Combining Analytical Sensors and NeSSI to Improve Process Understanding

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Analytical Sampling for Online Applications
Why Use Process Sensors?

Real-time analysis for ..

- Corrosion Monitoring
- Process development
- Process optimization
- Process control
- Production?
Process Challenges

- Analytical characterization
- Sampling and screening
- Data handling
  - Sensor fusing
  - Multi-sensor modeling
- Process modeling and feed back control
- Process optimization – move toward feed forward control???
Spectroscopic Analysis of a Process

- Possible problems with performing online spectroscopic measurements
  - Bubble formation
  - Solid Formation
  - Phase separation
  - Anything else that you could possibly imagine
- Most PAT problems are due to sampling not measurement device
- Need better systems to sample processes!!
NeSSI™ Modular Sampling Systems

- **New Sampling/Sensor Initiative**
- Surface-mount modular component based gas and fluid handling and conditioning systems
  - ISA SP76 interface specification
  - Elastomeric o-ring seals
- Offer flexibility in design and implementation
- Allows for optimal positioning of analyzers in a process stream
What is NeSSI?

• Industry-driven effort to define and promote a new standardized alternative to sample conditioning systems for analyzers and sensors
  • Standard fluidic interface for modular surface-mount components
  • Standard wiring and communications interfaces
  • Standard platform for micro analytics
What does NeSSI Provide

- Simple “Lego-like” assembly
  - Easy to re-configure
  - No special tools or skills required
- Standardized flow components
  - “Mix-and-match” compatibility between vendors
  - Growing list of components
- Standardized electrical and comm. (Gen II)
  - “Plug-and-play” integration of multiple devices
  - Simplified interface for programmatic I/O and control
- Advanced analytics (Gen III)
  - Micro-analyzers
  - Integrated analysis or “smart” systems
Where Does NeSSI Fit in the Lab

- Instrument/Sensor Interfaces
  - Design standards make development simpler
    - Reduced toolset to be mastered
    - Reduced sample variability to account for
  - Calibration/validation built-in
    - Consistent physical environment for measurement
    - Stream switching and/or mixing allow generation of standards to match analytical requirements

- Reaction monitoring
  - Microreactors and continuous flow reactors
  - Batch reactors (with fast loop)

- Sample Preparation
  - Gas handling (mixing, generation, delivery)
  - Liquid handling (mixing, dilution, conditioning, etc.)
NeSSI with an Array of Micro-Analytical Techniques will Impact Many Industries

- Process Control
- Process Optimization
- Product Development
NeSSI Sensing Technologies

- Gas Chromatography
  - Thermal Desorption
- Dielectric
- Spectroscopies
  - IR
  - NIR
  - UV-Vis
  - Raman
  - Fluorescence
- Impedance
- Conductivity
- Refractive Index

- Particle Sizing
  - Light scattering (?)
- Turbidity
- pH
- RGA
- Mass Spectrometry
- LC, SEC, IC
- Terahertz (?)
NeSSI™: Enabler for MicroAnalytical

- (the “rail” concept)

**Standard** Electrical (Digital) Interface “Rail”

Anyone’s Sensor

Anyone’s Actuator

**Standard** Mechanical Interface “Rail”

*Sensor/Actuator Manager

Standard “connectivity”

Standard “hockey-puckPC”

What technologies are available

Suitability for modular sampling systems

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*SAM*
At-Line GC’s with NeSSI Compatibility

ABB Natural GC

Siemens microSAM

Agilent 3000 Micro GC

Siemens microSAM
Calidus fast GC from Falcon Analytical
Thermo/C2V Fast Micro-GC

http://www.c2v.nl/ as well as http://www.thermo.com
Applied Analytics Inc. Diode Array

- OMA-300
- A Fiber-optics-diode-array process analyzer
- For on-line concentration monitoring
Applied Analytics Microspec IR

FEATURES

- Ideal for monitoring **PPM** level **WATER** in various solvents
- In stream quantitative measurements
- Contains no moving parts and
- Extremely robust allowing for installations in process stream environments
- Replaces analyzers such as process spectrometers in the process plant.
Small Diameter ATR-IR-Fiber Probes

Diamond ATR-IR-Fiber Probe of 2.7mm diameter in NeSSI

Fiber Photonics Inc.

www.fibrephotonics.com
micrOptix

Integrated Spectral Sensing System

Detector Array

Spectrally Balanced LEDs

The Spectral Measurement Sensor (SMS) is ideal for compact on-line liquid measurement applications.

Technology Overview

The Spectral Measurement Sensor features our patented, integrated sensing system technology. The technology consists of a linear variable filter that is optically coupled to a photodiode array detector and high stability, low power LED light sources.

i-PEL
The Process Spectral Measurement Sensor
H₂Scan Adaptation to NeSSI™ Platform

- Hydrogen specific: 0.5% H₂ to 100% H₂ v/v
- Response time (T90) < 30 sec
- In-line, real-time measurements in process gas streams up to 100°C
- Unique models for CO, H₂S, wet Cl₂
- 4-20mA, RS422 or RS232 serial connectivity
- Stable results
- On-site verification and calibration
- Approved for hazardous locations
  - Intrinsically safe design
  - ATEX certificate granted; UL pending
- Cost effective to buy / install / maintain
- Field verification and calibration kit available

http://www.h2scan.com/
Astute Sampling System

Sampling + Sensors & micro-analyzers

Astute System with C₂V Micro GC and H₂Scan hydrogen analyzer

www.eif-filters.com
Agilent NeSSI Dielectric Sensor

Cable to Agilent Network Analyzer

Swagelok 2-Port Valve Base

Dielectric Probe

Inner Body

O-ring (inside)

Outer Body

Close up of Coaxial Probe Tip

Exploded View
NeSSI™ IR Gas Cell

NDIRs. The Star NDIR has no moving parts.

- No Moving Parts or Special tools required for Easy Maintenance & Service
- No Critical Realignment
- Specific, Interference-Free CO₂ Detection
- Dual-Wavelength Ratioing Compensates for Drift
- Computer-Controlled for Accuracy
- Sapphire-Protected Optics
- Non-Corrosive, Non-Reflective Sample Cell

Sample Cell
NeSSI Compatible Optical Cells
Axiom Analytical, Inc.

- Currently Available
  - FFV Series Transmission Cells (Near-IR, UV-Visible)
  - FNL-120 UV-Visible ATR Cell

- In Development
  - Raman Cells (Single- and Multi-pass)

- Possible Development
  - Diffuse Reflectance Cells
  - Mid-IR ATR Cells

Courtesy of Mike Doyle
Axiom Analytical, Inc.
Chevron NeSSI/Analytical Unit

Specifications

- ASI Microfast GC
- Parker NeSSI gas handling/sampling system
- Carrier gas
- Mobility
NeSSI based Analytical Developments at CPAC
NeSSI Gas/Vapor System

ASI microFAST GC

Aspectrics EPIR w/ glass cell

Permeation Tower

N₂

NeSSI Gas/Vapor System

NeSSI Flow Cell

Waste
NeSSI Calib. Gas Generation System

Features of NeSSI System:

- Fully digital
- 4 Stage dilution, able to produce and maintain gas concentrations in ppb range
- Fully automated system, set and forget capability
- Integrated C2V NeSSI compat. GC
- Calib, platform for gas sensor dev.
Gas Calib. System LabView Control Program

- Perform automated DoE calibration runs
- input and log sensor, reference, temperature and pressure feeds
- System designed for full digital (plug and play) performance as h/w matures
Design of Small Fiber Optic Sensors

- vapochromic chemistry
- optical response to analyte
- simple design
- reversible response
- low power
- inexpensive
- fast response times
- high quantum efficiency
- long term sensor stability
- sensitive to a variety of analytes
- wireless communication
- battery powered

Analytes:
- Oxygen
- Moisture
- Ammonia
- Hydrogen
- Common Solvents
  - Alcohols
  - Esters
  - Amines
- Chlorinated Organics
- Organic Hydrocarbons (BTEX)
- Carbon Dioxide (in development)
- Hydrogen Sulfide (in development)
Modular NeSSI Oxygen Gas Sensor

Exploded View

1/16 in bifurcated fiber optic fiber
1/16 to 1/8 in Swagelok union
Sensor Body
Fiber optic ferrule with plastic housing
Close up of Outer Body Tip
Vapochromic Tip
Agilent NeSSI Mount

Exploded View
Vapochromic Humidity Sensor

- Measurement time – 100 ms
- 3 reps per concentration

• 2 PC calibration model
• Humidity range: 10 – 80%
• Ohmic feedback control humidity generator used for reference stds.

Elements: 6
Slope: 0.999824
Offset: 0.007585
Correlation: 0.999912
RMSEC: 0.342323
SEC: 0.374996
Bias: -1.272e-06
Vapochromic Benzene Sensor

Full spectrum response of the 0%, 10%, and 50% bubbler flow samples used to make the PLS model showing both the change in intensity and shift in peak maximum with changing benzene concentration.
Sensor response to $O_2$ Gas

20 replicates at each concentration
Concentration range: 0 - 100% Oxygen

$R^2 = 0.990$, $3$ PC
RMSEC = 1.0744
Response Time of Oxygen Gas Sensor

Sensor Response for $\text{O}_2$ in Solution

$R^2 = 0.998$

2 Latent Variables

RMSEC = 0.90163

Bias = $-7.1054 \times 10^{-15}$

5 replicates at each concentration

Concentration range: 1 $\mu$mol/L - 55 $\mu$mol/L

1 $\mu$mol/L = 32.5 ppb
Response Time of Dissolved $O_2$ Sensor

Nitrogen

$\approx 100\%$ 8 sec
$\approx 95\%$ 5 sec
3 Replicates Averaged

Air

$\approx 100\%$ 6 sec
$\approx 95\%$ 2 sec
3 replicates Averaged Oxygen

<table>
<thead>
<tr>
<th>Compound/polymer</th>
<th>Mean Response Time of Exchanges between $O_2$, $N_2$, Air ($T_{95%}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VCS/Teflon</td>
<td>3.7 s</td>
</tr>
<tr>
<td>Most other Oxygen Sensors</td>
<td>$\geq 30$ s</td>
</tr>
</tbody>
</table>

Future Miniature Oxygen Sensor

Oxygen Sensor and probe

Oxygen Sensing Tip
### Response of commercial optical DO sensors

<table>
<thead>
<tr>
<th>Company: Product</th>
<th>Sensor/Polymer</th>
<th>Detection Range</th>
<th>Response Time (water)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mettler-Toledo: InPro6880i</td>
<td>PtPorphine/Silicone</td>
<td>0-40 mg/L</td>
<td>20 sec</td>
</tr>
<tr>
<td>InSitu: RDO</td>
<td>PtPorphine/Polyester</td>
<td>0-20 mg/L</td>
<td>30 sec</td>
</tr>
<tr>
<td>Gobal water: D-Opto</td>
<td>RuPolpyrydyl/NA</td>
<td>0-25 mg/L</td>
<td>60 sec</td>
</tr>
<tr>
<td>YSI: ProODO</td>
<td>NA</td>
<td>0-50 mg/L</td>
<td>N/A</td>
</tr>
<tr>
<td>Hach: LDO</td>
<td>PtPorphine/Polystyrene</td>
<td>0-20 mg/L</td>
<td>90 sec</td>
</tr>
<tr>
<td>Ocean Optics: FOXY</td>
<td>RuPolpyrydyl/sol-gel</td>
<td>0-40 mg/L</td>
<td>50 sec</td>
</tr>
<tr>
<td><strong>Our Sensor</strong></td>
<td><strong>VCS/Teflon</strong></td>
<td><strong>0-50 mg/L</strong></td>
<td><strong>3.7 sec</strong></td>
</tr>
</tbody>
</table>

- Standard electrochemical Clark electrode response time to $T_{95}$ is over 2 minutes
- Vapo sensor is as sensitive, faster and more stable than current O$_2$ technology
Liquid Chromatography for NeSSI™

Scott Gilbert, CPAC Visiting Scholar
Crystal Vision Microsystems LLC
Atofluidic Technologies, LLC

- Split flow approach to sampling

- $\mu$-fluidic LC Chip for On-line Sample Pretreatment

- Pulsed electrochemical detection (on-chip)
Spreeta SPR sensing components

- SPIRIT system performs SPR detection using Texas Instruments’ Spreeta SPR chips
- Chips are mass-produced by TI, cost ~$4 in large quantities
- Each chip can perform three simultaneous measurements
- Systems contain 8 chips, for 24 total sensing channels

Clem Furlong, et al, UW
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