# From analysis to action: Process reliability and environmental protection through fast, automated $H_2S$ measurement technology

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Hydrogen sulphide ($H_2S$) is a widespread but dangerous by-product in wastewater treatment as well as in crude oil and natural gas processing. In wastewater treatment plants, it is produced during anaerobic digestion processes, while in the petroleum industry it is a component of many 'sour' crude oils and gases. In both cases, $H_2S$ poses a serious threat to humans, materials, and the environment - it is corrosive, toxic, harmful to the climate and has a strong odour.

Modern, automated $H_2S$ measurement technology not only enables the precise detection of critical concentrations in real time, but also provides the basis for targeted countermeasures, whether for odour control, plant safety, or compliance with legal limits.

The article shows how current measurement technologies can be used in wastewater and petrochemical processes to implement the necessary treatment measures in a targeted and cost-effective manner.

Hydrogen sulphide ($H_2S$) plays a significant role in wastewater treatment and the petroleum industry, as it can occur in various stages of the processes and poses a complex challenge. The main problems associated with $H_2S$ in industrial applications are:

1. Corrosion risk for steel and other metals used in refineries and pipelines, as well as for concrete components, which play an essential role in sewage systems. In Germany alone, an estimated €475 million worth of calcium nitrate and €54 million worth of iron(II) chloride chemical additives must be used annually to prevent odours and corrosion [1].

2. Safety risk, as hydrogen sulphide is a colourless, highly flammable gas that is toxic in high concentrations. Even low concentrations (from around 100 ppm) can cause serious health problems, and concentrations above 700 ppm can be fatal within a very short time. The industry must therefore implement rigorous safety measures and monitoring systems to protect workers and facilities from possible exposure.

3. Quality impairment of crude oil and natural gas: 'sour' oils require additional processing steps during refining, such as hydrodesulphurisation (desulphurisation), in order to reduce the sulphur content and comply with environmental regulations. Hydrogen sulphide is removed from petroleum and natural gas using various processes, such as gas scrubbing or the Claus process, in which hydrogen sulphide is converted into elemental sulphur. The sulphur is either used as a by-product or disposed of safely. According to USGS Mineral Commodity Summaries 2025, global sulphur production (mostly from Claus plants) is approximately 79–80 million tons per year (as elemental sulphur). Of this, >90% comes from the desulphurisation of natural gas and petroleum [2].

4. Environmental impact and regulations: Since hydrogen sulphide can release sulphur dioxide ($SO_2$) during combustion, leading to acid rain and other environmental problems, the petroleum industry is heavily regulated to limit emissions of sulphur compounds. The costs (OPEX) of complying with the older Euro standards for diesel (50 ppm) are usually in the range of $0.3–0.8/bbl., while for 10 ppm sulphur (ultra-low sulphur diesel, EU/USA) this cost is $0.8–2.0/bbl. With global production of approximately 28,342 kbbl./d of diesel products in 2024, this represents enormous additional costs [3].

In order to act effectively, the most important prerequisite is the reliable determination of sulphur contamination in the process. There are only a few specific measurement methods for detecting corrosive hydrogen sulphide. Some of these are very time-consuming or costly. This is due, on the one hand, to the very low levels that need to be determined and, on the other hand, to the difficult matrix that needs to be analysed: highly viscous petroleum oils, particulate-laden wastewater, heavily coloured samples and sludge, and solids with inclusions.

## Sulphide determination in water and wastewater

The new method for determining sulphide/$H_2S$ in aqueous solutions is carried out in accordance with the new ASTM D8536-25 and DIN 38405-27:2017 standards by combining highly efficient gas extraction with a selective electrochemical detection method. After dosing, the sample is acidified in the $H_2S$ analyser, which expels $H_2S$ gas from the solutions. The gas enters an amperometric sensor that detects $H_2S$ with high sensitivity. The precision and accuracy are higher than with the determination methods commonly used to date. The measurement time is between 5 and 15 minutes. The analysis of the sample without any sample pretreatment has a particularly beneficial effect on reproducibility. Matrix components of the sample are effectively separated due to the indirect determination method, so that cross-sensitivities hardly occur.

The sample volume to be dosed can be selected within a wide range (10 µL to 50 mL). This allows a linear measuring range from 0.01 mg/L to 1 g/L to be recorded without having to dilute the sample. The sample can be transferred directly from the sampling vessel to the analyser. This prevents oxidation losses. By selecting the pH value of the acidification, it is possible to distinguish between easily extractable sulphides and the total sulphide content. With the aid of phthalate buffer pH 4, it is thus possible to determine the non-firmly bound alkali sulphides in aqueous samples, which are also considered an immediate danger to humans, the environment, and corrosive plant components. With the addition of 8 % phosphoric acid, the sulphides bound to iron and other metals are also released and detected. This provides an excellent opportunity to monitor and control scrubber solutions or treatment strategies, for example by avoiding an excess of iron precipitants or detecting an underdose of treatment agents. The capacity of amine scrubber solutions for gases can also be monitored easily and in a very short time.

The measurement technology is used in corresponding industrial wastewater treatment plants for online monitoring of pressure pipes or gravity pipes by automatically drawing in and analysing a wastewater sample every 10 minutes *(Figure 1)*. Even the slightest signs of anaerobic processes can thus be detected at an early stage, even before gas sensors can detect $H_2S$ contamination. By transmitting the values to the control centre in real time, automatic control loops can be developed to optimise treatment strategies and achieve savings [4].

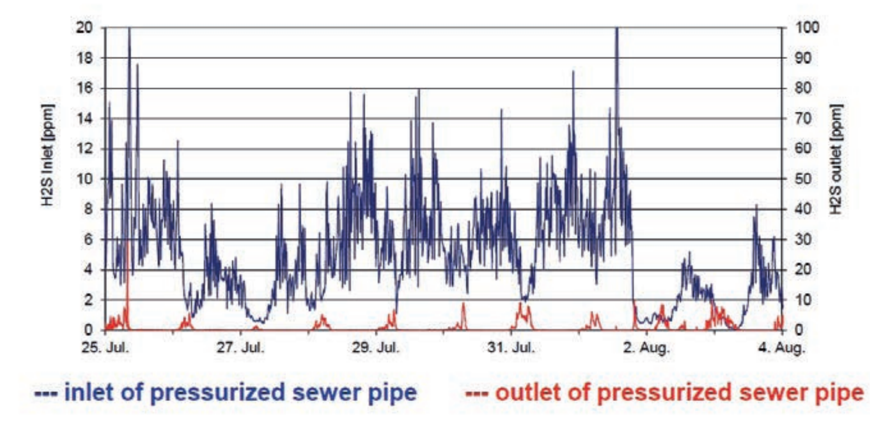


*Figure 1: Example of treatment of a sewage pipe with iron(II) salt solution using a two-channel online sulphide analysis.*

Usual wastewater samples are taken from the relevant areas of the wastewater network, stabilised on site with sodium hydroxide and zinc acetate, and then measured automatically in the laboratory using a 40-position autosampler. For the analysis, the autosampler automatically stirs the sample vial currently being measured in order to extract a homogeneous aliquot of the water sample *(Figure 2)*.

The analysis of amine washing solutions is possible in the same way, and leachate samples from landfills with high carbonate contents can also be analysed automatically *(Table 1)*. The foaming and high $CO_2$ content of these types of samples do not interfere with the extraction. Approximately 12 samples can be analysed per hour.



*Table 1: Sulphide measurement of leachate water samples in ppm.*

| No. | Sample name | 1 | 2 | 3 | Mean value [ppm] | Standard-deviation [ppm] | Relative Standard-deviation [%] |
|---|---|---|---|---|---|---|---|
| 1 | 3210-01 | 0.09 | 0.10 | 0.10 | 0.10 | 0.01 | 6.0 |
| 2 | 3877-01 | 1.10 | 1.07 | 1.10 | 1.09 | 0.02 | 1.6 |
| 3 | 6541-02 | 5.51 | 5.46 | 5.25 | 5.41 | 0.01 | 0.3 |
| 4 | 6623-02 | 6.66 | 6.61 | 6.45 | 6.57 | 0.11 | 1.7 |
| 5 | 7101-03 | 4.55 | 4.56 | 4.37 | 4.49 | 0.11 | 2.4 |
| 6 | 7155-03 | 1.98 | 1.97 | 2.03 | 1.99 | 0.03 | 1.6 |

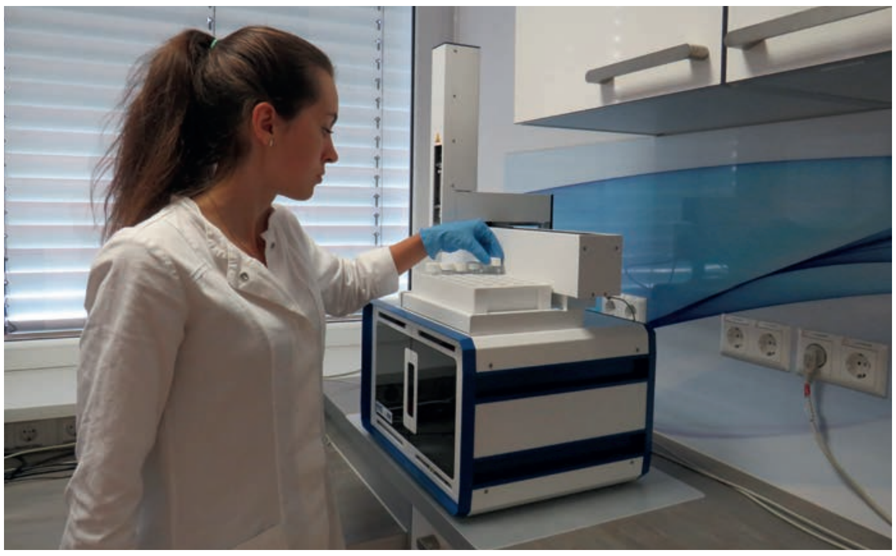

*Figure 2: Loading the autosampler with unfiltered wastewater samples for automatic homogenisation during analysis.*

Fully automatic dosing and emptying of reagents in a compact, well-protected design makes measurement possible even in the field *(Figure 3)*. This has the advantage that samples can be measured directly at the sampling point without stabilising reagents, which can prevent side reactions, particularly in some industrial wastewater treatment plants (e.g., leather industry, food industry, refineries, chemical industry).

*Figure 3: Measurements in the field without stabilizing reagents.*

## Sulphide determination in sludge and oils

Determining hydrogen sulphide contamination in oils and sludge is more challenging. In accordance with IP 570 (Procedure B) and ASTM D7621 (Procedure B), liquid petroleum products (crude oil, gasoline, diesel, marine fuels) are heated to 60 °C in a heating module and the gases released are analysed for $H_2S$.

The $H_2S$ headspace module consists of a heating oven that can be loaded with 20 mL vials or other vial sizes, a valve system with a bypass gas path, and a temperature control unit for a temperature range of 30 to 250 °C. The sample is weighed into the vial (max. approx. 10 g). The sample vial is sealed with a septum cap *(Figure 4)*.

With the additional $H_2S$ headspace module, all types of sludge with 1 - 85 % dry matter can be analysed. These are acidified in a gas-tight vial and then the gas phase is transferred to the analyser. *Figure 5* shows a comparison of a sulphide measurement with primary sludge (red curve), a measurement from a digestion tower sample (blue curve), and a measurement from excess sludge (black curve).

*Figure 4: $H_2S$ analyser coupled with an automated heating module for oils and solids.*

It can be seen that the analysis of samples containing solids can be carried out within 5 - 10 minutes. In order to verify the measurements, in addition to multiple determinations on different types of sludge, additions of 10 ppm sulphide solution were also carried out. *Table 2* below lists examples of these sample types. The recovery from the additions is very good. This demonstrates the high selectivity of the method for very complex sample compositions.

*Table 2: Repeated measurements of sulphides in sludge samples using heating and after evaluation of the step-up tests.*

| Measurement | Primary sludge [ppm] | Digested sludge [ppm] | Excess sludge [ppm] |
|---|---|---|---|
| 1 | 33.7 | 101.0 | 45.7 |
| 2 | 30.1 | 101.2 | 43.3 |
| 3 (recovery by step-up test) | 30.0 | 100.2 | 41.4 |

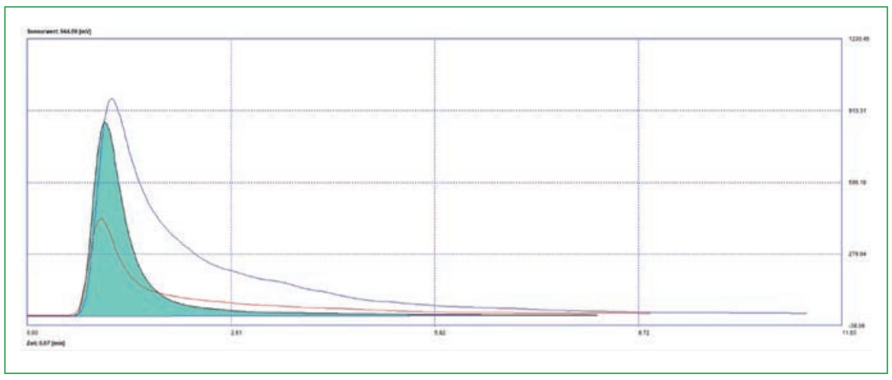

*Figure 5: Measurement curves for gas extraction of $H_2S$ from sewage sludge: primary sludge (red curve), digested sludge (blue curve), and excess sludge (black curve).*

In refineries, the variable measuring system with heating module has proven itself for many types of samples. Petroleum oils can be extracted at 60 °C in accordance with standard regulations, while other products such as bitumen, residues, and waste oils can also be extracted at higher temperatures, up to 180 °C.

After placing the vial in the oven and after a lead time (1 – 2 min), the gas flow of the $H_2S$ analyser transfers only the volatile $H_2S$ to the sensor unit.

One advantage of the headspace technique is that the vials used are disposable materials that do not require extensive cleaning, which significantly reduces both personnel costs due to the reduced workload and solvent consumption. Automation with up to 32 sample positions also makes it easy to tolerate longer measurement times caused by slower transport processes.

The electrochemical detection of hydrogen sulphide can be distorted by the presence of organic sulphur compounds (mercaptans). To reduce this influence, the detector is equipped with a diffusion barrier that reduces sensitivity to mercaptans by 75 %. Interposing an special oil trap can also wash out interfering volatile mercaptans.

The measurement results in *Table 3* show that mercaptan can be bound by > 90 % using a special Sulfimax light oil in the oil trap. At the same time, Sulfimax light oil binds hydrogen sulphide only to a small extent, enabling reliable measurement results in oil samples contaminated with mercaptans.

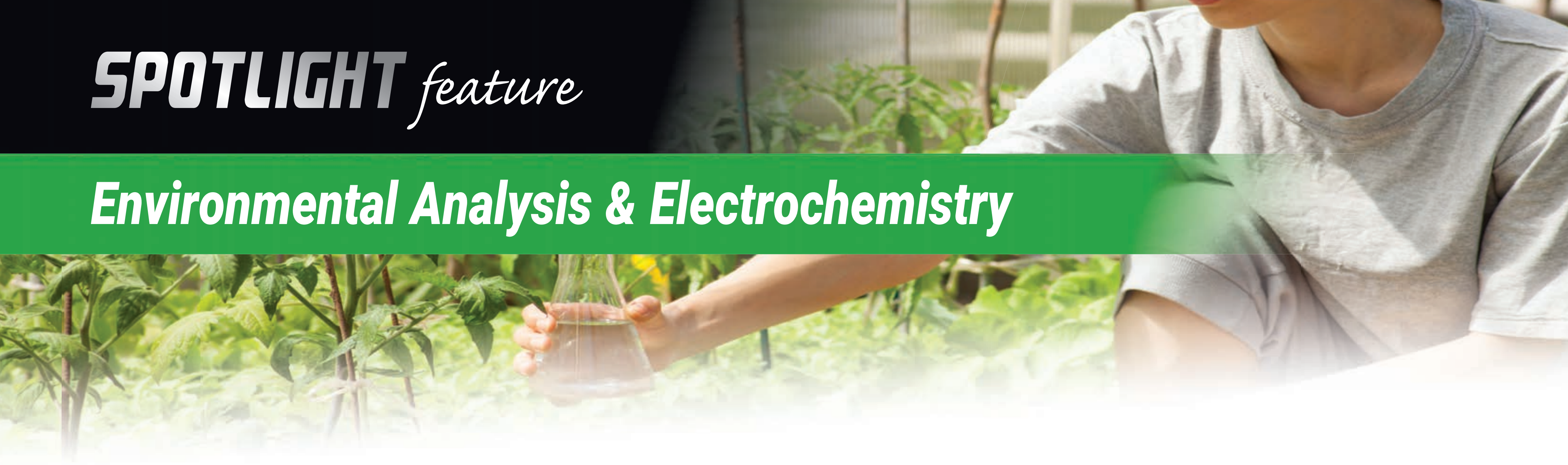


*Table 3: Repeated $H_2S$ measurements of mercaptan, $H_2S$ and mixed samples using the $H_2S$ heating module.*

| | 1-Propanethiol | | $H_2S$ standard | | $H_2S$ standard + 1-Propanethiol | |
|---|---|---|---|---|---|---|
| | Without scrubber | Oil scrubber | Without scrubber | Oil scrubber | Without scrubber | Oil scrubber |
| **Average** SD | **2.09** 0.07 | **0.20** 0.02 | **1.88** 0.08 | **1.77** 0.08 | **3.78** 0.14 | **1.74** 0.08 |
| [ppm] | 2.14 | 0.19 | 1.94 | 1.80 | 3.87 | 1.70 |
| [ppm] | 1.98 | 0.22 | 1.94 | 1.90 | 3.83 | 1.86 |
| [ppm] | 2.08 | 0.22 | 1.74 | 1.74 | 3.70 | 1.64 |
| [ppm] | 2.17 | 0.20 | 1.91 | 1.79 | 3.88 | 1.80 |
| [ppm] | 2.11 | 0.18 | 1.84 | 1.68 | 3.88 | 1.68 |
| [ppm] | 2.05 | 0.21 | 1.93 | 1.71 | 3.54 | 1.77 |

## Residual $H_2S$ determination in solid or molten elemental sulphur

The sulphur obtained from the Claus process must be highly purified for sale. Trapped $H_2S$ gas residues pose risks. Therefore, careful analysis is also in high demand in this area.

An example of the analysis of solid elemental sulphur in *Figure 6* shows that the effective extraction of volatile $H_2S$ is completed in a short time. Very low levels of 0.010 mg/kg - 1 mg/kg are typically detected.

A sample quantity of 1 to 15 g is filled into the headspace vials. In the case of molten sulphur, the melt is dosed directly into the vial or into suitable small portion moulds, e.g., in the shape of bars *(Figure 7)*. To prevent oxidation of the $H_2S$, the work must be carried out very quickly. Once the vial is sealed gas-tight, the effects of storage are minimal. The heating temperature must be set very accurately.

In addition to solids, gases from the Claus process and tail gas treatment can also be fed directly into the $H_2S$ analyser with electrochemical detection. 10 mL in a gas-tight syringe are injected into the gas extraction chamber via the sample inlet septum. The result is available within 2 minutes. Even oxygen-free gases, such as biogases or digester gases, can be analysed reproducibly. The measuring system with continuous gas extraction automatically conditions itself between each new measurement. This makes the electrochemical sensor durable and low-maintenance.

## From analysis to action – proactive $H_2S$ management pays off

Hydrogen sulphide ($H_2S$) is an invisible but serious hazard – for people, equipment, and the environment. Modern, automated measurement technology enables continuous real-time monitoring and creates the basis for rapid and targeted countermeasures. Early measurement allows for faster intervention, prevents damage, avoids limit value exceedance, and reduces long-term operating costs. Investing in modern, fast $H_2S$ analysis is therefore not only a matter of safety and environmental protection, but also an economically sensible step.

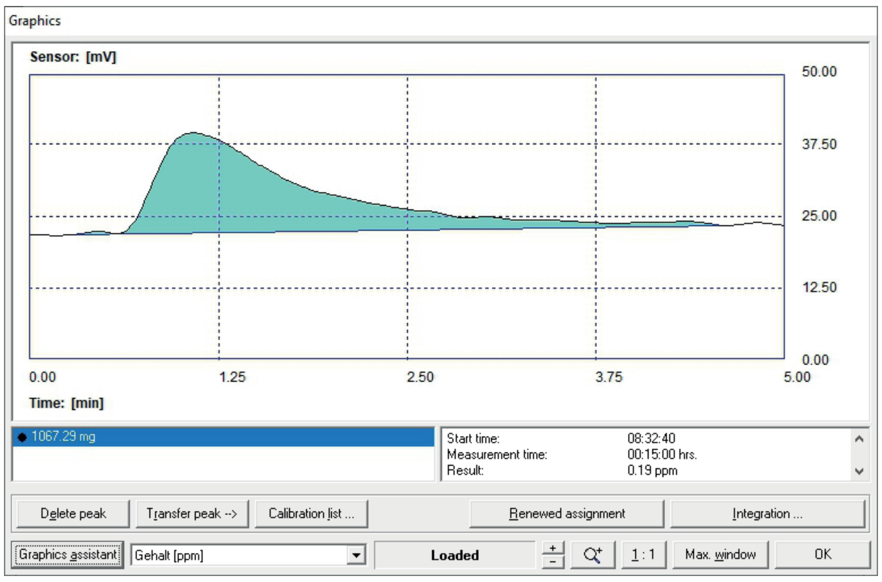


*Figure 6: Determination of volatile $H_2S$ from Claus-process-sulphur with the $H_2S$ analyser.*

*Figure 7: Sample of sulphur powdered or molten form.*

## References

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