Application Bulletin

Of interest to: Petrochemical industry A 1, 5

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

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.

Instruments and accessories

- 702 SET/MET Titrino, 716 DMS Titrino, 736 GP Titrino, 751 GPD Titrino or 785 DMP Titrino or
  726 or 796 Titroprocessor with 700 Dosino or 685 Dosimat
- 2.728.0040 Magnetic Stirrer
- 6.3014.223 Exchange Unit
- 6.0430.100 Ag Titrode with Ag_2S coating, 6.2104.020 electrode cable
- 6.1415.310 or 6.1415.250 titration vessel with 6.1414.010 lid as well as 6.1440.010 gas valve

Reagents

- Silver nitrate stock solution c($AgNO_3$) = 0.1 mol/L:
  16.988 g $AgNO_3$ is dissolved in 80 mL dist. water and made up to 1000 mL with ethanol or isopropanol (IPA).

  For the titer determination c(KCl) = 0.1000 mol/L is used, e.g. Metrohm no. 6.2301.060.
- 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 $CH_3COONa * 3 H_2O$ 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 $CH_3COONa * 3 H_2O$ is dissolved in 25 mL dist. water. Add 975 mL IPA as well as 4.6 mL glacial acetic acid and mix.

- Absorption solutions for gaseous samples:
  a) For the determination of H_2S and mercaptans:
  w(KOH) = 30% or w(NaOH) = 30% with an addition of 5 g/L Na_2EDTA (to complex heavy metals)
  b) For the determination of carbonyl sulfide:
  w(monoethanolamine) = 5% in ethanol [e.g. 5 g monoethanolamine (MEA) plus 95 g ethanol]

Analysis

1. Liquid samples

Depending on the expected sulfur content, a suitable volume of sample (see table) is added to 100 mL solvent* and titrated with alcoholic c($AgNO_3$) = 0.01 mol/L while passing nitrogen over the solution.

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

* Acidic solvent for aviation petrol, kerosene and distillate fuels, which normally contain higher molecular mercaptans. 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

Titration curves

Different titration curves can occur:

- Normal case: sample contains H_2S and mercaptans:
  The titration curve 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. The potential of the EP indicates which of the two compounds is present.
- 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^0 + R-SH $\rightarrow$ R-SSH

  The elementary sulfur is ignored when calculating the mercaptan sulfur (see below).

Calculations

Hydrogen sulfide:

mg H_2S-S / kg sample = EP1 * C01 * 16030 / C00

Mercaptans (besides H_2S):

mg RSH-S / kg sample = (EP2 – EP1) * C01 * 32060 / C00

Mercaptans in the presence of elementary sulfur:

mg RSH-S / kg sample = (EP3 – EP1) * C01 * 32060 / C00

C00 = sample mass in g (= sample volume in mL * density of the sample in g/mL)

C01 = ca. 0,01 (concentration of the titrant in mol/L * titer of the titrant)

Remarks

- 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 $AgNO_3$.

2. Gaseous samples

The sulfur compounds to be determined are absorbed in alkaline solutions (Apparatus see literature in appendix). 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).

H_2S and mercaptans:

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

Absorption solutions from refineries (refinery caustic solutions) usually contain little H_2S besides large quantities of mercaptans. In this case, stop the titration after the first equivalence point (which corresponds to H_2S) and carry out a second titration 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. Add 1 mL w(NH_3) = 25% and titrate with alcoholic c($AgNO_3$) = 0.01 mol/L while passing nitrogen over the solution.

Titration curves

- 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. The potential of the EP indicates which of the two compounds is present.
- Carbonyl sulfide yields only one single equivalence point.

Calculations

The sulfur content is given in mg S / m^3 dry gas under «standard conditions», i.e. at 273 K (0 °C).

Absorbed gas volume in L = time (min) * flow rate (L/min) * 273 / (273 + t)

t = temperature in °C

Example:

At 27 °C gas is passed through the apparatus for 30 min at a flow rate of 0.10 L/min.

Absorbed gas volume = 30 min * 0.1 L/min * 273 K / 300 K = **2.73 L**

Hydrogen sulfide:

mg H_2S-S / m^3 dry gas = EP1 * C01 * 16030 / V

Mercaptans (besides H_2S):

mg RSH-S / m^3 dry gas = (EP2 – EP1) * C01 * 32060 / V

Carbonyl sulfide (separate titration):

mg COS-S / m^3 dry gas = EP1 * C01 * 32060 / V

C01 = ca. 0,01 (concentration of the titrant in mol/L * titer of the titrant)
V = absorbed gas volume in L, converted to 273 K (see above)

Figures

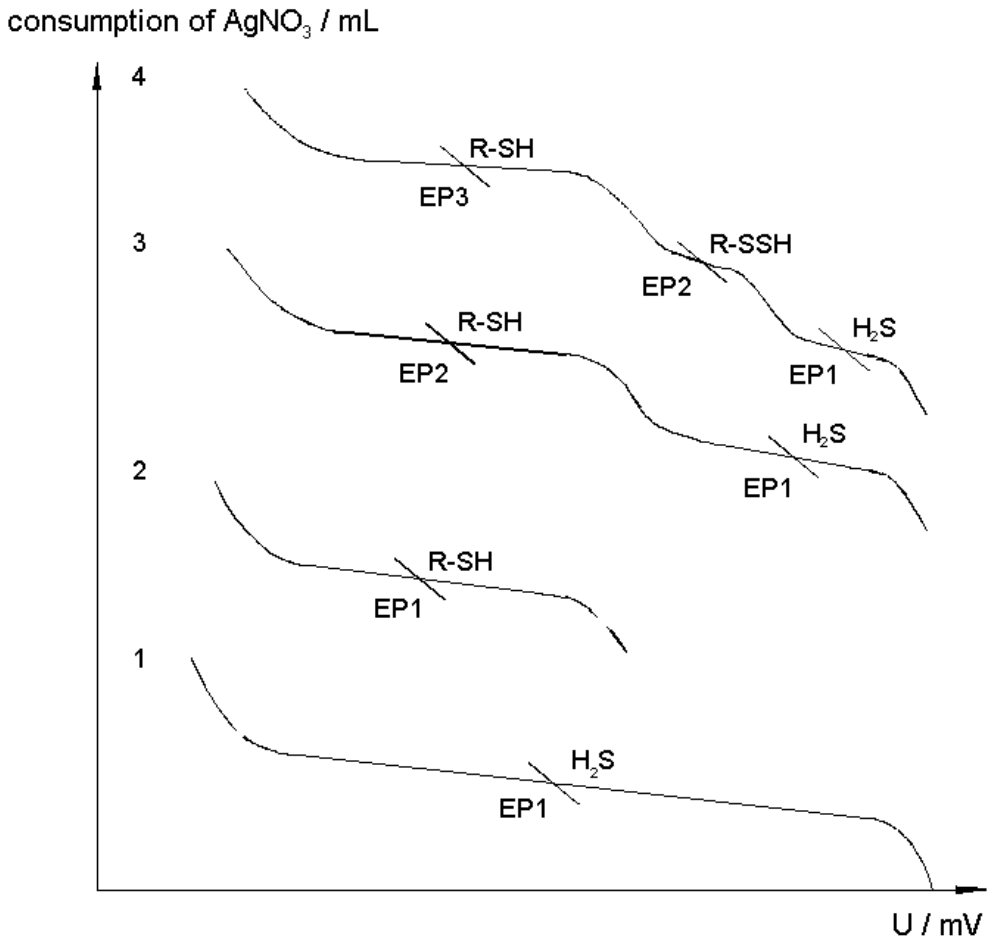

Fig. 1: *Possible titration curves when determining sulfur compounds in petroleum products.*

1 *H_2S alone*
2 *R-SH alone*
3 *H_2S + R-SH*
4 *H_2S + R-SSH + R-SH*

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 'pa
785 DMP Titrino          02287   785.0010
date  1999-07-13    time  14:41         9
DET  U                   H2S
parameters
>titration parameters
  meas.pt.density           2
  min.incr.                50 µl
  dos.rate                max. ml/min
  signal drift             10 mV/min
  equilibr.time            20 s
  start V:                 OFF
  pause                    20 s
  meas.input:               1
  temperature             25.0 °C
>stop conditions
  stop V:                 abs.
  stop V                    6 ml
  stop U                   OFF mV
  stop EP                   9
  filling rate            max. ml/min
>statistics
  status:                  OFF
>evaluation
  EPC                       5
  EP recognition:          all
  fix EP1 at U             OFF mV
  pK/HNP:                  OFF
>preselections
  req.ident:               OFF
  req.smpl size:         value
  limit smpl size:         OFF
  activate pulse:          OFF
          ------------
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Fig. 2: *Parameter settings on the 785 DMP Titrino.*

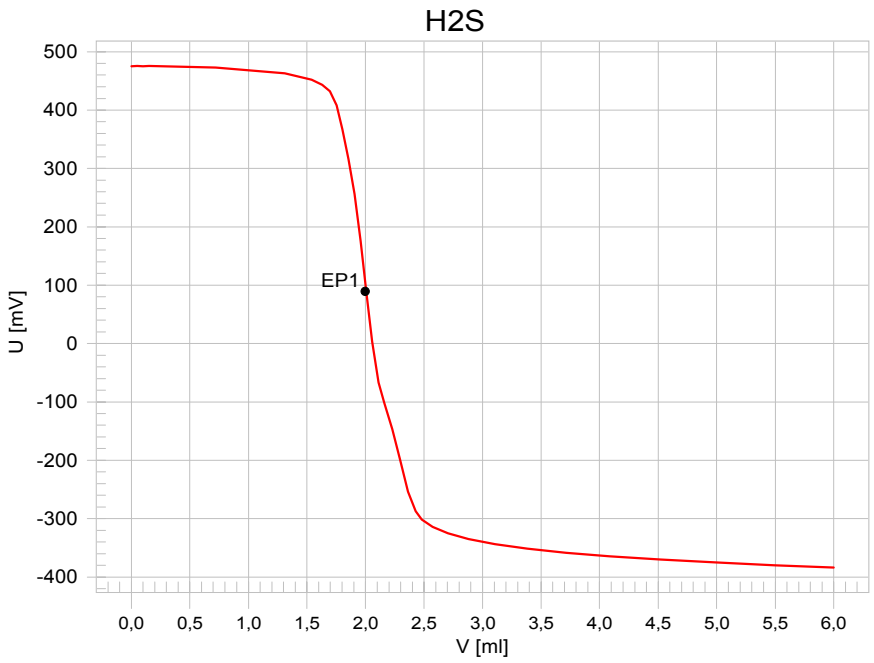

Fig. 3: *Titration curve H_2S alone.*

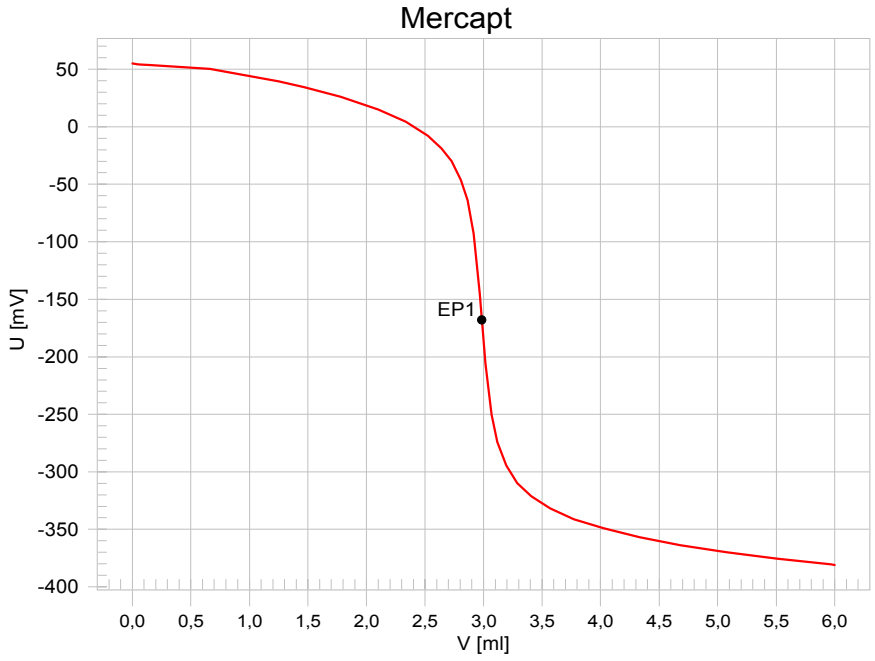

Fig. 4: *Titration curve mercaptans alone.*

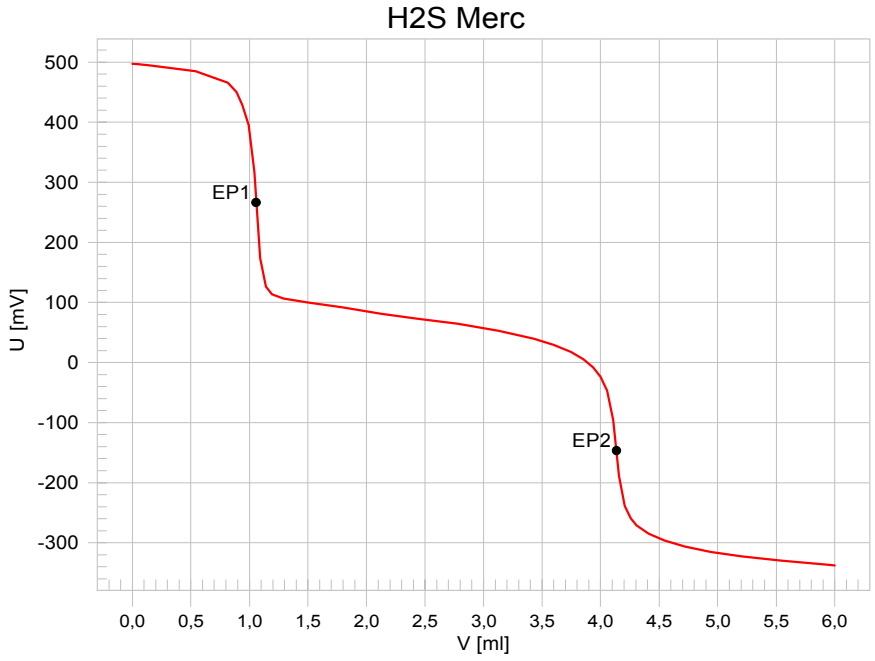

Fig. 5: *Titration curve H_2S + mercaptans.*

Literature

- ISO 3012: 1991
  Gasoline, kerosene and distillate fuels – Determination of mercaptan sulfur – Potentiometric method.
- ASTM D 3227-83
  Standard Test Method for Mercaptan Sulfur in Gasoline, Kerosene, Aviation Turbine and Distillate Fuels (Potentiometric Method).
- UOP Method 163-67
  Hydrogen sulfide and mercaptan sulfur in liquid hydrocarbons by potentiometric titration.
- 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 272/71 (1985)
  Determination of mercaptan sulfur and hydrogen sulfide content of LPG – Electrometric titration method.
- UOP Method 209-83
  Potentiometric analysis of used refinery caustic solutions. Part 2: Determination of sulfide and mercaptide.
- UOP Method 212-77
  Hydrogen sulfide, mercaptan sulfur and carbonyl sulfide in hydrocarbon gases by potentiometric titration.