H$_2$S-Determination in Wastewater

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1. Problem

In sewage system, Hydrogen sulfide and volatile organosulfur compounds are considered to have the greatest potential of creating health risks, apart from the odor nuisance. Even low concentration of them can cause significant health problems\[1\]. The generally accepted odor threshold of hydrogen sulfite is at 0.13 ppm while the significant odor nuisance can be perceived from 3 to 5 ppm. The MAC-value of H$_2$S in the air is at 10 ppm; however, the exact number hasn’t yet been officially clarified.

<table>
<thead>
<tr>
<th>H$_2$S Concentration / ppm</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.002 – 0.2</td>
<td>Odor threshold</td>
</tr>
<tr>
<td>3 – 5</td>
<td>Odor nuisance</td>
</tr>
<tr>
<td>10</td>
<td>MAC (Maximum Allowable Concentration) - Value</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 (cornea damage)</td>
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<tr>
<td>150 – 250</td>
<td>Loss of sense of smell</td>
</tr>
<tr>
<td>300 – 500</td>
<td>Respiratory System Damage</td>
</tr>
<tr>
<td>&gt;1000</td>
<td>Fatality in minutes or seconds</td>
</tr>
</tbody>
</table>

Tab. 1: Effects through hydrogen sulfide

Within the sewage system, a “slime layer”, which contains microorganism and fungi, is formed. Its thickness can pile up to several centimeters. Many different biological processes happen in this slime layer, in which the present sulfur bacteria (Desulfovibrio) in the anaerobic layer reduce sulfur organic compounds to sulfide. The sulfide diffuses from the anaerobic to the aerobic layer and is then oxidized to sulfate in the presence of oxygen or oxygen-containing compounds. If the amount of dissolved oxygen is insufficient, the oxidation process will not take place; therefore, sulfides enrich in the waste water. At oxygen concentration <0.1 mg/L and with the absence of other oxidants (e.g. nitrates or sulfates), the waste water will change to an
anaerobic state. This anaerobic milieu can be reached rapidly in long sewer pipes and pressure lines.

2. Impact on the sewerage

The impacts on the sewerage and waste water treatment plants are substantial:

1. Formidable odor nuisance from the sewers is observed, specifically at exchange points from printing systems into open channels.

2. Strong biogenic sulfuric acid corrosion of pipes, stand pipes and special structures occur. As biogas and sewers always contain a certain amount of water vapor, this vapor condenses on colder parts of sewer lines. The H$_2$S dissolved in the condensate is then oxidized to H$_2$SO$_4$ by oxygen in the air and microorganism. The result is that a strong acidic and corrosive solution is formed. As a consequence, metal components and concrete are destroyed$^{[2,3]}$.

3. When different waste water streams are flowing together, it is dangerous particularly for the staff working in sewage plants. Due to lethal high gas concentrations, the staff can suddenly be in danger as H$_2$S can spontaneously strip out from the anaerobic waste water.

4. Due to the deteriorated biological degradation of organic matrix, bulking sludge occurs increasingly, which substantially hinders the treatment in the waste water treatment plant. In the extreme case, the entire biology of the plant is affected.

A direct analysis of the H$_2$S-loading in waste water is mandatory in order to achieve goal-oriented regulation for waste water treatment as well as to create redevelopment concepts$^{[4]}$.

A new analysis technology for the selective determination of H$_2$S in the waste water is to be presented in the following.
3. H₂S-Analyzer for the examination of wastewater

Sulfide/H₂S in aqueous solutions is determined by the coupling of a highly effective gas extraction and a selective detection method. After dosing into the H₂S-analyzer, the sample is acidified. The released H₂S gas is stripped out from the solution by using a continuous gas flow and, subsequently, is selectively detected by an electrochemical sensor (Figure 1 and 2). By using this indirect method, the detector is not contaminated with the waste water sample. Therefore, compared with other conventional determination methods, a highly accurate analysis can be achieved.

The method is very robust. Regarding the reproducibility, the sample analysis without any sample preparation is particularly beneficial. Matrix components of the sample are effectively separated due to the indirect determination procedure and therefore cross-sensitivities can be avoided.
A typical trace/measured curve is shown in figure 3. The release of gas and detection take place very quickly, thus measuring times < 5min can be realized.

Figure 3: Typical trace/measured curve of the sulfide/H₂S-measurement in waste water
3.1 Application for laboratory use

Waste water samples can be dosed either manually by a syringe or automatically by an auto sampler. The volume of the sample to be dosed varies in a large range (10 µL to 50 ml). This enables a very wide linear measuring range between 0.01 ppm to 5000 ppm without the need for dilution of the sample.

3.2 Application for field/on-site analysis

For an automated field analysis/on-site use, the waste water sample is injected into the H₂S-Analyzer by a dosing pump. The sampling is realized directly from the sewer.

A typical measured curve of wastewater monitoring using on-line monitoring is shown in figure 4. It is obvious that typical peaks of H₂S are found, which ultimately caused by an increased release of H₂S from sewage system at those peaks.

Figure 4: Typical measured curve of H₂S on a pressurized water pipes

Hereby, the emission of H₂S shows a typical daily pattern and is dependent on other conditions in the sewage system such as:
- Changes of the inflows caused by indirect suppliers
- Changes of flow rates
- Various long residence times in the sewage system (waste water pumping regime)
- Aging state and H₂S-initial level of pollution at the input
- Weather conditions
- Temperature and season
Therefore, H₂S is the most important principle parameter for assessing the anaerobic processes in wastewater and, ultimately, a measure of the required dose of waste water chemicals.

With this new sulfide/H₂S-measuring method, extensive possibilities for a targeted wastewater treatment are created. The treatment can be related to the areas of municipal and industrial wastewater systems:

- Areas of the issues at grease separator systems inside and outside of building complexes and large buildings
- Pressurized water pipes
- Open channels
- Pump sumps
- Inflows of wastewater treatment plant
- Landfill leachate

4. Summary
The amount of sulfide/H₂S in wastewater can be determined accurately and reproducibly with the new H₂S-Analyzer. Therefore, the potential of H₂S-forming in sewage systems can be analyzed. Due to indirect dosing into the extraction module, the matrix elements of the samples do not interfere with the detection. Thus, additional steps of sample preparation are not required.

The application is very easy. The devices are very compact, easy-to-use and can be used for both laboratory analysis and online process control.

By using the direct analysis of waste water and its current amount of sulfide/H₂S, an evaluation for a precisely timed periodic application of treatment agents can be succeeded. This is how emissions of H₂S can be drastically reduced or avoided respectively, while the operating costs for the wastewater treatment can be kept at the optimum.

5. Literature

[2] ATV 'state of the systems in Germany - Results of the DWA Survey 2001 "; Correspondence wastewater 3 / 2002; p. 302-311
water, Ver. d. Inst
Hannover 1997