Moving towards full integration of Process Analysers using NESSI Modular Systems

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Agenda

- About SOLVAY
- Past experience using Nessi modular systems in SOLVAY
- Installing Tunable Diode Lasers (TDL) on Nessi/ASTUTE modular systems in the PVC industry
- Installing Chlorine moisture sensors on full plastic Nessi/ASTUTE modular systems
- Future Perspectives & Conclusions
About SOLVAY – Who we are

- **SOLVAY** is an **international industrial Group active in Chemistry**. It acquired **RHODIA** in September 2011 and now counts over 29 000 employees worldwide.

- It offers a broad range of products and solutions that contribute to improving quality of life.

- A strong commitment to **sustainable development** with a clear focus on **innovation & operational excellence**.

- Two main sectors of activity: **Chemicals** and **Plastics**.
About SOLVAY – Who we are

90% of Sales among the TOP 3

- **#1 Specialty Polymers**
  - High Barrier Polymers, High-Performance Engineering Polymers & Compounds, Fluorinated Polymers

- **#2 Polyamide & Intermediates**
  - PA 6.6 Polymers, Intermediates & Engineering Plastics

- **#1 Essential Chemicals**
  - Hydrogen Peroxide, Soda Ash & Sodium Bicarbonate

- **#1 Silica & Rare Earth Systems**
  - High-Performance Silicas, Rare Earths Systems

- **#1 Consumer Chemicals**
  - Specialty Surfactants, Phosphorus Chemistry & Diphenols

- **#3 Vinyls & Acetow**
  - PVC, Cellulose Acetate Fiber
About SOLVAY – Process Analytical Technologies

Process Analysers in SOLVAY
- Competence Centers in R&D-Brussels (2p) & Lyon (4p) for PAT research, development & engineering
- Local expert teams on each production site working as a network
- >8000 analyser systems installed worldwide

Primary Objective is improving
- Reliability
- Response time
- Maintenance work
- Footprint
- Standardisation (worldwide scale)
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Past Experience with Nessi Modular Systems

How we are proceeding in SOLVAY

- Step 1: building up experience with sampling
  - revamping old sampling systems
  - Introducing new systems (new projects)
  - “getting the feel” for maintenance

- Step 2: introducing the (micro)analysers
  - starting with traditional small analysers
  - then going for modern micro-analysers (µGC, µSpectr.)

- Step 3: … then we can think about connectivity (Nessi-Bus)
Past Experience with Nessi Modular Systems

- Focussing on NESSI 3D
  The ASTUD Concept (EIF)

- Installation:
  - On fast loop or derivation
  - On the sampling take-off point, reduces or eliminates the sampling line

- Integrated cross-flow filtration possibilities
- Improving on response time
- Easier t° control
- Low product and drain volumes
Past Experience with Nessi Modular Systems

- In the PVC process (2008) – Liquid EDC analysers
  - Sampling for Water in EDC analyser (7 barg – 50°C)
  - Sampling for EDC purity analyser (5 barg – 55°C)
Past Experience with Nessi Modular Systems

- In the H2O2 process (2011) – Reactor Vent gas analysers
  - Pre-sampling for Oxygen analyser in Oxydation reactor (8 barg – 60°C) - 95% N₂, 1,5% H₂O, organic/water aerosols
Past Experience with Nessi Modular Systems

- **In the Chlor-Alkali process (2010) – Chlorine analyser**
  - Sampling for Trace Moisture in Chlorine analyser outlet compression (0-20 mg/Kg - 4 barg - 30°C)
  - Perfectly adapted to Chlorine with PFA/PVDF body, Plastic or Hastelloy C screws, Kalrez/Chemraz O-rings
Past Experience with Nessi Modular Systems

- Experience limited to sampling but Nessi lives up to our hopes and expectations

- High reliability of the ASTUTE systems, low maintenance required (preventive replacement of critical o-rings once a year).

- No corrosion issues encountered

- Very corrosive processes may be addressed by using plastic modular systems. No dangerous leak issues encountered.

- Price remains an important discouraging issue

Ready to integrate analysers on the ASTUTE....
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Installing TDL on ASTUTE systems – PVC industry

PVC monomer production

Process Chemistry:
- Producing 1,2-Ethylene DiChloride (EDC)
- Cracking 1,2-EDC to Vinyl Chloride (VCM)

**Direct Chlorination**

\[ C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2 + \text{heat} \]

**Oxychlorination**

\[ C_2H_4 + 2 \text{HCl} + 1/2 \text{O}_2 \rightarrow C_2H_4Cl_2 + \text{H}_2\text{O} + \text{heat} \]

**Cracking of EDC**

\[ 2C_2H_4Cl_2 \rightarrow 2C_2H_3Cl + 2\text{HCl} - \text{heat} \]

Diagram: 
- Chlorine
- Ethylene
- Oxygen
- Water to WWT
- EDC
- HCl
- EDC Cracking
- VCM Purification
- EDC Purification
- Oxychlorination
- HT Direct Chlorination
Installing TDL on ASTUTE systems – PVC industry

- PVC monomer production

First observation of Nessi in SOLVAY plants (France):
Analyser #1 – Water in EDC
Analyser #2 – EDC purity

New TDL O2 Analysers installation (Belgium)
Installing TDL on ASTUTE systems – PVC industry

- **Traditional O₂ analyser on Oxychlorination reactor vent gas**

  - Principle: Paramagnetic
  - Goal: Security - Explosion prevention in OXY reactor
    (3 redundant analysers)
  - Process Conditions:
    - Pressure **6 Barg**; Temperature **40°C**
    - Composition 50% N₂, 30% CO₂, 5% CO, 5% C₂H₄, 4% EDC, <2% H₂O
  - [O₂] range: 0-5%vol (alarm @3%vol)
  - Enclosure: Analyser House
  - Other analysers on vent gas: CO, CO₂, C₂H₄ (Process control)
Installing TDL on ASTUTE systems – PVC industry

- Traditional $O_2$ analyser on Oxychlorination reactor vent gas

Sampling point

60 m $\varnothing 1/2''$ insulated sampling line

Analyser House
Installing TDL on ASTUTE systems – PVC industry

- Traditional $O_2$ analyser on Oxychlorination reactor vent gas

Common fast loop

Analyser loops

Sample conditioning

Analysers ($O_2$, CO, CO$_2$, C$_2$H$_4$)
Installing TDL on ASTUTE systems – PVC industry

Technical issues with traditional analysers

- Response time must be <30 sec (Process safety requirement)
  - Fast sample transport to analyser mandatory
  - Sample pressure must be near atmospheric (6 barg at sampling point) → Pressure reduction near sampling point mandatory!
  - Response time of paramagnetic analyser (+/-10 sec)

- Risk of Condensates
  - cold spots have to be avoided (fouling, flow disturbances)
  - gas toxicity
    - safety of analyser house must be respected (IEC61285)
  - sampled gas wasted to incinerator (not recycled).
    - to ensure fast response time, high flows/volumes are required (>2 m³/h) → Significant loss of EDC and C₂H₄
Installing TDL on ASTUTE systems – PVC industry

- Installing Tunable Diode Laser analysers

  - Advantages
    - Response time <3 sec
    - Very low maintenance (no moving parts)
    - High Specificity
    - Reliability (if well installed)
    - Stability (calibration 1/year)
    - Small footprint
    - Eex d version available
    - SIL rated

  - Disadvantages
    - limited to gas samples
    - Sensitive to process conditions (Pressure and t° compensation often mandatory, window protection with N₂ purge mandatory)
Installing TDL on ASTUTE systems – PVC industry

Installing a TDL On-Line with ASTUTE

Why?

- Retaining fast response time and all other advantages of TDL
- Limiting the flow (less waste to incinerator)
- Pressure control with Pressure regulators (adv. versus in-line config.)
- t° control (no condensation, no cold spots)
- Validation (zero and validation gases) (adv. versus in-line config.)
- No window purging necessary (adv. versus in-line config.)
- Independant of process, TDL may be dismounted and cleaned after process upsets (adv. versus in-line config.)
Installing TDL on ASTUTE systems – PVC industry

- Installing the $O_2$ TDL-ASTUTE on OXY vent gas
Installing TDL on ASTUTE systems – PVC industry

- Installing the O₂ TDL-ASTUTE on OXY vent gas
  - Total flow +/-350 l/h
  - Total Response time (T90) +/-12s
  - NEO Lasergas III TDL
  - No pressure compensation
Installing TDL on ASTUTE systems – PVC industry

- $O_2$ TDL-ASTUTE performances vs traditional analysers

Diagram showing TDL Analyser (Precision +/- 0.01% vol O2) vs Paramagnetic analysers (3x) (Precision +/- 0.05% vol O2). The graph illustrates the data from 22/05/2012 00:30:59 to 22/05/2012 02:32:38, with a 1h30' interval.
Installing TDL on ASTUTE systems – PVC industry

- $\text{O}_2$ TDL-ASTUTE performances vs traditional analysers

Response time improvement: +/- 25 seconds
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Installing H₂O sensor on Nessi systems – ChlorAlakali industry

- Chlorine Production (Cl₂ circuit after electrolysers)

First trials of Nessi on Chlorine in SOLVAY plants (Belgium): Moisture analyser
Installing H₂O sensor on Nessi systems – ChlorAlkali industry

Traditional trace moisture analyser in Cl₂ outlet compression

Traditional analysers:
- Principle: Electrolytic P₂O₅
- Goal: Corrosion prevention
- Process Conditions:
  Pressure 4 Barg; Temperature 30°C
- [H₂O] range: 0-20 mg H₂O / kg Cl₂
- Enclosure: Analyser Cabinet
- Sampling issues:
  - Strict control on sample pressure and flow to the sensor,
  - Adsorption/desorption of moisture in sample transport (tubing, filters, flowmeters) causing t° related memory effect,
  - gas toxicity,
  - corrosion.
Installing H₂O sensor on Nessi systems – ChlorAlakali industry

- Traditional trace moisture in Cl₂ analyser (P₂O₅ sensors)

Strong Corrosion Issues!!!
Memory effect in sampling line

Extern. Sampling
(Pressure control)

Intern. Sampling
(Flow control)

P₂O₅ Probe + holder
Installing $\text{H}_2\text{O}$ sensor on Nessi systems – ChlorAlakali industry

- Installing a $\text{P}_2\text{O}_5$ sensor on-line with ASTUTE
  - ASTUTE body PVDF (EIF)
  - Parts PVDF/PFA (EM-Technik)
  - Cabinet insulated and heated @30°C
Installing H$_2$O sensor on Nessi systems – ChlorAlakali industry

- Installing a P$_2$O$_5$ sensor on-line with ASTUTE
Installing H₂O sensor on Nessi systems – ChlorAlakali industry

Installing a P₂O₅ sensor on-line with ASTUTE

- Objectives:
  - minimising adsorption/desorption effect by reducing sample transport line (length and volume).
  - tighter control on t° in smaller insulated cabinet
  - reducing size/footprint

- First results obtained in parallel with an existing analyser expected July 2012

- Direct installation on sampling point (Process flange) expected before December 2012
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Future Perspectives

- TDL-ASTUTE with combined emitter-receiver unit (folded optical path)

Mettler-Toledo (GPro 500)

Quartz Corner-cube reflector

Eex D head
Future Perspectives

- TDL-ASTUTE with combined emitter-receiver unit (folded optical path)

Adapting to ASTUTE
Future Perspectives

- TDL-ASTUTE with combined emitter-receiver unit (folded optical path)

Spectra Sensors
Future Perspectives

- List of Nessi applications in preparation in SOLVAY

  - \( \text{H}_2\text{O}_2 \) process
    - TDL-Astute for \( \text{O}_2 \) in all reactors
    - Polarographic \( \text{O}_2 \) sensors and Resistivity \( \text{H}_2 \) sensor for \( \mu \)-pilot units
  - PVDF process
    - \( \text{O}_2 \) in VDF monomer return to reactor using TDL-Astute
  - PVC process
    - \( \text{O}_2 \) in chlorination reactors
    - \( \text{HCl} \) in liquid VCM (monomer)
    - \( \text{C}_2\text{H}_2 \) in return \( \text{HCl} \) to oxychlorination reactor
  - ....
Future Perspectives

- **Polarographic O\textsubscript{2} sensors and Resistivity H\textsubscript{2} sensor for μ-pilot units**
  
  - H2Scan Hydrogen sensor
    - HY-OPTIMA 1700
    - range 0-10\%v
  
  - Mettler-Toledo Oxygen sensor
    - InPro6850i
    - range 0-100\%v
Future Perspectives

- Polarographic $O_2$ sensors and Resistivity $H_2$ sensor for $\mu$-pilot units

Process Conditions:
- $P$ 5-50 barg
- $t^\circ$ 20-50°C
- $H_2$ measurement in ESD

Sample in

P Reducer

Sensor $O_2$

Sample out

Sensor $H_2$

Back P Reducer

Cal. gas in
Future Perspectives

Future technical developments for ASTUTE

- UV-NIR photometry
  - development of flow cells and fiber optics adapted to Astute

- Photoacoustic Infrared absorption photometry
  - development of source-sensor adapted to Astute

- µ-GC
  - something fast, something ATEX (NEMS) ….

- MultiLaser TDL (Multicomponent analyser), QCL
  - O2, CO, CO2, C2H4 in (oxy)chlorination reactor

- Raman (optograph) …. And many more.
Conclusions

- Past experience has proven the high flexibility and reliability of the ASTUTE system as a process sampling device even when applied to a corrosive process.

- It is now available in plastic material (PFA/PVDF) for processes where stainless steel may not be the most suitable material.

- Its modularity and versatility have enabled us to bring sensors as closely as possible to the process in order to improve response time and measurement stability.

- We have Integrated a TDL analyser to the ASTUTE system, retaining all the advantages of this technology while limiting the loss in response time caused by the extractive configuration and avoiding difficult/expensive window purging.

- The path is wide open to adapt other technologies to the ASTUTE system
Thank you