



## Thiols (Mercaptans) in Fuels

### Introduction

Thiols (or organic mercaptans) have an unpleasant odour and are corrosive. Thiols are removed during the manufacture of fuels such as gasoline, kerosene, aviation turbine and distillate fuels and it is important to check the efficiency of the treatment and the quality of the final product. Thiol titration uses the reaction of the R-SH group with Ag<sup>+</sup> in a nonaqueous media with a silver/silver sulphide measuring electrode.

### Principle

The Ag<sup>+</sup> ion reacts with the thiols according to



1 mole of thiol corresponds to 1 mole of Ag<sup>+</sup> ion

The titrant concentration is 0.01M

Results are expressed as a % (sometimes in mg/kg) of S (AW = 32.07 g/mol)

The titration is run using inflection point determination with a silver/silver sulphide measuring electrode and a glass reference electrode.

### Electrode and reagents

As the titration occurs in nonaqueous media, it is recommended to work with a three-electrode system (see electrode maintenance and storage notes).

M295Ag Metal Electrode (part no. E34M003) connected to the reference INPUT by means of a adapter part no. A94P807

pHG301 Glass Electrode (part no. E11M001) connected to measuring input E1 by means of cable part no. A94L114

M241Pt Metal Electrode (part no. E31M001) connected to GROUND

AgNO<sub>3</sub> 0.01M in isopropanol (2-propanol)

Prepare a 0.1M stock solution by dissolving 16.865 g of AgNO<sub>3</sub> in 100 ml of distilled water and complete to 1000 ml in a volumetric flask with 2-propanol.

Prepare the 0.01M titrant solution by diluting 100 ml of the stock solution to 1000 ml with 2-propanol in a volumetric flask.

Store the AgNO<sub>3</sub> solutions in brown glass bottles.

As aqueous AgNO<sub>3</sub> 0.1M is commercially available, you can also prepare the 0.01M titrant solution by

diluting 100 ml of the 0.1M aqueous solution to 1000 ml with 2-propanol using a volumetric flask.

### Alkaline titration solvent

Dissolve 1.6 g of anhydrous CH<sub>3</sub>COONa in 25 ml of free dissolved oxygen distilled water and complete to 1000 ml with 2-propanol

*This solvent is used if low molecular weight thiols are expected*

### Acidic titration solvent

Dissolve 1.6 g of anhydrous CH<sub>3</sub>COONa in 20 ml of free dissolved oxygen distilled water, add 4.6 ml of glacial acetic acid and complete to 1000 ml with 2-propanol

### Sodium sulphide solution

Dissolve 10 g of Na<sub>2</sub>S in 1000 ml of water

Warning: Reagents used in this application note are flammable. They can cause severe burns and are hazardous if swallowed, breathed or come into contact with the skin or eyes. Always respect laboratory health and safety regulations when using these reagents.

### Inflection Detection settings

#### CONTINUOUS IP

Cell grounding:	M241Pt
Burette volume:	10 ml
Max. volume:	10 ml
Stirring speed:	500 rpm
Working mode:	mV
Start timer:	45 s
Stop point:	-450 mV
Minimum speed:	0.20 ml/min
Maximum speed:	3.00 ml/min
Smoothing param: 4	
Titration:	Decreasing mV
Inflection number:	1
Inflection 1	
Min. ordinate:	-300 mV (see notes)
Max. ordinate:	-150 mV (see notes)
Stop at last IP:	YES
Sample	
Dilution:	NO
Sample unit:	g
Sample amount:	10 (see working range)
Number of results:	2
Result 1:	%
Reaction:	1 smp + 1 Titr
Molar weight:	32.060

Result 2: mg/kg  
 Reaction: 1 smp + 1 Titr  
 Molar weight: 32.060

Result: 5.18.10<sup>-4</sup> %  
 5.18 mg/kg

Sample amount around 30 g  
 Titrant volume around 0.45 ml

## Procedure

### Electrode preparation

A silver/silver sulphide electrode has to be used for this application.

To coat the silver electrode with silver sulphide proceed as follows:

For the first time, clean the silver electrode using an abrasive band (part no. 991-565).

Dip the silver electrode in a beaker with 100 ml of alkaline titration solvent and 8 ml of Na<sub>2</sub>S solution.

Using a pipette, add by increments over a 10 to 15 min. period 10 ml of AgNO<sub>3</sub> 0.1M solution.

Remove the electrode from the solution. If the sulphide coating is correct, the silver rod is black over its entire surface.

### Sample preparation

To determine thiols according to ASTM D3227, it is necessary to eliminate any hydrogen sulphide (H<sub>2</sub>S) present using acidic solution of CdSO<sub>4</sub>. Refer to the standard for the exact procedure.

### Titration

Weigh the recommended amount of sample (see working range). Add 100 ml of basic titration solvent

Dip electrodes and delivery tip in the beaker

Run the titration

## Results

**Expressed, according to the ASTM standard, as a % of S but also according to local rules in mg/kg or ppm of S**

$$R(\text{in } \%) = V(\text{titr}) * C(\text{titr}) * 32.06 * 100 / W(\text{smp}) * 1000$$

- 1000 = to have a result in g of S, the delivered volume is in ml
- V(titr) = total volume of titrant to reach the inflection point in ml
- C(titr) = Titrant concentration in mol/l (generally 0.01)
- W(smp) = sample amount in g
- 100 = to have a result for 100 g of sample
- 32.06 = Molar weight of S

The Titration manager calculates the result directly expressed as a % and mg/kg of S when the above inflection detection settings are applied.

### For 3 determinations on untreated kerosene

Mean: 0.012767%  
 127.67 mg/kg  
 Standard deviation: 0.000056 %  
 0.06 mg/kg

Sample amount around 10 g  
 Titrant volume around 3.6 ml

### Test on a gasoline S95

## Working Range

For low concentrations of thiols (around 5 mg/kg or 5.10<sup>-4</sup> %), weigh 30 to 50 g of sample to obtain a titration volume of around 0.4-1.0 ml.

For high concentrations of thiols, 10 g of sample are sufficient.

According to the formula for 20 g of sample, 1 ml of titrant corresponds to 0.0016% (or 1.6 mg/kg) of S.

## Notes

### ELECTRODE STORAGE AND MAINTENANCE

At the end of the titration, rinse electrodes with distilled water and wipe the glass electrode. Store the glass electrode as indicated in the operating instructions. Store the silver electrode in distilled water or in a solution of 100 ml of titration solvent containing 0.5 ml of the 0.1M AgNO<sub>3</sub> solution

Depending on local regulations, some laboratories use a combined Ag/Reference electrode as such as the MC6091Ag (part no. E34M004) instead of separate glass and silver electrodes.

### MIN AND MAX ORDINATES

The above values correspond to the alkaline titration solvent. When a glass electrode is used as "reference", it is necessary to change these values for those of the acidic titration solvent.

### NOTE REGARDING TITRATION DIRECTION

Using the Titration Manager, you need to connect glass and silver as indicated: pHG301 to the measuring input M291Ag to the reference input.

The titration direction is therefore the opposite of that using a (Hg/HgSO<sub>4</sub>) reference electrode and a silver electrode connected in the conventional way.

### NOTE REGARDING ELECTRODE CREATION

With the Titration Manager

#### First create the reference electrode

Function: Reference / ID from other / ID: M291Ag - (for example)

#### Next create the measuring electrode

Function: mV (i=0) / ID from catalogue / pHG301/ ID: Reference / from user / M291Ag

### Curve

