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# Comparison of lubricant oil antioxidant analysis by fluorescence spectroscopy and linear sweep voltammetry



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## ARTICLE INFO

### Article history:

Received 28 May 2015

Received in revised form

7 August 2015

Accepted 12 August 2015

Available online 21 August 2015

### Keywords:

Remaining useful life evaluation routine (RULER)

Excitation emission matrix (EEM) spectroscopy

Parallel factor (PARAFAC) analysis

Linear sweep voltammetry

## ABSTRACT

Synthetic lubricant oils based on a polyol ester base stock and containing amine-based antioxidants are characterised by fluorescence excitation–emission–matrix (EEM) spectroscopy. The main spectral features are attributed to antioxidants and are quantified using Parallel Factor (PARAFAC) analysis. The resulting PARAFAC component scores are compared to the relative antioxidant concentrations that were independently obtained with linear sweep voltammetry (LSV). An excellent correlation between the total intensity of the fluorescence signatures and the integrated LSV signal indicates that fluorescence EEM has a potential in the real-time – online or at-line – measurements of antioxidant concentrations. A modified fibre probe is presented that allows such measurements in strongly absorbing samples. The fibre probe contains a bevelled window to reduce the effects of fluorescence reabsorption and other “inner filter” effects.

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## 1. Introduction

Practically all rotary engines rely on lubricants to reduce friction between engine parts, as well as to help cool the engine and remove debris. Lubricants are typically changed after a predetermined service interval and not when the lubricant's quality starts to degrade. Even if the shutdown or servicing of the engine is expensive and/or dangerous, the maintenance periods are established based exclusively on the anticipated remaining useful lifetime of the lubricant in the engine. These service intervals are set such that the lubricant is changed “too early”, i.e. when it still has considerable remaining life; if the service interval is set too long, irreversible engine damage or even catastrophic failure may occur. Clearly, an on-line sensor for lubricant quality may help with protecting the engine, while also reducing the operating costs due to more realistic lubricant change intervals.

Several studies implied that antioxidants can be used as indicators of a lubricant's quality, meaning that the lubricant remains functional as long as the antioxidant concentration remains within a safe margin of the original concentration [1–5]. While a high antioxidant concentration is clearly not the only requirement for lubricant quality, a rapid decrease in this

concentration is assumed to be a good indicator of lubricant degradation. By quantitatively monitoring the concentration of the antioxidant additives and their chemical transformations with time one should therefore be able to estimate the lubricant's remaining useful life. This needs to yet be fully proved, and a chemical model of the lubricant degradation must be built.

Of course, in addition to the antioxidant stability, other factors affect the lubricant's performance, such as contamination with engine debris, water, coolants, and fuel [6]. As the oil ages the amount of contaminants increases and some of these contaminants may further accelerate oil degradation and additive depletion. A comprehensive chemical model must take at least some of these factors into account and, in turn, lead to a mechanical model linking the chemical degradation processes to the mechanical properties of a lubricant, for example its viscosity. However, this falls beyond the framework of this paper, which is concerned with comparing two very different methods of measuring concentrations of antioxidants. Obviously, the chemical model must be independent of the measurement method used.

Conventional, off-line, methods that monitor lubricant quality rely on the detection of degradation products. Volatile acids are recorded as the total acid number (TAN), or through the Rancimat method [7], whereas the formation of carboxyl and hydroxyl groups is recorded through their infrared spectroscopic signatures giving so-called “break-down numbers” [6,8–11]. Methods that detect degradation products are prone to underestimating the remaining useful life, since it is easy to contaminate functioning

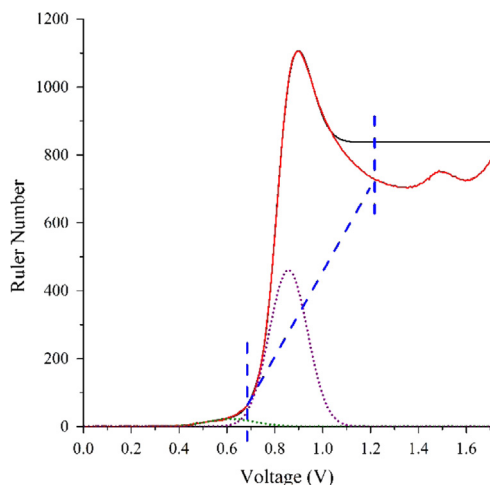
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lubricant with decomposition products. It is, for example, likely that fresh lubricant becomes contaminated with degradation products when the engine is not rinsed of decomposed lubricant at the service interval. Also these methods are far from being real-time or field-deployable.

Fluorescence Excitation–Emission–Matrix (EEM) spectroscopy has the potential of being field deployable and can be fibre-coupled to form an online sensor. Fluorescence EEM is a powerful tool that has been used to analyse and classify a multitude of liquid samples. Applications range from the detection of dissolved organic matter in water [12], classification of culinary liquids [13,14], drug testing [15], and characterisation of industrial liquids in marine environments [16]. It has been shown recently that antioxidant concentrations in lubricants can also be measured using fluorescence EEM spectroscopy [1]. By processing the EEM spectroscopic results with a multivariate analysis method, our group correlated the fluorescence matrix components with the presence of three different antioxidants. While two of these have been reliably identified as phenyl- $\alpha$ -naphthylamine (PAN) and its dimer (PAN<sub>2</sub>), the third could not be uniquely categorised, as it could be either a higher oligomer of PAN or a different fluorescing antioxidant. By oxidising jet turbine oil at three different temperatures, it was possible to derive a simple kinetic model that approximated well the three antioxidant concentrations over three orders of magnitude in time. Using the Rancimat measurements, it was established that the depletion of the total antioxidant concentration correlated with formation of the volatile acids as the degradation by-products.

The total antioxidant concentrations can also be measured electrochemically using a linear sweep voltammetry (LSV) technique, in the so-called RULER™ (Remaining Useful Lifetime Evaluation Routine) [2,17–21]. In this paper, the two techniques for measuring the antioxidant depletion in lubricating oils are experimentally compared. These are LSV, and fluorescence EEM spectroscopy. Both techniques are demonstrated to be nearly identically capable of determining the total antioxidant concentration, but EEM has two advantages. First, it provides information on the chemical identity of the lubricants and second, without the need for sample preparation, it is amenable for on-line measurements using a custom-designed fibre probe.



**Fig. 1.** Voltammogram of the fresh turbine oil sample shown as a solid red line. The solid black line represents the fit to the data using Eq. 3 whereas the green and purple dotted lines represent the two Gaussian functions in Eq. (1). Although at higher voltages Eq. (1) is no longer adequate, it does provide a good representation for the amine-based antioxidant peak at 900 mV. The RULER method of determining the antioxidant concentration is to integrate the area above and between the blue dashed lines [17]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## 2. Experimental

### 2.1. Sample preparation

Jet turbine oil, (NYCO, synthetic aviation turbine oil, Turbonyoil 600, ML-PRF-23699/F) graciously supplied by NYCO, was used for oil degradation experiments. The polyol ester-based oil was artificially aged by heating to three temperatures (195 °C, 180 °C, and 165 °C) that are typical for a jet turbine engine [22,23], while air was bubbled through the oil. The procedure was the same as used previously [1], but here a condenser was added to prevent evaporation loss of lubricant and lubricant degradation products as described by Besser et al. [24]. In addition to the artificially aged lubricant, field samples from the main rotor engine (BCA Engine Turbo Shaft T58-GE) of a Sikorsky Sea King helicopter were obtained at the engine's oil change intervals. All samples were analysed using both fluorescence EEM spectroscopy and linear sweep voltammetry.

### 2.2. Linear sweep voltammetry

The Remaining Useful Lifetime Evaluation Routine (RULER) is an ASTM standard for measuring the remaining antioxidant concentration in oils. RULER is a LSV method that relies on the difference of the signal from the sample to that obtained from fresh reference oil – similar to fluorescence EEM.

The LSV experiments were carried out using a commercial device (RULER, CE520, Fluitec). As jet turbine oil is being evaluated, the RULER “red” solution (Fluitec) was used. According to the supplier the “red” solution comprises of 5 ml of acetone, an electrolyte (lithium perchlorate), in addition to coarse and fine sand [17–20]. 100  $\mu$ L aliquots of turbine oil were added to each “red” solution vial. The vials were shaken so the antioxidants in the oil were extracted into the acetone electrolyte phase and the remaining base stock oil was agglomerated by the sand. The sand/oil suspension was then allowed to settle to the bottom to not interfere with the measurement. The instrument was calibrated using the neat “red” solution.

The probe consisted of a 3-electrode system containing two platinum working and auxiliary electrodes and a glassy carbon reference electrode. The potential across the electrodes was increased linearly at a rate of 100 mV/s and the resulting current was converted to a voltage by the voltammetric analyser, using a gain ratio of 1 V/20  $\mu$ A. The data was acquired through an analogue or digital recording device (0–1 V full scale) and scaled to a “RULER number”. Fig. 1 shows a typical LS voltammogram. The antioxidant N-phenyl-naphthalen-1-amine (phenyl- $\alpha$ -naphthylamine, PAN) present in the neat oil was oxidised resulting in a peak in the voltammogram at about 900 mV that was used to quantify the antioxidant concentration. Other amine-based antioxidants are also expected to contribute to the peak at 900 mV, whereas phenol-based antioxidants are expected to appear at around 1.5 V.

The LSV data can be fit to a combination of a step function and two Gaussian functions as shown in the following equation:

$$f(x) = a \exp(-\exp(-k(x-x_a))) + b \exp\left(-\frac{(x-x_b)^2}{w_b}\right) + c \exp\left(-\frac{(x-x_c)^2}{w_c}\right) \quad (1)$$

where  $a$ ,  $b$ ,  $c$ ,  $x_a$ ,  $x_b$ ,  $x_c$ ,  $k$ ,  $w_b$ , and  $w_c$  are fitting parameters (Fig. 1). To obtain the amine-based antioxidant concentrations, the larger Gaussian function was integrated. This integral,  $c\sqrt{w_c\pi}$ , was compared to that of the fresh sample at  $t=0$  min. The fit was found to be amenable to automation and slightly more robust compared to the manufacturer-recommended RULER method, which involves manually setting integration limits at each side of the main feature and thereby defining a sloping baseline before calculating the integral (Fig. 1).

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