Metrohm

Potentiometric determination of hydrogen sulfide, carbonyl sulfide and mercaptans in petroleum products

Branch

General analytical chemistry; petrochemistry, biofuels

Keywords

Potentiometric titration; automation; hydrogen sulfide; H_2S; carbonyl sulfide; mercaptan; petroleum products; natural gas; liquefied petroleum gas; petrol; gasoline; kerosene; branch 1; branch 5

Summary

This bulletin describes the potentiometric determination of hydrogen sulfide, carbonyl sulfide and mercaptans in gaseous and liquid products of the oil industry (natural gas, liquefied petroleum gas, used absorption solutions, distillate fuels, aviation petrol, gasoline, kerosene, etc.). The samples are titrated with alcoholic silver nitrate solution using the Ag Titrode for the equivalence point indication.

Instruments

- Titrator with DET mode
- Sample changer
- Rod stirrer
- Titration vessel with lid and gas inlet and overflow tube with valve

Electrodes

Ag Titrode with Ag_2S coating	6.0430.100S

Liquid samples

Reagents

- Silver nitrate ($AgNO_3$)
- Isopropanol (IPA) or ethanol (EtOH)
- Sodium acetate trihydrate ($CH_3COONa \cdot 3\ H_2O$)
- Glacial acetic acid
- Ammonia, $w(NH_3) = 25\%$
- Potassium chloride standard, $c(KCl) = 0.1000$ mol/L, Metrohm Article number 6.2301.060

Solutions

Stock solution titrant	$c(AgNO_3) = 0.1$ mol/L If possible this solution should be bought from a supplier 16.988 g $AgNO_3$ is dissolved in 80 mL dist. water and made up to 1000 mL with EtOH or IPA.
Titrant	$c(AgNO_3) = 0.01$ mol/L: 100 mL $AgNO_3$ stock solution is mixed with 80 mL dist. water and made up to 1000 mL with ethanol or IPA.
Alkaline solvent for low molecular mercaptans	2.7 g $NaCH_3COO \cdot 3\ H_2O$ is dissolved in 25 mL dist. water. Add 975 mL IPA as well as 10 mL $w(NH_3) = 25\%$ and mix.
Acidic solvent for higher molecular mercaptans	2.7 g $NaCH_3COO \cdot 3\ H_2O$ is dissolved in 25 mL dist. water. Add 975 mL IPA as well as 4.6 mL glacial acetic acid and mix.

Sample preparation

No sample preparation is required.

Analysis

Titer

To 1 mL $c(KCl) = 0.1$ mol/L standard solution 40 mL solvent is added and the solution then titrated with $c(AgNO_3) = 0.01$ mol/L until after the equivalence point.

Sample

Depending on the expected sulfur content a suitable volume of sample (see table below) is added to 100 mL solvent*. While passing nitrogen over the solution, the solution is titrated with alcoholic $c(AgNO_3) = 0.01$ mol/L until after the first or second equivalence point, depending on the sample.

If the sample contains only H_2S or mercaptans only one equivalence point is found, if the sample contains both two equivalence points are found.

If the sample does not dissolve completely in the solvent, some toluene can be added.

* For aviation petrol, kerosene and distillate fuels, which normally contain higher molecular mercaptans the acidic solvent is used.

For low boiling hydrocarbon fractions, which also contain low molecular mercaptans, the alkaline solvent is used.

Expected sulfur content / (mg S / kg sample)	Sample size / mL
1–50	50
50–100	25
100–300	10
300–500	5

Parameters

Titer

Mode	DET U
Stirring rate	8
Pause	20 s
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	32 s
Meas. point density	4
Min. increment	10 µL
ERC	5
EP recognition	greatest

Sample

Mode	DET U
Stirring rate	4
Pause	20 s
Signal drift	10 mV/min
Min. waiting time	0 s
Max. waiting time	20 s
Meas. point density	2
Min. increment	50 µL
ERC	5
EP recognition	all

Calculation

Titer

$$f = \frac{V_S \times c_{KCl}}{V_{EP1} \times c_{AgNO_3}}$$

f: Titer of $c(AgNO_3) = 0.01$ mol/L

V_S: Added volume of $c(KCl) = 0.1$ mol/L

c_{KCl}:   Concentration of the standard in mol/L; here $c(KCl) = 0.1$ mol/L

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{AgNO_3}:   Concentration of $c(AgNO_3) = 0.01$ mol/L

Hydrogen sulfide

$$H_2S = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_S}{\rho_S \times V_S \times 2} \times 1000$$

H_2S: mg of sulfur present as hydrogen sulfide per kg sample

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{AgNO_3}:   Concentration of titrant in mol/L; here $c(AgNO_3) = 0.01$ mol/L

f: Titer of $AgNO_3$

M_S: Molecular mass of sulfur, 32.066 g/mol

ρ_S: Density of the sample in g/mL

V_S: Sample volume in mL

2:      Stoichiometric factor

1000:   Conversion factor

Mercaptans (besides H₂S)

Mercaptans (besides H$_2$S)

$$RSH = \frac{(V_{EP2} - V_{EP1}) \times c_{AgNO_3} \times f \times M_S}{\rho_S \times V_S} \times 1000$$

RSH:	mg of sulfur present as mercaptans per kg sample
V_{EP2}:	Titrant consumption until the second equivalence point in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{AgNO_3}:	Concentration of titrant in mol/L; here c(AgNO$_3$) = 0.01 mol/L
f:	Titer of AgNO$_3$
M_S:	Molecular mass of sulfur, 32.066 g/mol
ρ_S:	Density of the sample in g/mL
V_S:	Sample volume in mL
1000:	Conversion factor

Mercaptans in presence of elementary sulfur

$$RSH = \frac{(V_{EP3} - V_{EP1}) \times c_{AgNO_3} \times f \times M_S}{\rho_S \times V_S} \times 1000$$

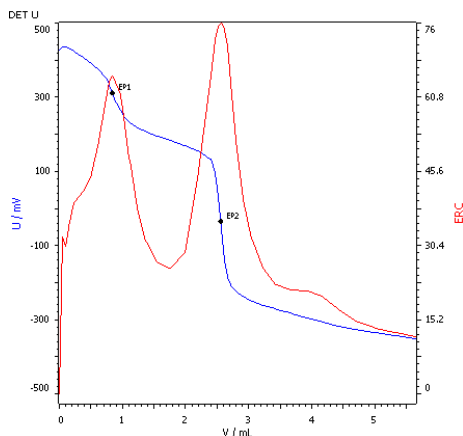|	
RSH:	mg of sulfur present as mercaptans per kg sample
V_{EP3}:	Titrant consumption until the third equivalence point in mL
V_{EP1}:	Titrant consumption until the first equivalence point in mL
c_{AgNO_3}:	Concentration of titrant in mol/L; here c(AgNO$_3$) = 0.01 mol/L
f:	Titer of AgNO$_3$
M_S:	Molecular mass of sulfur, 32.066 g/mol
ρ_S:	Density of the sample in g/mL
V_S:	Sample volume in mL
1000:	Conversion factor

Example determination

Fig. 1: Titration curve of H$_2$S and mercaptans (blue = titration curve, red = ERC)
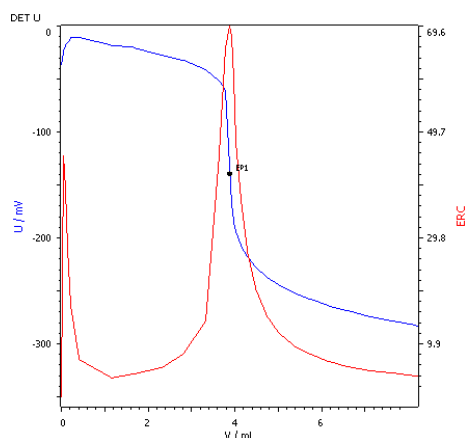

Fig. 2: Titration curve of only mercaptans (blue = titration curve, red = ERC)
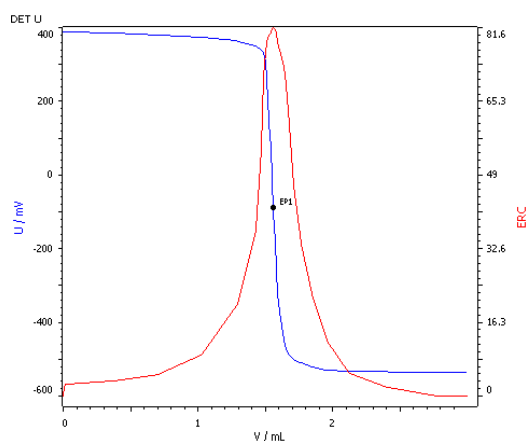

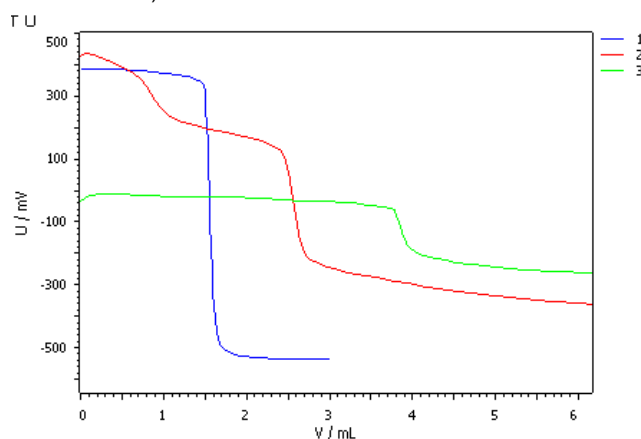Fig. 3: Titration curve of only H$_2$S (blue = titration curve, red = ERC)

Fig. 4: Titration curve overlay, 1 = only H$_2$S, 2 = H$_2$S and mercaptans, 3 = only mercaptans

Comments

- Different titration curves can occur:
    - Samples containing H_2S and mercaptans have a titration curve, which shows two equivalence points. EP1 corresponds to H_2S and EP2 to the mercaptans.
    - If the sample contains only H_2S or only mercaptans then only one single equivalence point is obtained. Generally samples containing mercaptans have smaller potential jumps and a lower initial measured value (see Fig. 4).
    - In the presence of elementary sulfur (besides H_2S and mercaptans) a third, flatter potential jump appears after the EP of H_2S. Free sulfur reacts with mercaptans to form the corresponding disulfides:
      $$S + R\text{-}SH \rightarrow R\text{-}SSH$$
      The elementary sulfur is ignored when calculating the mercaptan sulfur (see *Calculations*).

- Both H_2S and mercaptans are oxidized by atmospheric oxygen. It is therefore necessary to carry out the titration under an inert gas (nitrogen). The solvent used must be free from oxygen, too. In order to remove any oxygen, nitrogen is bubbled through the solvent in the titration vessel for 5 min prior to the analysis.

- Titration should not be too fast because mercaptans react only slowly with $AgNO_3$.

References

- ISO 3012:1999
  Petroleum products -- Determination of thiol (mercaptan) sulfur in light and middle distillate fuels -- Potentiometric method

- ASTM D3227-04a
  Standard Test Method for (Thiol Mercaptan) Sulfur in Gasoline, Kerosene, Aviation Turbine, and Distillate Fuels (Potentiometric Method).

- IP 342
  Petroleum products -- Determination of thiol (mercaptan) sulfur in light and middle distillate fuels -- Potentiometric method

- UOP163-10
  Hydrogen Sulfide and Mercaptan Sulfur in Liquid Hydrocarbons by Potentiometric Titration

- UOP209-00
  Alkalinity, Sulfide and Mercaptide Analyses of Used Refinery Caustic Solutions

Gaseous samples

Reagents

- Silver nitrate ($AgNO_3$)

- Isopropanol (IPA) or ethanol (EtOH)

- Sodium acetate trihydrate ($NaCH_3COO \cdot 3\,H_2O$)

- Glacial acetic acid

- Ammonia, $w(NH_3) = 25\%$

- Sodium hydroxide (NaOH) or potassium hydroxide (KOH)

- Disodium ethylendiaminetetraacetic acid (Na_2EDTA)

- Monoethanolamine (MEA)

- Potassium chloride standard, $c(KCl) = 0.1000$ mol/L, Metrohm 6.2301.060

Solutions

Stock solution titrant	$c(AgNO_3) = 0.1$ mol/L If possible this solution should be bought from a supplier. 16.988 g $AgNO_3$ is dissolved in 80 mL dist. water and made up to 1000 mL with ethanol or IPA.
Titrant	$c(AgNO_3) = 0.01$ mol/L: 100 mL $AgNO_3$ stock solution is mixed with 80 mL dist. water and made up to 1000 mL with ethanol or IPA.
Alkaline solvent for low molecular mercaptans	2.7 g $NaCH_3COO \cdot 3\,H_2O$ is dissolved in 25 mL dist. water. 975 mL IPA as well as 10 mL $w(NH_3) = 25\%$ is added and the solution is mixed.
Acidic solvent for higher molecular mercaptans	2.7 g $NaCH_3COO \cdot 3\,H_2O$ is dissolved in 25 mL dist. water. 975 mL IPA as well as 4.6 mL glacial acetic acid is added and the solution is mixed.
Absorption solution for H_2S and mercaptans	$w(KOH) = 30\%$ or $w(NaOH) = 30\%$; addition of 5 g/L Na_2EDTA (to complex heavy metals)
Absorption solution for carbonyl sulfide	$w(MEA) = 5\%$ in ethanol [e.g. 5 g MEA in 95 g ethanol]

Sample preparation

The sulfur compounds to be determined are absorbed in alkaline solutions (Apparatus see *References*). The first two absorption vessels are filled with $w(KOH) = 30\%$ or $w(NaOH) = 30\%$ (for the determination of H_2S and mercaptans), the third absorption vessel with $w(MEA) = 5\%$ in ethanol (for the determination of carbonyl sulfide).

Analysis

Titer

To 1 mL $c(KCl) = 0.1$ mol/L standard solution 40 mL solvent is added. The solution is then titrated with $c(AgNO_3) = 0.01$ mol/L until after the equivalence point.

H_2S and mercaptans

The contents of the absorption vessel are rinsed into the titration vessel with oxygen-free dist. water. The solution is titrated with alcoholic $c(AgNO_3) = 0.01$ mol/L while passing nitrogen over.

Absorption solutions from refineries (refinery caustic solutions) usually contain little H_2S besides large quantities of mercaptans. In this case, the titration is stopped after the first equivalence point (which corresponds to H_2S) and a second titration is carried out with a smaller sample size in order to determine the mercaptans.

Carbonyl sulfide

The absorption solution is rinsed into the titration vessel with oxygen-free ethanol. 1 mL $w(NH_3) = 25\%$ is added and titrated with alcoholic $c(AgNO_3) = 0.01$ mol/L while passing nitrogen over the solution.

Parameters

Titer

Mode	DET U
Stirring rate	8
Pause	20 s
Signal drift	30 mV/min
Min. waiting time	0 s
Max. waiting time	30 s
Meas. point density	4
Min. increment	10 µL
ERC	5
EP recognition	greatest

Sample

Mode	DET U
Stirring rate	4
Pause	20 s
Signal drift	10 mV/min
Min. waiting time	20 s
Max. waiting time	60 s
Meas. point density	4
Min. increment	10 µL
ERC	5
EP recognition	all

Calculation

Titer

$$f = \frac{V_S \times c_{KCl}}{V_{EP1} \times c_{AgNO_3}}$$

f: Titer of c(AgNO₃)= 0.01 mol/L

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{KCl}:   Concentration of the standard in mol/L; here c(KCl) = 0.1 mol/L

V_S: Added volume of c(KCl) = 0.1 mol/L

c_{AgNO_3}:   Concentration of c(AgNO₃) = 0.01 mol/L

The sulfur content is given in mg S/m³ dry gas under «standard conditions», i.e. at 273.15 K (0 °C).

Absorbed gas volume

$$V_S = \frac{t \times v_S \times 273}{T}$$

V_S: Absorbed gas volume in L

t: Temperature in °C

v_S: Flow rate of the gas in L/min

T: Temperature in K (t + 273.15)

Hydrogen sulfide

$$H_2S = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_S}{V_S \times 2} \times 1000$$

H_2S: mg of sulfur present as hydrogen sulfide per L dry gas

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{AgNO_3}:   Concentration of titrant in mol/L; here c(AgNO₃) = 0.01 mol/L

f: Titer of AgNO₃

M_S: Molecular mass of sulfur, 32.066 g/mol

V_S: Absorbed gas volume in L

2:      Stoichiometric factor

1000:   Conversion factor

Mercaptans (besides H₂S)

$$RSH = \frac{(V_{EP2} - V_{EP1}) \times c_{AgNO_3} \times f \times M_S}{V_S} \times 1000$$

RSH: mg of sulfur present as mercaptans per L dry gas

V_{EP2}:   Titrant consumption until the second equivalence point in mL

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{AgNO_3}:   Concentration of titrant in mol/L; here c(AgNO₃) = 0.01 mol/L

f: Titer of AgNO₃

M_S: Molecular mass of sulfur, 32.066 g/mol

V_S: Absorbed gas volume in L

1000:   Conversion factor

Carbonyl sulfide

$$COS = \frac{V_{EP1} \times c_{AgNO_3} \times f \times M_S}{V_S \times 2} \times 1000$$

COS: mg of sulfur present as carbonyl sulfide per L dry gas

V_{EP1}:   Titrant consumption until the first equivalence point in mL

c_{AgNO_3}:   Concentration of titrant in mol/L; here c(AgNO₃) = 0.01 mol/L

f: Titer of AgNO₃

M_S: Molecular mass of sulfur, 32.066 g/mol

V_S: Absorbed gas volume in L

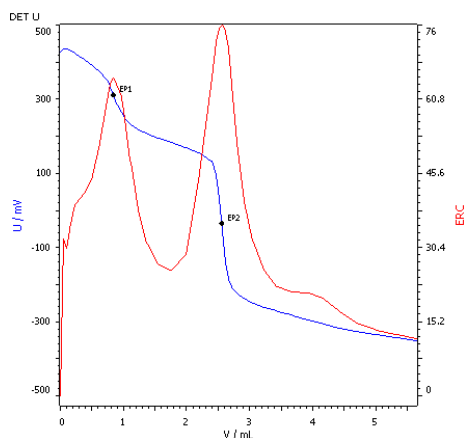2:   Stoichiometric factor

1000:   Conversion factor

Example determination

Fig. 5:   Titration curve of H₂S and mercaptans (blue = titration curve, red = ERC)

Application Bulletin 135/3
Potentiometric determination of hydrogen sulfide, carbonyl
sulfide and mercaptans in petroleum products
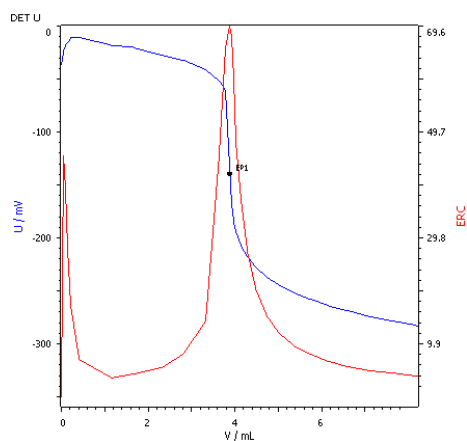

Fig. 6:   Titration curve of only mercaptans (blue = titration curve,
           red = ERC)

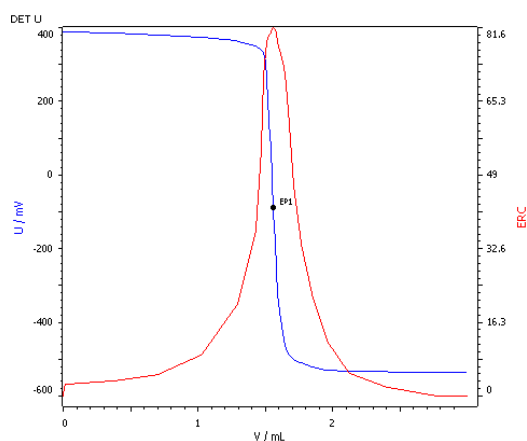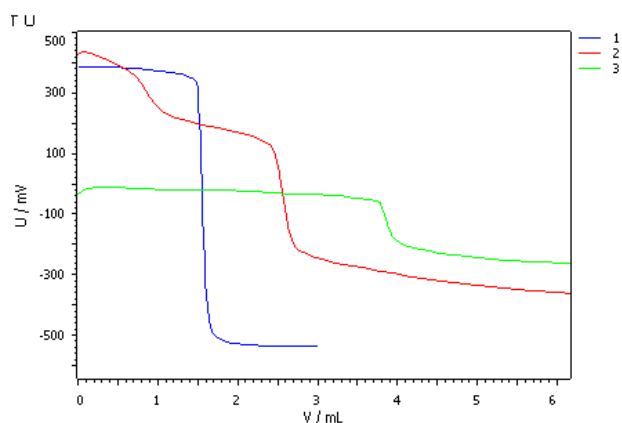Fig. 7:   Titration curve of only H₂S (blue = titration curve, red =
           ERC)

Fig. 8:   Titration curve overlay, 1 = only H2S, 2 = H2S and
           mercaptans, 3 = only mercaptans

Comments

- Normally two equivalence points appear. EP1 corresponds to H_2S and EP2 to the mercaptans.

- If the sample contains only H_2S or only mercaptans then only one single equivalence point is obtained. Generally samples containing mercaptans have smaller potential jumps and a lower initial measured value (see Fig. 8).

- Carbonyl sulfide yields only one single equivalence point.

- Both H_2S and mercaptans are oxidized by atmospheric oxygen. It is therefore necessary to carry out the titration under an inert gas (nitrogen). The solvent used must be free from oxygen, too. In order to remove any oxygen, nitrogen is bubbled through the solvent in the titration vessel for 5 min prior to the analysis.

- Titration should not be hurried because mercaptans react only slowly with $AgNO_3$.

References

- ISO 6326-3:1989
  Natural gas -- Determination of sulfur compounds -- Part 3: Determination of hydrogen sulfide, mercaptan sulfur and carbonyl sulfide sulfur by potentiometry

- IP 272
  Determination of mercaptan sulfur and hydrogen sulfide content of liquefied petroleum gases (LPG) - Electrometric titration method

- UOP212-05
  Hydrogen Sulfide, Mercaptan Sulfur, and Carbonyl Sulfide in Hydrocarbon Gases by Potentiometric Titration

Author

Competence Center Titration

Metrohm International Headquarters