

# On-line polyethylene additives analysis using a diode array uv / visible spectrophotometer and Charm Works

Ron Belchamber  
Process Analysis and Automation



株式会社 スペクトラ・コープ

〒164-0011 東京都中野区中央4-4-5第一小林ビル

Tel. 03-5328-2858 Fax. 03-5328-2859

URL <http://www.spectra.co.jp>

# Process Analysis & Automation

**Fernhill Road, Farnborough  
Hampshire  
GU14 9RX, UK**

**tel: +44 1252 373000**

**[www.paa.co.uk](http://www.paa.co.uk)**

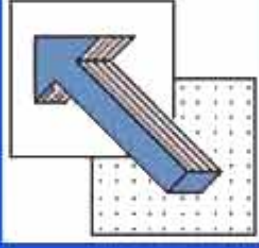
# Process Analysis & Automation

- Process analysis systems
- Multivariate process analysis software
  - ◆ Charm Works
- Sonic product development
- Acoustic emission monitoring systems
- Laboratory automation

# Applications - vertical markets

- Antioxidants in polyolefin melts
- Automation of standard tests
  - ◆ permanganate time
  - ◆ Hazen colour
- Batch processing
- Solvent purity
- Multicomponent stream composition

**HAMILTON**



**Custom Sensors  
& Technology**

**PROCESSES  
ANALYSIS  
AUTOMATION**

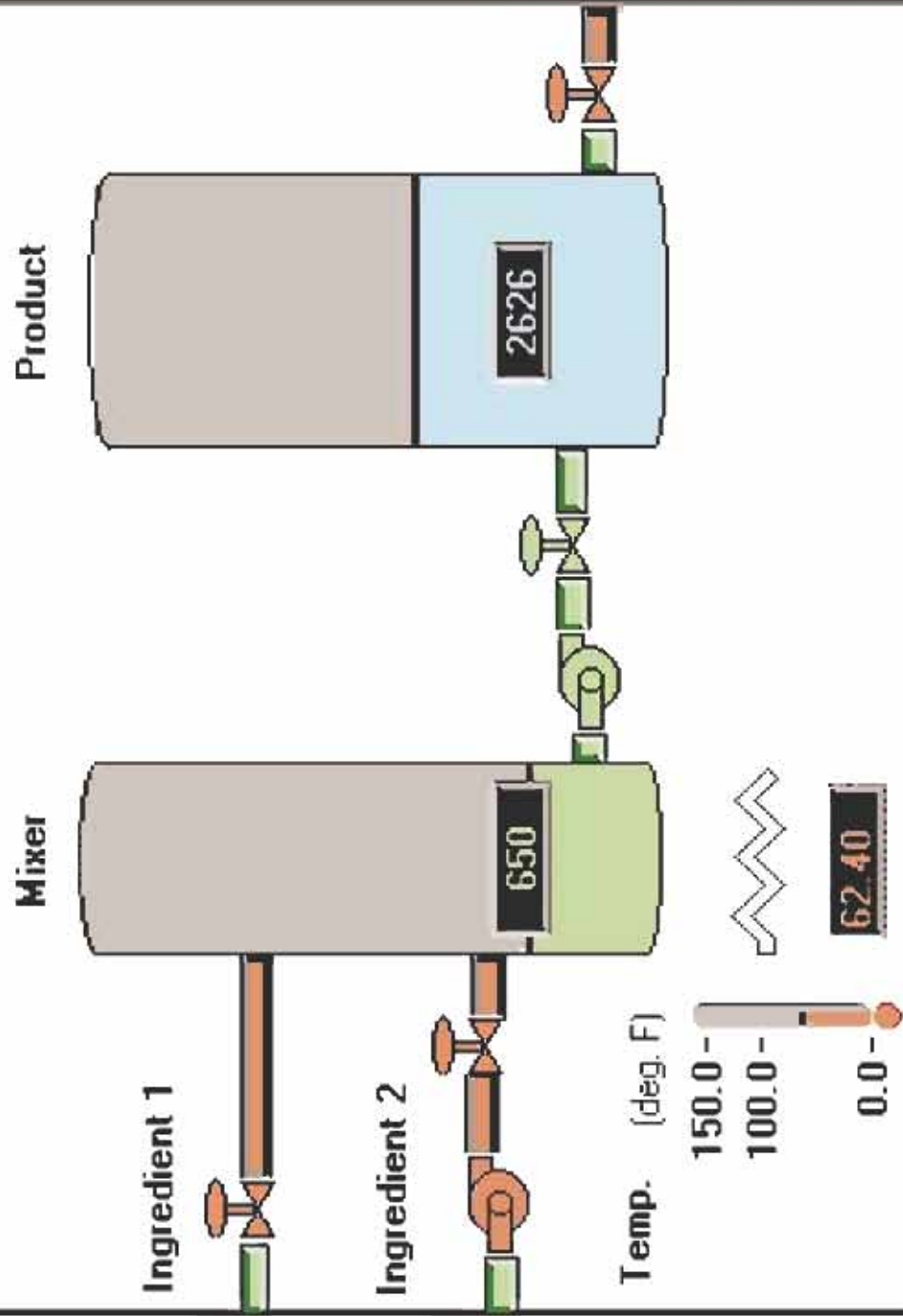


# LabVIEW

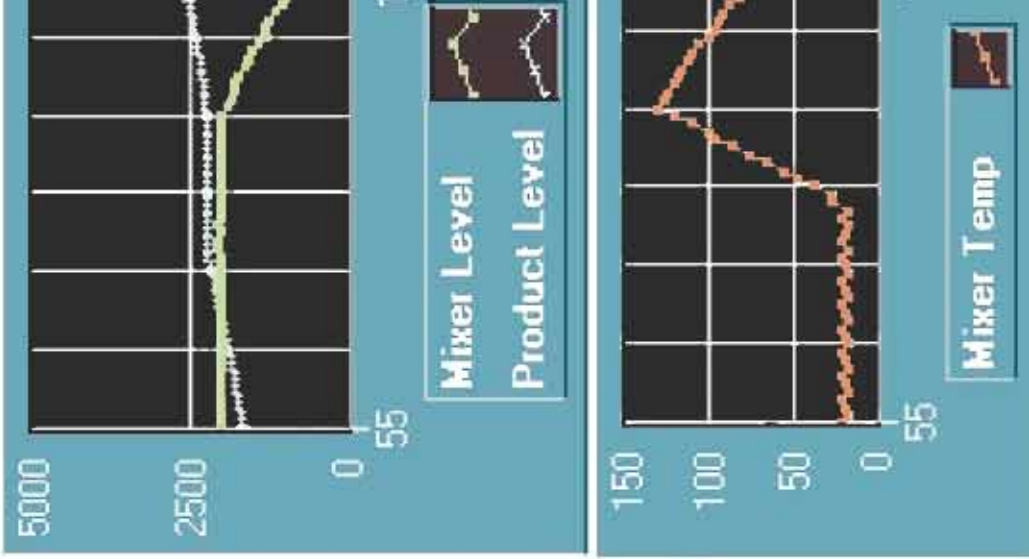
- Graphical programming environment
- Designed specifically for instrumentation
- Good graphical user interface
- High connectivity
- Charm Works add on toolkit provides chemometrics



Process



Operating Trends



RETURN [F4]

MORE INFO... [F5]

IN AUTO MODE

MANUAL [F3]

HELP [F1]

# Charm Works

- Chemometrics for real time process analysis
- LabVIEW tool kit
- PLS, PCA, SIMCA
- Easy to use



**Instrument  
drivers**

**SPC  
toolkit**

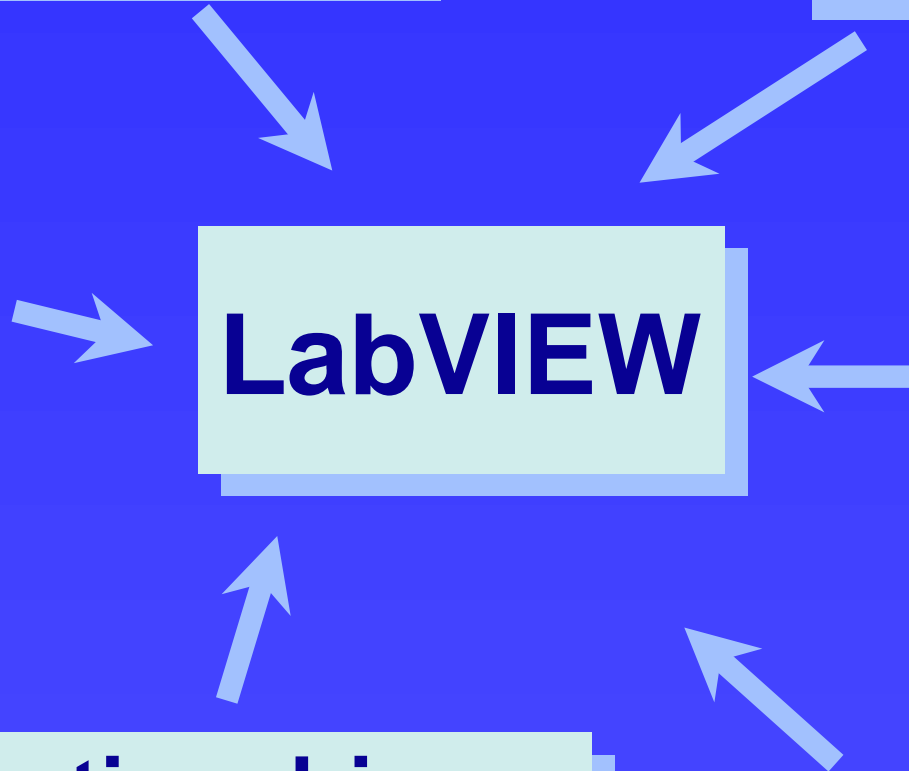
**Windows  
DLL,  
DDE, CINS**

**LabVIEW**

**SQL  
toolkit**

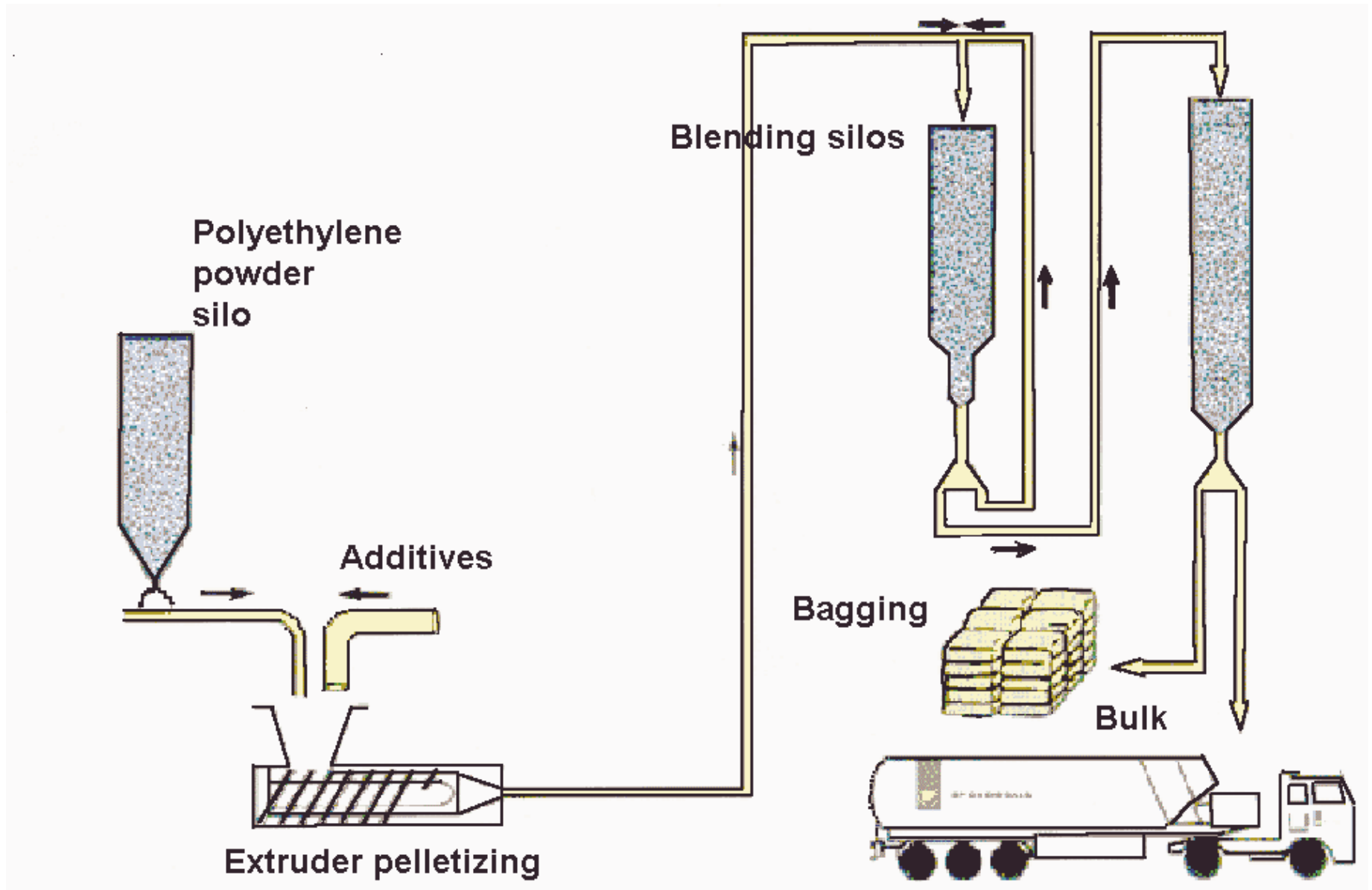
**Communication drivers  
TCP/IP, serial, ModBus,  
FieldBus**

**Charm Works**



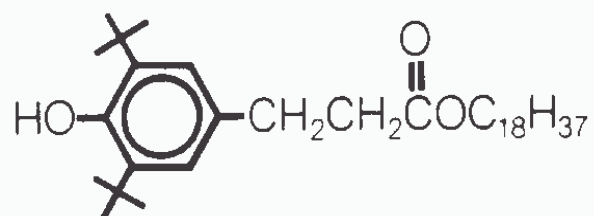
On-line polyethylene additives  
analysis using a diode array uv /  
visible spectrophotometer and  
Charm Works

# Polyethylene manufacturing

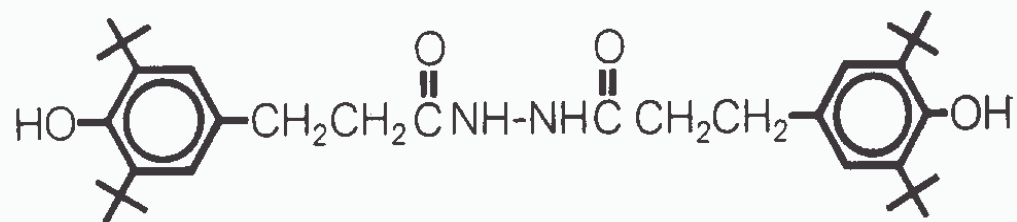


# Antioxidants

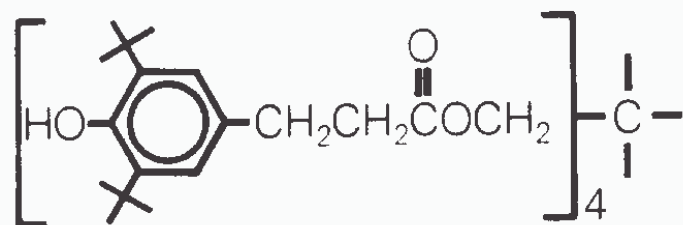
**IRGANOX 1076**



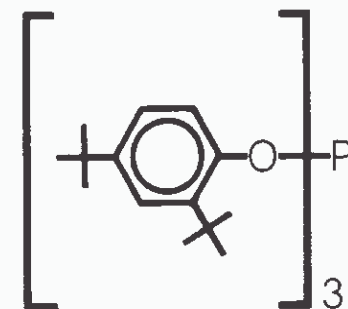
**IRGANOX MD 1024**



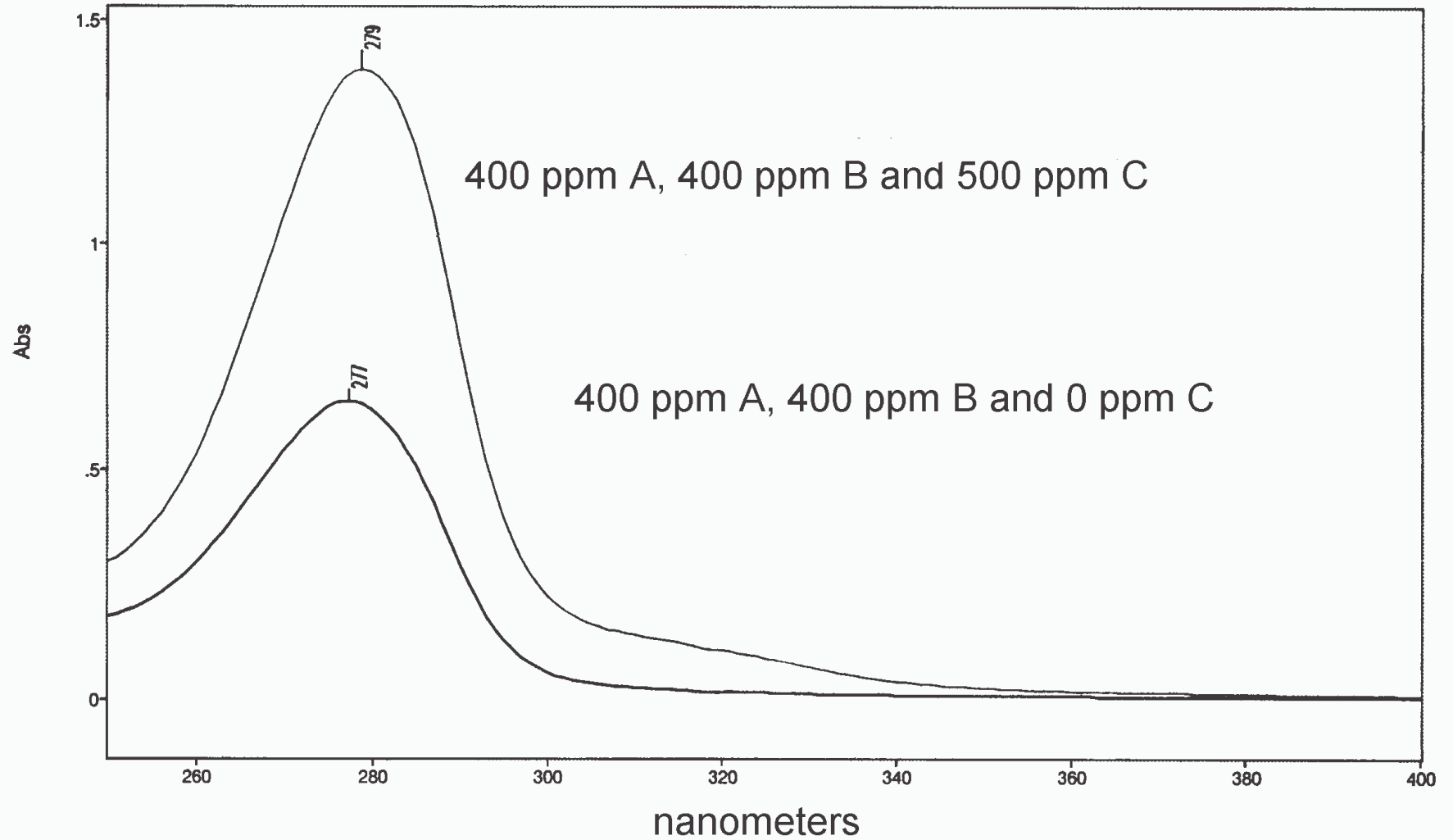
**IRGANOX 1010**

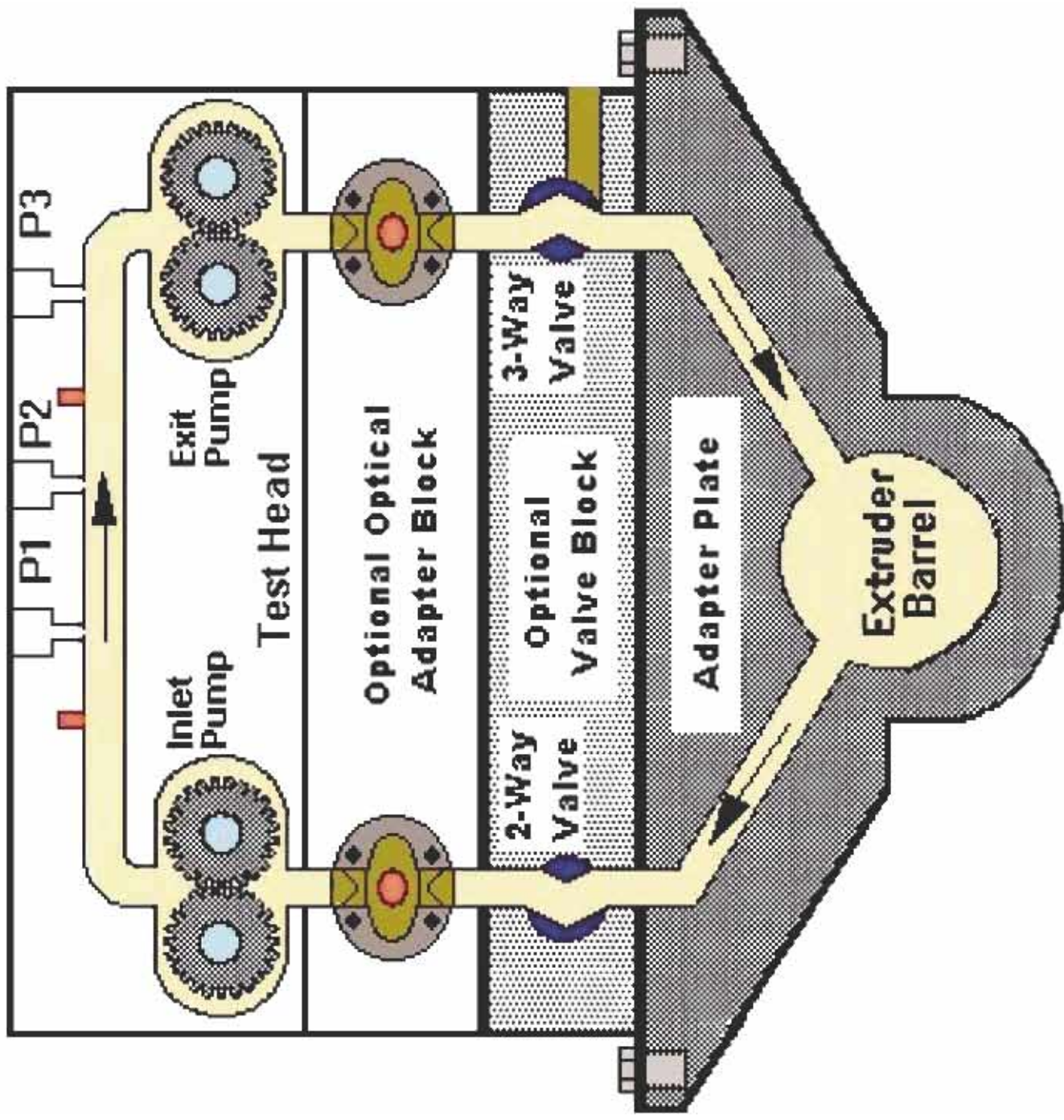


**IRGAFOS 168**



# Additives Spectra

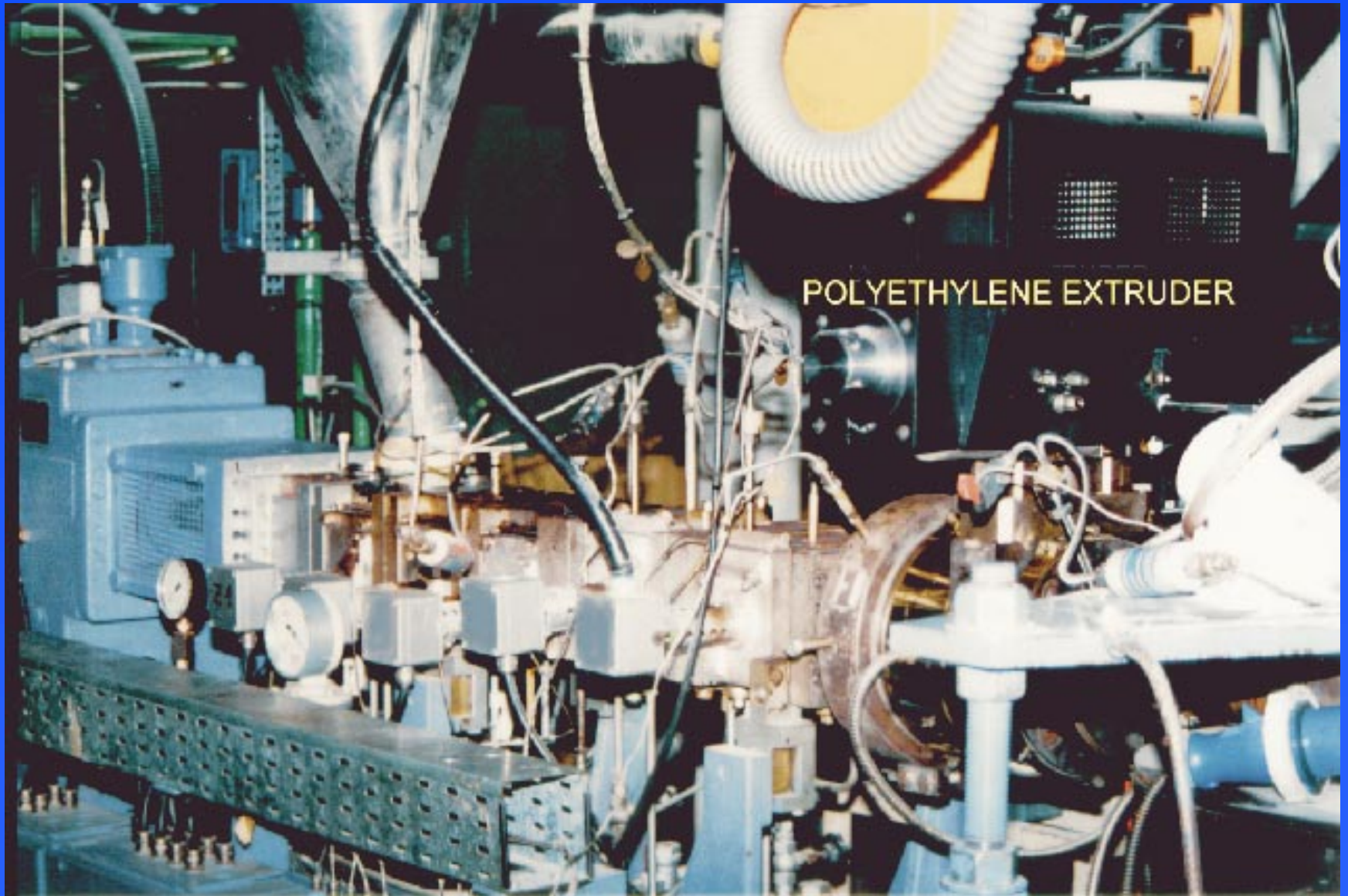




# Rheometric PCR-320



# The extruder





# Objectives

- Analyse three anti-oxidant additives concentration in real time
- On-line in the melt (up to 250°C)
- Manage all of the functions in a single, integrated, easily maintainable application

# Basic approach

- Spectroscopy (proven off-line)
- Probes and optical fibres
- Software environment (connectivity)
- PLS prediction model (1 off-line / 2 on-line)
- Reliable engineering (essential)
  - ◆ opto-isolation (analog + digital)
  - ◆ watchdog

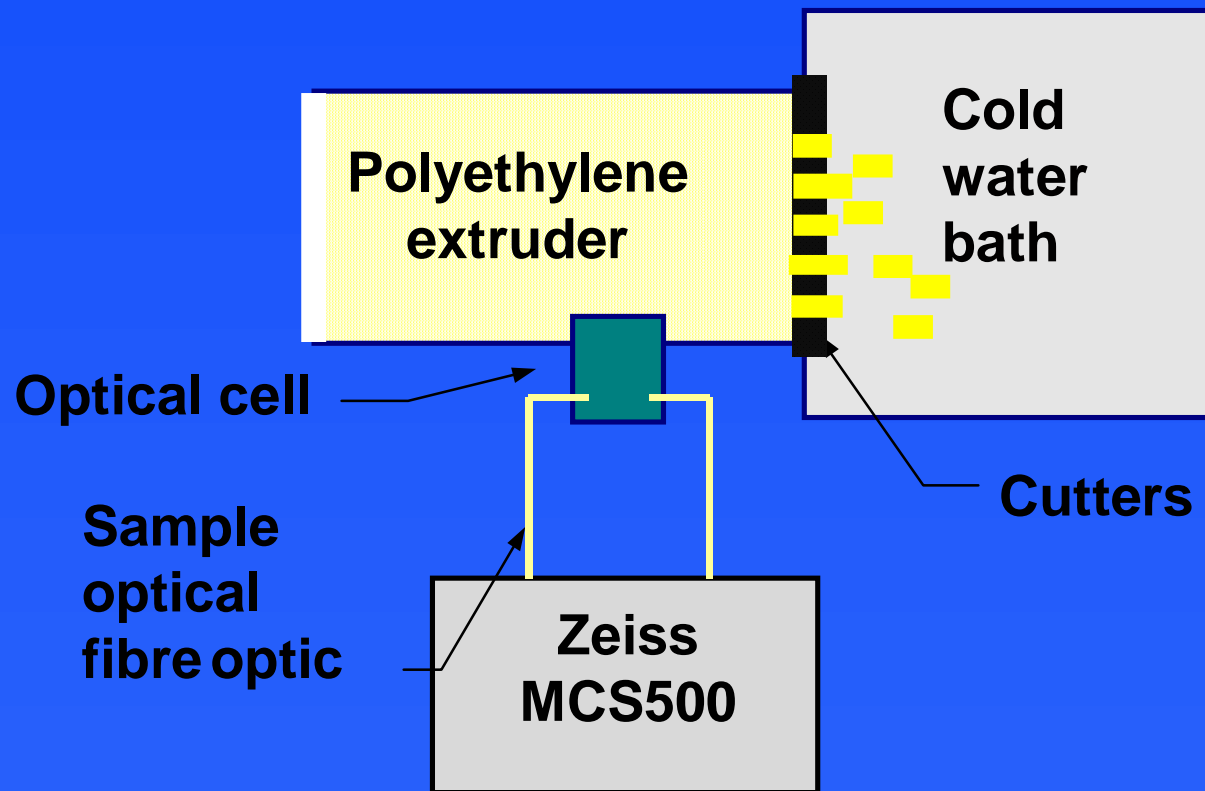
# Technology

- In-line probes (melt) - SpectrAlliance
- Fibre optics as interface  
(UV Quartz grade 600 $\mu$ m)
- Zeiss MCS500, PDA spectrometer
- National Instruments LabVIEW system
- PLS algorithm (Charm Works)

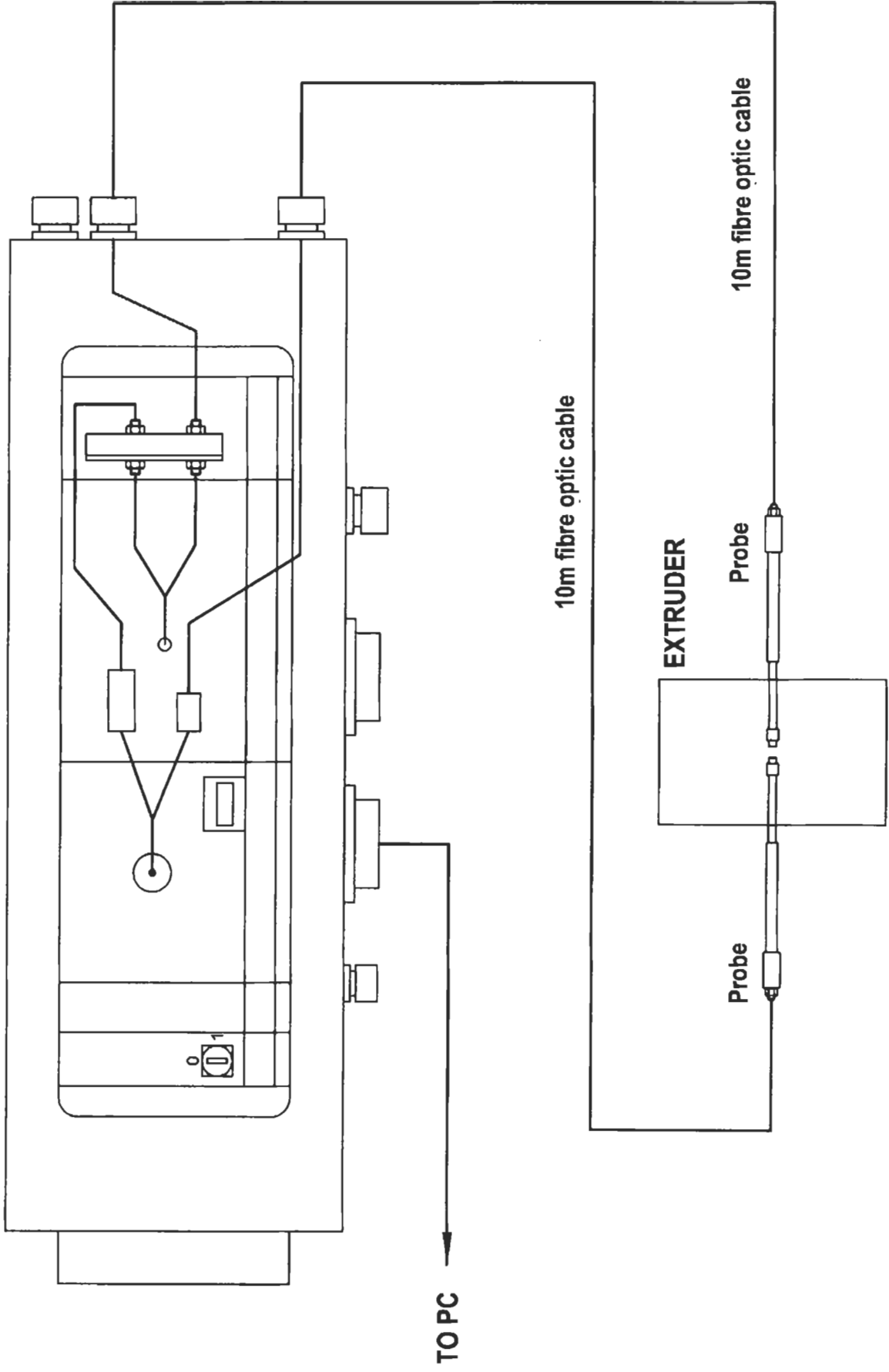
# Zeiss Spectrometer - MCS500



# Monitoring system



**SPECTROPHOTOMETER**



# Spectrometer functions

- Control and data transfer via RS-422
- Choose averaging time and spectral range
- Initiate scans and down load data
- Monitor reference spectrum (alarm on 60 % of initial integrated value for 370-400nm)

# Communications

- Serial communications with site VAX computer
  - ◆ incorporation of PLS predicted data into site database
- Digital alarms to local enunciator panel
- Digital inputs
  - ◆ reset alarms
  - ◆ rheometer fault



# Additional I/O

## ■ Digital outputs

- ◆ analyser fault
- ◆ bad prediction (high Mahalanobis distance)
- ◆ low additive concentration alarm
- ◆ low melt flow or extruder stopped
- ◆ PC Watchdog

## ■ Digital inputs

- ◆ sample temperature alarm
- ◆ reset low flow

# Error detection / correction

- Monitor reference spectrum (alarm on 60 % of initial integrated value for 370-400nm)
- Monitor prediction quality statistics to warn of calibration problems
- To detect flow problems in the rheometer by signal noise
- Correct for spectral offsets

# PLS2 modelling

## ■ X block

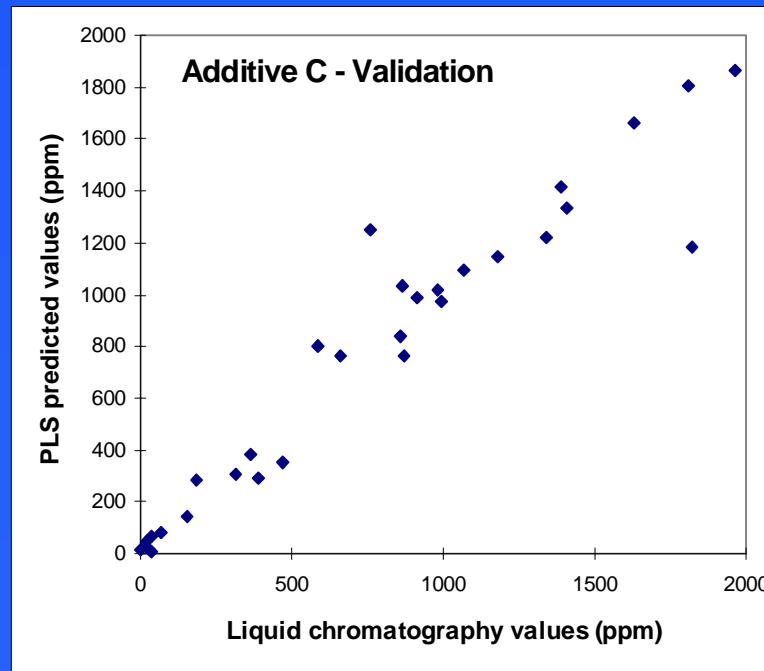
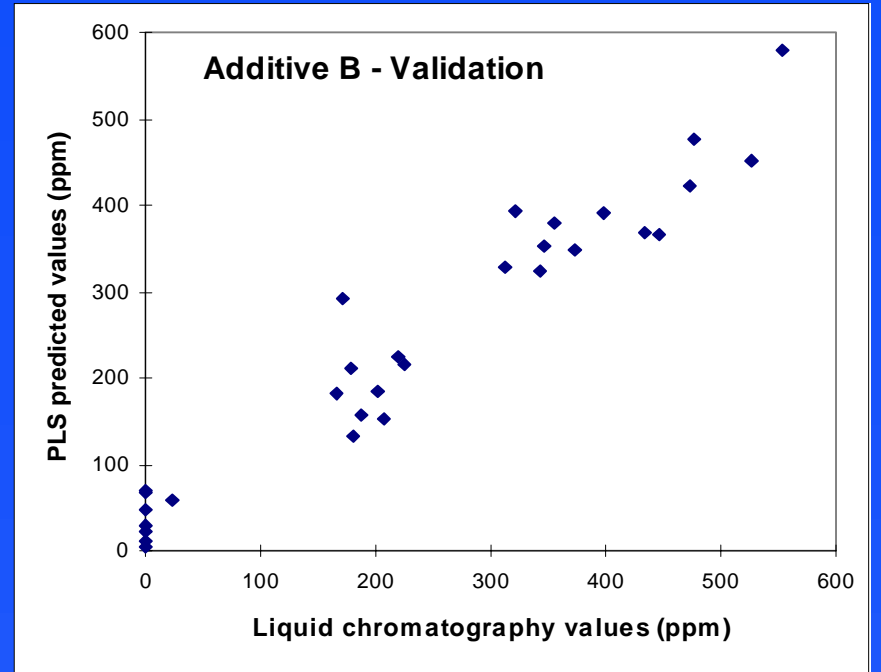
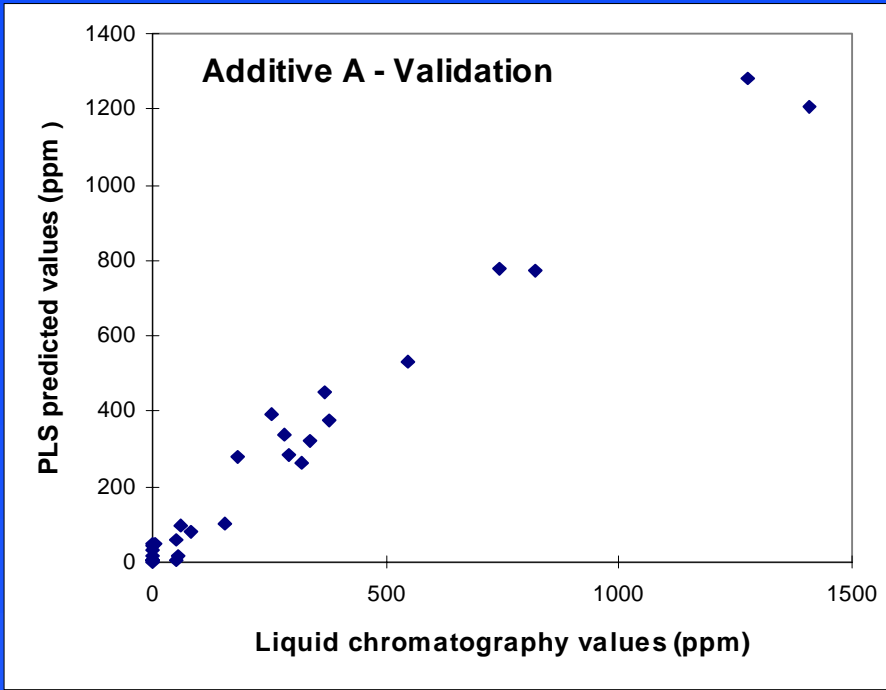
- ◆ spectra 243 - 400 nm (180 data points)
- ◆ mean centred scaling

## ■ Y block

- ◆ LC data (concentration of A, B and C)

■ 20 samples used initially to build model

■ Model extended on-line



# Conclusions

- The Zeiss MCS500 spectrometer has produced good spectral results for polyethylene/polypropylene additives
- PLS modelling has proved effective for analysing 3 non-resolvable anti-oxidant additives
- LabVIEW has enabled a fully integrated process analysis system to be developed in a short period of time at low cost

# New developments

## ■ Charm Works 99

- ◆ automatic baseline correction
- ◆ calibration free prediction

## ■ New applications

- ◆ batch processes
- ◆ reacting systems
- ◆ NIR