Hydrogen sulfide is a naturally-occurring, corrosive compound frequently present in oil and gas sources. It is also an irritant and a chemical asphyxiant. At levels greater than 100-ppm in air, it is immediately dangerous to life and health. Hydrogen sulfide will also cause corrosion by attacking iron to produce iron sulfide. Production of these sulfur-containing oil and gas sources therefore requires treatment to eliminate the hydrogen sulfide.

Newer sources of crude oil and gas tend to have higher hydrogen sulfide levels. The sulfur content in crude oil has trended higher over the past thirty years. In 1985, the average sulfur content at US oil refineries was 0.91%; in 2013, it reached 1.44%. The requirement to eliminate hydrogen sulfide are increasing.

Although there are many approaches to reduce $\text{H}_2\text{S}$ level, most rely upon amine- or triazine-based chemistries. Amines, such as monoethanolamine, are regenerative, and are often used in amine units for sulfur stripping at refineries. Triazines find applications in tower or flow-line applications; for example, in bubble towers near gas well-heads or for pipeline injection.

Triazine-based scavenger chemistry

One common triazine-based scavenger is 1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine, or MEA-triazine (CAS 4719-04-4). Consisting of a triazine ring with three monoethanolamine side groups, as shown in Figure 1, MEA-triazine offers significant $\text{H}_2\text{S}$ scavenging capacity. Not only does the triazine ring capture sulfur, but so also does the monoethanolamine released during the reaction.

During the reaction, MEA-triazine is converted into the two-sulfur-containing dithiazine, illustrated in Figure 2. The single-sulfur-substituted triazine has an exceedingly short lifetime, while a three-sulfur compound (trithiane) is uncommon. Therefore, dithiazine is the most prevalent scavenging by-product. Dithiazine can be problematic: it is not very soluble in water and tends to polymerize. The result is a build-up of material within the scavenging solution.

The question that operators must address is how to monitor the scavenging process. Portable, field-ready methods for analysis of scavenging solutions have not been available to date, and laboratory methods rely upon high-end mass spectrometry tools. The decision about when to replace the scavenger solution is therefore not optimal—solutions are potentially changed while scavenging potential remains. A field method for direct analysis of triazine-based scavengers and their by-products would enable process optimization, reducing costs while improving safety.

Spent scavenger solution analysis

Towards this end, OndaVia has developed a Raman-spectroscopy-based approach to spent scavenger analysis. The OndaVia Analysis System (P/N OV-PP-J003) consists of a portable analysis instrument, a laptop computer, and consumable analysis cartridges. The instrument weighs about sixteen pounds, requires a 12-VDC or 110-VAC power source, and uses less than a square foot of bench space; see Figure 3. Scavenger analysis requires nothing more than electrical power and a pipette.
The OndaVia system relies upon Raman spectroscopy for analysis. Raman spectroscopy provides a chemical fingerprint by exciting vibrations in molecular bonds using an infrared laser source. The resulting scattered light spectrum depends upon the chemical structure of the sample. As an optical approach, the sample does not contact the instrument, allowing the user to measure dirty samples without fear of instrument damage. The method is fast, simple, and versatile, with an ability to measure a wide-variety of compounds.

Samples are applied to consumable cartridges (P/N OV-PP-B010-PCT, Figure 4) for insertion into the instrument. The cartridge kit includes a proprietary reagent that enables accurate measurements. For MEA-triazine, the OndaVia Analysis System achieves ±10% over the range 300-pptm to 800-pptm (30- to 80-weight-%) with a two minute analysis. With ten repeat measurements from one sample vial, the accuracy can be improved to ±1-wt% at 60-wt%, a process that requires only twenty minutes. A second part number (P/N OV-PP-B010-LPT) is designed for 5-45% analysis, a range that covers concentrations typically found in spent scavenger solutions.

During analysis, the user mixes 100-µL of sample into a vial containing 500-µL of reagent, and applies ~15-ul of this mixture to the analysis cartridge. After inserting the cartridge into the instrument, the users begins analysis in the controller software. Analysis time takes under two minutes per sample, and the user is provided with a quantitative result: the weight-% concentration of MEA-triazine in the sample.

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Dithiazine may be subsequently measured with a similar procedure using our dithiazine analysis cartridge (P/N OV-PP-B011-LPT). With appropriate analysis procedures and detection ranges, both triazine and dithiazine may be determined from one spectrum, making the total analysis time for both compounds two minutes, a far cry from the hours of sample preparation and analysis required for mass spectroscopy and the days of transit time for shipping to the laboratory.

Summary
The OndaVia Analysis System offers a fast, easy-to-perform measurement of MEA-triazine and dithiazine in spent hydrogen sulfide scavenging solutions. The method requires minimal sample processing, and provides test results in under five minutes. The result is an ability to monitor the scavenging reaction, enabling process optimization while avoiding foiling and corrosion.

Figure 3. OndaVia Analysis System.

Figure 4. MEA-triazine Analysis Cartridge.

<table>
<thead>
<tr>
<th>Product</th>
<th>Part Number</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEA-Triazine Analysis Cartridges</td>
<td>OV-PP-B010-PCT</td>
</tr>
<tr>
<td>Dithiazine Analysis Cartridges</td>
<td>OV-PP-B011-LPT</td>
</tr>
<tr>
<td>OndaVia Analysis System</td>
<td>OV-PP-J003</td>
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