

Determination of Mercaptan Sulfur according to ASTM D 3227

Description

This application note describes the determination of mercaptan sulfur in gasoline, kerosene, aviation turbine and distillate fuels according to ASTM D 3227. This procedure is valid for a mercaptan content of 3 – 100ppm. Organic sulfides, disulfides, thiophene and elemental sulfur (less than 5 ppm do not interfere. Hydrogen sulfide (H_2S) must be removed with $CdSO_4$.

Normally an acidic titration solvent is used because of a higher titration speed. For low-molecular mercaptanes usually found in gasoline it is better to use an alkaline titration solvent, because the volatile low-molecular mercaptanes get lost in acidic solvent.

Instruments

Titration	TL 7000, TL 7750, TL 7800
Electrode	Ag 1100 (sulfidized)
Reference electrode	A 1180
Cable	L 1 A + L 1 N
Stirrer	Magnetic stirrer TM 235 or similar
Lab accessory	Beakers 150mL
	separator funnel
	Magnetic stirrer bar 30 mm

Reagents

1	Silver nitrate or Titrisol – $AgNO_3$ concentrate for 0.1 mol/L
2	Nitric acid conc. (65%)
3	Sulfuric acid conc. (96%)
4	Cadmium sulfate ($CdSO_4 \cdot 8H_2O$)
5	Potassium iodide
6	Sodium sulfide or Sodium sulfide nonahydrate
7	Isopropyl alcohol
8	Sodium acetate trihydrate or Sodium acetate anhydrous
9	Glacial acetic acid
10	Distilled water
All reagents should be of analytical grade or better.	

Titration procedure

Reagents

KI-solution 0.1 mol/L

About 17 g KI are dissolved in dist. Water and made up to 1l. The exact concentration is calculated. Only needed if titer determination should be done according to ASTM D 3227.

AgNO₃ – solution 0.1 mol/L (alcoholic solution)

17.0 g AgNO₃ are dissolved in 100ml dist. Water. After dissolution the mixture is made up to 1L with Isopropyl alcohol.

If Titrisol – AgNO₃ concentrate is used the content of one ampoule is made up to 1l in a volumetric flask with Isopropyl alcohol.

According to ASTM D 3227 the titer is determined with KI-solution: Six drops of concentrated HNO₃ are added to 100 mL of dist. Water. Nitrogen oxides are removed by boiling for 5 min. After cooling down 5 ml of the 0.1 mol/l KI solution are added and the solution is titrated with AgNO₃ 0.1 mol/L to an Equivalence point (EQ).

The titer of this solution can also be determined as described in our Application note "Titer determination of AgNO₃". We prefer this because this application uses NaCl as reference material which is available as certified reference material (CRM) for argentometric titrations.

AgNO₃ – solution 0.01 mol/L (alcoholic solution)

100ml of 0.1 mol/l alcoholic AgNO₃-solution are made up to 1l in a volumetric flask with Isopropyl alcohol. This 0.01 m AgNO₃ should be prepared fresh daily. The exact concentration is calculated.

Alkaline solvent

2,7g Sodium acetate trihydrate (or 1.6g anhydrous Sodium acetate) are dissolved in 25 mL dist. Water and made up to about 1L with Isopropyl alcohol. Dissolved oxygen can be removed by purging the solution with a rapid stream of nitrogen for about 10 min.

Acidic solvent

2,7g Sodium acetate trihydrate (or 1.6g anhydrous Sodium acetate) are dissolved in 25 mL dist. Water and 4.6 ml glacial acetic acid are added. The mixture is made up to about 1L with Isopropyl alcohol. Dissolved oxygen can be removed by purging the solution with a rapid stream of nitrogen for about 10 min.

Diluted H₂SO₄

100ml of conc. H₂SO₄ are added in portions to 500ml of dist. water.

CdSO₄ – solution

150g CdSO₄ x 8H₂O are dissolved in dist. Water. 10ml of diluted H₂SO₄ are added. The mixture is made up to 1l with dist. Water.

Na₂S – solution

10g of Na₂S or 30.6g of Na₂S x 9 H₂O are dissolved in dist. Water and made up to 1l.

Cleaning and storage of the electrode

The electrodes are rinsed with Isopropyl alcohol, then with distilled water. The sulfidized Ag 1100 electrode can be used as delivered. The A 1180 reference is stored in water. The Ag 1100 electrode can be sulfidized with the Na₂S – solution as described in the ASTM D3227. The A 1180 reference is stored in water.

Sample preparation

Test for free H₂S

5 mL of the sample are mixed with 5 mL of the acid CdSO₄ solution. The sample can be titrated directly, if no precipitate appears.

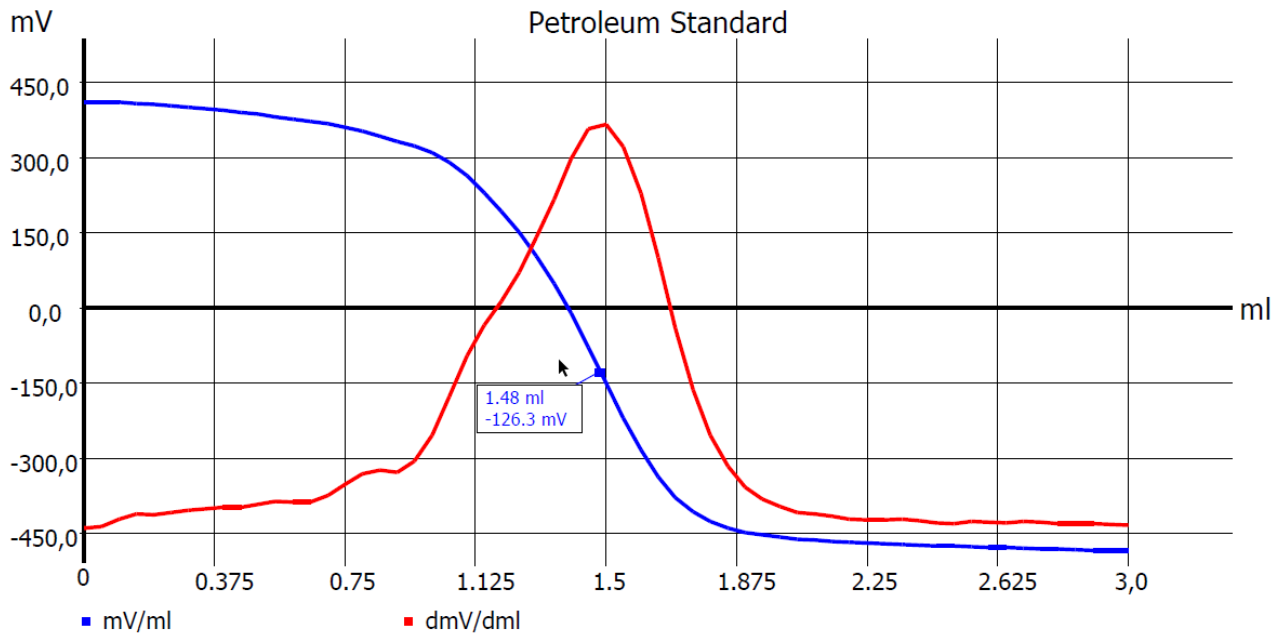
If a yellow precipitate appears, remove the H₂S in the following matter: Place a quantity of the sample (about 3 – 4 times the amount needed for the titration) in a separator funnel containing a volume of the acidic CdSO₄ solution equal to the half of the sample and shake vigorously. Draw off and discard the aqueous phase, and wash the sample 3 times with 25-30 mL portions of water, withdrawing the water after each washing. Repeat the extraction with CdSO₄ until all of the H₂S has been removed.

Sample titration

70mL of the solvent mixture (acidic or alkaline, depending on the sample) are placed in a beaker. 20 – 30mL of the sample are pipetted in this beaker. The sample is titrated immediately with 0.01 mol/L AgNO₃ solution to an EQ.

Important: The indicator electrode Ag 1100 must be connected with the reference connector of the titrator, using cable L 1 N. The reference electrode A 1180 must be connected to the DIN connector of the titrator with cable L 1 A.

Titration parameter



Default method	Mercaptane sulfur		
Method type	Automatic titration		
Modus	linear		
Measured value	mV		
Measuring speed / drift	Individual	Minimum holding time	5 s
		Maximum holding time	15 s
		Measuring time	4 s
		Drift	5 mV/min
Initial waiting time	10 s		
Linear step size	0.05 mL		
Damping	strong	Titration direction	Decrease
Pretitration	off	Delay time	0 s
End value	off		
EQ	On (1)	Slope value	250
Max. titration volume	10 mL		
Dosing speed	100%	Filling speed	30 s

Calculation:

$$R - SH [ppm] = \frac{(EQ1 - B) * T * M * F1}{V * F2}$$

B	0	Blank value
EQ1		Consumption of titrant at first Equivalence point
T	WA	Actual concentration of the titrant
M	32,06	Molecular weight
V	man	sample volume in mL
F1	1000	Conversion factor
F2	1	Conversion factor

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