Dithaizine in hydro-carbon liquids

OV-AN-0012

OndaVia

MEA-dithiazine in natural gas liquids

A midstream oil & gas company was facing a challenge in their collection system: solids were building up at their gas processing plant. Initially, the customer suspected their triazine-based sulfide treatment system. After attempting to adjust their treatment system to reduce byproduct formation, they started to look upstream at the stations feeding into their plant.

Quantitative Raman Spectroscopy is a set of proprietary tools that enable fast, easy chemical measurement using an all-optical technique. OndaVia has developed a large suite of analysis methods applicable to the oil & gas industry. Based on customer requests, we have developed a test method for monoethanolamine (MEA) and dithiazine in natural gas liquids and slop water samples. For hydrocarbon analysis, this method requires an extraction step into aqueous solution, followed by analysis via our standard amine part-per-million analysis methods. The result is a few-minute test with portable instrumentation that provides ppm-level amine or dithiazine content.

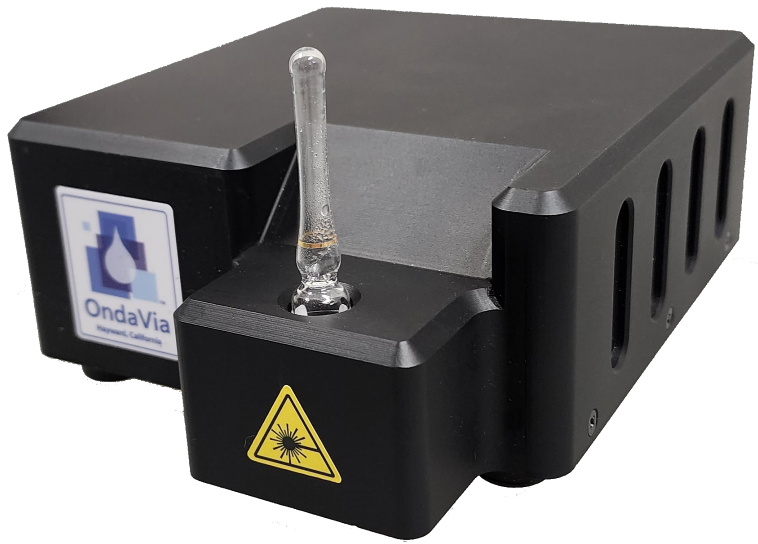

Figure 1. OPAL-103 OndaVia Portable Analysis Laboratory.

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.

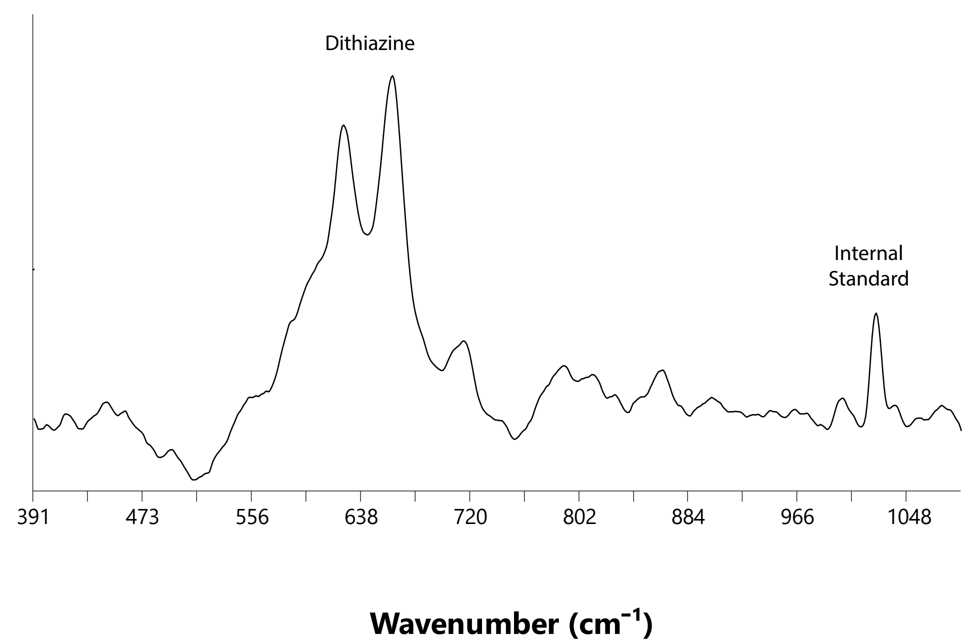

Figure 2. Dithiazine analysis via Quantitative Raman Spectroscopy. The C-S bonds in dithiazine have a clear, strong signal. The internal standard provides a reference signal against which the dithiazine can be quantified.

OndaVia Portable Analysis Laboratory

At OndaVia, we apply Raman spectroscopy for quantitative analytical chemistry. We combine proprietary methods, solvents, software, and algorithms to perform fast, accurate chemical analyses in a range of matrices. The OPAL-104 instrument, shown below in Figure 1, consists of a compact Raman spectrometer, proprietary reagents, and consumable, analyte-specific analysis cartridges. The spectrometer measures approximately 6” x 8” by 3”, operating on a regulated 2.5-A, 5-VDC supply using a “power brick”. The system is supplied with our Advanced ORC™ analysis software and an optional rugged case for transit and transport.

We currently offer analysis cartridges for an array of amines, anions, and organic compounds. We also offer pre-treatment kits for analysis in complex matrices. For example, our monoethanolamine (MEA) analysis method includes tools for pre-treating refinery sour water for quick, on-site MEA analysis. The OndaVia Analysis System works with all OndaVia analysis cartridges; only one instrument is required to measure any or all analysis cartridges. The result is a powerful water and/or chemical analysis platform. Furthermore, with OndaVia's analysis software, the user has access to spectral data for in-house method development or research.

Figure 3. NGL samples are provided in sampling cylinders. A few grams of sample is mixed with an equal mass 10-mM HCl (aq) for extraction.

Analysis of H_2S scavengers and by-products in hydrocarbon samples

MEA-triazine (hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine, CAS# 4719-04-4) is an important and popular hydrogen sulfide scavenger in natural gas treatment. Triazine-based scavengers are often applied shortly before transportation, resulting in residual scavenger within the gas. This scavenger can become a tramp amine, which in turn can lead corrosive heat stable salt deposits. More importantly for gas processing, the triazine converts to dithiazine during the scavenging process, a material that can polymerize, causing fouling problems.

OndaVia offers ppm-level analysis kits for MEA-triazine (OV-OP-B010-PPM), dithiazine (OV-OP-B011-PPM) and monoethanolamine (OV-OP-B003). These kits offer 10% accuracy over 5- to 100-ppm with a test that requires under two minute to perform. The user mixes the sample with our proprietary reagent, adds this mixture to a vial of nanoparticles, and then analyzes the nanoparticle-sample mixture in a portable Raman spectrometer.

Amine and dithiazine analysis in NGLs

Our analysis kit requires samples to be in an aqueous solution, as an amine signal in crude would be obscured by the organic background. To measure amine- and triazine-compounds in hydrocarbons, we developed an extraction method leveraging commonly used methods for amine analysis. For sample extraction, we weighed approximately 5-10-g of NGL sample from a cylinder, shown in Figure 2, into a 50-ml centrifuge vial. We then added an equal mass of 10-mM HCl. The vial was vortexed for two minutes, and then centrifuged to separate the water and hydrocarbon phases. Some gas evaporates during this process, but the non-volatility of MEA and dithiazine guarantees they remain in aqueous solution. We collect 100-uL of the aqueous phase, add reagent and 1M NaOH to adjust the pH above 12.7. This prepared sample was added to the nanoparticle vial, and analyzed using our calibration curves.

The results are presented in Table 1. The amine values are in the 20-40-ppm range with a clear, strong signal. These results are clear proof that triazine-based scavenging is occurring upstream of the gas collection site, Meanwhile, the dithiazine signal ranges from close to no detect to close to 40-ppm.

Table 1. Analysis of gas processing slop water for scavenging residuals.

Sample	MEA (ppm)	Dithiazine (ppm)
S1018	28	6
S1019	40	34
S1020	36	26
S1021	35	14
S1022	25	12

Amine and dithiazine analysis in slop water

Slop water analysis provides insights into system operation and performance over time. Amines will concentrate in the aqueous phase, while dithiazine will build in concentration to its relatively low solubility limit. Water analysis is even simpler than NGL analysis, as the extraction step is not needed.

The analysis results are presented in Table 2. In this case, we see a higher concentration of amine at all sites. The amine concentrates in the aqueous phase up to a few hundred parts-per-million. At two sites, however, the concentration is over 2% monoethanolamine in the water. This level amine could be an indicator of extreme overtreatment, high sulfide levels that require high triazine dosing, or slop water that has not been flushed for some time.

Looking at the dithiazine numbers, we see a similar trend to the amine concentration. Generally, there is a few hundred ppm. But at the sites with high amine there is also high dithiazine, over 0.6% by weight. These results point to these two sites as locations that should be investigated for problems.

Conclusion

OndaVia has developed analysis methods for ppm-level amines and triazines in aqueous solutions. Analysis of these compounds in NGLs requires an extraction step into dilute hydrochloric acid. This process uses generally available equipment to transfer the compounds of interest into an aqueous solution in under five minutes. This simple approach expands the capabilities of OndaVia's analysis approach into matrices heretofore unreachable with Raman spectroscopy.

Table 2. Analysis of gas processing slop water for scavenging residuals.

Sample	MEA (ppm)	Dithiazine (ppm)
S1010	500	540
S1011	280	690
S1012	460	360
S1013	20550	5970
S1014	460	160
S1015	29060	8690
S1016	360	380