

## Base number analysis by FTIR spectroscopy

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### Overview

A practical stoichiometric fourier-transform infrared (FTIR) Base Number (BN) method was developed in collaboration with Lubetech Pty Ltd., (Australia) to produce ASTM D4739-similar BN results. Thirty-six oils were analyzed by FTIR and ASTM D4739 and demonstrated to match up well, the overall SD for accuracy between methods being  $\sim\pm 1.0$  BN over a range of 0-10 BN, with the within-oil FTIR analytical reproducibility being  $\sim\pm 0.50$  BN. With samples prepared and reacted results are obtained in  $\sim 1$  min and the method is adaptable to standard FTIRs equipped with a conventional flow cell. As structured, service laboratories can achieve significant savings in time and labour while reducing the environmental and maintenance footprint associated with titration. This method is also a more reliable alternative to on-site filter-based IR instruments employing oil-dependent correlational chemometric calibrations as the simple Beer's Law calibration devised is universal, independent of oil type/condition and targets the acid-base reaction.

### Introduction

Potentiometric BN analysis is a determinative analytical procedure for in-service engine oils containing an acid neutralising base package. It is often carried out after FTIR condition monitoring/

screening (ASTM E2412) or the more specific measure of oxidative acidic products accumulating (ASTM D7418) or base related spectral signals being lost; all indicative of the oil being potentially compromised. The McGill IR group has been at the forefront of developing automated *quantitative* methods for the analysis of in-service oils by FTIR spectroscopy with a focus on automated methods (1), including Acid Number (AN) and BN. More recently, an effort has been undertaken with Australian collaborators to develop manual methods (2) focusing initially on AN as reported here previously (3). Lubetech Pty Ltd, an independent oil analysis and condition monitoring company based in Brisbane, Australia (4) has a vested interest in BN determinations. Like many oil analysis and condition monitoring laboratories optimising analytical efficiency while minimising its environmental footprint is high on its list of priorities. With an Agilent 5500t FTIR available in-house and having been apprised of the benefits derived from earlier AN methodology, a collaborative project was undertaken to prototype a manual stoichiometric FTIR BN method. The concept behind the manual FTIR AN and BN methods is to produce ASTM-similar results without investing in more sophisticated fully automated systems (5), but still achieve superior analytical rates and minimise reagents/solvent usage. This approach was also seen as an option to

facilitate on-site lubricant analysis where reliable BN information is critical. Here it is common to use ASTM D7889-approved IR in-service fluid property condition monitoring instruments that also generate non-ASTM approved AN/BN estimates. These estimates are not part of the ASTM method per se and are not considered adequately reliable for this purpose, but are being used as no practical, better options have been available to date.

### FTIR Spectroscopy and Calibration

The Agilent open-architecture Tumbler® accessory (nominal pathlength ~100 µm) for the 5500t FTIR Series is very convenient in terms of sample handling, requires minimal sample (~1.5 ml) to be prepared and only one or two drops for spectral analysis (Figure 1).



Figure 1: Agilent 5500t Tumbler open architecture sample handling accessory

Alternatively, any conventional FTIR spectrometer equipped with a ~100 µm transmission flow cell loaded by aspiration may also be used, albeit requiring more sample (~10 ml) to load and rinse out previous samples. What is unique about this BN method is that the calibration is based on a certified Conostan® 6 BN standard (6) which has all the characteristics of a lubricating oil and is simply diluted with mineral oil to produce a series of standards ranging from 0-6 BN (mg KOH/g) differing in 1.2 BN increments. The BN values are converted to apparent BN ( $BN_{App}$ ) expressed as mg KOH/ml in keeping with the volumetric nature of spectroscopy.

### Analytical Protocols

The BN sample analysis protocol is summarised in Figure 2, calibration following a similar route, trifluoroacetic acid (TFA) being used as the reagent for stoichiometric BN determination. Samples/standards (1.5 ml) are conveniently prepared and reacted in 2 ml self-capped plastic microfuge tubes.

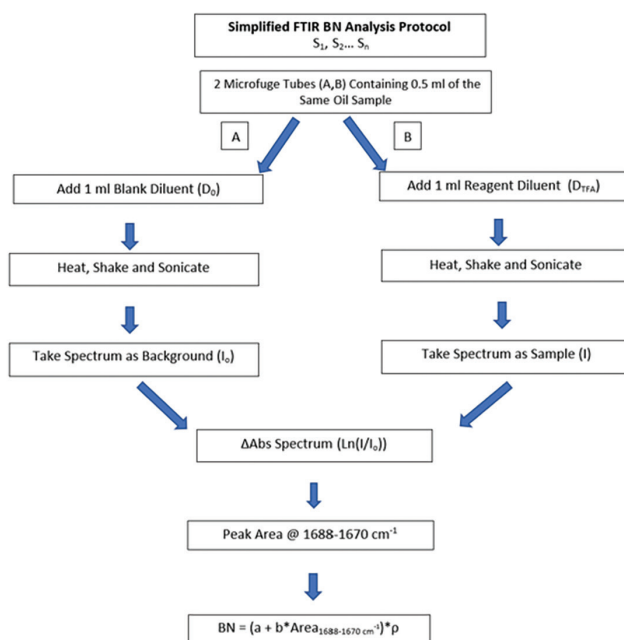


Figure 2: Simplified split-sample BN analytical protocol

If a standard transmission flow cell is used, 10 ml or more can be prepared in larger autosampler vials using the same oil:diluent ratios to load a new sample and wash out the previous one. In all cases sample preparation is based on split-sample analysis. For analysis two equivalent 0.5 ml aliquots are placed into two separate microfuge tubes, one treated with 1.0 ml of  $D_0$  and the other treated with 1 ml of  $D_{TFA}$ . The sample and diluent are not miscible but are thoroughly mixed and placed in a sonic bath to ensure the reaction/extraction is complete. Each split sample is scanned as a pair,  $D_0$  as the background spectrum ( $I_0$ ) followed by  $D_{TFA}$  as the sample spectrum ( $I$ ) to produce a differential absorbance spectrum ( $\Delta Abs = Ln(I_0/I)$ ) which ratios out the common spectral features of the oil matrix and emphasises the spectral changes associated with the acid-base reaction.

The calibration and analysis are based on the formation of the TFA salt (COO-) upon reacting with base, the signal change (area or peak height) being proportional to the  $BN_{App}$  of the sample.

### Calibration and Performance

#### Spectroscopy and Calibration

Figure 3 presents typical  $\Delta Abs$  calibration spectra obtained directly from the Agilent 5500t as well as typical calibration plot obtained from the Conostan® standard producing the following relation:

$$BN_{App} = 1.3163 * Area_{1688-1670} - 0.1886 \quad [1]$$

$$R^2 = 0.9958 \quad SD = \pm 0.151 \text{ BN}$$

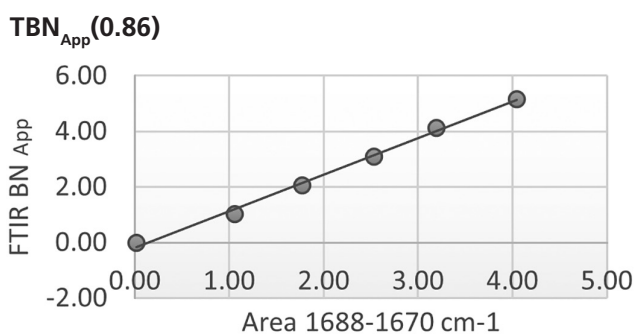
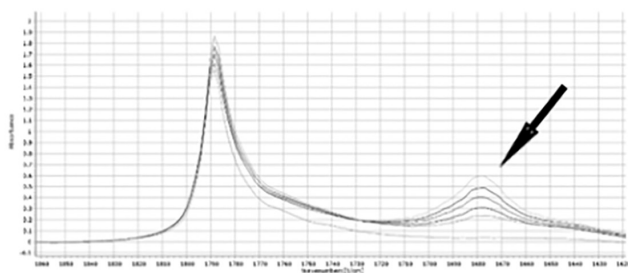


Figure 3: FTIR Calibration spectra (top) and resulting calibration plot (bottom)

Comparatively, the reproducibility of ASTM D4739 and FTIR BN for a new oil diluted with mineral oil were  $\pm 0.161 \text{ BN}$  and  $\pm 0.139 \text{ BN}$ , respectively. Thus, from a calibration standpoint, the performance of these two methods can be considered very similar for new oils. To some degree these results overstate the excellent performance of potentiometric titration when one

compares the results of the 6 BN standard and a new Delvac new oil, both serially diluted with mineral oil. Both have clear-cut inflection points relative to those obtained for used oils (Figure 4) which are clearly less determinative than the standard and a new oil. It is well recognised that oil titrations can be problematic when oils are degraded and can foul the electrodes (7), a problem not encountered with FTIR.

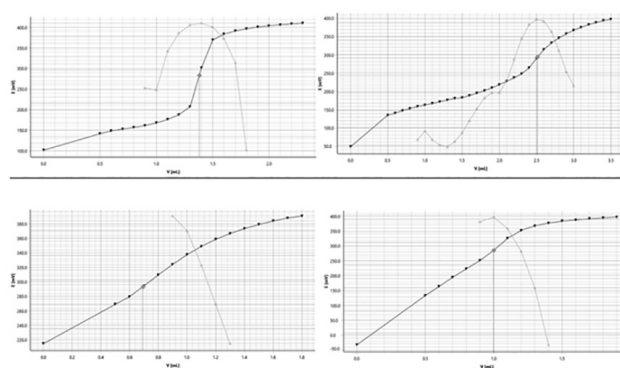


Figure 4: Potentiometric titration plots of (a) 6 BN standard, (b) new Delvac oil, (c) used Delvac oil and (d) used Pegasus oil

### Sample Analysis

Thirty-six lubricants, a combination of new and used oils were analysed for BN by both methods, the comparative responses plotted in in Figure 5.

#### D4739 TBN vs. FTIR BN

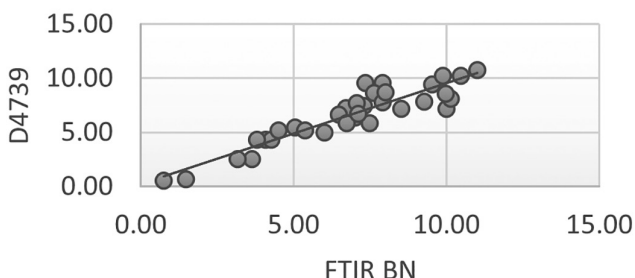


Figure 5: Relationship between ASTM D4739 titration vs. FTIR BN

The relationship between the two methods is:

$$ASTM \text{ D4739} = 0.9265 * FTIR \text{ BN} + 0.2678 \quad [4]$$

$$R^2 = 0.8493 \quad SD = \pm 1.005$$

This indicates that one can measure to within  $\sim\pm 1.0$  BN of what one would expect to determine by titration. Based on a more detailed comparative statistical assessment of the results and their stoichiometric basis, the FTIR BN determinations are very similar to those obtained by ASTM D4739 titration, hence the use of the term ASTM-similar.

### Method Performance/Benefits

One of the more noteworthy consequences of this study is the close concurrence of the magnitude of the FTIR BN results to those of D4739 given that a substantially weaker acid (TFA) is used instead of HCl. This is attributed to the fact that the TFA concentration used is  $\sim 6X$  greater than the 0.10 N HCl used in D4739. It is likely that with a minor adjustment in the TFA concentration, the FTIR method can be structured to match the ASTM method more directly. This may be useful in the longer run if proven correct and standardised but is eminently workable as is, converting from one measure to the other using linear regression. As a reference method, D4739 has no accuracy specifications per se, but the within-method SDDr of  $\pm 0.503$  BN obtained for the FTIR duplicates is very much in line with the reproducibility of  $\pm 0.530$  cited for a 10 BN certified standard (8) analysed by ASTM D4739.

One of the key benefits of the FTIR methodology is that it is a split-sample method, with both the calibration and analytical results being independent of oil-type as the common spectral elements of the oil are ratioed out and targets only the spectral changes specific to the acid-base reaction. The simple Beer's Law calibration devised is universal (e.g., independent of oil-type) and is readily assessed for performance (linearity and SD) and validated. This is significant because there are FTIRs and filter-based IRs that predict BN from neat oils using chemometrically-derived Library calibrations. These calibrations are based on spectral correlations of oils to their corresponding ASTM D4739 data and are strongly oil-type dependent

and do not target a specific spectral signal derived from an acid-base reaction. Such calibrations cannot be readily validated nor can instrument performance be assessed; users being reliant on the claims made by the manufacturers. As such, the results obtained can be problematic to rely on, especially if the oil is not represented, identified properly, or topped up with another oil-type. This sort of uncertainty is avoided in this BN approach, as one derives and evaluate one's own calibration rather than relying on the manufacturer's assurance. To date there have been few options for on-site BN determination, however, access to ASTM-similar data provides substantially more confidence that the information generated is valid and reliable for critical machine reliability decisions.

### Commercial Application

At Lubetech Pty Ltd, the manual FTIR BN method has replaced chemometrically derived BN values generated from the spectra of oils screened for in-service condition (ASTM E2412) but which was qualified in its accuracy. Interest in potentiometric titration, given its expense, has always been limited. The expense of this method versus its utility for most clients renders it commercially undesirable as most are looking for the cheapest, most reliable way to monitor the condition of their in-service oils. Additionally, modern oils have generally seen improvements in the BN stability and most clients are not seeing as dramatic drops in BN as they had been previously. Clients had been generally accepting of the fact that the previous FTIR TBN methods undertaken by most condition monitoring laboratories were not as accurate as D4739 but other results (viscosity, soot, wear results etc) were giving alternate indicators of the oil's condition. Being able to deliver ASTM quality data at a reasonable price has resulted in renewed interest in deterministic BN data. The independence of the stoichiometric method relative to oil type, formulation and condition is one of the distinct advantages over chemometric methods that are oil-type dependent. In the first instance, accuracy is obviously a primary factor, however, other

practical variables also play an important role in a method's success. Analytical time and the use of significant volumes of hazardous solvents/reagents are problematic for ASTM D4739, as is system maintenance.

The FTIR stoichiometric BN method is readily implemented at a substantially lower cost relative to potentiometric titration, in large part due to its generic nature, simplicity of sample preparation and straight-forward analytical protocol. In our laboratory the method has been implemented using generic software (SpectraGryph/Excel) to process the spectra collected and predict BN.

There is nothing to prevent FTIR manufacturers from packaging a turnkey version of the method for their own systems. Lubetech has been monitoring/tracking a wide range of client oils for some time, with BNs trending down with use/time, validating its diagnostic utility. Tracking oils in this manner is a cost-effective direct measure of oil degradation, with a significant number of clients now making stoichiometric FTIR BN a staple analysis. Thus the addition of this method to our analytical repertoire has not only been cost-efficient and an environmental plus, but has also provided users with value-added diagnostic information at a reasonable cost. Previous BN methods have been almost entirely replaced with the new method for clients at no further cost with far more accurate and environmentally-responsible results.

## Conclusion

The FTIR BN method devised for the Agilent 5500t equipped with the TumbIR handling accessory provides for rapid and accurate determination of ASTM D4739 BN-similar results.

As structured the method can readily be adapted to conventional FTIRs equipped with a demountable flow cell, requiring only somewhat more sample to

load and rinse. In both cases, sample preparation is straight-forward, requires minimal reagents/solvents and spectral analysis takes about one minute after the sample pairs have been prepared. In contrast, the titrimetric procedure takes between 30-45 minutes per sample and has a significant environmental/maintenance footprint. As a result of this collaborative development project, Lubetech Pty. Ltd. has implemented and provides FTIR BN as a cost effective, optional analysis.

A substantive data base is being built up to further refine the method as outlined here. As noted, the method may also serve for on-site use where quality BN data is required for critical machinery monitoring applications for which the Agilent 5500t is well suited, the analytical protocol simple enough to carry out in an on-site environment. Anyone interested in more detail can contact the authors directly or consult the pending issue of Lubrication Science (9).

Additional conceptual information is available in a comprehensive review related to the evolution of quantitative FTIR spectroscopy of lubricants, recently published in Tribology OnLine (10).

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