# Analysis of Spent $H_2S$ Scavenger Solutions

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OndaVia

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OndaVia offers a Raman-spectroscopy-based system for rapid, on-site chemical analysis. Based on customer requests, we have developed a test method for MEA-triazine and dithiazine in triazine-based hydrogen sulfide scavenging materials. This application note describes results when measuring spent scavenger solutions in gas treatment applications. A few dollars spent on testing can extend the lifetime of systems that consume hundreds to thousands of dollars per day in triazine-based scavengers. Process optimization that extends operations even a few days—or avoids costly shutdowns due to solids formation, corrosion issues, or out-of-specification products—will quickly pay for itself.


Figure 1. OndaVia Analysis System.

## Raman Spectroscopy

Raman spectroscopy is a powerful tool for chemical analysis—an optical technique that measures the vibrational and rotational modes within a molecular system. The sample is illuminated with monochromatic light (a 785-nm diode laser, in our case). The light interacts with the molecular bonds, causing some scattered photons to shift in energy. The resulting scattered light provides structural information that may be used as a "chemical fingerprint". The intensity of the Raman response is weak; however, it is directly proportional to the number of molecules—in other words, it is a direct measure of concentration.

## OndaVia Analysis System

At OndaVia, we rely upon Raman spectroscopy as a basis for our analysis methods. We combine proprietary methods, solvents, software, and algorithms to perform fast, accurate chemical analyses in a range matrices. The OndaVia Analysis System, shown in Figure 1, consists of a compact Raman spectrometer, proprietary reagents, and consumable, analyte-specific analysis cartridges. The spectrometer measures approximately 12" x 8" by 5". It operates on a regulated 2.5-A, 12-VDC supply using a "power brick". The system is supplied with Windows®-based analysis software and an optional rugged case for transit and transport.

We currently offer analysis cartridges for a wide range of amines, triazines, and anions. Our monoethanolamine (MEA) analysis method includes tools for pre-treating refinery sour water for quick, on-site MEA analysis. Our selenium measurement cartridge has a 5-ppb lower detection limit with an ability to speciate selenate and selenite. We are leveraging techniques from these cartridges to develop methods for arsenic, thiosulfate, and sulfate measurements.

The OndaVia Analysis System works with all OndaVia analysis cartridges; only one instrument is required. The result is a powerful water and/or chemical analysis platform. Furthermore, with OndaVia's Advanced ORC™ analysis software, the user has access to spectral data for in-house method development or research.

## Analysis method

The analysis of %-level triazine (Figure 2) and dithiazine (Figure 3) begins with an OndaVia test kit. Each kit contains a sample holding cartridge and a reagent vial. The reagent vial contains a precisely weighed quantity of material designed to provide a reference signal against which the sample is measured. The user adds 100-µl of sample to this vial and mixes well. A well-calibrated, fixed-volume, 100-µl pipette should be dedicated to this application for highest accuracy. A small quantity of this mixed sample (<10-µl) is introduced to the cartridge, inserted in the instrument, and analyzed using the corresponding calibration curve.

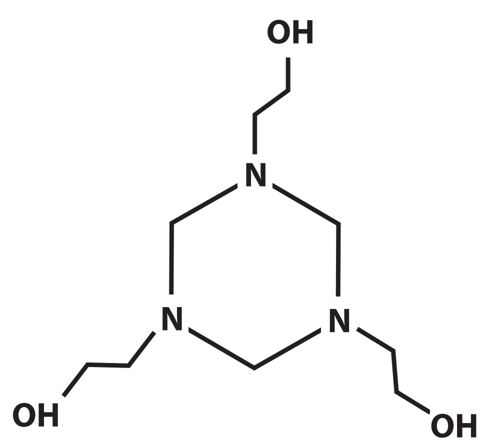

Figure 2. MEA-triazine chemical structure.

## Triazine and dithiazine in spent scavenger

OndaVia tested seven triazine-based $H_2S$ scavenger samples collected from wells in the Permian Basin. Each sample was shaken vigorously to mix the various phases before analysis. The resulting values are reported in Table 1. For some of the milkier solutions, adding methanol to the triazine determination clarified the translucency (dissolved the solids).

We also measured dithiazine in the samples. As the triazine level decreases, the dithiazine increases. In samples with very low triazine levels, the dithiazine is also low. At these levels, the dithiazine likely precipitates out of solution. We did not measure the dithiazine in the high triazine solutions, as dithiazine peaks were not visible in these samples.

The total weight-% of triazine plus dithiazine agrees with the starting weight-% of triazine (30-40%). As a check on samples #3 and #4, we diluted in water 1:1 by weight. The analysis results for MEA-triazine in these samples were 12.8% and 21.1%, respectively, in agreement with the undiluted result. Sample #6 appears to be overly depleted of triazine to where the dithiazine has precipitated from solution. It is interesting to note that these samples still contain significant levels of triazine. Disposal at this point would result in valuable scavenging material being discarded.

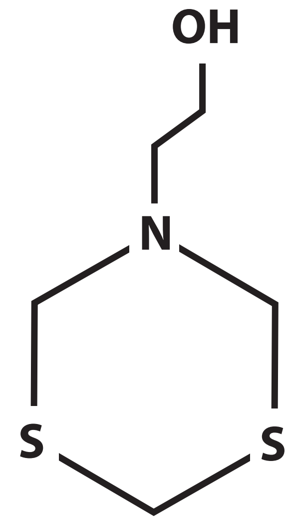

Figure 3. Dithiazine chemical structure. During scavenging, the monoethanolamine groups are substituted by sulfur from hydrogen sulfide. The free monoethanolamine can participate in further scavenging.

## Analysis of spent scavenger "layers"

Spent scavenger samples will often separate into layers. To understand the composition of these layers, we analyzed a spent scavenger sample before and after separation. The sample was first shaken vigorously to mix the sample. Analysis of the mixed sample determined the dithiazine content to be 19% and the triazine content to be 51%.

The sample was allowed to sit for four days, after which it separated into two distinct layers. The bottom layer was more viscous and cloudy, while the top layer remained clear. Analysis of the bottom layer showed a strong dithiazine signal, beyond the measurement limits of our calibration curve. We therefore diluted one part sample in three parts water by weight. The resulting measurements found the dithiazine and triazine content to be 52% and 35%, respectively. In the top layer, the two values were 11% and 52%, respectively. Based on the volume of the two layers, these values correspond to 18% and 49% total dithiazine and triazine, in agreement with our original measurements for the mixed sample.

This analysis yields a few interesting points. First, the dense, thick bottom layer has a high dithiazine content and little water. This result is not surprising, as dithiazine is soluble in water at only a few percent. However, the triazine content in this layer is relatively high; triazine is soluble in dithiazine. The top layer has a reduced dithiazine content, but still contains plenty of active triazine. Considering that this layer represents 82% of the sample volume, a recycling procedure in which the bottom layer is discarded could result in cost-savings and extension of scavenger lifetime.

## Conclusion

The OndaVia Analysis System provide a fast easy-to-use method for the analysis of $H_2S$ scavenger solutions. With tests for dithiazine and triazine, it is possible to monitor a scavenger solution during operation, enabling optimized process decisions. Instead of waiting for $H_2S$ breakthrough or dumping valuable scavenger before its useful lifetime is spent, an operator can directly monitor triazine content to measure scavenging capacity. Furthermore, by measuring dithiazine content, an operator can monitor for potential solids formation due to dithiazine polymerization, thereby avoiding more costly system faults.

Table 1. Spent scavenger analysis results

| Color, phases | Triazine (wt%) | Dithiazine (wt%) | Total (wt%) |
|---|---|---|---|
| Straw, 1 | 31.2 | | 31.2 |
| Orange, 3 | 26.7 | 15.7 | 42.4 |
| Golden, 2 | 26.0 | 10.0 | 36.0 |
| Straw, 1 | 49.2 | | 49.2 |
| Clear, 1 | 29.7 | | 29.7 |
| Straw, 2 | 7.4 | 2.7 | 10.1 |
| Red, 2 | 30.8 | 4.2 | 35.0 |