CCQTA

Canadian Crude Quality Technical Association

On-Line Contaminant Monitoring

Project Update

CCQTA/COQA Meeting

February 10 &11, 2010

New Orleans

On Line Contaminant Monitoring Project Update

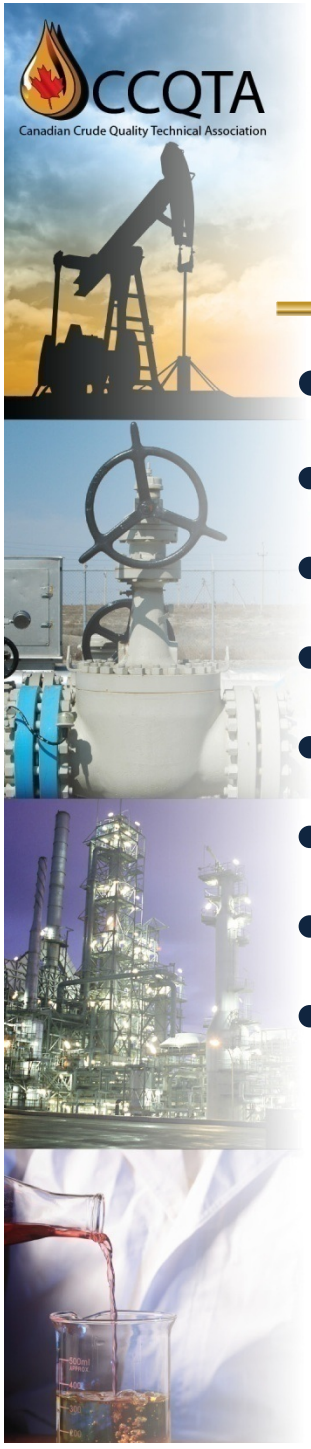
- **Overview**
- **Project Goals**
- **Interested Parties**
- **Project Scope**
- **Key Contaminants**
- **Work to Date**
  - **Technology Review**
  - **Ongoing work**

On Line Contaminant Monitoring Overview

- Contaminants in crude oil tend to be variable in concentration and poorly tracked in refinery feed
- Contaminants tend to impact plant operation more than finished product quality
- Most incidents of crude contamination impact on plant operation are poorly documented
  - Investigated post occurrence!
  - Insufficient data!

On Line Contaminant Monitoring Project Goals

- To develop on-line monitoring tools for the purpose of measuring key contaminants in refinery feed
- Use the data generated above to quantify the impact of contaminant concentrations and their variability on plant operation



On-Line Contaminant Monitoring Interested parties

- Cenovus
- Shell
- Nexen
- ConocoPhillips
- Corrillo Resources
- Maxxam Analytics
- ARC
- United Refining

On-Line Contaminant Monitoring Project Scope

- Identify target contaminants for monitoring
- Determine capabilities of existing technologies
- Select a location/plant for testing of existing/new technologies
- Determine effectiveness of monitoring tool(s)

On-Line Contaminant Monitoring Key Contaminants

- Possible contaminants of interest
  - Salt
  - Metals
  - Inorganic solids
  - Asphaltenes
  - Sulfur
- At this point no agreement has been reached on target contaminants

On-Line Contaminant Monitoring Technology Review

- Two potential technology providers have been identified
- Process NMR
  - Nuclear Magnetic Resonance
  - Electron Spin Resonance
  - FTIR with ATR
- Progression Inc.
  - Nuclear Magnetic Resonance
  - Laser Induced Breakdown Spectroscopy

On-Line Contaminant Monitoring NMR

- On-line NMR packages are already available for installation in Class 1, Div 1 areas, in a package similar in size and shape to a refrigerator
  - Most applications focused on measuring bulk properties of oil

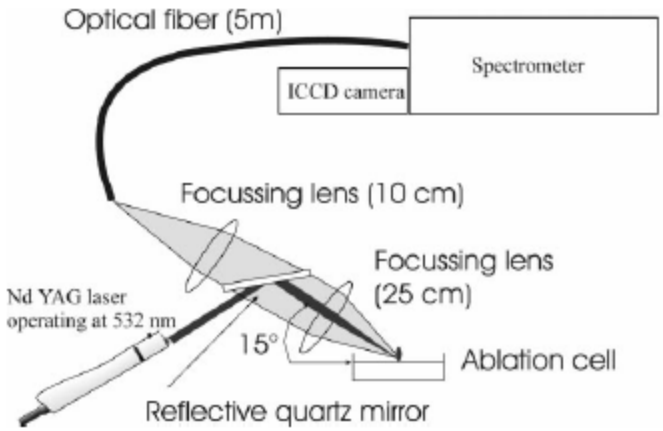
On-Line Contaminant Monitoring
ESR

- Measures concentration and composition of chemical species with unpaired electrons
- For crude oil, possible applications might include organic free radicals, condensed aromatics (such as asphaltenes), transition metal ions
- Seems to have potential for on-line application, more test work required

On-Line Contaminant Monitoring
LIBS background

- Laser induced breakdown spectroscopy
- LIBS well suited to on-line use as the laser beam and emissions beam can be carried by fiber optic to/from electronics unit

Example of LIBS hardware



On-Line Contaminant Monitoring LIBS background

- LIBS can be used in a laboratory or in a on-line configuration
- Capable of simultaneous multi-element detection with reasonable sensitivity
- Many applications have been tested, mostly on solids and gases, some liquids
  - Most liquid testing has focused on water, but some studies have been done on a petroleum based materials

On-Line Contaminant Monitoring
LIBS background

Results obtained for 12 elements in oil[a]

Element	Wavelength (nm)	Detection limit ($\mu g\,ml^{-1}$) (this work)
Pb	405.87	90
Si	288.1579	20
Ca	393.366	0.3
Na	588.995	0.7
Zn	334.502	130
Sn	283.999	80
Al	396.152	10
Cu	324.754	5
Ni	341.476	35
Fe	371.9935	20
Mg	285.213	1
Cr	425.43	20

[a] The sensitive lines are reported, as well as the detection limits obtained.

- Results extracted from Analytica Chimica Acta 429 (2001) 269 – 278

On-Line Contaminant Monitoring Work to Date

- Two refinery sites have expressed interest
- Technology suppliers presently testing equipment capabilities using crude oil samples supplied by the project
- Process NMR willing to assist/conduct LIBS application development testing, if an instrument can be provided (lease/loan)
- Once applicability has been established, an on-line analyzer can be designed by Process NMR/Progression Inc.

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