</sub>H<sub>25</sub>NaO<sub>4</sub>S, M = 288.38; z = 1
  - 5 mL 0.004 mol/L SDS

**Indication**

- DS500 SSE
- InLab®Mono ref. electrode (electrolyte: 3 mol/L KCl)

**Chemistry**

- Simplified scheme:
  - C<sub>27</sub>H<sub>42</sub>NO<sub>2</sub><sup>+</sup> + C<sub>12</sub>H<sub>25</sub>O<sub>4</sub>S<sup>-</sup> = C<sub>27</sub>H<sub>42</sub>NO<sub>2</sub> - C<sub>12</sub>H<sub>25</sub>O<sub>4</sub>S

**Calculation**

- Content (DL5x)
  - R<sub>1</sub> = Q*C/m (%)
  - C = M/(10*z)
  - R<sub>2</sub> = Q*C2/m (ppm)
  - C2 = M*1000/z

**Waste disposal**

- Neutralization of the titrated solution; special treatment is not necessary.

**Author, Version**

- Tang Lijuan, MT-CS
  - April 1999 / Revised January 2010

**Literature:** see M610, M613
Instruments
- DL58 Titrator
- AT261 Balance
This method can also be run with the G20 and T50/70/90 Titration Excellence (minor adaptations in their method), and with the DL50/53/55, and DL67/70ES/77 instruments.

Accessories
- 10 mL DV1010 burette
- Titration beaker ME-101974
- Sample changer with pump.
- Printer

Results

• Titer determination of 0.004 M Hyamine

<table>
<thead>
<tr>
<th>c(Hyamine)/mol/L</th>
<th>n</th>
<th>SDS / mmol</th>
<th>Titer</th>
<th>RSD(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.004</td>
<td>4</td>
<td>0.02</td>
<td>0.9645</td>
<td>0.50</td>
</tr>
</tbody>
</table>

• SPS content of drilling solution

<table>
<thead>
<tr>
<th>Sample size / g</th>
<th>n</th>
<th>Mean of results</th>
<th>RSD of mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25 ~ 8.00</td>
<td>6</td>
<td>5.3773 %</td>
<td>1.41%</td>
</tr>
</tbody>
</table>

• Determination limit of SPS in drilling solution

<table>
<thead>
<tr>
<th>SPS content</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal/mmol</td>
<td>Actual/mmol</td>
</tr>
<tr>
<td>0.0012</td>
<td>0.0014</td>
</tr>
<tr>
<td>0.0024</td>
<td>0.0025</td>
</tr>
<tr>
<td>0.0049</td>
<td>0.0048</td>
</tr>
<tr>
<td>0.0098</td>
<td>0.0097</td>
</tr>
<tr>
<td>0.0147</td>
<td>0.0148</td>
</tr>
<tr>
<td>0.0245</td>
<td>0.0247</td>
</tr>
<tr>
<td>0.0391</td>
<td>0.0386</td>
</tr>
</tbody>
</table>

Titration curves
Table of measured values

<table>
<thead>
<tr>
<th>Method</th>
<th>Mix 2-Phase</th>
<th>DS500</th>
<th>Manual 2-P</th>
</tr>
</thead>
<tbody>
<tr>
<td>Results:</td>
<td>12.43%</td>
<td>12.58%</td>
<td>12.24%</td>
</tr>
<tr>
<td>RSD</td>
<td>1.1%</td>
<td>0.79%</td>
<td></td>
</tr>
<tr>
<td>n</td>
<td>2</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

Mixed 2-Phase titration (Mix 2-P): Organic and aqueous phases continuously mixed, indication by the Photrode™ DP550.

Aqueous titration (DS500): Aqueous titration. Indication by surfactant sensitive electrode DS500.

Manual 2-P: 2-phase titration by customer, manually.

Comments

- The drilling emulsion contains a mixture of surfactants called sodium petroleum sulfonate (SPS) with an average molar mass of 420 g/mol. The main component is sodium dodecylbenzene sulfate.

- After each sample, the surfactant sensitive electrode and the reference electrode must be thoroughly rinsed and cleaned with water.

- A sample changer ST20A is used in this method for a fully automatic procedure. The method can easily be modified for manual operation: enter “Stand” as titration stand in the function SAMPLE.

Determination limit

The determination limit is defined as the smallest amount of substance that can be titrated with a good precision.

In this case, a RSD value of 3% was chosen. Depending on the analysis and quality management requirements, other values can be defined.

With potentiometric titration the smallest amount of SPS in the sample must be larger than 0.0025 mmol in order to achieve a reproducibility of 3% or better.

Additional Results

A customer sample was analysed by 3 different methods.

(Sample: LAS solution, Compound: Linear alkylbenzene sulphonate, LAS).

The results show a very good agreement:
### Method

**DL5x Titrator**

<table>
<thead>
<tr>
<th>Method</th>
<th>SPS content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Version</td>
<td>27-Apr-1999 15:03</td>
</tr>
</tbody>
</table>

#### Title

<table>
<thead>
<tr>
<th>Method ID</th>
<th>59</th>
</tr>
</thead>
<tbody>
<tr>
<td>Title</td>
<td>SPS content</td>
</tr>
<tr>
<td>Date/time</td>
<td>27-Apr-1999 15:03</td>
</tr>
</tbody>
</table>

#### Sample

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>SPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entry type</td>
<td>Weight</td>
</tr>
<tr>
<td>Lower limit [g]</td>
<td>0.0</td>
</tr>
<tr>
<td>Upper limit [g]</td>
<td>2.0</td>
</tr>
<tr>
<td>Molar mass M</td>
<td>420</td>
</tr>
<tr>
<td>Equivalent number z</td>
<td>1.0</td>
</tr>
<tr>
<td>Titrant stand</td>
<td>ST20A</td>
</tr>
<tr>
<td>Rinse</td>
<td>Yes</td>
</tr>
<tr>
<td>Solvent</td>
<td>H2O</td>
</tr>
<tr>
<td>Volume [mL]</td>
<td>15.0</td>
</tr>
<tr>
<td>Conditioning</td>
<td>Yes</td>
</tr>
<tr>
<td>Time [s]</td>
<td>10</td>
</tr>
<tr>
<td>Interval</td>
<td>1</td>
</tr>
<tr>
<td>Rinse</td>
<td>Yes</td>
</tr>
<tr>
<td>Solvent</td>
<td>H2O</td>
</tr>
<tr>
<td>Volume [mL]</td>
<td>18.0</td>
</tr>
<tr>
<td>Temperature sensor</td>
<td>Manual</td>
</tr>
</tbody>
</table>

#### Stir

| Speed [%] | 50 |
| Time [s] | 15 |

#### EQP titration

<table>
<thead>
<tr>
<th>Titrant/Sensor</th>
<th>Hyamine 1622</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration [mol/L]</td>
<td>0.004</td>
</tr>
<tr>
<td>Sensor</td>
<td>SSE</td>
</tr>
<tr>
<td>Unit</td>
<td>mV</td>
</tr>
<tr>
<td>Temperature acquisition</td>
<td>No</td>
</tr>
<tr>
<td>Stir</td>
<td>50%</td>
</tr>
<tr>
<td>Speed [%]</td>
<td>35</td>
</tr>
<tr>
<td>Predispense</td>
<td>None</td>
</tr>
<tr>
<td>Wait time</td>
<td>0 s</td>
</tr>
<tr>
<td>Control</td>
<td>User</td>
</tr>
<tr>
<td>Titrant addition</td>
<td>Dynamic</td>
</tr>
<tr>
<td>dE(set)</td>
<td>8.0 mV</td>
</tr>
<tr>
<td>dV(min) [mL]</td>
<td>0.02 mL</td>
</tr>
<tr>
<td>dV(max) [mL]</td>
<td>0.2 mL</td>
</tr>
<tr>
<td>Measure mode</td>
<td>Equilibrium controlled</td>
</tr>
<tr>
<td>Meas val. acquisition</td>
<td>Equilibrium controlled</td>
</tr>
<tr>
<td>dE</td>
<td>0.5 mV</td>
</tr>
<tr>
<td>dt</td>
<td>1.0 s</td>
</tr>
<tr>
<td>t(min) [s]</td>
<td>3.0 s</td>
</tr>
<tr>
<td>t(max) [s]</td>
<td>20 s</td>
</tr>
<tr>
<td>Recognition</td>
<td>Positive</td>
</tr>
<tr>
<td>Threshold</td>
<td>20 mV/mL</td>
</tr>
<tr>
<td>Tendency</td>
<td>Positive</td>
</tr>
<tr>
<td>Measurement</td>
<td>1</td>
</tr>
<tr>
<td>Evaluation and recognition</td>
<td>Standard</td>
</tr>
</tbody>
</table>

#### Calculation

**Formula**

\[ R = \frac{Q \cdot C}{m} \]

- **Result unit** SPS Content
- **Decimal places** 4

<table>
<thead>
<tr>
<th>Result name</th>
<th>SPS Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistics</td>
<td>Yes</td>
</tr>
</tbody>
</table>

#### Report

| Output unit | Printer |
| Results | Yes |
| All results | Yes |

---

### Titration Excellence

<table>
<thead>
<tr>
<th>001 Title</th>
<th>General titration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type</td>
<td>Compatible with T50 / T70 / T90</td>
</tr>
<tr>
<td>ID</td>
<td>59</td>
</tr>
<tr>
<td>Title</td>
<td>SPS content</td>
</tr>
<tr>
<td>Date/time</td>
<td>01.01.2010 15:00:00</td>
</tr>
<tr>
<td>Modified</td>
<td>No</td>
</tr>
<tr>
<td>Modified by</td>
<td>--</td>
</tr>
</tbody>
</table>

#### Sample (Titer)

| Number of IDs | 1 |
| Entry type | SPS |
| Lower limit [g] | 0.0 g |
| Upper limit [g] | 2.0 g |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0°C |

#### 003 Titration stand (Manual stand)

| Type | Manual stand |
| Titration stand | Manual stand 1 |

#### 004 Stir

| Speed [%] | 50 |
| Duration | 15 s |

#### 005 Titration (EQP) [1]

| Titrant | Hyamine 1622 |
| Sensor | Sensor |
| Unit | mV |
| Temperature acquisition | No |
| Stir | 50% |
| Speed [%] | 35 |
| Predispense | None |
| Wait time | 0 s |
| Control | User |
| Titrant addition | Dynamic |
| dE(set) | 8.0 mV |
| dV(min) [mL] | 0.02 mL |
| dV(max) [mL] | 0.2 mL |
| Meas val. acquisition | Equilibrium controlled |
| dE | 0.5 mV |
| dt | 1.0 s |
| t(min) [s] | 3.0 s |
| t(max) [s] | 20 s |
| Evaluation and recognition | Standard |
| Threshold | 20 mV/mL |

#### Calculation

**Formula**

\[ R = \frac{Q \cdot C}{m} \]

- **Result unit** SPS Content
- **Decimal places** 4

<table>
<thead>
<tr>
<th>Result name</th>
<th>SPS Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Statistics</td>
<td>Yes</td>
</tr>
</tbody>
</table>

#### Report

**Output unit** Printer

---

**009 End of sample**
# Potentiometric Two-Phase Titrations

<table>
<thead>
<tr>
<th>Method</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>M376</td>
<td>Anionics Content in Shower Gels by Potentiometric Two-Phase Titration</td>
</tr>
<tr>
<td>M377</td>
<td>Anionics Content in Cutting Oils by Potentiometric Two-Phase Titration</td>
</tr>
<tr>
<td>M378</td>
<td>Titer Determination of Hyamine by Potentiometric Two-Phase Titration</td>
</tr>
</tbody>
</table>
Determination of the anionic surfactant content in shower gels by titration with 0.004 mol/L Hyamine®1622 in a two-phase mixed system at pH 3 using a DS800 TwoPhase electrode according to DIN EN 14480-2004.

### Preparation and Procedures

**Note:** MIBK is an intensively smelling organic solvent. It is recommended to work in a fume hood.

- 40 mL deionized water is added to 5 mL sample.
- pH-adjustment to pH 3 with HCl by means of the second titration burette (EN DIN 14480).
- 20 mL MIBK:EtOH 1:1 solvent are dispensed by an additional dosing unit (20 mL burette).
- Stir at a high speed (80%) to get an emulsion.
- Anionics content is expressed as SDS content.

**DS800 TwoPhase Surfactant Sensitive Electrode:**

- Fill the shaft and electrode tip with electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the electrode 2-3 times to avoid air bubbles and rinse it with deionized water.
- Condition the DS800 in deionized water for e.g. 15 minutes, and then perform 1-2 test titrations with the sample.

### Remarks

1) The method parameters have been optimized for the sample used in this application. It may be necessary to slightly adapt the method to your specific sample.

2) This method allows for an automated analysis with a Rondolino sample changer. The conditioning time was set to 120 s (e.g. Rondolino settings: 5) to clean the sensor in deionized water.

3) The method can be modified for manual operation. Select "Manual stand" in the method function "Titration stand".

4) Standard solutions of the different products are prepared by dissolving in 1 L volumetric flask approx. 5-10 g of the products. The resulting concentration in g/mL is stored as auxiliary value e.g. H[SDS] in the titrator.

**Literature:**

DIN EN 14480-2004, [www.din.de](http://www.din.de)
Instruments
- Titration Excellence T70/T90
- 2 additional dosing units
- Rondolino Sample Changer

Accessories
- 2 x 10 mL DV1010 + 1 x 20 mL DV1020 burettes
- Titration beaker ME-101974
- XS205 Balance
- Olivetti Printer JobJet 210

Results

Method ID: 0214LAS
Date / Time: 09/07/2007 07:50:32
User name: Administrator

All results
Method ID: 0214LAS
Sample 1/5
R1 24.726 %
Sample 2/5
R1 24.677 %
Sample 3/5
R1 24.669 %
Sample 4/5
R1 24.622 %
Sample 5/5
R1 24.641 %

Statistics
Method ID: 0214LAS
R1 (Content)
Number of samples: 5
Mean value: 24.667 %
Std. Deviation: 0.040 %
Std. Error of the mean: 0.161 %

Different samples
<table>
<thead>
<tr>
<th>Sample type</th>
<th>expected content (%SDS)</th>
<th>n</th>
<th>Result (%SDS)</th>
<th>s (%SDS)</th>
<th>srel (%)</th>
<th>Auxiliary value</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0214 viscous</td>
<td>24</td>
<td>5</td>
<td>24.667</td>
<td>0.040</td>
<td>0.161</td>
<td>pH 3</td>
<td>H[0214]=0.005056 g/L</td>
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<tr>
<td>0273 viscous</td>
<td>25</td>
<td>8</td>
<td>25.290</td>
<td>0.034</td>
<td>0.136</td>
<td>pH 3</td>
<td>H[0273]=0.005019 g/L</td>
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<tr>
<td>0411 powder</td>
<td>20</td>
<td>3</td>
<td>20.274</td>
<td>0.055</td>
<td>0.273</td>
<td>pH 3</td>
<td>H[0411]=0.010012 g/L</td>
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<tr>
<td>0193 formulation</td>
<td>8-9</td>
<td>5</td>
<td>9.303</td>
<td>0.031</td>
<td>0.332</td>
<td>pH 3</td>
<td>H[0193]=0.010033 g/L</td>
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<tr>
<td>0Liq liquid det.</td>
<td>5-15</td>
<td>6</td>
<td>7.317</td>
<td>0.060</td>
<td>0.817</td>
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<td>H[0Liq]=0.00805 g/L</td>
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</table>
Titration curve

Table of measured values

<table>
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<tr>
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<tbody>
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<td>mL</td>
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<td>s</td>
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<td>°C</td>
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<td>192</td>
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<td></td>
</tr>
</tbody>
</table>
Comments

- The determination is performed at pH 3 according to DIN EN 14480. The pH adjustment is necessary to avoid interference due to the presence of free fatty acids (FFA) in the products. In fact, at pH 3 the FFA are fully protonated, therefore they can not be precipitated by addition of Hyamine®1622.

- The DS800 electrode has been optimized for the use in a MBK:water two-phase system. Therefore, optimum performance of this electrode can mainly be achieved in this mixed solution.

- When working with the LabX Software, select "Rondolino Mode" in the LabX window at the PC and activate it.

Method

<table>
<thead>
<tr>
<th>001 Title</th>
<th>Type General titration</th>
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</thead>
<tbody>
<tr>
<td>ID</td>
<td>T70 / T90</td>
</tr>
<tr>
<td>Title</td>
<td>SDS content potentiometric</td>
</tr>
<tr>
<td>Author</td>
<td>Administrator</td>
</tr>
<tr>
<td>Date/Time</td>
<td>06/07/2007 17:56:59</td>
</tr>
<tr>
<td>Modified at</td>
<td>06/07/2007 07:50:32</td>
</tr>
<tr>
<td>Modified by</td>
<td>--</td>
</tr>
<tr>
<td>SOV</td>
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<table>
<thead>
<tr>
<th>002 Sample</th>
<th>Number of IDs 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>ID</td>
<td>0214</td>
</tr>
<tr>
<td>Entry type</td>
<td>Fixed volume</td>
</tr>
<tr>
<td>Volume</td>
<td>5.0 mL</td>
</tr>
<tr>
<td>Density</td>
<td>1.0 g/mL</td>
</tr>
<tr>
<td>Correction factor</td>
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</tr>
<tr>
<td>Temperature</td>
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</table>

<table>
<thead>
<tr>
<th>003 Titration stand (Rondolino TTL)</th>
<th>Type Rondolino TTL</th>
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<tbody>
<tr>
<td>Titration stand</td>
<td>Rondolino TTL 1</td>
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<table>
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<tr>
<th>004 Stir</th>
<th>Speed 35%</th>
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<tbody>
<tr>
<td>Duration</td>
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<tr>
<td>Condition</td>
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<table>
<thead>
<tr>
<th>005 Titration (EP) [1]</th>
<th>Titrant HCl</th>
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</thead>
<tbody>
<tr>
<td>Sensor Type</td>
<td>pH</td>
</tr>
<tr>
<td>Sensor</td>
<td>DG111-SC</td>
</tr>
<tr>
<td>Unit</td>
<td>pH</td>
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| Temperature acquisition | Temperature acquisition No |

<table>
<thead>
<tr>
<th>Stir</th>
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<tr>
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<td>Wait time</td>
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<table>
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<tbody>
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</tr>
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<td>End point value</td>
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<tr>
<td>Control band</td>
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</tr>
<tr>
<td>Dosing rate (max)</td>
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</tr>
<tr>
<td>Dosing rate (min)</td>
<td>50 µL/min</td>
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<table>
<thead>
<tr>
<th>006 Dispense (normal) [1]</th>
<th>Titrant MIBK : EtOH 1:1</th>
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<tbody>
<tr>
<td>Concentration</td>
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<tr>
<td>Volume</td>
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</tr>
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<table>
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<table>
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<th>Titrant Hyamine 1622</th>
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<td>Sensor Type</td>
<td>mV</td>
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<td>Sensor</td>
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<td>mV</td>
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| Temperature acquisition | Temperature acquisition No |

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<tbody>
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<tr>
<td>Control</td>
<td>User</td>
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<tr>
<td>Titrant addition</td>
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<td>dE(set value)</td>
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<td>dV(max)</td>
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<tr>
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<td>1 s</td>
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Evaluation and recognition

| Procedure | Standard |
| Threshold | 100 mV/mL |
| Tendency  | Positive |
| Ranges    | 0         |
| Add. EQP criteria | No |

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<td>At slope</td>
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| Accompanying stating | Accompanying stating No |

| Condition | No |

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<th>Result Content</th>
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<tr>
<td>Formula</td>
<td>R1 = q[2] * C / (m * z)</td>
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</tr>
<tr>
<td>M</td>
<td>M[Sodium dodecyl sulfate]</td>
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<tr>
<td>z</td>
<td>z[Sodium dodecyl sulfate]</td>
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<th>Results Per sample</th>
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<td>Per sample</td>
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<td>Table of meas. values</td>
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<th>Summary Results</th>
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<table>
<thead>
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<th>Summary Results</th>
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| Extra statistical func. | No |
| Send to buffer | No |
Anionics Content in Cutting Oils by Potentiometric Two-Phase Titration

Determination of the anionic surfactant content in cutting oils by titration with 0.004 mol/L Hyamine®1622 in a two-phase mixed system at pH 3 using a DS800 TwoPhase electrode according to DIN EN 14480-2004.

### Preparation and Procedures

Note: MIBK is an intensively smelling organic solvent. It is recommended to work in a fume hood.

- 40 mL deionized water is added to 5 mL sample.
- pH-adjustment to pH 3 (EN DIN 14480) with HCl or to pH 11 by means of the second burette.
- 20 mL MIBK-OH 1:1 solvent are dispensed by an additional dosing unit (20 mL burette).
- Stir at a high speed (80%) to get an emulsion.
- Anionics content is expressed as SDS content.

#### DS800 TwoPhase Surfactant Sensitive Electrode:

- Fill the shaft and electrode tip with electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the electrode 2-3 times to avoid air bubbles and rinse it with deionized water.
- Condition the DS800 in deionized water for e.g. 15 minutes, and then perform 1-2 test titrations with the sample.

### Remarks

1) The method parameters have been optimized for the sample used in this application. It may be necessary to slightly adapt the method to your specific sample.

2) This method allows for an automated analysis with a Rondolino sample changer. The conditioning time was set to 120 s (e.g. Rondolino settings: 5) to clean the sensor in deionized water.

3) The method can be modified for manual operation. Select "Manual stand" in the method function "Titration stand".

### Literature:

- DIN EN 14480-2004,
- DIN EN 14669-2005, [www.din.de](http://www.din.de)

---

<table>
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<tr>
<th>Sample</th>
<th>0.1-0.3 g cutting oil, depending on anionic surfactant content.</th>
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<td>Anionics expressed as sodium dodecyl sulfate SDS, C₁₂H₂₅NaO₄S</td>
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<tr>
<td></td>
<td>M(SDS) = 288.38 g/mol, z = 1</td>
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<tr>
<td>Chemicals</td>
<td>40 mL deionized water</td>
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<tr>
<td></td>
<td>20 mL MIBK:EtOH 1:1 solvent</td>
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<tr>
<td></td>
<td>MIBK: Methyl isobutyl ketone, 4-Methylpentan-2-one EtOH: ethanol</td>
</tr>
<tr>
<td>Titrant</td>
<td>Hyamine®1622, C₂₇H₄₂ClNO₂, c(Hyamine) = 0.004 M</td>
</tr>
<tr>
<td></td>
<td>Hydrochloric acid, HCl, 0.1 M</td>
</tr>
<tr>
<td></td>
<td>Sodium hydroxide, NaOH, 0.1 M</td>
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<tr>
<td>Standard</td>
<td>SDS (for Hyamine), THAM (for HCl), KHP (for NaOH)</td>
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<tr>
<td>Indication</td>
<td>DS800 TwoPhase Surfactant Electrode DX200 or InLab® Reference (3 M KCl) DGi111-SC pH glass electrode</td>
</tr>
<tr>
<td>Chemistry</td>
<td>Simplified scheme: C₂₇H₄₂NO₂⁺ + C₁₂H₂₅O₄S⁻ = C₂₇H₄₂NO₂⁻·C₁₂H₂₅O₄S</td>
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<tr>
<td>Calculation</td>
<td>R1: SDS-Content (%)</td>
</tr>
<tr>
<td></td>
<td>R1 = Q[2]<em>C/m, C = M/(10</em>z); z = 1</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>Neutralize the sample solution before final disposal as organic solvent.</td>
</tr>
<tr>
<td>Author, Version</td>
<td>Cosimo De Caro, MSG Anachem, November 2007</td>
</tr>
</tbody>
</table>
### Instruments
- Titration Excellence T70/T90
- 2 additional dosing units
- Rondolino Sample Changer

### Accessories
- 2 x 10 mL DV1010 + 1 x 10 mL DV1020 burettes
- Titration beaker ME-101974
- XS205 Balance
- Olivetti Printer JobJet 210

## Results

<table>
<thead>
<tr>
<th>Method ID:</th>
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<th>Sample series ID: --</th>
<th>User name: Administrator</th>
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<tr>
<td>Date / Time:</td>
<td>11/12/2007 09:02:23 am</td>
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</table>

### Samples

<table>
<thead>
<tr>
<th>No.</th>
<th>ID</th>
<th>Sample size and results</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>00883-03</td>
<td>0.1773 g R1(Anionics Content) 4.91 %</td>
</tr>
<tr>
<td>2</td>
<td>00883-03</td>
<td>0.1873 g R1(Anionics Content) 4.88 %</td>
</tr>
<tr>
<td>3</td>
<td>00883-03</td>
<td>0.1537 g R1(Anionics Content) 4.82 %</td>
</tr>
<tr>
<td>4</td>
<td>00883-03</td>
<td>0.2101 g R1(Anionics Content) 4.86 %</td>
</tr>
<tr>
<td>5</td>
<td>00883-03</td>
<td>0.1782 g R1(Anionics Content) 4.86 %</td>
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<tr>
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<td>00883-03</td>
<td>0.1624 g R1(Anionics Content) 4.88 %</td>
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### Statistics

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<tr>
<th>R1 (Anionics Content)</th>
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<th>s</th>
<th>srel</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>6</td>
<td>4.87 %</td>
<td>0.03 %</td>
<td>0.636 %</td>
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</table>

### Various samples

<table>
<thead>
<tr>
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<th>s</th>
<th>srel (%)</th>
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<td>02800-01</td>
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Titration curve

Table of measured values

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<th>Meas. value mV</th>
<th>1. Derivative mV/mL</th>
<th>Time s</th>
<th>Temperature °C</th>
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</table>
**Comments**

- The analysis is performed at pH 3 to avoid interference due to the presence of free fatty acids (FFA). At pH 3, FFA are fully protonated, thus they can not be precipitated by addition of Hyamine®1622.
- However, when samples such as cutting oil 11675-01 and 01125-02 contain anionics with R-COOH end groups, they are titrated at an alkaline pH value of e.g. pH 11 to be able to precipitate them with Hyamine®1622 (see also DIN EN 14669).
- The DS800 electrode has been optimized for the use in a MIBK:water two-phase system. Therefore, optimum performance of this electrode can mainly be achieved in this mixed solution.

**Method**

### 001 Title

<table>
<thead>
<tr>
<th>Type</th>
<th>General titration</th>
</tr>
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<tbody>
<tr>
<td>ID</td>
<td>m377</td>
</tr>
<tr>
<td>Title</td>
<td>SDS content potentiometric</td>
</tr>
<tr>
<td>Author</td>
<td>Administrator</td>
</tr>
<tr>
<td>Date/Time</td>
<td>11/12/2007 07:22:42 am</td>
</tr>
<tr>
<td>Modified at</td>
<td>11/12/2007 09:02:23 am</td>
</tr>
<tr>
<td>Modified by</td>
<td>--</td>
</tr>
<tr>
<td>EDV</td>
<td>None</td>
</tr>
</tbody>
</table>

### 002 Sample

| Number of IDs | 1 |
| Entry type | Weight |
| Lower limit | 0 g |
| Upper limit | 5 g |
| Density | 1.0 g/mL |
| Correction factor | 1.0 |
| Temperature | 25.0°C |

### 003 Titration stand (Rondolino TTL)

| Type | Rondolino TTL |
| Titration stand | Rondolino TTL 1 |

### 004 Stir

| Speed | 35% |
| Duration | 60 s |
| Condition | No |

### 005 Titration (EP) [1]

| Titrant | HCl |
| Sensor | pH |
| Type | DG111-SC |
| Unit | pH |
| Temperature acquisition | Temperature acquisition No |
| Speed | 35% |
| Predispense | None |
| Wait time | 0 |
| Control | Absolute |
| Tendency | Negative |
| End point value | 3 pH |
| Control limit | 2.0 pH |
| Dosing rate (max) | 10.0 mL/min |
| Dosing rate (min) | 500 µL/min |
| Termination | At Vmax |
| Termination delay | 0 s |
| At Vmax | 10 mL |
| Max. time | Infinite |
| Accompanying stating | No |
| Condition | No |

### 006 Dispense (normal) [1]

| Titrant | MIBK:EtOH 1:1 |
| Concentration | 1 |
| Volume | 20 mL |
| Dosing rate | 60.0 mL/min |
| Condition | No |

### 007 Stir

| Speed | 80% |
| Duration | 60 s |
| Condition | No |

### 008 Titration (EQP) [2]

| Titrant | Hyamine 1622 |
| Concentration | 0.004 mol/L |
| Sensor | pV |
| Type | Dynamic |
| Unit | pH |
| Temperature acquisition | Temperature acquisition No |
| Speed | 80% |
| Predispense | None |
| Wait time | 0 s |
| Control | User |
| Titrant addition | Dynamic |
| dE(set value) | 8.0 mV |
| dV(min) | 0.1 mL |
| dV(max) | 0.5 mL |
| Measure. val. acquisition | Equilibrium controlled |
| dE | 0.5 mV |
| dt | 2 s |
| t(min) | 8 s |
| t(max) | 45 s |

**Evaluation and recognition**

| Procedure | Standard |
| Threshold | 30 mL/mL |
| Tendency | Positive |
| Ranges | 0 |
| Add. EQP criteria | No |

**Termination**

| At Vmax | 20 mL |
| At potential | No |
| At slope | No |
| After number of recognized EQPs | No |
| Combined termination criteria | No |
| Accompanying stating | No |
| Condition | No |

### 009 Calculation R1

| Result | Anionics Content |
| Formula | R1=Q*[C/m] |
| Constant | C=M/(10*z) |
| M | Sodium dodecyl sulfate |
| z | Sodium dodecyl sulfate |
| Decimal places | 3 |
| Result limits | No |
| Record statistics | Yes |
| Extra statistical func. | No |
| Send to buffer | No |

### 010 Record

| Results Per sample | Per sample |
| Raw results Per sample | Per sample |
| Table of meas. values Last titration function | No |
| Sample data | No |
| Resource data | No |
| E - V Last titration function | No |
| dE/dV - V Last titration function | No |

### 011 End of sample

#### 012 Record

| Summary | Results |
| Results | Yes |
Titer Determination of Hyamine® 1622 by Potentiometric Two-Phase Titration

Titer determination of 0.004 mol/L Hyamine® 1622 with sodium dodecyl sulfate (SDS) as a standard in a two-phase mixed system at pH 3 using a DS800 TwoPhase electrode according to DIN EN 14480-2004.

<table>
<thead>
<tr>
<th>Sample</th>
<th>5 mL 0.004 SDS SDS: Sodium dodecylsulfate.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Sodium dodecyl sulfate SDS, C_{12}H_{25}NaO_{4}S M(SDS) = 288.38 g/mol, z = 1</td>
</tr>
<tr>
<td>Chemicals</td>
<td>40 mL deionized water 20 mL MIBK:EtOH 1:1 solvent MIBK: Methyl isobutyl ketone, 4-Methylpentan-2-one EtOH: ethanol</td>
</tr>
<tr>
<td>Titrant</td>
<td>Hyamine® 1622, C_{27}H_{42}ClNO_{2} c(Hyamine) = 0.004 M Hydrochloric acid, HCl, c(HCl) = 0.1 M</td>
</tr>
<tr>
<td>Standard</td>
<td>SDS (for Hyamine), THAM (for HCl),</td>
</tr>
<tr>
<td>Indication</td>
<td>DS800 TwoPhase Surfactant Electrode DX200 or InLab® Reference (3 M KCl) DGi111-SC pH glass electrode</td>
</tr>
<tr>
<td>Chemistry</td>
<td>Simplified scheme: C_{27}H_{42}NO_{2}^{+} + C_{12}H_{25}O_{4}S^{-} = C_{27}H_{42}NO_{2}C_{12}H_{25}O_{4}S</td>
</tr>
<tr>
<td>Calculation</td>
<td>Titer R1 = m/(VEQ[2]*c[2]<em>C) C = 1/(cst</em>z) z = 1</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>Neutralize the sample solution before final disposal as organic solvent.</td>
</tr>
<tr>
<td>Author, Version</td>
<td>Cosimo De Caro, MSG Anachem, July 2007</td>
</tr>
</tbody>
</table>

Preparation and Procedures

Note: MIBK is an intensively smelling organic solvent. It is recommended to work in a fume hood.

- 40 mL deionized water is added to 5 mL sample.
- pH-adjustment to pH 3 (EN DIN 14480) with HCl by means of the second burette.
- 20 mL MIBK-OH 1:1 solvent are dispensed by an additional dosing unit (20 mL burette).
- Stir at a high speed (80%) to get an emulsion.

DS800 TwoPhase Surfactant Sensitive Electrode:

- Fill the shaft and electrode tip with electrolyte.
- Screw the electrode tip onto the shaft.
- Shake the electrode 2-3 times to avoid air bubbles and rinse it with deionized water.
- Condition the DS800 in deionized water for e.g. 15 minutes, and then perform 1-2 test titrations with the sample.

Remarks

1) This method allows for an automated analysis with a Rondolino sample changer. The conditioning time was set to 120 s (e.g. Rondolino settings: 5) to clean the sensor in deionized water.

2) The method can be modified for manual operation. Select "Manual stand" in the method function "Titration stand".

3) When working with the LabX Software, select "Rondolino Mode" in the LabX window at the PC and activate it.

Literature:

Instruments
- Titration Excellence T70/T90
- 2 additional dosing units
- Rondolino Sample Changer

Accessories
- 2 x 10 mL DV1010 + 1 x 20 mL DV1020 burettes
- Titration beaker ME-101974
- XS205 Balance
- Olivetti Printer JobJet 210

Results

<table>
<thead>
<tr>
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<th>414Titer</th>
<th>Sample series ID</th>
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<td>06/07/2007 17:15:16</td>
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<td>Samples</td>
<td>No.</td>
<td>ID</td>
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<td>SDSTiter414</td>
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Statistics
- R1 (Titer)
  - Number of samples: 6
  - Mean value: 0.999866
  - s: 0.001784
  - srel: 0.178%

Titer
- Titrant: Hyamine 1622
- New titer: 0.99987

Results
- R2 (Hyamine): 0.999866

Titration curve
### Table of measured values

<table>
<thead>
<tr>
<th>Volume/mL</th>
<th>mV</th>
<th>mV/mL</th>
<th>s</th>
<th>°C</th>
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### Comments

- The DS800 electrode has been optimized for the use in a MIBK:water two-phase system. Therefore, optimum performance of this electrode can mainly be achieved in this mixed solution.
Method

001 Title
Type: General titration
Compatible with: T70 / T90
ID: 414Titer
Title: Titer Hyamine 1622
Author: Administrator
Date/Time: 28/08/2006 14:53:16
Modified at: 06/07/2007 17:15:16
Modified by: --
Protect: No
SOP: None

002 Sample (Titer)
Titrant: Hyamine 1622
Concentration: 0.004 mol/L
Standard: DSSTiter414
Type of standard: liquid
Entry type: Fixed volume
Volume: 5 mL
Correction factor: 1.0
Temperature: 25.0°C

003 Titration stand (Rondolino TTL)
Type: Rondolino TTL
Titration stand: Rondolino TTL 1

004 Stir
Speed: 35%
Duration: 45 s
Condition: No

005 Titration (EP) [1]
Titrant: HCl
Concentration: 0.1 mol/L
Sensor:
Type: pH
Sensor: DG111-SC
Unit: pH
Temperature acquisition: No
Stir:
Speed: 35%
Fidepresses:
Mode: None
Wait time: 0
Control:
End point type: Absolute
Tendency: Negative
End point value: 3 pH
Control band: 2.0 pH
Dosing rate (max): 0.2 mL/min
Dosing rate (min): 50 µL/min
Termination:
At EP: Yes
Termination delay: 0 s
At Vmax: 10 mL
Max. time: Infinite
Accompanying stating:
Accompanying stating: No
Condition:
Condition: No

006 Dispense (normal) [1]
Titrant: MIBK:EtOH 1:1
Concentration: 1:1
Volume: 20 mL
Dosing rate: 60.0 mL/min
Condition: No

007 Stir
Speed: 80%
Duration: 60 s
Condition: No

008 Titration (EQP) [2]
Titrant: Hyamine 1622
Concentration: 0.004 mol/L
Sensor:
Type: mV
Sensor: DS800
Unit: mV
Temperature acquisition: No

Stir:
Speed: 80%
Fidepresses:
Mode: Volume
Volume: 1.5 mL
Wait time: 15 s

Control:
Control: User
Titrant addition: Dynamic
dE(set value): 8.0 mV
dV(min): 0.1 mL
dV(max): 0.5 mL
Measure. val. acquisition: Equilibrium controlled
dE: 1.0 mV
dt: 1 s
t(min): 5 s
t(max): 30 s

Evaluation and recognition:
Procedure: Standard
Threshold: 100 mV/mL
Tendency: Positive
Ranges: 0
Add. EQP criteria: No
Termination:
At Vmax: 10 mL
At potential: No
At slope: No
After number of recognized EQPs: Yes
Number of EQPs: 1
Combined termination criteria: No
Accompanying stating:
Accompanying stating: No
Condition:
Condition: No

009 Calculation R1
Result:
Result unit: Titer
Formula: R1=m/(VEQ*2*c*2*C)
Constant:
M [Sodium dodecyl sulfate]: 1/(cst*z)
z [Sodium dodecyl sulfate]: z
Decimal places: 6
Result limits: No
Record statistics: Yes
Extra statistical func.: No
Send to buffer: No

010 Record
Results:
Per sample
Raw results:
Per sample
Table of meas. values:
Last titration function
Sample data: No
Resource data: No
E - V:
Last titration function
dE/dV – V:
Last titration function

011 End of sample

012 Titer
Titrant: Hyamine 1622
Concentration: 0.004 mol/L
Titer:
Mean [R]
Limits: No
Condition:
Condition: No

013 Calculation R2
Result:
Titer: Hyamine
Result unit:
Formula: R2=mean[R1]
Constant:
M [None]: M
z [None]: z
Decimal places: 6
Result limits: No
Record statistics: Yes
Extra statistical func.: No
Send to buffer: No

014 Record
Summary:
Results: No
Raw results: No
Resource data: No
Calibration curve: No
Literature


**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.**
Selected Application for Surfactant Titration

This brochure contains dedicated applications for the determination of surfactant content in various samples. Four techniques have been illustrated in detail, namely:

1. the turbidimetric titration,
2. the automated, colorimetric two-phase titration,
3. the potentiometric titration in aqueous phase with a surfactant sensitive electrode (SSE), and
4. the potentiometric two-phase titration with a SSE

METTLER TOLEDO offers you various powerful tools for the surfactant titration which are meant to facilitate your content determination analyses and to contribute to reliable results over the whole lifetime of your instrument.