Application Note

Energy & Chemicals

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Quantitative Analysis of MEA-Triazine Hydrogen Sulfide Scavengers Through Innovative Transmission FTIR Spectroscopy

The Agilent Cary 630 FTIR spectrometer with DialPath module: transmission FTIR with variable path lengths

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Abstract

A common contaminant in oil and gas extraction is hydrogen sulfide (H_2S). Monoethanolamine-triazine (MEA-triazine) is one of the most used scavengers for H_2S. Industrially, there are many challenges in measuring MEA-triazine concentration in aqueous solutions. This application note aims to develop a mid-infrared (mid-IR) method using an Agilent DialPath transmission module to measure the concentration of MEA-triazine in aqueous solutions. The analytical method described meets the requirements for quantifying MEA-triazine with different solvents, providing time savings, ease of use, and reduced susceptibility to pipetting errors due to viscosity.

Introduction

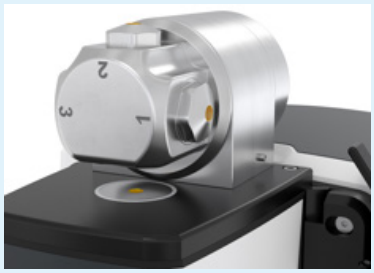
A common contaminant in the oil and gas industry is H_2S. H_2S can already be present in oil and gas reservoirs, or can be formed by thermal, bacterial, or thermochemical action.[1] A common and efficient way to treat such contamination is by using amine-based scavengers.[2] MEA-triazine (1,3,5-tri-(2-hydroxyethyl)-hexahydro-s-triazine) is one of the most commonly used scavengers of H_2S.[2] MEA-triazine is generally synthesized as a highly viscous, clear to light-yellow solution with a concentration of 80% when using pure MEA as substrate.[3]

Several analytical techniques have been developed in the past to measure the purity of MEA-triazine solutions. A good approximation of the remaining triazine after synthesis can be done by measuring the total amine content. This can be done using the Kjeldahl method or ion-exchange chromatography; however, measuring the total amine content is time-consuming as it involves digestion, steam distillation, and titration/chromatography.[4] In addition, the methods provide results with low accuracy.[5] Because MEA-triazine is not thermally stable, gas chromatography analysis is complicated, time-consuming, and prone to errors.[6]

This application note demonstrates the benefits of the Agilent Cary 630 FTIR spectrometer fitted with an innovative Agilent DialPath module for easy and efficient measurement of MEA-triazine concentration.

The unique DialPath sampling module eliminates the need for traditional flow or demountable liquid cells, simplifying the analysis of liquid samples in transmission mode. A small drop of liquid sample is placed between two horizontally positioned windows of the DialPath module, as shown in Figure 1. The distance between the two windows defines the optical path length. The DialPath module provides instant selection of three preset path lengths that can be selected ("dialed in") by turning the module head.

The DialPath – eliminating the need for liquid cells



The DialPath can bypass common difficulties with traditional cells such as:

- The cells are fragile, and spacers and windows can be difficult to assemble.
- The cell design makes it hard to achieve a reproducible path length.
- Cells tend to leak.
- Air bubbles can interfere with the analysis.
- Cleaning and assembling the cells are time-consuming tasks.
- Sticky and viscous samples are difficult to measure.
- Significant amounts of sample volume and rinsing solvent are required.

1 Ensure that the crystal is clean.

2 Place your sample on the window.

3 Turn the Agilent DialPath to your required path length to analyze.

Figure 1. Three simple steps allow the analysis of liquid samples using an Agilent Cary 630 FTIR spectrometer equipped with an Agilent DialPath module.

Experimental

Preparation of the calibration curve (standards)

Eight standards were prepared by diluting MEA-triazine (CRIKEM Industries Limited) in aqueous solution to percentages of 15, 20, 25, 30, 40, 50, 60, and 75% (by mass wt%).

Preparation of interference test samples

To investigate the interference effect, two standards (25 and 50% triazine) were prepared using two common additives, 99.9% methanol (MeOH) from Fisher Scientific (part number A456-212) and 99.9% isopropyl alcohol (IPA) from Fluka (part number 34965) at three different concentrations, 10, 15, and 25%, in aqueous solution, as shown in Table 1.

Table 1. MEA-triazene interference test samples preparation.

Sample	Nominal MEA-Triazene Concentration (wt%)	Additive	Added Additive Concentration (v/v%)
1	25	MeOH	10
2	25	MeOH	15
3	25	MeOH	25
4	25	IPA	10
5	25	IPA	15
6	25	IPA	25
7	50	MeOH	10
8	50	MeOH	15
9	50	MeOH	25
10	50	IPA	10
11	50	IPA	15
12	50	IPA	25

Instrumentation

A Cary 630 FTIR spectrometer with ZnSe optics (part number G8043-64002) and a DialPath accessory with three variable path lengths (part number G8043-68303) were used in this study (Figure 2). For both standard and interference samples, spectra were collected using the settings specified in Table 2 with 50 µm path length. Before each measurement, the upper and lower windows of the DialPath module were cleaned between samples, first with a dry cotton tissue, then with a cotton tissue soaked in acetone.

Table 2. FTIR data collection parameters using the Agilent DialPath module.

Parameter	Setting
Number of Scans (Background and Sample)	32
Spectral Range	4,000 to 650 cm^{-1}
Sample Volume	7 µL
Resolution	4 cm^{-1}
Path Length	50 µm
Background Collection	Air
Number of Standards	8 (n = 4)
Number of Samples	12 (n = 4)

Results and discussion

As the MEA-triazine standards and samples were prepared in an aqueous solution, water IR absorption peaks at 3,600 to 3,000, and 1,640 cm^{-1} were observed. To select the optimal region for quantification analysis of MEA-triazine, the peak area between 1,284.07 and 1,203.93 cm^{-1}, which reflects the distinctive infrared characteristics of MEA-triazine, was selected (Figure 3).

Figure 2. The liquid sample is placed onto the sample window of the Agilent DialPath module fitted to the Agilent Cary 630 FTIR spectrometer.

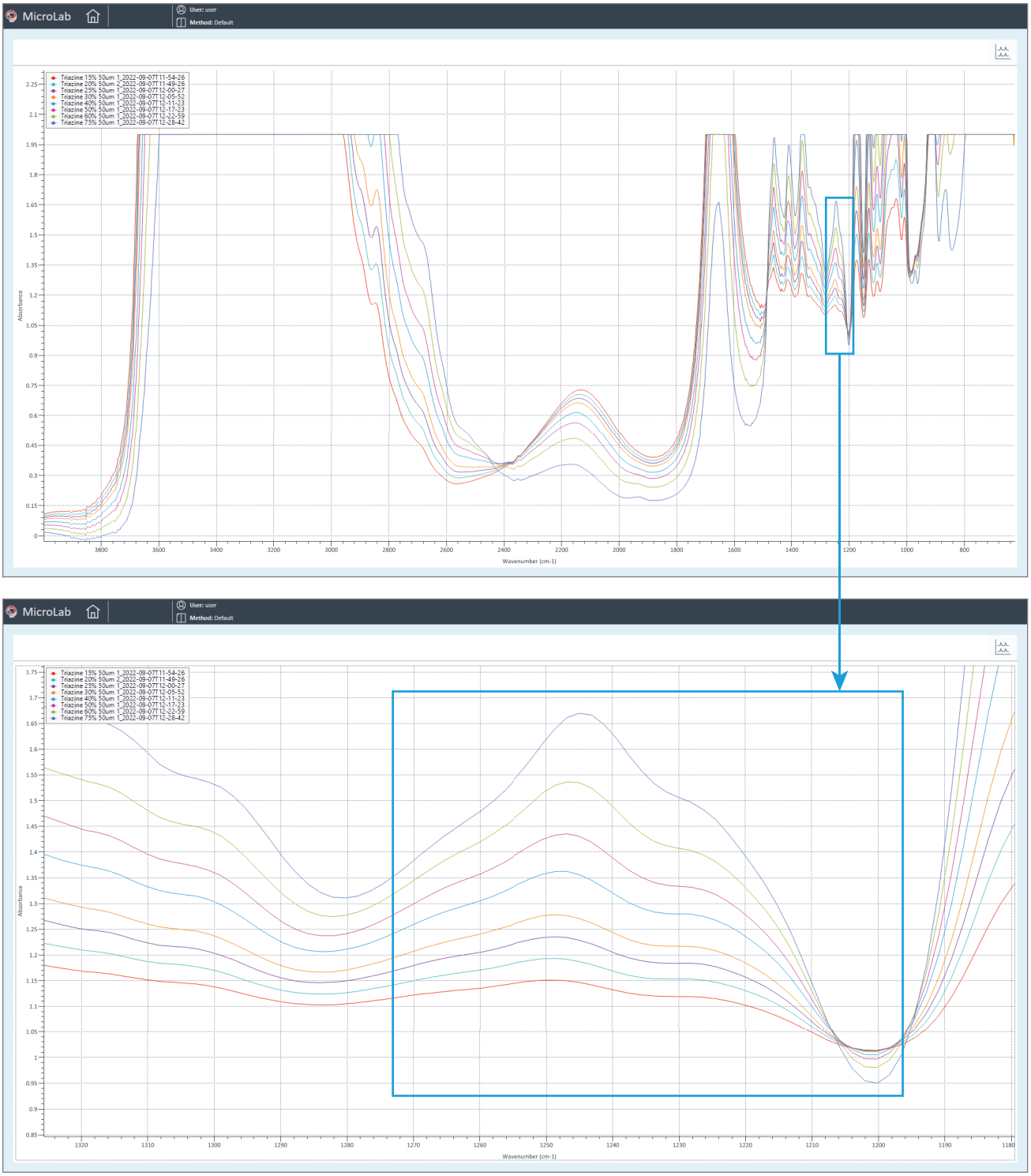


Figure 3. FTIR spectrum overlay of the MEA-triazine standard solutions. The blue box indicates the peak area used for quantification analysis.

Linearity and calibration curve

MEA-triazine standards containing different concentrations (15 to 75%) of MEA-triazine in aqueous media were measured in quadruplicate. Using the peak area defined in the previous section, a calibration curve was built using Agilent MicroLab Quant software, which is included in the Agilent MicroLab FTIR software suite.

Using Agilent MicroLab Quant software, a simple Beer-Lambert law based on peak area was used to instantly produce a calibration curve. The calibration curve displayed excellent linearity with a correlation coefficient (R^2) value of 0.9993 (Figure 4). Calibration curves and correlation coefficient calculations are performed automatically in the software. Users can report the obtained results for documentation purposes. MicroLab Quant is a powerful, intuitive tool for method development that guides the user through each step in building a quantitative method. Built-in checks make sure that simple user errors do not affect the calibration.

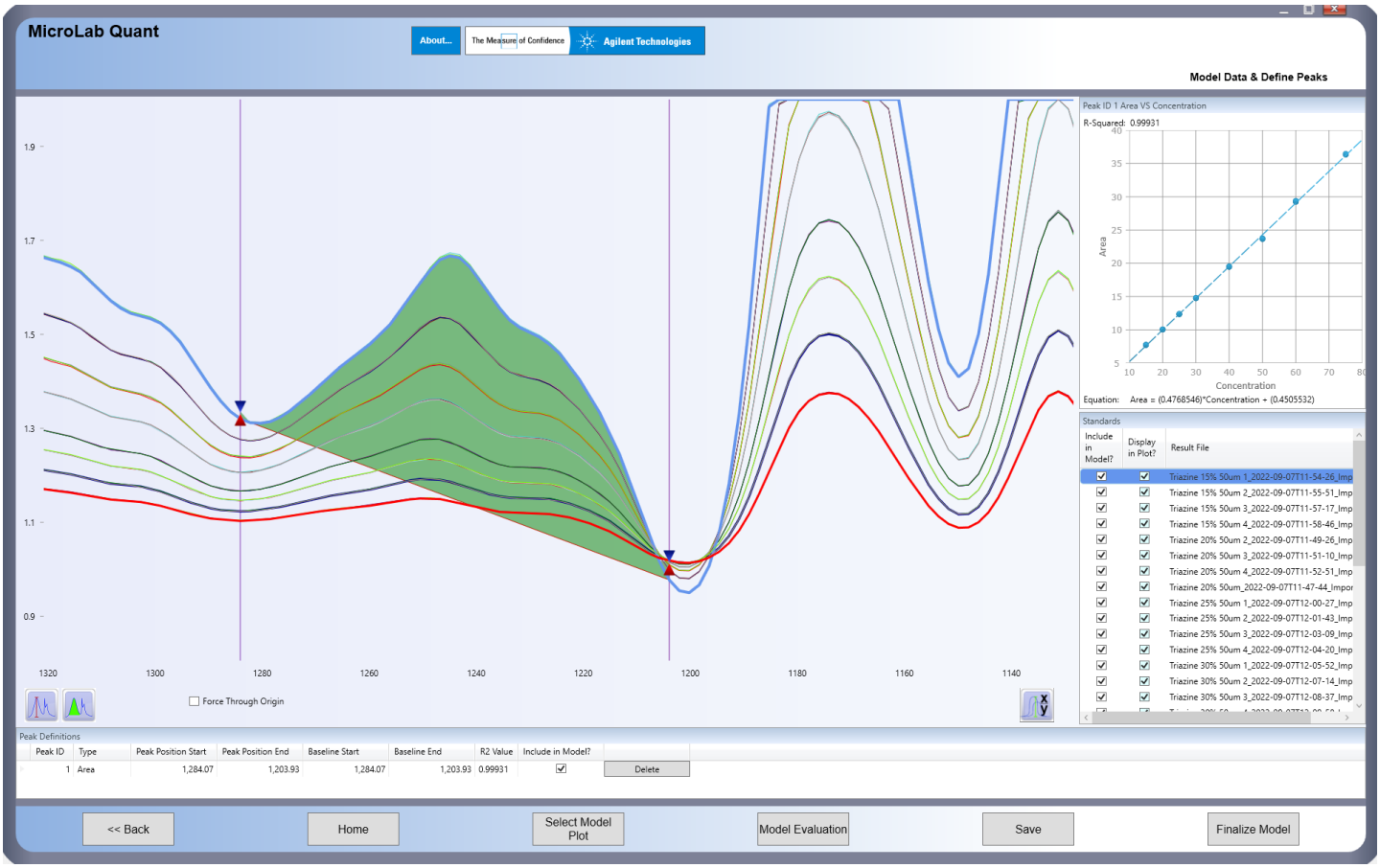


Figure 4. Linearity evaluation of MEA-triazine standards using an Agilent DialPath module and Agilent MicroLab Quant software.

MicroLab Quant software includes a quick and convenient Cross Validation feature for the calibration curve, which can be performed using the same dataset. As shown in Figure 5, the Cross Validation results predicted values closely matching the known concentrations, with an overall standard error of 0.116%.

Interference samples measurements

To assess the model using an independent dataset, samples with nominal concentrations of MEA-triazene at 25 and 50% containing 10, 15, and 25% (v/v) MeOH and IPA were used. These solvents are commonly used to decrease the viscosity of MEA-triazine and extend the usable temperature range for triazine scavengers, thus improving their applicability.[3] Subsequently, the samples were analyzed to detect any potential effects on the MEA-triazene concentration readings. The results were obtained using the Independent Set function in MicroLab Quant, comparing the predicted concentrations against known values.

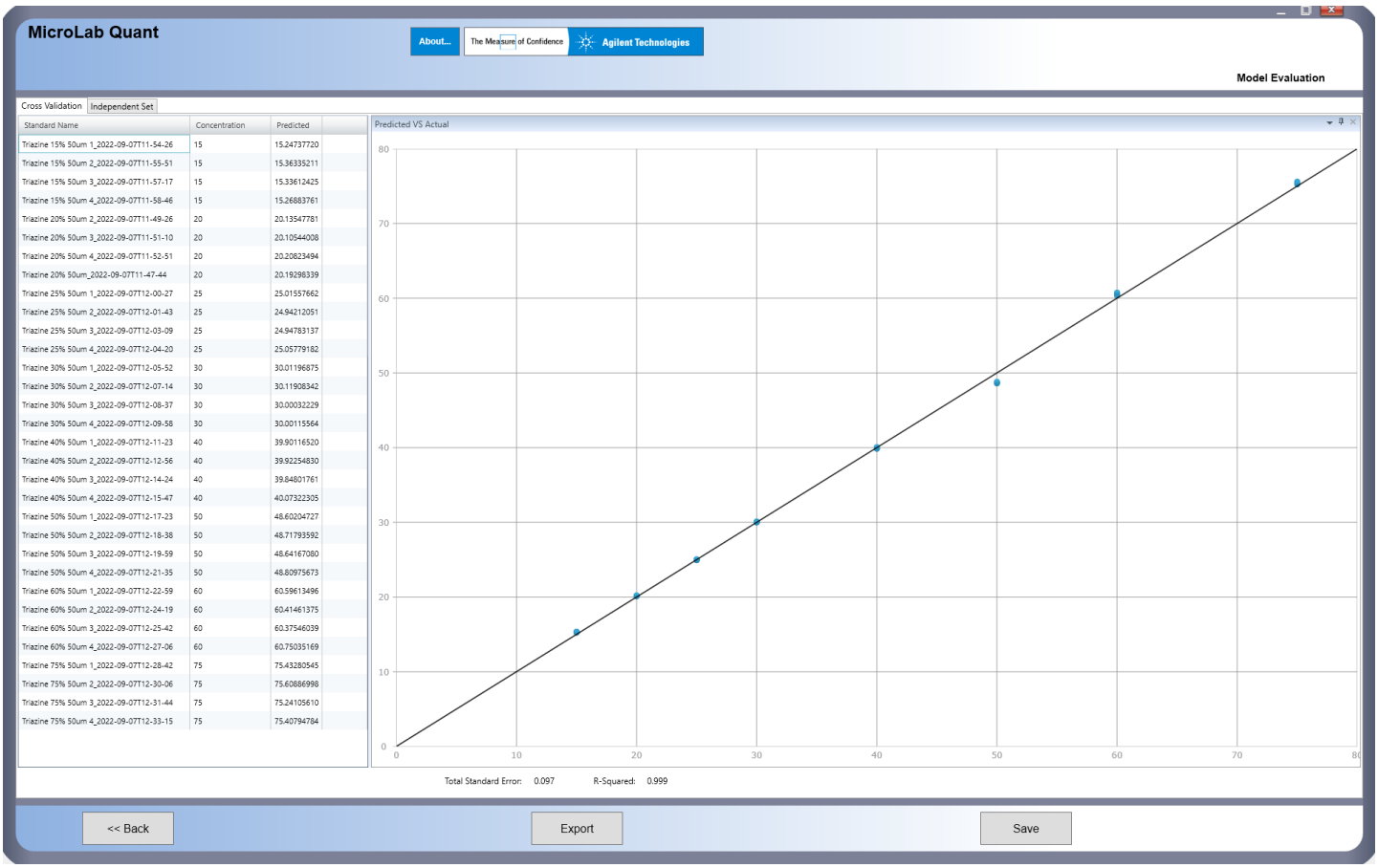


Figure 5. Agilent MicroLab Quant software Cross Validation feature, ideal for model evaluation.

Influence of MeOH on MEA-triazene concentration

As shown in Table 3, at a nominal MEA-triazene concentration of 25%, increasing MeOH concentration from 10 to 25% resulted in a small but noticeable decrease in the measured concentration, with differences from nominal values increasing from 0.2104 to 0.9831%. Similarly, at a nominal concentration of 50%, higher MeOH levels led to larger discrepancies, with the difference growing from 2.4477% at 10% MeOH to 4.3634% at 25% MeOH. The standard total error for six samples measured (n = 4 each) was calculated to be 0.284.

Influence of IPA on MEA-triazene concentration

The data with added IPA show a distinct trend where increasing IPA concentrations overestimate the MEA-triazene concentrations. For a nominal concentration of 25%, the measured concentrations exceeded the nominal values by 2.7026% at 10% IPA and rose to 5.7845% at 25% IPA. At 50% nominal concentration, the difference increased from 3.4670 to 6.5482% as IPA concentration increased. The standard total error for six samples measured (n = 4 each) was calculated to be 0.327.

Table 3. Effect of added MeOH on MEA-triazene concentration measurements.

Nominal MEA-Triazene Concentration (wt%)	Added MeOH Concentration (v/v%)	Average Measured MEA-Triazene Concentration (wt%)	Standard Deviation (wt%)	Difference Between Nominal and Measured MEA-Triazene Concentration (wt%)
25	10	24.7895	0.0914	0.2104
25	15	24.6059	0.0392	0.3940
25	25	24.0169	0.0817	0.9831
50	10	50.9477	0.0566	2.4477
50	15	51.4533	0.1890	2.9533
50	25	52.8634	0.3100	4.3634

Table 4. Effect of added IPA on MEA-triazene concentration measurements.

Nominal MEA-Triazene Concentration (wt%)	Added IPA Concentration (v/v%)	Average Measured MEA-Triazene Concentration (wt%)	Standard Deviation (wt%)	Difference Between Nominal and Measured MEA-Triazene Concentration (wt%)
25	10	27.7026	0.0557	2.7026
25	15	28.6802	0.0094	3.6802
25	25	30.7845	0.5485	5.7845
50	10	53.4671	0.0566	3.4670
50	15	54.2989	0.2276	4.2989
50	25	56.5482	0.1065	6.5482

Both MeOH and IPA solvents influenced the measured concentrations of MEA-triazene, with a larger error observed with IPA compared to MeOH, particularly at higher solvent concentrations. As shown in Figure 6, this can be explained by the change in the area under the curve upon the addition of IPA, resulting in a new peak at 1,325 to 1,275 cm^{-1} and a reduction in absorption; yet, with MeOH, only a reduction in absorption was observed. The minimal standard deviations in both datasets suggest that precise measurements can be achieved using the DialPath and Cary 630 FTIR spectrometer.

A separate calibration curve with MEA-triazine containing a certain concentration of these solvents could be generated to enhance the quantification accuracy of MEA-triazine.

High sample throughput and usability

The modular design of the Cary 630 FTIR allows for effortless switching between different measurement modes, notably including the DialPath. The DialPath significantly improves sample throughput over traditional liquid cell methods. It requires only a small sample volume directly on the module's surface for each measurement, streamlining the preparation process. This approach eliminates common problems such as bubbles, leaks, and the need for lengthy assembly.

Also, the DialPath offers flexibility in path length adjustment, allowing users to optimize measurements based on specific sample requirements. Shorter path lengths can be used to reduce IR absorption effects of water, which can interfere with accurate readings. This is beneficial for aqueous samples where minimizing water interference is crucial. The design also accommodates samples of varying viscosities, reducing handling issues and measurement inaccuracies associated with high-viscosity liquids.

Paired with the user-friendly MicroLab Quant software, which simplifies model evaluations within the software itself, the Cary 630 FTIR becomes a powerful tool for high-throughput and accurate MEA-triazine quantification.

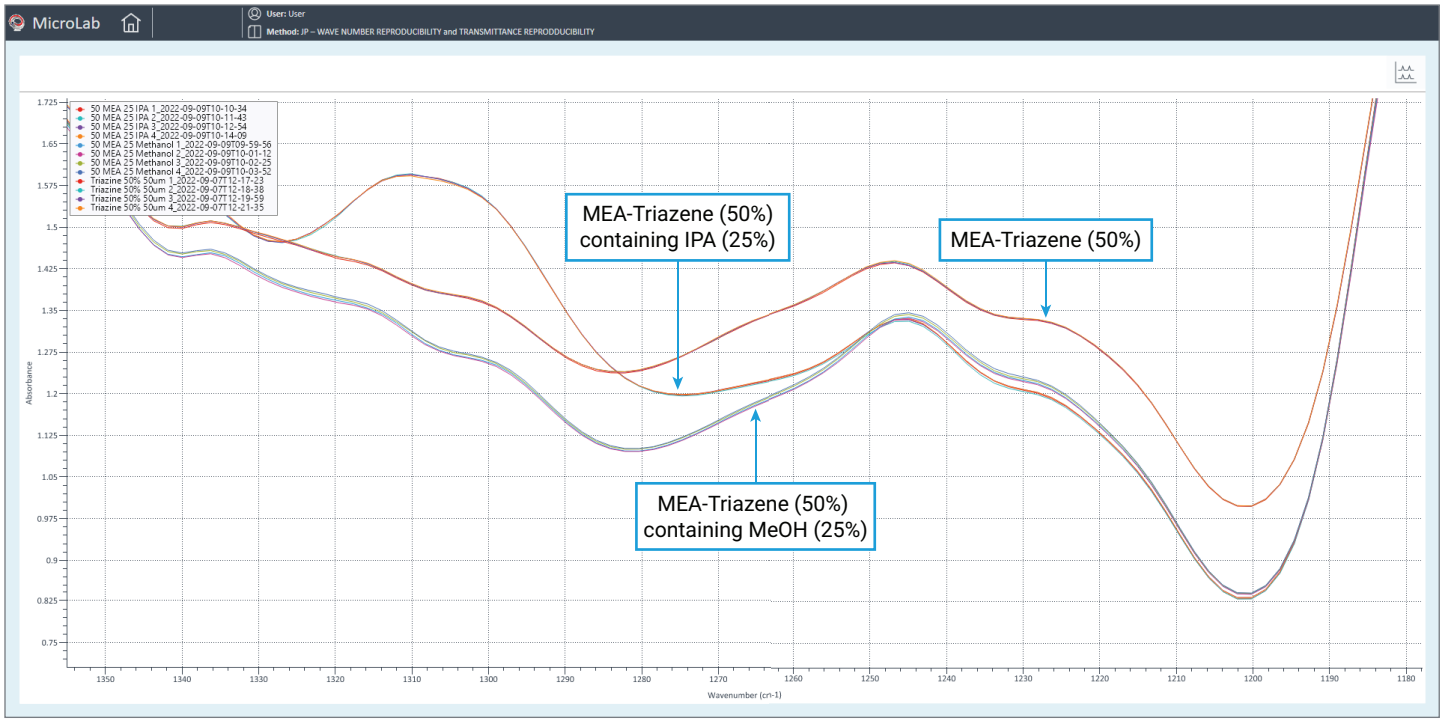


Figure 6. Overlay of MEA-triazine 50%, highlighting the spectral changes upon the addition of 25% MeOH and IPA.

Conclusion

The Agilent Cary 630 FTIR spectrometer with DialPath module proves to be a highly effective, accurate, and user-friendly method for the quantitative analysis of MEA-triazine in aqueous solutions. The technique's excellent linearity and robustness against additives such as MeOH and IPA highlight its reliability. The DialPath module's innovative design simplifies the measurement process, enhances sample throughput, and reduces common issues such as leaks and air bubbles. This method offers a significant improvement over traditional analytical techniques, providing a practical solution for both field and laboratory measurements in the oil and gas industry.

Acknowledgment

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Further information

Agilent Cary 630 FTIR Spectrometer

MicroLab FTIR Software

MicroLab Expert

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