

Portable Hydrocarbon Sensor for Environmental Applications

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ABSTRACT - Current environmental monitoring techniques depend upon use of analytical chemistry facilities, a costly and time-consuming activity. To overcome these issues, a rapid, low-cost, field-portable fluorescence sensor capable of detecting hydrocarbons in water has been developed. Such systems provide rapid feedback in the field, improving response time for environmental monitoring and remediation applications. The device uses ultraviolet light-emitting diodes and a compact charge-coupled device spectrometer to excite and measure fluorescence signatures. In this paper, we will describe our instrument and its performance when testing oil-sands process affected water and diesel contaminated soils and outline avenues for improvement of a second-generation prototype.

1. INTRODUCTION

Environmental monitoring techniques are an important prerequisite for sustainable development of Canada's natural resources. Current monitoring techniques require collected samples to be sent to an analytical chemistry facility. This is a costly and time-consuming step that hinders environmental monitoring and remediation efforts. To address this limitation, we have developed a rapid, low-cost, field-portable fluorescence sensor capable of detecting hydrocarbons in liquid and soil matrices. Of particular interest is its application for environmental monitoring of contaminants relevant to the oil sands industry in Alberta.

Naphthenic acids (NA) are found in bitumen deposits, and are a useful component of the oil sands extraction process. Since NA in process-affected (PA) water have been identified as toxic, monitoring NA levels in oil sands process-affected (PA) water is an important component of assessing and mitigating their environmental and operational impacts. These NA also promote corrosion in process vessels during bitumen upgrading. A low-cost, portable sensor capable of detecting NA at environmentally and industrially relevant concentrations would be of great interest to the oil sands industry.

Previous work has studied the characteristic fluorescence signatures of NA when excited by ultraviolet (UV) light in the range of 260 nm to 350 nm [1].

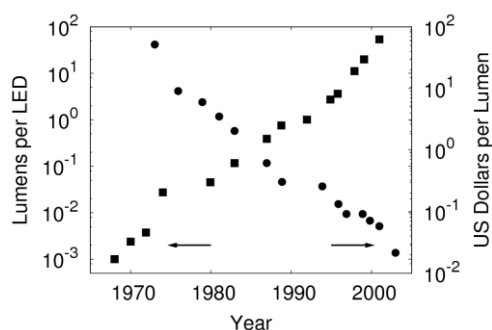


Figure 1: Light emitting diode cost and output power over the last 40 years. Similar to Moore's Law, describing computer technology, Haitz's law describes the doubling of output power every 2.3 years while cost drops in half every 3 years [2].

Our prototype device uses UV light-emitting diodes (LED) to excite and measure fluorescence signatures. LED cost and power has followed a trend similar to Moore's law over the past 40 years, shown in Figure 1. For LEDs, the trend is known as Haitz's law: power per LED doubles every 2.3 years while cost per lumen decreases by half every 3 years. This rapid scaling, coupled with the commercial availability of UV LEDs, allows for development of an instrument that duplicates much of the functionality of current bench top laboratory instruments.

The prototype is capable of six UV excitation wavelengths between 265 nm and 340 nm. A compact charge-coupled device (CCD) spectrometer monitors emission wavelengths from UV to near-infrared between 200 nm and 800 nm. Commercial, off-the-shelf components are used in the device, and the

prototype is capable of detecting contaminants at the parts-per-million level.

In this paper, we will describe our instrument and its performance when testing oil-sands PA water and diesel contaminated soils and outline avenues for improvement of the next generation of our device.

2. METHODOLOGY

A schematic of our prototype is shown in Figure 2. Four LEDs of each wavelength are used, for a total of 24 (Sensor Electronic Technology, Inc.). Peak output powers (10 μ s pulses at 1 kHz) between 11 mW and 25 mW were obtained. The emitted light is focused on the sample by a parabolic mirror. The sample absorbs UV light, and emits fluorescence that is characteristic of the sample's composition and concentration. The parabolic mirror is also used to collect the fluorescence light, which is subsequently focused (1" diameter, f/4 lens) for analysis using a compact CCD spectrometer (Ocean Optics). The complete prototype is shown in Figure 3; this version has been encased in ABS plastic pipe to provide a robust container for use in the field.

This prototype was evaluated using PA water samples obtained from three industrial sites in northern Alberta. For initial testing and evaluation, the samples were filtered to remove particles larger than 450 nm. Fourier-transform infrared spectroscopy was used to determine the concentration of NA, using an industry standard technique [3]. We used commercially available NA (Sigma Aldrich) for calibration, rather than petroleum-derived NA.

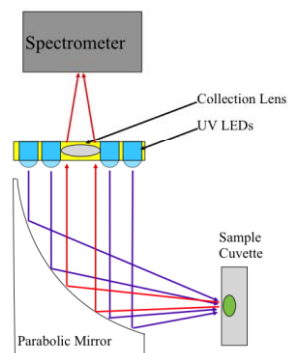


Figure 2: Schematic of our prototype's operating principle. The ultraviolet LEDs emit light (purple lines) that is focused by a parabolic mirror onto an environmental sample. The sample fluoresces (green) emitting light (red lines), that is measured by a spectrometer, identifying and quantifying contaminants.



Figure 3: Dr. Manisha Gupta (left), Debbie Ha (middle), and Yu Zhou (right) demonstrate the prototype (black cylinder, left) at the 2010 International Oil Sands Tailings Conference.

3. RESULTS

We verified the operation of our prototype by comparing collected data with that collected using a commercial bench-top fluorescence spectrophotometer (Varian Eclipse). Figure 4 shows excellent agreement between the prototype and the Varian data.

The analytic performance of our prototype was tested using the filtered process-affected water samples. Samples were then diluted with de-ionized or distilled water to produce samples at different concentrations. One sample result from these measurements is shown in Figure 5. We observe different sensitivities for the different industrial sites, but good linearity within a particular site. Limits of detection are below 10 mg L⁻¹ for a measurement time of 25 seconds.

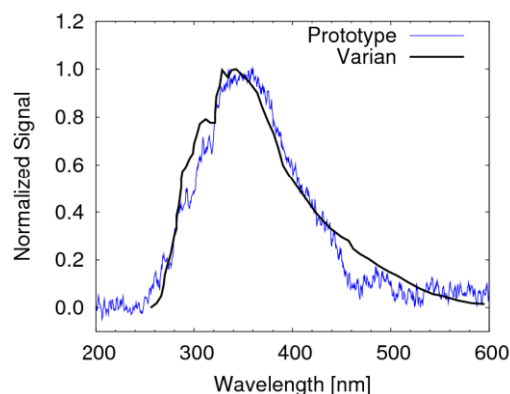


Figure 4: Comparison between prototype and bench-top fluorescence data for naphthenic acids for an excitation wavelength of 280 nm. The LED signature has been removed. The agreement is excellent, indicating the prototype is functioning correctly.

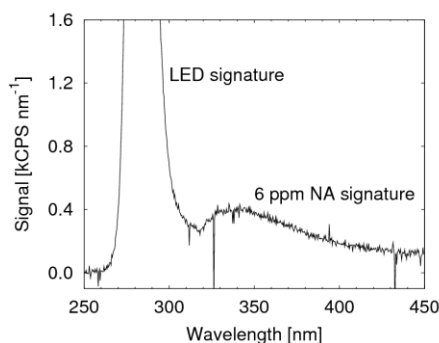


Figure 5: Characteristic signature of NA in filtered PA water. The large peak on the left is scattered light from the 280 nm LED excitation. The peak at 340 nm is the fluorescence for 6 parts-per-million naphthenic acid concentrations. Total acquisition time was 25 seconds.

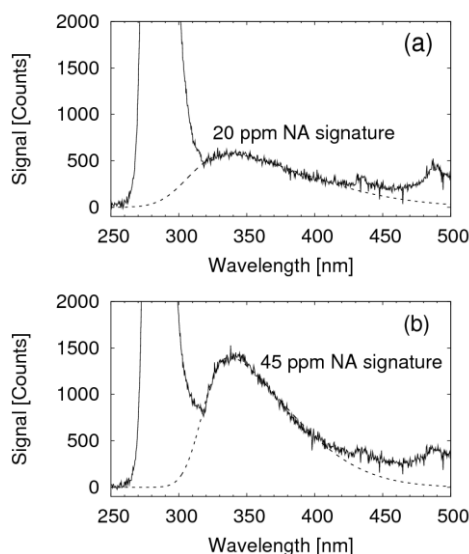


Figure 6: Fluorescence signature produced by our prototype using unfiltered process-affected water from (a) Albian and (b) Suncor tailings ponds. Despite the lack of sample preparation, we are still able to easily detect naphthenic acids at concentrations between 20 parts-per-million and 45 parts-per-million, indicating that our device could be used in the field to provide real-time feedback to environmental efforts.

Finally, the device was tested with PA water samples with no preparation – direct from the tailings ponds. The results are given in Figure 6, where the NA signature is clearly visible for both samples. These results indicate that this technology may be of use in an environmental or process control application for the Alberta oil sands industries.

While the initial results are encouraging (For additional details, see [4]), there are substantial

improvements to be made to this prototype. Improving the optics through increased LED density, improving $f/\#$ and using achromatic collection optics could yield as much as a factor of 100 improvement in performance. Combined with the expected cost reduction and improved power of UV LEDs in the near future, it is expected that an ultra-low-cost hand-held instrument will be available in the near future.

4. CONCLUSIONS

Current environmental monitoring techniques that require analytical chemistry facilities can act as a bottleneck for environmental monitoring and remediation applications. We have developed a low-cost, field-portable fluorescence sensor capable of rapidly detecting hydrocarbons in liquids at the parts-per-million level to address these issues. With continued effort, we anticipate hand-held instruments will be available in the near future.

CIPI SUPPORT

This work was supported by CIPI TEN project "Fluorescent sensor for geo-environmental site characterization" partially supported by CIPI and ConeTec Investigations, Ltd.

OTHER ACKNOWLEDGEMENTS

We would like to acknowledge Qing Wang and Steve Drake for technical support, and the Integrated Nanosystems Research Facility at the University of Alberta. We gratefully acknowledge funding from the Oil Sands Tailings Research Facility (OSTRF), the Natural Sciences and Engineering Council (NSERC), the University of Alberta, and the Canada School of Energy and Environment.

REFERENCES

- [1] Brown, L. D., M. Alostaz, A. C. Ulrich (2009). In 62nd Canadian Geotechnical Conference, Halifax, Nova Scotia, 1–7.
- [2] Steele, R. V. (2007). *Nat. Photonics*, 1:25–26
- [3] Jivraj, M., M. Mackinnon, B. Fung (1995). In Syncrude Analytical Manuals, 4th Edition, Research Department, Syncrude Canada Ltd., Edmonton, AB
- [4] M.T. Taschuk, Q. Wang, S. Drake, A. Ewanchuk, M. Gupta, M. Alostaz, A. Ulrich, D. Segó, Y.Y. Tsui, In International Oil Sands Tailings Conference 2010, Edmonton, AB, Canada, December 5th - 9th (2010).