HOT ARTICLE
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Fluorescence excitation–emission matrix (EEM) spectroscopy and cavity ring-down (CRD) absorption spectroscopy of oil-contaminated jet fuel using fiber-optic probes†

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Received 17th January 2012, Accepted 18th March 2012
DOI: 10.1039/c2an35091b

Excitation emission matrix (EEM) and cavity ring-down (CRD) spectral signatures have been used to detect and quantitatively assess contamination of jet fuels with aero-turbine lubricating oil. The EEM spectrometer has been fiber-coupled to permit in situ measurements of jet turbine oil contamination of jet fuel. Parallel Factor (PARAFAC) analysis as well as Principal Component Analysis and Regression (PCA/PCR) were used to quantify oil contamination in a range from the limit of detection (10 ppm) to 1000 ppm. Fiber-loop cavity ring-down spectroscopy using a pulsed 355 nm laser was used to quantify the oil contamination in the range of 400 ppm to 100 000 ppm. Both methods in combination therefore permit the detection of oil contamination with a linear dynamic range of about 10 000.

Introduction

On its journey from the refinery to an airplane’s fuel tank, aviation jet fuel will spend time in storage and may be transferred many times. Each time a transfer occurs, there is a potential for fuel contamination. As a result of contamination, engine and fuel system parts can be damaged leading to potentially high costs and lost time. More importantly, fuel contamination remains to be a notable factor in accidents caused by engine fuel starvation.1 Contaminations also have a direct impact on the service life and performance of jet engines. Since contaminants may be corrosive and abrasive to the fuel system and engine components, they may cause inefficiencies or failures in filters and separators by plugging them. It is not possible to completely prevent fuel contamination during transport and storage, and on-site monitoring of jet fuel contamination is, consequently, a high priority for aviation safety.2,3

With this current suite of projects we design fiber-coupled fuel and lubricant oil monitoring systems that encompass classes of contaminants which presently can only be quantified off-line. In the current study we focus on online monitoring of the contamination of fuel with lubricants. Other meaningful indicators of lubricant and fuel quality are contamination of both fuel and lubricants with water and with glycol, as well as the presence of oxidation products in lubricants due to aging.

Optical techniques, such as absorption and fluorescence spectroscopy, are well-suited for rapid data collection with minimal sample pre-treatment. Fluorescence spectroscopy, in particular, has demonstrated high sensitivity with respect to the aromatic content of complex hydrocarbon mixtures and allows for fast data acquisition. Accurate data treatment can be carried out on fluorescence spectroscopic data at relatively low costs. Since excitation or emission spectra by themselves do not contain sufficient information to differentiate hydrocarbon mixtures of similar composition, we propose to correlate UV/Vis (and eventually IR-) absorption with UV-induced fluorescence. In this report we demonstrate that fiber-based Cavity-Ring-Down (CRD) absorption spectroscopy, and fluorescence Excitation–Emission Matrix (EEM) spectroscopy can provide the information that is needed to detect and quantify contamination and degradation products in machinery fluids.

Fiber-coupled EEM spectroscopy

Excitation–Emission Matrix (EEM) spectroscopy has long been recognized as a powerful method for complex mixture analysis. EEM spectra are typically generated by scanning the complete emission spectrum for each excitation wavelength.4 The emission intensity as a function of both excitation and emission wave-lengths can be presented by a three-dimensional response feature, which may be visualized as a topographical map.5

The representation of the whole three-dimensional intensity matrix realises the full potential of the fluorescence technique. Cross-sections of this excitation/emission matrix at fixed excitation wavelengths and at fixed emission wavelengths are, respectively, standard single line emission and excitation spectra. The advantage of the EEM technique is its ability to deconstruct the...
broad, overlapped bands characteristic for a single-line excited fluorescence spectrum into recognizable patterns, which can then be used as indicators for sample composition.

Excitation–emission matrix spectroscopy has been widely used as a tracking tool in different areas of research such as water quality control,5,7 sea water contamination with oil,8,9 medical studies,10 characterization of alcoholic drinks,11,12 classification of edible oils13–16 and discrimination of fuel.17,18 The EEM data were subjected to different multivariate data analysis methods to identify and quantify the constituents.

Fiber-optic probes have been developed as accessories for some commercial EEM spectrometers. We have constructed a probe using a bifurcated fiber bundle to collinearly excite and collect the fluorescence of a liquid sample. By designing a custom fiber bundle we were able to reduce the cost compared to the commercially available accessory and we also had better control over the chemical and thermal resistance as well as the light throughput. The main advantage of collinear but counter-propagating excitation and detection is the compensation for fluorescence reabsorption. A hydrocarbon sample can be excited only over a distance that is related to the absorption length, /εC, and the red-shifted fluorescence is collected only after having passed some distance through the sample. In our arrangement the absorption pathlengths for the excitation and emission are the same. A strongly absorbing sample emits fluorescence close to the fiber probe, giving the fluorescence emission a small probability for reabsorption. A weakly absorbing sample, on the other hand, permits excitation of a larger sample volume, and the resulting fluorescence is similarly generated by a larger volume. As a consequence, a fiber optic probe permits EEM spectroscopy over a larger range of intensities compared to the more commonly used fluorescence collection at right angles.

Principles of multi-way data analysis

Fluorescence EEM spectra can be analysed using a second-order multivariate algorithm such as parallel factor analysis (PARAFAC).19,20 Other multivariate techniques have also been applied for the determination and quantification of individual analytes within mixtures. For example principal component analysis and regression (PCA/PCR) is a common multivariate calibration technique due to its ability to deal even with highly collinear data by reducing the dimensionality of the original dataset.21,22 Both data analysis methods can be applied to broadband, overlapping spectra, and even when components contribute to the EEM spectra that were not considered in the calibration step.19,20,22 PARAFAC analysis and PCA/PCR will be discussed below and applied to our EEM datasets.

Fluorescence EEMs collected for several samples give rise to “three-way data”, i.e. the data may be arranged in a cube, which has the dimensions of excitation wavelength, emission wavelength and sample number. With three-dimensional data structures the analyte signal can be separated mathematically from the background signal. The PARAFAC model can then be used to decompose the collected excitation–emission matrices into the spectral profiles of the pure component species. For a pure compound an EEM is a bilinear matrix which can be described as a scaled outer product of two column vectors, i.e. the excitation profile of the compound at any one emission wavelength, and the emission profile of the compound at a single excitation wavelength.9,23,24

The PARAFAC model is a generalization of principle component analysis (PCA) to an n-way dataset X. An appropriate dataset consists of a number of spectra that may be from either mixtures or pure compounds and any spectra from unknown samples that may even contain unknown interferences. In the present case of a three-way data cube, X (of dimension I × J × K) is decomposed into components. Each component consists of three loading vectors. When xijk (fluorescence intensity) denotes the element in position i, j, k in the data cube X, the structural model of PARAFAC can be expressed as

\[ x_{ijk} = \sum_{f=1}^{F} a_{if} b_{jf} c_{kf} + e_{ijk} \]  

here F corresponds to the number of components (“factors”) in the model. The emission profile of a factor can be the fluorescence of an analyte, the fluorescence of an interference, or part of the instrumental background (i.e. due to the Raman or Rayleigh scattering). In our case F is identical to the number of fluorophores. The elements of three loading vectors aif, bjf, ckf together with the residual error, eijk, determine the fluorescence intensity, xijk. Here, aif is the concentration of fluorophore f in the ith sample, bjf is the relative absorption of fluorophore f at wavelength λej, and ckf is the relative emission of this fluorophore, f, at wavelength λek. The indices stand for the sample, i = 1, …, I, the excitation wavelengths λej, j = 1, …, J and the emission wavelengths λek, k = 1, …, K.19,20

Choosing the appropriate number of factors/components is the first step for constructing a PARAFAC model. This decision can be made based on the calculation of core consistency and residual for each selected value of component numbers19,25 as will be illustrated below.

Principal component regression (PCR) has also been applied to our datasets. In PCR latent variables are extracted in the form of scores by principal component analysis (PCA). The PCA technique transforms the original data to a space of lower dimensionality and thereby compresses the data. PCA operates by successively finding components that have as high a variance as possible. After extracting the component, the remaining “projections” of the multidimensional dataset are in turn analysed to find the next principal component which describes the highest variance in the new space.

After the regression vector is determined, a method is needed to measure the predictive ability of the PCA/PCR model. Typically the original data is split into two parts, i.e. a calibration (training) dataset that is used to build the model and a prediction/validation dataset that is used to optimize and assess the predictive abilities of the model. The calibration and prediction set do not need to be the same size, and samples for the two groups should be picked randomly. In our analysis we compared for both sets the minimal number of components that is needed for a fit (“Scree-plot” see below), the uncertainties of the predicted concentrations, and the square of the correlation coefficient, R². When all these values are comparable within their respective uncertainties, the combined dataset may be used for the calibration of the system.
Fiber-loop cavity ring-down spectroscopy

As was shown previously, absorption spectroscopy in combination with fluorescence and scattering measurements permits sensitive determination of lubricant quality metrics, such as total acid number (TAN), phosphorus content, and the Joint Oil Analysis Program (JOAP) “anti-wear” index.26

Cavity ring-down (CRD) absorption spectroscopy (CRDS) is a sensitive absorption technique for quantitative measurements of analytes in gas or condensed samples. CRD spectroscopy obtains its sensitivity from enhancement of the optical loss measurement in a high finesse optical cavity, and can be performed with either pulsed or continuous wave light sources.27,28 In CRDS not the absolute amount of absorbed light is measured, but the temporal decay of the intensity in the optical cavity is recorded.

In a typical CRD setup light is coupled into an optical cavity, the light intensity is allowed to build up and then to decay. The lifetime of the photons trapped in the cavity is related to the optical loss, such as absorption and scattering. This lifetime, or ring-down time, is equal to the time in which the light intensity decreases to 1/e of its initial value. The ring-down time, \( \tau \), is independent of intensity fluctuations and detection efficiency and only depends on the total losses in the optical cavity.29 Eqn (2) expresses the ring-down time as a function of the round trip time of the cavity, \( nL/c_0 \), and the transmission per round trip, \( T_{rt} \):

\[
\tau = \frac{nL}{c_0(-\ln T_{rt})} = \frac{nL}{c_0\left(-\ln T_{\text{blank}} + \sum C_i \frac{\varepsilon_i d}{L}\right)}
\]

Here, \( T_{\text{blank}} \) is the transmission per round-trip for a blank sample, \( n \) is the refractive index of the cavity medium, \( L \) is the roundtrip length, \( d \) is the length of the path through the sample with concentration \( C \), and \( c_0 \) the vacuum speed of light. The absorption coefficients of the analytes, \( \varepsilon \), are given with respect to base \( e \). In the experiments described below, the optical cavity consists of a loop made from multimode optical fiber and the interaction length with the sample, \( d \), corresponds to the distance between the two fiber ends.30,31 In this case \(-\ln T_{\text{blank}} \approx -\ln T_{\text{gap}} + nL \), where \( T_{\text{gap}} \) is the transmission across the gap in the absence of analyte and \( \alpha \) is the absorption coefficient of the cavity medium.

Materials and methods

Fluorescence measurements

Fifty-two samples of JetA1 type fuel (Shell Corp.) mixed with jet turbine oil (NYCO, synthetic aviation turbine oil, MIL-PRF-23699 F Class STD) were included in this study. Samples were prepared at different concentration levels from 5 ppmv to 1000 ppmv. The prepared samples were distributed between a calibration and a prediction set.

Fluorescence measurements of all samples were completed with a spectrophotometer (Varian, Cary Eclipse). The fluorescence excitation and emission were delivered using a bifurcated optical fiber bundle, which contains 6 multimode fibers for irradiation and 13 fibers for fluorescence collection (core/cladding diameters: 400/440 \( \mu \)m, CeramOptec). The end face of the fiber probe containing all 19 fiber ends is immersed in the sample material (Fig. 1).

The spectrofluorometer contains a pulsed xenon lamp and a red-sensitive photomultiplier tube as grating-coupled light source and detector, respectively. For each sample the EEM spectrum was obtained in the emission wavelength range from 305 to 600 nm with a 1 nm increment, while the excitation wavelengths were stepped in the range of 300 to 363 nm in 3 nm increments. The bandwidth of both excitation and emission was 5 nm and PMT voltages and scan speed were set to 850 V and 21 nm s\(^{-1} \), respectively.

Fig. 1 Sketch of the bifurcated fiber bundle used for EEM experiments. Top row: (A) fiber end immersed in sample, light is guided into the sample through 6 fiber ends (purple) and is collected by 13 fiber ends (yellow). (B) Fiber bundle in front of the light source. (C) Fiber bundle in front of the detector. Each fiber has a 400 \( \mu \)m core and a 440 \( \mu \)m cladding and the diameter of the fiber bundle (shown in (D)) is about \( d = 2.2 \) mm.

Fig. 2 Schematic of the fiber-loop cavity ring-down setup. Light from the third harmonic of a Nd:YAG laser (A) is coupled into a 99 : 1 fiber-fiber coupler (B) and then circulates in the loop. With every roundtrip the pulse interacts with the liquid sample that is introduced into a microcross (C) using a capillary (D). Light scattered form the loop is detected with a photomultiplier tube (E).

Fiber-loop cavity ring-down measurements

Absorption measurements on 13 fuel samples with oil concentrations between 200 and 100 000 ppmv were performed using a fiber-loop CRD setup as shown in Fig. 2. The loop was formed from a multimode silica fiber (Fiber Optic Network Technology (C) using a capillary (D)). Light scattered form the loop is detected with a photomultiplier tube (E).
FONT, 440/400 μm) with a length of \( L = 11 \) m. A Nd:YAG laser at 355 nm (Spectra-Physics GCR-11, ~7 to 10 ns; power 20–50 mJ per pulse) and a photomultiplier tube (Hamamatsu R928) were used as light source and detector. To couple the light into the loop a fused fiber-fiber coupler (FONT) with a coupling ratio of 99 : 1 was used. The fiber-loop was closed using a micro-cross (Upchurch, P-729 PEEK cross) as an interface between the fiber optic cables and the capillary containing the liquid. The gap between the fiber ends \( (d = 200 \mu m) \) created a detection volume of 25 nL. The samples were delivered into the gap using a sample injector (Rheodyne 7725; injection volume: 20 μL). To detect the scattered light from the fiber a small part of fiber was uncoated and placed on top of the PMT detector.

**Results and discussion**

**EEM spectra and analysis**

Typical EEMs corresponding to pure fuel and to oil at a 1000 ppm concentration in fuel are shown in Fig. 3 together with emission and excitation spectra, which were extracted from these matrices by integration over the entire excitation and emission wavelength range. Neat fuel fluoresces in the range from about 340 and 355 nm, when it is excited between 330 nm and 335 nm. A weaker emission feature is observed between 380 and 420 nm following excitation at 340 to 380 nm (Fig. 3A). Neat oil shows two broad emission peaks centred at wavelengths of 410 nm and 550 nm (see ESI†). Fluorescence at 410 nm is caused by a tri-modal absorption spectrum with peaks at 250, 350 and 380 nm, whereas the fluorescence at longer wavelength is initiated by absorption at 410 nm. The EEM spectrum of oil diluted in fuel is much simpler and exhibits a dominant absorption feature at 340–355 nm and a broad fluorescence band centred at 400 nm (Fig. 3B). EEM spectra of oil and fuel therefore overlap to some extent. It is not possible to scale the fluorescence EEM spectrum of neat oil to low concentrations, since quenching effects and re-absorption of fluorescence make a linear extrapolation impossible.

Fig. 4 shows the EEM spectra of nine samples containing between 5 ppm, and 650 ppm, of jet turbine oil. It is apparent that even at the level of 10 ppm, the EEM spectra show an enhancement of the long wavelength feature, and that quantitative concentration measurements at the low ppm level should be possible. The intensity scales for the EEM spectra in Fig. 3(A) and (B) are identical and by inspection it is apparent that the EEM spectra may be understood as a linear combination of the two features corresponding to “oil” and “fuel”, i.e. wavelength shifts, self-absorption or quenching do not appear to be strong.

**Parallel factor (PARAFAC) analysis**

The excitation and emission profiles of the main components in the fuel/oil mixtures were extracted from 52 EEM spectra (20 spectra in the calibration set and 32 in the prediction set) by applying the PARAFAC analysis procedure. The PARAFAC model was implemented in Matlab ver 7.10.0 using the n-way toolbox provided by Andersson and Bro. The calculation of core consistency and residual indicated that a two-component model provides the best fit to our samples. The selection of the number of components and calculation of, both, the core consistency percentage and the residuals is done by the software and the decision was made by repeatedly applying the PARAFAC model using between 1 and 5 components. The stability of the model was tested using the validation dataset.

The PARAFAC model yields integrated emission and excitation spectra for both components. Comparison with the experimental integrated emission and excitation spectra for fuel (Fig. 3C) and 1000 ppm, oil in fuel (Fig. 3D) indicates that the two PARAFAC components can indeed be correlated to the fuel and oil constituents. While the excitation and emission spectra for oil show excellent agreement with the PARAFAC component 2, there are noticeable differences between the experimental spectra for fuel and those predicted by the model for component 1. In both, excitation and emission spectra of neat fuel, the long-wavelength features are not well reproduced. We suspect that the PARAFAC procedure attributes those features to component 2 (oil) which indeed shows maxima at these longer wavelengths. From this observation we expect that the model predicts a finite amount of component 2 even in pure fuel.

The scores of the two components were extracted separately for the calibration set and the prediction set and are shown in Fig. 5. The two scores are inversely correlated and show the expected negative slope. Scores for the calibration set and prediction set were also correlated to concentration (Fig. 6). The scores are scattered and not well described by a linear correlation to concentration, possibly due to fluctuations in the excitation and emission intensity, but also due to fluorescence reabsorption. On the other hand, the ratio of the scores, which is independent of intensity, shows a strong linear correlation to concentration \((R^2 = 0.95)\) and permits the construction of a linear calibration curve (Fig. 7A). Even the contribution of fluorescence reabsorption, which is already reduced by collecting fluorescence at 180 degrees, should not affect the ratio of scores as long as the fluorescence intensity of both components is attenuated by the same fraction.

Using the equations by Currie and Svehla\(^1\) we determine that a measured score ratio of 4 corresponds to a concentration (410 ppm,\() that is with 99% confidence larger than that of the neat fuel. This value is not the true detection limit, however, since it is assumed, that the uncertainty of the measured ratio is constant for all concentrations. This assumption of a constant error is incorrect as is shown by the reduced scatter of the measurements at low concentrations. Instead, the detection limit has to be determined by repeated measurements at low oil concentrations.

EEM measurements and PARAFAC analysis of 8 independently prepared samples at 10 ppm, and of 8 neat fuel samples demonstrate that even this low level of contamination may be distinguished from neat jet fuel and be quantified (Fig. 7B). The ratio of PARAFAC scores is 0.97(0.10) for the 10 ppm, samples and 0.69 (0.01) for neat fuel, where the values in brackets indicate one standard deviation. When setting the decision threshold at the 10 ppm, level the likelihood that an average of 8 measurements would result in a “false positive” measurement, is about one in one hundred.

From Fig. 7 it is apparent that a simple fiber-coupled EEM sensor has the potential to identify and quantify the
contamination of jet fuel with jet turbine oil at levels of 10 ppm\text{v} and higher.

**Principal component analysis and regression**

A related analysis model is presented by Principal Component Analysis (PCA) and Regression (PCR). Since the collected EEM data is arranged in a 3D-matrix, the first step consists of a process in which the data is reduced to a lower dimension. The unfolding process can be understood as the rearrangement of the 3D data cube as a product of mutually orthogonal 2D-data arrays. Here, the 3D-EEM spectra of all 20 calibration and 32 prediction samples were truncated, applying PCA, in a Matlab environment (ver. 7.10.0). Scree plots for calibration and prediction set indicate that 5 components are sufficient to describe the dataset (Fig. 8). The calculated regression vectors from the calibration set were applied to the unfolded EEM data of, both, the calibration and the prediction set to determine the concentration of oil in fuel. Fig. 9 represents the result of the PCA/PCR process and shows as a linear fit the concentration that the model predicts. The slope for the combined set is $0.998 \pm 0.02$ with a squared correlation coefficient of $R^2 = 0.978$. Again, using the confidence intervals of the linear fit in Fig. 9, the oil concentration that falls with 99\% certainty outside the confidence interval (272 ppm\text{v} for the combined set) is higher than the actual detection limit (10 ppm\text{v}) but consistent with the results of the PARAFAC analysis.

![Excitation–Emission Matrix Spectra](image)

**Fig. 3** Excitation–Emission Matrix Spectra of (A) neat jet fuel and (B) jet fuel containing 1000 ppm\text{v} of jet turbine oil. The colour bars on the right of each panel indicate the colours associated with low intensity (top) to high intensity (bottom). In the right panels the excitation spectra are obtained by integrating the experimental EEM spectra over all emission wavelengths (black dots) and the emission spectra by integrating over all excitation wavelengths (red dots). The respective solid lines are integrated spectra of component 1 (C) and component 2 (D) from the PARAFAC analysis. The dashed lines are absorption spectra recorded using a 1 cm cuvette.
Fig. 4 Selection of Excitation–Emission Matrix Spectra of jet fuel containing the indicated amount of jet turbine oil. In total 52 of these 2-dimensional spectra were recorded.

Fig. 5 PARAFAC scores of the component 1 (fuel) and component 2 (oil). The empty circles were extracted from the 20 samples in the calibration set and the solid points correspond to the 32 EEM spectra of the prediction set.

Fig. 6 PARAFAC scores of components “oil” (black) and “fuel” (red) as in Fig. 5, but as a function of concentration of oil in fuel. The calibration set is indicated with hollow circles, whereas the prediction set is shown as solid circles.
It appears that both analysis procedures are equally robust for the present dataset and give similar results. One may consider as an advantage of the PARAFAC analysis, that the “factors” or “components” have a physical meaning, i.e. the EEM spectra of the two components are closely related to those of the two constituents of our mixture. By comparison, the components in the PCA/PCR analysis are not related to the chemical components of the mixture.

**Fiber-loop cavity ring-down spectroscopy**

Samples at 13 different concentrations of jet turbine oil in jet fuel ranging from 200 ppm, to 100 000 ppm, (10%) were injected into the 25 nL gap between two ends in a multimode fiber loop. The decay of a 7 ns laser pulse at 355 nm is measured. This wavelength was chosen because fuel is largely transparent at this wavelength, whereas oil absorbs strongly (see Fig. 3). Fig. 10 presents the waveform obtained when the gap is filled with a blank solution containing neat fuel. The intensities were fit using a single exponential decay and Gaussian functions with constant widths for each peak. Since the first peak contains a considerable amount of scattered light, it is very strong and saturates the PMT. It was therefore excluded from the fitting.

**Fig. 7** (A) Calibration curve from all 52 samples analysed by the PARAFAC model. The vertical error bars were assumed to be constant and obtained as in ref. 33. The red line is the result of a linear least squares fit, whereas the blue lines are the limits of the 99% confidence interval. (B) PARAFAC scores obtained from the EEM spectra of neat fuel (red circles) and 10 ppm, oil in fuel (black circles). The ovals indicate the 99% confidence limit and their lack of overlap shows that the samples can be readily distinguished.

**Fig. 8** Scree plot showing the logarithm of the sum of squares of the residual, as a function of the number of factors for the calibration sample set (red) and the prediction set (black). It is apparent that 5 factors are sufficient to model the EEM spectra.

**Fig. 9** Result of the PCA/PCR analysis. 20 EEM spectra of the calibration set (red) and 32 EEM spectra of the prediction set were analysed using 5 factors and the regression obtained from the calibration set. The linear fits for both datasets agree well and fall on top of the linear least square fit for the combined EEM dataset (red line, $R^2 = 0.978$; slope 0.998 ± 0.02). A concentration of 272 ppm is with 99% confidence larger than that of a blank jet fuel sample (blue lines).
routine. Similar measurements have been completed for the 13 oil-contaminated fuel samples (Fig. 11). The samples were injected in 20 μL plugs and the detection limit (390 ppmv) was obtained by measuring the concentration at which the ring-down time signal differs by more than three standard deviations from the baseline. The repeatability of the measurements was tested using 10 identical injections of 2000 ppmv oil in fuel (not shown). At this concentration the ring-down time changed by 5.0 /C6 0.2 ns compared to that of neat fuel.

After rearranging eqn (2) the inverse of the ring-down time can be expressed as a linear function of the oil concentration in fuel

$$\frac{1}{\tau_{\text{sample}}} = \frac{c_0}{n L} d C + \frac{1}{\tau_{\text{blank}}} \quad (3)$$

here, the length of the fiber loop, $L = 11$ m, the width of the gap, $d = 200 \text{ μm}$, and the speed of light in the fiber $c_0/n = 2.07 \times 10^8 \text{ m s}^{-1}$. From the slope of the calibration curve in Fig. 12 (279 s$^{-1}$ ppnv$^{-1}$) we determine the absorption coefficient as $\varepsilon = 7.44 \times 10^{-4} \text{ ppmv}^{-1} \text{ cm}^{-1}$ to base $e$. An absorption spectrum of 1000 ppmv of oil in fuel recorded using a conventional absorption spectrometer shows a decadic absorption coefficient of 3.37 $\times 10^{-4} \text{ ppmv}^{-1} \text{ cm}^{-1}$, corresponding to 7.75 $\times 10^{-4} \text{ ppmv}^{-1} \text{ cm}^{-1}$ given with respect to base-$e$ in good agreement with the values from fiber-loop CRD spectroscopy. The small difference is likely due to the uncertainty in the gap width, $d$.

**Discussion and conclusion**

We used two different types of fiber optic probes to determine the concentration of oil in fuel. The fluorescence EEM spectra were analysed in two different ways, i.e. by PARAFAC and PCA/PCR giving calibration curves with very similar properties and a measurement range from about 10 ppmv to 1000 ppmv. The PARAFAC analysis technique demonstrated that the EEM spectra may be understood as arising from only two components (five components when using PCA/PCR) and that up to 1000 ppmv their ratio is linearly correlated to the concentration. At higher concentrations we expect that quenching and other non-linear effects contribute and more components would be required.

The absorption measurements were performed on small sample volumes of 20 μL and with a detection volume of only 25 nL. Since the absorption measurements were conducted at only one wavelength, we were not able to identify the spectral signatures of the oil sample. The detection limit of the CRD method was about 390 ppmv, with a dynamic range that extended to 100 000 ppmv (10%). When combining both fiber-coupled techniques, one should therefore be able to identify and quantify contaminants at low concentrations by fiber-coupled EEM spectroscopy while measuring their concentrations at selected wavelengths up to 10% concentrations using fiber-coupled absorption spectroscopy.

Aside from the simple optical configuration the fiber-coupled EEM method furthermore permits *in situ* sampling of the fuel, *i.e.* identification of contaminants without removal of the sample. We note that this method may be useful when
monitoring the contamination of any corrosive, inflammable or explosive liquid, including jet fuel, of course.

The present methods should be readily extendable to mixtures of more than two components. We then expect PARAFAC analysis to be particularly useful as it permits us to quantify and possibly identify the different components in the mixture. Fiber coupled absorption measurements may have to be extended to multiple wavelengths. While this is straightforward using pulses from different lightsources and time-domain multiplexing, we note that an alternative method using multi-wavelength phase-shift cavity ring-down spectroscopy may be more practical and less expensive.\(^5\)

**Acknowledgements**

The authors thank Klaus Bescherer and Adam Gribble for technical assistance, and GasTOPS Ltd. (Ottawa) and the Natural Sciences and Engineering Research Council (NSERC) of Canada for funding. HPL and HO also thank Peter Wentzell (Dalhousie University) for advice and many insightful comments.

**Notes and references**