Determination of $\text{H}_2\text{S}$ in Waste Water and Petrochemical Products

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Outline

1. ECH – Area of Business

2. H₂S Analyzer by ECH
   - Basics
   - Applications for petrochemical products,
     e.g. liquids, viscous samples, solids and gases
   - Applications for water, typical measurements and
     methods for waste water treatment

3. Summary
1. ECH – Area of Business

- Development, manufacturing and marketing of analytical instruments and measurement methods
- Main fields of application are:
  (A) laboratory analysis
  (B) factory- and process monitoring for technical control
  (C) on-site, online and mobile analysis
(A) Products for Laboratory Analysis

- Titrator AQUA 40.00
- Gas Module
- H₂S-Analyzer
- Electrochemical Analyzer SnLayer
- ECH Laboratory GC
(B) Typical On-Site Products

B.1 Analyzers

B.2 Analyzer including sample preparation

ECH MobilGC

H₂S-Analyzer: automatic gas analyzer for 2 sample points (e.g.: biofilters or waste water tanks)

H₂S-Analyzer (manual injection)
(C) Typical Online Products

Online $\text{H}_2\text{S}$-Analyzer

- liquid samples

- gaseous samples

Online gas chromatograph

online monitoring system based on the measuring principle of gas chromatography
2. H₂S-Analyzer by ECH

Applications for the determination of H₂S:

- ✔ water and waste water
- ✔ solids, oil and gas
- ✔ in the laboratory, on-site or online

http://www.deutschebp.de
Problems caused by H₂S

1. Odour trouble
   - sensitization of population

2. Health risk
   - toxicity is comparable to hydrogen cyanide (HCN)

3. Sulphuric acid corrosion
   - concrete reducing up to 10 mm per year
   - high investment costs to repair

4. Blocking of biological activity of microorganisms
   - increasing of bulking sludge inside aeration tanks of waste water treatment plants
## Effects of H$_2$S

<table>
<thead>
<tr>
<th>$c$(H$_2$S) [ppm]</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002 – 0.2</td>
<td>Odour threshold</td>
</tr>
<tr>
<td>3 – 5</td>
<td>Odour nuisance</td>
</tr>
<tr>
<td>10</td>
<td>MAC (Maximum Allowable Concentration)</td>
</tr>
<tr>
<td>&gt; 10</td>
<td>Irritation to eyes and respiratory tract</td>
</tr>
<tr>
<td>&gt; 50</td>
<td>Serious eye defect (damage of cornea)</td>
</tr>
<tr>
<td>150 – 250</td>
<td>Loss of sense of smell</td>
</tr>
<tr>
<td>300 – 500</td>
<td>Damage of breathing</td>
</tr>
<tr>
<td>&gt; 1000</td>
<td>Mortal danger in minutes or seconds</td>
</tr>
</tbody>
</table>
Different Types of H₂S-containing Samples in Refineries

<table>
<thead>
<tr>
<th>Sample</th>
<th>Example</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1 liquid</td>
<td>gasoline, kerosene, diesel fuel, crude oil, mineral oil, hydraulic oil, engine oil, transformer oil</td>
<td>indirect by oven and gas extraction chamber</td>
</tr>
<tr>
<td>#2 highly viscous and solid</td>
<td>tar, oil sludge bitumen, sulphur</td>
<td>indirect by oven and headspace-technique</td>
</tr>
<tr>
<td>#3 gaseous</td>
<td>LPG, LNG, CNG</td>
<td>gas injection module</td>
</tr>
<tr>
<td>#4 water</td>
<td>extraction and washing solutions, waste water</td>
<td>indirect by gas extraction chamber and acidification</td>
</tr>
</tbody>
</table>
Principle of H₂S-Analyzer

Advantages:
- no sample preparation
- fast gas extraction procedure of H₂S from sample
- low cross sensitivity
- H₂S is purged completely from sample and transferred to the sensor
**H₂S-Analyzer Cubiform**

**Features:**

- Short measuring time 5 – 10 min
- Free adjustable sample volume 0.01 – 20 mL
- Wide measuring range and low detection limit of 0.01 ppm
- Automatic peak evaluation at the end of the measurement
H$_2$S – Analyzer with Autosampler

Advantages:

- fully automated analytical procedure
- sample volume 0.01 – 20 mL
- low demand of chemicals
- robust and fast analysis (up to 40 measurements per hour)
Headspace-Module for the Determination of $\text{H}_2\text{S}$

Without sample preparation

Headspace vial is inserted into the oven and the measurement is started
Principle of the Headspace-Module

Temperature: up to 250°C
Application:
Determination of $\text{H}_2\text{S}$ in Oil

Determination of $\text{H}_2\text{S}$ in a mineral oil sample
Application:
Determination of $\text{H}_2\text{S}$ in heavy Oil
Determination of $\text{H}_2\text{S}$ in Oil

Result list shows the high repeatability of the measurement
Online H$_2$S- Analyzer

Features:

- automatic sampling
- direct analysis of sulphide/H$_2$S-content of waste water and light oils
- low demand of chemicals ($H_3PO_4$)
- data transfer via 4-20 mA or modem/internet
- alarm settings

Online application directly in the waste water
Typical Applications

- surface water
- ground water
- mineral water
- leachate
- seweage water
- pressure pipes
- pump sumps
- grease separators
- refineries, chemical industries
- mineral oil, crude oil
Special Features

- detector is separated from the sample by the gas extraction chamber
- high sensitivity (>0,01 ppm)
- high accuracy of the sample injection (1%)
- sample inlet can be rinsed backwards to prevent biofouling and sedimentation
Self Cleaning Sampling

**Problem:**
Biofouling on surface of electrodes or measuring systems

**Answer:**
- back flushing of sample tubes with fresh water (4 bar)
- immediate cleaning after injection of waste water sample
- low maintenance and high robustness
Determination of Sulphide in the Waste Water of Refineries

Online-analysis of waste water
Comparison of Results from the Laboratory and Online H₂S-Analyzer

Back flush cleaning of the waste water pipe

Sulphide [mg/L]

Online-sulphide
Lab results
The odour nuisance was caused by peaks of H$_2$S from the waste water.
Self-Learning Treatment System

Formation of $\text{H}_2\text{S}$ depends on:

- flow rate of waste water
- residence time of waste water in pressure pipes
- ageing characteristics of waste water
- inflowing $\text{H}_2\text{S}$-content
- weather conditions, temperature and season
Optimized Waste Water Treatment

--- inlet of pressurized sewer pipe
--- outlet of pressurized sewer pipe

waste water chemical: Fe(II)-salt-solution
consumption: 1.800 L / d
waste water: 10.000 m³ / d
length of pressure pipe: 3 km

Mean H₂S value at outlet: 1.1 ppm
Summary

- High sensitivity and accuracy
- Low detection limit
- Wide linear measuring range
- Low demand of chemicals
- Low maintenance effort
- Different kinds of petrochemical samples
- No sample preparation is needed
- For laboratory, on-site and online applications

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