PORLA Stability and Compatibility Analyzer

Dr Juha Vilhunen – Managing Director
Mr Jurg Walvogel – Product Manager
Finnish Measurement Systems Ltd
FMS Ltd is developer and manufacturer of laboratory and on-line analyzers for oil industry, production and research.

Analyzers in product range of FMS Ltd:

- Porla Crude and heavy fuel oil stability and compatibility analyzer
- New Generation Porla analyzer
- Porsas On-line p-value analyzer
- Samuli On-line cloud point analyzer
- Bisom Porla bitumen solubility analyzer
Our main product is **New Generation PORLA Analyzer** for oil refining process optimization, for blending of heavy fuel oils, crude oils and bitumen, as well as for developing new oil products and processes.

**New Generation PORLA** will produce a full set of stability and compatibility parameters such as: **P-value**, **Pa**, **Po**, **Xmin**, **FRmax**, **FR5/1**, **In** and **Sbn** by one run.
HISTORY OF FMS LTD

• FMS was established as subsidiary of Neste Oil Plc 1996
• A planned gradual dilution of Neste ownership was agreed upon
• First, business activities focused to Scandinavia and Russia
• Application development was carried out in close collaboration with prominent global partners
• FMS Ltd spin-offed from Neste Oil Plc totally 2010
• Company privately owned, fully independent global
• Investing to product/application development with prominent players has been continued during history of the company
• The present main market areas of FMS Ltd are Scandinavia, Europe, Asia and Russia
Experience of FMS key persons on oil industry and development of analytical instruments for oil and petrochemical industry:

**Dr Juha Vilhunen, MD of FMS (PhD Analytical Chemistry)**
- Neste Oil Ltd, Corporate technology, Director 12 years 1985-1997
- FMS Ltd, Managing Director since 1997
- ACA Systems Ltd, President 2002-2008
- Adjunct Professor, Jyväskylä University, since 2002
- Senior Business Development Advisor, Kuopio Innovation Ltd, since 2009

**Jurg Waldvogel, Product Manager of FMS**
- Neste Oil Ltd, Corporate technology, Senior Technologist 16 years
- FMS Ltd, Product Manager since 2002

During their career FMS Ltd key persons have developed more than 100 measuring instruments for oil, petrochemical and paper industry.
Porla analyzer, standard method ASTM D7112 since 2005

Applications developed in collaboration with:

• ExxonMobil/Soluble Solutions, USA
• IFP/Axens, France
• NCUT, Canada
• Neste Oil Ltd, Finland
• Nynas, Sweden
PORLA HISTORY

• 1986 Monitoring and optimization of different refinery units, reporting only P-value (Neste)
• 1994 Developing of new detector design (Light reflection)
• 1999 Change of measurement procedure to obtain full set of parameters (IFP)
• 2001 Addition calculation of compatibility parameters (NCUT, ExxonMobil)
• 2005 ASTM standard method accepted
• 2009 Developing of special Bisom model for bitumen (Nynäs)
• 2013 Addition of measurement program for asphatene-free oils
• 2015 Launching of New Generation Porla analyzer
PORLA APPLICATIONS

- Monitoring blending of heavy fuel oils
- Monitoring blending of marine fuels
- Optimization of thermal cracking/visbreaking processes
- Optimization of hydrocracking processes
- Monitoring mixing of crude oil and feedstock blends for refineries
- Monitoring mixing of crude oil export blends
- Monitoring blending of bitumen
- Facilitating tar sand production processes
- Cargo based monitoring of opportunity crudes
- Supporting tendering, dosing and control of process chemicals (antifoulants)
ADVANTAGES OF PORLA ANALYZER

• Enables oil refineries to select more economic crude oil blends with minimized risk of fouling problems
• Determination full set of stability and compatibility parameters (FRmax, Xmin, P, Pa, Po, FR5/1, TE, In and Sbn) by one run
• Reporting also ExxonMobil heavy and crude oil blending model parameters In and Sbn
• Capability to analyze stability and compatibility parameters of low asphaltene content oils
• Offer unique method to analyze compatibility parameters of asphaltene-free oils
• ASTM test method D7112 since 2005
OTHER ADVANTAGES OF PORLA

• User-friendly, highly automated sample preparation and analytical procedure minimizing operator time and mistakes
• Fast screening mode to determine optimal running parameters for unknown samples
• Self cleans at the end of the test procedure
• Possibility to use different paraffinic and aromatic solvent combinations
BENEFITS OF PORLA

• Maximizing profitability of refinery processes
• Minimizing production of off-spec products
• Selecting crude oil and feedstock blends more economically and preventing shutdowns of refinery units/refineries
• Enabling optimal and profitable use of opportunity crudes
• Preventing production of incompatible crude oil and feedstock blends for refineries
• Minimizing production of incompatible crude oil export blends
• Optimized selection, use and costs of process chemicals (antif.)
• Increasing profitability of tar sand production processes
• Production of bitumen, which corresponds to customer needs
PORLA Flow Chart

- Paraffin Pump
- Circulation Pump
- Detector
- Exhaust Pump
- Mixer
- Sample Cup
- Sample Solution
- Heater
PORLA Detector
Definition of parameters

- P-value, define state of peptization of asphaltenes in oil
- Pa, peptizability of asphaltenes
- Po, peptization power of oil medium,
- FR5/1 or xylene equivalent, measure of oil aromaticity, the smaller the value the more aromatic is oil
- FRmax, flocculation ratio at infinite dilution
- Xmin, paraffinic solvent consumption of pure oil
- In, insolubility number, the higher the bigger precipitation risk
- INmix, is the highest IN of components of the blend
- SBN, solubility blending number, ability of oil to keep asphaltenes in solution, the higher the lower precipitation risk
- SBNmix, volumetric average of SBNs of blend components
Definition of parameters

• P-value, smallest 1 i.e. oil is unstable and can precipitate asphaltenes without addition of any paraffins; bigger P-values indicate higher stability of oil with respect of asphaltene precipitation

• Typical P values: P>1.35 for usual fuels, P>1.5 with Pa>.45 and Po>0.8 for bunker fuels

• FR5/1 or xylene equivalent, measure of oil aromaticity, the smaller the value the more aromatic is the oil

• A high aromaticity means that more paraffinic fluids can be added without flocculation of asphaltenes

• IN, insolubility number, inverse measure of ability of asphaltenes to stay in solution. The higher the number, the higher the risk of asphaltene flocculation. IN of asphaltene-free fluids is 0. IN of a blend is equal to the highest IN of all fluids of the blend.

• SBN, solubility blending number, ability of oil to keep asphaltenes in solution, the higher the lower precipitation risk

• SBNmix, volumetric average of SBNs of blend components, all hydrocarbon fluids have a SBN number.
CALCULATION OF STABILITY FIGURES

\[
FR = \frac{\text{Varom}}{\text{Varom} + \text{Vpara}}
\]

\[
TE = \frac{FR_{5/1}}{100}\%
\]

\[
X = \frac{\text{Varom} + \text{Vpara}}{\text{Moil}}
\]

\[
P = 1 + X_{\text{min}}
\]
CALCULATION OF STABILITY FIGURES

\[ P = 1 + X_{\text{min}} \text{ or } P_o / (1 - P_a) \]

\[ P_a = 1 - FR_{\text{max}} \]

\[ P_o = FR_{\text{max}} \times P \]

\[ P_a = \text{peptizability of asphaltenes} \]
\[ P_o = \text{peptizing power of the oil matrix} \]
\[ FR_{\text{max}} = \text{maximum flocculation ratio (at } 1/X=0) \]
Blending Model Parameters

\[
\text{TE} = \frac{I_N}{(1 - VH/25d)}
\]

\[
S_{BN} = I_N \left( 1 + \frac{V_H}{5} \right)
\]

\(TE = \) toluene equivalent

\(V_H = \) maximum n-heptane can be added to 5 ml of oil without precipit.

\(d = \) density of oil

COMPATIBILITY MODEL:

Compatibility criterion

\[
S_{BNmix} > I_{Nmax}
\]

\[
S_{BNmix} = \frac{V_1S_{NB1} + V_2S_{BN2} + \cdots}{V_1 + V_2 + \cdots}
\]
Blends are compatible when the volumetric average solubility blending number is greater than the insolubility number of any component of the blend.
PORLA PROCEDURE

• Select method
• Prepare stock solution from oil and aromatic solvent
• Weigh stock solution to three sample cups
• Load sample cups to carroussel of analyzer
• Type sample data to operating screen
• Start measurement
• Store and print results
PORLA METHOD

• Detector system: based on reflection of visible light
• Limit of the method: depends on sample, users have reported direct analysis of oils down to 0.05-0.1% asphaltenes, special analytical procedure for asphaltene-free oils,
• Sensitivity of method for suspended coke particles: principle and wavelength of detector (reflection of light) make it asphaltene sensitive with minor disturbance of coke particles
• Potential improvement of fidelity data: operation is based on continuous development, new solutions realized with steps (generations of analyzers)
• Duration of measurement: full procedure 3 titrations 60-90 min, sample preparation few min.
• Automatic aspects of measurement: fully automatic and guided procedure, sample prep few min
• Advancements in the optical detection system: minor interferences due to coke or other particles. No detector change for different samples.
PORLA METHOD AND MARKET

• Correlation between parameters of PORLA and other method: different methods applying different solvent combinations give different results.

• Routine or research analyzer: Porla has been used both for routine laboratory analyses and research purposes.

• Reliability of Porla (does it require frequent calibrations and maintenance): automated calibration procedure of solvent pumps is carried out by balance, is simple and takes few minutes, pumps are very stable and durable, minor maintenance actions.

• Availability of Porla analyzer: FMS Ltd is manufacturer, distribution by local representatives or directly by FMS.

• Overview of customers/users of the equipment over the world: operation of FMS has focused so far mainly to Scandinavia, Europe, Russia and Asia; Worth mention: half of the biggest oil companies of the world are business partners of FMS and have acquired Porla analyze.
BUSINESS PARTNERS OF FMS LTD
On One Screen....

1 Sample
(Few minutes preparation)

10 parameters

All in one run

In 60-90 minutes
### PARAMETERS AND PUMP CALIBRATION MENU

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mixing time (s)</td>
<td>20</td>
</tr>
<tr>
<td>Circulation time (s)</td>
<td>20</td>
</tr>
<tr>
<td>Suction line empty time (s)</td>
<td>25</td>
</tr>
<tr>
<td>Aromat dose time (s)</td>
<td>45</td>
</tr>
<tr>
<td>Cleanse time (s)</td>
<td>45</td>
</tr>
<tr>
<td>Cleanse cycles</td>
<td>3</td>
</tr>
<tr>
<td>Paraffin pump rate (ml/s)</td>
<td>0.061</td>
</tr>
<tr>
<td>Aromat pump rate (g/s)</td>
<td>0.109</td>
</tr>
<tr>
<td>Exhaust pump rate (g/s)</td>
<td>0.4</td>
</tr>
<tr>
<td>Cup capacity (ml)</td>
<td>70</td>
</tr>
<tr>
<td>Test Run Int. Limit</td>
<td>6</td>
</tr>
<tr>
<td>Detection Sensitivity</td>
<td>0.005</td>
</tr>
<tr>
<td>Aromat evaporate rate (g/h)</td>
<td>0.9</td>
</tr>
<tr>
<td>Step wait time (s)</td>
<td>70</td>
</tr>
<tr>
<td>Paraffin step size (ml)</td>
<td>0.7</td>
</tr>
</tbody>
</table>

- **Pump calibration**: Paraffin pump
- **Paraffin**: Heptane
- **D g/cm³**: 0.694
Repetitive analyses of Visbreaker residues obtained at different process temperatures

<table>
<thead>
<tr>
<th>Repetitive analysis</th>
<th>P-val (450°C)</th>
<th>P-val (435°C)</th>
<th>P-val (420°C)</th>
<th>P-val Feedst</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 1</td>
<td>1.24</td>
<td>1.92</td>
<td>2.48</td>
<td>5.50</td>
</tr>
<tr>
<td>Run 2</td>
<td>1.32</td>
<td>1.98</td>
<td>2.45</td>
<td>5.14</td>
</tr>
<tr>
<td>Run 3</td>
<td>1.27</td>
<td>1.98</td>
<td>2.40</td>
<td>4.92</td>
</tr>
<tr>
<td>Run 4</td>
<td>1.29</td>
<td>1.98</td>
<td>2.49</td>
<td>5.02</td>
</tr>
<tr>
<td>Run 5</td>
<td>1.22</td>
<td>1.98</td>
<td>2.53</td>
<td>4.92</td>
</tr>
<tr>
<td>Run 6</td>
<td>1.27</td>
<td>1.98</td>
<td>2.47</td>
<td>4.92</td>
</tr>
<tr>
<td>Average</td>
<td><strong>1.27</strong></td>
<td><strong>1.97</strong></td>
<td><strong>2.47</strong></td>
<td><strong>5.07</strong></td>
</tr>
<tr>
<td>s</td>
<td>0.035</td>
<td>0.024</td>
<td>0.041</td>
<td>0.23</td>
</tr>
<tr>
<td>r</td>
<td>0.028</td>
<td>0.019</td>
<td>0.033</td>
<td>0.18</td>
</tr>
</tbody>
</table>
### Stability and Compatibility Analyses of Athabasca Crude/Bitumen

<table>
<thead>
<tr>
<th>QC</th>
<th>P-Value</th>
<th>IN</th>
<th>SBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.66</td>
<td>28.1</td>
<td>102.1</td>
</tr>
<tr>
<td>2</td>
<td>3.61</td>
<td>26.9</td>
<td>96.4</td>
</tr>
<tr>
<td>3</td>
<td>3.80</td>
<td>26.3</td>
<td>99.3</td>
</tr>
<tr>
<td>4</td>
<td>3.79</td>
<td>26.1</td>
<td>98.2</td>
</tr>
<tr>
<td>5</td>
<td>3.89</td>
<td>26.9</td>
<td>103.6</td>
</tr>
<tr>
<td>6</td>
<td>3.67</td>
<td>25.2</td>
<td>91.8</td>
</tr>
<tr>
<td>7</td>
<td>3.85</td>
<td>25.3</td>
<td>96.7</td>
</tr>
<tr>
<td>8</td>
<td>3.86</td>
<td>24.7</td>
<td>94.7</td>
</tr>
<tr>
<td>9</td>
<td>3.64</td>
<td>25.9</td>
<td>93.5</td>
</tr>
<tr>
<td>10</td>
<td>3.81</td>
<td>25.3</td>
<td>95.6</td>
</tr>
</tbody>
</table>

Average: P-Value 3.76, IN 26.1, SBN 97.2

**SD:**

- $s = 0.10$
- $r = 0.06$
High asphaltene content is not necessary to associate with high risk of trouble

Oil # from Venezuela oil fields

Evaluation of compatibility risks of opportunity crudes of oil refineries in Europe for crude assay using blending model parameters

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>P-value</th>
<th>$I_N$</th>
<th>$S_{BN}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude 1</td>
<td></td>
<td></td>
<td>31,7</td>
</tr>
<tr>
<td>Crude 2</td>
<td>2,6</td>
<td>50,4</td>
<td>75,8</td>
</tr>
<tr>
<td>Crude 3A</td>
<td>-</td>
<td>-</td>
<td>11,9</td>
</tr>
<tr>
<td>Crude 3B</td>
<td>-</td>
<td>-</td>
<td>38,9</td>
</tr>
<tr>
<td>Crude 4</td>
<td>1,9</td>
<td>39,8</td>
<td>71,8</td>
</tr>
<tr>
<td>Crude 5</td>
<td>-</td>
<td>-</td>
<td>44,6</td>
</tr>
<tr>
<td>Crude 6</td>
<td>2,4</td>
<td>30,2</td>
<td>67,5</td>
</tr>
<tr>
<td>Crude 7</td>
<td>4,1</td>
<td>23,8</td>
<td>97,1</td>
</tr>
<tr>
<td>Crude 8</td>
<td>3,0</td>
<td>23,0</td>
<td>63,0</td>
</tr>
</tbody>
</table>

Blending Crude 2 with Crudes 1, 3A, 3B and 5 can be a risk
Blending Crude 4 with Crude 1, 3A and 3B can be a risk
Blending Crude 3A with any asphaltene containing 2, 4, 6, 7 and 8 can be a risk
Variations of stability and compatibility parameters of different cargos of same brand crudes

<table>
<thead>
<tr>
<th>Crude oil</th>
<th>P-value</th>
<th>( I_N )</th>
<th>( S_{BN} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bashra</td>
<td>2,6</td>
<td>34,2</td>
<td>89,1</td>
</tr>
<tr>
<td>Bashra 2</td>
<td>2,4</td>
<td>30,5</td>
<td>72,0</td>
</tr>
<tr>
<td>CPC</td>
<td>-</td>
<td>-</td>
<td>11,9</td>
</tr>
<tr>
<td>CPC 2</td>
<td>-</td>
<td>-</td>
<td>38,9</td>
</tr>
<tr>
<td>Iran Heavy</td>
<td>2,2</td>
<td>36,9</td>
<td>81,1</td>
</tr>
<tr>
<td>Iran Heavy 2</td>
<td>2,3</td>
<td>32,9</td>
<td>74,3</td>
</tr>
<tr>
<td>Iran Light</td>
<td>2,3</td>
<td>23,5</td>
<td>54,6</td>
</tr>
<tr>
<td>Iran Light 2</td>
<td>4,1</td>
<td>23,8</td>
<td>97,1</td>
</tr>
<tr>
<td>REB</td>
<td>3,7</td>
<td>24,3</td>
<td>81,4</td>
</tr>
<tr>
<td>REB 2</td>
<td>3,0</td>
<td>23,0</td>
<td>63,0</td>
</tr>
</tbody>
</table>
Conclusions

• Porla is used by prominent oil and service companies
• Easy check for potential compatibility issues
• Usable for crude, residue, heavy and light fuel oils and bitumen
• High automatisation level and self diagnostic
• Easy use with less work power
• Porla is a powerful tool to otimize feedstocks and processes of oil industry
• Opportunity crudes will be a fast growing new application area
Thank you for your interest!

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