Thiols (mercaptans) in Fuels (ASTM D3227-13)

DOC316.52.93109

Potentiometric titration
Applications: gasolines, kerosenes, aviation turbine fuels, distillate fuels

1. Introduction

This test method covers the determination of mercaptan sulfur in gasolines, kerosenes, aviation turbine fuels, and distillate fuels. Organic sulfur compounds such as sulfides, disulfides, and tiophene, do not interfere. Elemental sulfur in amounts of less than 0.0005 mass % does not interfere. Hydrogen sulfide will interfere if not removed.

2. Principle

The hydrogen sulfide-free sample is dissolved in an alcoholic sodium acetate titration solvent and titrated potentiometrically with silver nitrate solution, using as an indicator the potential difference between a glass electrode and a silver/silver-sulfide electrode. Under these conditions, the mercaptan sulfur is precipitated as silver mercaptide and the end point of the titration is shown by a change in cell potential.

3. Electrodes and reagents

PHG301 + CL114 cable: Glass pH electrode

M295Ag: Metal electrode (silver rod)

Legacy adapter: The pH electrode PHG301 is plugged into the BNC socket using the CL114 cable, and the silver electrode is plugged into the banana socket

Titrant: $AgNO_3$ 0.01 mol/L: Prepare a 0.1 mol/L stock solution by dissolving 16.865 g of $AgNO_3$ in 100 mL of distilled water and complete to 1000 mL in a volumetric flask with propan-2-ol. Prepare the 0.01 mol/L titrant solution by diluting 100 mL of the stock solution to 1000 mL with propan-2-ol in a volumetric flask. Store the $AgNO_3$ solutions in brown glass bottles

Note: *As aqueous $AgNO_3$ 0.1 mol/L is commercially available, you can also prepare the 0.01 mol/L titrant solution by diluting 100 mL of the 0.1 mol/L aqueous solution to 1000 mL with propan-2-ol using a volumetric flask*

Alkaline titration solvent: Dissolve 2.7 g of sodium acetate trihydrate ($NaC_2H_3O_2.3H_2O$) or 1.6 g of anhydrous sodium acetate ($NaC_2H_3O_2$) in 25 mL of water (free of dissolved oxygen), and pour into 975 mL of propan-2-ol

Acidic titration solvent: Dissolve 2.7 g of sodium acetate trihydrate ($NaC_2H_3O_2.3H_2O$) or 1.6 g of anhydrous sodium acetate ($NaC_2H_3O_2$) in 20 mL of water (free of dissolved oxygen), pour into 975 mL of propan-2-ol and add 4.6 mL of glacial acetic acid

Standard for titrant calibration: Potassium iodide approximately 0.01 mol/L: Dissolve 1.7 g of KI (weigh to 0.01 g) in 100 mL of water in a 1-L volumetric flask and dilute to 1 L. Calculate the exact molarity

Cadmium sulfate, acid solution (150 g/L): Dissolve 150 g of cadmium sulfate ($3CdSO_4.8H_2O$) in water. Add 10 mL of dilute H_2SO_4 and dilute to 1 L with water

Sodium sulfide solution (10 g/L): Dissolve 10 g of Na_2S in water and dilute to 1 L with water. Prepare fresh as needed

3.1. Preparation and storage of silver/silver-sulfide electrode

Prepare the silver sulfide coating on the silver electrode using the following method:

- Gently polish the electrode until a clean silver surface shows
- Prepare a solution of 100 mL of titration solvent containing 8 mL of Na_2S solution.
  Note: *To improve the deposition, add a few drops of nitric acid HNO_3 to adjust the pH to around 9 and heat the solution to 60 °C*
- Immerse the electrode
- Add slowly, with stirring, 10 mL of 0.1 mol/l $AgNO_3$ solution over a period of 30 min
- Remove the electrode from the solution, wash with water and wipe with a soft tissue

Between batches of titrations, store the electrode for a minimum of 5 min in 100 mL of titration solvent containing 0.5 mL of the 0.1 mol/L $AgNO_3$ solution.

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4. Ranges and settings

4.1. Default parameters

The working procedure is described using the following parameters:

- m sample = 20 g, but can be between 10 and 50 g depending on the expected mercaptan content. Indicative sample masses are given as a guide:

Expected mercaptan sulfur (mg/kg)	m sample (g)
50-100	10-20
10-50	20-40
<10	30-50

- Burette volume = 10 mL

4.2. Working range

ASTM D3227-13 standard specifies that this test method can be used to determine mercaptan sulfur content between 3 and 100 mg/kg.

The method has been tested for low contents of up to 1.5 mg/kg, using a sample weighing at least 30 g.

4.3. Settings

Name	Default parameter	Unit
Application		
Application name	Thiols	
Sample		
Name	Sample	
Amount	20.000	[g]
Probes		
Recommended pH probe	PHG301	
Recommended Ag probe	M295Ag	
Titrant		
Name	$AgNO_3$	
Titrant concentration	0.01000	[eq/L]
Syringe	Syringe 1	
Rinsing step (propan-2-ol)		
Active	Yes	
Time	30	[s]
Stirring speed	25	[%]
IP titration		
Stirring speed	20	[%]
Measured parameter		[mV]
Predose	0	[mL]
Max volume stop point	10	[mL]
Stop on last EQP	Yes	
Delay	15	[s]
Stability criteria	6	[mV/min]
Min increment size	0.05	[mL]
Max increment size	0.5	[mL]
Result 1 name	Mercaptan sulfur	[%]
R1 resolution	5 decimals	
R1 min	0.00015	[%]
R1 max	0.01	[%]
R1 QC min	0.00015	[%]
R1 QC max	0.01	[%]
R1 EQP index	1	
R1 molar weight	32.06	[g/mol]
Result 2 name	Mercaptan sulfur	[mg/kg]
R2 resolution	1 decimal	

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R2 min	1.5	[mg/kg]
R2 max	100	[mg/kg]
R2 QC min	1.5	[mg/kg]
R2 QC max	100	[mg/kg]
R2 EQP index	1	
R2 molar weight	32.06	[g/mol]

4.4. Modification of the settings

The parameters are defined in order to have the best compromise between accuracy and titration time. The stability criteria of 6 mV/min is defined by the ASTM D3227-13 standard.

For higher concentrations with a high titrant volume, the titration time can be reduced with an addition of titrant (predose) at the beginning of the titration. Enter the predose volume (in mL) and the stirring time after the addition in the application edit window.

5. Titration procedure

A titration is divided into several parts:

- A rinsing step for the electrodes (pH probe and Ag probe): 30 seconds in propan-2-ol
- A blank determination to determine the equivalent volume induced by the solvent
- A second rinsing procedure
- A titration of mercaptan sulfur

5.1. Sample analysis

Before titration, qualitatively test the sample for hydrogen sulfide H_2S according to the ASTM D3227 standard and if needed pre-treat the sample following the given procedure.

The choice of titration solvent (alkaline or acidic) depends on the type of sample. Refer to the ASTM D3227 standard for more information.

1. Launch the application **Thiols**.
2. On the first screen, in **Sample type** choose **Define blank** and press **Start**.
3. Follow the rinsing indications on the screen. Then, place an empty beaker with a stir bar under the probe holder. 100 mL of solvent will be automatically added by the pump and blank determination will start[1]. Make sure that both electrodes are immersed. At the end of the titration, the equivalent volume corresponding to the blank is displayed and automatically recorded. Press **Next** and choose **New sample**.
   Note: *Make a blank on 100 mL of titration solvent at least daily.*
4. Weigh the sample in the titration beaker according to the recommendations given in section **4.1**.
5. In **Sample type** choose **Sample with blank** (or **Sample** if blank was 0 mL) and press **Start**.
6. Follow the rinsing indications on the screen. Then, place the beaker containing the sample and a stir bar under the probe holder and press **OK**. 100 mL of solvent will be automatically added by the pump and the titration will start[1]. Always make sure that both electrodes are immersed. At the end of the titration, mercaptan sulfur content is displayed in mass % and mg/kg.
7. By pressing **Next** it is possible to:
   - Replicate the sample. This is used to study the repeatability by analyzing several samples successively. At the end of each titration, a window displays the average value, the standard deviation (SD in % and mg/kg) and the relative standard deviation (RSD in %).
   - Analyze a new sample. Another titration can be started but no Standard Deviation and RSD value will be made.

[1] Manual addition of the solvent is also possible: in **Edit** mode, deactivate **Automatic addition** and activate **Manual addition.**

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6. Results

6.1. Result calculation

The calculation used is:

$$\text{Mercaptan sulfur (\%)} = \frac{C_{titrant}\,(mol/L) \times (V_{titrant} - V_{blank})\,(mL)}{n_{e-\ titrant} \times m_{sample}\,(g)} \times M_S\,(g/mol) \times \frac{100}{1000}$$

$$= \frac{0.01\,(mol/L) \times (V_{titrant} - V_{blank})\,(mL)}{1 \times m_{sample}\,(g)} \times 36.02\,(g/mol) \times \frac{100}{1000}$$

$$\text{Mercaptan sulfur (mg/kg)} = \frac{C_{titrant}\,(mol/L) \times (V_{titrant} - V_{blank})\,(mL)}{n_{e-\ titrant} \times m_{sample}\,(g)} \times M_S\,(g/mol) \times 1000$$

$$= \frac{0.01\,(mol/L) \times (V_{titrant} - V_{blank})\,(mL)}{1 \times m_{sample}\,(g)} \times 36.02\,(g/mol) \times 1000$$

6.2. Experimental results

These results are indicative.

Eight successive determinations were made on unleaded 95 gasoline. Sample masses were around 30 g and equivalent volumes of around 0.16 mL for a mean titration duration of 16 minutes.

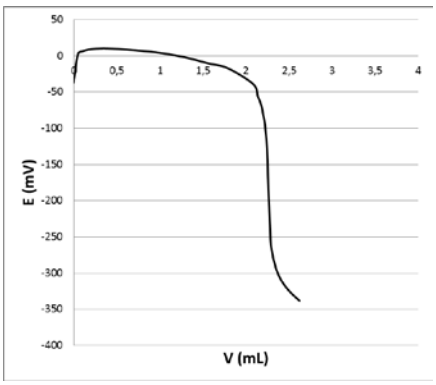
Unleaded 95	
Mercaptan sulfur (%)	0.00017
Mercaptan sulfur (mg/kg)	1.7
Standard deviation (mg/kg)	0.1
Relative standard deviation (%)	7.4

Kerosene 32 mg/kg	
Mercaptan sulfur (%)	0.00333
Mercaptan sulfur (mg/kg)	33.3
Standard deviation (mg/kg)	0.5
Relative standard deviation (%)	1.6

Kerosene 47 mg/kg	
Mercaptan sulfur (%)	0.00485
Mercaptan sulfur (mg/kg)	48.5
Standard deviation (mg/kg)	0.3
Relative standard deviation (%)	0.6

6.3. Example of a titration curve

This curve has been obtained during the analysis of one of the kerosene samples:



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7. Recommendations

The rinsing step can be skipped (right button) or disabled (in **Edit** mode), although it is highly recommended to consistently rinse the electrodes between each measurement in order to maintain good accuracy.

8. Bibliography

- *Standard ASTM D3227-13*

9. Appendix: Titrant calibration

The silver nitrate solution can be calibrated. Its exact concentration can be determined from a titration using potassium iodide.

Add 6 drops of nitric acid HNO_3 to 100 mL of water in a beaker. Remove oxides of nitrogen by boiling for 5 min and cool to an ambient temperature. Pipette 5 mL of 0.01 mol/L KI solution into the beaker. Put in a stir bar, dip the probes and the delivery tip into the solution and launch the titrant calibration sequence.

At the end of the titrant calibration, titer (mol/L) is displayed and the user can reject, replicate, or save the result. The saved value will be used for calculations.

Default settings for titrant calibration

Name	Setting	Unit
IP titration		
Stirring speed	20	[%]
Predose	3	[mL]
Stop on last EQP	Yes	
Delay	0	[s]
Min increment size	0.05	[mL]
Max increment size	0.5	[mL]
Titer result		
Resolution	5 decimals	
Min titer	0.00900	[mol/L]
Max titer	0.01100	[mol/L]
Standard		
Name	KI	
Amount	5	[mL]
Concentration	0.01	[mol/L]

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