

The determination of chloroacetic acid (chloroacetate) in surfactants

Chromatographic method

Method One---HPLC method

1 Scope

This International Standard specifies a method for the determination of mono-chloroacetic acid (mono-chloroacetate) and di -chloroacetic acid (di-chloroacetate) in surfactants.

The method applies to surfactants which are anionic surfactant such as alkyl (phenyl) ethoxylated carboxylate, amphoteric surfactant such as alkyl imidazoline carboxylate and cationic surfactants such as alkyl dimethyl betaine and fatty acetyl propyl dimethyl betaine.

2 Normative references

Omitted

3 Principle

The sample was dissolved in mobile phase solution. After injection, it flow through an C₈ bonded silicone gel column. The mono-chloroacetic acid (mono-chloroacetate) and di -chloroacetic acid (di-chloroacetate) were seperated with sample and eluted by the mobile phase one after another successfully. The eluate was detected by an UV detector or photo diode array detector.

4 Reagents

4.1 Water: Appropriate for HPLC analysis.

4.2 Mono-chloroacetic acid(ClCH_2COOH): chromatographic grade or analytical grade, purity > 99%

4.3 Di -chloroacetic acid($\text{Cl}_2\text{CH}_2\text{COOH}$): chromatographic grade or analytical grade, purity > 99%

4.4 Acetone nitrile(CH_3CN) , HPLC Grade.

4.5 N-Phosphorous acid(H_3PO_4): analytical grade.

4.6 Hydrochloric acid (HCl): analytical grade.

4.7 Hydrochloric acid(1+1) :10ml of Hydro chloric acid(4.6) and 10ml of water(4.1) mix well.

5 Apparatus

Use usual laboratory apparatus and, in particular, the following.

5.1 HPLC instrument equipped with a proper data analysis system and a high resolution UV detector or photo diode array detector. The instrument must be meet the following specifications: The noise of base line at 254nm $< 2 \times 10^{-5}$ AU/s (blank cell);

the base line drift at 254nm $< 1 \times 10^{-3}$ AU/h (blank cell, after stabilizing for 60 minutes).

5.2 HPLC column: C₈ boned silicone gel with particle size about 5 μ m , dimension: 250mm \times 4.6mm (ID), pH : 1-8; or equivalent.

5.3 Injection syrenge:25 μ L.

5.4 Analytical balance: minimum 0.1mg.

5.5.Ultra sonic device for the degasing of reagents.

5.6 Device for filtration, with filters of suitable porosity (nominal aperture diameter of 0,2 μ m or 0,45 μ m) and syringe filter, for the filtration of reagents and sample before analyzing.

5.7 Vacuum pump.

5.8 pH- meter.

5.9 Volumetric flask: of appropriate capacity (100ml or so).

5.10 Glass beaker. of appropriate capacity (50ml or so).

6 Procedures

6.1 HPLC conditions:

Mobile phase: 900ml of filtrated water(4.1) was mixed with 100ml of filtrated acetone nitrile(4.4), and 2.0ml of phosphorous acid was added, mix well. Degassing before use (with ultra -sonic device(5.5))

Flow rate: 1.0ml/min.

Wave length: 214nm.

Injection volume: 20ul.

6.2 Preparation of the stock solution

Weigh about 0.1g of standard mono mono-chloroacetic acid(4.2) and 0.1g of di-cloroacetic acid(4.3)(accurate to 0.0001g) in a 50ml beaker, add about 20ml of mobile phase solution(6.1) and stir. Transfer to a 100ml volumetric flask, rinse the beaker at least twice with mobile phase solution and transfer to the volumetric flask. Make up to the mark and shake well. This solution is the stock solution .The concentrations of this solution are following: mono-chloroacetic acid about 1mg/ml and di-cloroacetic acid about 1mg/ml.

The stock solution shall be preserved at 4°C in refrigerator and expire after 7 days of storage.

6.3 Preparation of the standard solution

Transfer 0.1ml, 0.5ml,1.0ml,1.5ml, 2.5ml of stock solution into 5 100ml volumetric flasks, dilute to the mark with mobile phase solution. These are standard solutions for calibration curve. The standard solutions shall be prepared before injection and expired after analyzing.

Filter the standard solutions with syringe filter and inject 20ul for analysis. Calculate the linear correlation coefficient with proper calculator or software. R obtained shall be 0.999 or more.

6.4 Analysis of sample

6.4.1 AEC and imidazoline samples

Weigh about 5-10g of samples (accurate to 0.0001g) in a 100ml beaker, add about 30ml of mobile phase solution(6.1) and stir till the sample dissolved completely. Measure the pH in a pH-meter(5.8). Pipette the hydrochloric acid solution(4.7) into the sample slowly and stir, till the same pH of the sample as that of mobile phase solution obtained. Transfer into a 100ml volumetric flask, rinse at least twice and make up to the mark with mobile phase solution. Filter with syringe filter and inject 20ul for analysis.

6.4.2 Betaine samples

Prepare the sample solution according to the method in appendix A using ion-exchange column. After treatment, the sample solution shall be filtered by syringe filter and inject 20ul for analysis.

7 Result and calculation

7.1 Calculate the content of sodium mono-chloroacetic acid (sodium chloroacetate)by equation(1):

$$X(mg/kg) = \frac{A \times V \times 116.5}{m \times 94.5} \dots\dots\dots(1)$$

Where :

X: The content of sodium mono-chloroacetic acid (sodium chloro acetate), mg/kg.

A: The calculated concentration of sodium mono-chloroacetic acid (sodium chloro acetate) in test sample solution, $\mu\text{g/mL}$.

V: The volume of test sample, mL.

M: the weight of test sample, g.

116.5: The mole weight of sodium mono-chloroacetic acid (sodium chloro acetate),g.

94.5: The mole weight of mono-chloroacetic acid, g.

7.2 Calculate the content of sodium di-chloroacetic acid (sodium di-chloro acetate)by equation(2):

$$X(mg / kg) = \frac{A \times V \times 150.9}{m \times 128.9} \dots\dots\dots(2)$$

Where :

X: The content of sodium di-chloroacetic acid (sodium di-chloro acetate), mg/kg.

A: The calculated concentration of sodium di-chloroacetic acid (sodium di-chloro acetate) in test sample solution, $\mu\text{g/mL}$.

V: The volume of test sample, mL.

M: the weight of test sample, g.

150.9: The mole weight of sodium mono-chloroacetic acid (sodium chloro acetate),g.

128.9: The mole weight of mono-chloroacetic acid, g.

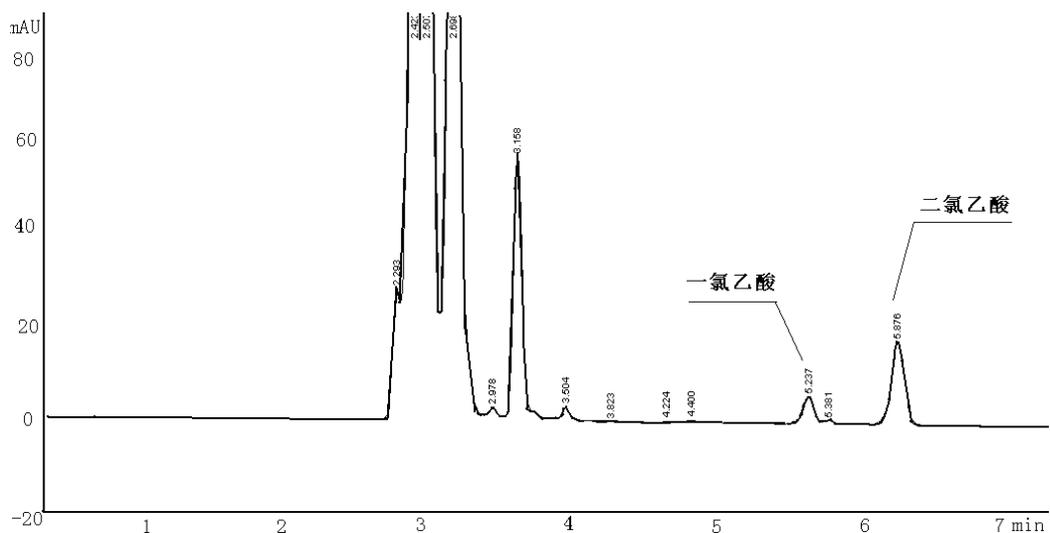


Fig 1 The chromatography of mono-chloroacetic acid and di-chloroacetic acid in betaine sample

8 Test report

This test report shall contain at least the following information:

- a) The test method used, with reference to this International Standard;
- b) All information necessary for the complete identification of the test compound;
- c) All the data (e.g. in tabular form) obtained and the calibration curve;
- d) All operating details not specified in this International Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s).

Method Two--- IC method

1 Scope

This International Standard specifies a method for the determination of mono-chloroacetic acid (mono-chloroacetate) and di -chloroacetic acid (di-chloroacetate) in surfactants.

The method applies to surfactants which are anionic surfactant such as alkyl(phenyl) ethoxyl carboxylate, amphoteric surfactant such as alkyl imidazoline carboxylate and cationic surfactants such as alkyl dimethyl betaine and fatty acetyl propyl dimethyl betaine.

2 Normative references

Omitted

6 Principle

The sample solution was diluted to a proper concentration and flow through an anionic ionexchange column. The mono-chloroacetic acid (mono-chloroacetate) and di -chloroacetic acid (di-chloroacetate) were absorbed in the column first, then eluted by the mobile phase one after another successfully. The eluate was detected by electric conductivity detector.

7 Reagents

4.1 Water(H₂O): Resistivity > 18.2MΩ

4.2 Mono-chloroacetic acid(ClCH₂COOH): chromatographic grade or analytical grade, purity > 99%

4.3 Di -chloroacetic acid(Cl₂CH₂COOH): chromatographic grade or analytical grade, purity > 99%

4.4 Sulfuric acid(H_2SO_4) , analytical grade.

4.5 Disodium carbonate (Na_2CO_3): chromatographic grade.

4.6 Sodium hydro carbonate ($NaHCO_3$): chromatographic grade.

4.7 Sodium Hydroxide: chromatographic grade

8 Apparatus

Use usual laboratory apparatus and, in particular, the following.

5.1 Ion chromatography instrument equipped with separation column, protection column, proper suppressor, data analysis system and a high resolution electric conductivity detector.

5.2 IC column: quaternary ammonium modified anionic ion-exchange column.

5.3 Injection syringe: 50 μ L.

5.4 Analytical balance: minimum 0.1mg.

5.5 Device for filtration, with filters of suitable porosity (nominal aperture diameter of 0,2 μ m to 0,45 μ m) and syringe filter, for the filtration of reagents and sample before analyzing.

5.6 Vacuum pump.

5.7 Volumetric flask: of appropriate capacity (100ml,1000mL).

5.8 Glass beaker. of appropriate capacity (25ml ,100mL).

6 Procedure

The proper analytical condition was associated with equipment, please choose one of the following conditions when analyzing or consult the manufacturer before modification of following conditions for better separation.

6.1 IC condition 1:

Quaternary ammonium modified ion-exchange column, 4mm \times 25mm, with proper protection column and suppressor.

a) Mobile phase: 3.2mmol/L disodium carbonate(4.5) solution, and 1.0mmol/L sodium hydro carbonate(4.6) solution.

b) Flow rate:0.70min/min.

c) Temperature: 25 $^{\circ}$ C.

d) Injection volume: 20 μ L.

e) Recovery solution: 50mmol/L sulfuric acid(4.4) solution.

Based on above conditions, a typical chromatogram was as following, the MDL are 0.012 μ g/mL for Mono-chloroacetic acid ($ClCH_2COOH$) and 0.032 μ g/mL for Di-chloroacetic acid ($Cl_2CHCOOH$) respectively.

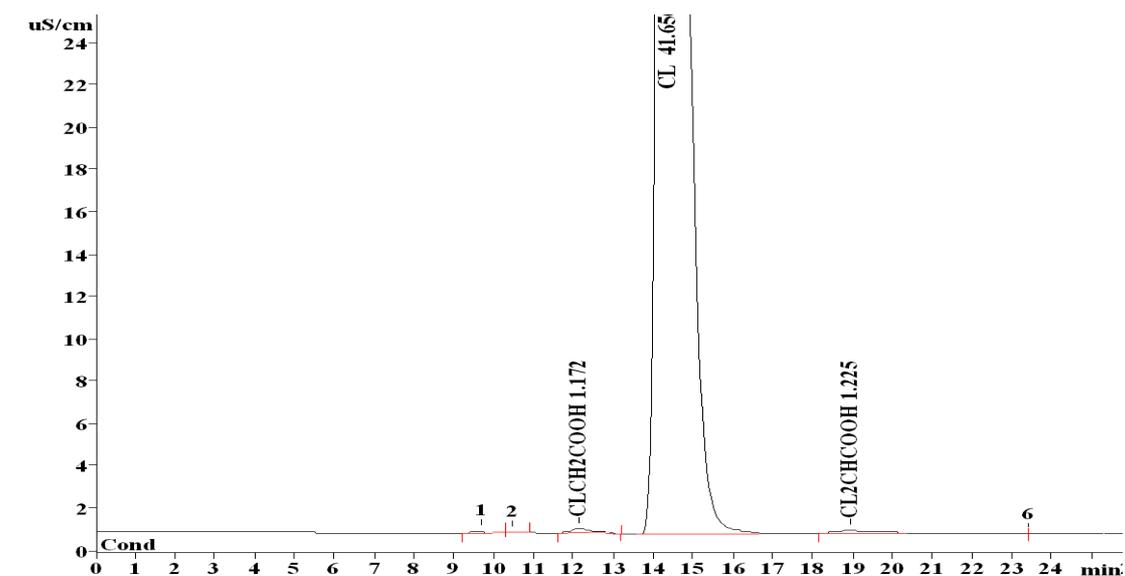


Fig 1 The chromatogram of mono-chloroacetic acid and di-chloroacetic acid in sample (under condition 1)

6.2 IC condition 2:

Quaternary ammonium modified ion-exchange column, 4mm×25mm, with proper protection column and suppressor.

a) Mobile phase: 15mmol/L sodium hydroxide(4.7) solution.

b) Flow rate: 0.85min/min.

c) Temperature: 25°C.

d) Injection volume: 20ul.

Based on above conditions, a typical chromatogram was as following, the MDL are 0.012ug/mL for Mono-chloroacetic acid (ClCH_2COOH) and 0.051ug/mL for Di-chloroacetic acid (Cl_2CHCOOH) respectively.

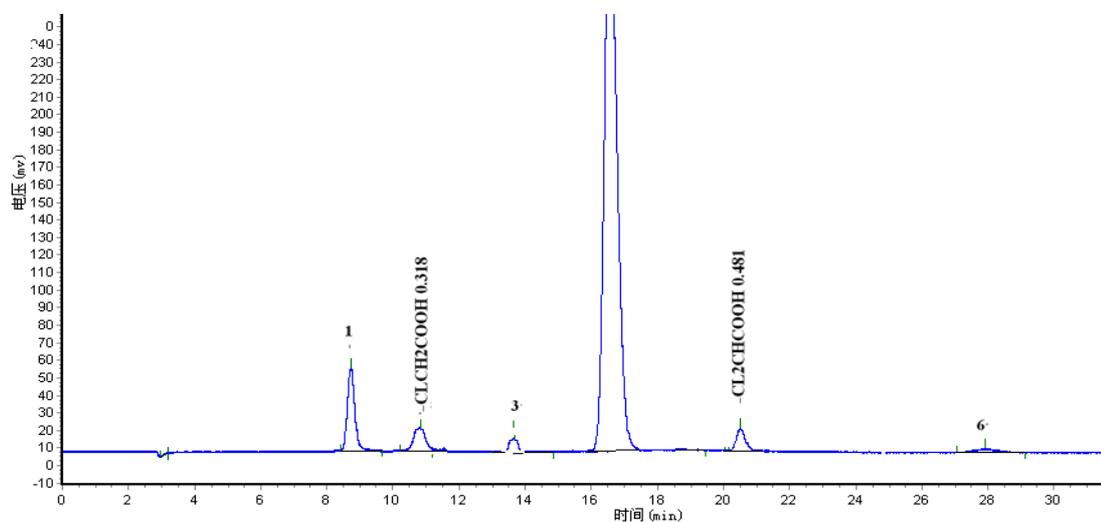


Fig 2 The chromatogram of mono-chloroacetic acid and di-chloroacetic acid in sample(under condition 2)

6.3 Preparation of the stock solution

Weigh about 0.1g of standard mono-chloroacetic acid(4.2) and 0.1g of di-chloroacetic acid(4.3)(accurate to 0.0001g) in a 50ml beaker, add about 20ml of water (4.1) and stir. Transfer to a 1000ml volumetric flask, rinse the beaker at least twice with water(4.1) and transfer to the volumetric flask. Make up to the mark and shake well. This solution is the stock solution .The concentration of this solution are following: mono-chloroacetic acid about 0.1mg/ml and di-chloroacetic acid about 0.1mg/ml.

The stock solution shall be preserved at 4°C in refrigerator and expire after 7 days of storage.

6.4 Preparation of the standard solution

Transfer 0.1ml, 0.5ml, 1.0ml, 5.0ml, 10.0ml of stock solution into 5 100ml volumetric flasks, dilute to the mark with water and shake well. These are standard solutions for calibration curve. The standard solutions shall be prepared before injection and expired after analyzing.

Filter the standard solutions with syringe filter and inject 20ul for analysis. Calculate the linear correlation coefficient with proper calculator or software. R obtained shall be 0.999 or more.

This is the calibration curve.

6.5 Analysis of sample

Weigh about 1- 5g of sample (accurate to 0.0001g) in a 100ml beaker, add about 30ml of water(4.1) and stir till the sample dissolved completely. Transfer into a 100ml volumetric flask, rinse at least twice. Make up to the mark with water and shake well. Filter with syringe filter and inject 20ul for analysis.

7 Result and calculation

7.1 Calculate the content of sodium mono-chloroacetic acid (sodium chloro acetate) by equation(1):

$$X (mg / kg) = \frac{A \times V \times 116.5}{m \times 94.5} \dots\dots\dots(2)$$

Where :

X: The content of sodium mono-chloroacetic acid (sodium chloro acetate), mg/kg.

A: The calculated concentration of sodium mono-chloroacetic acid (sodium chloro acetate) in test sample solution, µg/mL.

V: The volume of test sample, mL.

M: The weight of test sample, g.

116.5: The mole weight of sodium mono-chloroacetic acid (sodium chloro acetate), g.

94.5: The mole weight of mono-chloroacetic acid, g.

7.2 Calculate the content of sodium di-chloroacetic acid (sodium di-chloro acetate) by equation(2):

$$X (mg / kg) = \frac{A \times V \times 150.9}{m \times 128.9} \dots\dots\dots(2)$$

Where :

X: The content of sodium di-chloroacetic acid (sodium di-chloro acetate), mg/kg.

A: The calculated concentration of sodium di-chloroacetic acid (sodium di-chloro acetate) in test sample solution, $\mu\text{g/mL}$.

V: The volume of test sample, mL.

M: the weight of test sample, g.

150.9: The mole weight of sodium mono-chloroacetic acid (sodium chloro acetate),g.

128.9: The mole weight of mono-chloroacetic acid, g.

8 Test report

This test report shall contain at least the following information:

- a) the test method used, with reference to this International Standard
- b) all information necessary for the complete identification of the test compound;
- c) all the data (e.g. in tabular form) obtained and the calibration curve;
- d) all operating details not specified in this International Standard, or regarded as optional, together with details of any incidents which may have influenced the test result(s).