

Validation of a FTIR Spectroscopy Method for Measuring and Monitoring Fuel Dilution in Lubricating Oils

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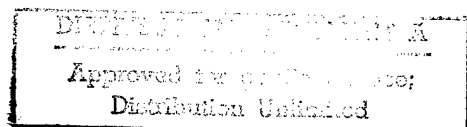
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Abstract: A FT-IR based fuel dilution analysis system was validated for long term reliability and precision. Frequency shift and spectral reproducibility tests showed that the instrument could operate for up to 10 months without maintenance. Changes in ambient temperature and humidity levels and the proximity to mechanical and acoustic noise generators did not affect the performance of the instrument. This was accomplished due to the methodic analytical procedures, data analysis and isolation devices developed and employed. The system was calibrated using actual used oils and fuel dilution values determined by the standard ASTM Gas Chromatography method. The calibration model developed with multivariate algorithms was able to predict fuel in SAE 30, 40, 50 and Mil-L-9000 engine oils down to 0.4% dilution.

Key Words: Condition monitoring; Failure prevention; FT-IR; Fuel Dilution; Infrared Spectroscopy; Oil Analysis; Used Lubricating Oil;

Introduction: Lubricant condition monitoring programs are widely accepted as preventive measures to premature machinery failures [1, 2]. Analytical testing of lubricating oils is an efficient cost-effective tool commonly used to track fluid degradation and assess operating conditions of mechanical equipment. The results when properly interpreted can be useful for the detection of mechanical faults in critical equipment before equipment failure. A successful implementation and application of such programs however require *a)* the acquisition of data that provides information pertaining to the performance status of the monitored lubricant, *b)* a reliable instrumentation, *c)* a robust and rapid analytical method to detect and identify the problems and provide the necessary corrections. Machinery failure prevention based on



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lubricant condition monitoring is applicable to industries such as paper mills, metal processing and petroleum refineries, which rely on high performance lubricants.

The objective of continuous condition monitoring programs is to perform fast and reliable analyses for on-time correction of problematic situations. This objective is often defeated by delayed analytical results of third party laboratories. One case that well illustrates this situation is the analysis of fuel dilution in diesel engine lubricating oils on board naval ships. The seepage of fuel into the lubricant reservoir can induce deleterious changes that inevitably affect the performance of the fluid and the engine. As part of its failure prevention program, tests for fuel dilution in used diesel oils represent a significant element of the Oil and Coolant Condition Analysis Program (OCCAP) of the Canadian Forces Navy. The currently accepted ASTM standard procedure for determining fuel dilution in lubricating oils is based on Gas Chromatography (GC) methods. GC test equipment requires daily calibrations, which can take from one to several hours depending on the number of standards used for a particular testing procedure. Furthermore, samples have to be shipped to land based GC laboratories thereby delaying the implementation of the necessary corrective measures.

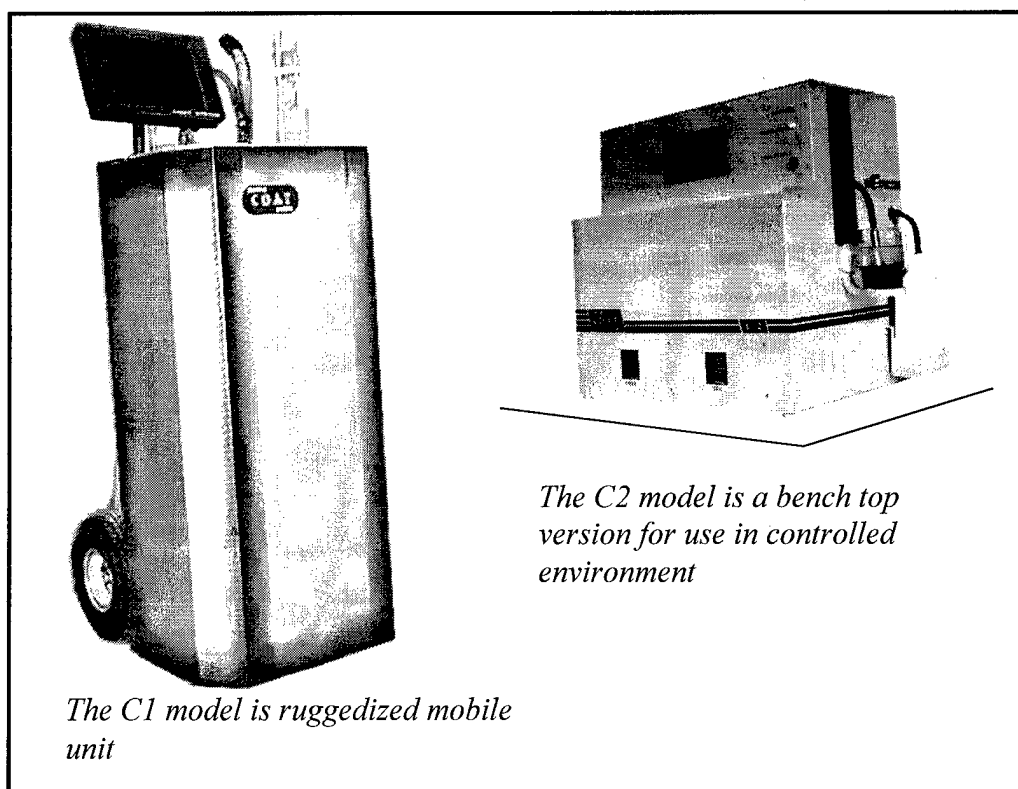


Figure 1: Two models of the COAT system used for fuel dilution analysis.

In a previous report [3], we have described the design and calibration of a Fourier Transform Infrared (FTIR) based analytical instrument for measuring fuel dilution in lubricating oil. The method is incorporated into a Continuous Oil Analysis and Treatment (COAT[®]) system (Fig.1) and calibrated against fuel dilution data obtained from an

external laboratory using the standard ASTM D3524 gas chromatography (GC) method. The FTIR method is rapid, accurate, and could be used on-board ship to provide immediate results. There are no hazardous chemical reagents, no sample burning, no lengthy sample preparation involved and a daily calibration is not required. Furthermore, advanced data analysis tools such as multivariate algorithms of partial least square (PLS), can be applied to the development of robust calibration models thereby increasing accuracy and reliability in the assessment of fuel dilution in lubricants. This paper describes the validation of the FTIR based system for fuel dilution analysis under the conditions described below.

Instrumentation and Procedures: The validation was carried out using the ruggedized mobile version of the COAT[®] system (Fig. 1). The system was operated for ten continuous months without maintenance. The testing proceeded as follows:

1. Evaluation of the instrument reliability in terms of frequency shift and spectral reproducibility. Testing environments were *a)* temperature controlled laboratory and 'plant floor' machinery control room with low acoustic noise, mechanical vibration, and humidity levels; *b)* 'plant floor' exposed to temperature and humidity level changes, high acoustic noise, and significant mechanical vibration level.
2. Evaluation of the calibration for long term stability and method consistency.
3. Evaluation of the performance of the FTIR based fuel dilution method by participating in a Round-Robin test setup for the GC method (ASTM D3524). The FTIR results are compared to GC data from approximately nine different commercial and governmental GC laboratories. Unknown samples were predicted using the calibration and system parameters established 10 months earlier. A new calibration was also built and the predictions were compared to the existing calibration results.

Results and Discussion: A formulated polyalphaolefin (PAO) based synthetic oil was used as reference for the evaluation of the COAT[®] system and the calibration method. The reference oil spectra (Fig.2) provided information on pathlength change, cross-contamination, cell filling and presence of contaminants in the lines or on the cell crystal surfaces. The absorbance band around 892 cm⁻¹ was mainly used for frequency shift and spectral reproducibility tests.

1. System Validation: Instrument reliability tests conducted in laboratory and machinery control room with stable temperature and humidity levels showed the system was not affected by "normal" operating conditions. Figure 3 represents the monitoring of absorbance bands at 892 cm⁻¹ from the spectra of the PAO reference oil. The error on the frequency after 40 weeks of operation is ± 0.01 cm⁻¹. The frequency stability of the COAT[®] system is made possible due to corner cube mirror technology that allows permanent alignment of the infrared interferometer. This feature is desirable especially for instruments designed to be mobile because a frequency shift of the order of 0.1 cm⁻¹ can induce up to 0.2 % error. Spectral reproducibility tests were conducted by evaluating the residual spectra of reference oils and comparing the peak height at 892 cm⁻¹. After 40 weeks of operation, spectral error was in the order of 3 milli absorbance unit

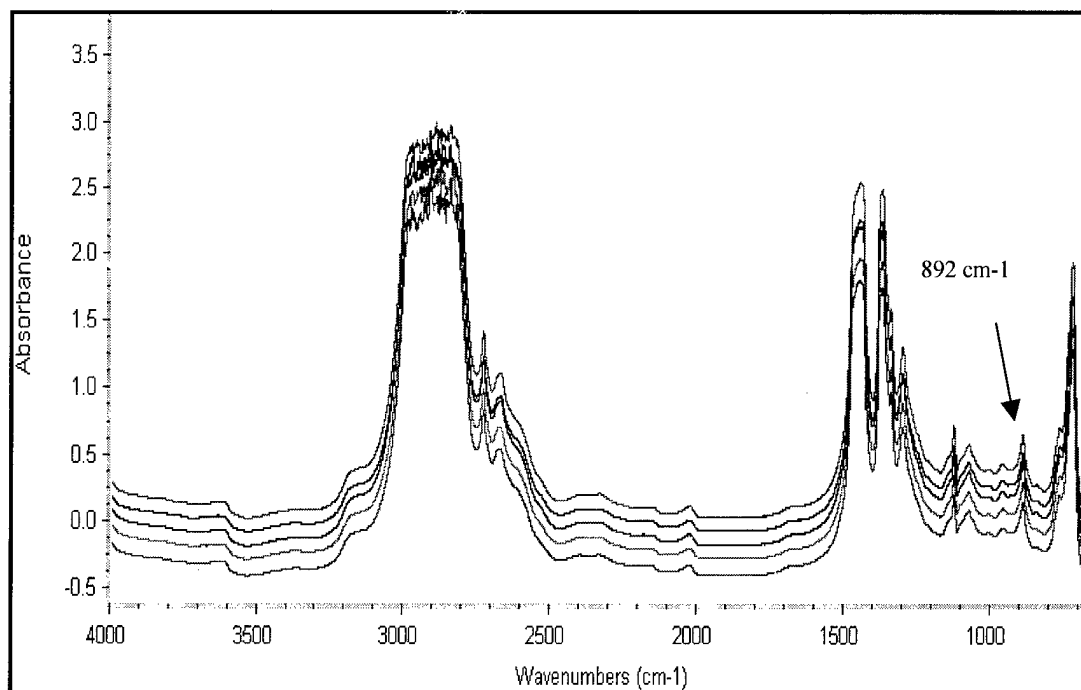


Figure 2: Infrared spectra of reference synthetic oil

and there was no sign of increase. These results demonstrate the long-term reliability and stability of the COAT[®] system, an important requirement for a maintenance free analytical instrument.

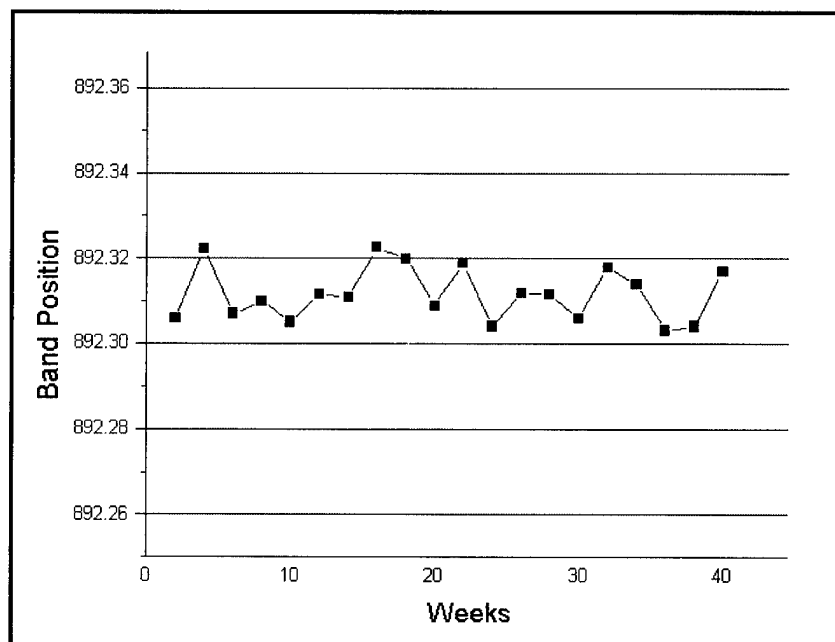


Figure 3: Frequency reproducibility of the COAT[®] system

The performance of the system was however affected when operated on the plant floor where vibration and noise levels exceeded 20 Hz and 3k Hz, respectively. The situation was corrected after mechanical dampening, insulation and noise barriers were installed. Figure 4 shows the results obtained before and after noise and vibration control devices were installed. Scan rejections due to bad data was eliminated and the precision on the measurements was greatly increased. The additive level was monitored with accuracy ($\pm 0.02\%$) within the upper and lower limits required for this particular application. The varying humidity levels on the plant floor were compensated for by including an algorithm in the sampling procedure to automatically record a background spectrum before every sample. This is made possible due to the proprietary movable transmission flow-through cell sampling accessory of the COAT[®] system [3].

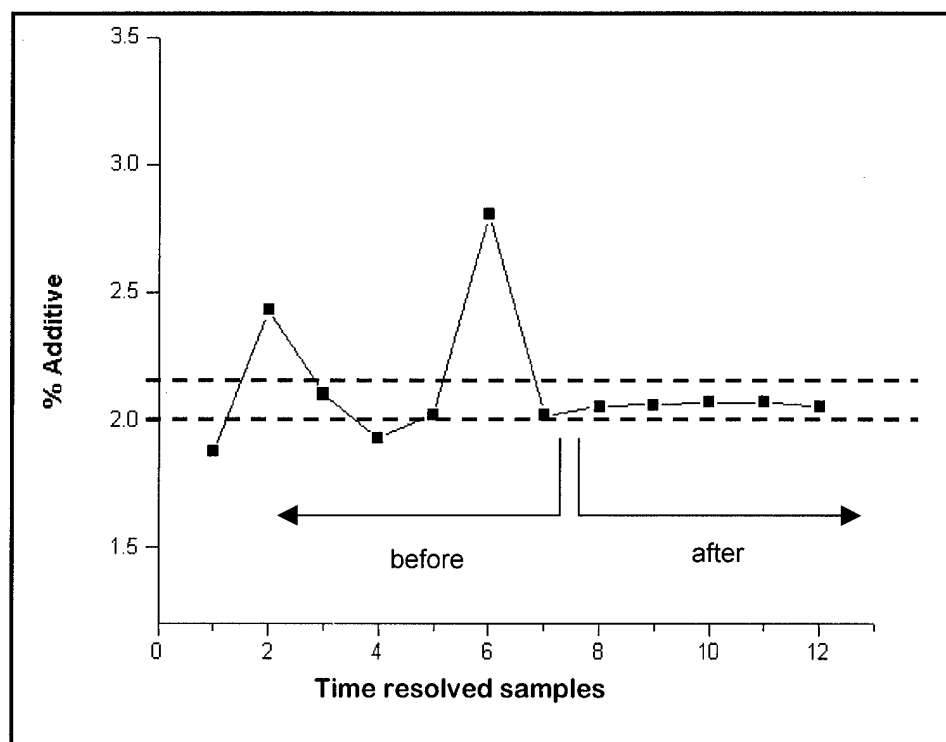


Figure 4: Monitoring of additive levels before and after system isolation.

2. Validation of Infrared Fuel Dilution Method: The quantitative calibration method for fuel dilution by infrared is based on multivariate statistical analysis. The application of partial least-squares (PLS) modeling to both mid and near infrared data analysis is well documented [4, 5]. A number of steps were considered for the development of a robust calibration since the model is developed against GC fuel dilution data, a method with considerable inherent sources of errors. Furthermore, for reasons we have previously reported [3], the calibration standards are all actual diesel fuel contaminated used oils obtained from the Canadian Forces Navy. Although full spectrum features can be used when working with PLS, due to the nature of the standards and the reference data, we have identified a unique spectral region that best describes the fuel dilution status of all

standards [3]. In the mid-infrared, diesel fuel appears around 810 cm^{-1} , however the exact position of the band is affected by the lubricant source, type (synthetic or petroleum based etc...) and lubricant. Figure 5 shows the scaled spectra of 5 lubricants with the same fuel dilution value of 2.5%. To minimize the model

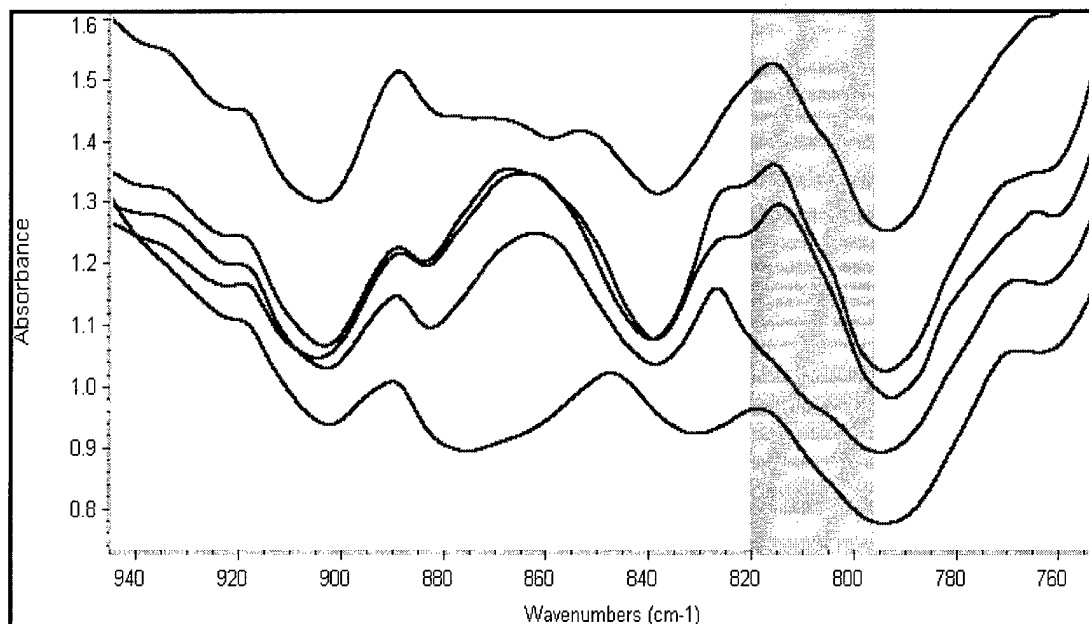


Figure 5: Grayed area illustrates different peak shapes around 810 cm^{-1} band. All 5 spectra have a fuel dilution value of 2.5%.

sensitivity to lubricant and fuel sources, the calibration standards are balanced so that the source and type information becomes redundant and is therefore neglected by PLS. This is important for naval applications where ships in deployment may acquire lubricants and diesel fuels from various sources. Using a narrow spectral region with base point anchors minimized non-linearity caused by “normal” instrument drift and the presence of contaminants such as soot in the standards. With this approach, the automatic baseline correction feature of the software becomes more reliable. Figure 6 shows the calibration curve obtained for diesel fuel dilution using 7 loading factors decided upon after a cross-validation evaluation ($R^2 = 0.97$ and $\text{STD} = 0.25$). It is worth mentioning that the accuracy of this calibration is dependent on the accuracy of the associated reference GC method. The performance of the FT-IR fuel dilution method during the Round-Robin evaluation of the GC method (ASTM D3524) has proved the method’s capability to quantitate fuel dilution in both used and new oil. As expected the calibration model developed with fuel contaminated used oils could not predict the fuel content of new oils and vis versa. The new and used oil samples were predicted using the appropriate calibrations. Table 1 shows the prediction results and statistics for new oils. Five new oil samples were spiked with fuel and their predictions compared to the mean triplicates of non-spiked samples. The results show calibration consistency and accuracy. The overall prediction error for the non-spiked samples was 0.05 % while error between the calculated and the predicted spiked samples was 0.08% fuel dilution.

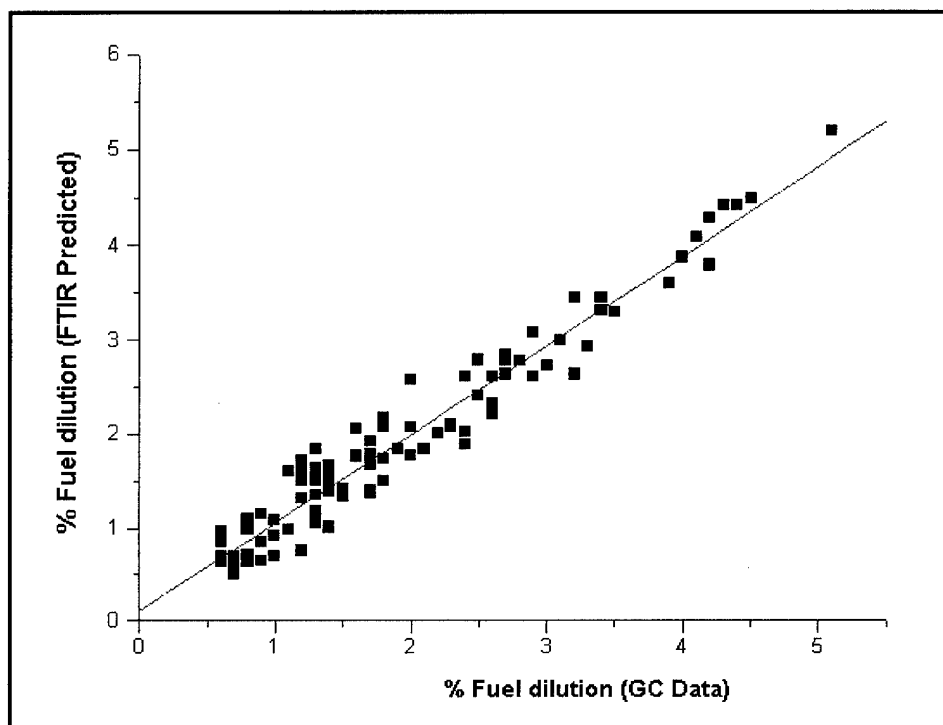


Figure 6: Calibration curve showing the correlation between the FT-IR predicted fuel values and the reference data

Table 1: Prediction of fuel dilution in new oil samples

Sample code	% Fuel ¹	STD	Spiked Samples		
			Prediction	Calculated	STD ²
NO7	1.13	0.04	3.68	3.89	0.11
NO8	3.18	0.03	5.43	5.71	0.14
NO11	1.79	0.13	4.38	4.50	0.06
NOS1	0.99	0.01	3.31	3.44	0.06
NOS2	2.02	0.04	4.56	4.59	0.02

1. % Fuel refers to the mean of triplicate analyses

2. STD² is the standard deviation from the mean of predicted and calculated fuel values

Similar results were obtained for the prediction of used oil samples. The overall error on the prediction of non spiked used samples was 0.13% fuel value while the comparison between the predicted spiked samples and the calculated values shows an overall error of 0.25% fuel.

Table 2: Prediction of fuel dilution in used oil samples

Sample code	% Fuel ¹	STD	Spiked Samples		
			Prediction	Calculated	STD ²
UO1	7.04	0.40	9.22	9.94	0.36
UO2	3.79	0.12	6.04	6.40	0.18
UO3	2.46	0.08	4.72	5.07	0.18
UO4	2.22	0.10	3.92	4.74	0.40
UO5	2.62	0.15	5.28	5.62	0.17
UO6	1.59	0.00	4.43	4.50	0.04
UO9	0.52	0.04	2.61	3.32	0.40

1. % Fuel refers to the mean of triplicate analyses

2. STD² is the standard deviation from the mean of predicted and calculated fuel values

Long term stability tests of the calibration model were conducted by recording and predicting 40 samples not included in the calibration after 6 and 10 months. The global prediction error of the model for both predictions remained around 0.4 % fuel. Prediction error due to calibration drift was significant towards the end of the testing period. To minimize this source of error, the calibration should be revised every 4 to 5 months by adding new standards in order to actuate the standards pool with respect to actual lubricants and fuel in use.

Conclusion: The validation of the COAT[®] system for fuel dilution analysis was successful. Fuel dilution is measured in 5 minutes or less without jeopardizing accuracy. Furthermore, there are no hazardous chemical reagents, no sample burning, no lengthy sample preparation involved and daily calibration is not required. Although the validation was conducted on land, the results described herein can be reproduced on board ship. A tremendous gain is envisaged analytically where the operator has a total control over the lubricant monitoring process. The historical data of the lubricant is available and corrective measures can be applied as new data that reflect its actual status is acquired. The stability of the system will provide accurate data for up to 5 months before any calibration correction is necessary.

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