**ThermoFisher**
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*The world leader in serving science*

# ARL ADVANT'X Intellipower™ Series

## Analysis of Polymers

# Advances in X-ray Fluorescence

## ARL ADVANT'X Intellipower Series

# ARL ADVANT'X Intellipower Series:

- A new generation of sequential XRF instruments for the 21$^{st}$ century

- Four spectrometers with a choice of power for various levels of performance and speed of analysis:
  - ARL ADVANT'X Intellipower 1200/2500
    - 1200W or 2500W
    - no external water chiller required

  - ARL ADVANT'X Intellipower 3600/4200
    - 3.6 kW – high performance
    - 4.2 kW – top performance

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# ARL ADVANT'X Family : Features & Benefits

- Built around unique ARL universal goniometer updated for faster operation

- New X-ray tubes (4GN, 5GN) bring higher sensitivity

- Modular approach for flexibility in price / performance

- Multiple sample loading capabilities

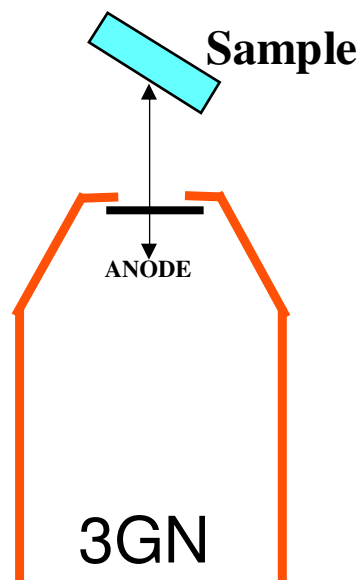- Unique features for highest performance on ultra-light elements analysis

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# ARL ADVANT'X Intellipower Series: Side View
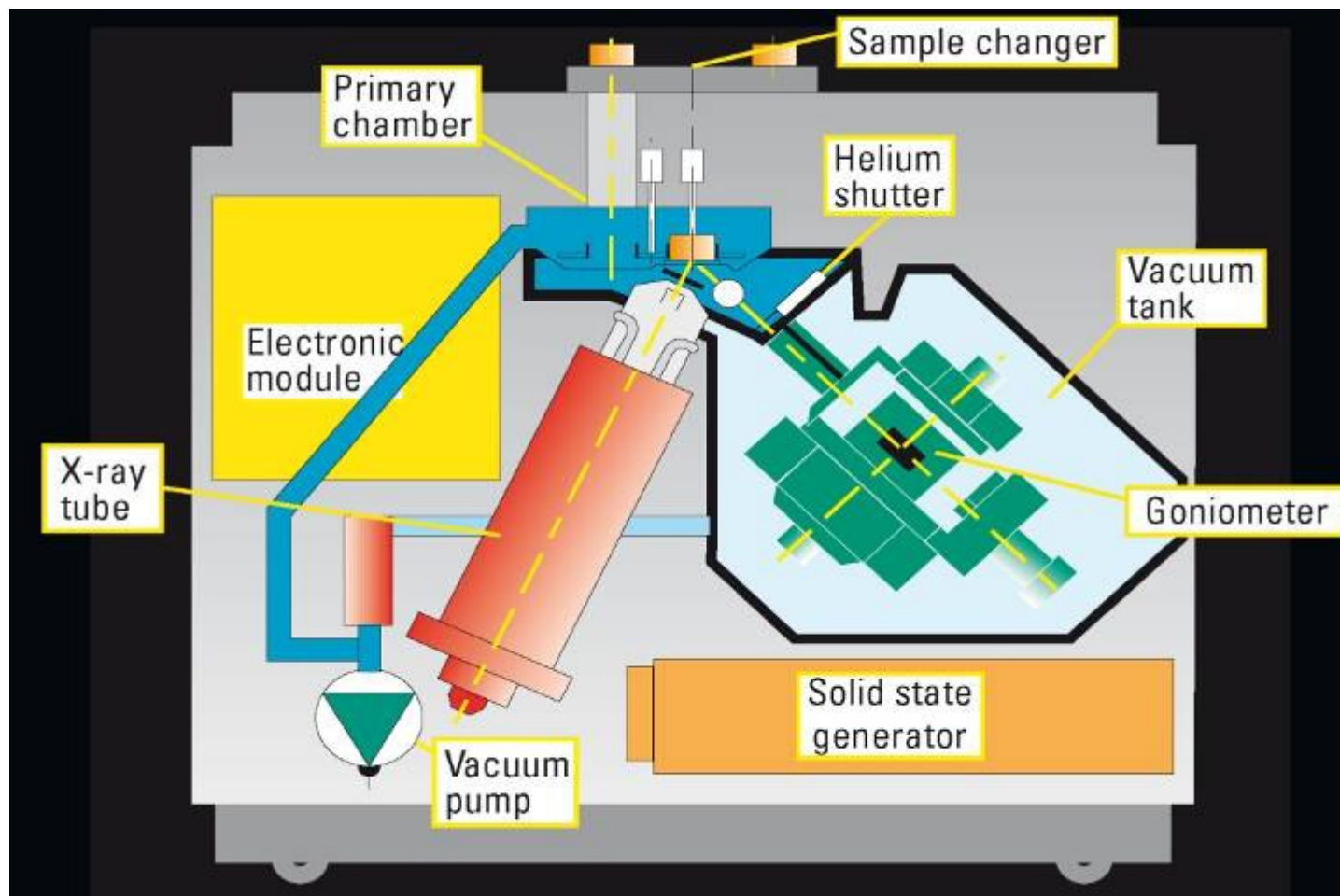
# X-ray tube evolution : closer coupling for higher sensitivities



ANODE

3GN

4GN
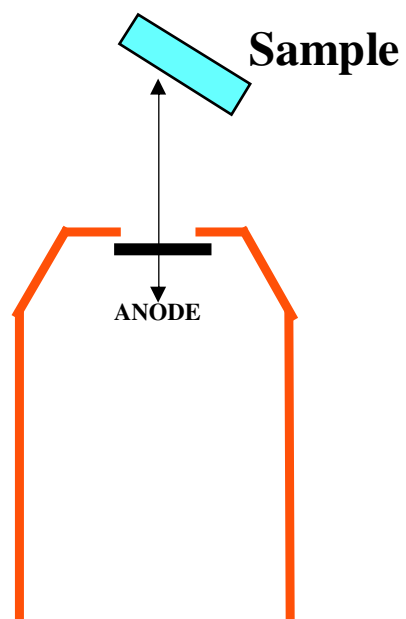
**ARL 8400**

**ARL 9400**

**ARL ADVANT'X Series**

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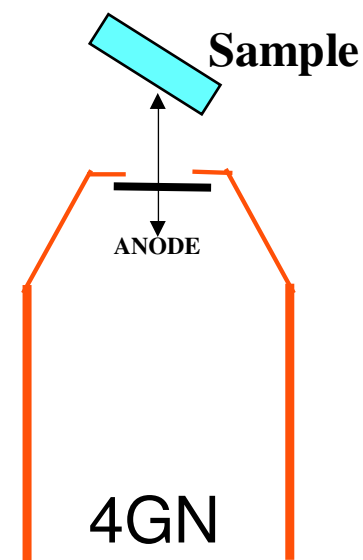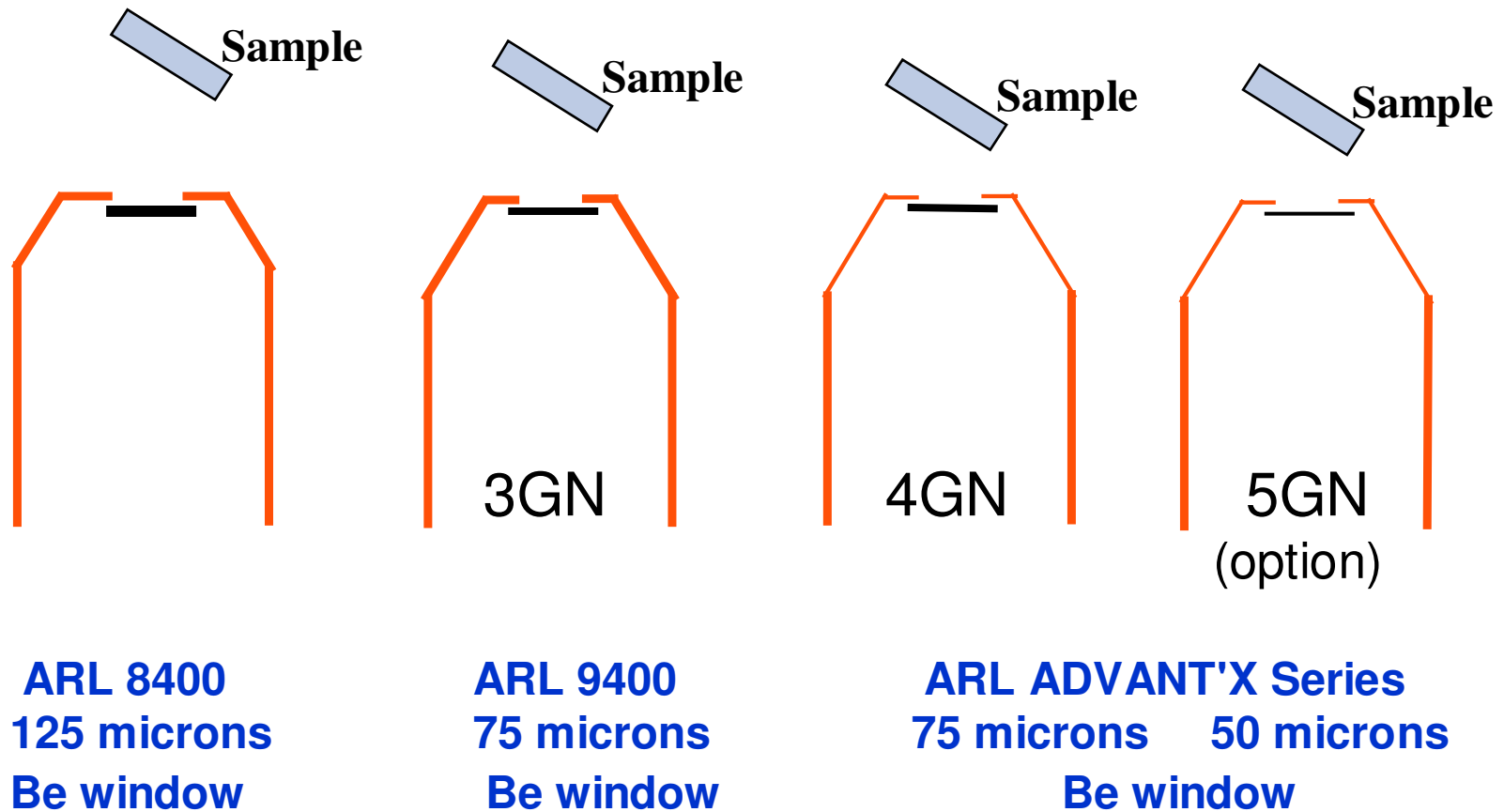
# X-ray tube evolution : thinner windows

- Thinner window for enhanced excitation of ultra-light elements (Be to Cl)



**ARL 8400**
**125 microns**
**Be window**

**ARL 9400**
**75 microns**
**Be window**

**ARL ADVANT'X Series**
**75 microns    50 microns**
**Be window**

# 5GN X-ray tube with 50μm Be window (optional)

- 50μm Be window brings enhanced sensitivity compared to 75μm Be window



**Sensitivity comparison
5GN tube (50micron Be) vs. 4 GN tube (75micron Be)**
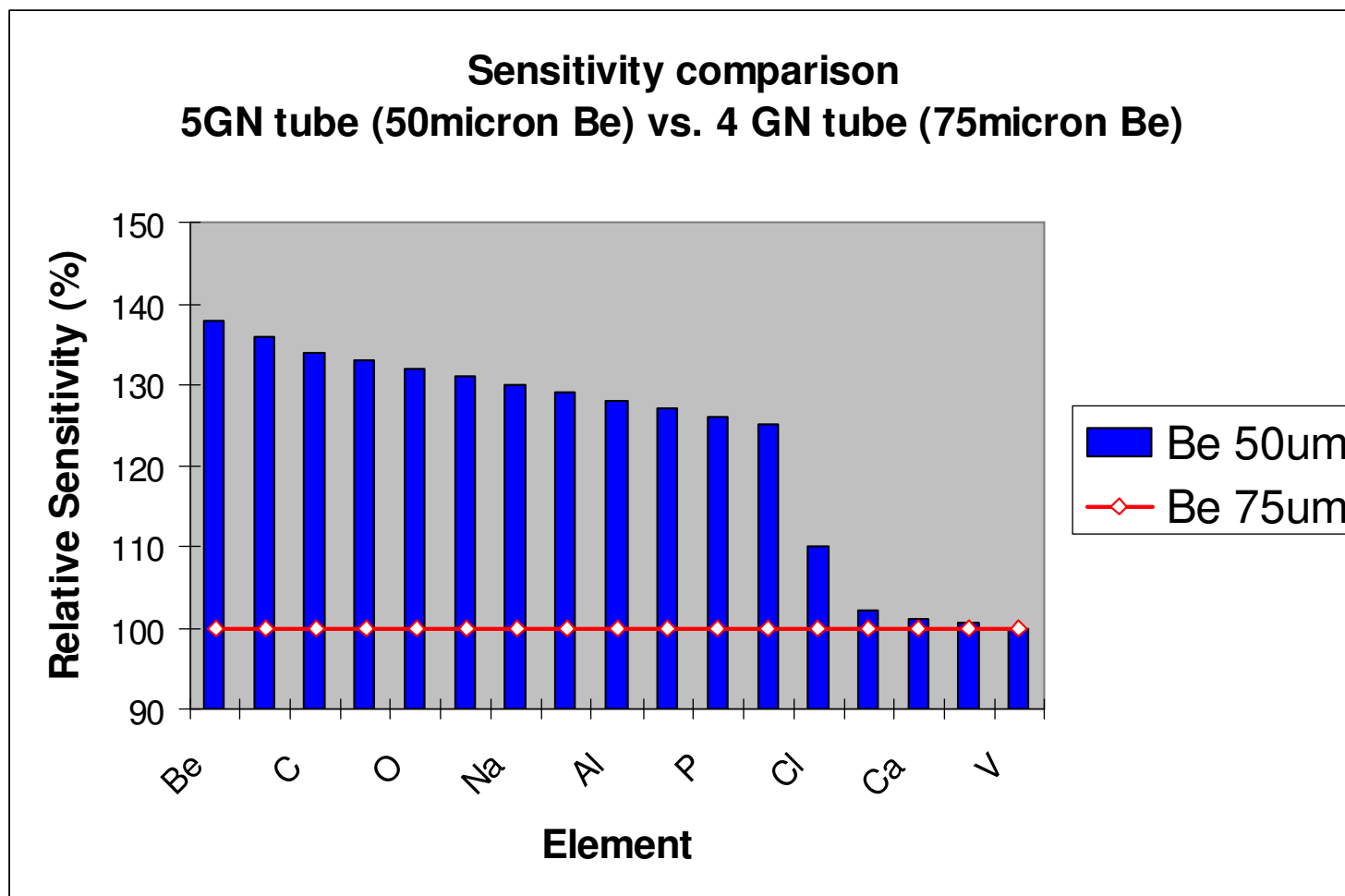
# Exclusive Gearless Goniometer

View of the latest Moiré fringe gearless goniometer, version F45

# … 10 Year Warranty
# on the angular positioning
# of the XRF goniometer

eXtra Performance in sequential XRF

# Exclusive Gearless Goniometer

- 5th Generation Goniometer

- Quantitative analysis of any element from Oxygen to Uranium (in basic configuration)

- Elements from Beryllium to Nitrogen when specific multilayer crystals are fitted

- Full capability for analysis of non-routine samples
  - Semi-quantitative analysis (QuantAS)
  - Stardardless analysis (UniQuant 5)

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# Exclusive Gearless Goniometer

- Moiré Fringe positioning
  - Digital precision < +/- 0.0002°
- Slewing speed up to 4800 deg/min
- Accuracy +/- 0.01 degree on LiF crystals
- Up to 4 collimators
- Up to 9 crystals
- Two detectors with angular range of 0° to 155°
- Fifth generation system with 25 years experience and 2500 gearless goniometers installed worldwide
- Automatic alignment of crystal and detector
  - No human errors & no radiation hazard
- Automatic self quality control

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# Exclusive Gearless Goniometer

## Moiré Fringe Positioning

- Crystal and detector systems are each linked to a circular glass diffraction grating

- Reader heads contain the smaller angled grating and the optical detector

- Crystal grating is rotated by a θ drive, while the detectors are moved at angle 2θ in order to satisfy Bragg's law :
  n λ = 2d sin θ
  - n = order of radiation
  - λ = wavelength of radiation
  - 2d = interplanar spacing of crystal
  - θ = angle of incidence on the crystal
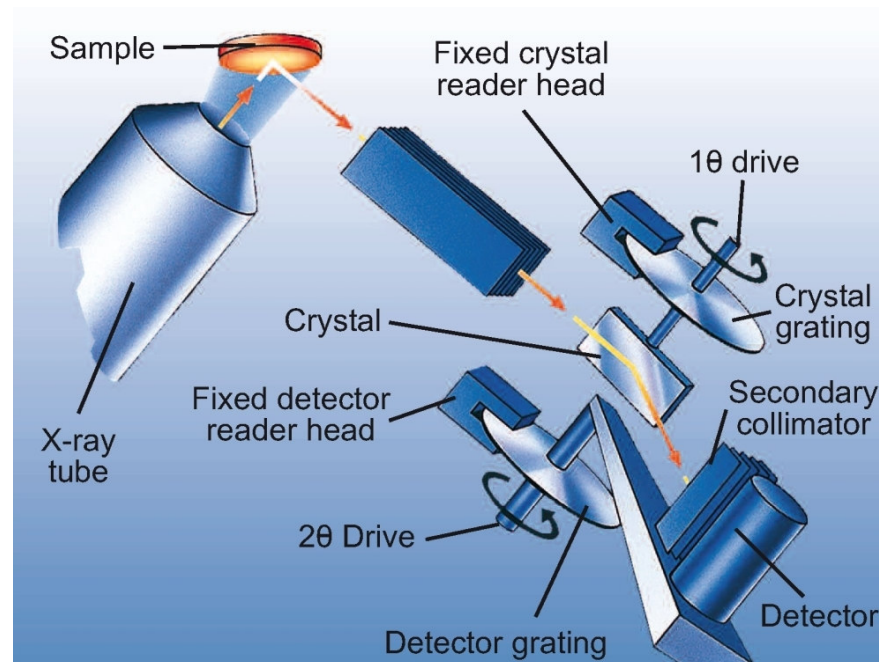


**Goniometer Principle of Operation**

# Choice of Collimators, Crystals & Detectors

| FEATURE | Sensitivity | Resolution | Be | B | C | N | O -F -Na | Mg | Al | Si | P -S -Cl | K | Ca...Ti...Fe Sn...Yb | Co...Zn...Sn Hf...U |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **K Spectra / L Spectra** | | | | | | | | | | | | | | |
| **COLLIMAT.** | | | | | | | | | | | | | | |
| X-Coarse 2.6° | V.High | Low | | | | | | | | | | | | |
| Coarse 0.6° | High | Fair | | | | | | | | | | | | |
| Medium 0.25° | Good | Good | | | | | | | | | | | | |
| Fine 0.15° | Low | High | | | | | | | | | | | | |
| **CRYSTAL** | | | | | | | | | | | | | | |
| AXBeB | High | Low | Be | | | | | | | | | | | |
| AX20 | Good | Low | | B | | | | | | | | | | |
| AX16 | High | Low | | | C | | | | | | | | | |
| AX09 | Good | Low | | | | N | | | | | | | | |
| AX06 | High | Low | | | | | O | | | | | | | |
| AX03 | Good | Good | | | | | O | | | | | | | |
| TIAP | Good | Good | | | | | O | | | | | | | |
| ADP | Low | High | | | | | | Mg | | | | | | |
| PET | Good | Fair | | | | | | | Al | | | | | |
| InSb | High | High | | | | | | | | Si | | | | |
| Ge111 | Good | High | | | | | | | | | P | | | |
| LiF 200 | Good | Good | | | | | | | | | | K | | |
| LiF 220 | Fair | High | | | | | | | | | | | Ti | |
| LiF420 | Low | V.High | | | | | | | | | | | | |
| **DETECTOR** | | | | | | | | | | | | | | |
| FPC | | | | | | | | | | | | | | Zn |
| Scintillation | | | | | | | | | | | | | | |

FPC = flow proportional counter

# ARL ADVANT'X Intellipower Series

## Comprehensive sample loading systems
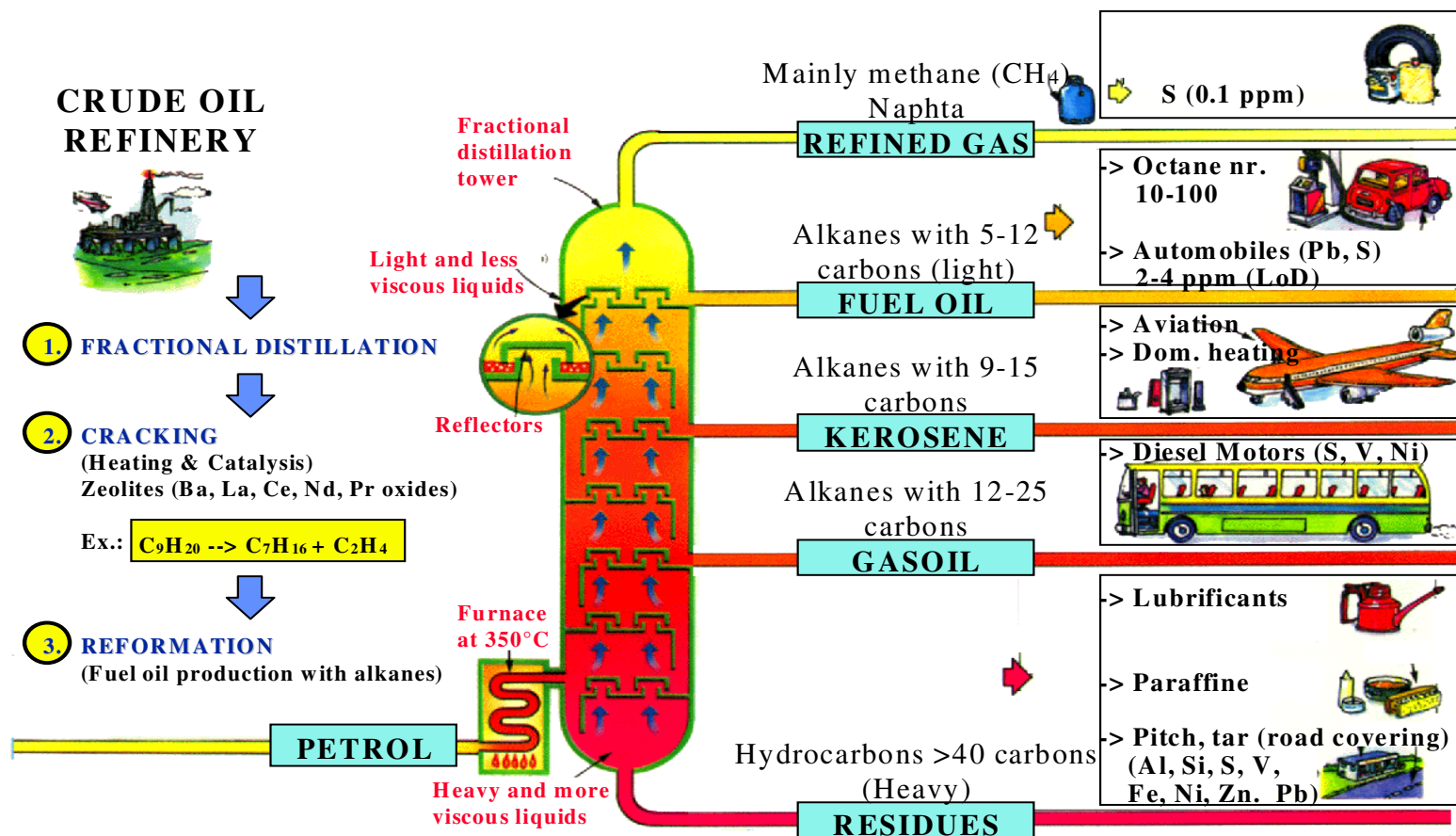
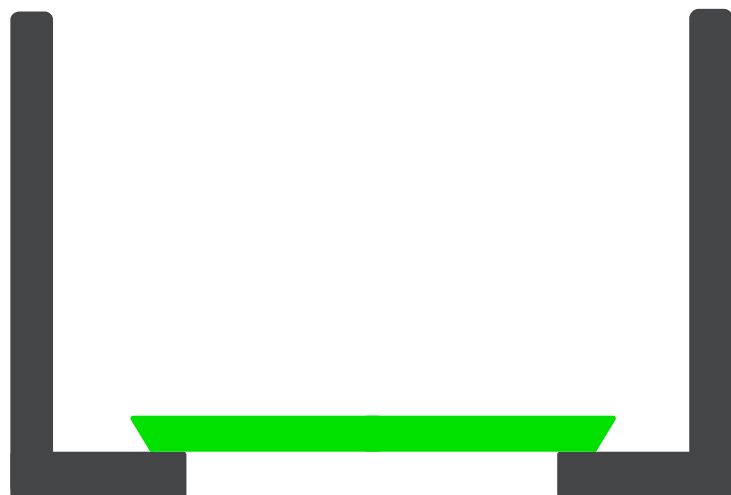Single position      12 positions      Large X-Y auto-sampler

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## PETROCHEMICALS: Process, Products & Analysis

**CRUDE OIL REFINERY**

**1.** FRACTIONAL DISTILLATION

**2.** CRACKING
(Heating & Catalysis)
Zeolites (Ba, La, Ce, Nd, Pr oxides)

Ex.: $C_9H_{20} \rightarrow C_7H_{16} + C_2H_4$

**3.** REFORMATION
(Fuel oil production with alkanes)

PETROL

Fractional distillation tower

Light and less viscous liquids

Reflectors

Furnace at 350°C

Heavy and more viscous liquids

Mainly methane (CH$_4$)
Naphta
REFINED GAS

Alkanes with 5-12 carbons (light)
FUEL OIL

Alkanes with 9-15 carbons
KEROSENE

Alkanes with 12-25 carbons
GASOIL

Hydrocarbons >40 carbons (Heavy)
RESIDUES

S (0.1 ppm)

-> Octane nr. 10-100
-> Automobiles (Pb, S) 2-4 ppm (LoD)

-> Aviation
-> Dom. heating

-> Diesel Motors (S, V, Ni)

-> Lubrificants
-> Paraffine
-> Pitch, tar (road covering) (Al, Si, S, V, Fe, Ni, Zn. Pb)

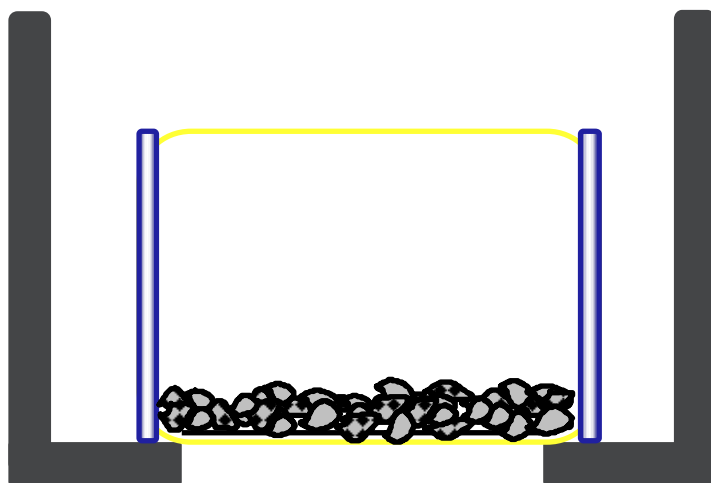# Sample preparation: Conventional Solid Samples

**Fused Glass Bead
or Polymer disc**
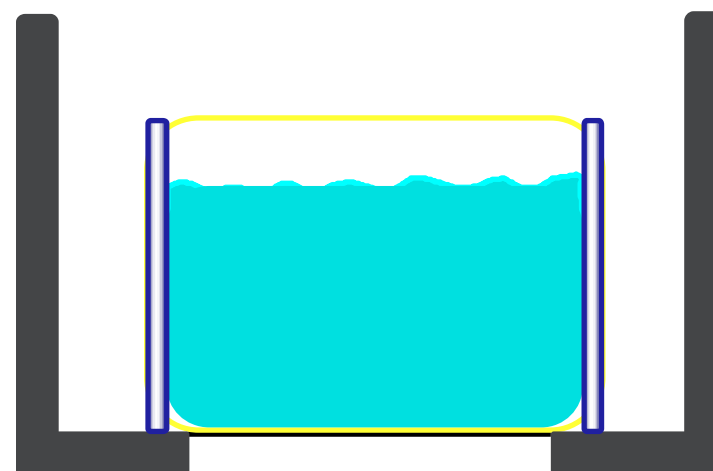(prepared by hot pressing)
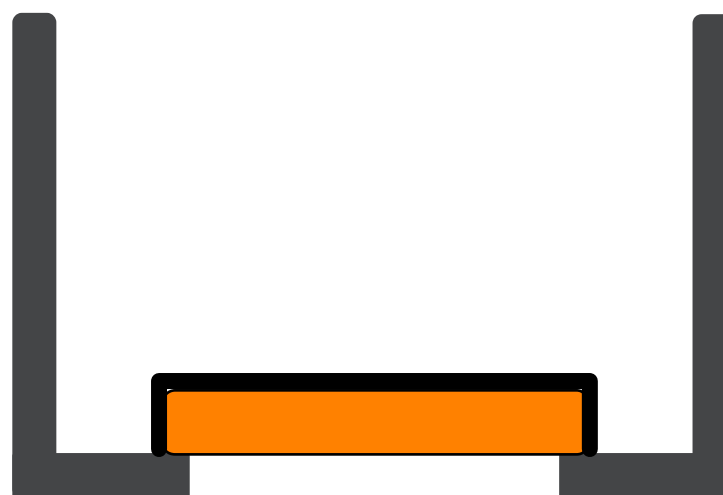
**Bulk Sample**
(Metal, Glass or Pressed
Powder)

# Other Sample Types



**Loose Granules**
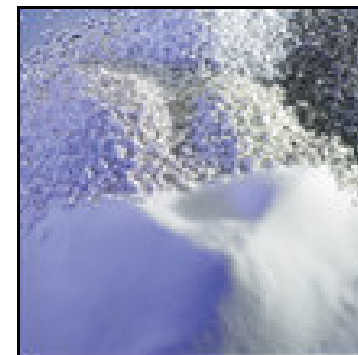- loss of precision
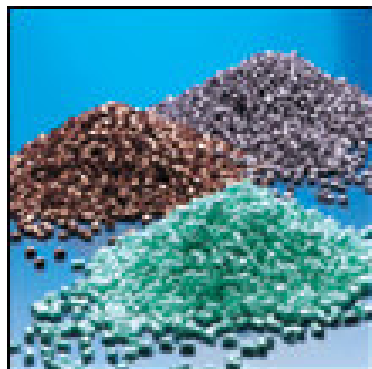- loss of accuracy

**Liquids**
(oils, solvants)
- no dilution required

# Analysis of traces in polymers

- **Catalysts for polymerization**
  - Al, Ti and Zn
- **Charges and additives**
  - Plasticizers
  - Lubricants
  - Stabilizing agents
  - Neutralizers
  - Anti-oxidants
  - Pigments
    - Mg, Si, P, S, Cl and Ca

# Analysis of traces in polymers



**TYPICAL LOD ON ARL ADVANT'X INTELLIPOWER SERIES**

| ELEMENT | 4200W (3 SIGMA) [PPM] | 3600W (3 SIGMA) [PPM] | 2500W (3 SIGMA) [PPM] | 1200W (3 SIGMA) [PPM] |
|---------|------|------|------|------|
| Mg | 0.86 | 0.93 | 1.11 | 1.61 |
| Al | 0.23 | 0.25 | 0.30 | 0.43 |
| P | 0.16 | 0.17 | 0.21 | 0.30 |
| Cl | 0.30 | 0.32 | 0.39 | 0.56 |
| Ca | 0.14 | 0.15 | 0.18 | 0.26 |
| Ti | 0.10 | 0.11 | 0.13 | 0.19 |
| Cr | 0.11 | 0.12 | 0.14 | 0.21 |
| Fe | 0.07 | 0.08 | 0.09 | 0.13 |

- Limits of detection for various elements in polymers (100s counting time)

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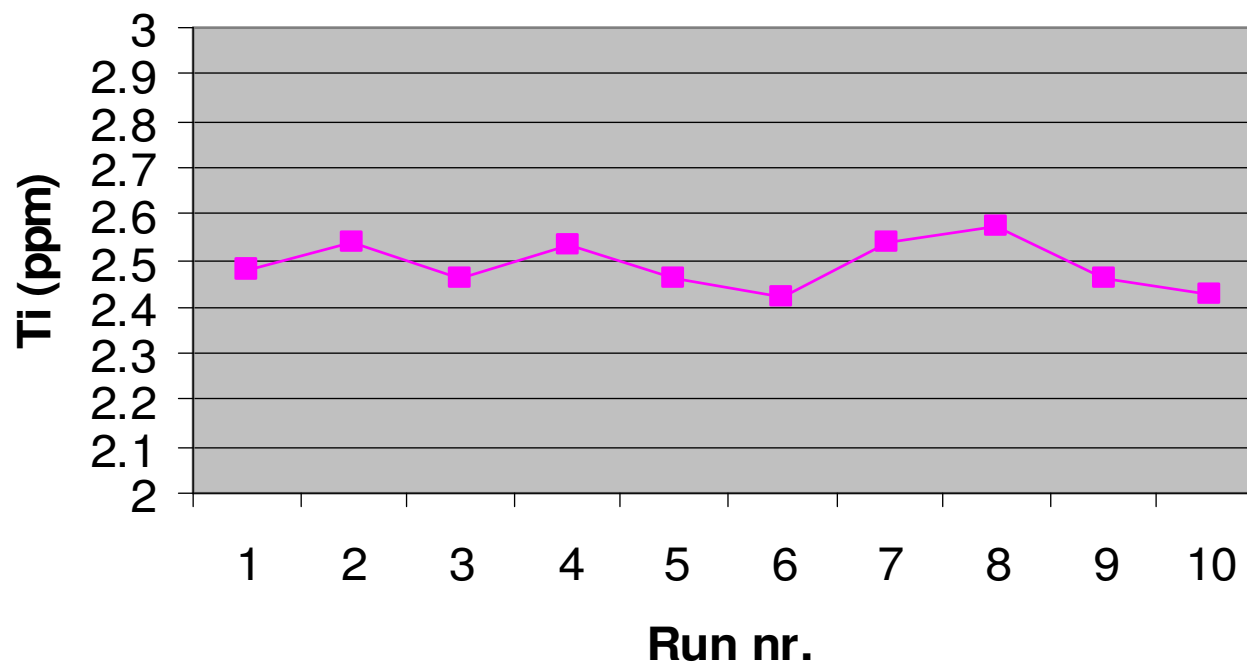**Thermo Fisher** SCIENTIFIC

# Demands on Ti analysis in polymers

- Ti used as catalyst
- Undesirable rest in the polymer
- Monitoring required
- $\pm$ 0.1 ppm on a range from 0.5 to 5 ppm

# Repeatability for Ti analysis in polymers

- 10 runs – 60 seconds analysis time
- Sample comes out of spectrometer after each run
- Standard deviation : 0.052 ppm

# Repeatability for trace analysis in polymers

| RUN | Al [PPM] | Ca [PPM] | Fe [PPM] | Mg [PPM] | Ti [PPM] | P [PPM] | Ce [PPM] |
|---|---|---|---|---|---|---|---|
| 1 | 71.3 | 104.4 | 11.4 | 60.1 | 2.1 | 15.6 | 24.2 |
| 2 | 72.0 | 104.2 | 11.6 | 59.9 | 2.0 | 15.6 | 24.0 |
| 3 | 71.6 | 104.1 | 11.6 | 60.8 | 2.0 | 15.6 | 23.0 |
| 4 | 71.5 | 105.1 | 11.4 | 60.6 | 2.1 | 15.7 | 23.5 |
| 5 | 72.5 | 104.9 | 11.6 | 61.3 | 2.0 | 15.6 | 23.2 |
| 6 | 73.5 | 105.2 | 11.4 | 61.5 | 2.0 | 15.9 | 23.7 |
| 7 | 72.7 | 105.6 | 11.6 | 61.7 | 2.2 | 16.1 | 23.6 |
| 8 | 73.4 | 105.8 | 11.6 | 60.5 | 2.1 | 16.2 | 22.4 |
| Avg. | 72.3 | 104.9 | 11.5 | 60.8 | 2.0 | 15.8 | 23.5 |
| SD | 1.4 | 1.0 | 0.1 | 0.2 8 | 0.1 | 0.4 | 1.3 |

- 8 runs on the same polymer disc
- 20 seconds analysis time per element
- Power: 4200W

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# References in polymers analysis



**Masterbatches**
- **Schulman Plastics (Belgium)**
- **Clariant (Italy)**

**Tapes and adhesives**
- **MacTac Europe (Belgium)**
- **Nitto Europe (Belgium)**

**Polymers films**
- **Toray Plastics (France)**
- **Huntsman Chemicals (USA)**
- **Mitsubishi Chemicals (ex-Hoechst Diafoil) USA**

**Tyres and rubber**
- **Pirelli (Italy)**

# References in polymers analysis

**Polyolefins**
- **Montell (Italy)**
- **Borealis (Finland)**
- **Tecnip Qatar (QR)**
- **SABIC Ibn Zahr (Saudi Arabia)**
- **Saudi Polyolefins (Saudi Arabia)**
- **The Polyolefin Company (Singapore)**
- **Technimont (UAE)**
- **PolyOne (USA)**

**Monomers, Polymers, Resins**
- **Arkema (ex-Atofina Chemicals) (USA)**
- **Lubrizol (USA)**
- **BP Amoco Chemicals (USA)**
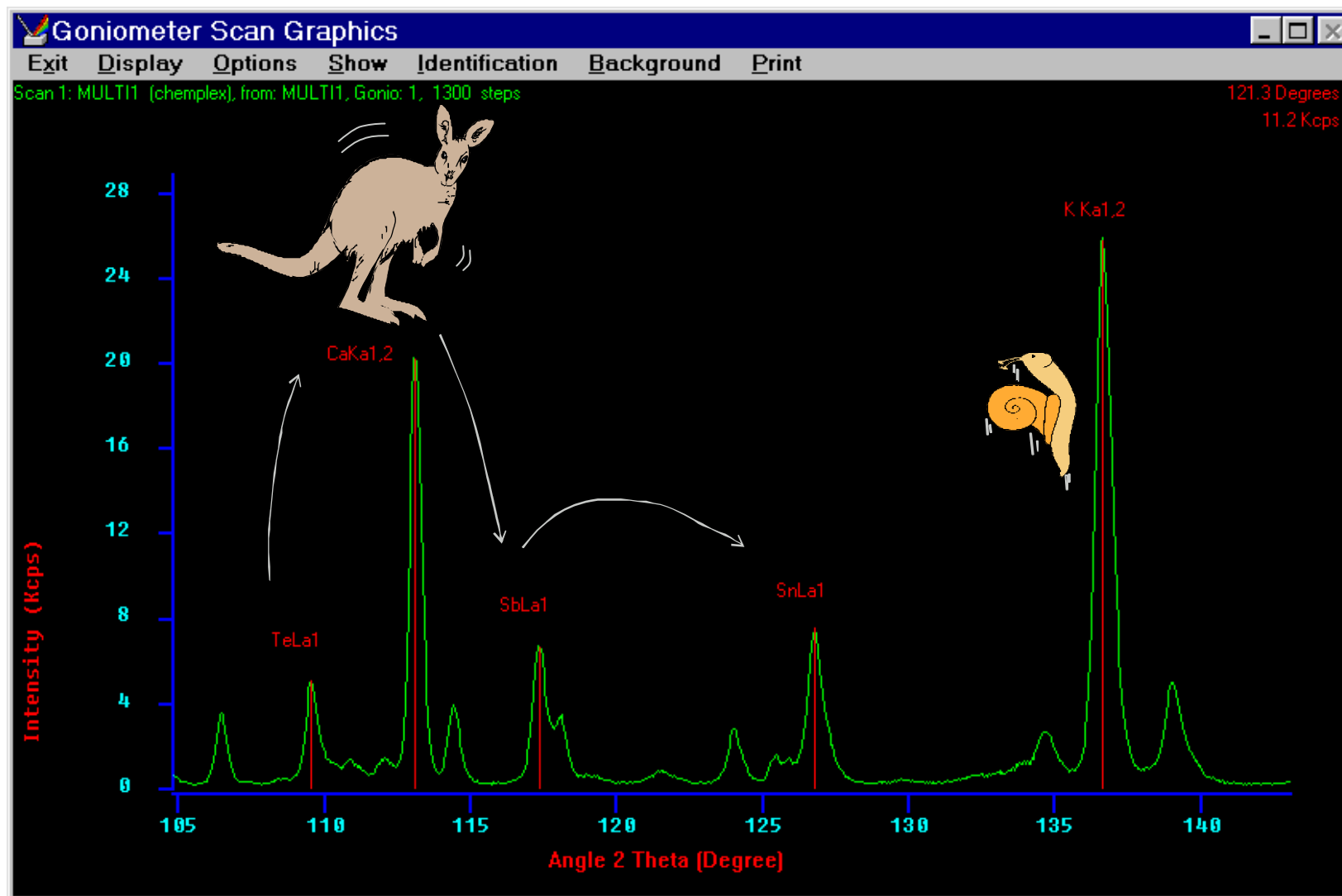- **G.E. Plastics (USA)**
- **etc..**

WDXRF has the distinction of being unique and powerful technique by virtue of

## Standard-less analysis

Made possible by advancement of mathematical formulation of XRF through Fundamental Parameters and thorough understanding of the physics behind XRF.

# Standard-less XRF analysis
# Two methods used: Peak hopping vs. Scanning

# Versatility of standard-less program UniQuant v.5

## Variety of samples types and nature

- Solids such as polymers, alloys and pressed powders

- Liquids with variable mass (catch weight)

- Fused beads with varying dilution (catch weights)

- Small amounts, as little a 10 mg powder.

- Odd shapes, small components.

- Monolayer on substrate. Composition and thickness

- Multilayer on substrate. Thickness of layers.

# Limits of detection in oils

| Element | Crystal/ Detector | LoD [ ppm] | LoD [ ppm] | LoD [ ppm] |
|---|---|---|---|---|
| | | Intellipower | Intellipower | Intellipower |
| | | 3600 W | 2500 W | 1200 W |
| Mg | AX06/FPC | 2.2 | 2.65 | 3.74 |
| Al | PET/FPC | 0.67 | 0.81 | 1.14 |
| Si | PET/FPC | 0.38 | 0.46 | 0.65 |
| S | GE111/FPC | 0.25 | 0.30 | 0.43 |
| Ca | LIF200/FPC | 0.17 | 0.21 | 0.29 |
| Cr | LIF200/FPC | 0.14 | 0.17 | 0.24 |
| Mn | LIF200/FPC | 0.14 | 0.17 | 0.24 |
| Fe | LIF200/FPC | 0.15 | 0.18 | 0.26 |
| Cu | LIF200/SC | 0.12 | 0.14 | 0.2 |
| Zn | LIF200/SC | 0.11 | 0.13 | 0.19 |
| Sn | LIF200/FPC | 0.57 | 0.69 | 0.97 |
| Pb | LIF200/SC | 0.14 | 0.17 | 0.24 |

**3 sigma – 100s counting time – 6 micron PP film**

# ARL OPTIM'X

High performance at affordable price

Unique WDXRF system

# ARL OPTIM'X

- Optimized configuration for optimum analytical results

# ARL OPTIM'X: Unique WDXRF product
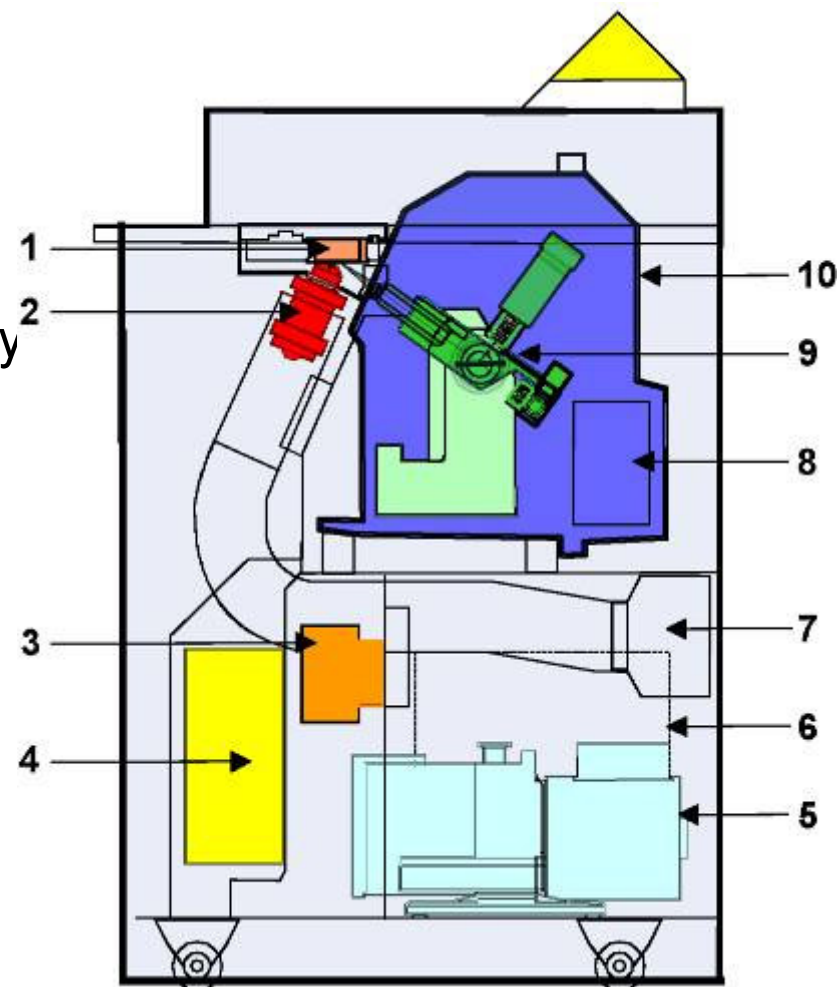
**WD-XRF**
SmartGonio™
Flexible, versatile,
elemental analysis

**WD-XRF**
Multichromators™
Rapid, dedicated
routine analysis
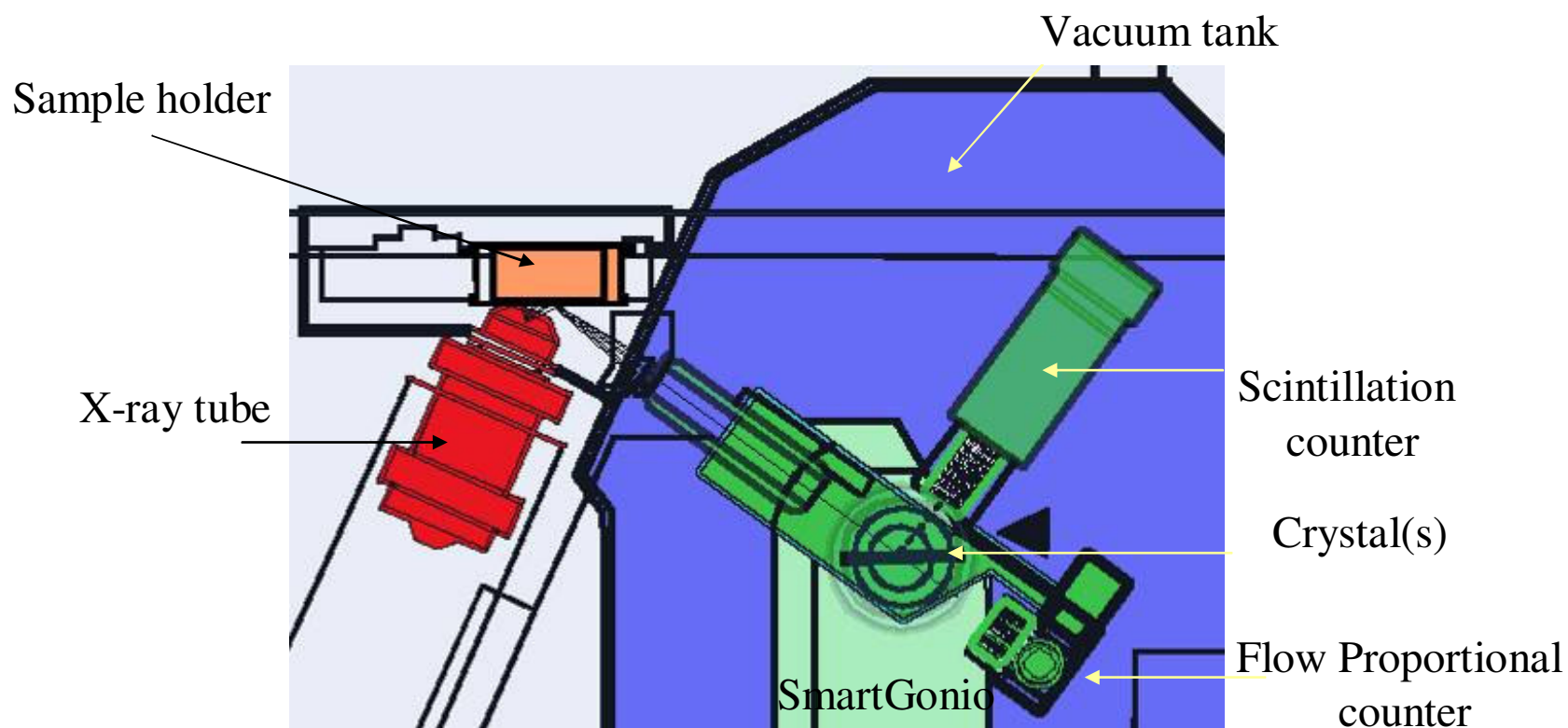
# ARL OPTIM'X

- **Side view**
  - 1 Sample
  - 2 X-ray Tube
  - 3 High voltage Power Supply
  - 4 Low voltage power supply
  - 5 Vacuum Pump
  - 6 Electronic Rack
  - 7 X-ray Tube cooling
  - 8 Carte XMI
  - 9 SmartGonio™
  - 10 Vacuum tank
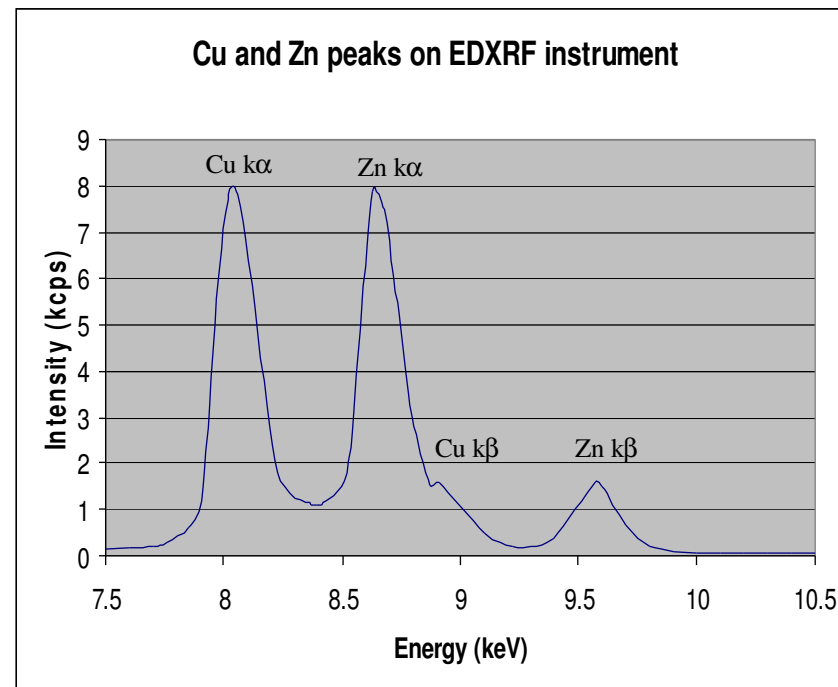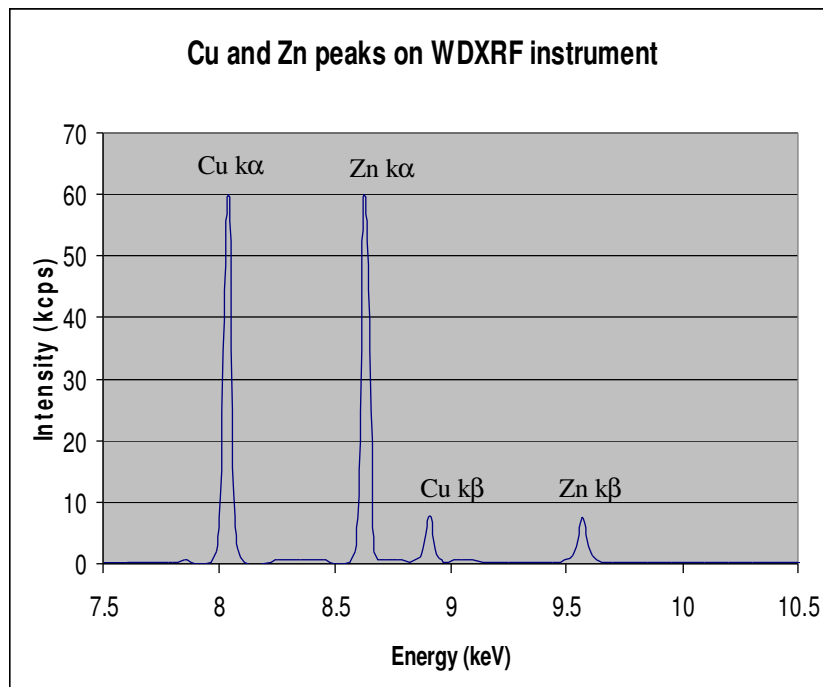
# Close coupling

- Mini X-ray tube (50W - air cooled)
- Close coupling of optics for optimized sensitivity equivalent to 200 W



Sample holder

X-ray tube

Vacuum tank

Scintillation counter

Crystal(s)

Flow Proportional counter

SmartGonio

# Superior Spectral Resolution

**Cu and Zn peaks on WDXRF instrument**

Intensity (kcps) vs Energy (keV)

Cu kα, Zn kα, Cu kβ, Zn kβ

**Cu and Zn peaks on EDXRF instrument**

Intensity (kcps) vs Energy (keV)

Cu kα, Zn kα, Cu kβ, Zn kβ

- 10 times better resolution compared to EDX
- 8 to 10 times higher count rates

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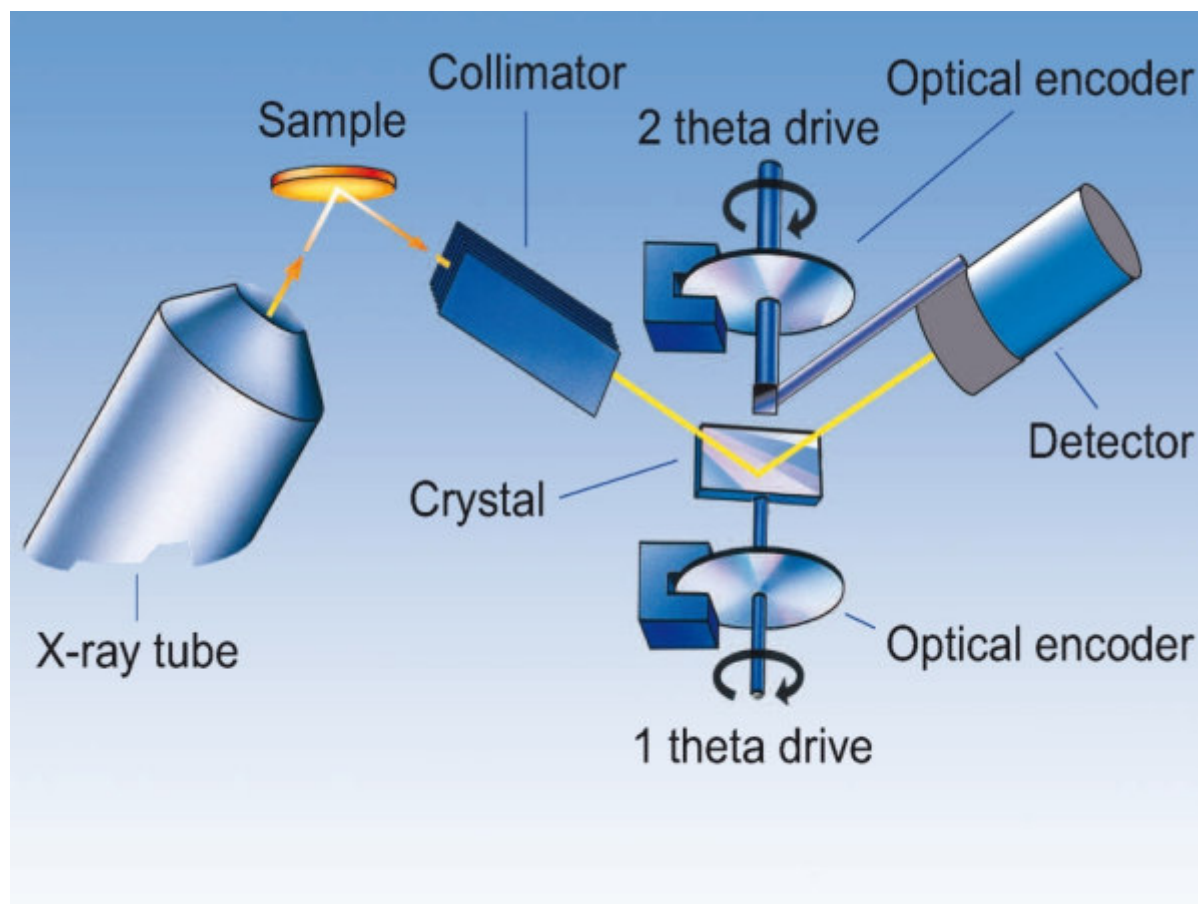
**View of the Moiré fringe SmartGonio<sup>TM</sup>**
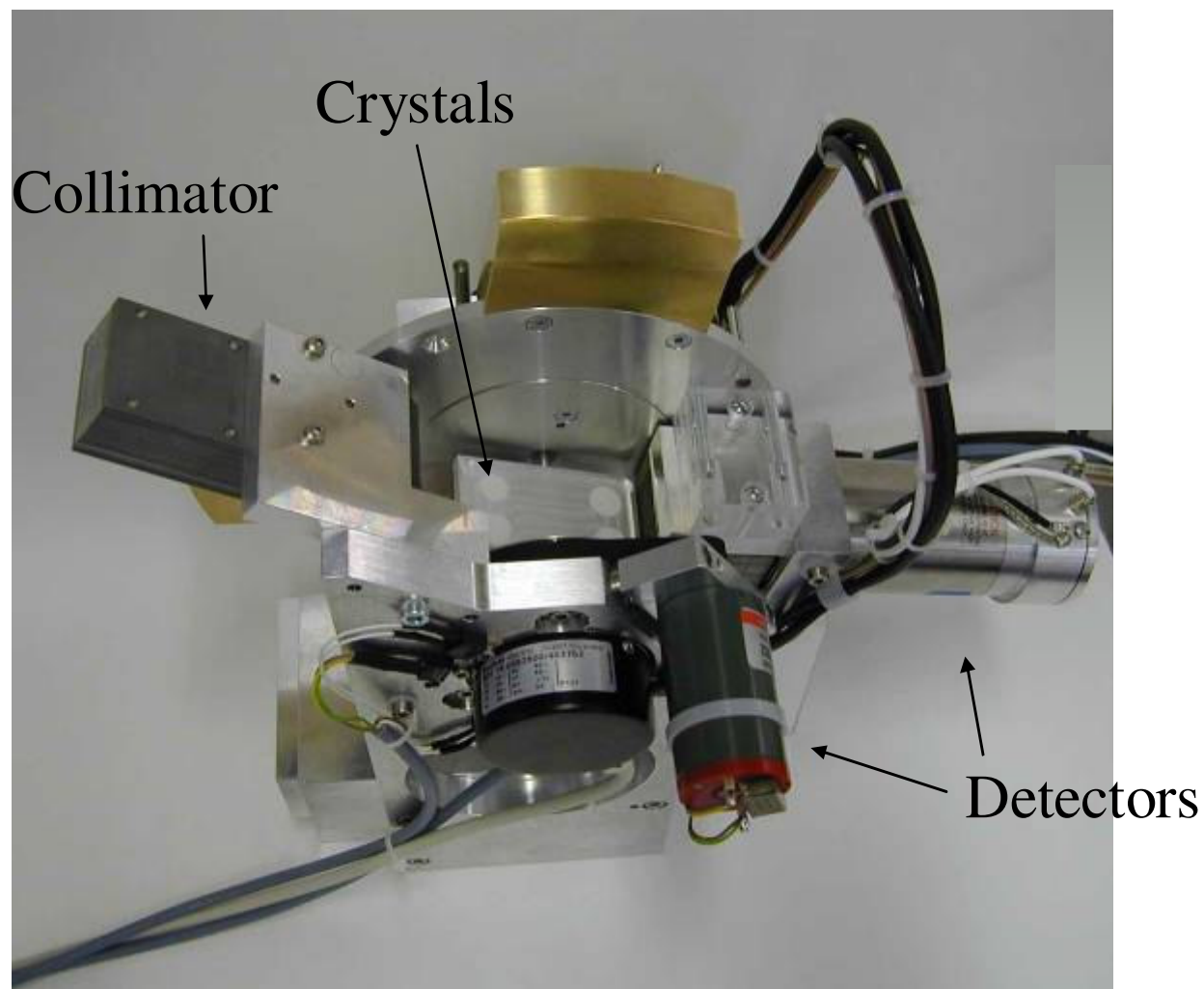
# Up to 3 crystals fitted !!

# Gives access to all elements
# from F to U
## (when 2 detectors fitted)

# Integrated Analytical Assistant
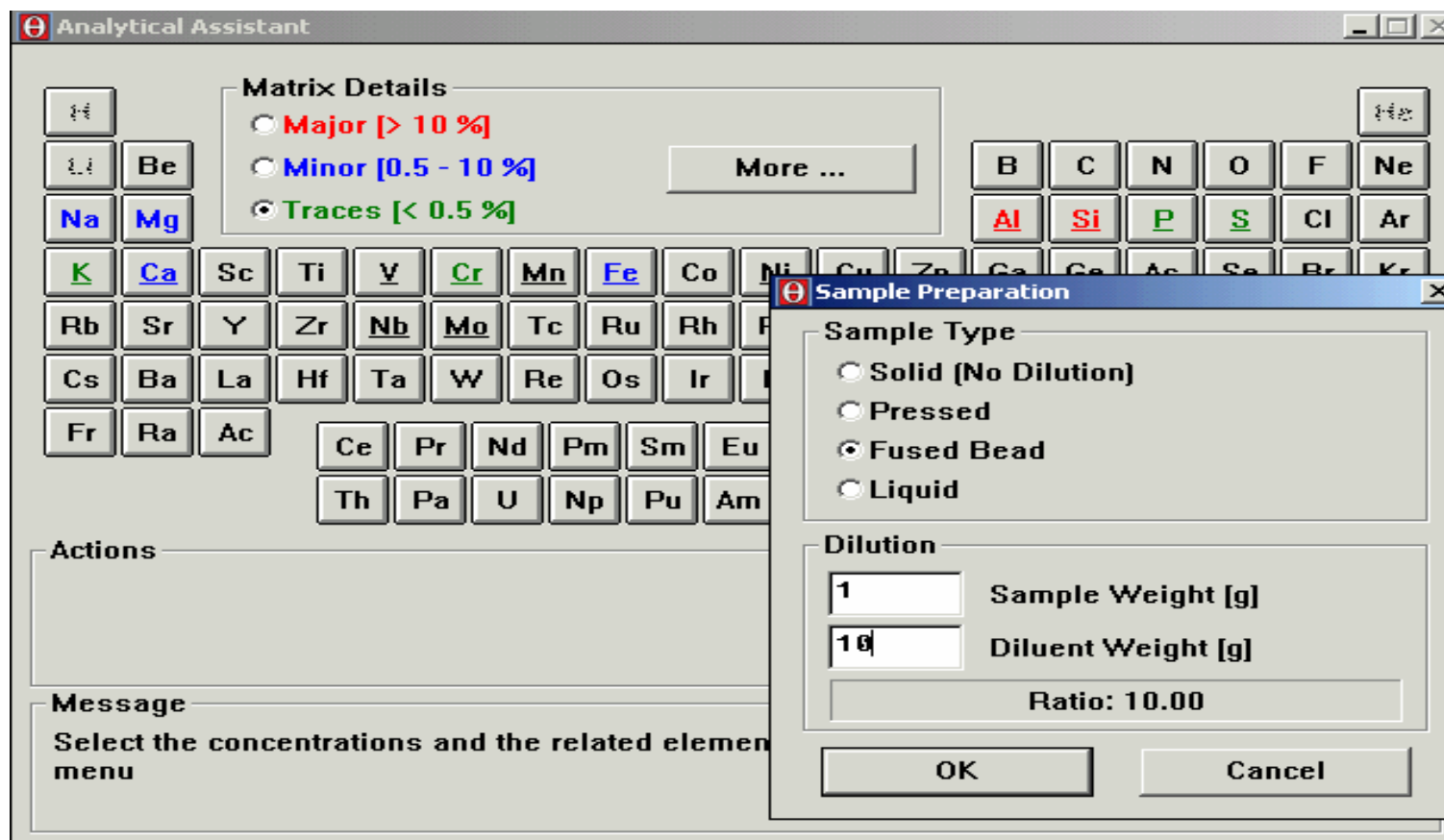


Analytical information on all analyzed elements
Ease of use and help through Analytical Assistant

# ARL Optim'X: Unique WDXRF Spectrometer

- Attractive price/performance ratio

- No water cooling required

- Low power consumption

- Very low detector gas consumption

- Most modern and intelligent electronics platform

- Minimized operating costs
  - no external water supply necessary (neither city water nor external water cooler circuit required)

- Modem connection for remote diagnostics

# Typical applications

**Oils, gasoline and other petrochemical products**

# Elemental analysis of oils and gasoline

- ISO 14596 or prEN ISO 20884 (S)
- ASTM D2622 (S)
- ISO 15597 (Cl and Br)
- ISO 14597 (Ni and V)
- ASTM D5059 (Pb)
- DIN 51577 (Cl)
- DIN 51391 (Ca, Zn)
- DIN 51431 (Mg)
- DIN 51363 (P)
- .....

# Elemental Analysis of oils and gasoline

SULPHUR IN GASOLINE AND DIESEL

- Environmental regulations worldwide are getting tighter
- Diesel fuel with $S \leq 10$ppm is already produced in some European countries
- By 2006 the limit for diesel has been set at 15ppm in USA
- In order to be sure to have less than 10ppm S in the market, the producer must produce at 4ppm S maximum.
- The XRF instrument must have a maximum LoD of 1.5 ppm to do the job

# ARL Optim'X: S in oil and gasoline

**ASTM D 2622 oder prEN ISO 20884**

**Limit of detection:**        1.4 ppm in 100s

                                       1.0 ppm in 200s
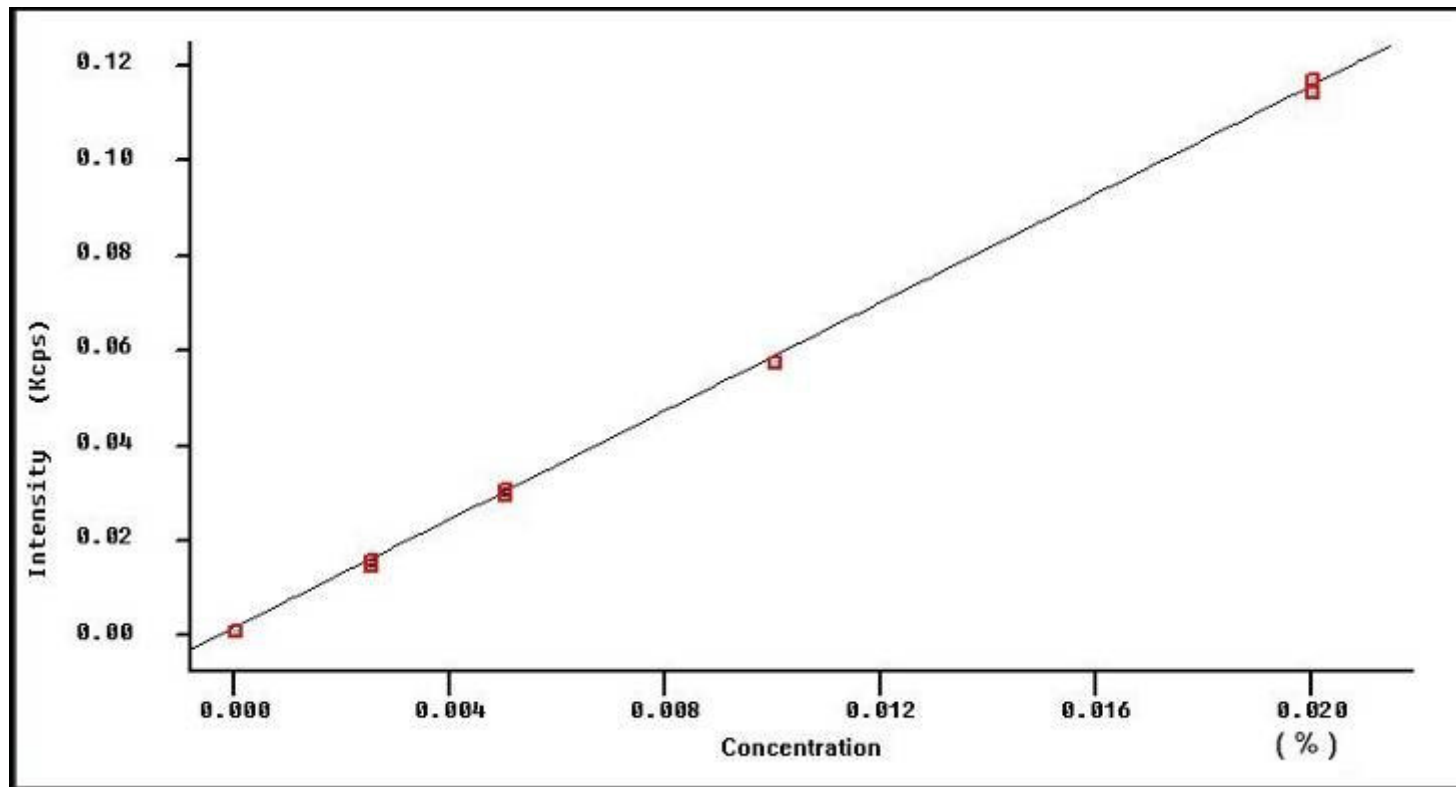
# ARL Optim'X: S in oil and gasoline

Short term repeatability (120 s)

Two samples - new cell at each run

| Sample | 25ppm | 100ppm |
|---|---|---|
| Run  1 | 25.4 | 100.6 |
| Run  2 | 25.7 | 100.7 |
| Run  3 | 26.4 | 101.8 |
| Run  4 | 26 | 102.3 |
| Run  5 | 25 | 98.4 |
| Run  6 | 25.9 | 100.5 |
| Run  7 | 26.7 | 101.5 |
| Average | 25.9 | 100.8 |
| Std. Dev. | 0.58 | 1.27 |

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# ARL Optim'X: Limits of detection

| Element | Fixed channel LOD [ppm] 120s |
|---------|------------------------------|
| Mg | 8 |
| Al | 3.1 |
| Si | 3.2 |
| P | 1.5 |
| S | 1.2 |
| Ca | 1.7 |
| Fe | 0.8 |
| Pb | 1 |

Oil matrix - Fixed channels - 120 s counting time

# ARL Optim'X: Limits of detection

| Element | SmartGonio configuration | Smart Gonio LOD [ppm] 120s |
|---|---|---|
| Al | PET/FPC | 4.2 |
| Si | PET/FPC | 4 |
| P | PET/FPC | 2 |
| S | PET/FPC | 1.7 |
| K | LIF200/FPC | 1.4 |
| Ca | LIF200/FPC | 1.5 |
| V | LIF200/FPC | 1 |
| Cr | LIF200/FPC | 1 |
| Mn | LIF200/FPC | 1 |
| Fe | LIF200/FPC | 1.1 |
| Ni | LIF200/SC | 0.6 |
| Cu | LIF200/SC | 0.8 |
| Zn | LIF200/SC | 0.6 |
| Pb | LIF200/SC | 1.7 |

Oil matrix
SmartGonio™
120 s counting time

*FPC :    Flow proportional counter*
*SC :       Scintillation counter*

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# Typical applications

- Polymers and masterbatch products

# ARL Optim'X: Application in Polymers

- **Limits of detection in Polymers**

| Elem. | Line | Crystal | Detector | Collima. | Time | Kv/mA | LOD |
|-------|------|---------|----------|----------|------|---------|----------|
| F | Ka | AX06 | FPC | 0.29 | 120 | 40/1.25 | 500 ppm |
| S | Ka | PET | FPC | 0.29 | 120 | 40/1.25 | 4.1 ppm |
| P | Ka | PET | FPC | 0.29 | 120 | 40/1.25 | 4.3 ppm |
| K | Ka | LIF200 | FPC | 0.29 | 120 | 40/1.25 | 1.5 ppm |
| Ti | Ka | LIF200 | FPC | 0.29 | 120 | 40/1.25 | 1.2 ppm |
| Cr | Ka | LIF200 | FPC | 0.29 | 120 | 40/1.25 | 1.1 ppm |
| Br | Ka | LIF200 | FPC | 0.29 | 120 | 40/1.25 | 0.9 ppm |

# ARL Optim'X: Application in Polymers

- **Repeatability in Polymers**

| | Run | F | Si | P | S | K | Ti | Cr | Br |
|---|---|---|---|---|---|---|---|---|---|
| sample 4 | 1 | 0.0098 | 0.0046 | 0.0023 | 0.0463 | 0.0174 | 0.00014 | 0.00002 | 0.0291 |
| sample 4 | 2 | 0.0032 | 0.0045 | 0.0022 | 0.0470 | 0.0173 | 0.00010 | 0.00005 | 0.0290 |
| sample 4 | 3 | 0.0211 | 0.0047 | 0.0020 | 0.0463 | 0.0175 | 0.00003 | -0.00003 | 0.0289 |
| sample 4 | 4 | 0.0239 | 0.0047 | 0.0023 | 0.0467 | 0.0172 | 0.00018 | 0.00000 | 0.0291 |
| sample 4 | 5 | -0.0147 | 0.0047 | 0.0022 | 0.0471 | 0.0177 | 0.00004 | -0.00003 | 0.0290 |
| sample 4 | 6 | 0.0343 | 0.0047 | 0.0022 | 0.0477 | 0.0172 | 0.00008 | -0.00007 | 0.0290 |
| sample 4 | 7 | 0.0305 | 0.0045 | 0.0020 | 0.0469 | 0.0173 | 0.00010 | -0.00003 | 0.0290 |
| sample 4 | 8 | -0.0015 | 0.0046 | 0.0023 | 0.0467 | 0.0172 | 0.00001 | 0.00000 | 0.0291 |
| sample 4 | 9 | 0.0239 | 0.0048 | 0.0027 | 0.0468 | 0.0172 | 0.00011 | 0.00008 | 0.0290 |
| sample 4 | 10 | 0.0220 | 0.0046 | 0.0028 | 0.0472 | 0.0175 | 0.00011 | 0.00006 | 0.0291 |
| sample 4 | 11 | 0.0042 | 0.0046 | 0.0024 | 0.0473 | 0.0174 | 0.00008 | -0.00001 | 0.0290 |
| | | | | | | | | | |
| | Ave. | 0.0143 | 0.0046 | 0.0023 | 0.0469 | 0.0174 | 0.00009 | 0.00000 | 0.0290 |
| | SD | 0.0151 | 0.00010 | 0.00023 | 0.00042 | 0.00015 | 0.00005 | 0.00005 | 0.00005 |

All results given in %

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