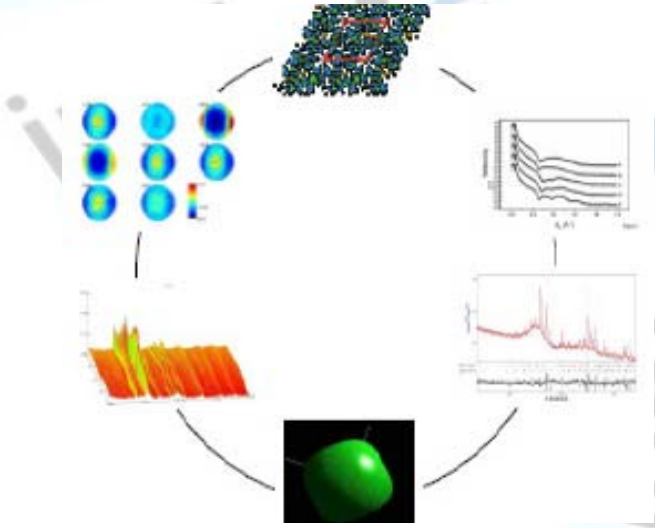
Description of some XRD techniques

1st workshop « Combined Analysis Using X-ray and Neutron Scattering »

Henry Pillière, Inel



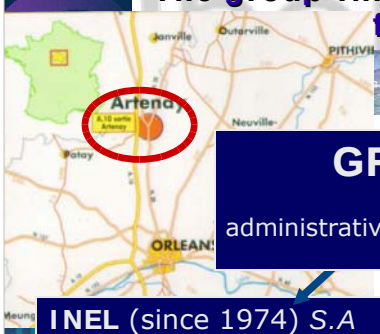
Caen, 28 juin 2010

Description of some XRD techniques

- Presentation
- Interaction X-ray and matter
- Instrumental function
- XRD setup
  - Laboratory
  - on-line
- examples

Caen, 23 juin 2010

The group Innoveurope, a flexible structure for dynamic SMEs



GROUP INNOVEUROPE

Activity :
administrative tasks for managing Inel and Ionix

INEL (since 1974) *S.A*

Activity :
- Design, manufacture and marketing of materials for studies by using X-ray diffraction for public research centers and private.

IONIX (2001) *S.A.R.L*

Activity :
Design, manufacture and marketing of equipment for radiography in nondestructive testing for industrial environments.

INEL Inc (1989) *USA*
US Subsidiary

INEL Ltd (2006) *UK*
UK Subsidiary

http://www.inel.fr

More than 40 distributors around the world

Inel company, since 1974

Our mission is to study and to design scientific instruments adapted to your needs.
Our know-how, resources and methods have been reinforced from year to year.

Instru-mentation

- XRD instrumentation
- X-ray radiography
- EUV instrumentation

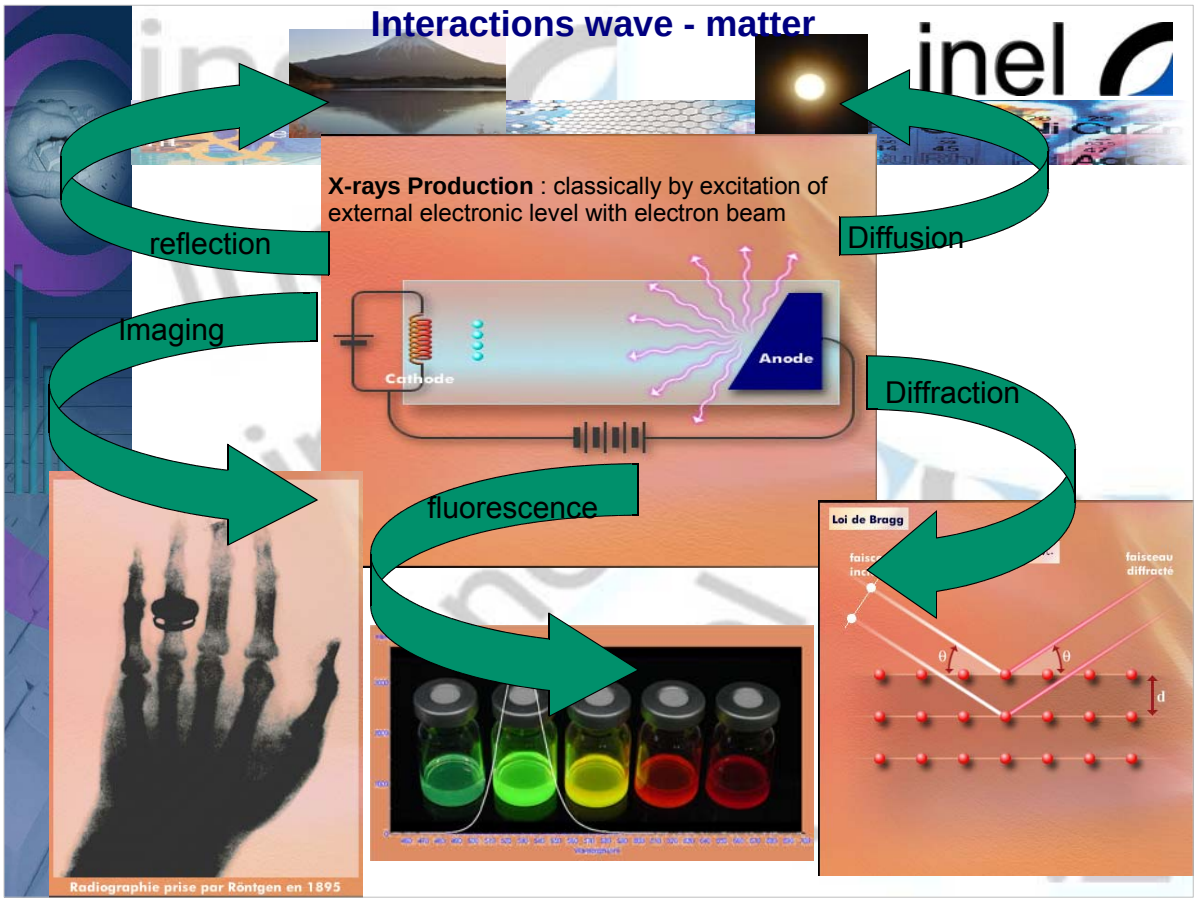
Engineering

- Conception and integration of industrial XRD instruments
- Conception and integration environmental cells for XRD instruments (anvils, reactors, environmental cells, …)
- Techniques coupling with XRD (1)
- Up-grade of X-ray diffractometers

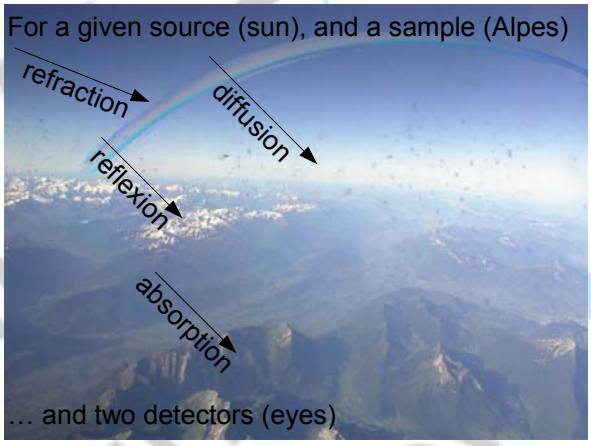
Study

- Advice and management of projects
- Thesis, Patent
- partnership

Interactions wave - matter

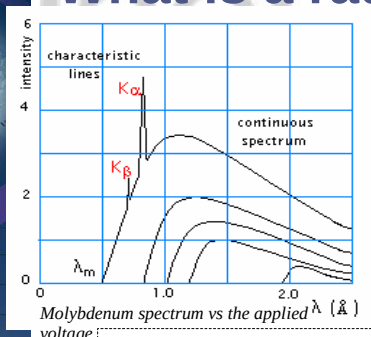


In reality, not so easy !



Instrumentations using radiation for material analysis need to be optimized :
- source characteristics
- detection characteristics
- sample environment
- mechanical design

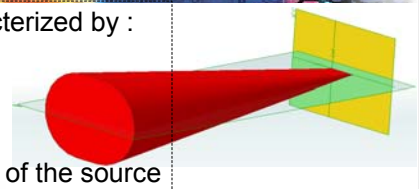
What is a radiation ?



Molybdenum spectrum vs the applied voltage

A light emission characterized by :

- a spectral range
- a solid angle
- intensity
- dimension and shape of the source



Optimizing the characteristics of a source allows to focus on a given interaction

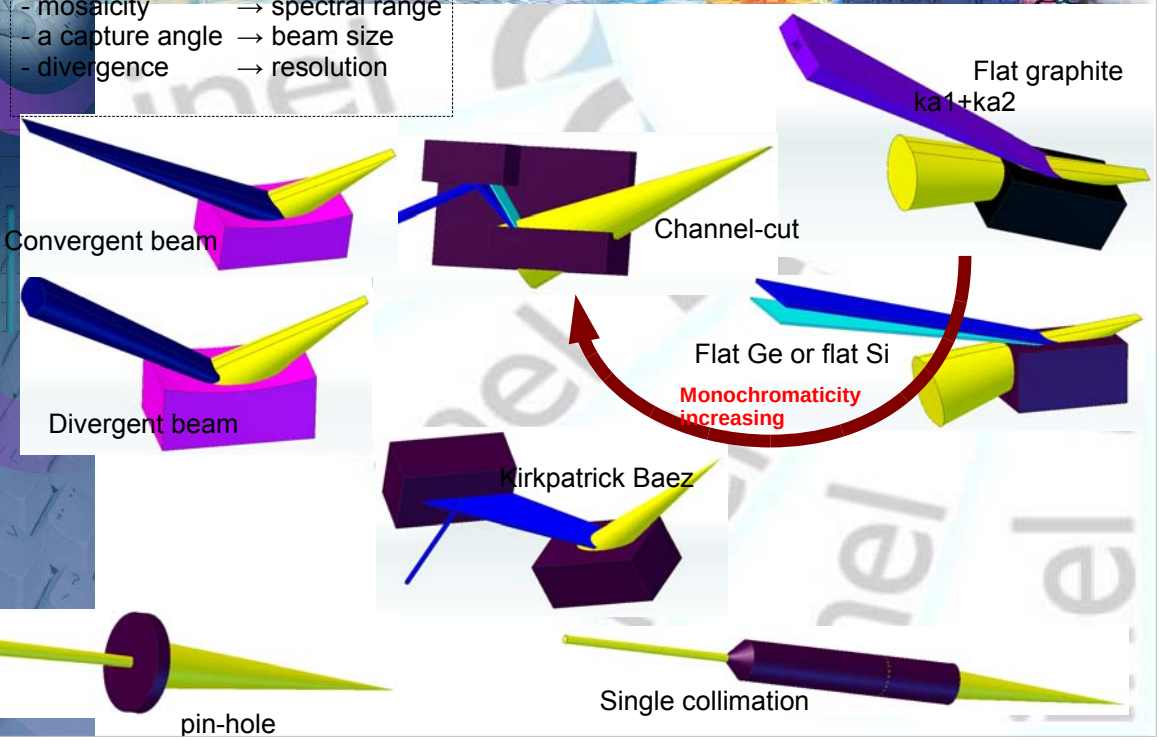
	fluorescence	imaging	diffraction	reflection	diffusion
Spectral range	large	large	Monochromatic (excepted Laue)	monochromatic	monochromatic
Solid angle	Few degrees	Large (60°)	Small to parallel or focusing	Very small	Very small or focusing
Source size	Small or large	Small for resolution improvment	small	small	small
Source shape	point/linear	point	Point or linear	linear	Point or linear

This is achieved by using appropriate optics
(1D, 2D, monochromator, mirror, collimator, slits ...)

What kind of optic ?

An optic is characterized by :

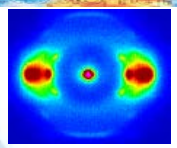
- mosaicity → spectral range
- a capture angle → beam size
- divergence → resolution



How to detect a radiation ?

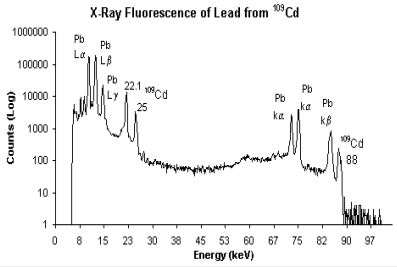
A detector is characterized by :

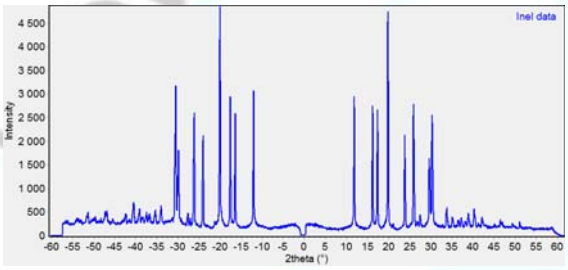
- spacial resolution
- dynamic range
- energy resolution
- dimension



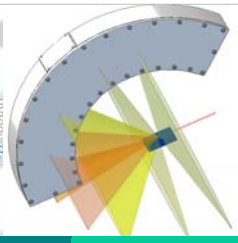
Optimizing the characteristics of a detector allows to improve the measurement

	fluorescence	imaging	diffraction	reflectivity	diffusion
Spacial resolution	none	good	good	none	medium
Dynamic range	3	4~5	3~5	6~8	3~4
Energy resolution	~200eV	None Filtering possible	None or 1KeV	None or 1KeV	None or 1KeV
dimension	0D	2D (1D)	0D, 1D, (2D)	0D(1D)	1D-2D



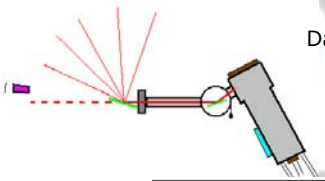


detection types



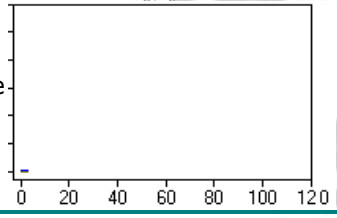
OD detector : principle θ / 2θ

θ/2θ : is the most classic principle in X-ray diffraction



Data acquisition Is done stepwisely.

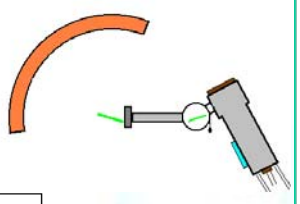
2θ and statistics are time dependent

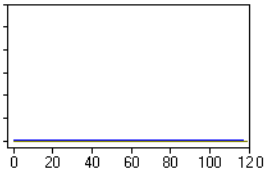


1D detector : PSD principle

CPS intercepts Debye cones over 120° in 2θ.

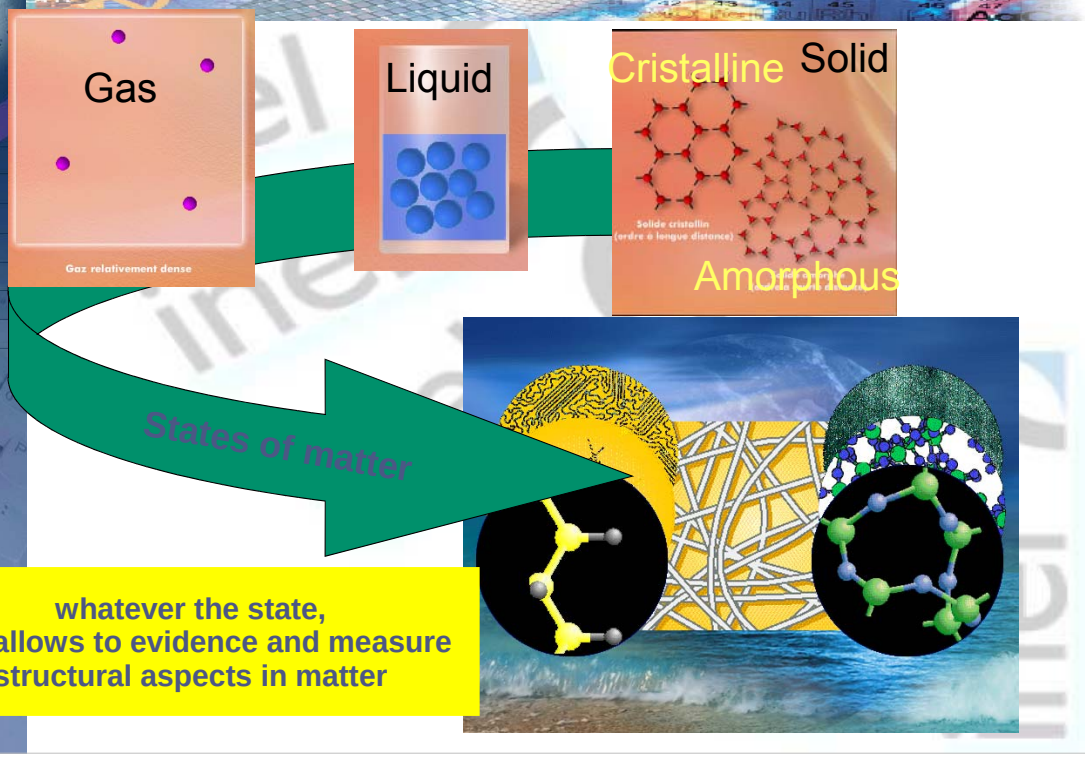
2θ acquisition consists in recording snapshot records





Statistics is time dependent.

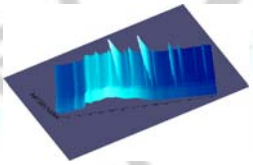
Let's consider X-ray diffraction (XRD)

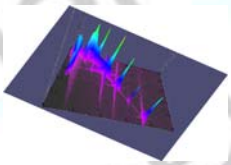


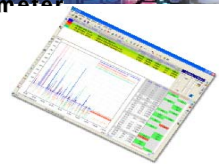
**whatever the state,
XRD allows to evidence and measure
structural aspects in matter**

1D XRD System

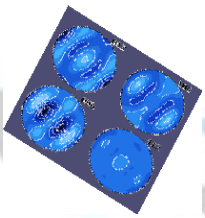
Real Time X-Ray Diffraction Systems for laboratory uses
From bench top XRD to complex goniometer



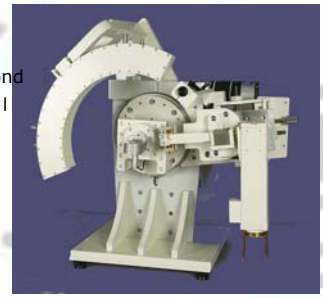




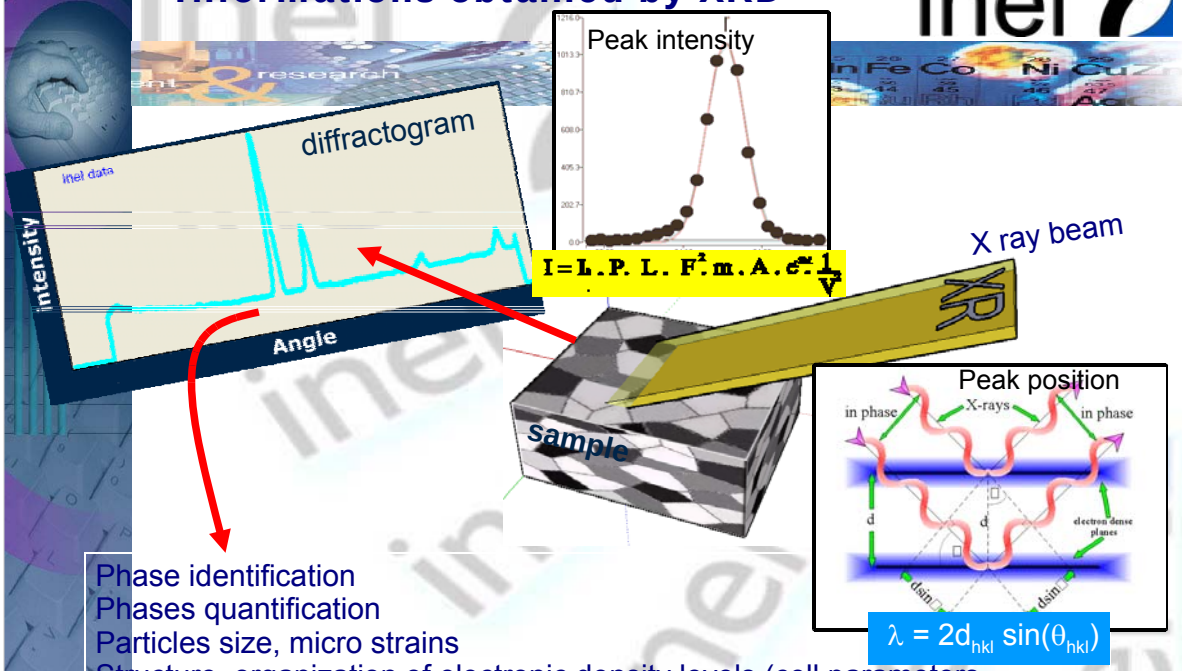
Phases identification
Phase quantification
Crystallography
Microstructure
In-situ experiment progress
Texture analysis
Stress measurement
Thin film characterization
Small angle X-ray scattering



- Real time detection by PSD detector
- Simultaneous data acquisition up to 120°/2θ
- Very high resolution, up to 0.05°/2θ
- Complete 2θ measurement time of just 1 second
- Multi axis goniometer with real time detection l
- Micro diffraction capability down to 10 µm
- Monochromatic optic
- Sample holders
- Reflection / Transmission mode
- Variable temperature furnaces (up to 2700°C)
- Treatments software



Informations obtained by XRD



Phase identification
Phases quantification
Particles size, micro strains
Structure, organization of electronic density levels (cell parameters, valence, atomic occupation, ...)
Structural anisotropy (stress, texture, thin film characterization ...)
Distribution of structures
Phase transition, kinetics study

Instrumental function for XRD

Some basis :

- Instrumental function is governed by all components of the XRD instrument :
  - source characteristics
  - optics and collimation
  - detection device
  - sample environment

- XRD components should be compatible to each other
  - Example : 1D optic is not recommended with a 2D detector (equatorial aberration)

- The good knowledge of the instrumental function allows to estimate as well the quality of the result
  - Example : absorption correction or LP correction are not the same in Bragg Brentano or in Debye Scherrer

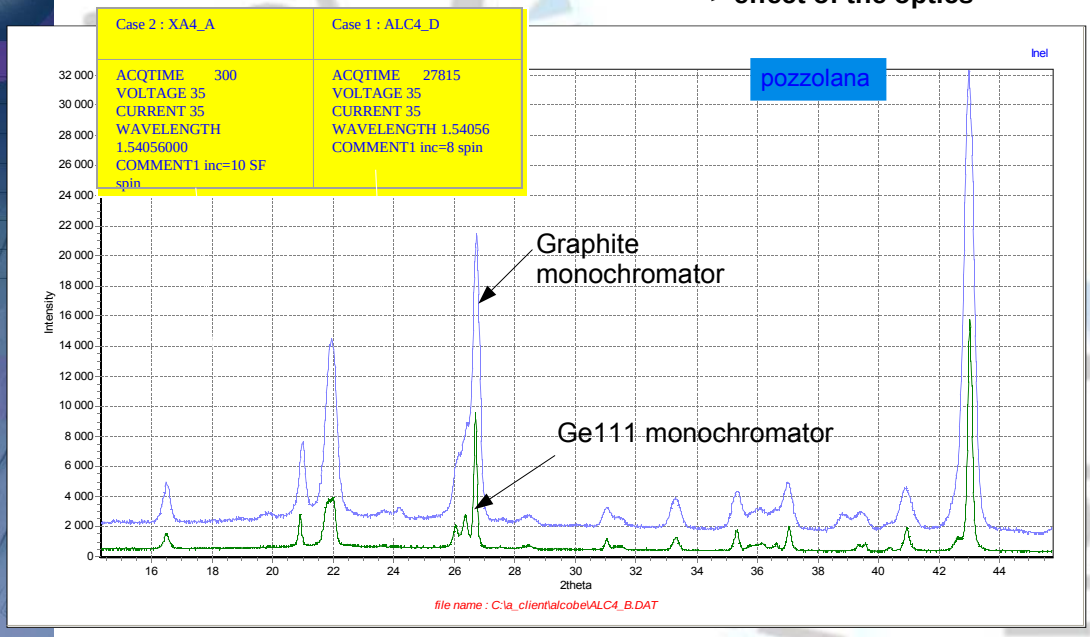
- The instrument must be adapted to the requested measurement
  - Example : performing transmission measurement with Bragg-Brentano XRD is not appropriate

- Instrumental conditions must be correctly chosen (reproducibility of results)
  - Example : choose of the appropriate wavelength vs sample

- Use of appropriate standards
  - Example : in reflexion, eccentricity is influenced by transparency. Using standard with same absorption can correct this

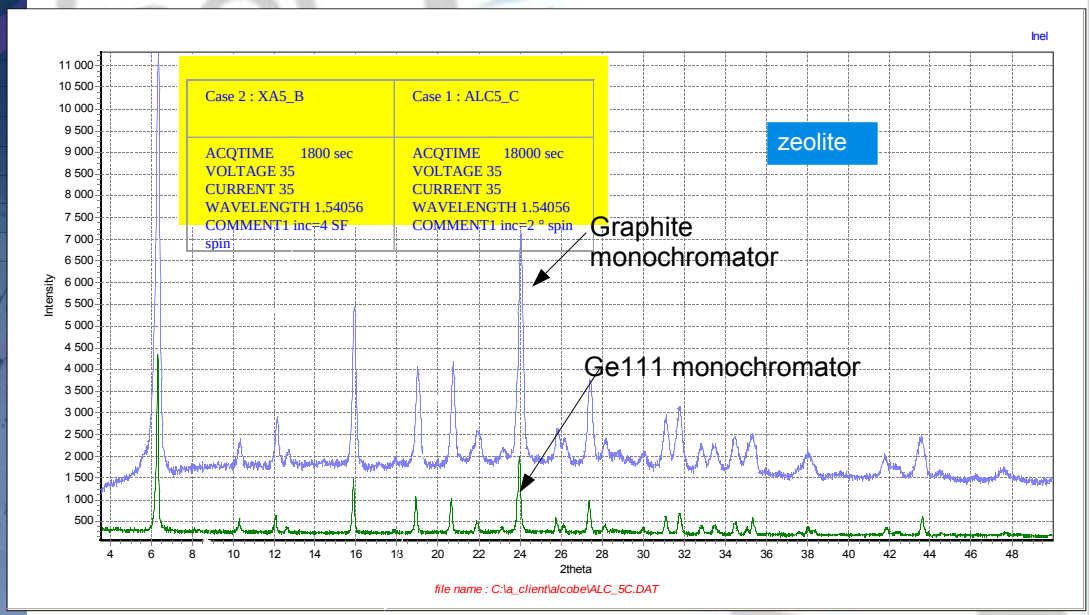
Comparison between high resolution and high flux

-> effect of the optics



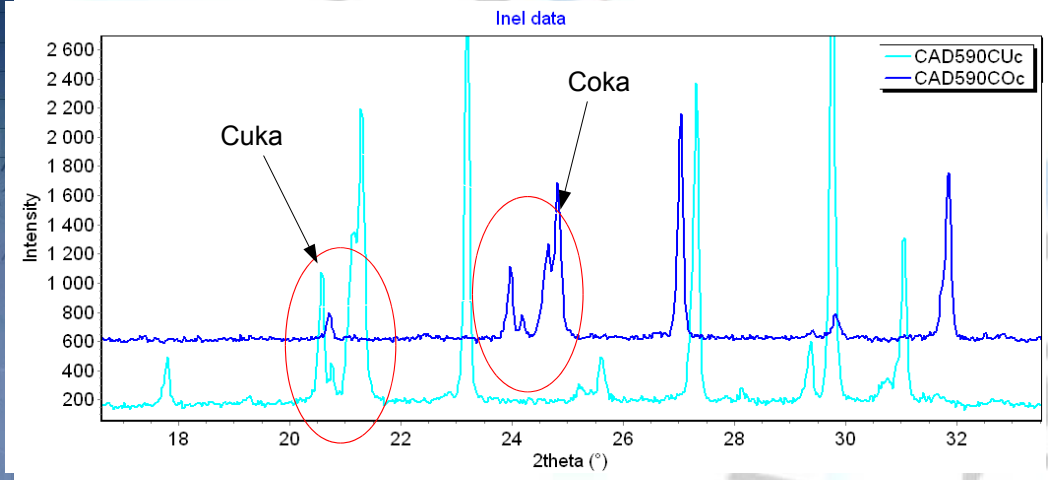
Comparison between high resolution and high flux

-> Effect on optic



Comparison between 2 different wavelengths

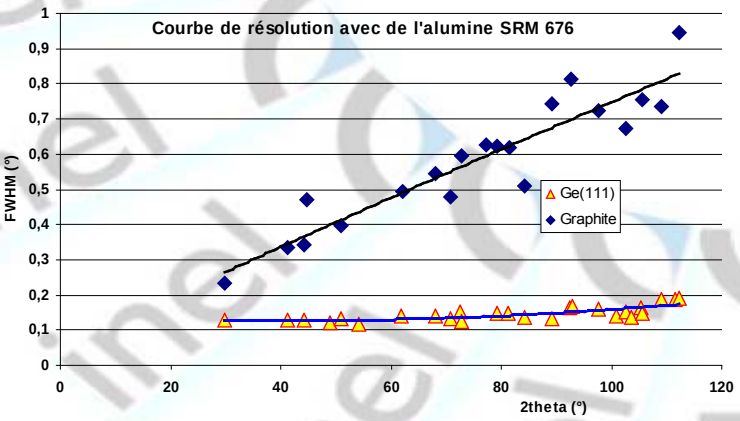
Mixture of minerals



Resolution of the instrument

-> effect of the optics

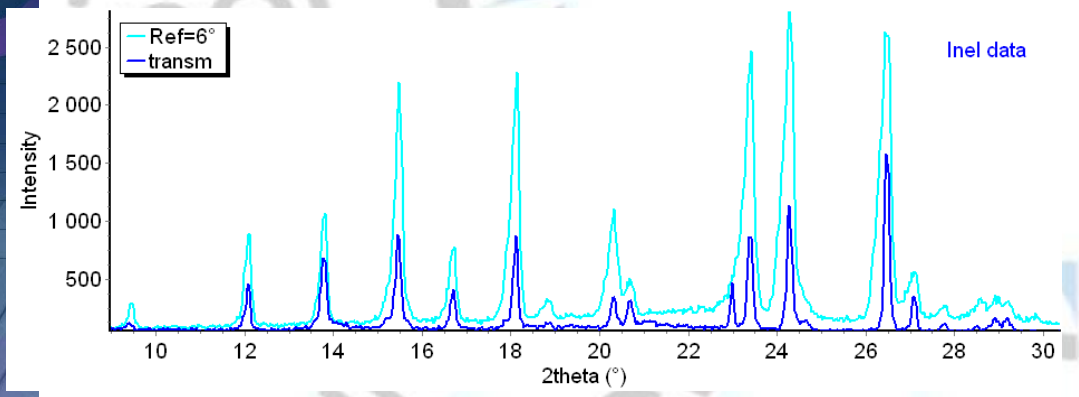
Flux ratio	
Ge(111)	1
Graphite	5
parab. mirror	10



Resolution curves from alumina patterns (SRM 676), with 2 different flat monochromators : Ge(111) and graphite (002). With graphite, ka1/ka2 doublet is considered as a single peak. Diffraction lines have been refined by using a gaussian shape.

Resolution of the instrument

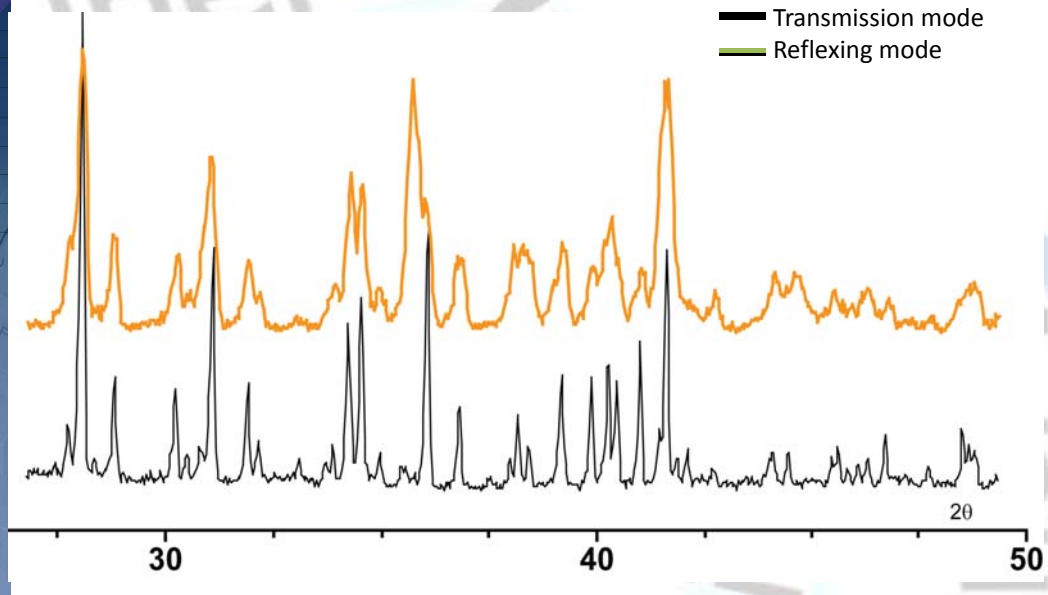
-> Effect of the recording mode



Considering a given diffractometer, equiped with a CPS120, a Ge(111) monochromator and a copper source. Comparing the recording mode, between reflection (light blue) and transmission (dark blue), a paracetamol sample has been recorded. In transmission, the curve is better resolved than in reflection. However the intensity is higher in reflection than in transmission (absorption effect).

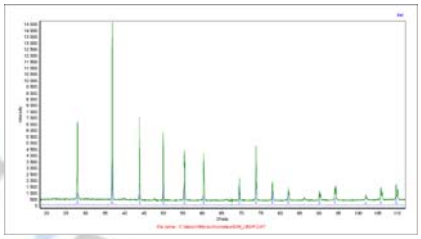
Resolution of the instrument

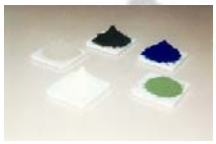
-> Effect of the recording mode on Na-gluten



Powder Applications

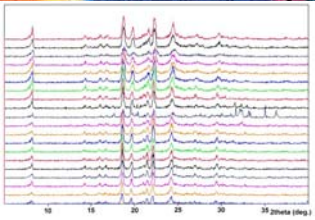
- **Identification**
  - Police (narcotics, explosives, pigments, …)
  - Museum (work of art, …)
  - Pharmacy, cosmetic, mining, geology, …
- **Quantification**
  - Environment (quartz, asbestos, dust analysis …)
  - Mining industry, …
- **Cristallography**
  - Analysis of new phases (pharmacy, electronic, …)
- **Microstructure**
  - Information about crystalline defects :
    - Physico chemistry : reactivity (catalysis), oxidation
    - Mechanical : joints of grain, fragility area
    - Conducting : atomic replacement, doping





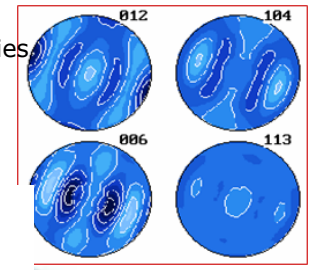
In-situ Applications

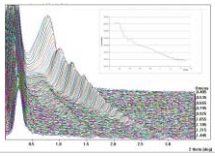
- **Temperature / Pressure**
  - Phase transitions
- **Electrochemistry**
  - Following the phase transition : load, unload
    from a battery (ageing, reversibility, functioning)
- **Reactivity**
  - Search match on metastable components during a chemistry reaction
    Cement hydratation / Gas absorption in zeolithe
- **Industrial control on line**
  - Cement quality control,
  - phosphate industries
  - Solar panel control
- **Following the product state in the time**
  - Product evolution with the temperature and the humidity



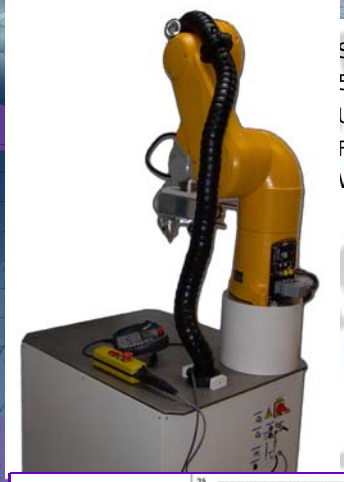
Goniometric Applications

- **Texture, crystalline orientation**
  - Phase in a rock, information about the area tectonic
  - Deposition on a substrate, consequence for electronic properties
  - On metal, determination of the oxidation resistance
    OR acceptance of a particular cover
    Fiber materials (C,PET),
- **Residual stress (metallurgy)**
  - Stress state measurements of a mechanic pie
    (Young module and stress vector)
- **Micro-diffraction**
  - Homogeneity analysis of a bulk sample
- **Grazing diffraction**
  - Thickness measurement of a thin film
  - Deposition identification (irradiated zirconia)





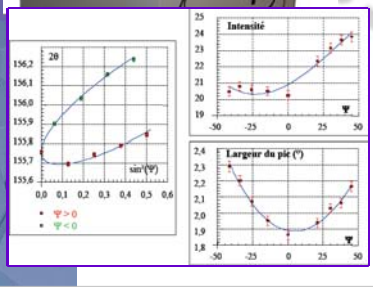
PRECIX : Residual stress measurements with a robot



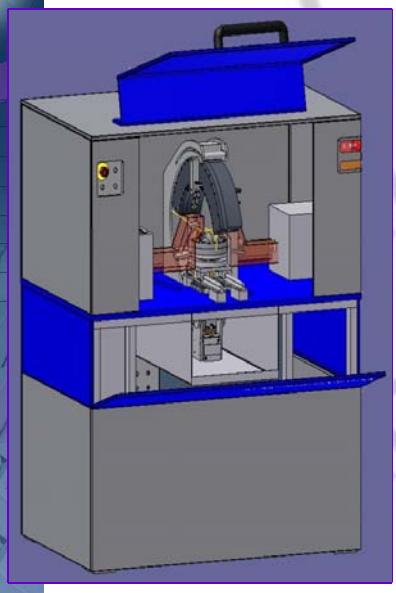
Stress measurements on big parts
50mm PSD
Unique laser positioning system
Fast
Works with standard software!

Nothing comparable on the market !!!

Head of analysis
A compact diffraction device, combined with optical metrology

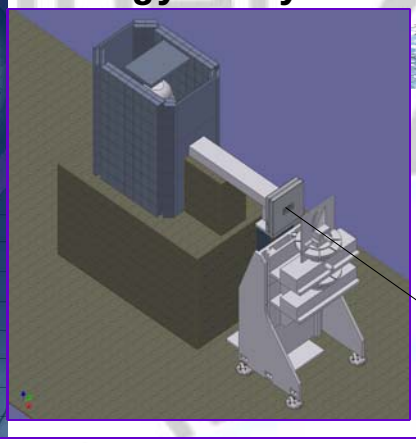


Combined system DRIFT-DRX

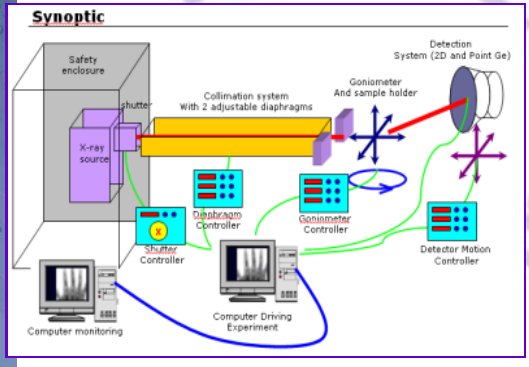


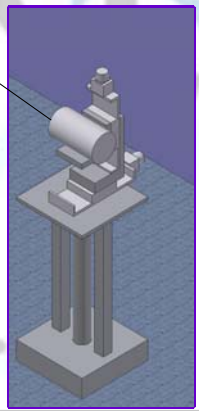
- Development of a laboratory system, combining XRD and DRIFT, to perform in-situ measurement
- Development of an adapted environmental cell pressure-temperature
- Concept of instrumented system, with an appropriate expert software

High energy X-ray diffraction



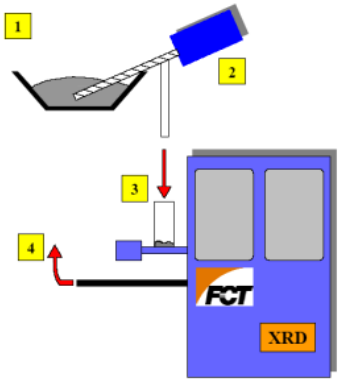
- Development of a high energy X-ray diffractometer (200-400keV) for the quality control of large crystal
- Miscut determination
- Sample monitoring and image acquisition
- Possible extrapolation of the instrument for stress and texture analysis



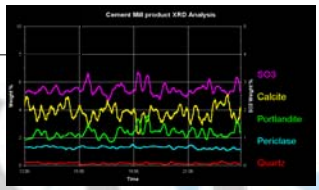


Industrial XRD

COSMA, on line XRD



C_3S, C_2S, C_3A, C_4AF, CaO, $Ca(OH)_2$, $CaCO_3$, $CaSO_4.2H2O$, $CaSO_4.^1/_2H2O$, Other minerals



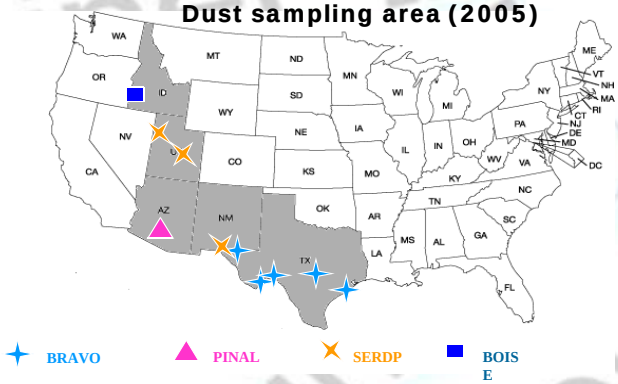
Features

Real time monitoring taken	Process changes shown as they happen, remedial action can be immediately
Continuous measurement levels	Trends dearly show success of control actions to maintain target
Bulk sample presented process	Provides confidence that results reflect actual changes in the
Direct analysis of minerals result	No assumptions, no back calculation, no guess work, just accurate
Total composition identified dealt	Process disturbances from rogue minerals quickly identified and with

Quantitative Mineralogical Analysis of Aerosol Samples by X-ray Diffraction (XRD)

Desert Research Institute

Dust sampling area (2005)



Importance

- Globally 50% of aerosol particulate mass
- Significant impact on earth's radiation budget
- Substantial contribution to global climate
- Impact on visibility and health

Examples of mineral contained in aerosol

Quartz, Aragonite, Hematite, Halite, Muscovite, argiles (Illite, Kaolinite, Montmorillonite), Calcite, Dolomite, Magnetite

Definitions

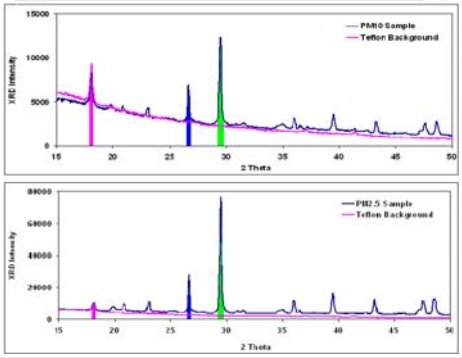
- PM10 and PM2,5 (Particulate Matter) : particle with an aerodynamic diameter lower 10microns (PM10) or 2,5 microns (PM2,5)
- PM10 : Local dust, severe dust storms
- PM2,5 : Health effects - Long-range transport – low Visibility

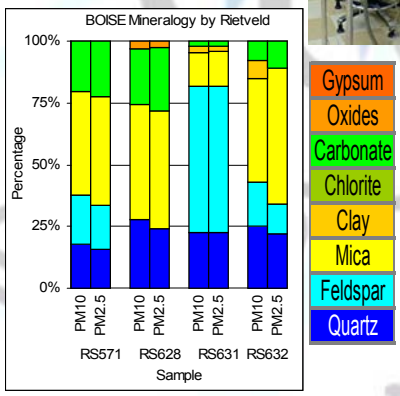
Quantitative Mineralogical Analysis of Aerosol Samples by X-ray Diffraction (XRD)

Dust inlet

Optimised XRD : Equinox 3000

- High intensity source
- Rapid detection
- Data treatment (Rietveld)





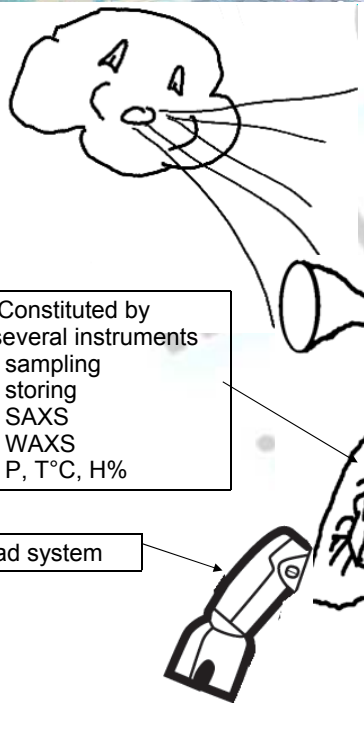
Quantitative Mineralogical Analysis of Aerosol Samples by X-ray Diffraction (XRD)

Inel diffractometer is the most adapted instrument for such a study

- Chemical speciation alone does not adequately distinguish amongst mineral dusts
- Optical properties of minerals vary substantially
- XRD provides a methodology to quantify the mineral constituency of crustal material in aerosols
- Knowledge of the mineralogy of dusts could enhance aerosol modeling

NanoAir, concept

Investigation on an instrumented system



=> system for controlling and surveying

Real time data measurement

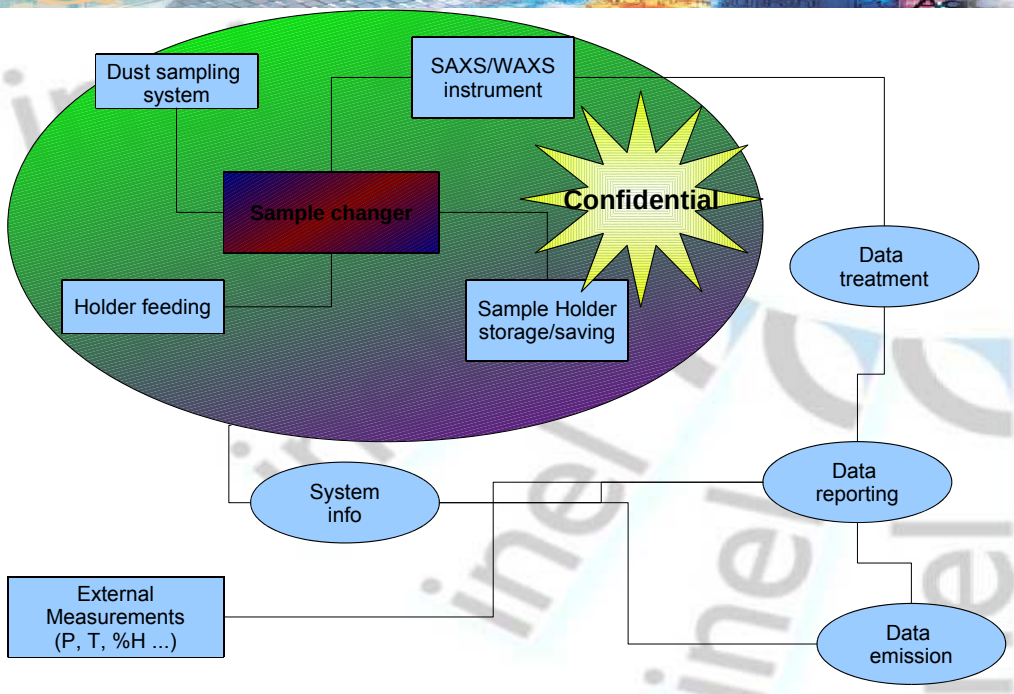
Communicating system

Constituted by several instruments
- sampling
- storing
- SAXS
- WAXS
- P, T°C, H%

Nomad system

expertise of measurements in real time

NanoAir, synoptique



NanoAir, partners

Validation

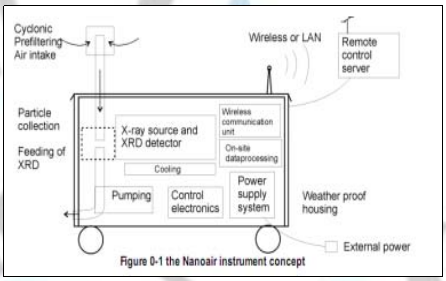


Figure 0-1 the Nanoair instrument concept

Distributors

Integration

Supply materials

Data treatment

Aerosol collection

Quality control in detergent

Phosphates are used in many domains :
Fertilizing agent, food additives, hydraulic fluids, pharmacy
Provenance : sodium and potassium phosphate salts

Phosphates

sodium Phosphate

potassium Phosphate

Ortho-
MSP, DSP, TSP
- Water softening
- Metal treatment
- Hard surface cleaning
- Emulsifiers

Pyro
SAPP, TSPP
- acid cleaner
- water treatment
-dispersants
- Sequestrant

TripolyP
STPP1, STPP2 ..
- laundry detergents
- dishwasher detergents
- water softening
- industrial cleaners

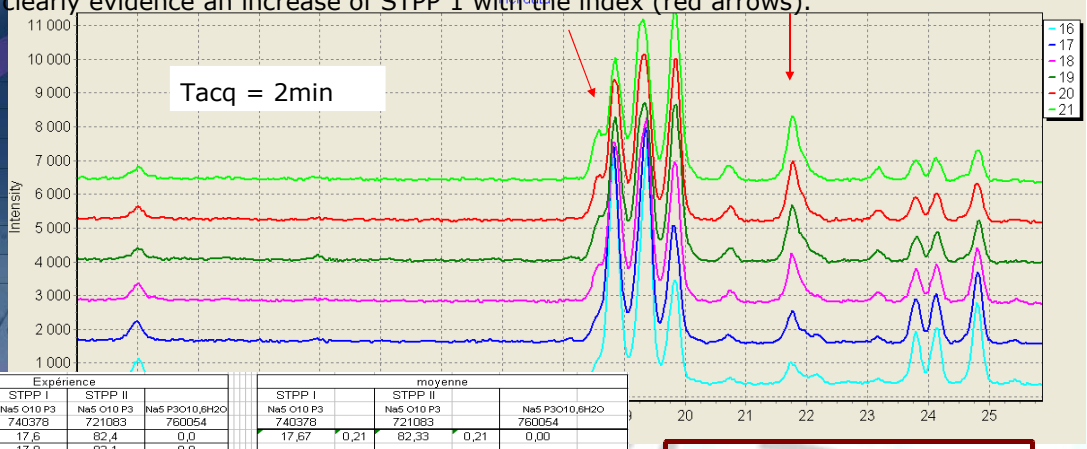
glassy
SHMP
- water treatment
- bath salts
- Dispersant

Analytic techniques for phosphates quality control

- Gravimetry : estimate of the total amount of phosphates
- Chromatography : quantitative determination of ortho, pyro, tripoly and glassy
- XRF and atomic absorption : elements analysis
- XRD : phase analysis of all crystallized products

Quality control in detergent

On the graph below, are represented diffractograms recorded for each sample. We can clearly evidence an increase of STPP 1 with the index (red arrows).



Echantillons		Expérience STPP I Na5 O10 P3 740378	STPP II Na5 O10 P3 721083	Na5 P3O10,6H2O 760054	moyenne STPP I Na5 O10 P3 740378		STPP II Na5 O10 P3 721083		Na5 P3O10,6H2O 760054	
16	a	17,6	82,4	0,0	17,67	0,21	82,33	0,21	0,00	
	b	17,9	82,1	0,0						
	c	17,5	82,5	0,0						
17	a	25,9	70,7	3,4	25,90	0,20	70,73	0,35	3,03	0,32
	b	25,7	70,4	2,9						
	c	26,1	71,1	2,8						
18	a	40,8	57,0	2,2	40,90	0,17	56,93	0,31	2,17	0,58
	b	40,8	57,2	2,0						
	c	41,1	56,6	2,3						
19	a	50,6	46,1	3,3	51,35	0,54	45,23	0,60	3,43	0,13
	b	51,3	45,1	3,6						
	c	51,7	44,9	3,4						
	d	51,8	44,8	3,4						
20	a	51,2	46,3	2,5	51,17	0,45	46,57	0,38	2,27	0,25
	b	51,6	46,4	2,0						
	c	50,7	47,0	2,3						
21	a	60,7	37,4	1,9	60,20	0,56	37,93	0,50	1,87	0,15
	b	60,3	38,0	1,7						
	c	59,6	38,4	2,0						

Quantitative analysis has been performed by using the Rietveld method.
Good reproducibilité, and good agreement with other techniques (chemistry)

Phase transition at low 2theta

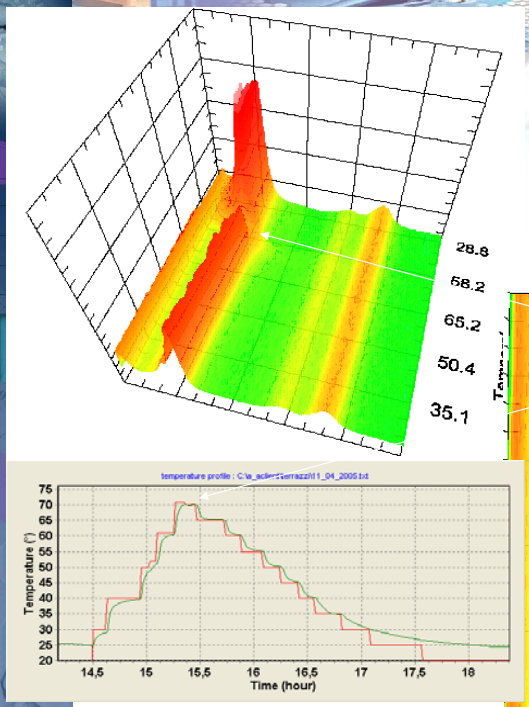


figure 1 : temperature profil; every 10°C up to 70°C, and then everay 5° in cooling.

Source : Copper
Generator : 3,5 kW
Optique : Parabolic mirror
Incidence :in transmission (1mm capillary)
Sample holder: non spinning
furnace type FURCAP
Detector : CPS120
power : 35 kV – 35 mA
Acquisition time: 3min
setting : MPD

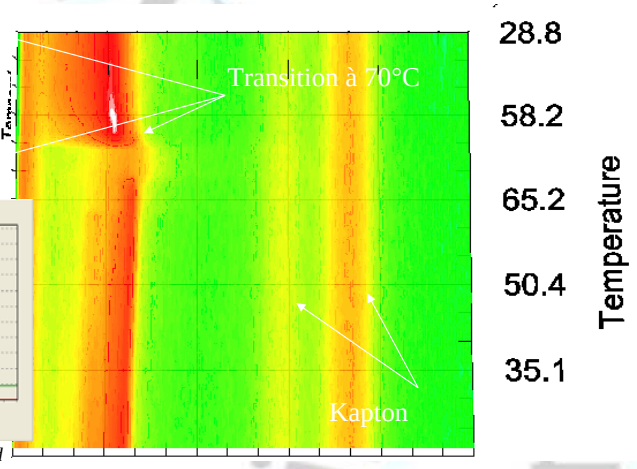
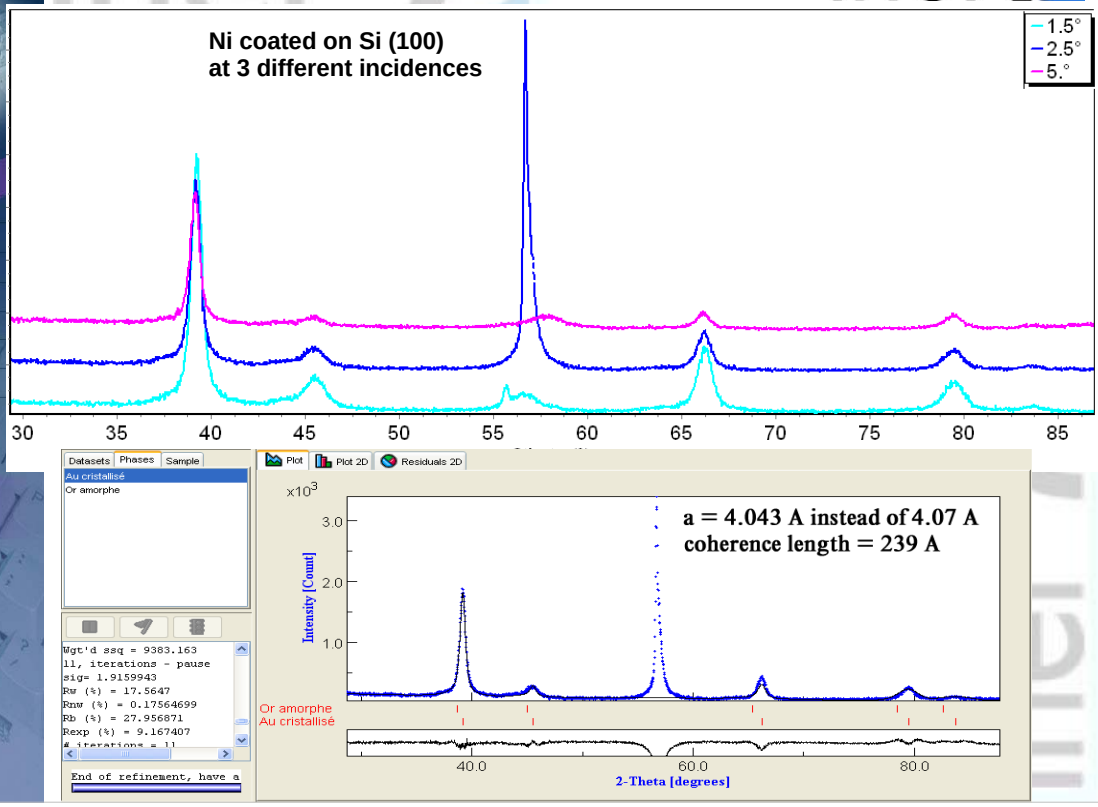
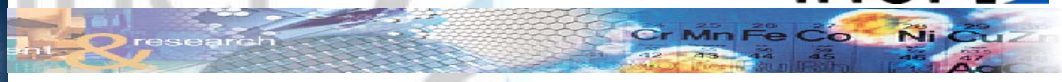


figure 2 : 3D plot

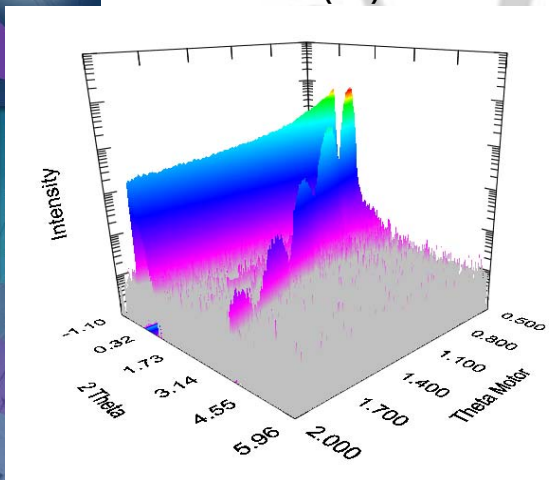
Grazing diffraction

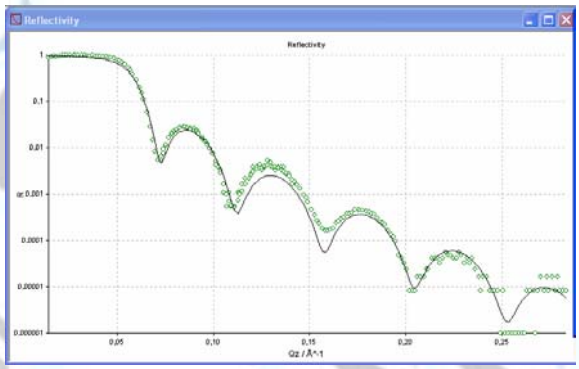


Reflectometry



Ni coated on Si (100)



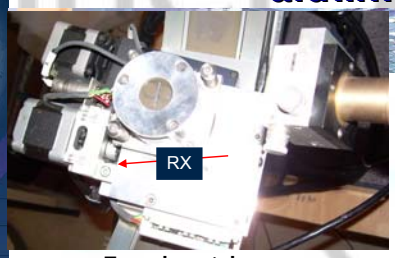


sample type:
- independent layers
- analytical profile function
- multiple layers
- symmetric film

number of layers: 1

	d / Å	rho / Å^-2	Im(rho) / Å^-2	sigma / Å	R(mag)	I(mag)
air	N/A	0E+0	0E+00	N/A	0	0
Ni	127,26	5,545E-5	2,528E-06	6,487	0	0
Si	N/A	2,015E-5	4,588E-07	6,752	0	0

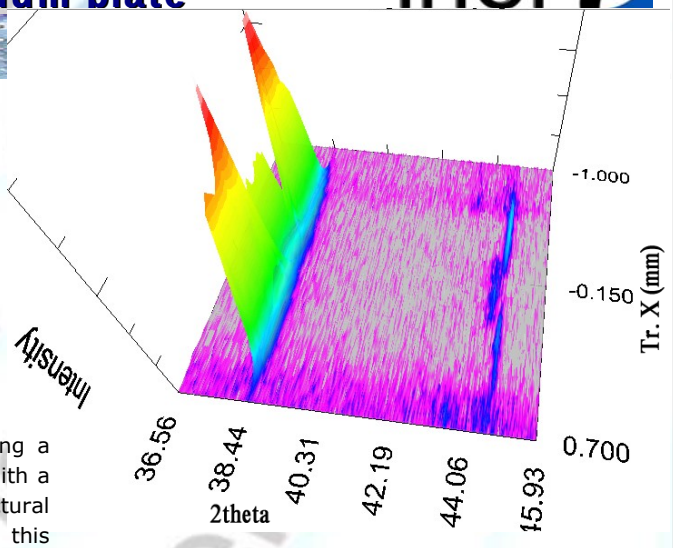
Microdiffraction on the side of aluminum plate

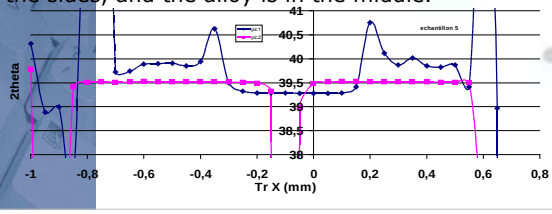


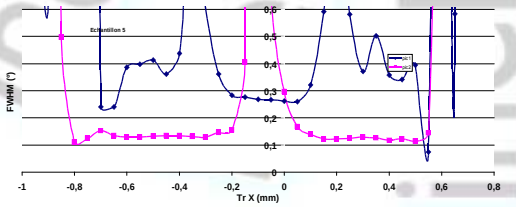
Experimental

Power = 40mA – 30 kV
Scan step in X = 50 mic
Time per scan = 2 min
Beam size = 20mic x 2mm
Incidence = 20°

The sample is an aluminum alloy, containing a low amount of Mg. By probing the sample with a small beam, we have identified structural modification within the plate. From this expertise, was can say that pure aluminum is on the sides, and the alloy is in the middle.

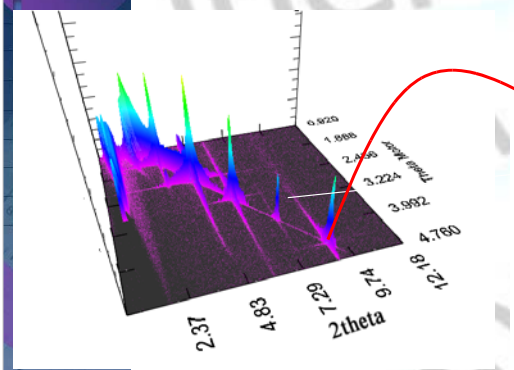


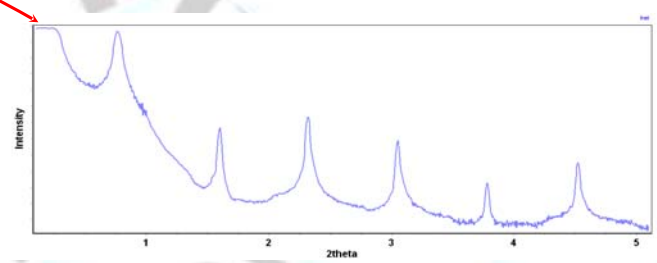




Multilayer measurement by reflectometry

Reflectometry on nanometric thin film allows to measure the 2D structure of a composite material





128 stackings of W/Si on Silicon
W = 1.1nm
Si = 2.2nm

Thin films informations

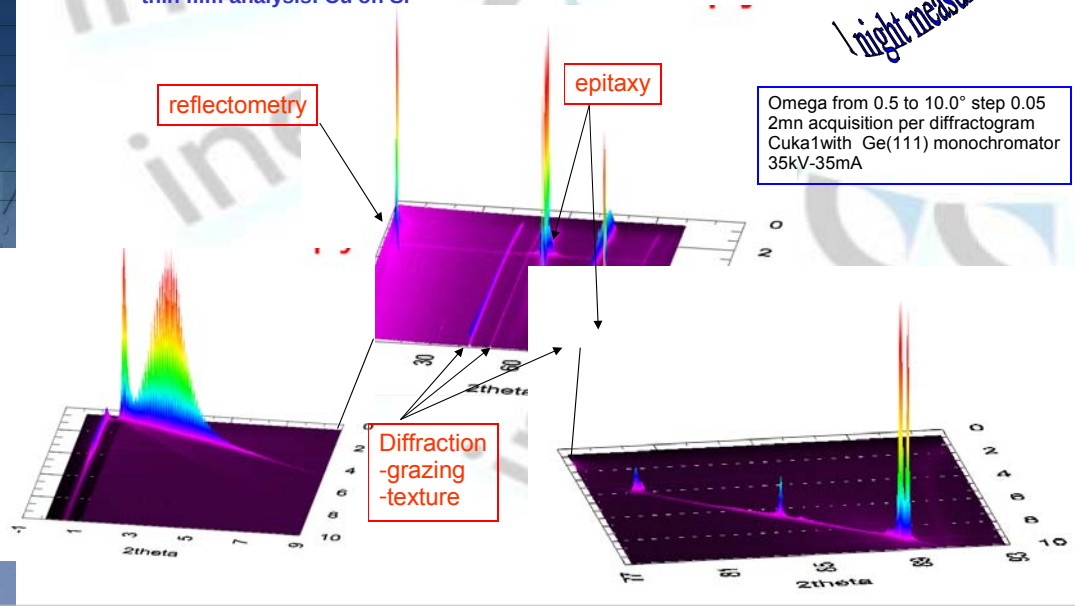
One experiment = « a huge of informations »
thin film analysis: Cu on Si

night measurement

reflectometry

epitaxy

Omega from 0.5 to 10.0° step 0.05
2mn acquisition per diffractogram
Cuka1with Ge(111) monochromator
35kV-35mA

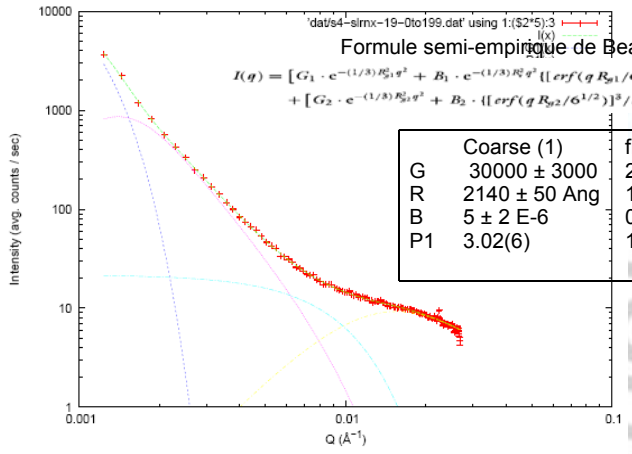


Diffraction
-grazing
-texture

SAXS informations

The University of Edinburgh
One of the world's top 20 universities

Particules de 20nm d'oxyde de titane.

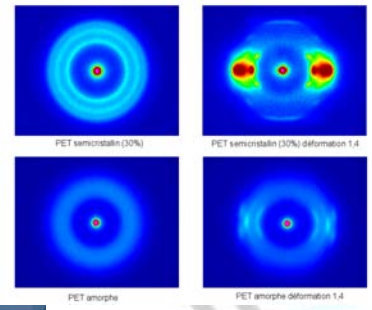


Formule semi-empirique de Beaucage

$$I(q) = [G_1 \cdot e^{-(1/3)R_{g1}^2 q^2} + B_1 \cdot e^{-(1/3)R_1^2 q^2} \{[erf(q R_{g1}/6^{1/2})]^3/q\}^{P_1}]$$
$$+ [G_2 \cdot e^{-(1/3)R_{g2}^2 q^2} + B_2 \cdot \{[erf(q R_{g2}/6^{1/2})]^3/q\}^{P_2}] \cdot S(q)$$

	Coarse (1)	fine (2)
G	30000 ± 3000	20 ± 10
R	2140 ± 50 Ang	190 ± 60 Ang
B	5 ± 2 E-6	0.04 ± 0.07
P1	3.02(6)	1.4 ± 0.4

SAXS WAXS Diffusion



Detection

1D linear detection

2D detection

Optic

Crossed coupled X-ray mirrors (Kb optic)

Parabolic mirror with collimation

Monochromator with collimation

X-ray capillary

Sample

Transmission mode

Sample changer

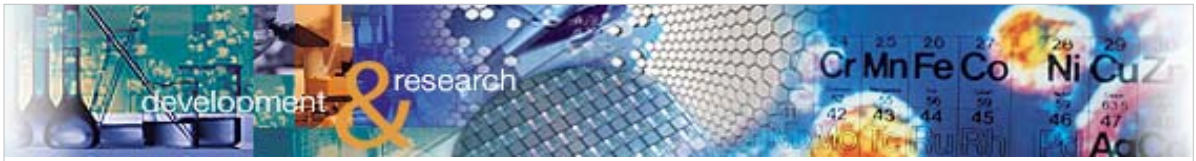
Environmental chamber

Under vacuum

Sample holder

Optic line

Distance between the sample and the detector



- X rays diffraction is an appropriate techniques to perform phases identification and quantification
- Investigation at the nano scale
- XRD is a non destructive techniques, without special conditioning
- A huge of databases is available (ICDD, ICSD, COD …)
- data modeling is a real performance for a lot of applications