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Determination of Nitrite Levels in Engine Coolant by UV/Vis Spectroscopy

Introduction

Engine coolants are an important fluid sometimes neglected in motor vehicles. Some citations in the literature report that a major cause of engine failure behind lubricant failure, is that of the coolant[1]. Formulations of engine coolant (also known as antifreeze) consist of glycol, water and an additive package[2]. Although the additives can differ by their chemistry and formulation, the function of the additives in the fluid is to prevent corrosion and promote operational efficiency. Most in-service lubricant analysis programs have testing procedures for the analysis of coolants.

Nitrite (NO_2-) is a common additive to coolant formulations that is used to prevent pitting of the cylinder liner by creating an oxide patina protective layer[1]. The nitrite additive in the fluid is consumed as it is in use however, and as such requires frequent testing to maintain appropriate levels. Testing of nitrite in coolants is done using several techniques such as the paper test strip and ion chromatography. The paper test strip method is a quick manual analysis of coolants that can indicate the relative amount of nitrite in a coolant. Ion chromatography is a common chromatographic technique used for quantitative analysis of nitrite and other anions in coolant samples[3]. Another technique to consider for testing nitrites in aqueous samples is UV/Vis spectroscopy. The UV/Vis technique for analysis of nitrite in aqueous samples is easy and offers the advantage of accuracy, speed and automation for high volume testing.

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There are several methods cited in the literature for analysis of nitrites. In this application, we use EPA method 354.1 as a template to accurately determine nitrite levels as ppm NO_2^- in glycol based aqueous engine coolant using the PerkinElmer LAMBDA® 365+ UV/Vis Spectrometer (Figure 1). All data was processed with UV Winlab™ software.

Figure 1: PerkinElmer LAMBDA 365+ Spectrometer.

Principle

According to EPA 354.1, nitrite in aqueous solution can be determined by a diazotization reaction with sulfanilamide under acidic conditions[4]. The product of this reaction is then coupled with N-(1-Naphthyl)ethylenediamine dihydrochloride to obtain a purple coloured product that can be detected spectrophotometrically at 540 nm. The resulting UV/Vis absorbance at 540 nm is directly proportional to the nitrite concentration of the aqueous sample based on the Beer's Law principle. Reagents used for the preparation for samples and standards according to EPA 354.1 are listed below:

1. N-(1-Naphthyl)ethylenediamine Dihydrochloride
2. Anhydrous Sodium Nitrite
3. Sulfanilamide
4. Nitrite and Nitrate-free distilled water
5. Concentrated Hydrochloric Acid
6. Chloroform
7. Sodium Acetate

EPA 354.1 reports nitrites as mg/L NO_2^- N (Nitrite - Nitrogen) over a calibration range of 0 – 10 mg/L in water, wastewater, and sludge. For this application, we used reagents and standards to report nitrites as ppm NO_2^- (Nitrite). Ready-made reagents and standards are available from numerous chemical suppliers and these were used where possible. As the concentration of nitrite in engine coolants exceeds 1000 ppm in a new sample a dilution factor will need to be applied for the analysis.

It was determined that a UV/Vis cuvette with a nominal pathlength of 1 mm should be used rather than the standard 10 mm cuvette used for the EPA method. Using a cuvette with a shorter pathlength allows us to analyse more concentrated samples and therefore reduce the total dilution factor applied to the results.

Method

To make the buffer colour change reagent, 0.25 g N-(1-Napthyl) ethylenediamine Dihydrochloride is added to 25 mL sulfanilamide reagent (1 % (w/v) sulfanilamide in 10 % HCl). This reagent is light sensitive and should be stored appropriately. The reagent was tested for stability and has a shelf life of up to two weeks.

To make the calibration standards a premade 1000 ppm nitrite standard was purchased (1.0 mL of standard solution is equivalent to 1.0 mg NO_2^-). The premade nitrite standard was diluted with nitrite and nitrate free distilled water to make a working standard of 100 ppm NO_2^-. This working standard was further diluted to make up the range indicated in Table 1.

Table 1: Calibration range for nitrite standards

Description	NO_2^- concentration (ppm)
Standard 1	0.25
Standard 2	0.50
Standard 3	1.00
Standard 4	5.00
Standard 5	10.00

For sample preparation 5 mL of nitrite and nitrate free distilled water was added to a 10 mL volumetric flask. To this volume of water 40 µL of sample of standard was added followed by 250 µL of the buffer colour change reagent. The flasks were then made up to the mark with distilled water and shaken to achieve a 250-fold dilution factor.

Standards and samples were allowed to sit for 30 minutes before analysis to allow the colour to develop and stabilize after the addition of the buffer colour reagent. A Wavelength Quant method on UVWinlab™ software was created using a wavelength of 540 nm. Standards and samples were measured in a UV/Vis cell with a nominal pathlength of 1 mm.

Results

The spectra of the nitrite standards as well as the resulting calibration curve are shown in Figures 2 and 3. The linear regression coefficient (R2) obtained from the calibration curve displayed in Figure 3 is 0.9996 indicating an excellent level of data correlation within the specified calibration range.
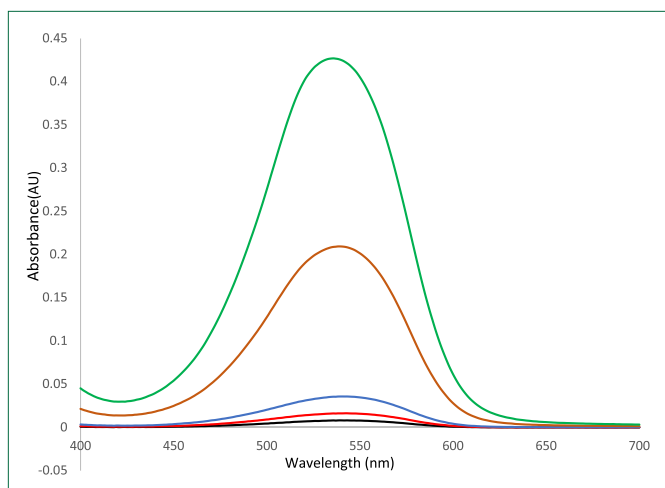
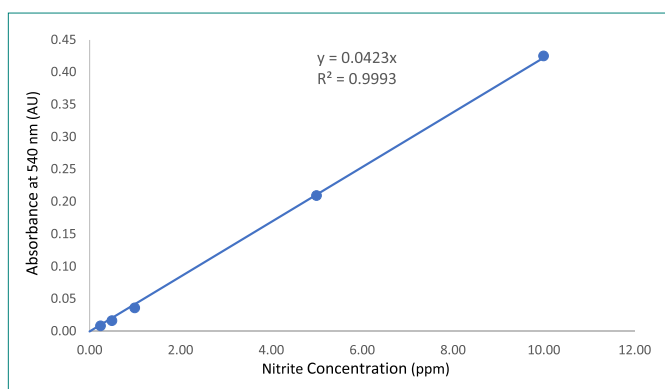Figure 2: Overlay of nitrite standard spectra (700 nm – 400 nm).

Figure 3: Nitrite calibration curve in ppm..

Table 2 below shows the values calculated for some different coolant samples using the UV/Vis calibration method. The values were compared to reference samples with a known nitrite value to determine the accuracy of the method. The 250-fold dilution factor was applied to the results to calculate the final adjusted amount. A 1000 ppm control sample was included in the middle of a sample set as well as at the end of the sample set to monitor the accuracy of the analysis. The sample values agreed well with the reference values after applying the 250-fold dilution factor.

Table 2: Sample result set

Sample	Adjusted Nitrite (ppm)	Reference Value (ppm)
Coolant 1	205	193
Coolant 2	1180	1225
Coolant 3	628	620
Coolant 4	1669	1677
Coolant 5	1404	1388
1000ppm std (QC)	1023	1000

Conclusion

The adaptation of EPA method 354.1 for the quantitation of nitrite levels in engine coolant was achieved with a high degree of accuracy. Ready-made reagents allow for a much easier preparation of samples and standards. Using less reagents also provides a better opportunity to automate the sample and standard preparation procedures to improve accuracy and efficiency in future work.

Coolant additives did not appear to have a significant effect on the accuracy of the results when compared to real world samples and as such the method is suitable for the coolant sample matrix. The LAMBDA 365+ and UV UVWinlab software provide a reliable solution for accurately determining nitrite levels in engine coolant.

References

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