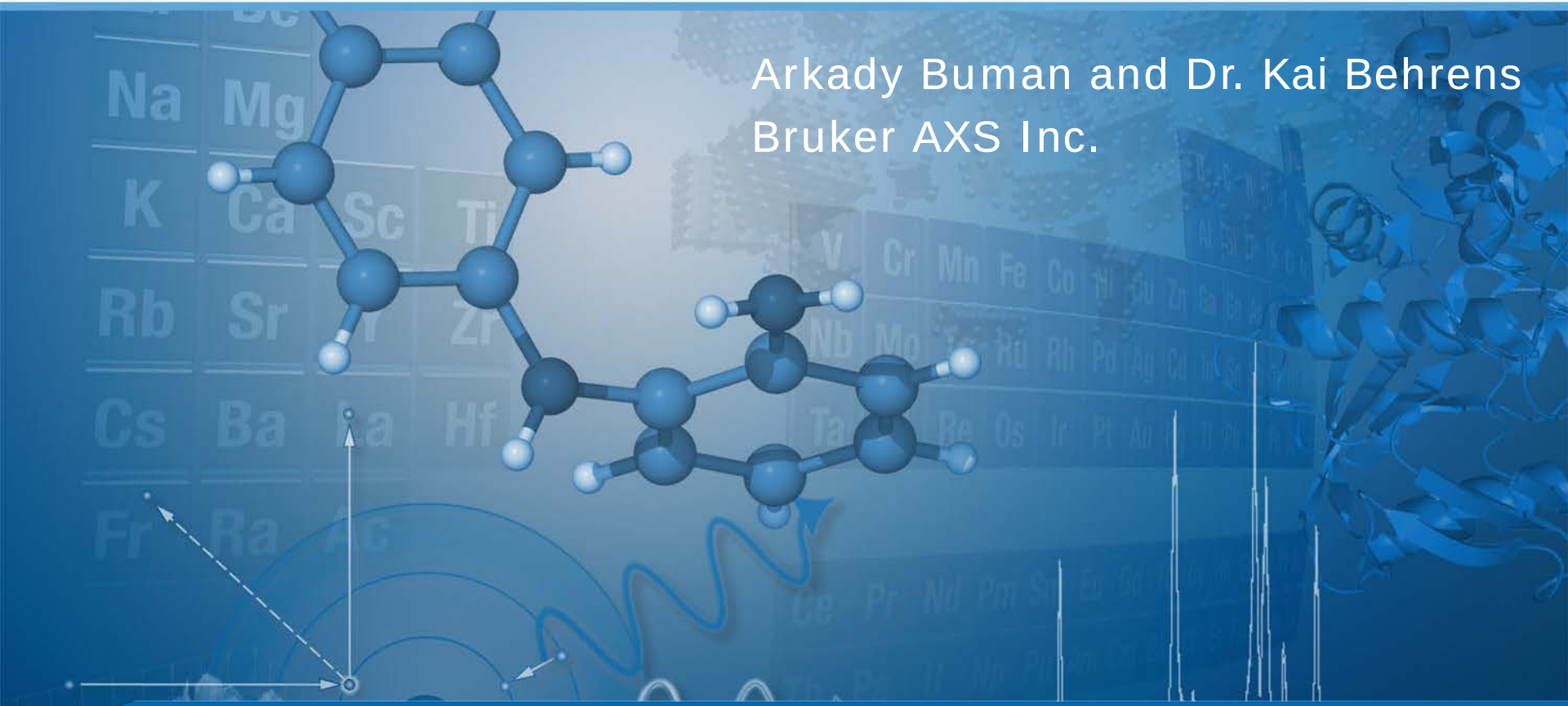
XRF Analysis of Polymers
Additives, Initiator Residues and Toxic Elements



Arkady Buman and Dr. Kai Behrens
Bruker AXS Inc.

Welcome
Today's Speakers

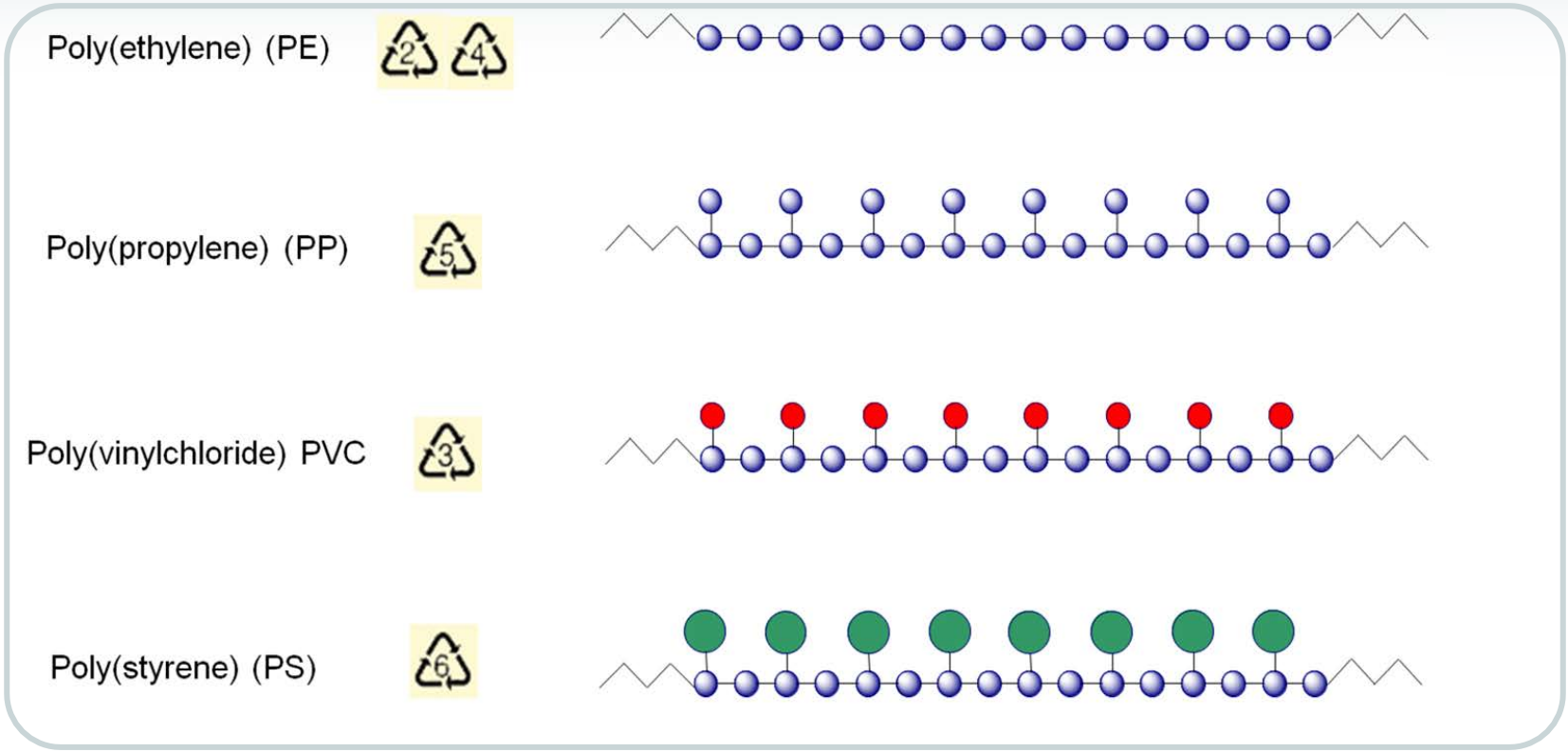
Arkady Buman
Product Manager XRF
Madison, WI, USA

Dr. Kai Behrens
Global Product Manager XRF
Karlsruhe, Germany

Webinar: XRF Analysis of Polymers
Topics

- Analytical tasks in polymer and plastics production
  - Process control
  - Quality control
- Analytical technology: WDXRF
- Results
  - Additives
  - Initiator residues
  - Impurities
  - Regulated toxic elements
- Ready-to-analyze solutions
- Q&A

Polymers and Plastics
Homopolymers



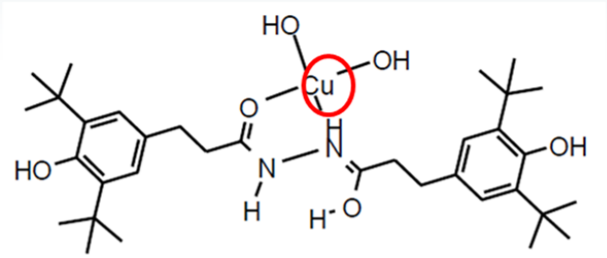
- PE, PP, PVC and PS are very popular polymers and have replaced a lot of traditional materials, such as metal or wood, due to longer lifetime and weight, better shaping and coloring characteristics
- ABS, PET, and Teflon are replacing other materials, such as ceramics and glass, in technolgically advanced products

Polymers and Plastics Additives

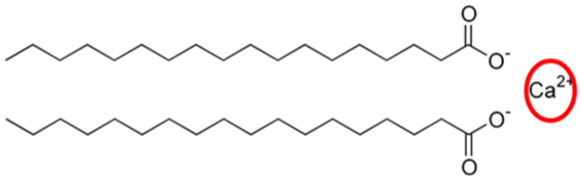
- Thermal stabilizers (processing, long term)
- UV stabilizers
- Pigments
- Carbon black
- Processing aids
- Anti-block
- Anti-statics
- Slip agents
- Flame retardants

Polymers and Plastics
Stabilizer and Processing Aids

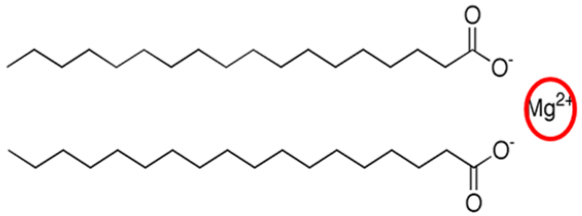
- Metal deactivators form stable complexes with metal ions thus improving stability



- Calciumstearate



- Magnesiumstearate



- Mg, P, Cu and Ca are indicators for additives
- Mg, Al, Ti, Ni, Mo are typical residues from initiators
- F, Cl, Fe, Zn are impurities from production processes
- Pb, Hg, Br, Cd, Cr are regulated substances (RoHS, WEEE), other regulations such as consumer product safety and end of life of vehicles (ELV) also regulate other elements such as Sb

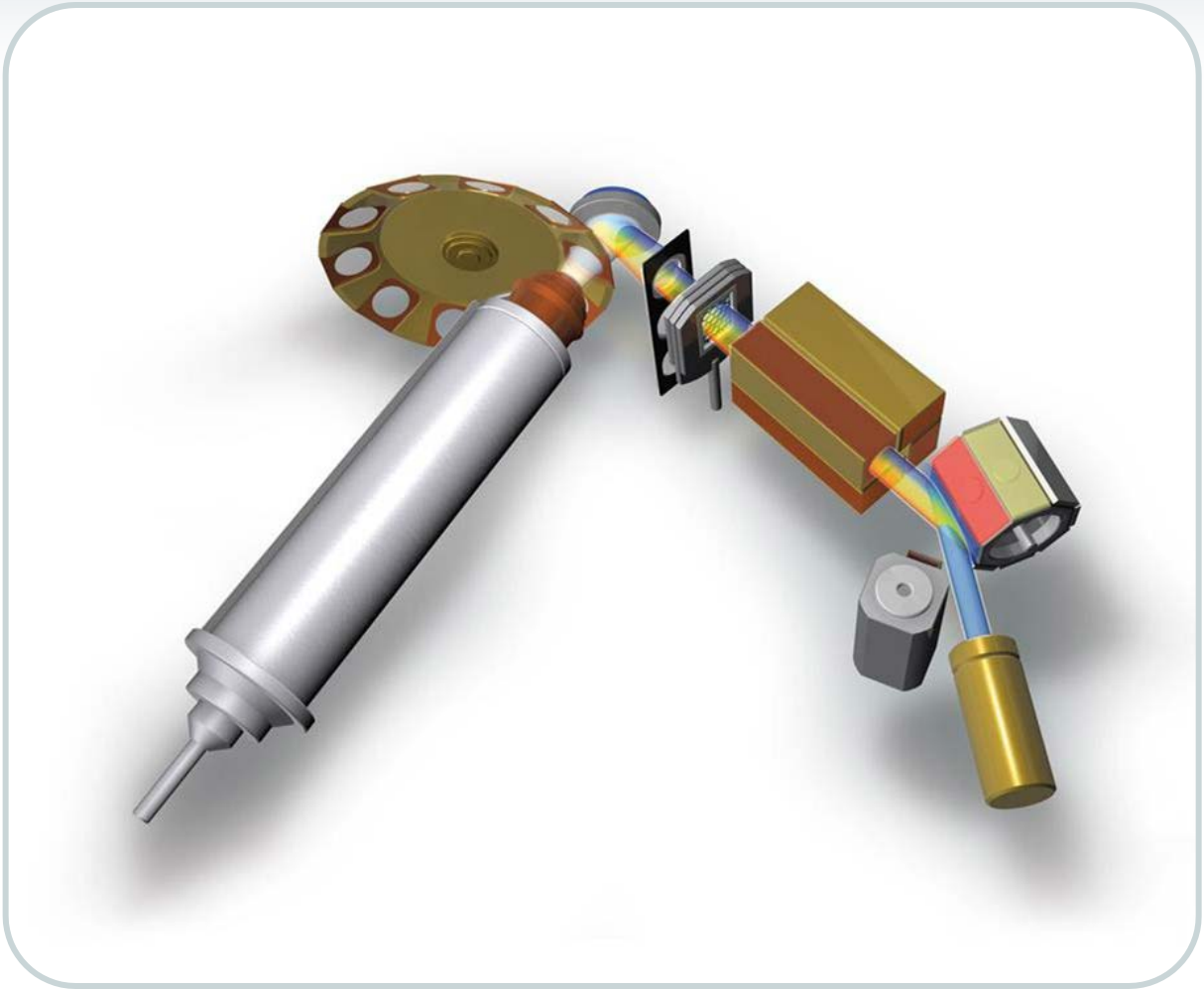
S8 TIGER
WDXRF Spectrometer Series

S8 TIGER(((WDXRF spectrometers are the latest models on the market with most modern technology!

Available in three basic configurations:

- S8 TIGER 1K
- S8 TIGER 3K
- S8 TIGER 4K

S8 TIGER
Sequential WDXRF Spectrometer



Analytical flexibility:

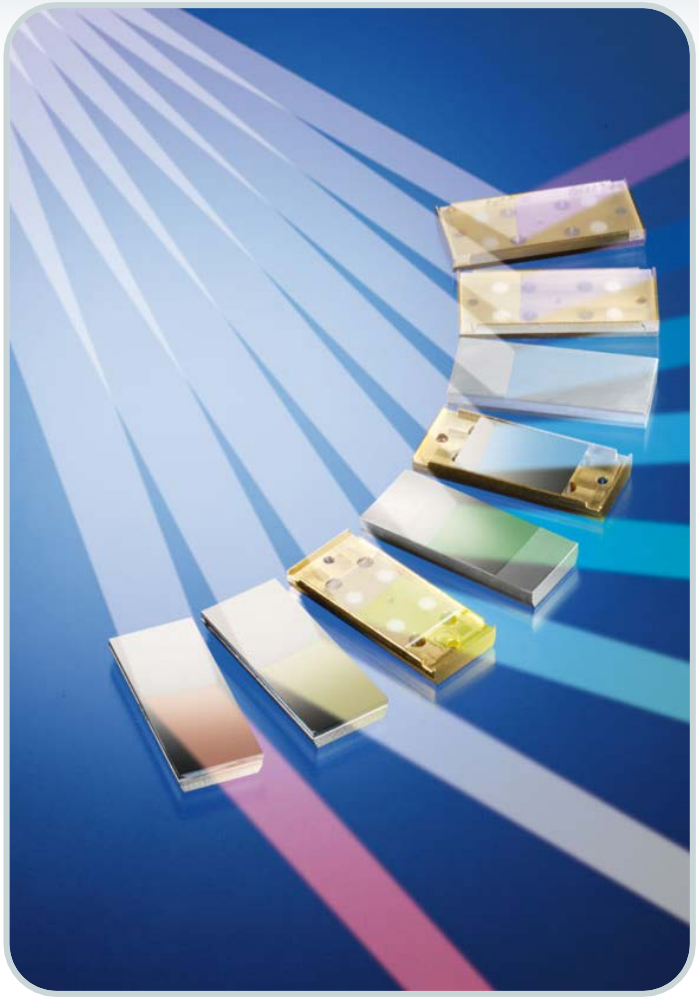
- 4 kW excitation
  20 – 60 kV
- 5 – 170 mA
- 10 beam filters
- 4 collimators
- 8 crystals
- 2 detectors

WDXRF Spectrometer Series: S8 TIGER 4K

Superior analytical performance with clear benefits by design:

- Best in the market:
- max. 170mA - 4 kW for best light element analysis
- No compressed air
- Dust-sealed spectrometer cabinet
- Smallest footprint (~0.8 m^2)
- Reduced helium consumption
- Reduced cooling water consumption, independent of short fluctuations

S8 TIGER
Superior Analytical Performance



Unrivalled analytical flexibility:

- 10-position beam filter changer
- 4-position collimator changer
  (6 different divergence settings)
- 8-position crystal changer
  (15 different crystals)

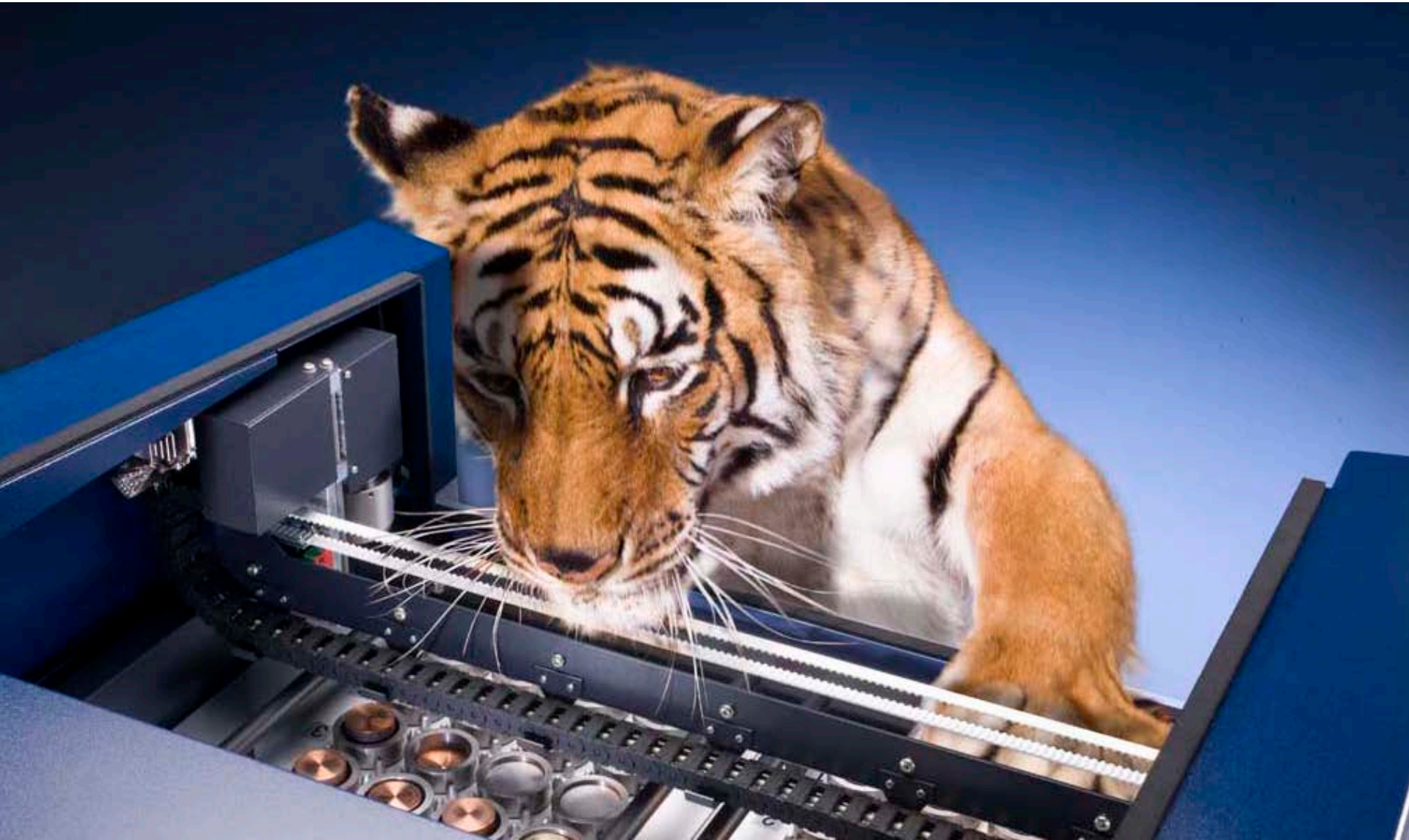
Application-optimized crystals:

- XS-CEM: long-term stable, temperature-independent
- XS-GE-C: plus 40% intensity for P, plus 20% intensity for S
- XS-PET-C: plus 20% intensity for Al
- XS-B: plus 100% intensity for B

S8 TIGER
X-ray Technology – High Performance

- Highest excitation intensity for all elements
  - Optimized beam path with highest flexibility
  - Compact beam path with lowest distance anode – sample - detector
- Best light element excitation
  - Low kV excitation voltage for reduced background
  - Full 4 kW excitation power up to 170 mA for best element sensitivities
- Excellent precision
  - Direct loading of the sample in the reference position, no inaccurate positioning in comparison to turret systems
  - Reliable analysis of liquid samples
- No heat-up and burning of samples in comparison to conventional XRF systems
  - Efficient tube head cooling

S8 TIGER
SampleCare™



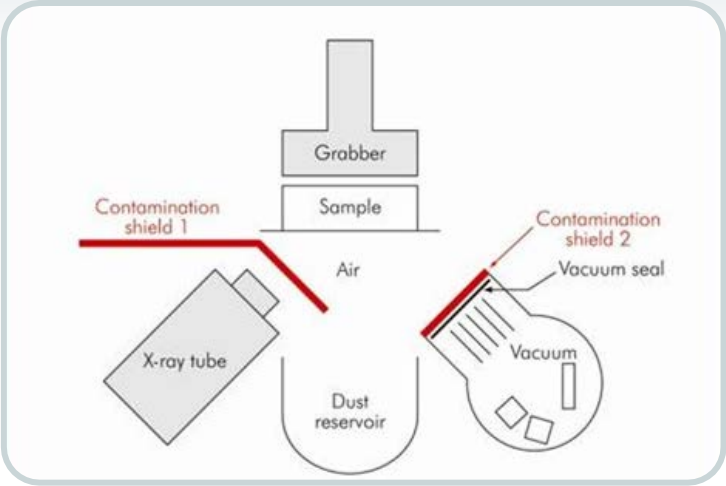
S8 TIGER SampleCare™

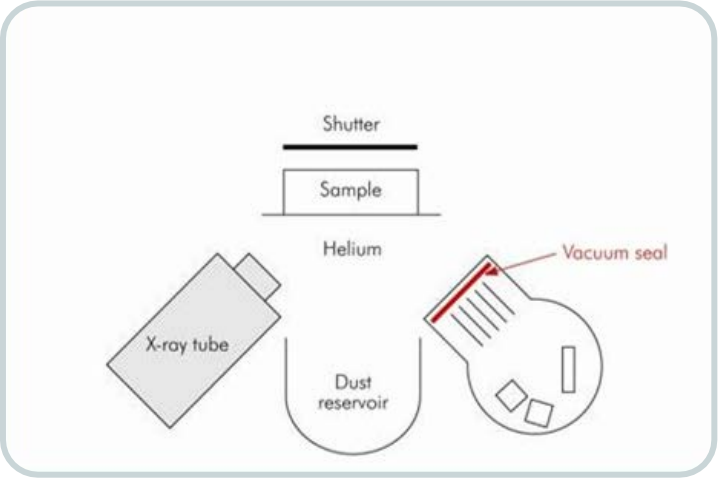
Four Times Protection:

- Low maintenance cost and time, high instrument uptime due to unique protection during loading and unloading:
- Two contamination shields to protect tube window and goniometer
- Dust reservoir to collect sample particles and droplets

Unique protection during measurements:

- Duraberyllium™ shield for tube window protection
- Unique vacuum seal with high transmission window for goniometer protection





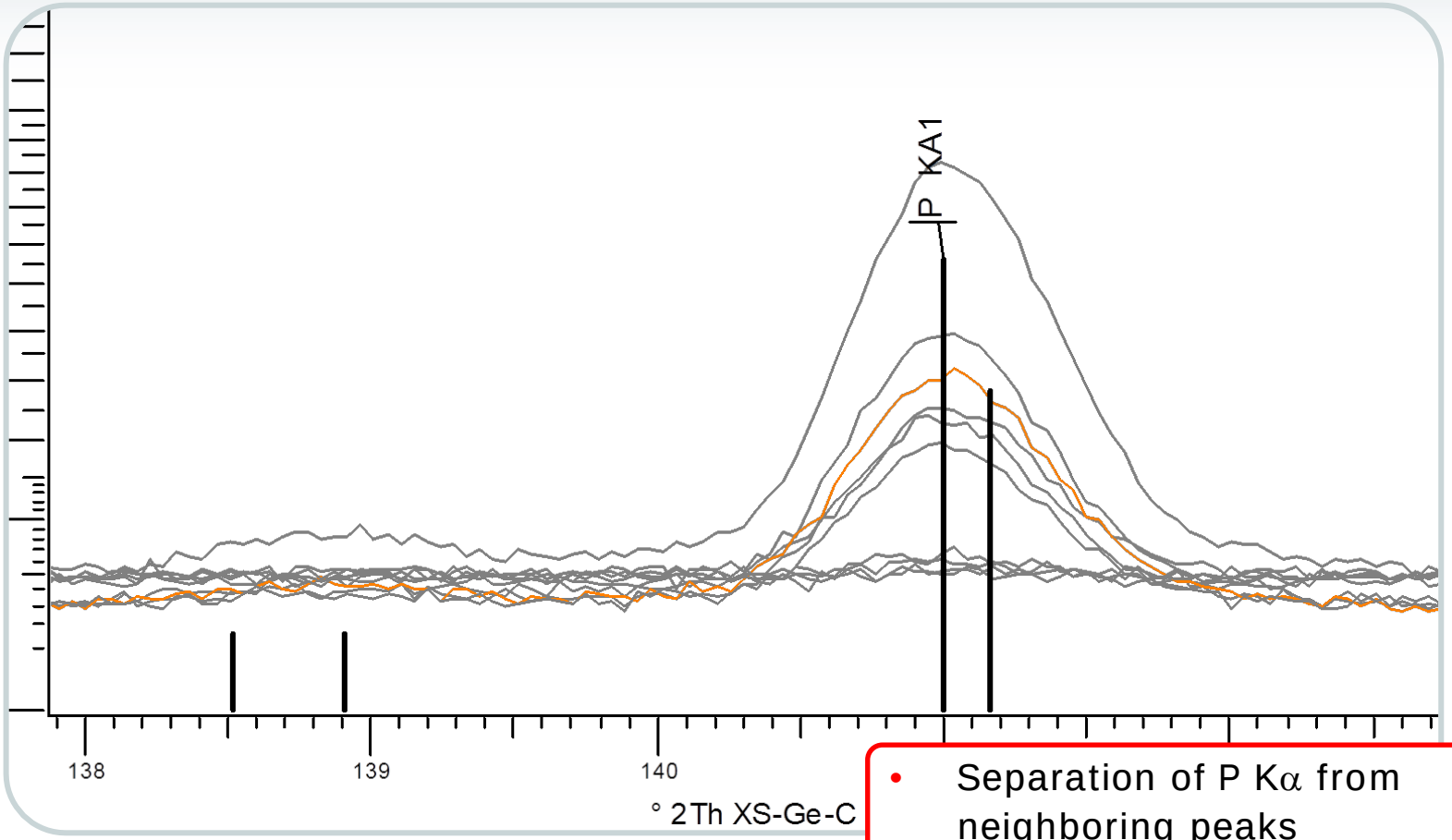
S8 TIGER
Polymer Applications

S8 TIGER
Analysis of Additives

- Determination of additives
  - Precise evaluation of the concentration level for the optimal dosing of valuable substances
  - Selection of tracer element for organic additives, which cannot be determined directly
    - e.g. P as marker for PS 38 or PS P-EPQ

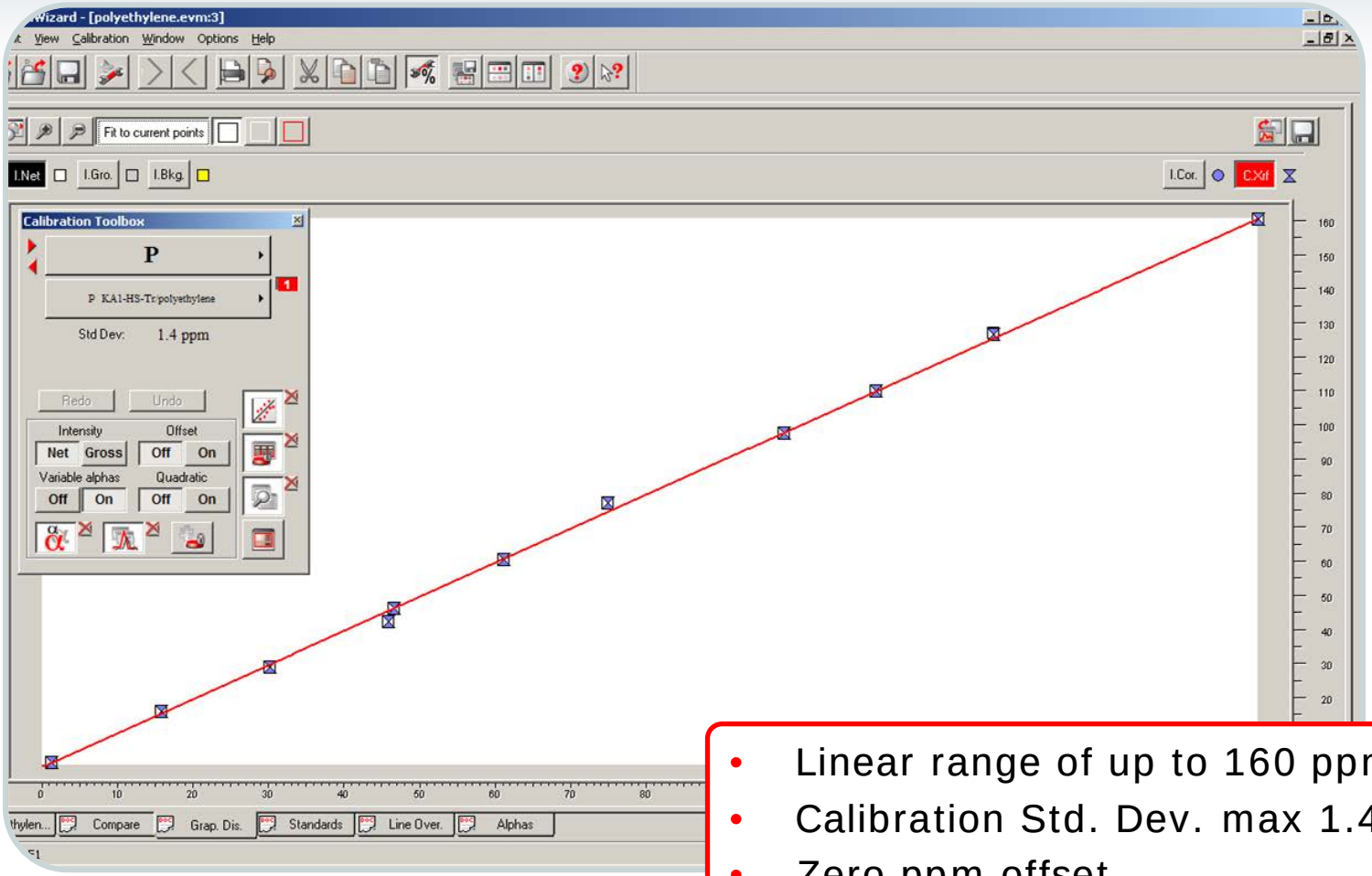
- Analysis of solids as hot pressed PUK under vacuum
- Analysis of granules in sample cups under helium
- Selection of soft excitation condition to reduce the heat dissipation from tube to sample

Additives in PE
Analysis of Phosphorus with the S8 TIGER



- Separation of P Kα from neighboring peaks
- Use of high intensity and best resolution crystal XS-Ge-C

Additives in PE
Analysis of Phosphorus with the S8 TIGER



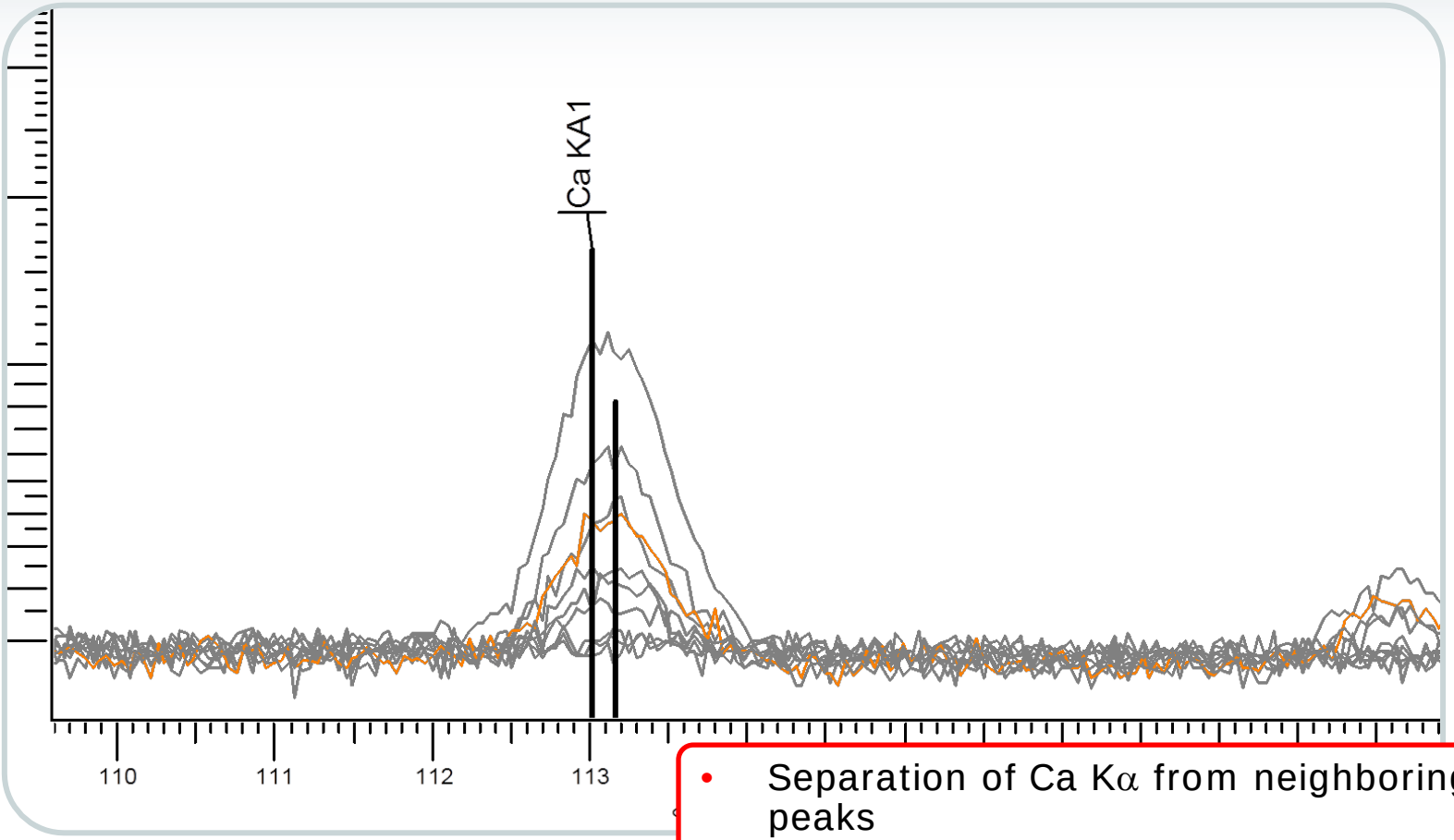
- Linear range of up to 160 ppm
- Calibration Std. Dev. max 1.4 ppm
- Zero ppm offset

Additives in PE
Analysis of Phosphorus with the S8 TIGER

Number	Standard Name	Chemical Concentration	XRF Concentration	Absolute Deviation	Relative Deviation	LLD (PPM)
14	AB-1	1.3	1.2	-0.1		0.3
10	AB-2	15.7	16	0.3	1.7	0.3
20	AB-3	30.1	29	-1.1	-3.5	0.3
17	AB-4	45.8	42.6	-3.2	-7.1	0.3
15	AB-5	46.6	46.4	-0.2	-0.36	0.3
13	AB-6	61	60.5	-0.5	-0.75	0.3
11	AB-7	74.8	77.4	2.6	3.4	0.4
16	AB-8	98.2	97.7	-0.5	-0.48	0.5
12	AB-9	110.3	110.1	-0.2	-0.16	0.5
18	AB-10	125.8	126.9	1.1	0.87	0.5
19	AB-11	160.8	160.4	-0.4	-0.23	0.6

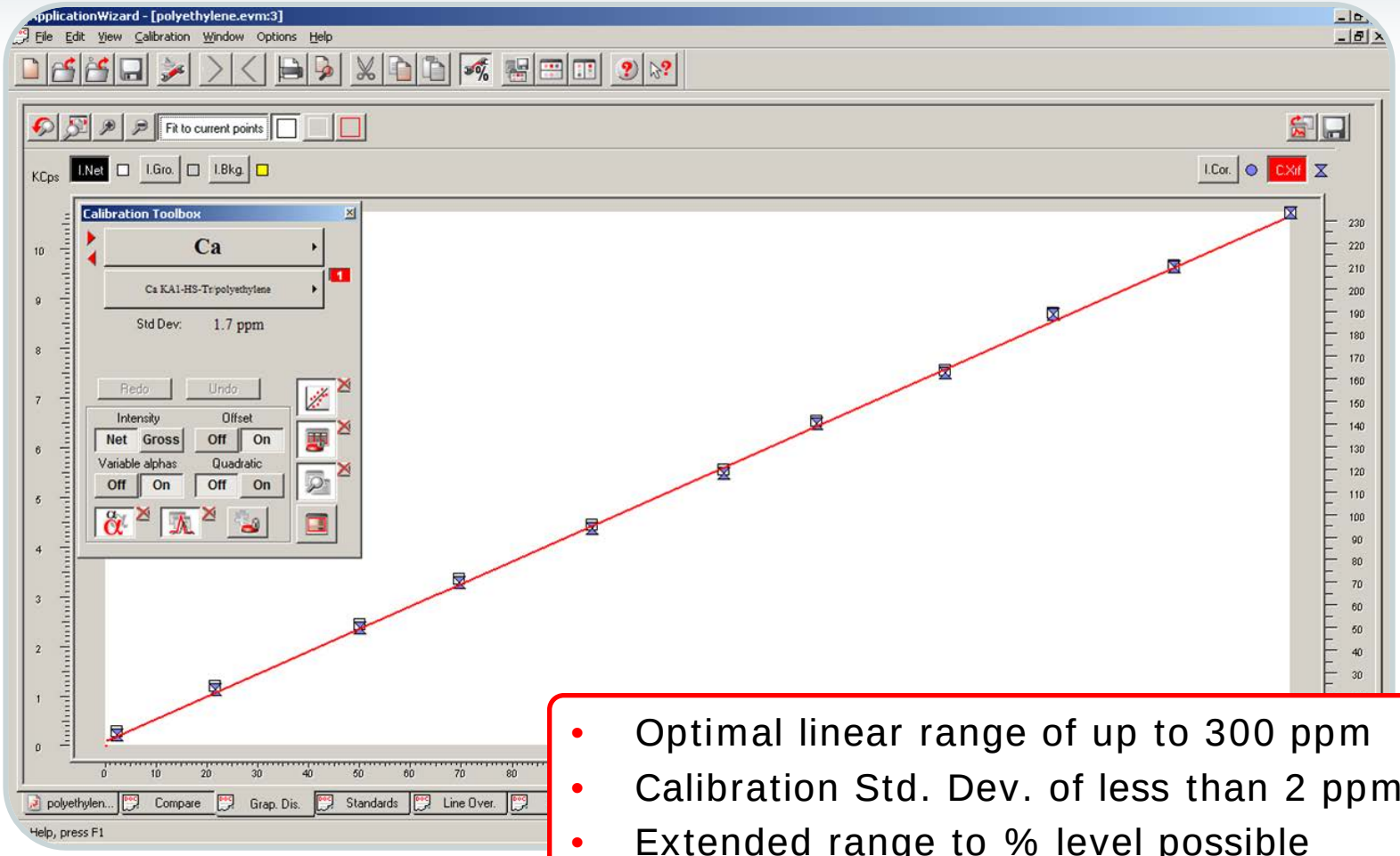
- Direct analysis of solid samples (disks - PUK) from a hot press or as granules
- Detection limit of 0.3 ppm (3 σ, 60 s)
- Optimal detection with clear separation from other elements

Additives in PE
Analysis of Calcium with the S8 TIGER



- Separation of Ca Kα from neighboring peaks
- Flat background, no background determination required

Additives in PE
Analysis of Calcium with the S8 TIGER



- Optimal linear range of up to 300 ppm
- Calibration Std. Dev. of less than 2 ppm
- Extended range to % level possible

Additives in PE
Analysis of Calcium with the S8 TIGER

Number	Standard Name	Chemical Concentration	XRF Concentration	Absolute Deviation	Relative Deviation	LLD (PPM)
1	P1	2.3	2.5	0.2		0.5
2	p2	21.6	22.8	1.2	5.4	0.5
3	p3	50	50.1	0.1	0.24	0.6
4	p4	69.4	70.2	0.8	1.2	0.7
5	p5	95.6	94	-1.6	-1.7	0.9
6	p6	121.5	118.5	-3	-2.5	1
7	p7	139.6	140.4	0.8	0.6	1.1
8	p8	165	162.9	-2.1	-1.2	1.1
9	p9	186.2	189	2.8	1.5	1.1
10	p10	210	209.8	-0.2	-0.073	1.4
11	p11	232.7	233.6	0.9	0.37	1.4

- High accuracy allows exact determination of the mixture of polymer with the additive
- Maximum deviation 2 ppm (1% relative)
- Detection limit of 1 ppm (3 σ, 60 s)
- Less thermal stress on samples reducing the measurement time
- No background measurements required

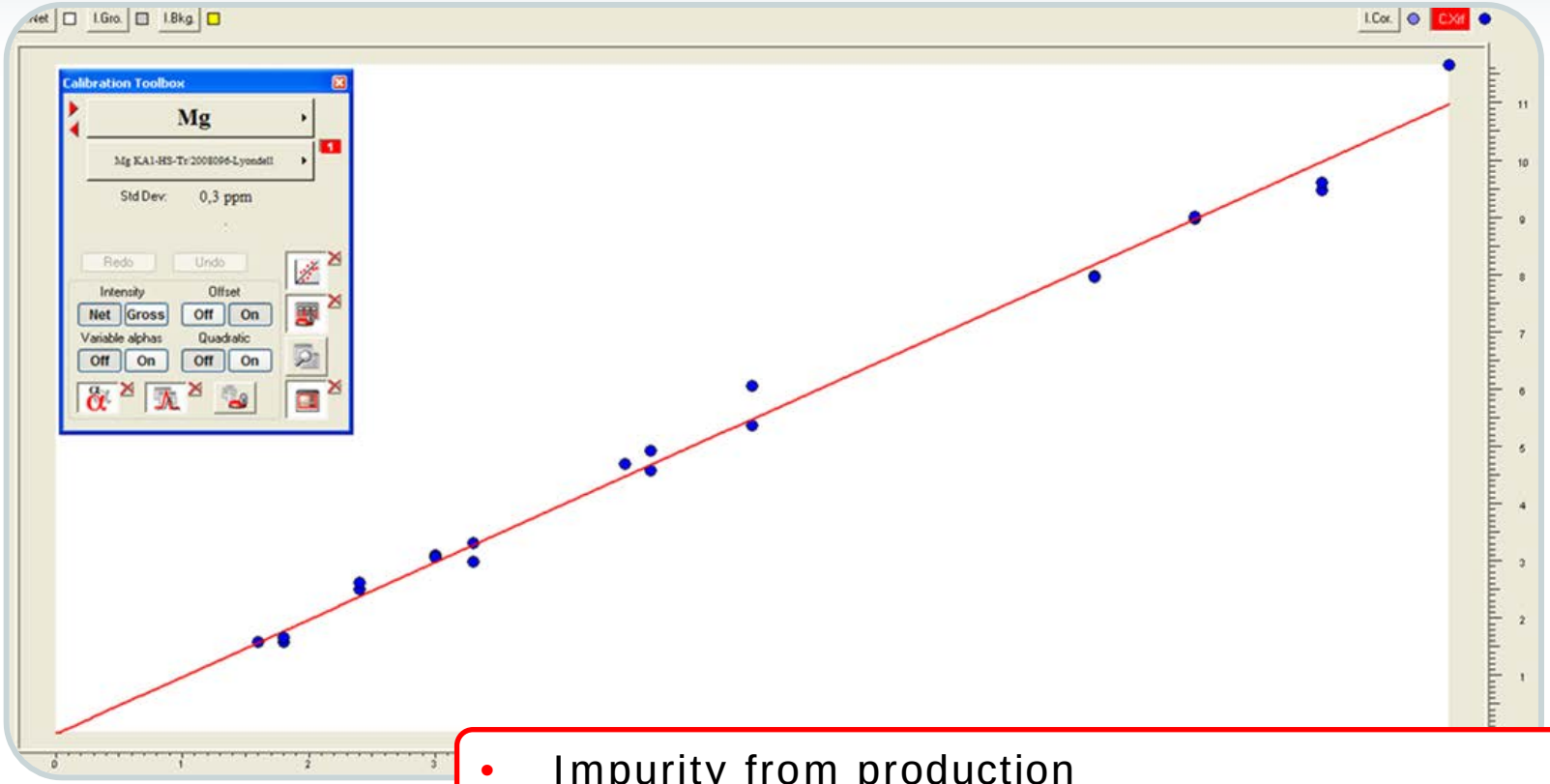
S8 TIGER
Analysis of Additives

- Additives are easily determined by WDXRF
- Detectable elements such as P used as marker for organic substances
  - Providing chemical formula allows the direct calculation of the compound concentration
- Reducing the measurement time allows the analysis of a wide element range without stressing the sample
  - Low temperature tube head with efficient cooling reduces the heat dissipation to the sample
- Analysis of solid samples or granules without complicated sample preparation

S8 TIGER
Analysis of Initiator Residues

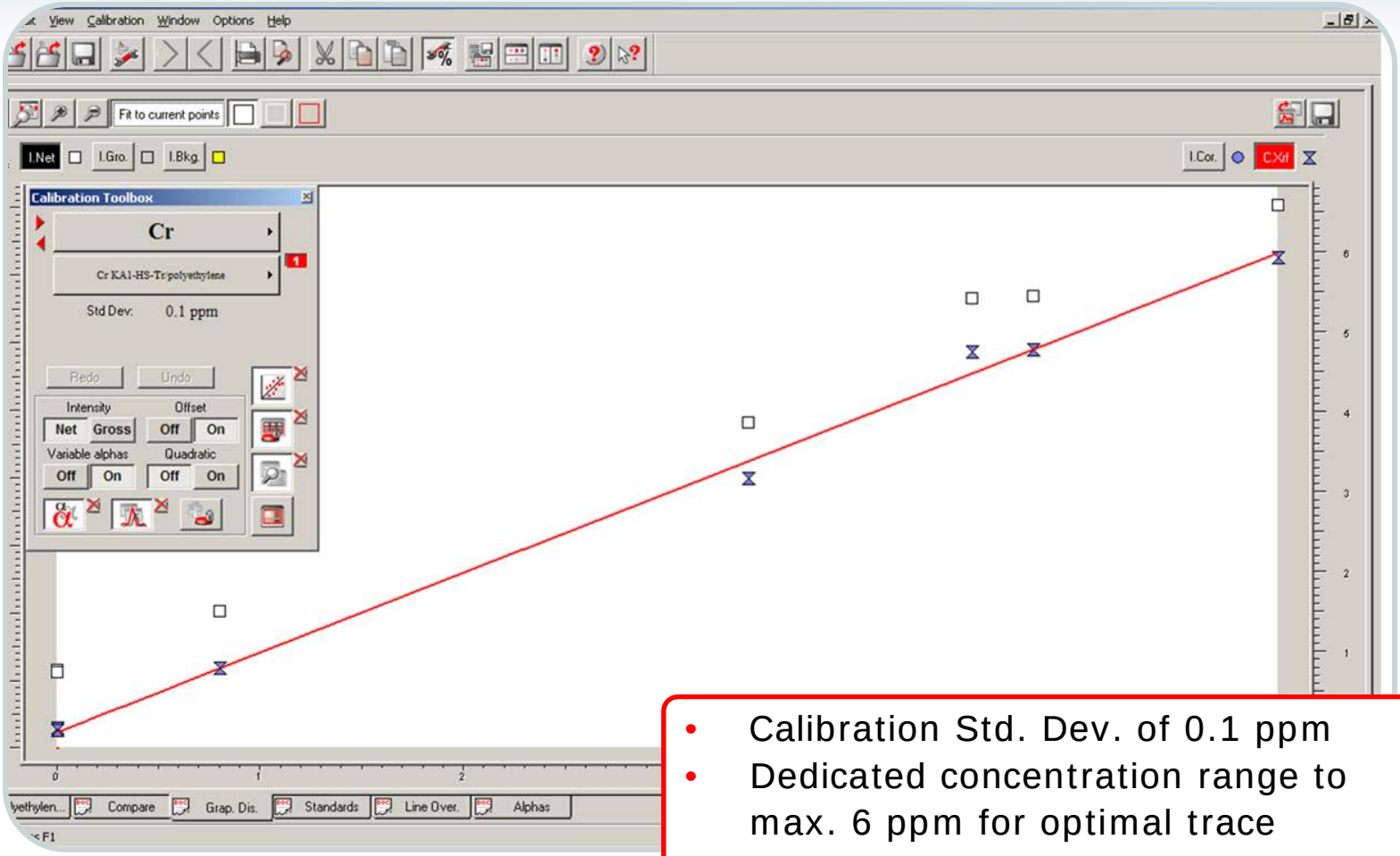
- Analysis of initiator residues
  - Mg beside high Al concentration in Ziegler-Natta Systems
  - Cr or Ti in 3d-element based initiator system
- Early recognition of initiator losses requires precise trace element determination
- Avoidance of high initiator concentrations in order to maintain long polymer life
- Meet regulation such as packaging directives, food safety and consumer product safety

Initiator Residues in PE
Analysis of Magnesium with the S8 TIGER



- Impurity from production
- Efficiency improved by reduced Mg concentration
- LLD: 0.2 ppm

Initiator Residues in PE
Analysis of Chromium with the S8 TIGER



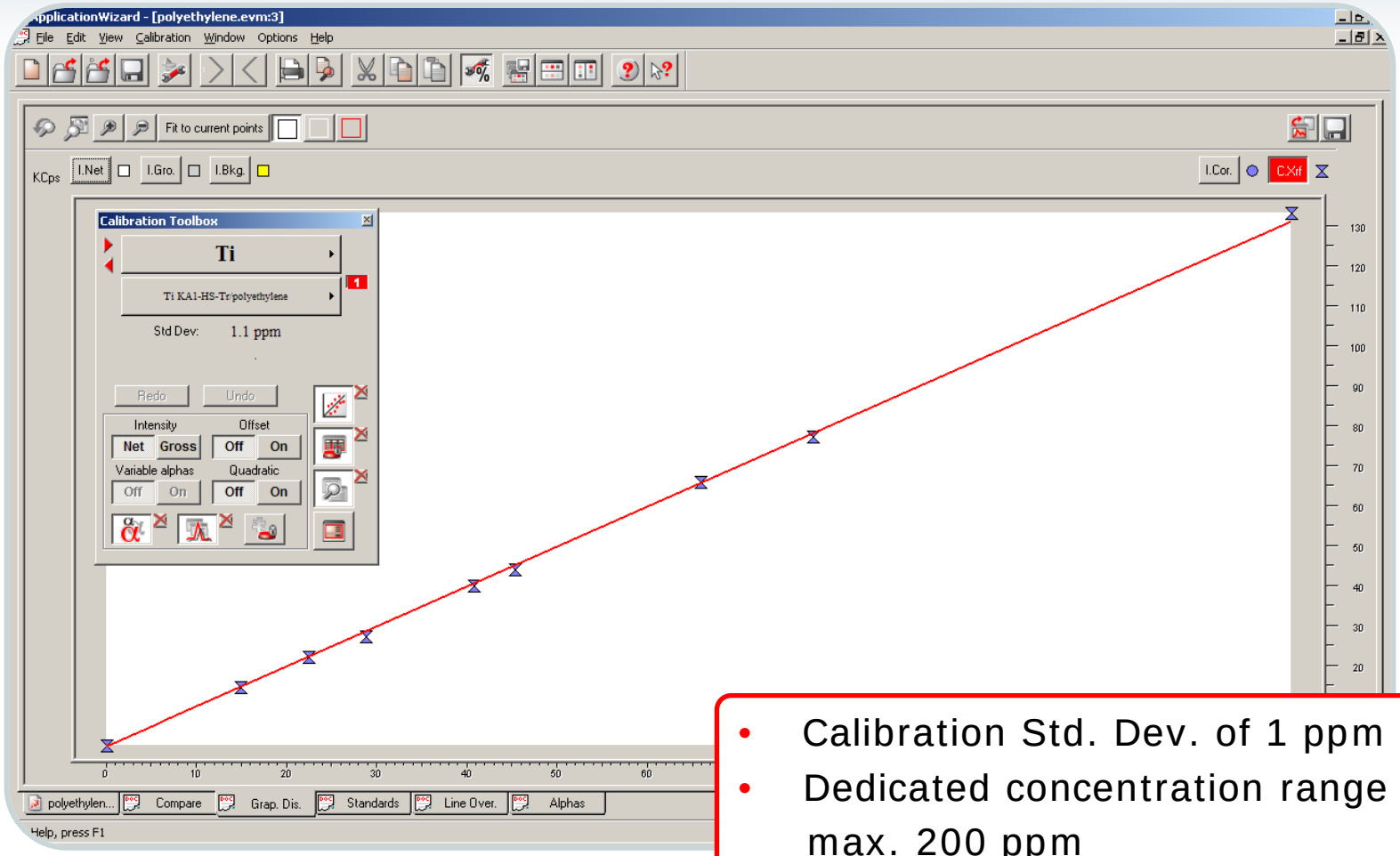
- Calibration Std. Dev. of 0.1 ppm
- Dedicated concentration range to max. 6 ppm for optimal trace detection

Initiator Residues in PE
Analysis of Chromium with the S8 TIGER

Number	Standard Name	Chemical Concentration	XRF Concentration	Absolute Deviation	Relative Deviatio	LLD (PPM)
1	CR1	0.8	0.8	0		0.2
2	CR2	3.4	3.2	-0.2		0.2
3	CR5	4.5	4.8	0.3		0.2
4	CR4	4.8	4.8	0		0.2
5	CR3	6	5.9	-0.1		0.3

- Optimal accuracy of less than 0.3 ppm deviation allows early recognition of initiator losses
- Detection limit of 0.2 ppm (3 σ, 60 s)
- Excellent precision
- Dedicated trace calibration enhances WDXRF performance
- Unrivalled accuracy of WDXRF in comparison to other methods such as ICP or AAS – due to little sample preparation

Initiator Residues in PE
Analysis of Titanium with the S8 TIGER



- Calibration Std. Dev. of 1 ppm
- Dedicated concentration range to max. 200 ppm

Initiator Residues in PE
Analysis of Titanium with the S8 TIGER

Number	Standard Name	Chemical Concentration	XRF Concentration	Absolute Deviation	Relative Deviation	LLD (PPM)
1	TITAN003	0.1	0	-0.1		0.2
2	TITAN009	14.9	14.4	-0.5	-3.3	0.3
3	TITAN019	22.4	22.1	-0.3	-1.1	0.4
4	TITAN023	28.8	27.1	-1.7	-5.8	0.5
5	TITAN034	40.8	39.9	-0.9	-2.3	0.6
6	TITAN038	45.3	44	-1.3	-2.9	0.7
7	TITAN048	65.9	65.9	0	-0.025	1
8	TITAN052	78.3	77.2	-1.1	-1.4	1
9	TITAN061	131.3	133.1	1.8	1.4	1

- Direct analysis of solid samples (disks - PUK) from a hot press or as granules
- Detection limit of 0.3 ppm (3 σ, 60 s) for low ranges or 1 ppm for higher ranges
- 1 ppm deviation for higher concentration ranges

S8 TIGER
New X-ray Tube

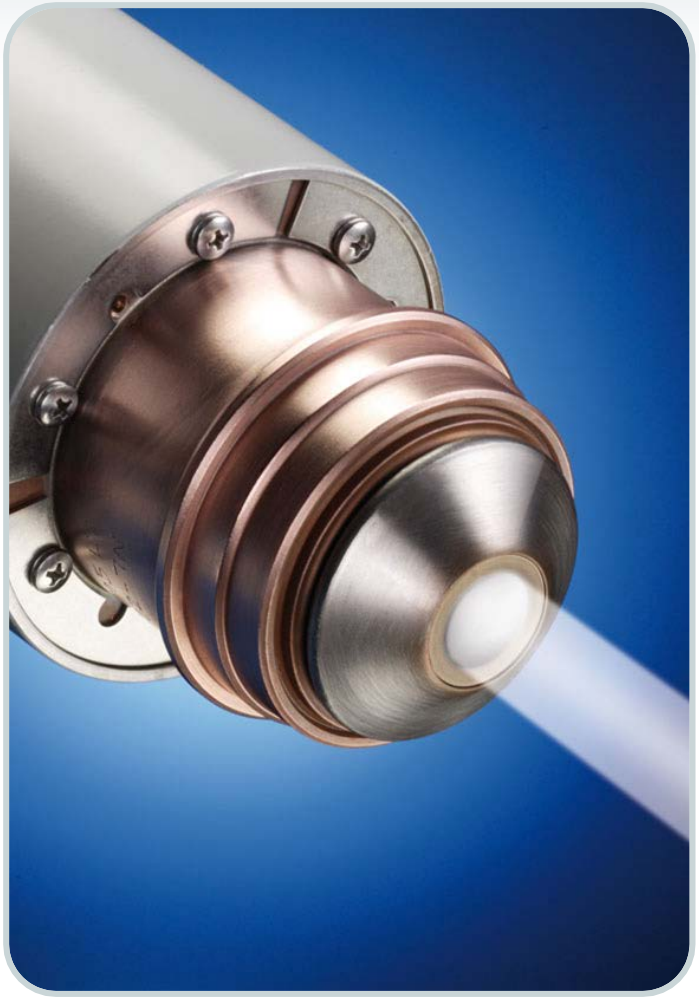
High-intensity X-ray tube with Cr target
Operating at 3.3 kW

Target applications:

- Petrochemistry
- Polymers

Available for

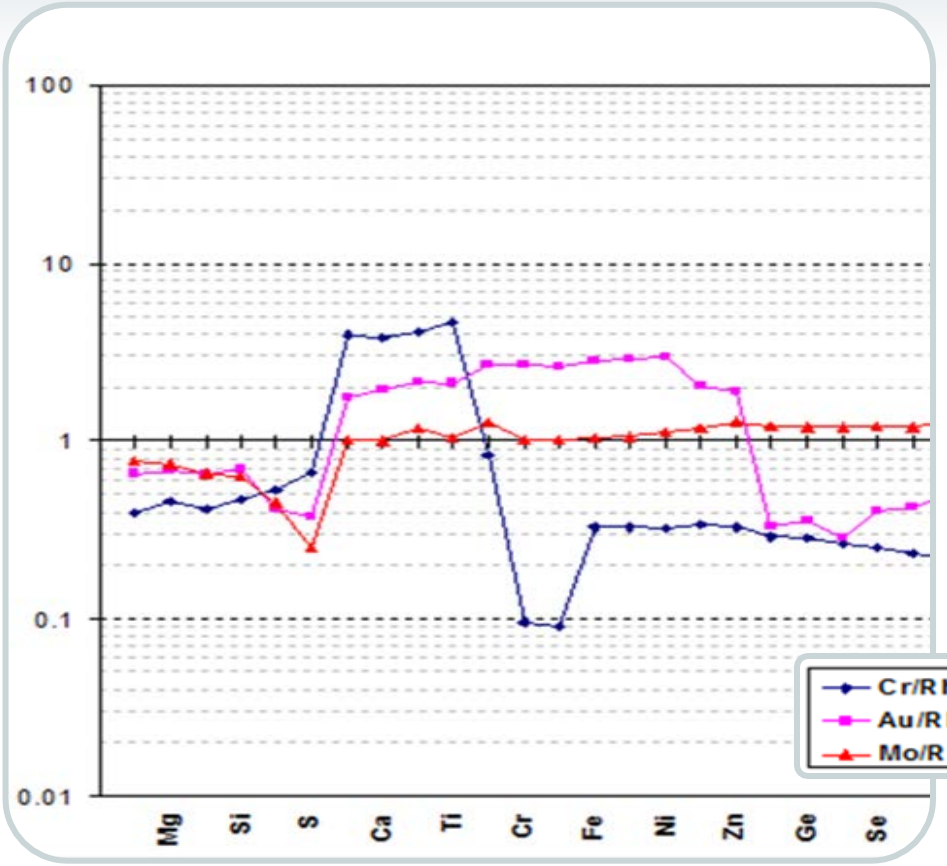
- S8 TIGER



S8 TIGER
New Cr X-ray tube

Intensity gain (Cr over Rh tube)

- For Cl - factor of 3
- For Ca - factor of 4
- For Ti - factor of 5



- LLD in polymers
  - 0.4 ppm for Cl
    (0.7 ppm with Rh)
  - 0.1 ppm for Ca
    (0.2 ppm with Rh)
  - 0.05 ppm for Ti
    (0.2 ppm with Rh)

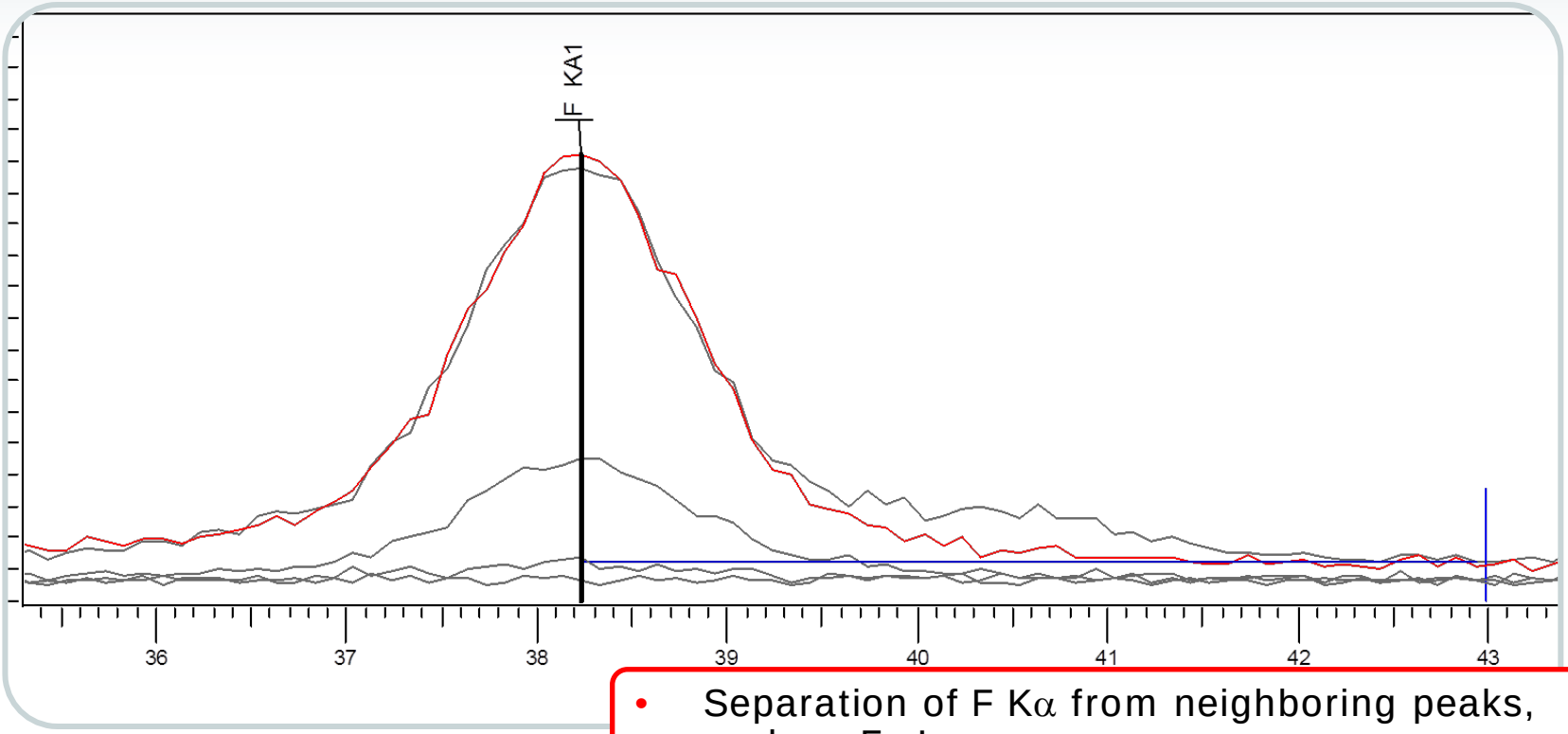
- Less stress on valuable samples due to 3.3 kW max power

S8 TIGER
Analysis of Impurities

- Impurities from the production process influences polymer quality, such as iron and other elements from steel used for the piping and machineries

- Halogens decrease polymer life
- In solid samples the detection of F is possible with WDXRF in hot pressed samples

Impurities in PE
Analysis of Fluorine with the S8 TIGER



- Separation of F Kα from neighboring peaks, such as Fe L
- Use of the high resolution crystal XS-55 (multilayer optic)

Impurities in PE
Analysis of Fluorine with the S8 TIGER

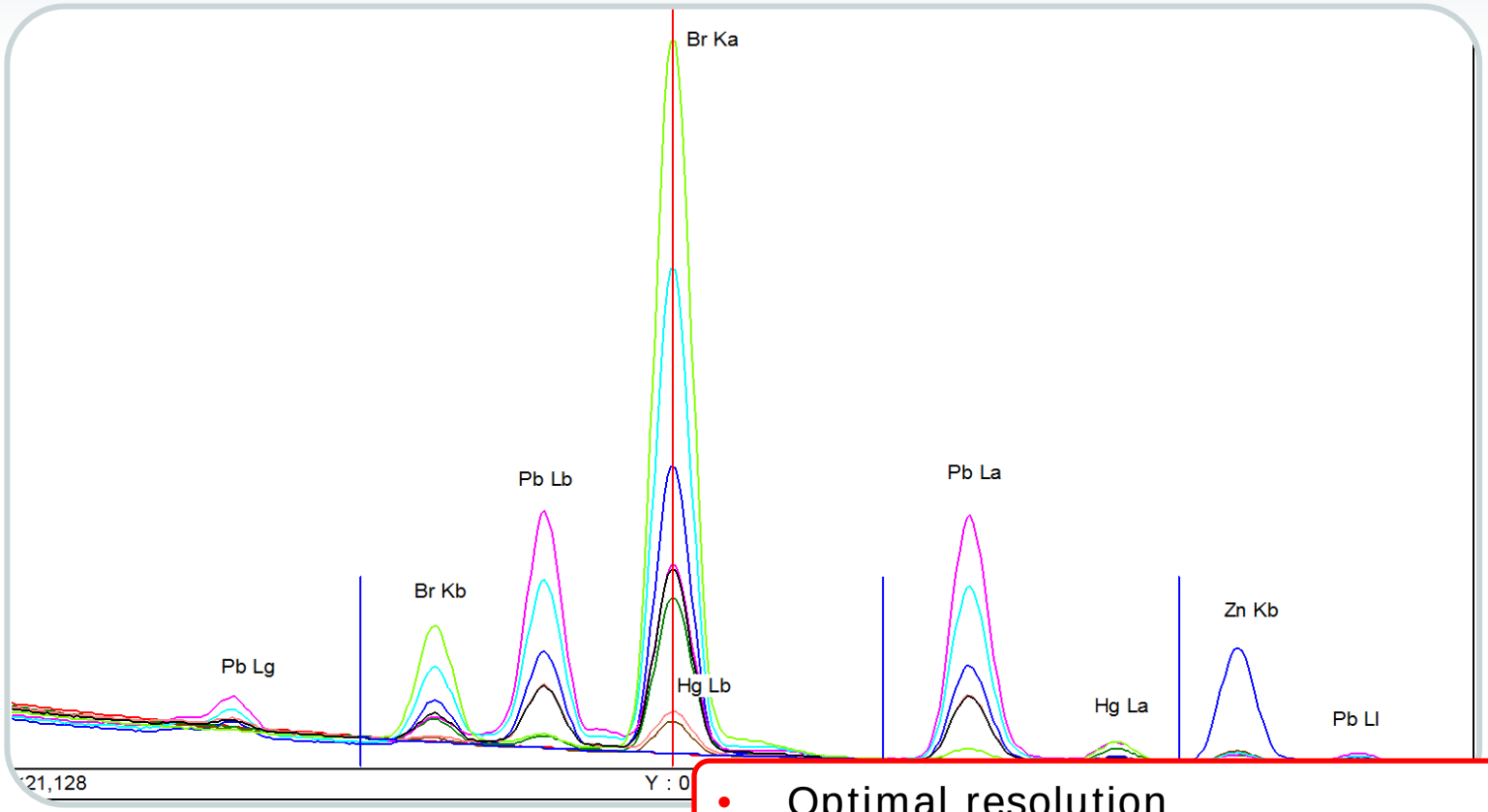
Number	Standard Name	Chemical Concentration	XRF Concentration	Absolute Deviation	Relative Deviation	LLD (PPM)
1	F1	0	-1	-1		11.7
2	F2	1630	1904	274	17	12
3	F3	3418	4667	1249	37	12.9
4	F4	4378	4424	46	1	12.8
5	F5	6543	6264	-279	-4	13.3
6	F6	7444	6400	-1044	-14	13.4
7	F7	10238	10409	171	2	15.2

- Direct analysis of solid samples (disks - PUK) from a hot press in vacuum
- Analysis of granules in polymer cups is not feasible due to absorption of F Kα in the foil
- Detection limit of 13 ppm
- Excellent precision

S8 TIGER
Analysis of Regulated Hazardous Elements

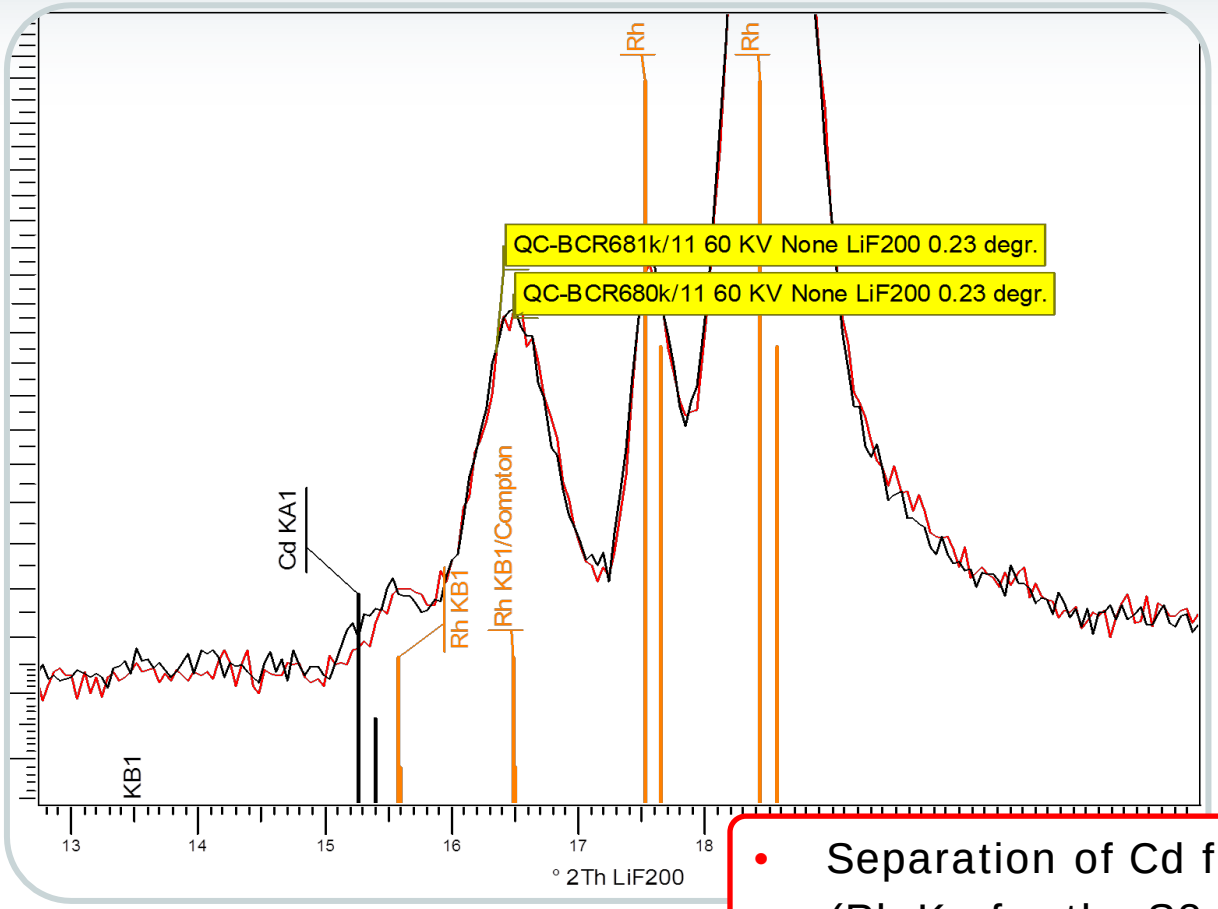
- Detection and analysis of regulated toxic elements are possible with WDXRF down to the sub-ppm range
- EDXRF is not capable of separating elements such as Hg, Br and Pb from each other
  - Low spectral resolution

Regulated Toxic Elements
Analysis of RoHS Elements with the S8 TIGER



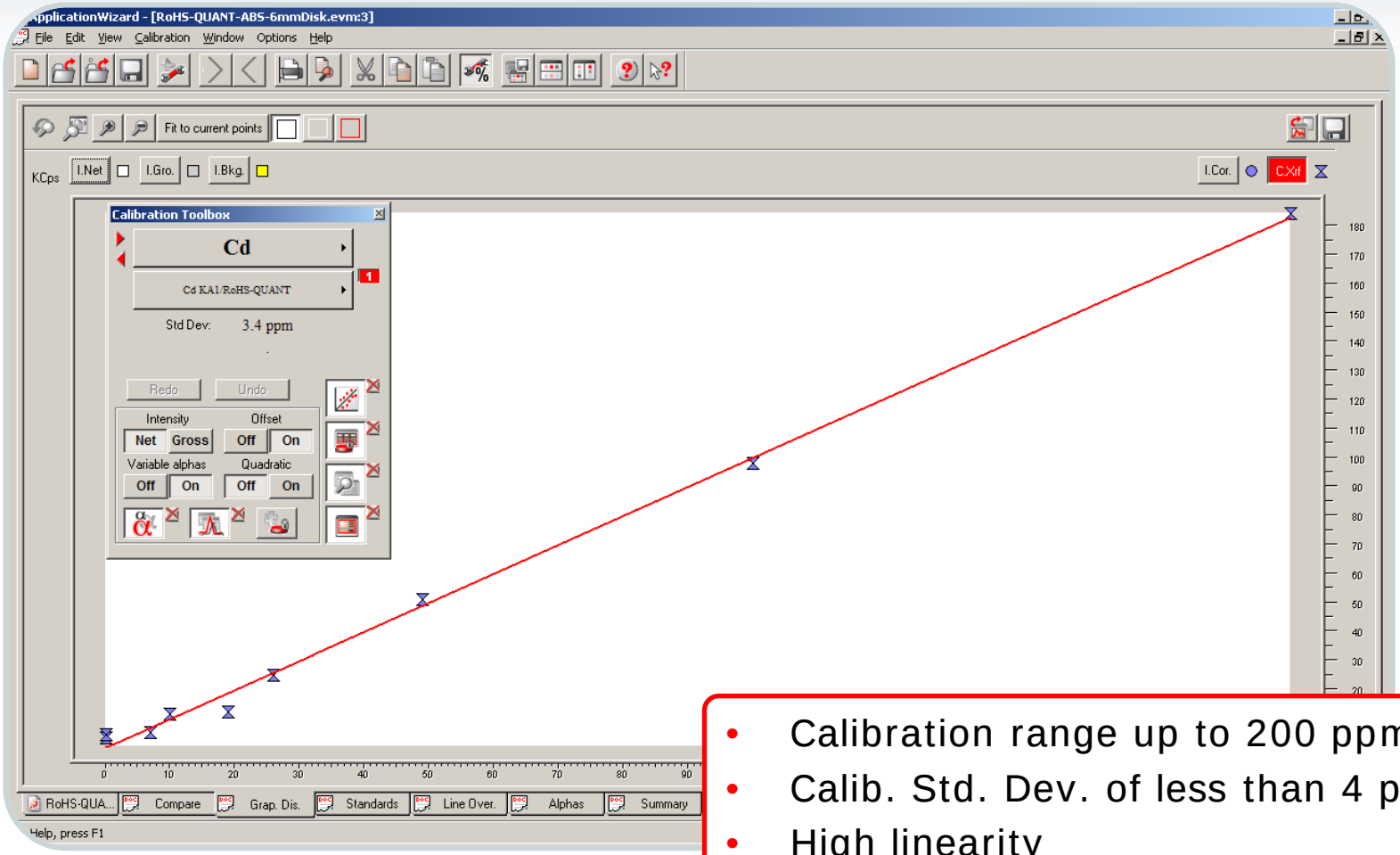
- Optimal resolution
- WDXRF separates neighboring lines
- Clear identification of Hg, Pb, and Br

Regulated Toxic Elements
Analysis of Cadmium with the S8 TIGER



- Separation of Cd from tube lines
- (Rh Kα for the S8 TIGER)
- with LiF 200, better with LiF 220

Regulated Toxic Elements
Analysis of Cadmium with the S8 TIGER



- Calibration range up to 200 ppm
- Calib. Std. Dev. of less than 4 ppm
- High linearity

Regulated Toxic Elements
Analysis of RoHS Elements with the S8 TIGER

Sample	Date	Cr (%)	Br (%)	Hg (%)	Pb (%)	Cd (%)
Average (n=83)	every 10 min	0.0479	0.0346	0.0288	0.0333	0.0017
Stdev		0.0002	0.0005	0.0001	0.0001	0.0001
COV		0.5%	1.4%	0.4%	0.4%	6.0%

Sample	Date	Cr (PPM)	Br (PPM)	Cd (PPM)	Hg (PPM)	Pb (PPM)
QC_RoHS-QUANT-ABS-6mmDisk	12/10/2008 9:18	503	227	95	401	475
QC_RoHS-QUANT-ABS-6mmDisk/1	12/10/2008 9:27	504	227	95	402	473
QC_RoHS-QUANT-ABS-6mmDisk/2	12/10/2008 9:36	503	227	93	403	474
QC_RoHS-QUANT-ABS-6mmDisk/3	12/10/2008 9:45	504	227	93	400	474
QC_RoHS-QUANT-ABS-6mmDisk/4	12/10/2008 9:54	503	227	92	402	474
QC_RoHS-QUANT-ABS-6mmDisk/5	12/10/2008 10:03	504	226	94	401	474
QC_RoHS-QUANT-ABS-6mmDisk/6	12/10/2008 10:11	504	226	95	401	475
QC_RoHS-QUANT-ABS-6mmDisk/7	12/10/2008 10:20	503	227	94	403	475
QC_RoHS-QUANT-ABS-6mmDisk/8	12/10/2008 10:29	505	227	97	402	476
QC_RoHS-QUANT-ABS-6mmDisk/9	12/10/2008 10:38	504	226	96	402	475
QC_RoHS-QUANT-ABS-6mmDisk/10	12/10/2008 10:47	504	227	94	400	476
QC_RoHS-QUANT-ABS-6mmDisk/11	12/10/2008 10:56	503	227	94	400	473
QC_RoHS-QUANT-ABS-6mmDisk/12	12/10/2008 11:05	504	226	96	401	474
Average		**504**	**227**	**94**	**401**	**475**
Std.Dev.		**1**	**0**	**1**	**1**	**1**
Rel.Std.Dev.		0.14%	0.20%	1.32%	0.26%	0.17%

- Excellent precision of less than 1.5 % relative in ppm levels

S8 TIGER
WDXRF Performance

- Accuracy and precision fit to demands for the analysis of
  - Additives
  - Initiator residues
  - Impurities
  - Regulated elements
- Simple sample preparation
  - For integration into process control regime and quality checks close to production
- Detection of traces to sub-ppm with standard instrument configuration
- Ready to analyze solutions available

S8 TIGER
Ready-To-Analyze Solutions

GEO-QUANT T

GEO-QUANT M

GEO-QUANT F

METAL-QUANT

CEMENT-QUANT

POLYMER-QUANT A

PETRO-QUANT

RoHS-QUANT

QUANT EXPRESS

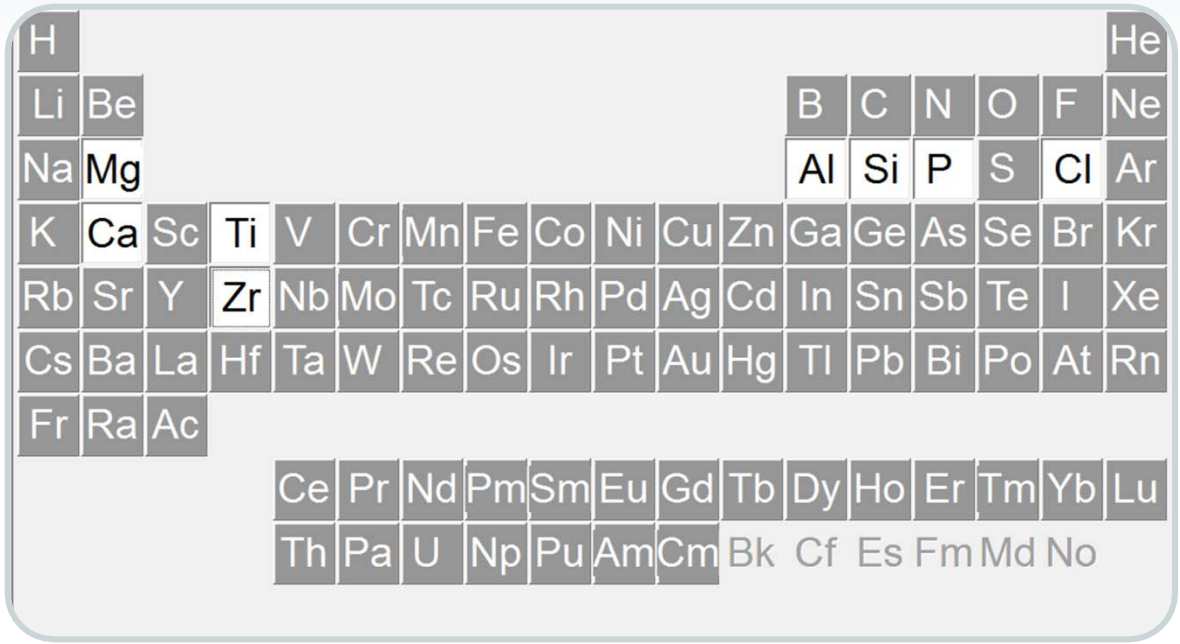
POLYMER-QUANT A for the S8 TIGER

POLYMER-QUANT is the ready-to-analyze solution for additives in polymers:

- Covering more than 8 elements
- In polymer disks and granules
- Contains certified standard materials from NIST as acceptance test sample

POLYMER-QUANT A APPLICATIONS

- Contains all relevant additive elements and initiator residues in polymers
- Covers the analysis of virgin polymers with typical concentration ranges
- In all CH-based polymer types with the variable alpha model (PE, PP, PET, ABS, ...)



POLYMER-QUANT A
Covered Concentration Range

	Mg (ppm)	Al (ppm)	Si (ppm)	P (ppm)	Cl (ppm)	Ca (ppm)	Ti (ppm)	Zr (ppm)
MIN	2	26	5	1	10	0	0	3.5
MAX	495	260	1198	210	1250	125	99	76

- Covered polymer types: PE, PP, PET, ABS, ...
- Combination with QUANT-EXPRESS for PVC and similar polymers
- Combination with RoHS-QUANT ABS
- Typical measurement: 14 min (S8 TIGER 4 K)
  Adjustable to requirements

POLYMER-QUANT A
Standards

POLYMER-QUANT A

- Contains calibration standards (Polyethylene and Polypropylene) as granules
- NIST certified reference material as acceptance test samples
- Drift correction samples
- Operators Manual
- Installation CD

S8 TIGER
Ready-To-Analyze Solutions

GEO-QUANT T

GEO-QUANT M

GEO-QUANT F

METAL-QUANT

CEMENT-QUANT

POLYMER-QUANT A

PETRO-QUANT

RoHS-QUANT

QUANT EXPRESS

RoHS-QUANT ABS
S8 TIGER

- Is the analytical ready-made solution for RoHS for quick & easy qualitative screening and quantitative analysis of regulated substances in polymers of electrical and electronic devices

  for the

  - S2 RANGER
  - S8 TIGER

RoHS - Lead-free
Limits of elements and compounds

Elements	Defined Limits	Use
Lead	1000 ppm	paint, solder, PVC stabilizer, plastic pigment
Mercury	1000 ppm	batteries, contacts in microswitches, lightning equipments, plastic pigment
Cadmium	100 ppm	stabilizer and pigment in plastics, semiconductors, batteries
Chromium	1000 ppm (Hexavalent)	anti-corrosion coatings, plasticizers, paints, plastic processing
Bromine	1000 ppm (as PBB and PBDE in total)	fire retardent in plastics and polymers

RoHS Quantitative Screening
Mandatory Detection Limits

- Basic requirements for the safe and error-free identification of elements and the quantitative analysis of regulated elements are the resolution and detection power of the XRF instrument.

- Not every XRF instrument is capable of distinguishing between Br and Hg or to detect safely Cd in RoHS samples.

- Mandatory detection limits in ppm for XRF used for RoHS compliance screening acc. to IEC/ACEA:

	Polymer	Metals	Electronics
Cd	15	30	30
Pb	30	60	60
Hg	30	60	60
Br	15	30	
Cr	30	60	30

S8 TIGER
RoHS-QUANT

RoHS-QUANT is based on fast and simple sample preparation:

Benefits:

- Quick and instant results
- Flexible for different kind of samples
- Low costs for sample preparation equipment or accessories

RoHS-QUANT ABS
S8 TIGER

- 10 ABS polymer standards (100 g granules each)
- 10 ABS polymer standards prepared as 2- and 6-mm disks
- 1 QC sample (100 g, 2- and 6-mm disks)
- CRM BR680 PE standard (47 g and 2-mm disk)
- CRM BR681 PE standard (47 g and 2-mm disk)

S8 TIGER
Ready-To-Analyze Solutions

GEO-QUANT T

GEO-QUANT M

GEO-QUANT F

METAL-QUANT

CEMENT-QUANT

POLYMER-QUANT A

PETRO-QUANT

RoHS-QUANT

QUANT EXPRESS

Refinery Products

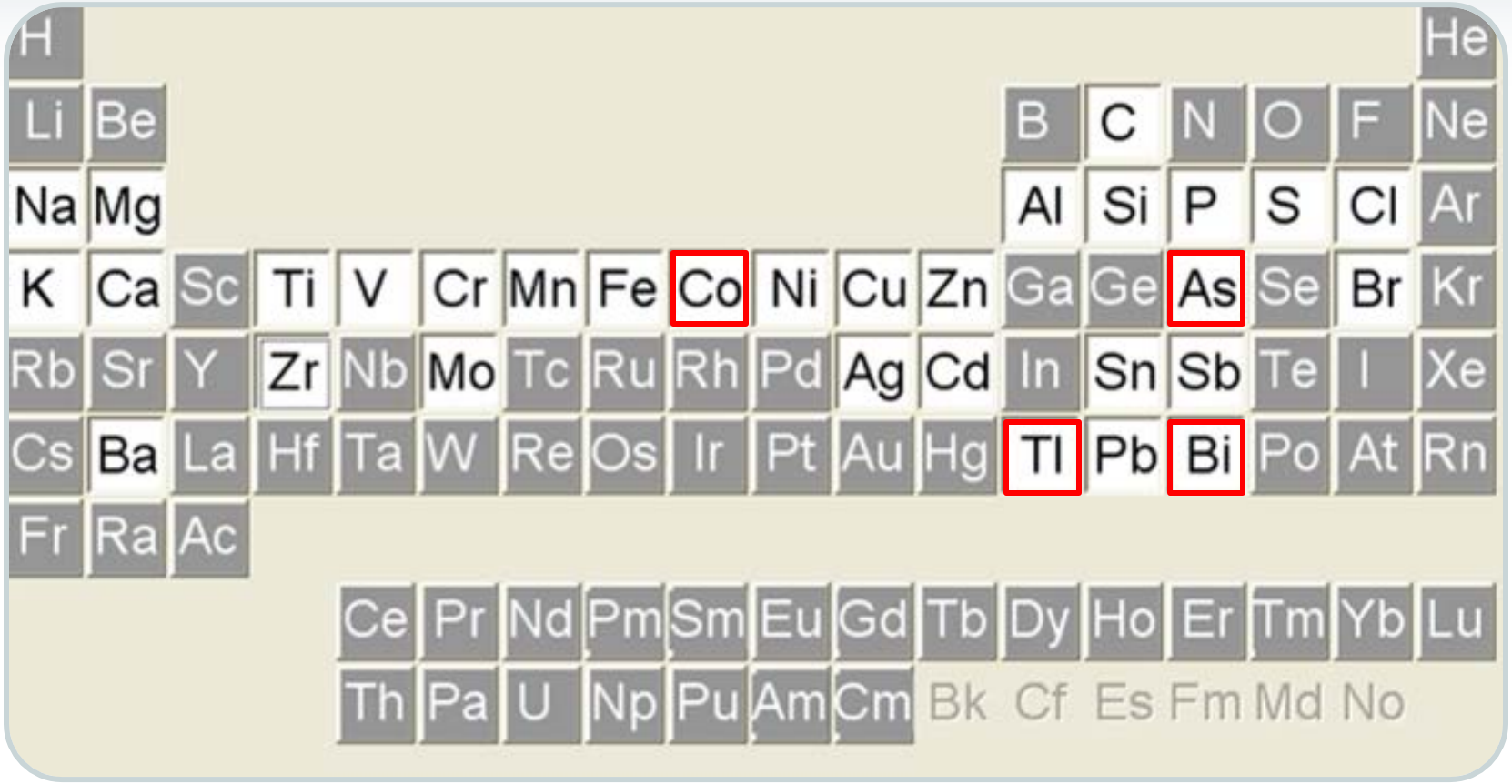
Crude Oil

20°	**$C_1 – C_4$**	**Gas (for PE, PP)**
70°	$C_5 – C_9$	Naphtha (Chemicals)
120°	$C_5 – C_{10}$	Gazoline
170°	$C_{10} – C_{16}$	Kerosene, Paraffin
270°	$C_{14} – C_{20}$	Diesel
	$C_{20} – C_{50}$	Lubricating Oil
600°	$C_{20} – C_{70}$	Fuel Oil (Ships, Heating)
	$> C_{70}$	Residue (Bitumen, Petcoke)

PETRO-QUANT
Solutions for the Petrochemical Industry

- Norm-compliant to ASTM, EN, ISO, DIN
- Sulfur and lead in automotive fuels, lubricants
- Additives and stabilizers in oils, greases, …
- Wear metals to detect engine debris
- Impurities of initiators in oils and polymers
- Additives in polymers and plastics
- Toxic elements according to RoHS/WEEE
- Pet coke / coal anodes
- Alternative fuels in cement production
- …

PETRO-QUANT
Unique Solutions for Petrochemicals



Universal petrochemical calibration for up to 30 elements in hydrocarbon-based matrices – straight out of the box
NEW: 4 additional elements: Co, As, Tl, Bi as additives and contaminants

Bruker AXS
Ready-to-Analyze Solutions - Benefits

POLYMER-QUANT A, ROHS-QUANT and PETRO-QUANT are fully calibrated for the analysis of additives, initiator residues, impurities and regulated elements in plastic matrices.

Benefits:

- Time saving – ready to start
- Routine analysis right from the beginning
- No XRF expert needed to do calibrations
- Minimum operator training
- QC procedure integrated
- Drift correction for the life of the instrument established

Standards included, flexibility integrated

- Quick adaptation to own applications
- Upgrade path

Q&A

Any questions?

Please type any questions you may have for our speakers in the Q&A panel and click Send.

How did we do?

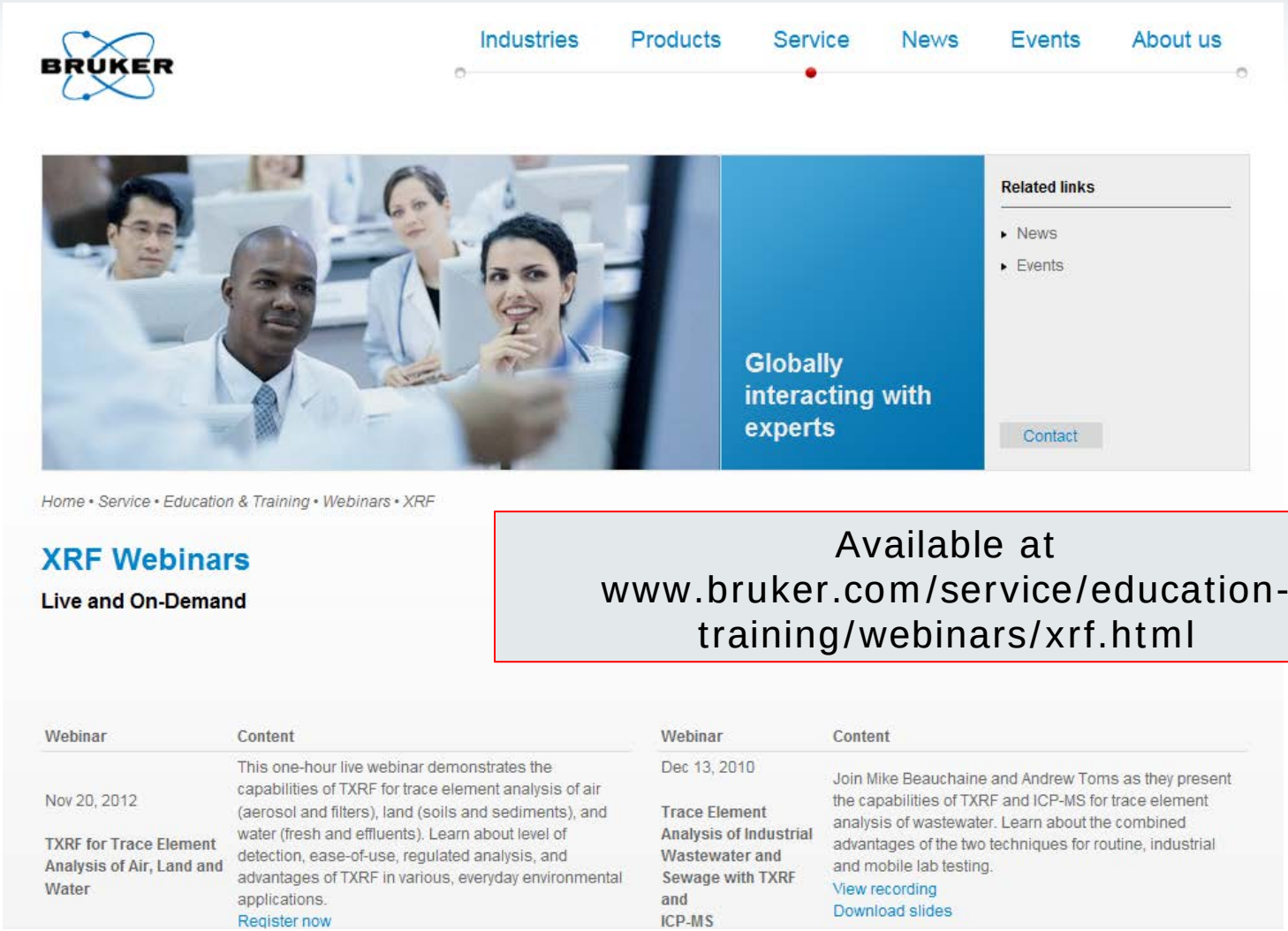
When you exit the webinar, please fill out our evaluation survey to let us know. We appreciate your feedback.

Thank you!

Arkady Buman
Product Manager XRF
Madison, WI, USA

Dr. Kai Behrens
Global Product Manager XRF
Karlsruhe, Germany

Past and Future XRF Webinars



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APS – American Physical Society – Baltimore, MD – Mar 18-22

Pittcon – Philadelphia, PA – Mar 18-21

MRS Spring – San Francisco, CA - Apr 1-5

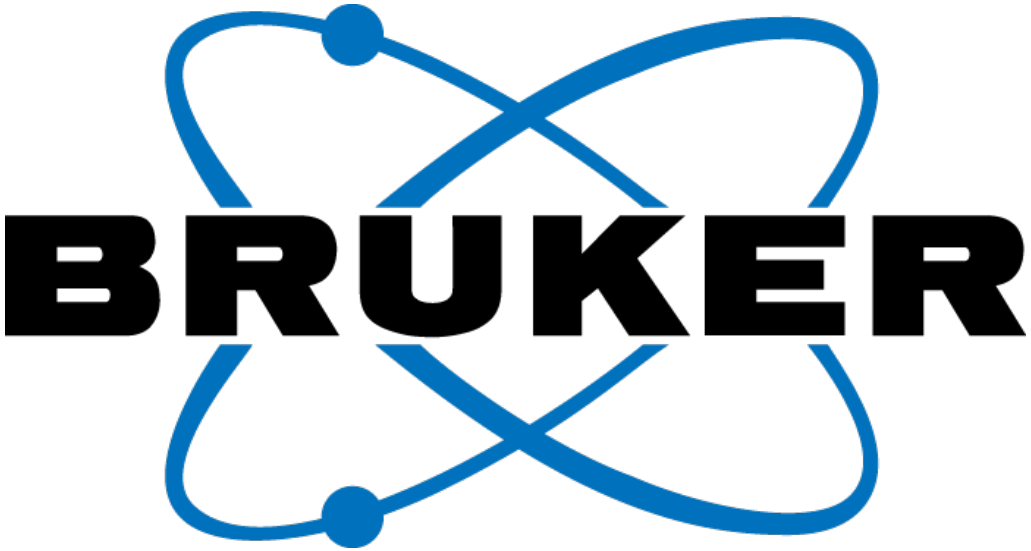
AEROMAT – Bellevue, WA - Apr 2-5

Cast Expo – St. Louis, MO - Apr 6-9

ACS Spring – New Orleans, LA - Apr 7-11

ICDD XRF Clinic – Newtown Square, PA - Apr 29 - May 3

AISTech – Pittsburgh, PA – May 6-9



Innovation with Integrity

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