Analysis of MEA-triazine and dithaizine in crude oil

OV-AN-0006

OndaVia

Analysis of MEA-triazine and dithiazine in crude oil

OndaVia offers a Raman-spectroscopy-based system for rapid, on-site chemical analysis. Based on customer requests, we have developed a test method for monoethanolamine (MEA), MEA-triazine, and dithiazine in crude oil samples. The method requires an extraction step into aqueous solution, followed by analysis via our standard MEA and MEA-triazine part-per-million analysis methods. The result is a few-minute test with portable instrumentation that provides ppm-level amine or triazine content in crude oil.

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 1. OndaVia Analysis System.

OndaVia Analysis System

At OndaVia, we apply Raman spectroscopy to analytical chemistry. We combine proprietary methods, solvents, software, and algorithms to perform fast, accurate chemical analyses in a range matrices. The OndaVia Analysis System (OV-PP-J003), shown below 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” to convert 120-VAC. 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 Advanced ORC™ analysis software, the user has access to spectral data for in-house method development or research.

Analysis of amines and triazines in crude oil

MEA-triazine (hexahydro-1,3,5-tris(hydroxyethyl)-s-triazine, CAS# 4719-04-4) is an important and popular hydrogen sulfide scavenger in crude oil production. Triazine-based scavengers are often applied shortly before transportation, resulting in residual scavenger within the crude. This scavenger can become a tramp amine at the refinery, which in turn can lead corrosive heat stable salt deposits. Moreover, 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-PP-B018), dithiazine (OV-PP-B011-PPM) and monoethanolamine (OV-PP-B003). These kits offer 10% accuracy over 0- 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.

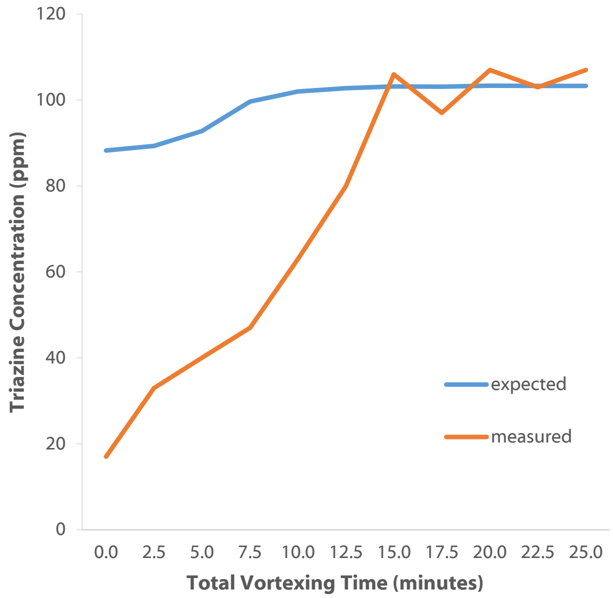

Figure 2. Effects of mixing time on sample preparation. The addition of triazine to crude oil requires extensive mixing to ensure the expected concentration is reached.

Sample preparation

Mixing triazine into a crude sample is not trivial. Care must be taken to ensure that triazine is completely and properly mixed. To demonstrate this challenge, we added 5-mg of a 62% MEA-triazine commercial triazine product to a 35-g crude sample; the resulting final concentration should be 86-ppm triazine. This sample was placed on a rotary lab mixer for four hours, after which the triazine was extracted and measured at 17-ppm. The sample was returned to the lab mixer for an additional twenty-four hours, aggressively vortexed for 2.5 minutes, and then measured at 30-ppm.

We started a cycle of mixing the sample on a rotary stage for 2-4 hours followed by an additional 2.5 minutes of vortex mixing. The measured concentration as a function of time is shown in Figure 2. Note that due to the removal of sample for analysis (and sample lost due to leaks during vortex mixing), the expected concentration increases with time. After twenty minutes of vortex mixing and three days on a rotary mixer, the sample reached the expected concentration.

Triazine analysis results

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 crude oil, we developed an extraction method leveraging commonly used methods for amine analysis. For sample extraction, we weighed approximately 0.5-g of crude sample into a 1.5-ml centrifuge vial and added an equal mass of 1-mM HCl. The vial was vortexed for two minutes, and then centrifuged to separate the water and oil phases. We collected 100-uL of the aqueous phase, added 40-ul of MEA-triazine reagent, and 10-uL of 1M NaOH to adjust the pH above 12.7. This prepared sample was added to the nanoparticle vial, and analyzed using our MEA-triazine-ppm calibration curve. The measured concentration was 120-ppm, near the prepared concentration at 125-ppm.

In order to confirm the triazine was completely extracted, a second extraction was tested on the highest concentration samples. The crude oil portion of the first extraction was removed from the centrifuge vial, introduced to a second vial, and an equal mass quantity of 1-mM HCl was added. After vortex mixing, sonication, and centrifugation, the analysis reported zero MEA-triazine. The first extraction collected all extractable MEA-triazine.

Starting from the crude oil spiked with 125-ppm of triazine, we created dilutions using unspiked crude. The results are presented in Figure 3. The dilutions show a linear decrease in triazine content, reporting values that are expected. Analysis of the unspiked crude sample reports zero triazine.

High triazine concentration analysis

Our method is capable of extracting high triazine concentrations, although a dilution step is necessary to determine the triazine concentration using our 0-100-ppm curve. To demonstrate this approach, we performed an extraction test on a Brazilian crude oil sample spiked with 2,500-ppm of MEA-triazine. We extracted the triazine using our standard method, and then diluted the aqueous sample 100:1, finding 25-ppm of MEA-triazine.

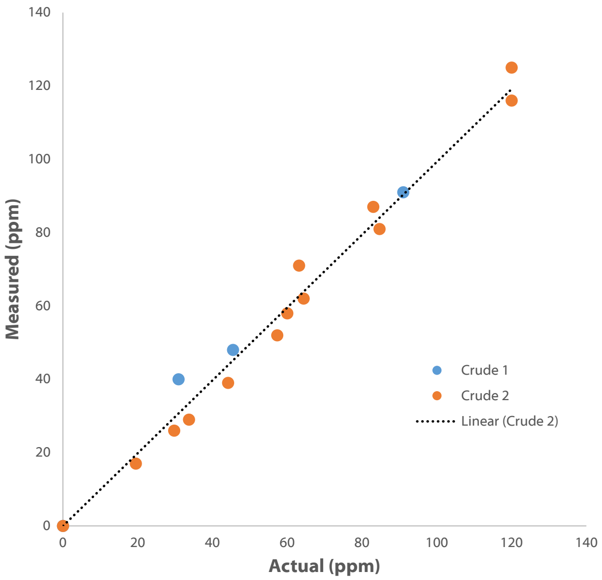

Figure 3. MEA-triazine content in two different crude oil samples. The samples were spiked with MEA-triazine to a known concentration, and then diluted to various levels. The triazine was extracted and measured.

Additional crude oil samples

Given the encouraging results for the first three samples, we expanded our test method to an additional seven samples. These samples are from a variety of locations world-wide across a wide range of APIs. The more viscous samples required the addition of xylene (up to 2× crude volume) during the triazine spiking step in order to mix the sample properly. Xylene had no impact upon the measured result.

The spiked concentration and measured values are shown in Table 1. The results closely follow the expected values, all within 10% except for the most viscous sample (S0073). This sample had to be heated to 40°C in order to dispense oil into the mixing vial. Even with xylene:crude at 2:1, the sample was difficult to prepare. Nevertheless, the final error is under 20%. With optimization of the xylene content and preparation temperature, this method could easily be improved further for more viscous samples.

Table 1. Extractions across a range of crude oil samples of varying compositions, sources, and properties.

Sample	Expected (ppm)	Measured (ppm)
S0072	45	44
S0072	22	21
S0073	43	36
S0074	46	42
S0075	40	42
S0076	43	45
S0077	36	39
S0078	49	46

Dithiazine analysis

Our dithiazine extraction method proceeds similarly, although preparation of dithiazine-spiked crude samples required a few microliters of xylene to help solubility. The sample is mixed 1:1 by weight with 1-mM HCl, vortexed for two minutes, and centrifuged to separate the phases. Dithiazine analysis requires mixing 100-µl of the aqueous phase with 100-µl of dithiazine reagent, and then adding 20-µl of 1M NaOH.

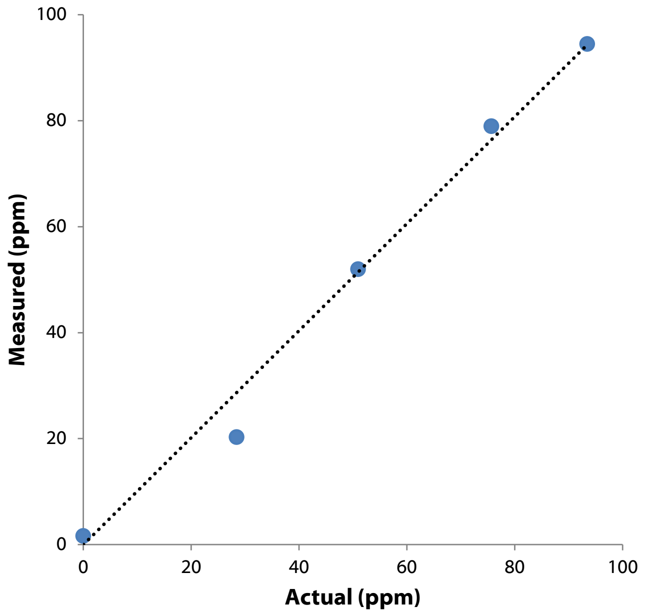

Figure 4. Dithiazine extracted from crude oil sample 2. The samples were spiked with dithiazine at 129-ppm, and then diluted to various levels. The dithiazine was extracted and measured using our ppm-level dithiazine analysis kit.

The results are shown in Figure 4. The concentration of extracted dithiazine from serial dilutions of a 129-ppm sample followed the expected curve.

Conclusion

OndaVia has developed analysis methods for ppm-level amines and triazines in aqueous solutions. Analysis of these compounds in crude oil 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.