Application Note

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Quantification and Chemical Identification of NOx Reduction Agent AdBlue (AUS32) Using ATR-FTIR

Agilent Cary 630 FTIR benefits for performing easy, fast, and reliable liquid measurements

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Abstract

The Agilent Cary 630 FTIR spectrometer is a simple and easy-to-use instrument for the analysis of commercial AdBlue. In this study, a Cary 630 FTIR equipped with the single reflection diamond ATR module was used in identifying commercial AdBlue, as specified in the ISO 22241-2 standard. The study was extended to quantifying urea in commercial AdBlue using a linear calibration curve constructed using the Agilent MicroLab Quant application. This FTIR-based quantification provides an easier and more economical alternative to ISO 22241-2 methods for routine quantifications of urea content in AdBlue using Agilent MicroLab FTIR software.

Introduction

AdBlue is the trade name for the 32.5% w/w aqueous urea solution of high purity, whose quality specifications are regulated by the ISO 22241 standard. It is also known as DEF (Diesel Exhaust Fluid) in the USA, ARLA32 in Brazil, and under the technical name AUS32 outside Europe. Irrespective of the name, this substance is always required to meet the same specifications. AdBlue is used in vehicles running diesel engines, where the selective catalyst reduction (SCR) is implemented. In practice, AdBlue is injected into the exhaust emissions of a diesel-powered engine to reduce harmful nitrogen oxide (NOx) emissions, which cause damage to the environment. During this process, AdBlue is injected into the exhaust pipe upstream of the SCR catalytic converter. As a result of heat, urea decomposes into ammonia, and harmful NOx gases undergo selective catalytic reduction to form nitrogen gas and water vapor (Figure 1).[1]

AdBlue is in high demand and is currently facing a shortage of refined urea, the key ingredient of AdBlue. Increased demand in AdBlue has followed stricter global fuel standards, particularly in Europe. Therefore, it is important to determine the identity, quality, and chemical characteristics of AdBlue to ensure that it meets the requirements specified in ISO 22241 standards. In the ISO 22241-2, Annex J, FTIR spectroscopy is specified as the analytical technique for the identification of AdBlue, with a urea concentration greater than 10% w/w. The ISO 22241-2 standard also specifies a combustion method (Annex B) and a refractive index method (Annex C) for quantifying urea content in AdBlue.

However, applying these quantification methods can be time-consuming, and requires chemicals, lab equipment, and experienced personnel. This application note explores FTIR spectroscopy as an easier and more economical alternative for routine quantifications.

FTIR spectroscopy is a rapid and easily implemented technique that provides both identity and quantity information of a sample. FTIR analysis requires only minimal sample volume, and in most cases, no sample preparation and consumables are required. When light is transmitted through a solution of urea (AdBlue), infrared light is absorbed and produces a spectrum with characteristic peaks that allow identification. The FTIR spectra collected for commercial AdBlue samples are compared with the 32.5% w/w standard urea solution for quick and easy identifications.

The Agilent Cary 630 FTIR spectrometer, equipped with a diamond attenuated total reflection (ATR) sampling module is well-suited for analyzing commercial AdBlue (Figure 2). As the world's smallest benchtop FTIR spectrometer, the Cary 630 FTIR combines robustness, flexibility, and high performance in an

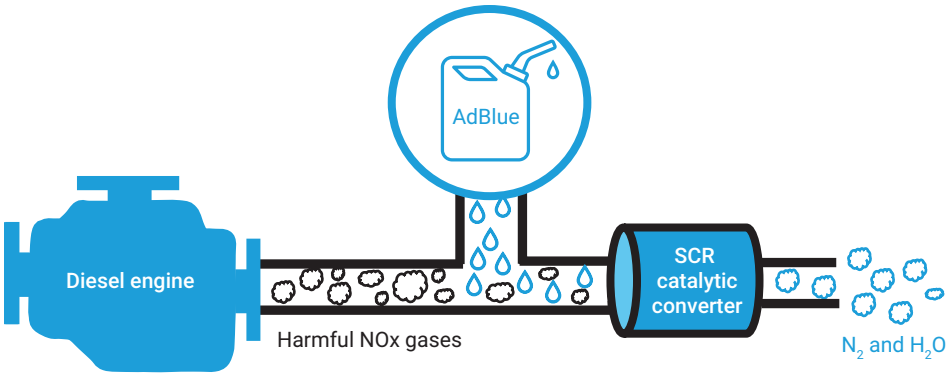

Figure 1. AdBlue, together with selective catalyst reduction technology, converts harmful NOx gasses into nitrogen gas and water vapor.

Figure 2. Agilent Cary 630 FTIR spectrometer with Diamond Attenuated Total Reflection sampling module attached.

ultracompact design, ideal for routine analysis. The Cary 630 FTIR can be quickly reconfigured with a sample module, requiring no user alignment. For ease-of-use, the Agilent MicroLab software provides step-by-step guidance with instructive pictures to intuitively navigate users through the entire analytical workflow. The software uses a method-based approach that enables setting up methods for identification, as well as for quantification. Results are displayed in an easy-to-understand format, color-coding the results based on customizable limits, making data review quick and intuitive (Figure 3).

Experimental

Instrumentation

The Agilent Cary 630 FTIR spectrometer equipped with a single reflection diamond ATR module was used in this study. A small volume of a sample was placed on the ATR crystal, and data acquisition was carried out using Agilent MicroLab software, version 5.7. Parameters were selected as shown in Table 1 (the ATR crystal was cleaned with distilled water before each analysis).

Table 1. Experimental parameters for the Agilent Cary 630 FTIR-ATR module.

Parameters	Setting
Spectral Range	4,000 to 650* cm^{-1}
Sample Scans	256
Spectral Resolution	4* cm^{-1}

* Specified in ISO -22241

Materials and methods

Part A: Determination of identity of commercial AdBlue

Preparation of standard 32.5% w/w urea solution: The 32.5% w/w standard urea solution was prepared in a 10 mL volumetric flask, by fully dissolving 3.25 g of urea crystals (CAS 57-13-6) in distilled water.

Samples for the analysis:

- An internally prepared urea solution of 32.5% w/w concentration was used.
- A commercial AdBlue sample was purchased from a local gasoline station.

Part B: Quantifying urea in commercial AdBlue

Preparation of standard samples: Ten standard samples of urea (CAS 57-13-6) with known concentrations (10, 15, 20, 25, 30, 35, 40, 45, 50, and 60% w/w) were prepared in 10 mL volumetric flasks, through appropriate dilutions. These standard samples were used to create a quantification method with a linear calibration curve constructed using the MicroLab Quant application which is included in the Agilent MicroLab software suite.

Control samples: To evaluate the quantification method, five urea (CAS 57-13-6) samples with known concentrations (6, 12, 29, 33, and 43% w/w) were prepared as the control in 10 mL volumetric flasks, by fully dissolving appropriate amounts of urea crystals in distilled water.

Samples for the analysis:

- The standard 32.5% w/w urea solution prepared in Part A was used.
- A commercial AdBlue sample was purchased from a local gasoline station.

Figure 3. Agilent MicroLab software automatically recognizes the attached sampling module and applies the correct parameters. The software navigates the user, step-by-step, through the analytical workflow using instructive pictures. Color-coded results, directly reported after data acquisition, make data review quick and intuitive.

Results and discussion

Part A: Determination of identity of commercial AdBlue

The MicroLab software guides users through the entire analytical workflow, using instructive pictures and an easy-to-navigate design. A FTIR method for the routine identification of AdBlue solutions was created in the MicroLab software, as specified in the ISO 22241-2 standard. The AdBlue Identification method was created by adding the FTIR spectrum of the 32.5% w/w standard urea sample into a new spectral library. Using this method, FTIR spectra of the commercial AdBlue samples are compared with the reference sample. Following data acquisition, the software automatically performs the library comparison, and automatically calculates the Hit Quality Index (HQI) for each sample. The HQI indicates how well the measured spectrum matches the reference spectrum in the library. The HQI can then be used as pass/fail criteria. Users can set color-coding thresholds, and the software automatically applies color-coding. This allows for easy interpretation and identification of out-of-spectrum samples. Samples that are identified with high confidence are displayed in green, while samples that are identified with low confidence are displayed in red.

To test the AdBlue identification method created above; the 32.5% w/w internally prepared urea solution and a commercial AdBlue solution were analyzed. Following data acquisition, the software automatically applied the similarity search algorithm and provided

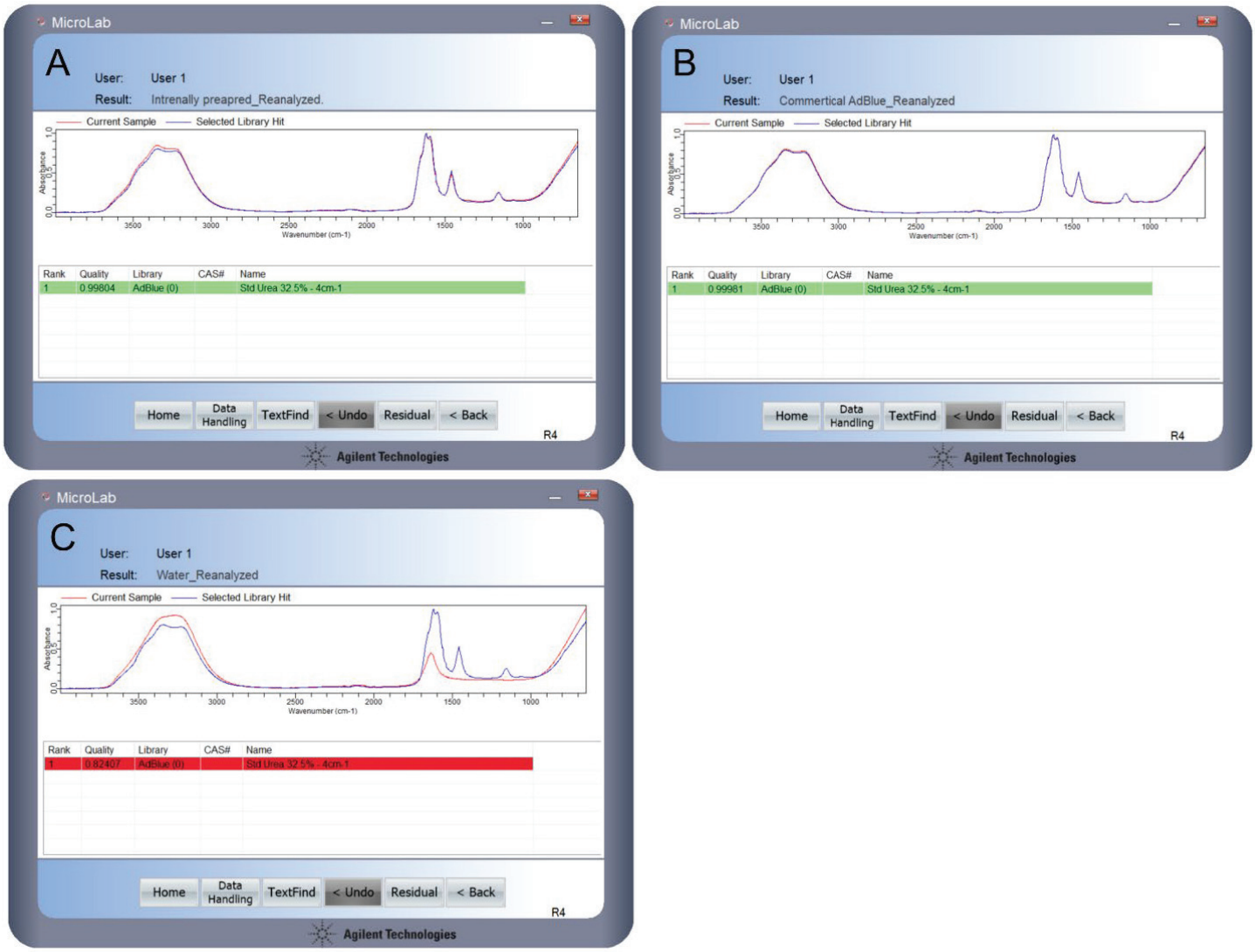

Figure 4. A routine qualitative method for identifying commercial AdBlue samples with a high degree of confidence. Color coded results report (A) an internally prepared 32.5% w/w urea sample, (B) a commercial AdBlue sample, and (C) water. The color-coding makes result interpretation easy and reduces the risk of operator error.

the identification results. As shown in Figures 4A and 4B, the software correctly identified the samples with an HQI of 0.99804 and 0.9998 (with 1 being the highest theoretical value), respectively, with green color-coded results. When a FTIR spectrum of water was analyzed, a red color-coded result displayed an HQI of 0.82407, confirming the spectral mismatch (Figure 4C). These results demonstrate that the Cary 630 FTIR with a diamond ATR module provides a quick and easy method for automatically identifying commercial AdBlue, as specified in the ISO 2224-2 (Annex J) standard.

Part B: Quantifying urea in commercial AdBlue

According to the ISO 22241-2 standard, both the combustion method and the refractive index method can be used for determining the urea content of AdBlue. However, applying these methods can be time-consuming for routine analysis. In addition, these methods require a certified reference material, lab equipment, experienced personnel, and are only applicable for determining the urea content in the range of 30 to 35% w/w. Thus, it is important to evaluate alternative methods for routine analysis of urea content in commercial AdBlue.[2] This application note explores FTIR spectroscopy as an easier and more economical alternative to the ISO 22241 methods for routine quantifications.

Creating a quantification model (calibration curve)

The MicroLab Quant application was used to create a linear calibration curve. See the Agilent instruction sheet "Alcohol level determination in hand sanitizers by FTIR" (5994-2827EN) for step-by-step instructions on creating a quantification model. FTIR spectra of ten standard samples of urea with known concentrations (10, 15, 20, 25, 30, 35, 40, 45, 50, and 60% w/w) were collected. The characteristic peak of urea, located at 1,157 cm^{-1} was used to develop the calibration curve, using the area under the curve. As shown in Figure 5, the plot of the peak area as a function of concentration indicates that quantification model has excellent linearity, with a correlation coefficient of R = 0.99934. This model was saved as "AdBlue Quantification" for analyzing samples. The newly created AdBlue quantification method was evaluated using: 1) total standard errors, calculated using the MicroLab Quant application, and 2) precision measurements based on repeatability studies.[2]

Quantification model evaluation

Once the quantification model has been created, it can be further evaluated within the MicroLab Quant application. This can be done in two ways: using the **Cross Validation** or **Independent Set** function under the **Model Evaluation** tab (Figure 5).

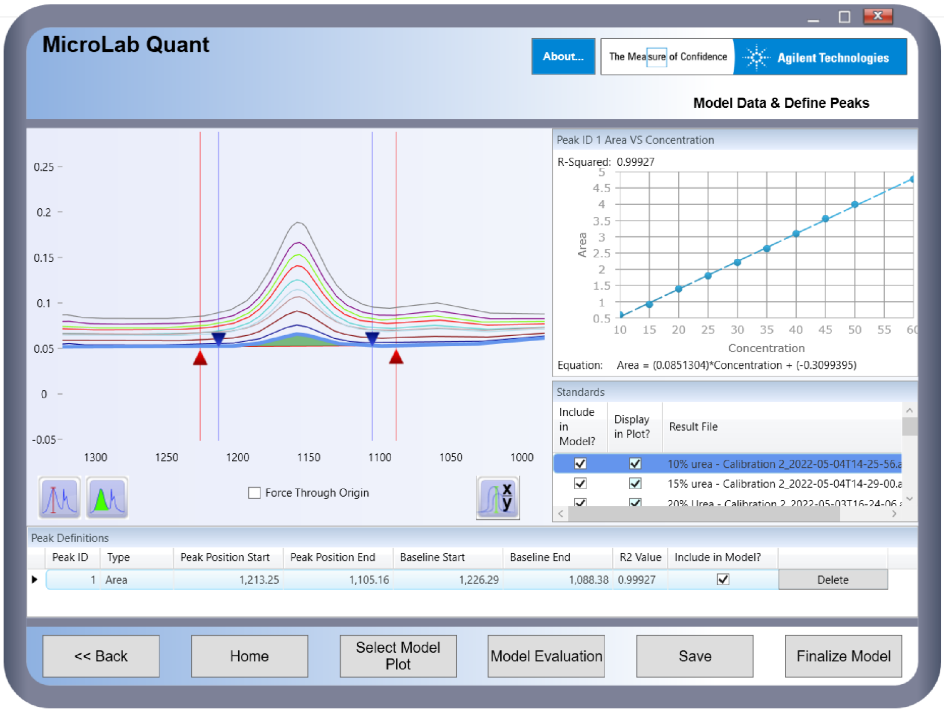

Figure 5. The peak area between 1,213.25 cm^{-1} and 1,105.16 cm^{-1} was used to evaluate the linearity of the ATR-FTIR spectral response. The calibration curve and the correlation coefficient calculations are performed automatically in the software.

Cross validation: This function was used to predict the concentrations of the standard samples that were used to create the calibration curve. As shown in Figure 6, predicted concentrations have high accuracy, with a 0.18 total standard error.

Independent set validation: This function was used to evaluate the AdBlue quantification model using control samples with known urea concentrations (6, 12, 29, 33, and 43% w/w). FTIR spectra of these samples were collected, and corresponding data files were added by clicking the **Add Files** button. The sample concentration was then entered in the table. Predicted concentrations and total associated error were obtained automatically by clicking the **Predict** button. As shown in Figure 7, the AdBlue quantification model accurately predicted the concentrations of control samples with a total standard error of 0.19.

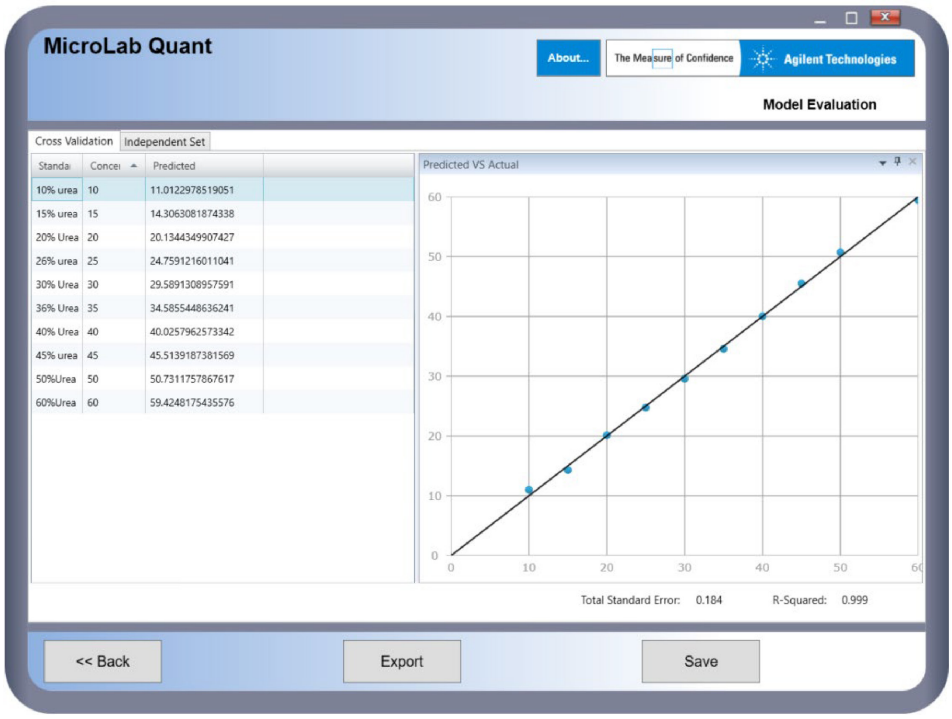

Figure 6. Cross validation of the AdBlue quantification model. Calculations were performed automatically using the Cross Validation function, available within the Agilent MicroLab Quant application.

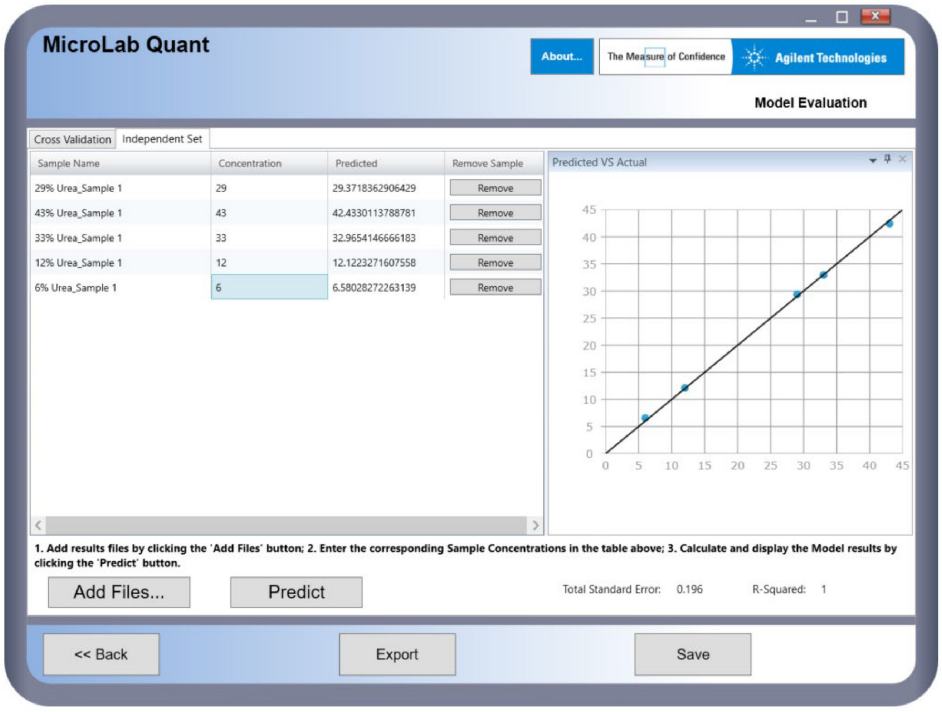

Figure 7. Evaluation of the AdBlue quantification model using the Independent Set function available within the MicroLab Quant application.

Measurement precision and accuracy.

Measurement precision and accuracy were evaluated using the 32.5% w/w standard urea sample following the procedure outlined in Fojtikova, P. *et al.*[2] Accuracy is expressed as a percent recovery of the theoretical amount of the analyte in the sample, and precision is expressed as a repeatability by the relative standard deviation. The 32.5% w/w standard urea sample was split into six portions, and each portion was analyzed using the AdBlue quantification method (The ATR crystal was cleaned with distilled water before each analysis). As shown in Table 2, the Cary 630 FTIR with single reflection diamond ATR module showed excellent precision with a standard deviation of only 0.3%, and >99% accuracy in concentration measurements.

Table 2. Repeatability over six portions of 32.5% w/w standard urea sample using the Agilent Cary 630 FTIR with single-reflection diamond ATR module.

Sample (32.5% w/w Standard Urea)	Concentration (% w/w)
Sample Portion 1	31.9
Sample Portion 2	32.5
Sample Portion 3	32.7
Sample Portion 4	32.3
Sample Portion 5	32.9
Sample Portion 6	32.4
Average Concentration	32.5
Accuracy (%)	>99%
Precision (Standard Deviation %)	0.3

Analysis of commercial AdBlue samples

A commercial AdBlue sample purchased from a local gasoline station and the 32.5% w/w standard urea solution were used for the analysis. The urea concentration of a AdBlue sample is defined in ISO 22241-2 standard as the arithmetic mean of the three measurements rounded to the nearest 0.1%. To be consistent with the ISO method, each sample was split into three portions, and the FTIR spectra were collected. Each FTIR spectrum was analyzed using the AdBlue quantification method. Highly accurate results were obtained for the average concentrations of each sample. The calculated standard deviations were 0.4% for the 32.5% w/w standard urea solution and 0.6% for the commercial AdBlue sample (Table 3). These results suggest that the Agilent MicroLab software provides an easy, accurate, and economical alternative for the routine analysis of urea content in commercial AdBlue.

A fast, accurate, and simple alternative method for AdBlue quantification

Creating the quantification model, which consisted of 10 standard samples, required approximately 30 minutes. This included cleaning the crystal, collecting a background, collecting data for 10 standards (256 scans per sample), as well as generating the corresponding quantification model. Once the quantification model was implemented in a MicroLab method for routine analysis, the analysis of one sample took approximately 2.5 minutes, which included cleaning the crystal, collecting background, and collecting the sample spectrum (256 scans per sample). However, reducing number of scans per sample allows faster analysis and higher sample throughput (e.g., 128 scans required approximately 1.5 minutes). The Cary 630 FTIR, with a single reflection diamond ATR module, provided a fast and reliable alternative method for quantifying urea content in commercial AdBlue and with minimum risk of operator error.

Table 3. Analysis of commercial AdBlue and internally prepared 32.5% w/w urea solutions using the Agilent Cary 630 FTIR ATR module together with the AdBlue quantification model created using the MicroLab Quant application.

Sample		Concentration (% w/w)	Average Concentration (% w/w)
32.5% w/w Standard Urea Solution	Sample Portion 1	31.9	32.4 ± 0.4
	Sample Portion 2	32.5	
	Sample Portion 3	31.7	
Commercial AdBlue	Sample Portion 1	32.9	32.4 ± 0.6
	Sample Portion 2	32.6	
	Sample Portion 3	31.8	

Conclusion

The Agilent Cary 630 FTIR spectrometer is a simple and easy-to-use instrument for the analysis of commercial AdBlue. In this application note, the Cary 630 FTIR with a single-reflection diamond ATR module was used to create a quick and easy method for identifying commercial AdBlue, as specified in the ISO 22241-2 standard. FTIR spectroscopy is an easier and more economical alternative to the ISO 22241-2 methods for routine quantifications of urea content in AdBlue using Agilent MicroLab software. The Cary 630 FTIR-ATR generates a highly linear calibration curve with excellent repeatability, demonstrating the effectiveness of the instrumentation, method, and analytical results.

References

1. Foerter, D. C; Whiteman, C. S. Typical Installation Timelines for NOx Emissions Control Technologies on Industrial Sources. *Institute of Clean Air Companies (ICAC)* December **2006**.
2. Fojtikova, P. *et al.* Tracking AdBlue Properties During Tests of Selective Catalytic Reduction (SCR) Systems - the Suitability of Various Analytical Methods for Urea Content Determination. *Int. J. Energy Res.* **2020**, *44*, 2549–2559.

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