



OPTICAL CHEMICAL SENSORS FOR PROCESS CHEMICAL ANALYSIS



UCM

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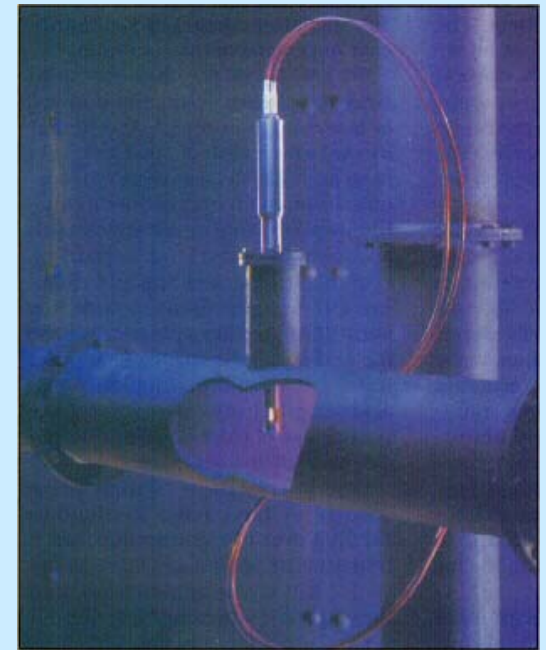
Concept of “process analysis”

Real-time measurements of reactants, intermediates and/or products that provide **direct information** about the process or reaction, its efficiency and yield for *control, optimization* and other *decision-making* steps.



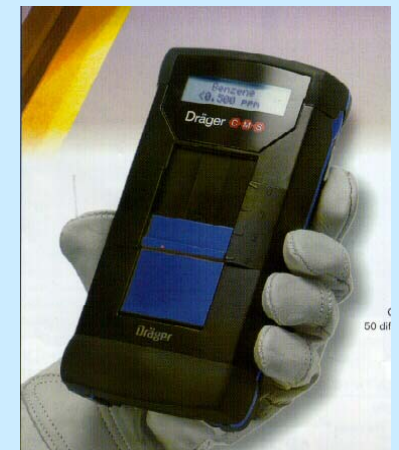
Includes...

- ✓ sampling
- ✓ pretreatment
- ✓ measurement
- ✓ interpretation
- ✓ application of data



Industrial incentives for process analyzer technology

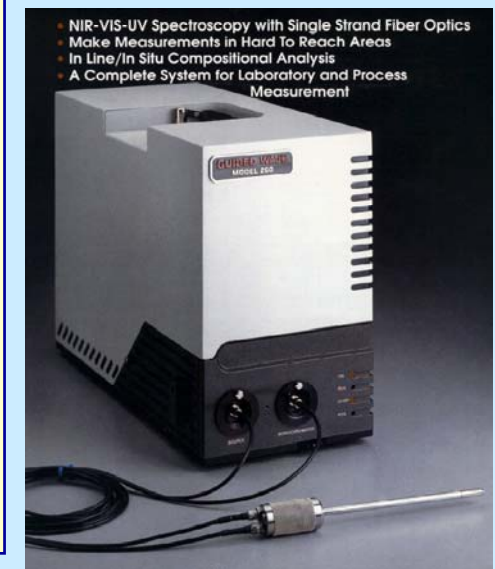
- ❑ Automated process control
- ❑ Optimal operating efficiency
- ❑ Total product quality control
- ❑ Comply with governmental regulations
 - industrial safety
 - hygiene
 - air/water/land quality



K.J. Clevett, *Process Control Qual.* 1994, 6, 81

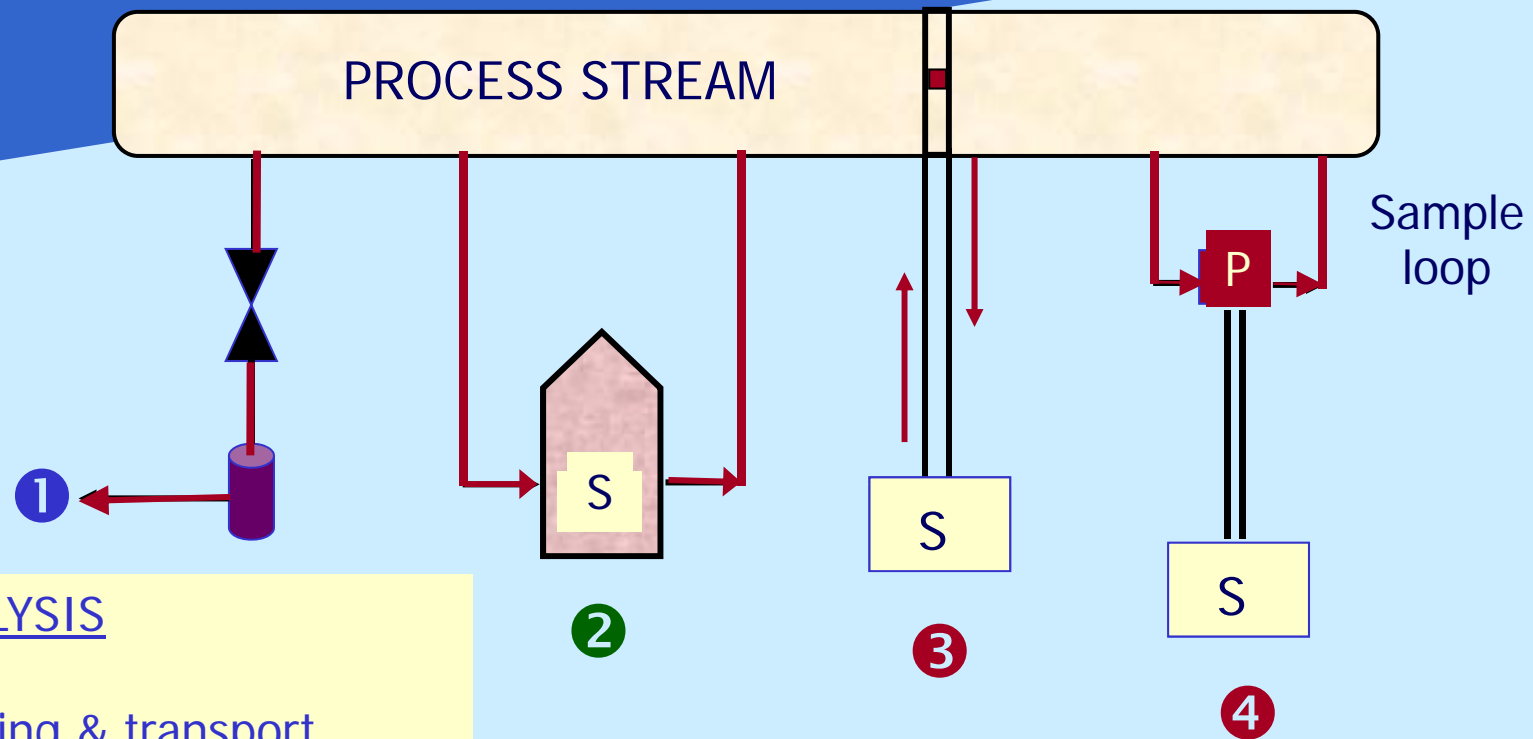
Development of process analyzers is also driven by analytical technology

- Origins: *IR* absorption recorders and paramagnetic *oxygen* analyzers (late '30s)
- Differential *thermal* conductimeters & *distillation*-type analyzers ('40s)
- UV/vis spectrometers ('50s)
- Gas chromatographs ('60s)
- Process mass spectrometers ('70s)
- NIR analyzers ('80s)
- FT-IR, NIR, Raman/fiber optics/**chemometrics**



R.E. Sherman, “Analytical Instrumentation: Practical Guides for Measurement and Control”, Instrum. Soc. of America, NC, 1996

Main categories of process measurements



OFF-LINE ANALYSIS

- ☹ Discontinuous
- ☹ Manual sampling & transport
- ☺ Sophisticated lab instruments
- ☺ Detailed quality control (long-term)

AT-LINE ANALYSIS

- ☹ Manual sampling
- ☹ Trained personnel
- ☺ Reduced time delays

ON-LINE PROBES

- ☺ Automatic sampling & transport
- ☺ Autonomous analysis
- ☹ Intermittent measurements

IN-LINE PROBES

- ☺ Eliminates sampling
- ☺ Continuous measurements

F. McLennan & B.R. Kowalski (eds.), *Process Analytical Chemistry*, Blackie, London, 1995

Requirements of process analyzers

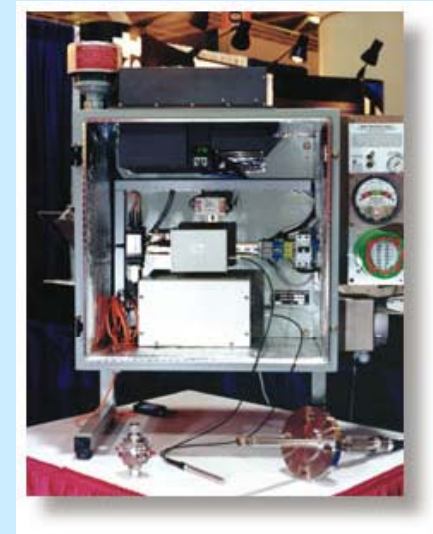
- ❑ Highly **automated** (unattended operation)
- ❑ **Rugged**, operable in *hazardous* areas
- ❑ **Simple**, serviceable by untrained personnel
- ❑ Adequate vendor technical **support**
- ❑ **Calibrated** for long time/automatic recalibration
- ❑ Fast enough **measurement rate**

$$\tau = \frac{\tau_R}{1 + k\tau_R}$$

τ : process time constant

k : chemical reaction rate constant

τ_R : reactor volume/volumetric flow rate



Sampling strategies

A **sampling system** is “an assembly of components and equipment with the function of taking a *representative* sample from the process, *condition* it, *transporting* and *presenting* it to the analyzer, and *disposing* of it”.

Depends on the nature of...

- ✓ the type of *line analysis*
- ✓ the process *analytes*
- ✓ the *information* required
- ✓ the type of *analyzer*



Analyzer interfacing is one of the most important issues!

(e.g. sampling handling issues are **85%** of the problems with uv/vis process analyzers, light source failures contribute 5%, opto-electronic problems and others make the rest) (Sherman, 1996)

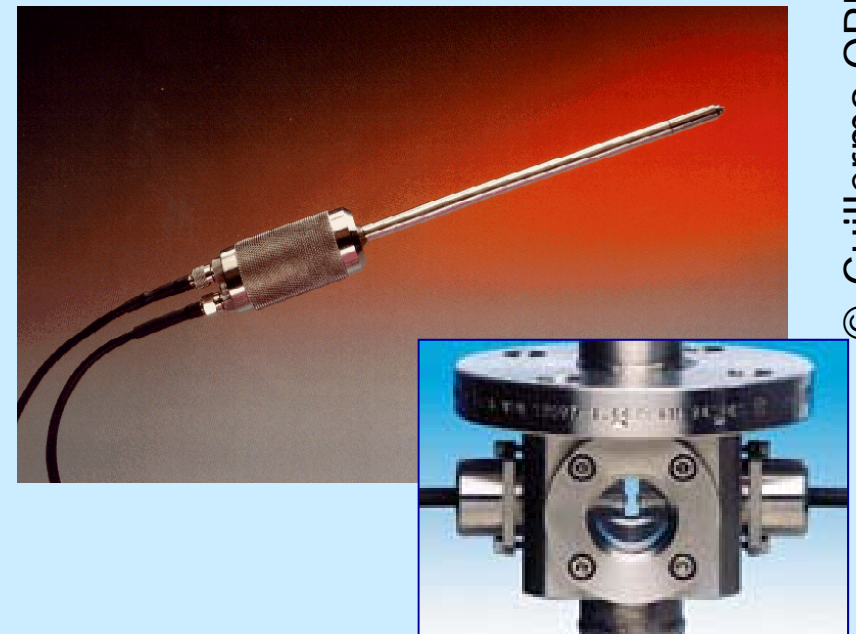
Pay attention to spatial heterogeneity of the sampled material

E.A. Houser, “*Principles of Sample Handling and Sampling Systems Design for Process Analysis*”, ISA, Pittsburgh, PA, **1972**

Process optical spectroscopic techniques

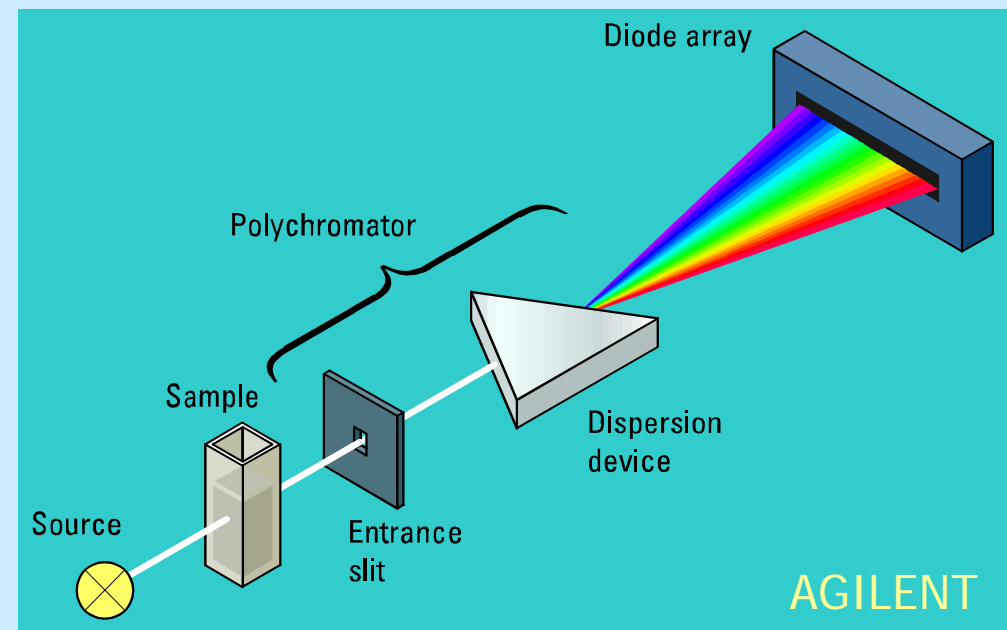
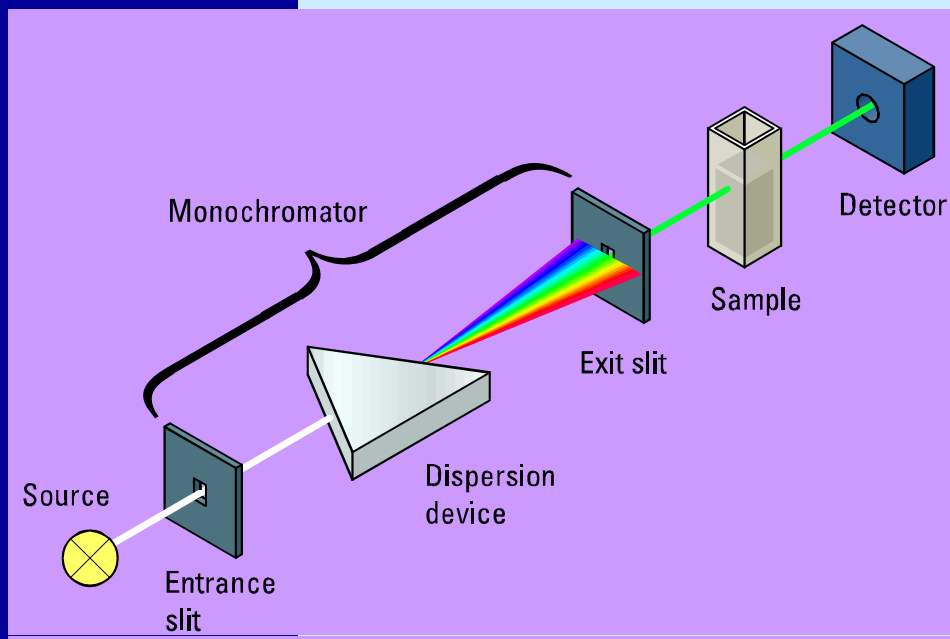
- **Electronic** spectroscopies
 - UV
 - VIS
 - *Fluorescence*
- **Vibrational** spectroscopies
 - NIR
 - IR
 - Raman
- Refraction index
- Image analysis

+ optical fiber (+sensor)



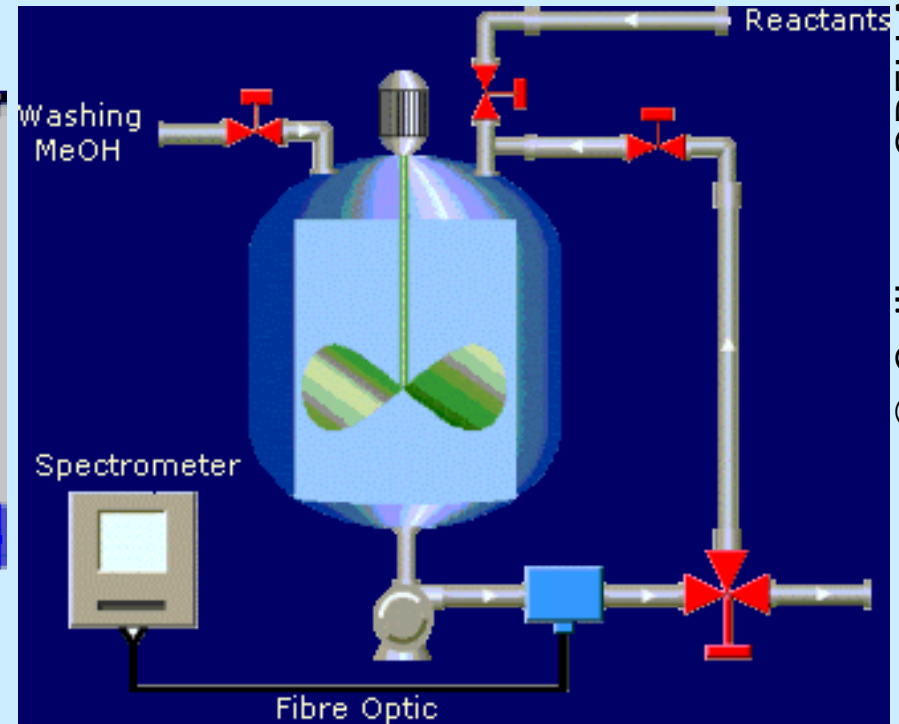
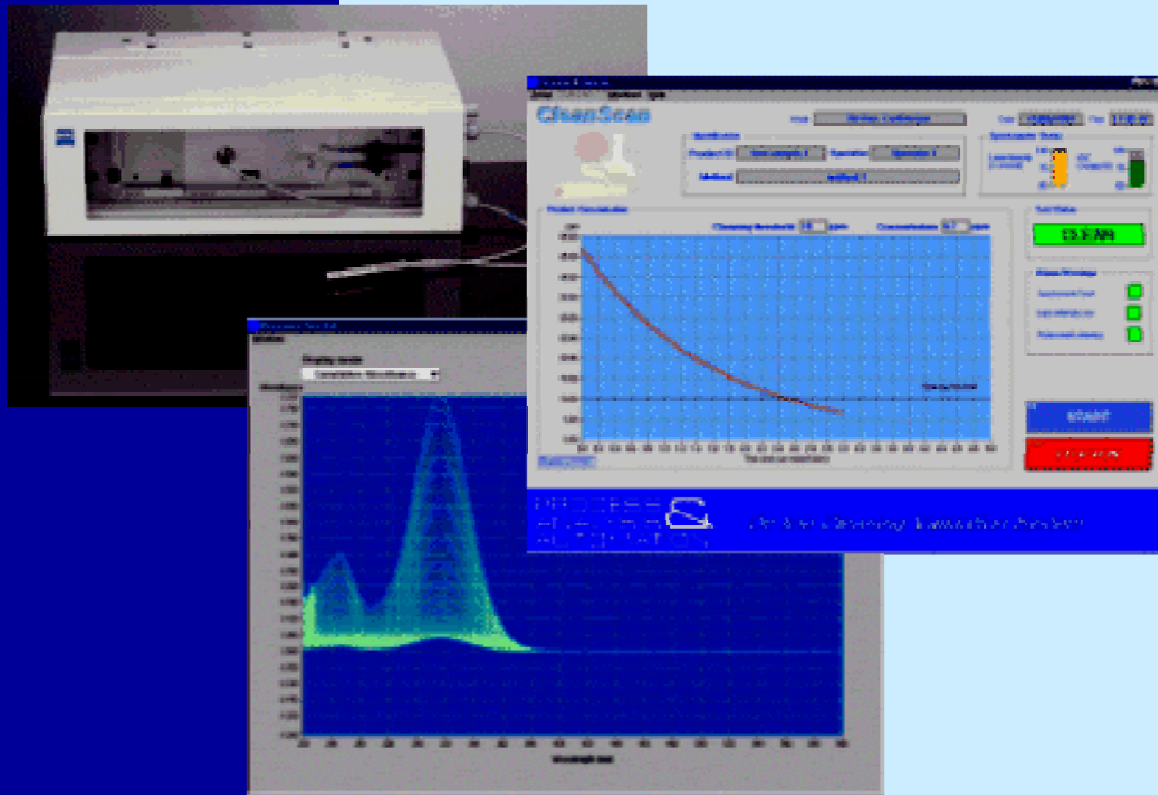
Process UV/Vis spectroscopy

- Scanning analyzers
- **Photodiode array analyzers**



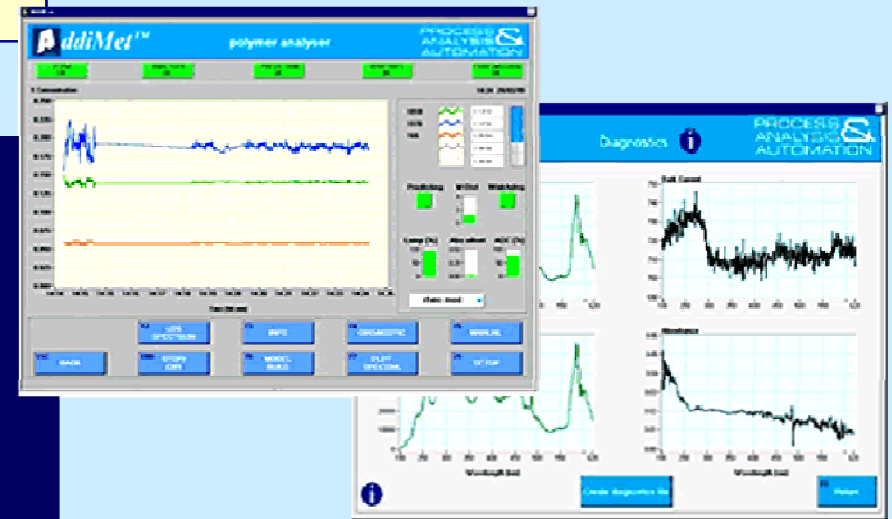
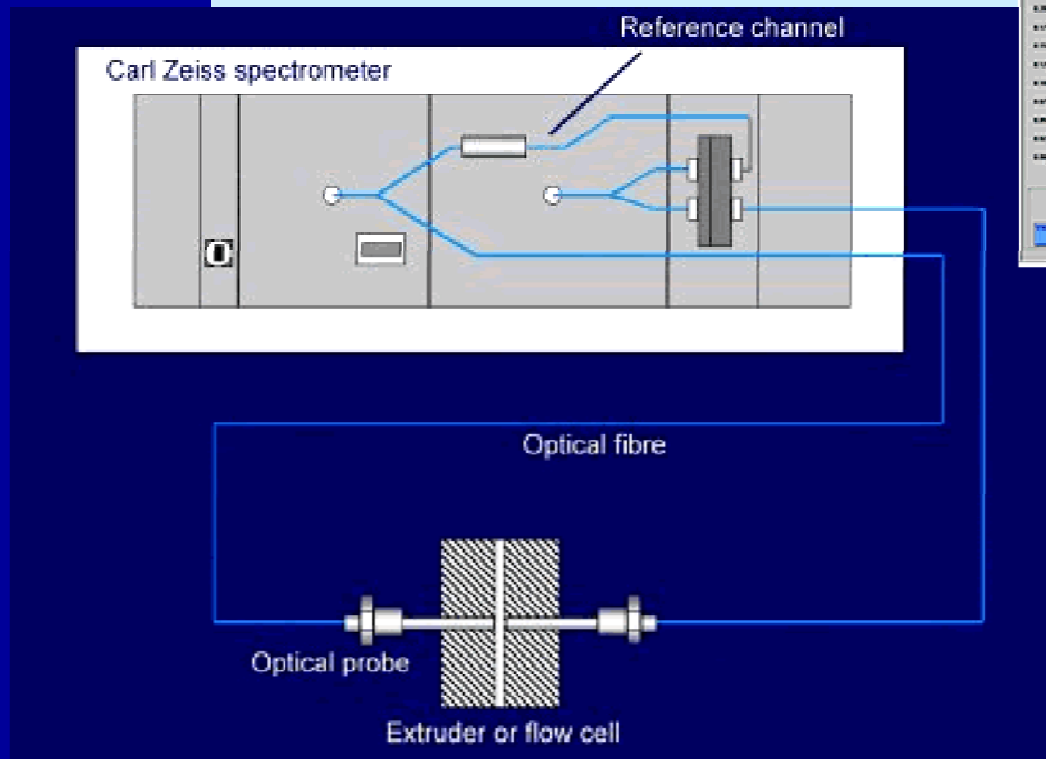
Process analysis by UV-VIS sensors

Industrial cleaning validation



Process analysis by UV-VIS sensors

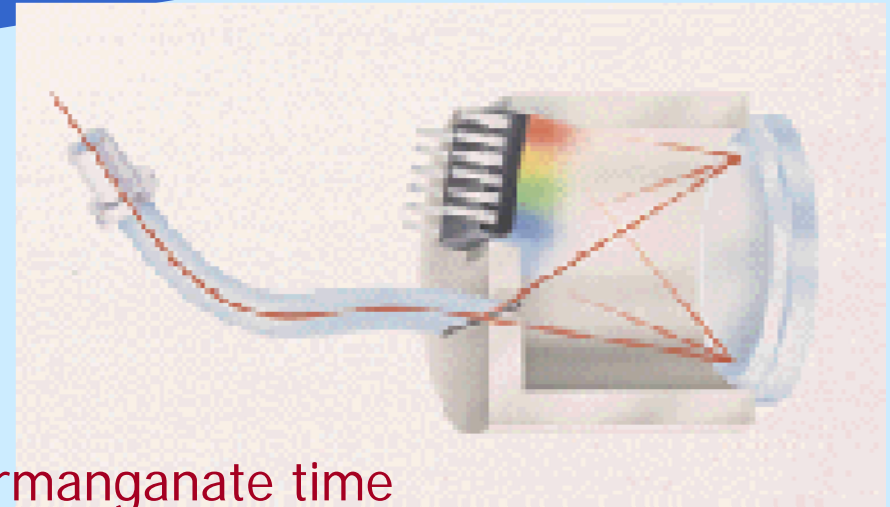
On-line analysis of **polymers** and **additives**



Process analysis by UV-VIS sensors

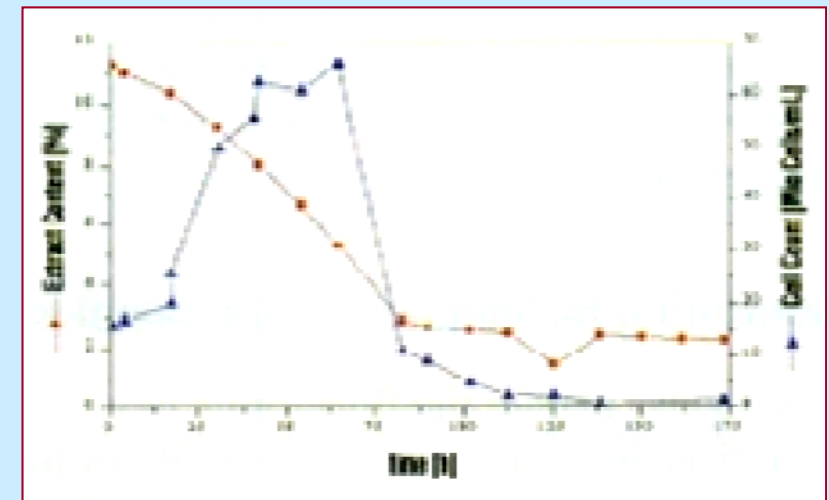
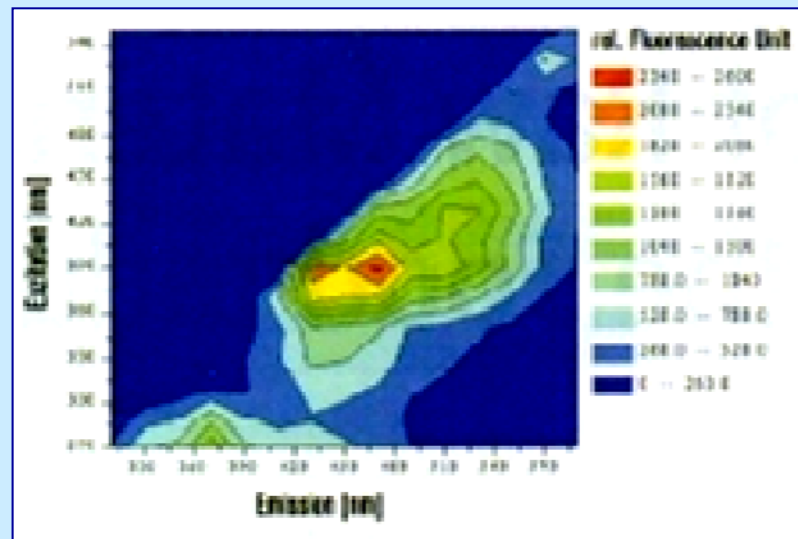
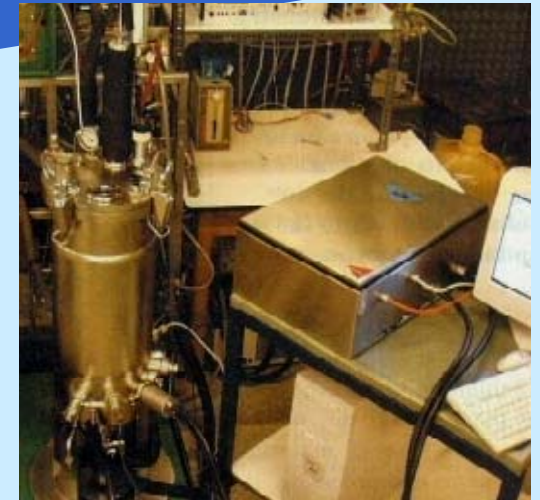
Monolithic spectrometers

- Automated measurements of permanganate time
- Analysis of aromatic hydrocarbons (BTX) in process water
- Optical dissolution analysis and control
- In-line analysis of flavored waters
- Agricultural harvest machines
- Color measurements



Process analysis by fluorescent sensors

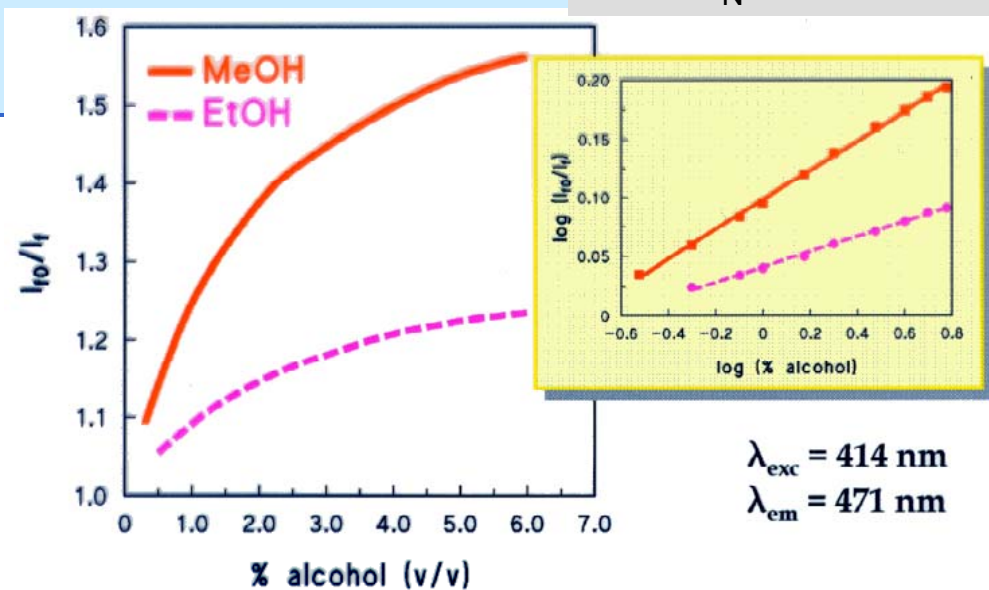
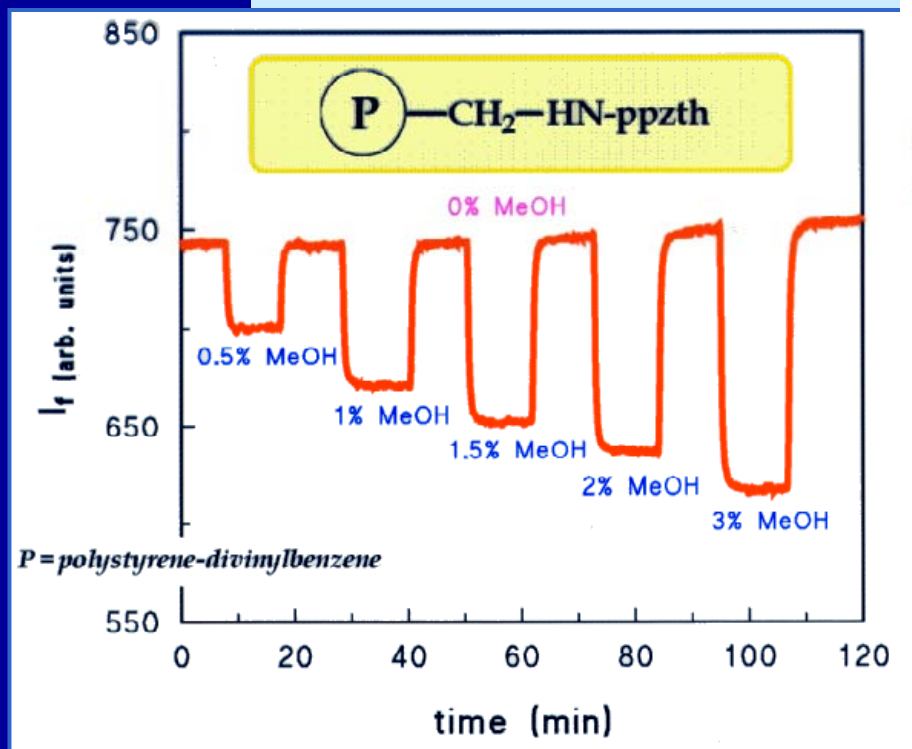
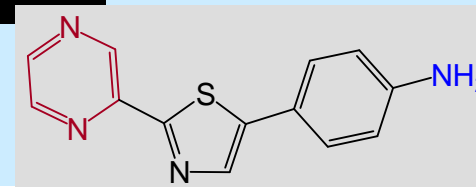
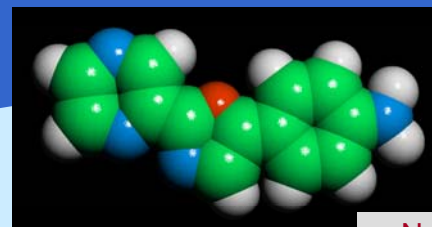
Monitorization of **extract** content and **cell** count in **beer brewing**



T. Scheper et al. *Uni. Hanover*
Gilde Brauerei AG, *Hanover*
Delta Light & Optics, *Denmark*

Process analysis by fluorescent sensors

Monitorization of **alcohols** in **unleaded petrol** blending lines



G. Orellana et al., *Span. Pat.* **2065268**

G. Orellana et al., *Anal. Chem.* **1995**, *34*, 2231

Process analysis by luminescent sensors

Smart food packaging

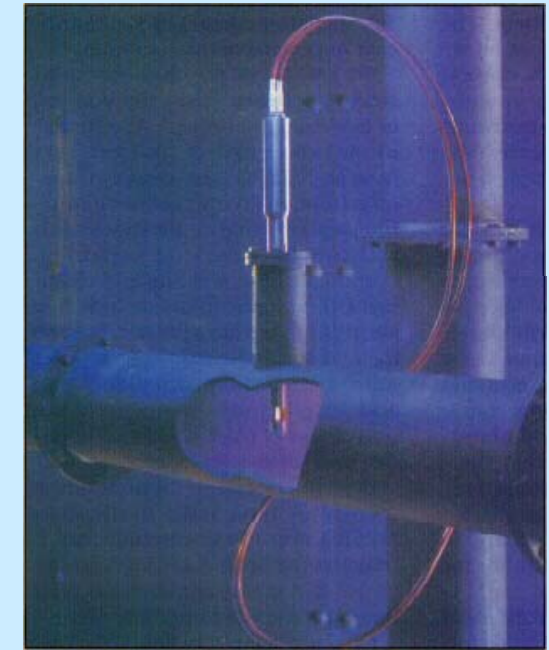
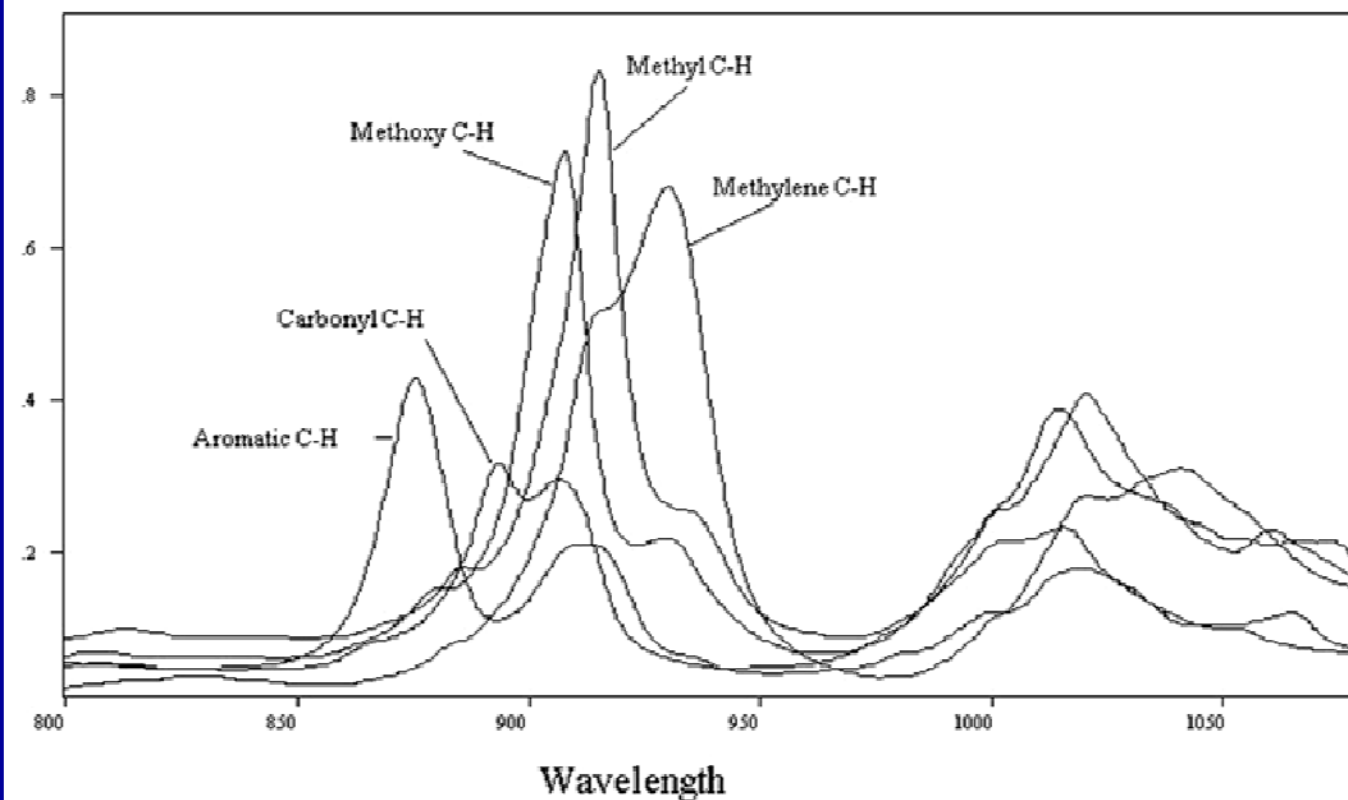


O_2 $[Ru(dip)_3]^{2+}$

CO_2
 $[Ru(dip)_3]^{2+} / BTB$

Process analysis by NIR sensors

Determination of **octane number**



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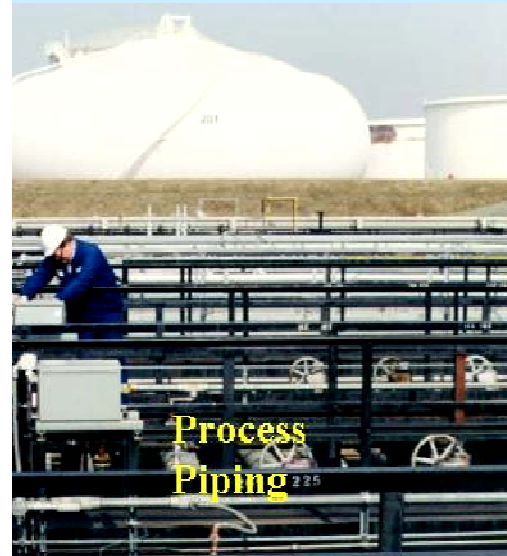
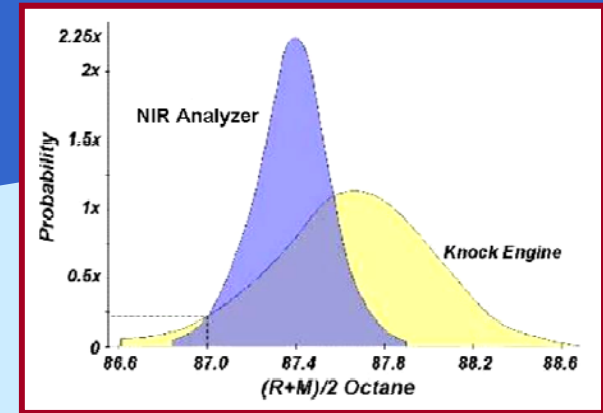
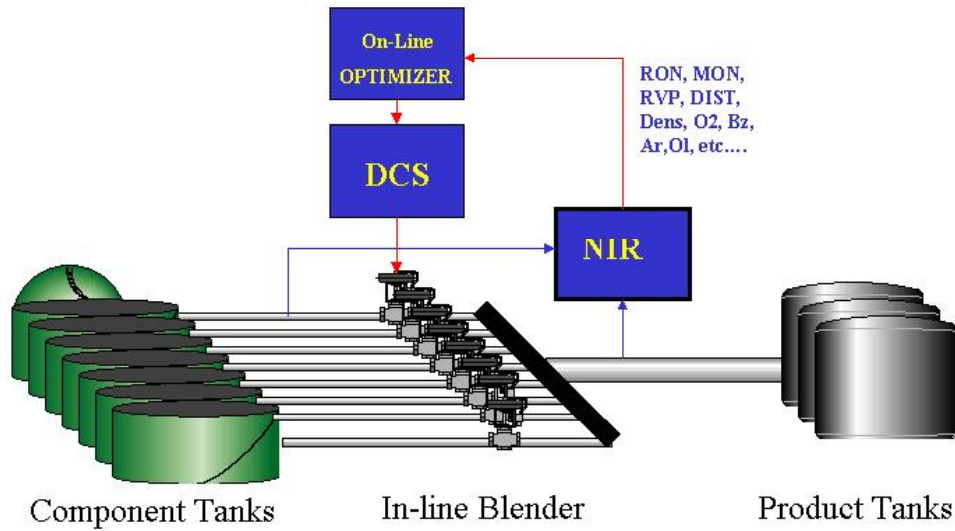
Chemometrics!!!

Patented wavelengths:
Maggard, *US Pat. 5,349,189*
(1994)

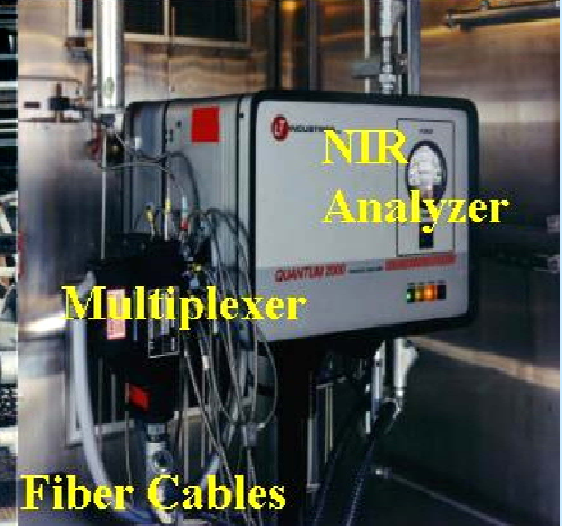
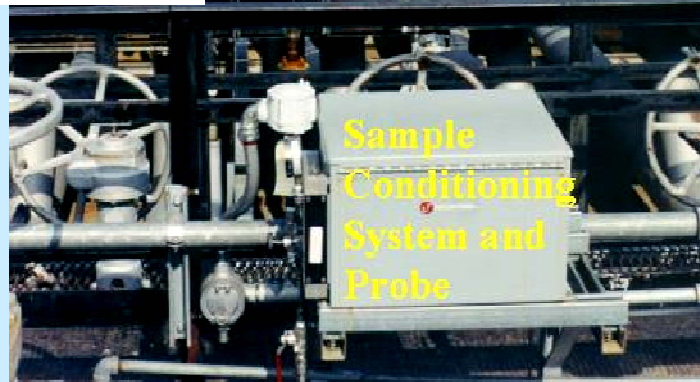
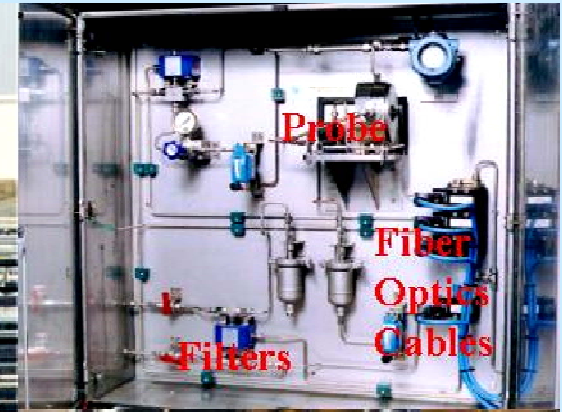
Process analysis by NIR sensors

Determination of octane number

Most of Savings Due to Blend Optimizer With NIR

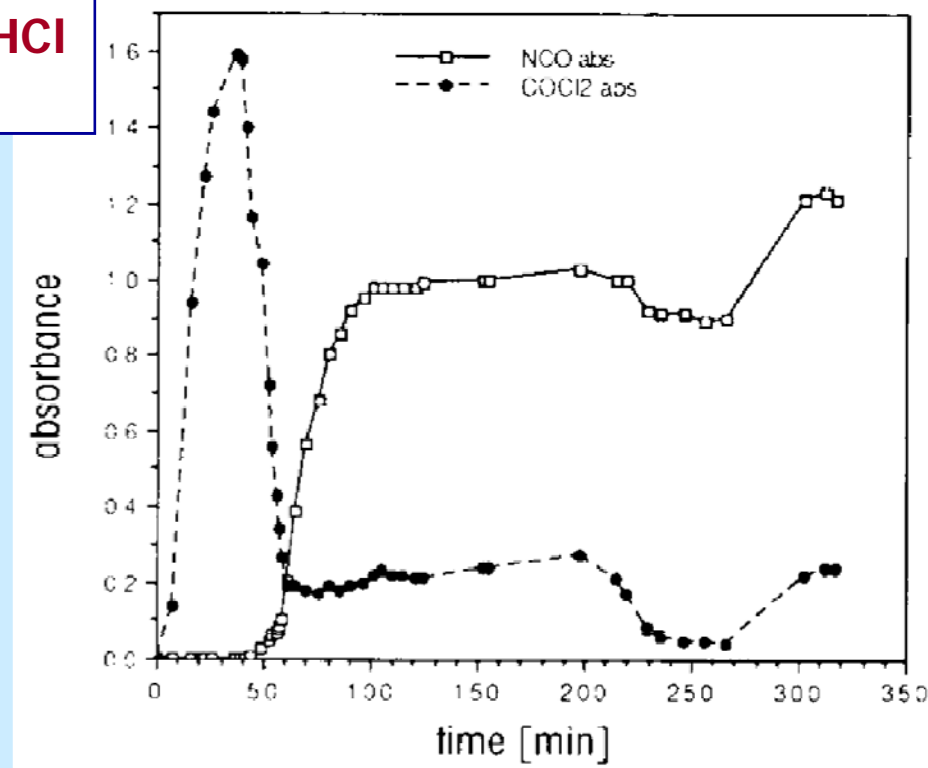
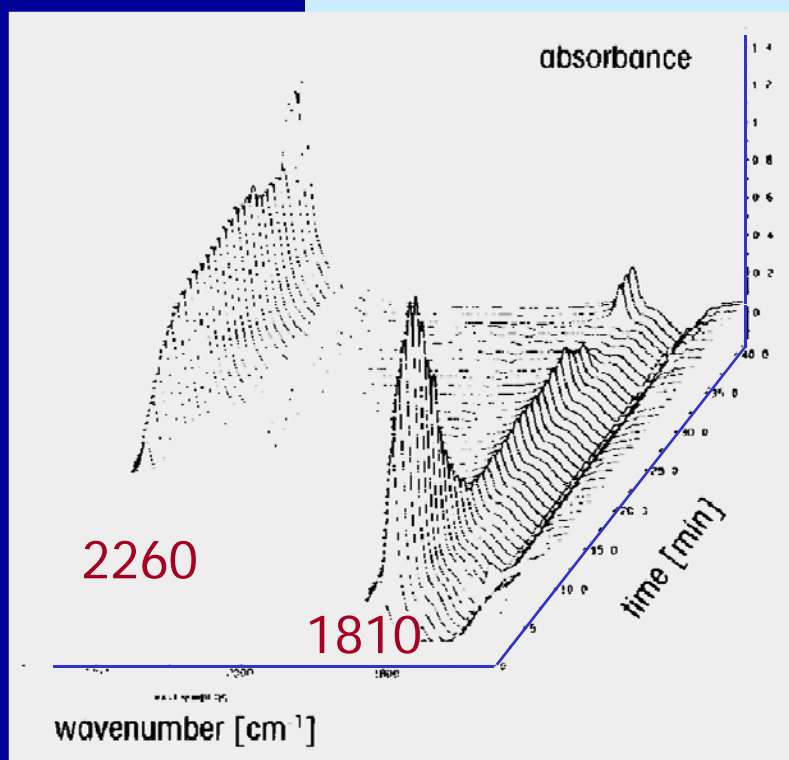
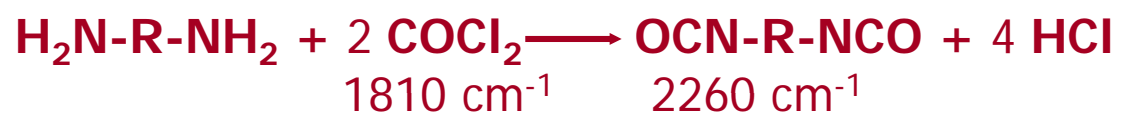


Process Piping



Process analysis by FT-IR fiberoptic sensors

Phosgenation of diamines



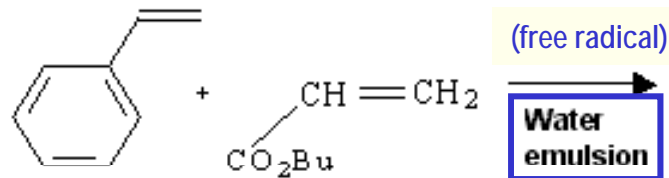
ReactIR®



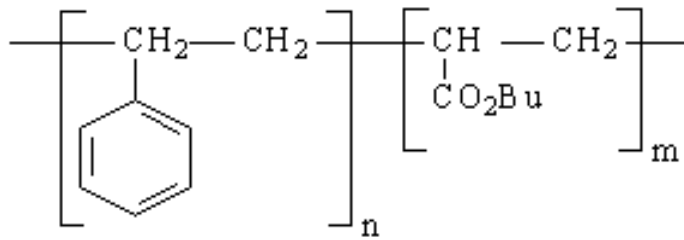
Process analysis by Raman sensors

Monitorization of **emulsion polymerization** reactions

Reaction Summary



Monomers



Copolymer

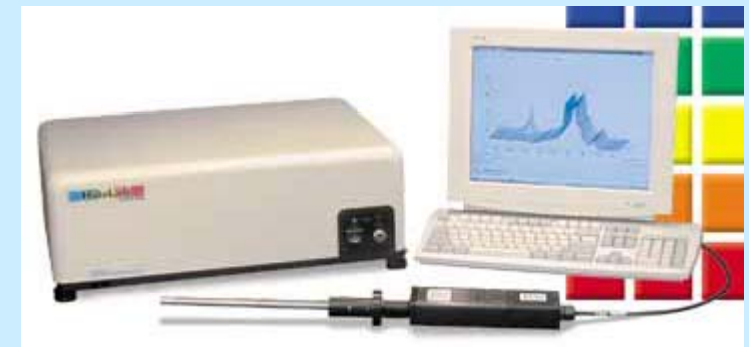
785 nm LD exc.

50 μm opt. fiber (excit.)

100 μm opt. fiber (return)

Important process for:

- paints
- adhesive products
- synthetic rubbers
- solid supports

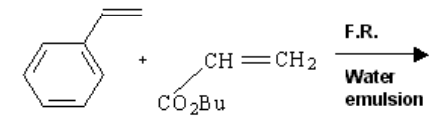


KAISER OPTICAL SYSTEMS, Inc.

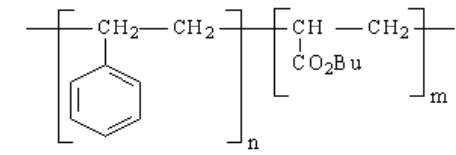
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Monitorization of **emulsion polymerization** reactions

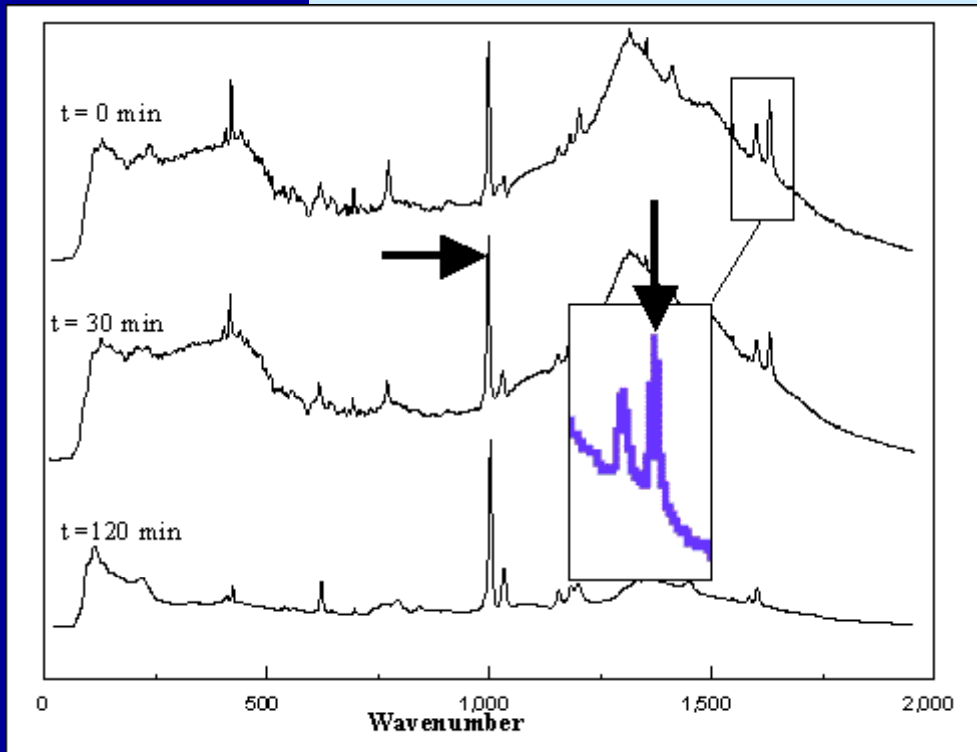
Reaction Summary



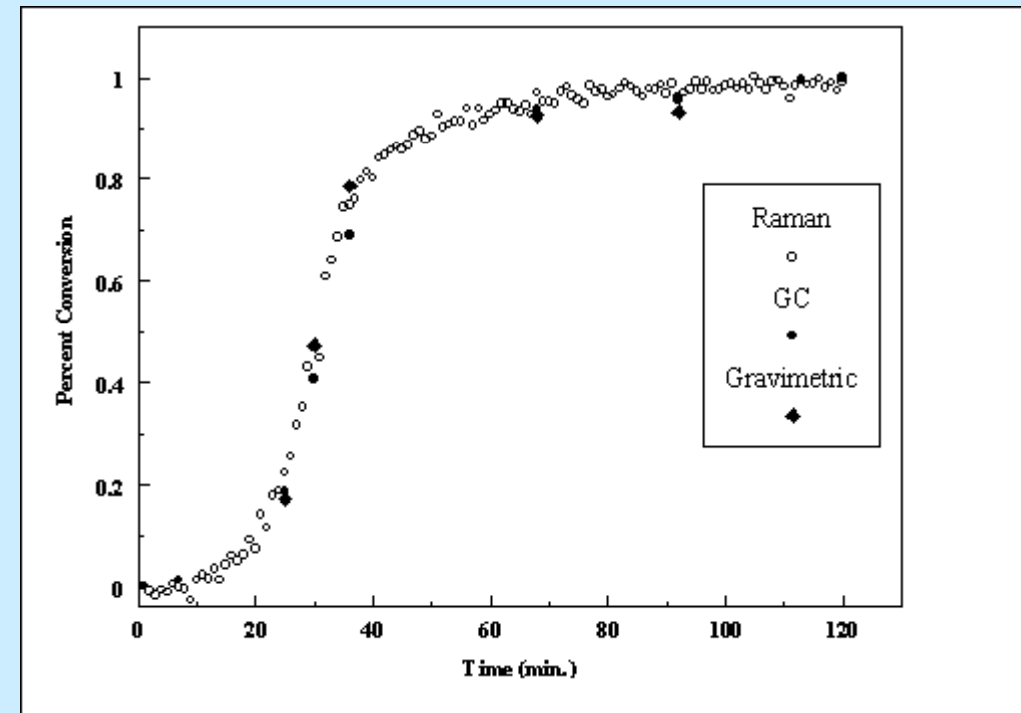
Monomers



Copolymer



(ratiometric)



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