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# XRF Applications in Polymers

Thermo Fisher Scientific
X-Ray Elemental Analysis
Ecublens, Switzerland

# Thermo Scientific XRF and XRD Product Portfolio: Strong And Complementary Technologies

## EDXRF

**ARL QUANT'X**
Top performance bench-top EDXRF

## WDXRF

**ARL PERFORM'X**
High performance sequential XRF

**ARL OPTIM'X:** Surprising performance in WDXRF

## Integrated XRF and XRD

**ARL 9900 Series**
Integrated XRF-XRD

## Stand-alone Powder XRD

**ARL EQUINOX Series**
from benchtop XRD to advanced research XRD

**XRF: Elemental analysis**

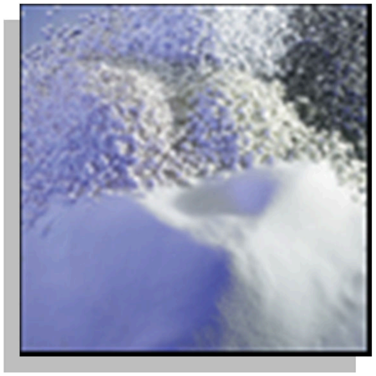
**XRD: Analysis of structure, crystallograph, phases or compounds**

# Polymers and additives

- Performance of today's polymers is synonymous with additives:
  - Accelerants
  - Anti-degradants
  - Anti-foams
  - Anti-oxidants
  - Anti-ozonates
  - Blowing agents
  - Coupling agents
  - Cross linking agents
  - Fillers
  - Flame retardants
  - Plasticizers
  - Processing aids
  - Retarders
  - Stearates
  - UV stabilizers
  - Vegetable oils
  - Others

# Polymer additives and contaminants

- Despite performance and consumer benefits, polymers and additives may contain hazardous constituents
- Some intentionally formulated (additives)
- Some unintentional (contaminants)



# Partial list of regulations requiring polymer analysis

- Consumer Product Safety Improvement Act (CPSIA) since 10 February 2009 limits lead and phthalates in toys and a large number of consumer goods.
- EU Directive 2002/96/EC WEEE (Waste Electrical and Electronic Equipment) that establishes limits for product content that must be recyclable or reusable.
- EU Directive 2003/11/EC ROHS (Restriction Of the use of certain Hazardous Substances) restricting six toxins from most electronic and electrical equipment
- EU Directive 90/128/EC for monomers and plastics additives for food contact
- EU Directive 2002/72/EC relating to plastic materials and articles intended to come in contact with foodstuffs
- EU Directive 2002/61/EC Aryl Amine Breakdown Products in Azo Dyes
- EU Directive 67/548/EEC Carcinogenic and Regulated Dyes
- FDA and The United States Code of Federal Regulations (CFR) – 21 CFR Parts 175-178 that regulate adhesives, components of coatings, paper and paperboard components, polymers and adjuvants and production aids.
- United States Environmental Protection Agency (USEPA) – Methods 606, 506-1 and 8061 regulating Phthalates and Adipates

# Regulations and testing standards

- Easier to find regulations limiting heavy metals than test standards for analyzing them
- For example ASTM F963 – 08, Standard Consumer Safety Specification for Toy Safety
- Provides an acid extraction method for heavy metals
- Provides mg/kg limits for Pb, Sb, As, Ba, Cd, Cr, Pb, Hg, Se
- Yet subsequent quantification by ICP-OES has no standard

# ASTM D 5577 – 94 (2003)

- Standard Guide for Techniques to Separate and Indentify Contaminants in Recycled Plastics (*no XRF*)

**TABLE X1.1 Identification of Contaminants Addressed by Specific Test Procedures**

| Test Procedure (Section Number) | ASTM or ISO Method | Components Detected |
|---|---|---|
| Ash test (7.4.1) | ISO 3451/1 | Inorganic fillers, some metals |
| Chlorinated polymers (8.5) | | Chlorinated materials |
| Chromatographic analysis (7.7) | Practice E 355; Practice E 682 | Chemicals, original-use contents |
| Color or yellowness index (7.2.1) | Test Method D 1925 | Colored or degraded materials |
| Density or specific gravity (7.3) | Test Methods D 792; Test Method D 1505 | Contamination by other polymers |
| Density separations, water or propanol/water (8.3) | | Paper, other polymers, metals |
| Extrusion/melt flow test (8.4; 7.2.2) | Test Method D 1238 | Incompatible polymers, metals, dirt, insoluble material |
| Flame or beilstein test (8.4.1) | | Chlorinated materials |
| Haze or transmittance (7.2.1) | Test Method D 1003 | Moisture; incompatible polymers |
| Inspection table (8.2.1 | | Visible contaminants (specks, particles) |
| Infrared spectroscopy (7.6) | Practice E 1252 | Contaminant functional groups |
| Magnets (7.4.2) | | Ferrous metals |
| Moisture (7.1) | Test Methods D 789; Test Method D 1003; Test Method D 4019 | Water content |
| Molded specimens or plaques (8.2.2) | | Paper, adhesives, poly(vinyl chloride), incompatible polymers |
| Polystyrene contaminant (8.8) | | Polystyrene; other aromatic polymers |
| Product uniformity (7.4) | | |
| Solvent extraction procedures, hexane or xylene (8.7) | | Glues, soluble contaminants |
| Specimen preparation (8.1) | | |
| Stain 5 test (8.6) | | Nylon, polyesters, paper |
| Stain K test (8.5.2) | | Chlorinated polymers |
| Thermal analysis (7.5) | Test Method D 3418; Test Method E 794 | Polymer identity |
| Ultraviolet spectroscopy (8.8) | | Aromatic polymers |
| Visible inspection procedures (7.2; 8.2) | | Dirt, specks, particles, materials with color different from bulk polymer |

# International XRF standard test methods

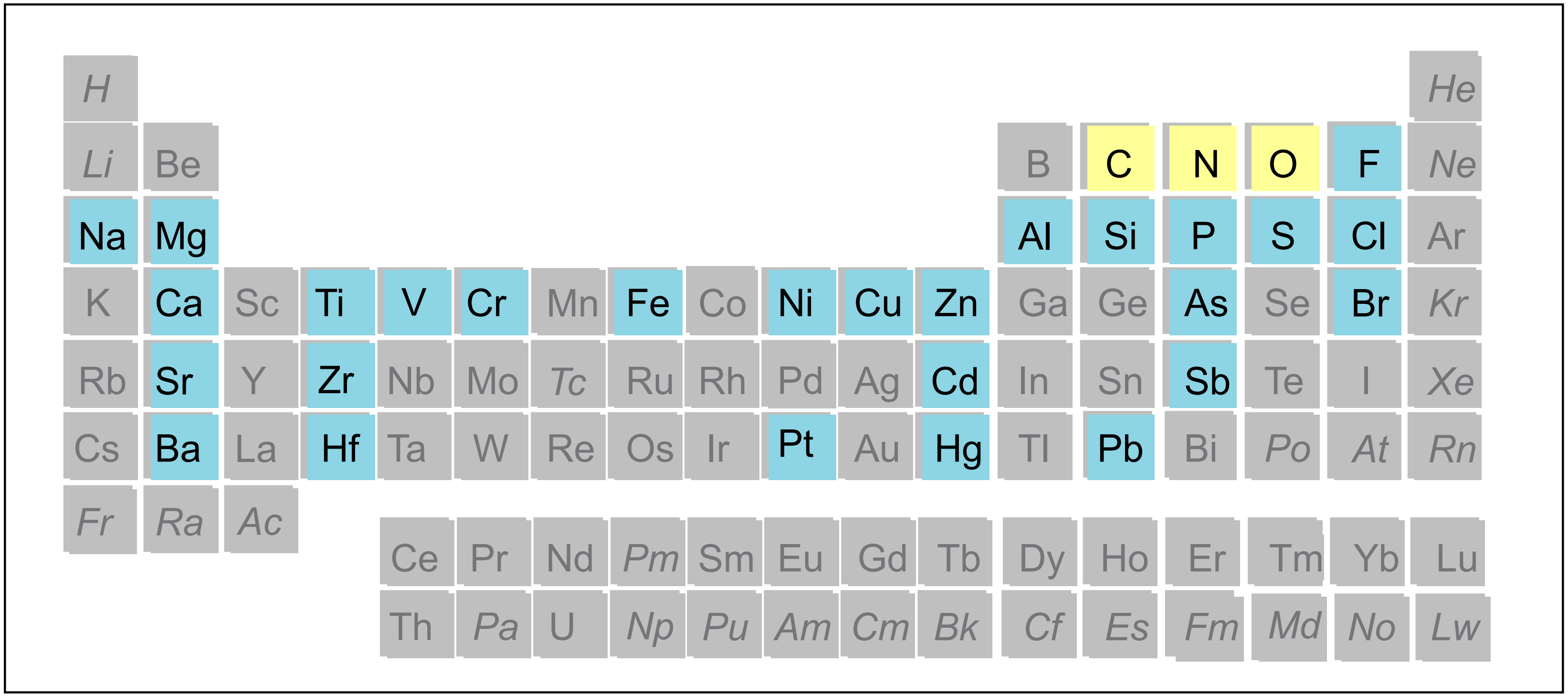
- Many EDXRF and WDXRF methods exist for *petroleum products*
  - 13+ ASTM methods (including one dedicated to catalysts)
  - 4+ ISO methods
  - Plus others

- Only a few methods for *polymer products*
  - 2 ASTM methods (+ another for pigments)
  - No ISO methods

- Why?
  - The XRF matrix effect for uniquely formulated polymers makes standardization more difficult
  - This *does not* make XRF's typical benefits less useful

# XRF elemental analysis in polymers (I)

- One view of the periodic table:




Elements of primary interest in polymers and related materials

Elements requiring special XRF config-urations



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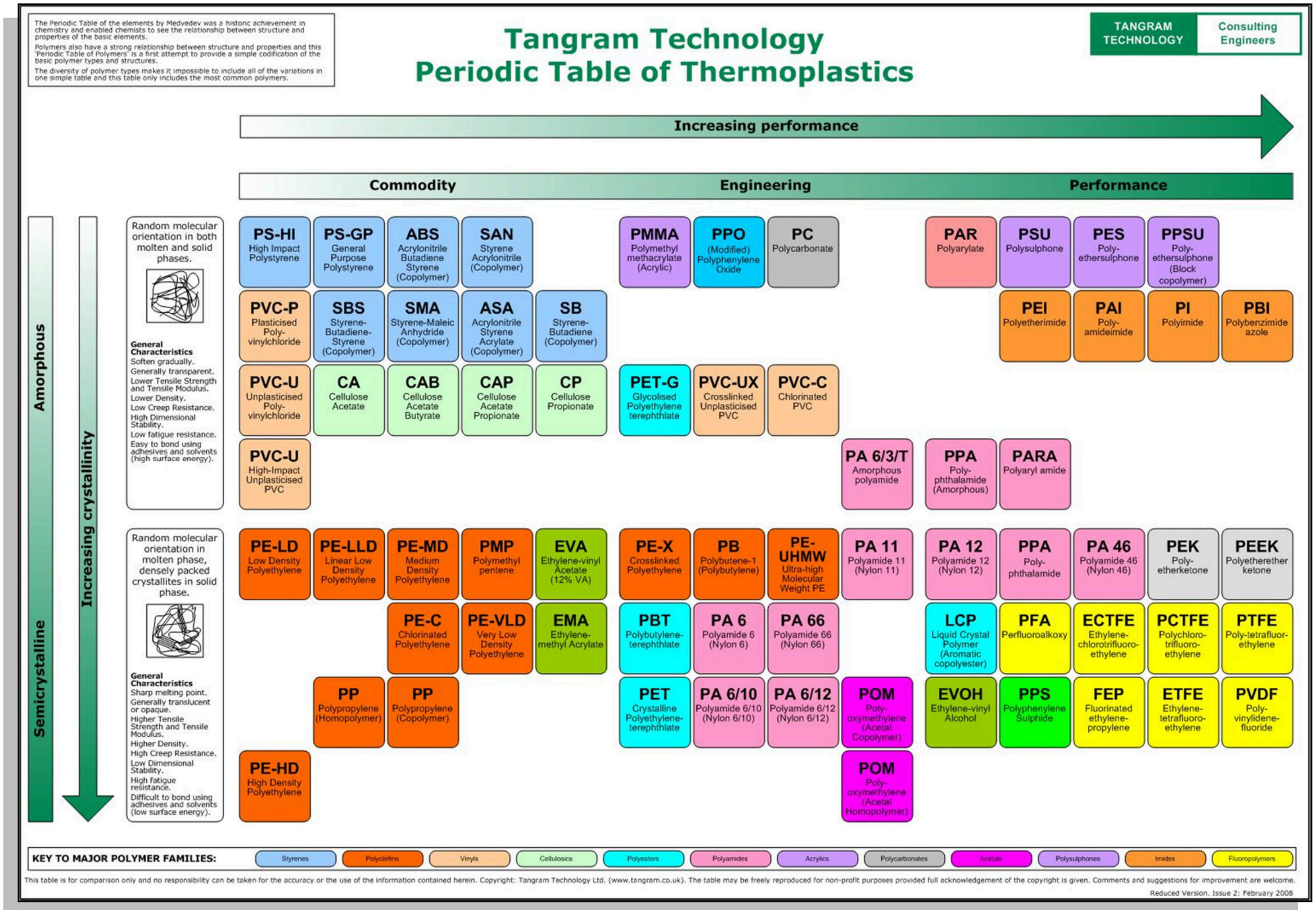
# XRF elemental analysis in polymers (II)

- XRF works on virtually any polymer, thermoplastic or thermoset

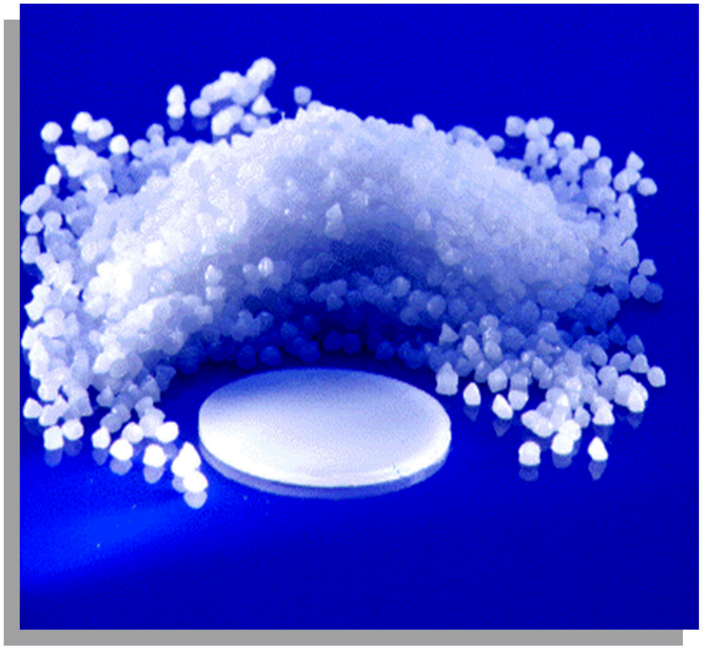


# Calibration reference materials

- Polymer reference materials are available through…
  - Metrology institutes
  - Commercial sources
  - Can be discs, granules or pellets
  - Including certified additive compounds

- Certified custom compounding services for ppm levels of multiple elements are available in polyolefins

- In-house standards can be blended and melt-homogenized
  - Most common





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# Thermo polymer calibration set (I)

- Set of custom polymer standards in polyolefins
- Tailored for customer elements and analytical ranges

# Thermo polymer calibration set (II)

- Example of a customer calibration set
- 10 elements, variable ranges from 0 - 500ppm

Product Code: PL(PE)10-10E(P) Lot Number: 121206

Standard Deviation (1 Sigma)-4.0 % (Relative) *

| Sample Number | Parts Per Million | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Al | Ca | Cl | Cr | Mg | P | Si | Ti | Zn | Zr |
| 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 5 | 30 | 75 | 20 | 0 | 120 | 50 | 10 | 20 | 25 |
| 3 | 10 | 5 | 151 | 4 | 20 | 206 | 502 | 25 | 0 | 30 |
| 4 | 20 | 20 | 301 | 0 | 30 | 100 | 100 | 40 | 0 | 40 |
| 5 | 25 | 50 | 0 | 10 | 0 | 0 | 200 | 0 | 40 | 5 |
| 6 | 30 | 0 | 50 | 8 | 5 | 81 | 0 | 50 | 5 | 0 |
| 7 | 40 | 0 | 0 | 12 | 40 | 42 | 251 | 0 | 30 | 50 |
| 8 | 51 | 10 | 103 | 0 | 26 | 0 | 0 | 31 | 51 | 20 |
| 9 | 0 | 25 | 202 | 16 | 51 | 162 | 303 | 20 | 25 | 0 |
| 10 | 0 | 40 | 253 | 2 | 10 | 25 | 417 | 5 | 10 | 10 |
| QC | 25 | 25 | 150 | 10 | 25 | 100 | 100 | 25 | 25 | 25 |

* THE RELATIVE DEGREE OF UNCERTAINTY IS 4 %. THIS IS THE ESTIMATED ACCUMULATION OF ERRORS FROM ASSAY ANALYSIS AND WEIGHING OF RAW MATERIALS.

# Other sample preparation

- Field samples or competitive samples can be ground and pressed into a pellet with binding wax
- Unknown samples can be analyzed directly with a Fundamental Parameters program (= semi-quantitative)
- XRF is an easy and quick complement to “wet chemistry” techniques such as ICP / AA, in which…
  - Polyolefins can require 5-30 minutes digestion in nitric acid under microwaves
  - Followed by acid evaporation, volume dilution with water and filtering of any precipitate before analysis

# XRF standard test methods

- ASTM
  F 2617 – 08
  (heavy metals)

- ASTM
  D 6247 – 98
  (2004)
  (polyolefins)

Designation: F 2617 – 08

**Standard Test Method for Identification and Quantification of Chromium, Bromine, Cadmium, Mercury, and Lead in Polymeric Material Using Energy Dispersive X-ray Spectrometry[1]**

This standard is issued under the fixed designation F 2617; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

**1. Scope**

1.1 This t... fluorescence... tion and qu... mercury, and...

1.2 This t... concentratio... minated diph... test method ... atoms or ion...

Designation: D 6247 – 98 (Reapproved 2004)

**Standard Test Method for Analysis of Elemental Content in Polyolefins By X-ray Fluorescence Spectrometry[1]**

This standard is issued under the fixed designation D 6247; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

**1. Scope**

1.1 This test method covers a general procedure for the determination of elemental content in polyolefins by X-ray fluorescence spectrometry, in concentration levels typical of those contributed by additives and reactor processes.

NOTE 1—Specific methods and capabilities of users may vary with differences in interelement effects and sensitivities, instrumentation and applications software, and practices between laboratories. Development and use of test procedures to measure particular elements, concentration ranges or matrices is the responsibility of individual users.

NOTE 2—One general method is outlined herein; alternative analytical practices can be followed, and are attached in notes, where appropriate.

E 691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method

E 1361 Guide for Correction of Interelement Effects in X-ray Spectrometric Analysis

E 1621 Guide for X-ray Emission Spectrometric Analysis

**3. Terminology**

3.1 *Definitions:*

3.1.1 Definitions of terms applying to XRF and plastics appear in Terminology E 135 and Terminology D 883, respectively.

3.2 *Definitions of Terms Specific to This Standard:*

# EDXRF: ASTM F 2617 – 08

- Chromium, Bromine, Cadmium, Mercury, and Lead by *EDXRF* in polymeric materials
- Application range: from 20 mg/kg (ppm) to ~1% for each element
- Repeatability and reproducibility limit example for Bromine:

**TABLE 4 Bromine Content Results from the Interlaboratory Study**

NOTE—All values are expressed as mass fractions in mg/kg (ppm).

| Material | Certified Value[A,B] and Uncertainty | Average | Repeatability Standard Deviation | Reproducibility Standard Deviation | Repeatability Limit | Reproducibility Limit |
|---|---|---|---|---|---|---|
| | | $\bar{X}$ | $s_r$ | $s_R$ | $r$ | $R$ |
| A | < 0.1 | 2.9 | 0.33 | 4.2 | 0.92 | 11.7 |
| B | 1007 ± 12 | 982.8 | 3.8 | 9.4 | 10.7 | 26.4 |
| C | 51 ± 3 | 52.5 | 1.4 | 3.8 | 4.1 | 10.7 |
| D | 383 ± 14 | 386.4 | 2.3 | 2.9 | 6.4 | 8.2 |
| E | 101 ± 4 | 101.5 | 0.80 | 4.4 | 2.2 | 12.2 |
| F | 808 ± 19 | 781.1 | 2.9 | 61.2 | 8.1 | 171.3 |
| G | 98 ± 5 | 101.5 | 2.8 | 2.8 | 7.8 | 7.8 |

[A] The certified values were taken from the certificate of analysis of each material and are typically derived from multiple methods of determination in different laboratories.
[B] The uncertainty listed for each certified value was taken from the certificate of analysis of the material. The certificate provides a definition of the uncertainty estimate, typically expressed at a 95 % level of confidence.

# Heavy metals application: RoHS

- EU Directive 2003/11/EC – RoHS
  - “Restriction of the use of certain Hazardous Substances”
  - Sets maximum content of six elements/compounds in electronics goods

- Less than 100 ppm of
  - Cadmium (Cd)

- Less than 1,000 ppm of
  - Lead (Pb)
  - Mercury (Hg)
  - Hexavalent chromium (Cr (VI))
  - Polybrominated biphenyls (PBBs)
  - Polybrominated diphenyl ethers (PBDEs)

# EDXRF result:  Si(Li) detector, low power (50W)

- ARL QUANT'X with Peltier-cooled Si(Li) detector
- Total 500s counting time
- Limits of detection achieved:
  - Cr  2.0 ppm
  - Br  1.0 ppm
  - Cd  1.5 ppm
  - Hg  1.3 ppm
  - Pb  1.3 ppm

# EDXRF result: RoHS pass/fail

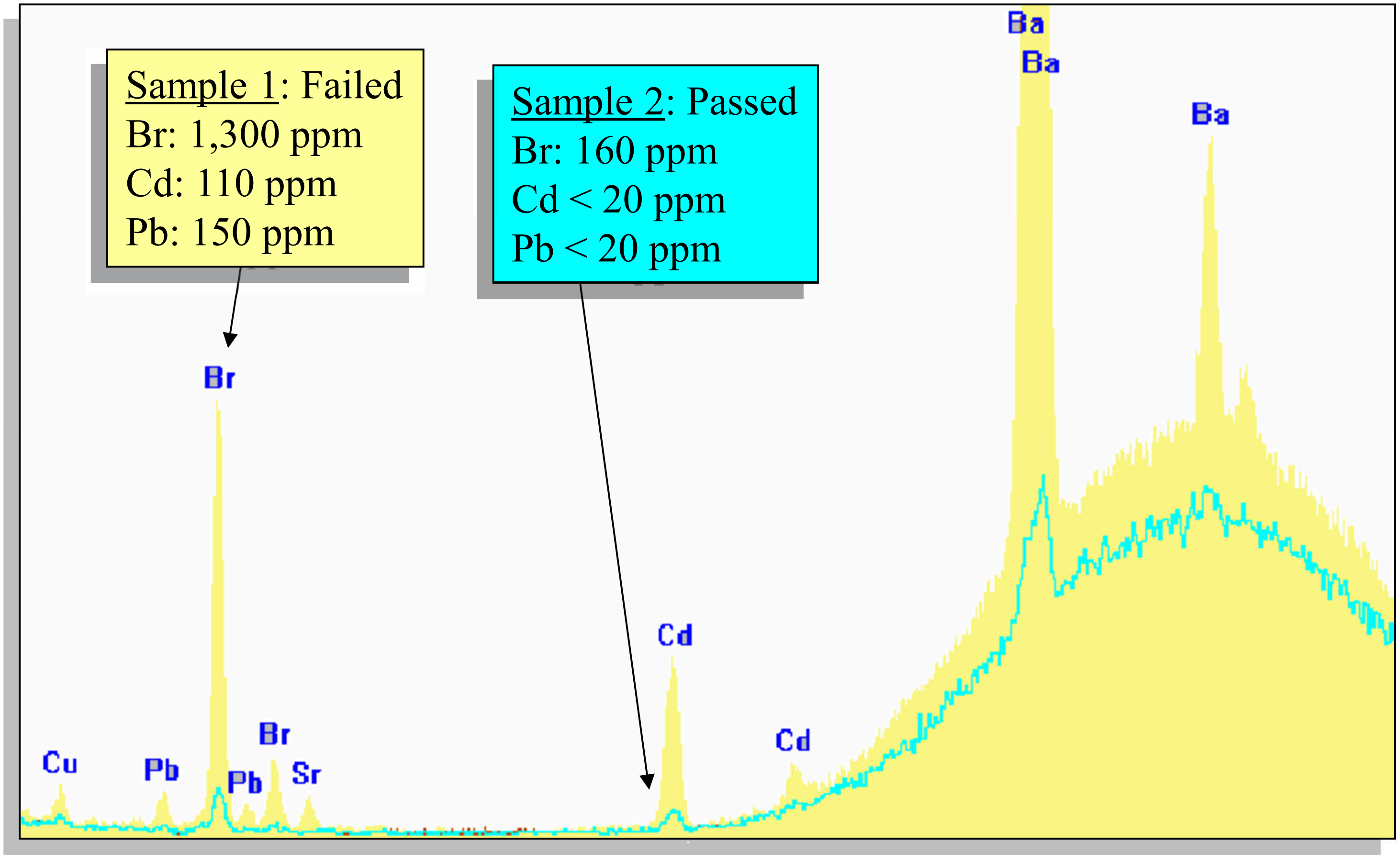


**Figure 1**: Results obtained with ARL QUAN'TX EDXRF with 500s counting time

# EDXRF result: PVC containing Cd and Pb

- ARL QUANT'X with Peltier-cooled Si(Li) detector
- Total 200s counting time
- Difference between 85 ppm and 35 ppm is easy to ascertain

| | Cd | Pb |
|---|---|---|
| LoD | 0.9 ppm | 1 ppm |
| Precision | 1.8 @ 35 ppm | 5.2 @ 89 ppm |
| Precision | 3.7 @ 85 ppm | 14.1 @ 837 ppm |

Table 2: Limits of detection (LoD) and precisions

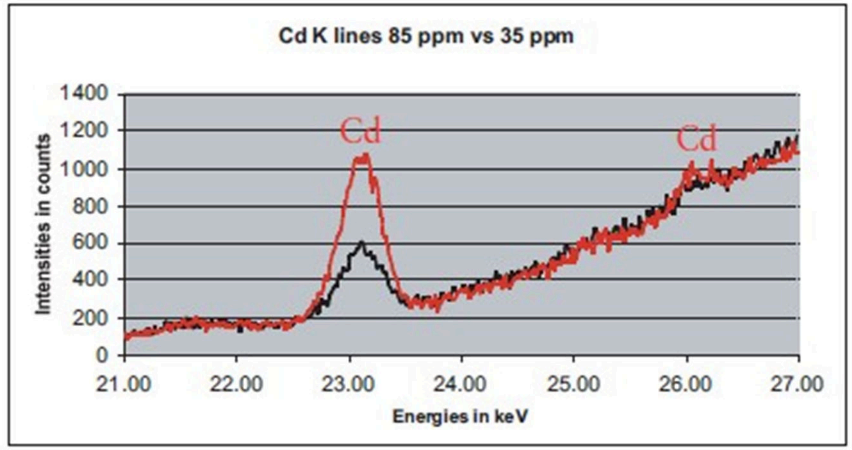


Figure 1: Comparison of the spectrum of PVC containing 35 ppm of cadmium (black) with the spectrum of PVC containing 85 ppm of cadmium (Red)

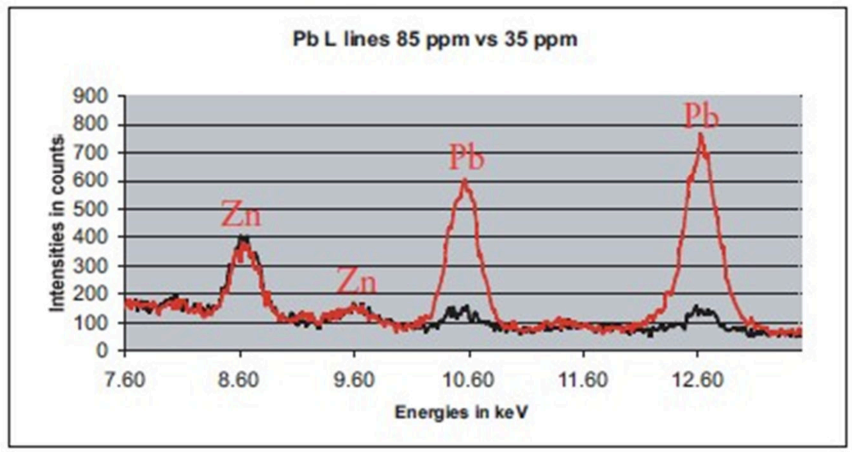


Figure 2: Comparison of the spectrum of PVC containing 35 ppm of lead (black) with the spectrum of PVC containing 85 ppm of lead (Red)

# EDXRF result – fundamental parameters

- Polyethylene sample with no prior calibration, i.e., “standard-less”
- Quick results give a good screen for RoHS/WEEE compliance
- Can be improved with further matrix-matching

| | Certified value (ppm) | UniQuant v6 result (ppm) |
|---|---|---|
| As | 4 | 4.1 |
| Br | 96 | 46 |
| Cd | 19.6 | 21 |
| Cr | 20.2 | 13 |
| Hg | 5 | 1 |
| Pb | 13.6 | 6.2 |
| S | 76 | 62 |

# WDXRF: ASTM D 6247 – 98 (2004)

- Various elements in polyolefins by *WDXRF*
- Application range: "…in concentration levels typical of additives and reactor processes"
- Outline of elements and concentration levels for PE and PP:

| Element | Metal PE1 | Metal PE2 | Metal PE3 | Metal PP1 | Metal PP2 | Metal PP3 |
|---|---|---|---|---|---|---|
| Al | 134 | 2.9 | 116 | 80 | 62 | 29 |
| Ca | ... | ... | 100 | ... | 25 | 45 |
| Cr | ... | 1.16 | ... | ... | ... | ... |
| Fe | 33 ± 4 | ... | ... | ... | ... | ... |
| Mg | 12 ± 2 | ... | 23 ± 3 | 13 ± 2 | ... | ... |
| P | ... | 90 | 74 | 69 | 36 | ... |
| Si | 1503 | 206 ± 20 | 3338 | 827 | 349 | ... |
| S | ... | ... | ... | ... | < 85 | 64 ± 20 |
| Ti | 5.3 | ... | 7.7 | 2.5 | 2.2 | 0.74 |
| Zn | ... | 63 | ... | 199 | ... | ... |

# WDXRF result – low power (50W)

- ARL OPTIM'X with Ultra Closely Coupled Optics
- Additive elements in polyethylene (40mm discs)
- Low ppm detection limits in 60s counting time
- Lighter elements, e.g., Fluorine, can be improved with longer counting time

**Instrumentation**

| Element | Line | Ana. Time (seconds) | Limits of detection [ppm] | SEE | Std Dev. | At ppm |
|---|---|---|---|---|---|---|
| **Al** | Ka1,2 | 60 | 3.3 | 6.4 | 1.3 | 28 |
| **Ca** | Ka1,2 | 60 | 2.1 | 2.7 | 0.8 | 12 |
| **Cr** | Ka1,2 | 60 | 1.4 | 1.1 | 0.5 | 1 |
| **F** | Ka1,2 | 60 | 260 | 69 | 105 | 140 |
| **Mg** | Ka1,2 | 60 | 6.6 | 30 | 2.7 | 30 |
| **P** | Ka1,2 | 60 | 2.8 | 1.9 | 40 ? | 20 |
| **Si** | Ka1,2 | 60 | 3.3 | 16 | 1.4 | 35 |
| **Ti** | Ka1,2 | 60 | 1.7 | 1.2 | 0.5 | 4 |
| **Zn** | Ka1,2 | 60 | 0.9 | 1.6 | 0.3 | 3 |

**SEE**: Standard Error of Estimate, a measure of accuracy


Figure 1. Innovative UCCO technology

# WDXRF result – low power (50W)

- ARL OPTIM'X with Ultra Closely Coupled Optics
- Typical results, high precision (short term repeatability)

| | 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 %

# WDXRF result – higher power (2500 to 4200W)

- ARL PERFORM'X
- Higher power WDXRF achieves sub-ppm LoD on all elements

TYPICAL LOD

| ELEMENT | 4200W (3 SIGMA) [PPM] | 2500W (3 SIGMA) [PPM] |
|---|---|---|
| Mg | 0.86 | 1.11 |
| Al | 0.23 | 0.30 |
| P | 0.16 | 0.21 |
| Cl | 0.30 | 0.39 |
| Ca | 0.14 | 0.18 |
| Ti | 0.10 | 0.13 |
| Cr | 0.11 | 0.14 |
| Fe | 0.07 | 0.09 |

Table 2: Limits of detection for various elements in polymers (100 sec. counting time)



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# WDXRF result – high power (4200W)

- 8 consecutive runs on the same polymer disc
- 20s counting time on each element
- Typical results, high precision of analysis

| 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 |

# WDXRF application – ultra low traces

- Traces of Titanium catalyst can negatively affect polymer performance
- Customer need to monitor Ti at ultra low levels
- Goal of ±0.1 ppm on a range from 0.5 to 5 ppm
- High power (4200W) XRF



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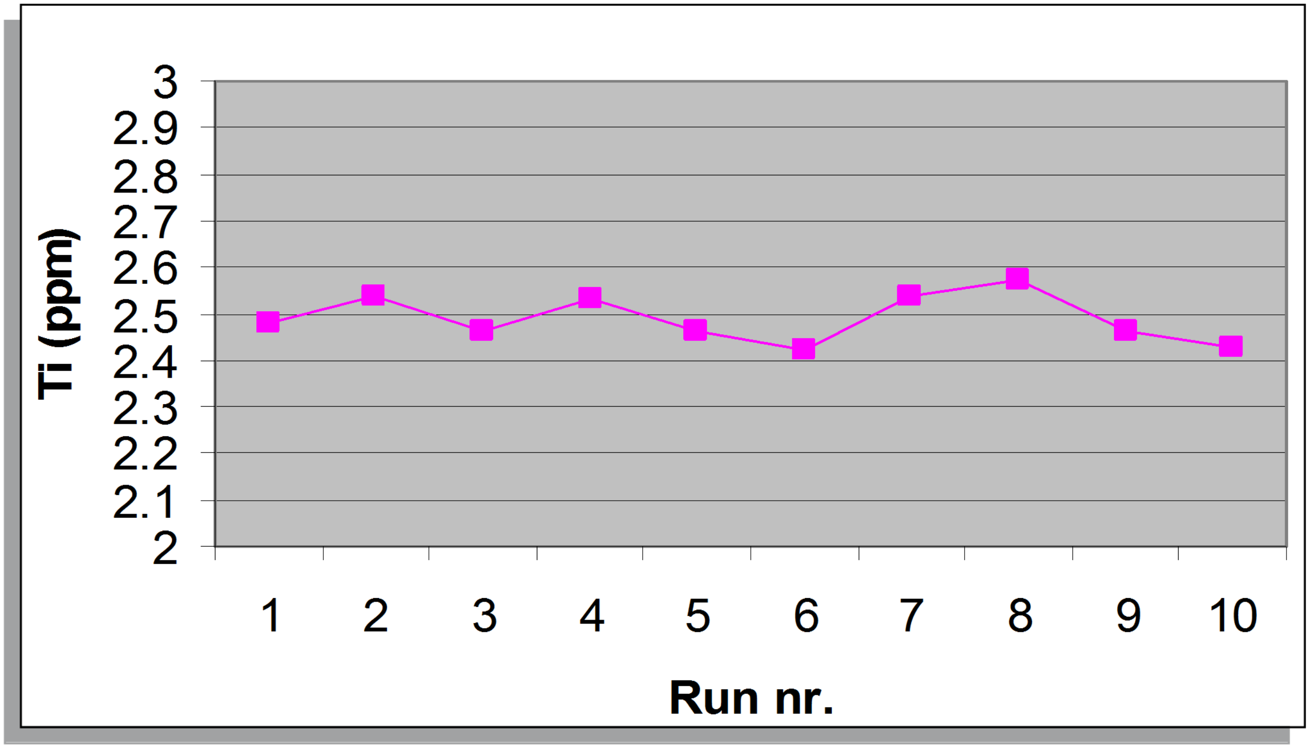
# Repeatability for ultra low traces of Ti

- 10 runs, each for 60 seconds analysis time
- Sample removed from spectrometer after each run
- Standard deviation:  0.052 ppm exceeded the goal



# Calibration for RoHS/WEEE and other elements

**Elements:**

**As, Cd, Cl, Hg, S, Ti, Pb, Zn, Cr, Cu, Ni, Br and Ba**

Note: 3.6kW is used in order to avoid deterioration of the sample surface due to heat



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# Limits of detection in polymer matrix

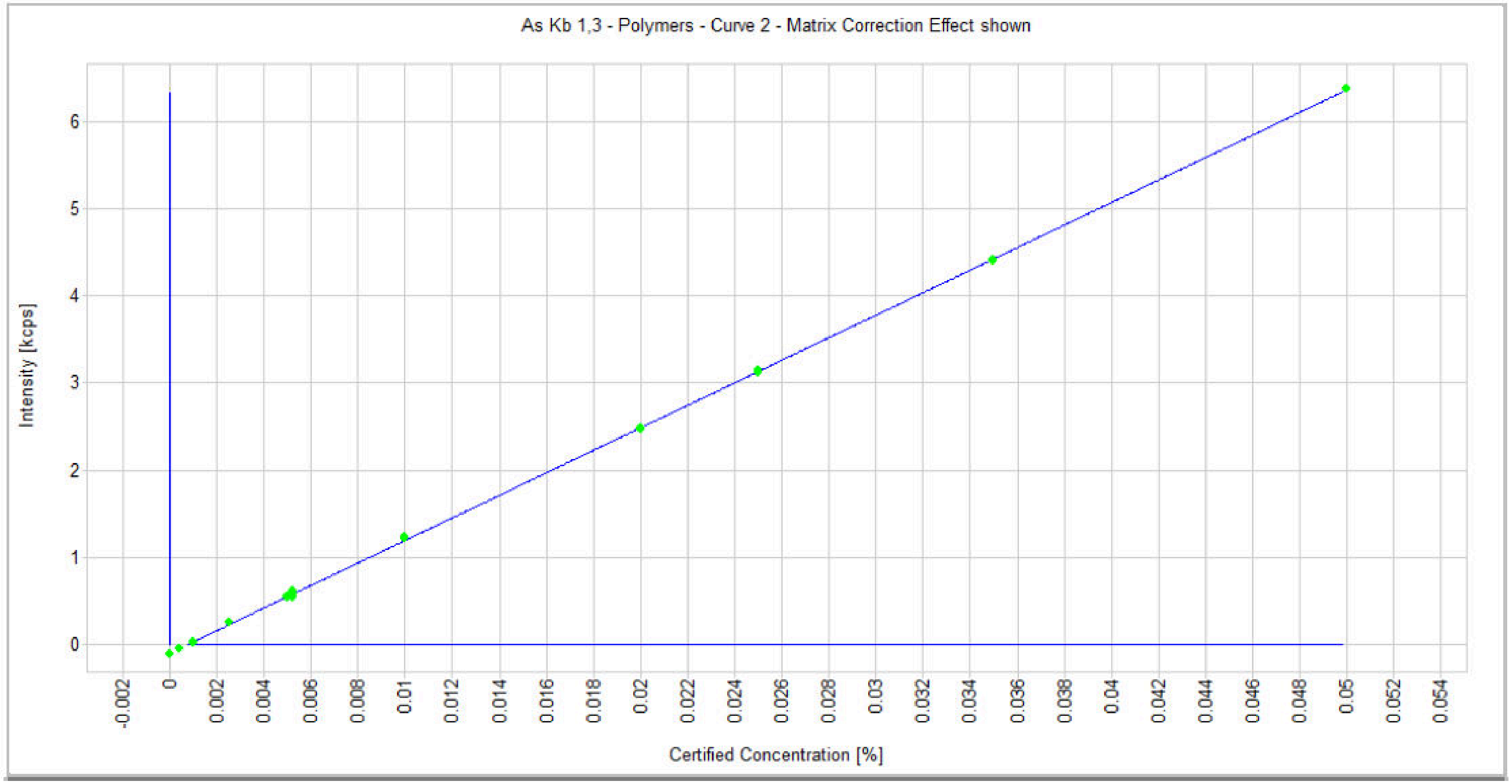
**Limits of detection calculated as 3 times Std deviation on a blank sample**

| Element | As | Cd | Cl | Hg | S | Ti | Pb | Zn | Cr | Cu | Ni | Br | Ba |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| kV/mA | 60/60 | 60/60 | 30/120 | 60/60 | 30/120 | 30/120 | 60/60 | 60/60 | 60/60 | 60/60 | 60/60 | 60/60 | 30/120 |
| PBF | Yes | Yes | | Yes | | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes |
| LoD (100s) ppm | 1.7 | 3.5 | 1.4 | 1.6 | 3.4 | 0.2 | 1.3 | 0.2 | 0.3 | 0.2 | 0.2 | 0.2 | 0.9 |

Note: 3.6kW is used in order to avoid deterioration of the sample surface due to heat

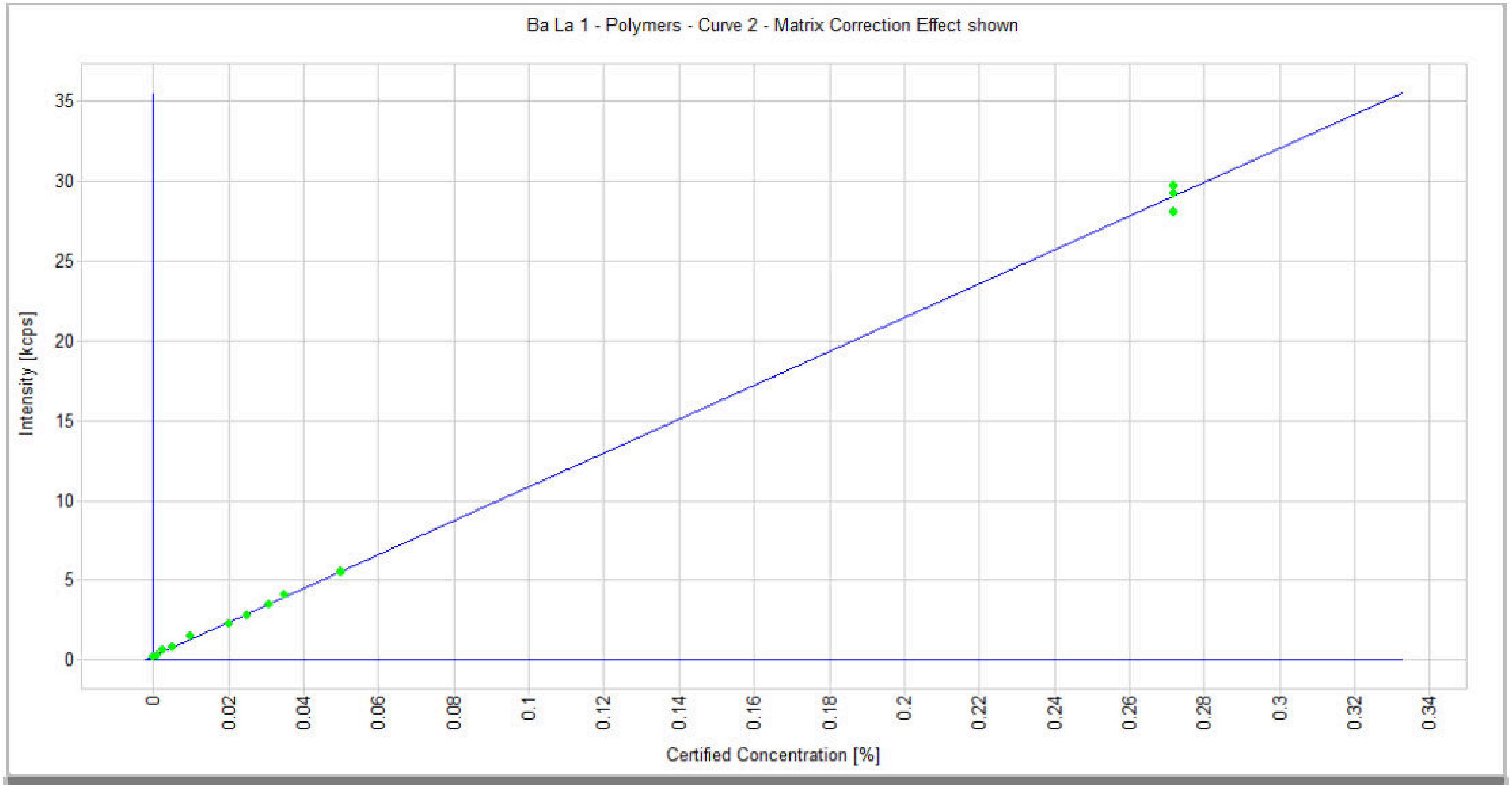
# Arsenic in polymer – calibration curve

- SEE = 0.00017%



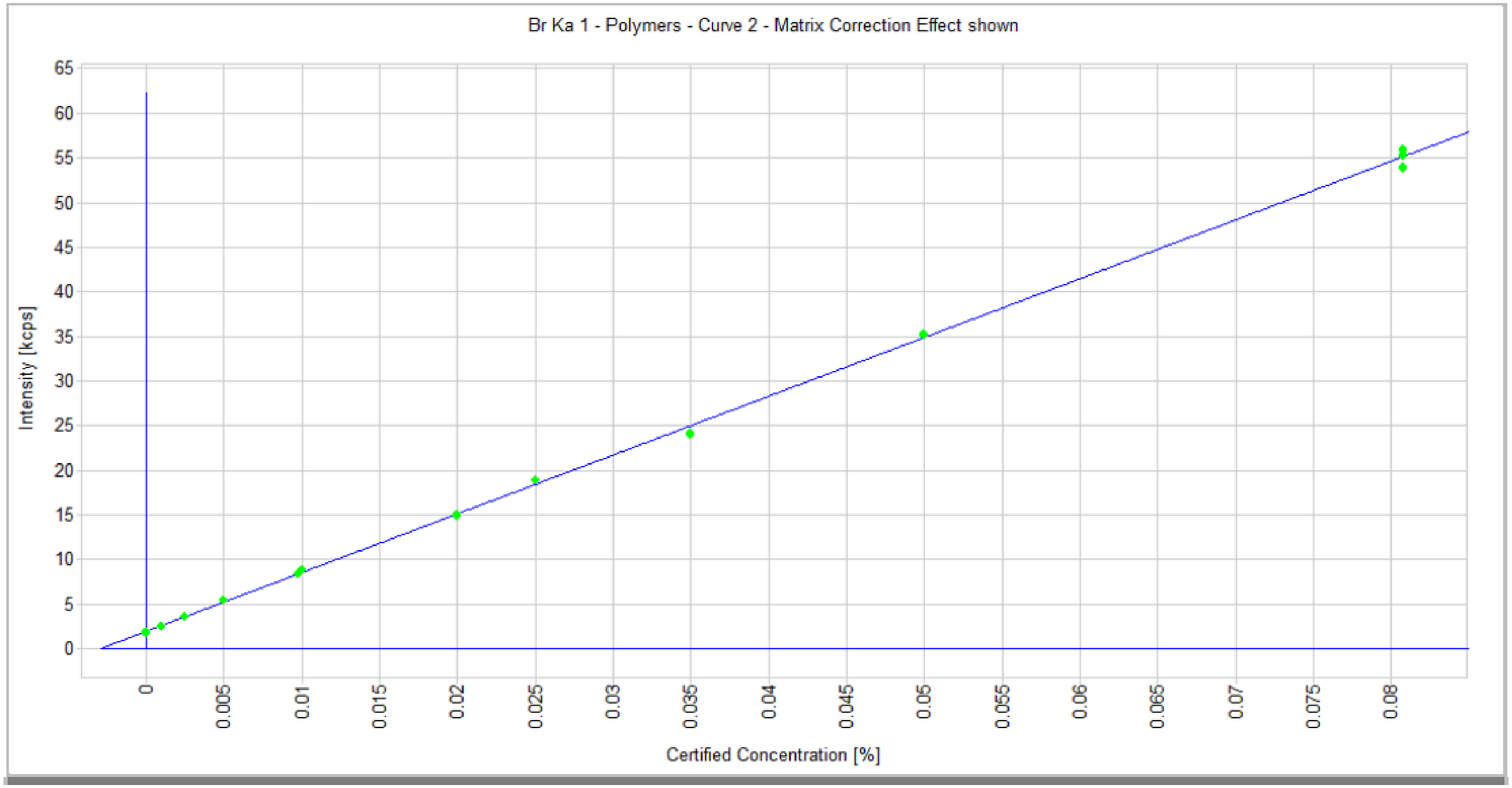
# Barium in polymer – calibration curve

- Ba La line – up to 0.27% – SEE = 0.0033%



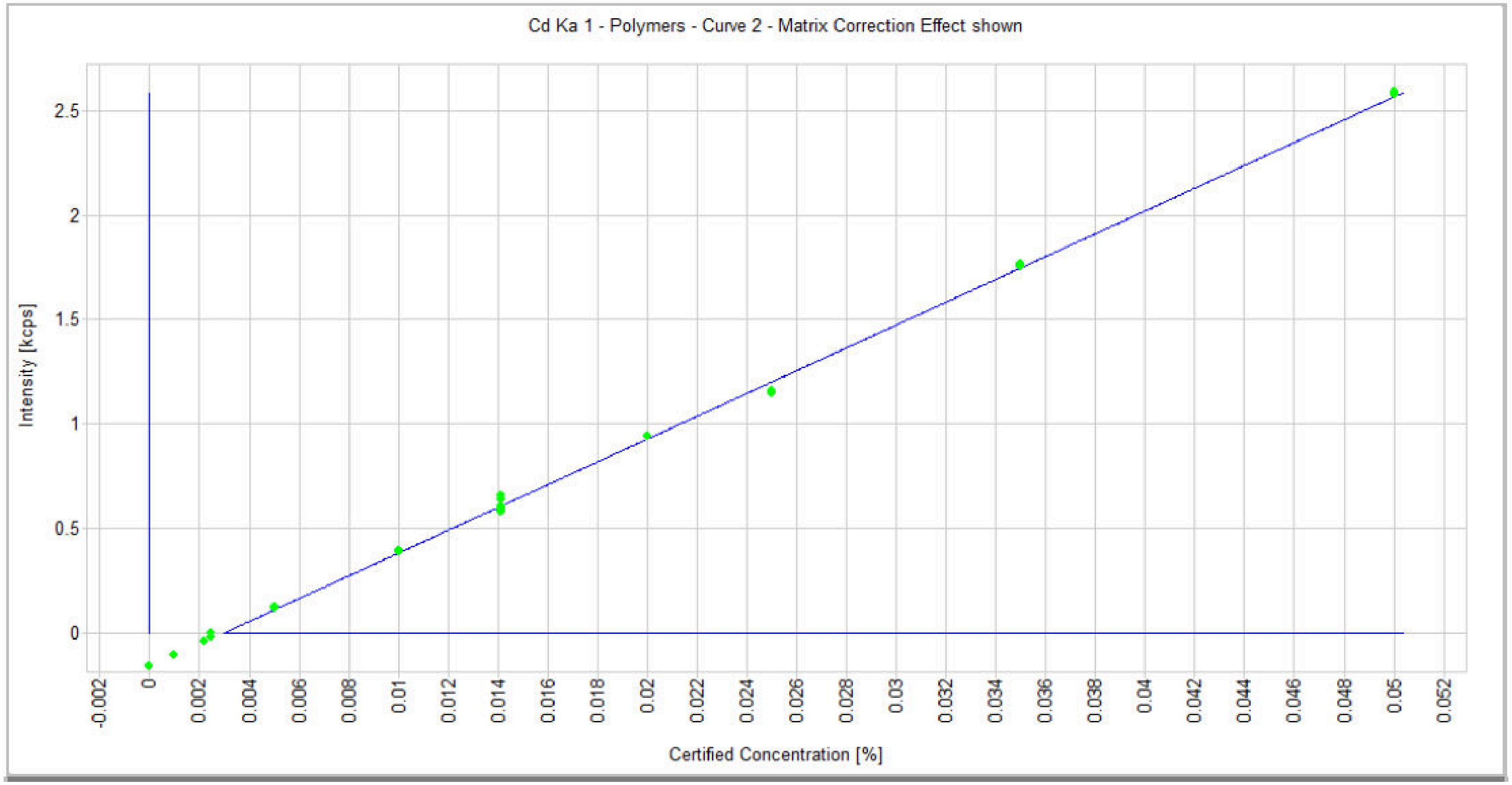
# Bromine in polymer – calibration curve

- Br up to 0.08% – SEE = 0.0085%



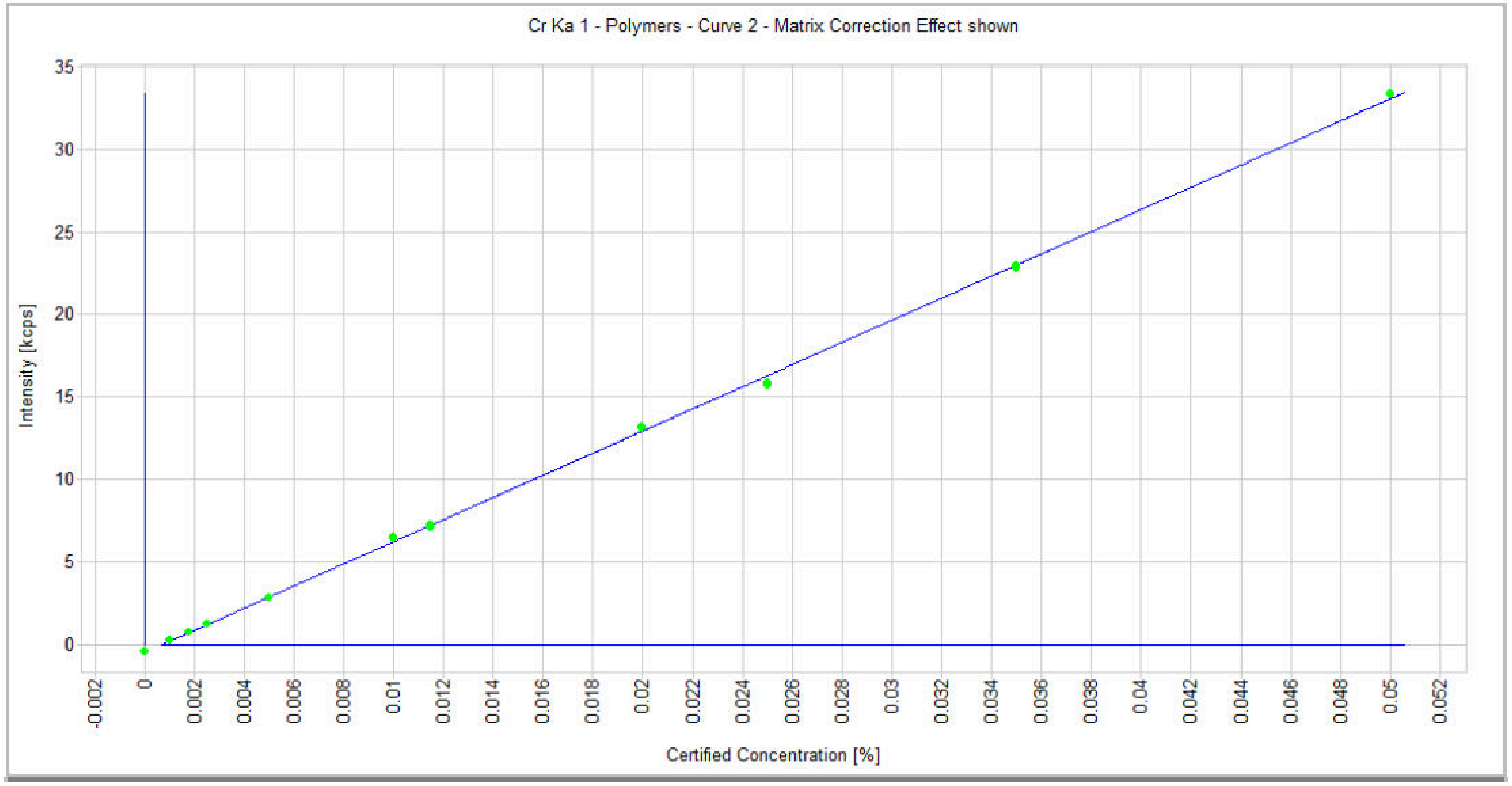
# Cadmium in polymer – calibration curve

- Cd up to 0.05% – SEE = 0.00046%
- Copper Primary beam filter used



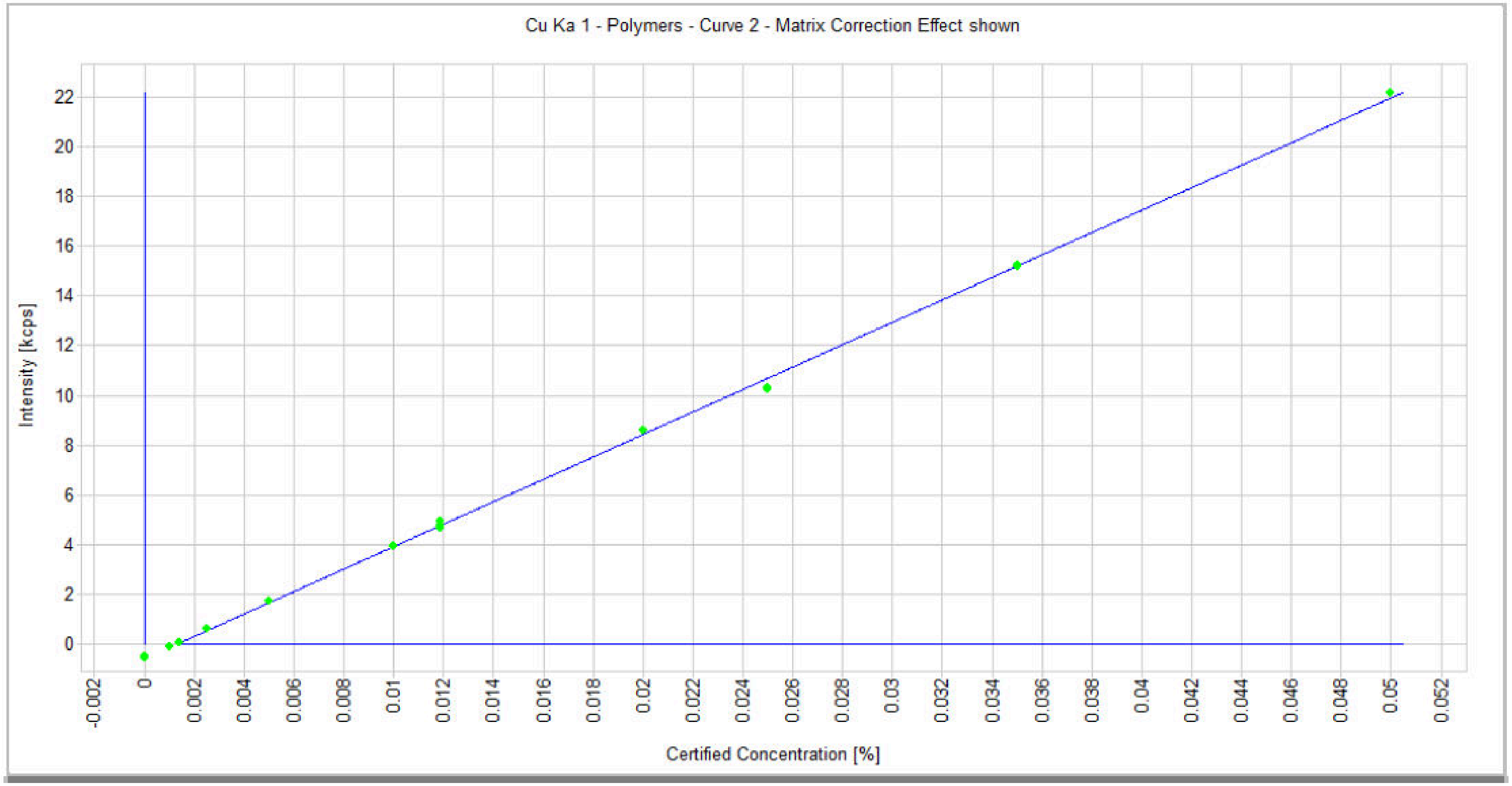
# Chromium in polymer – calibration curve

- Cr up to 0.05% – SEE = 0.00034%



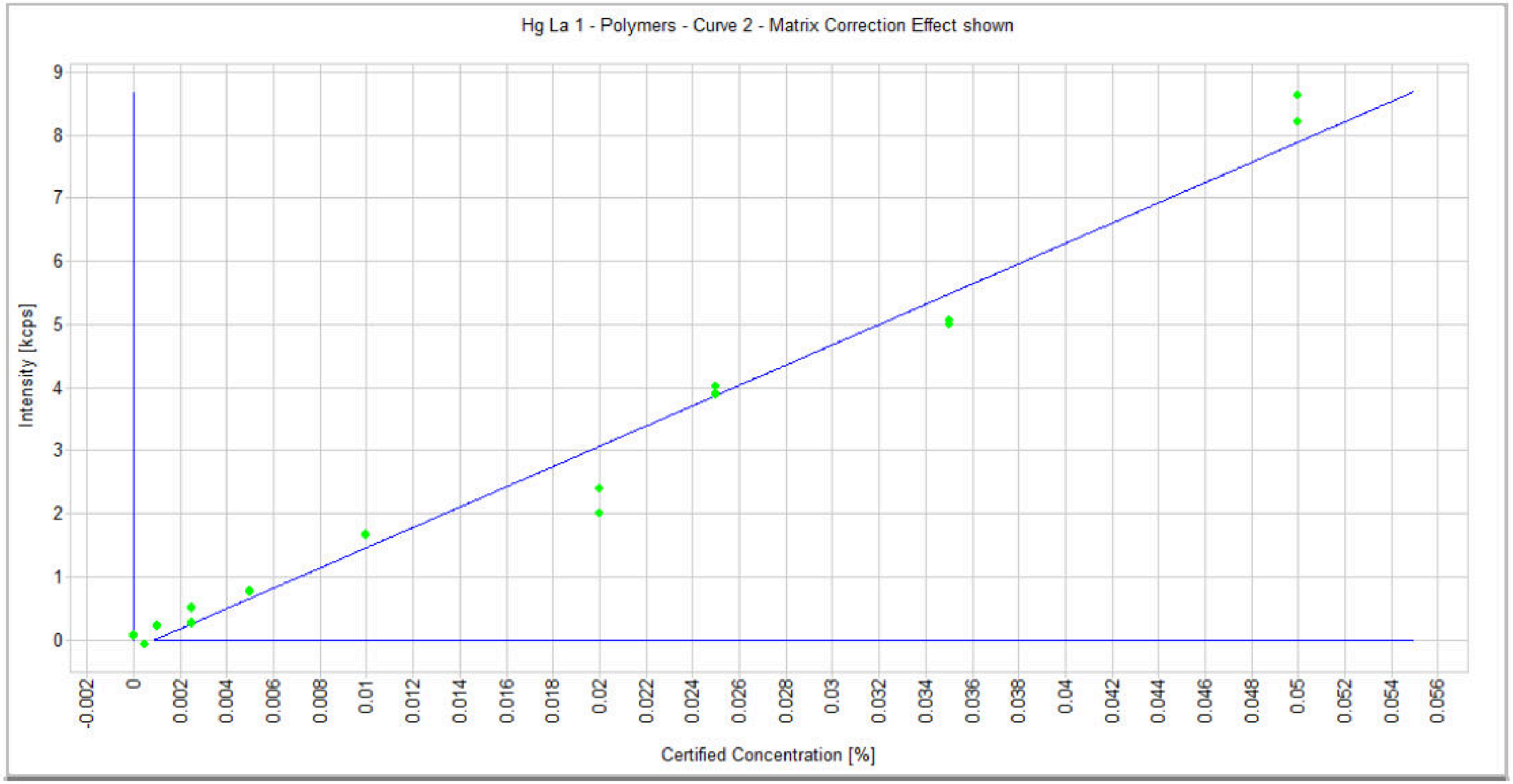
# Copper in polymer – calibration curve

- Cu up to 0.05% – SEE = 0.00038%



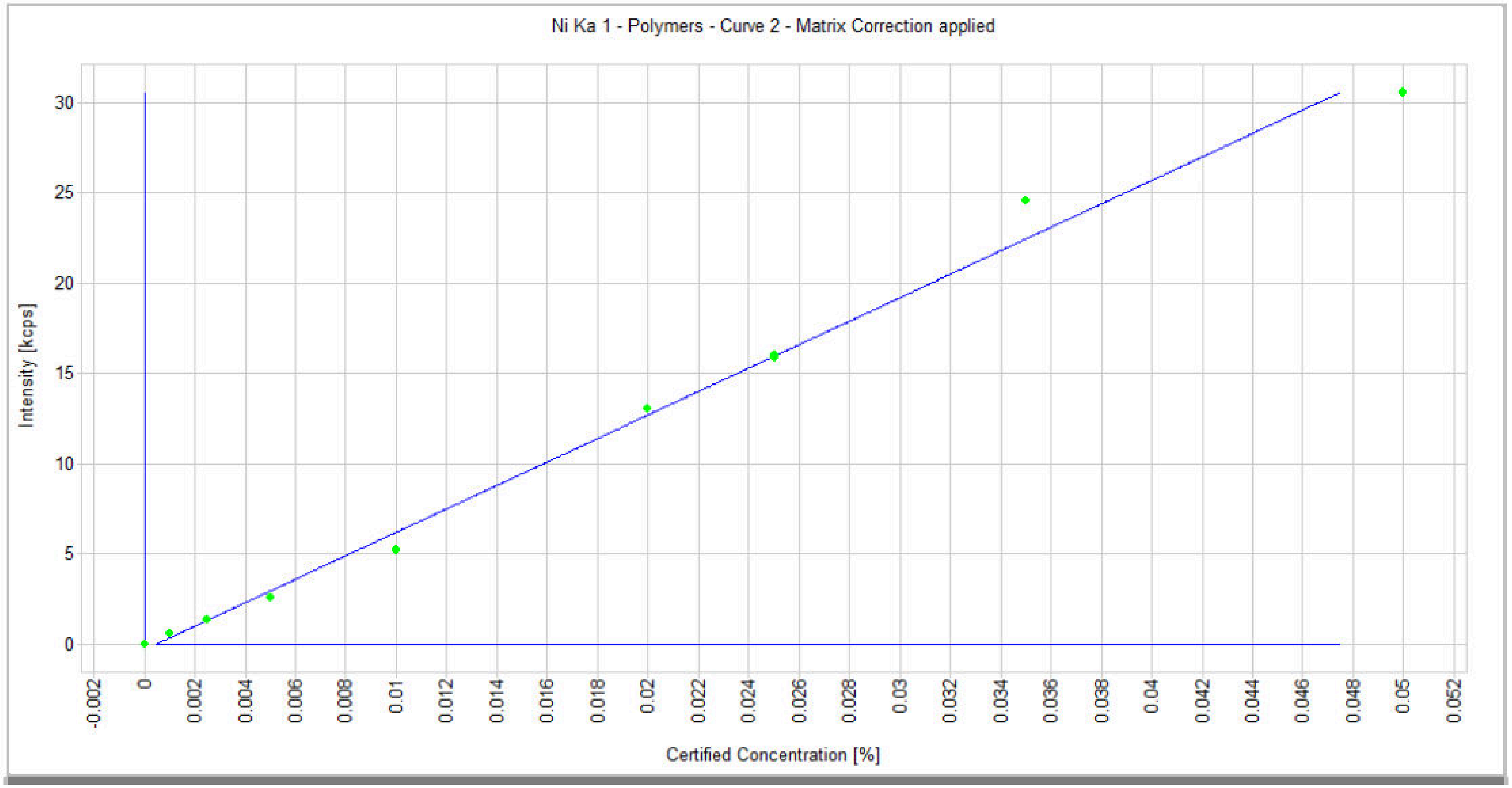
# Mercury in polymer – calibration curve

- Hg up to 0.05% – SEE = 0.0022%



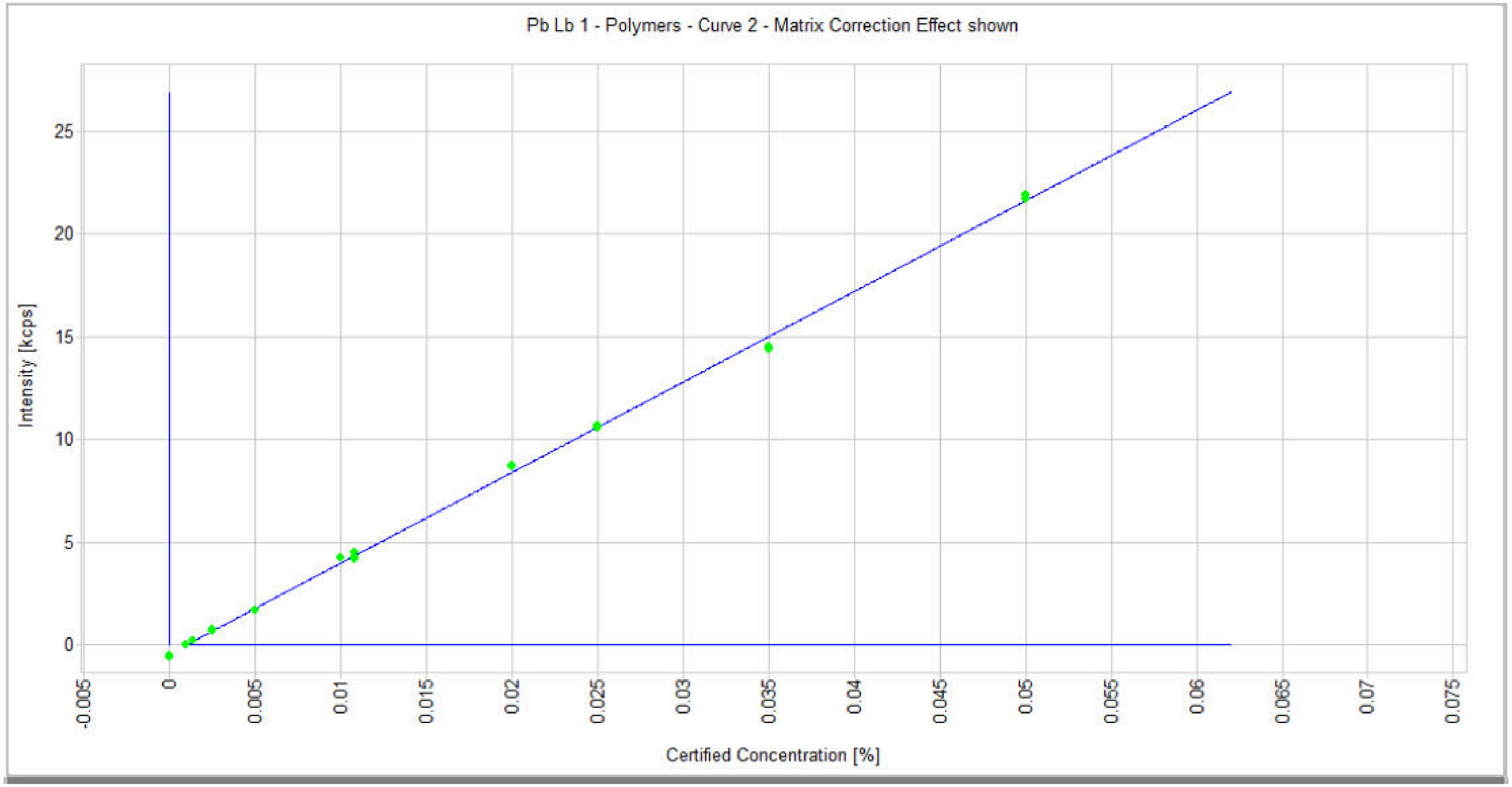
# Nickel in polymer – calibration curve

- Ni up to 0.05% – SEE = 0.0013%



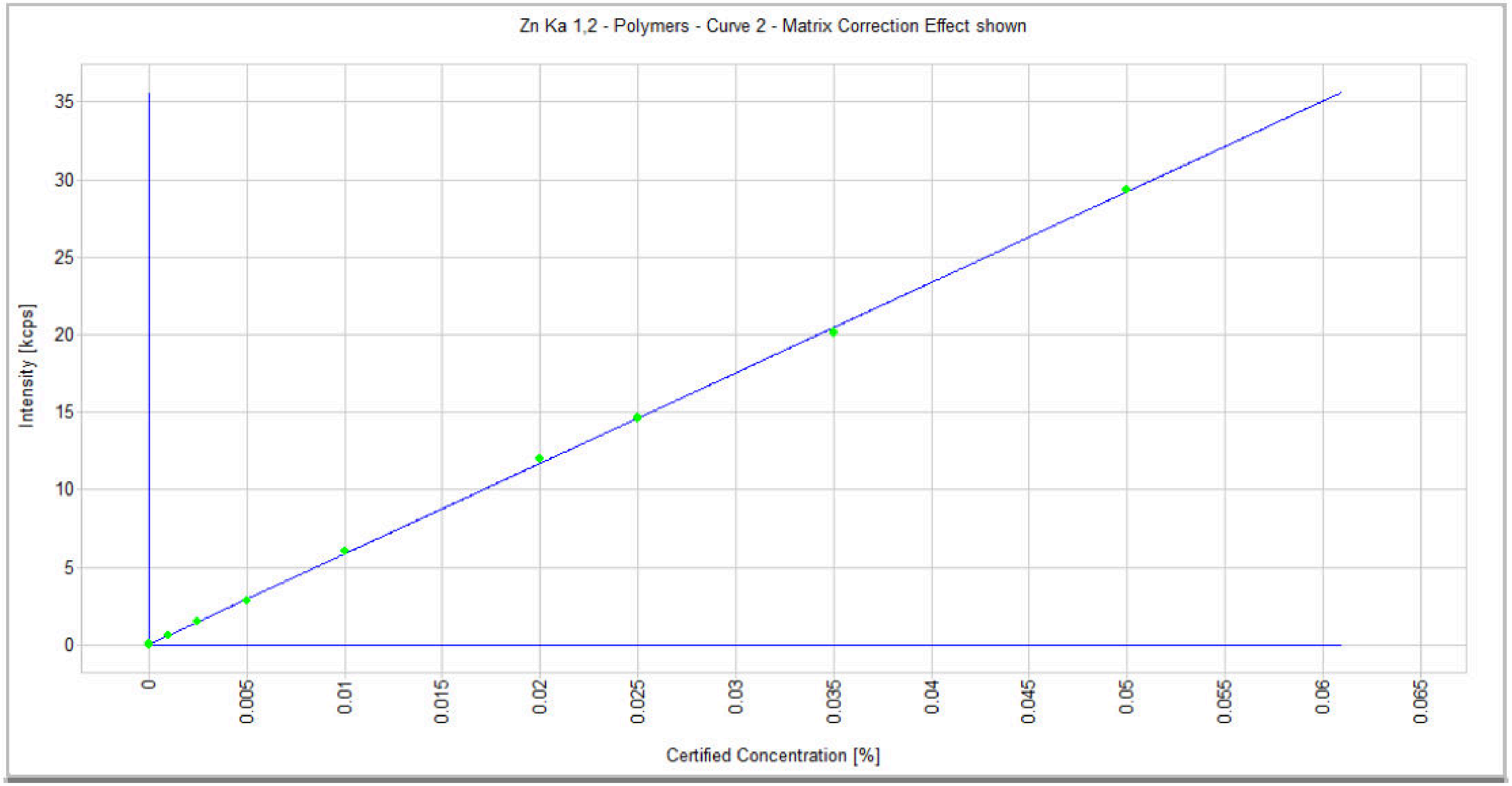
# Lead in polymer – calibration curve

- Pb up to 0.05% – SEE = 0.0005%



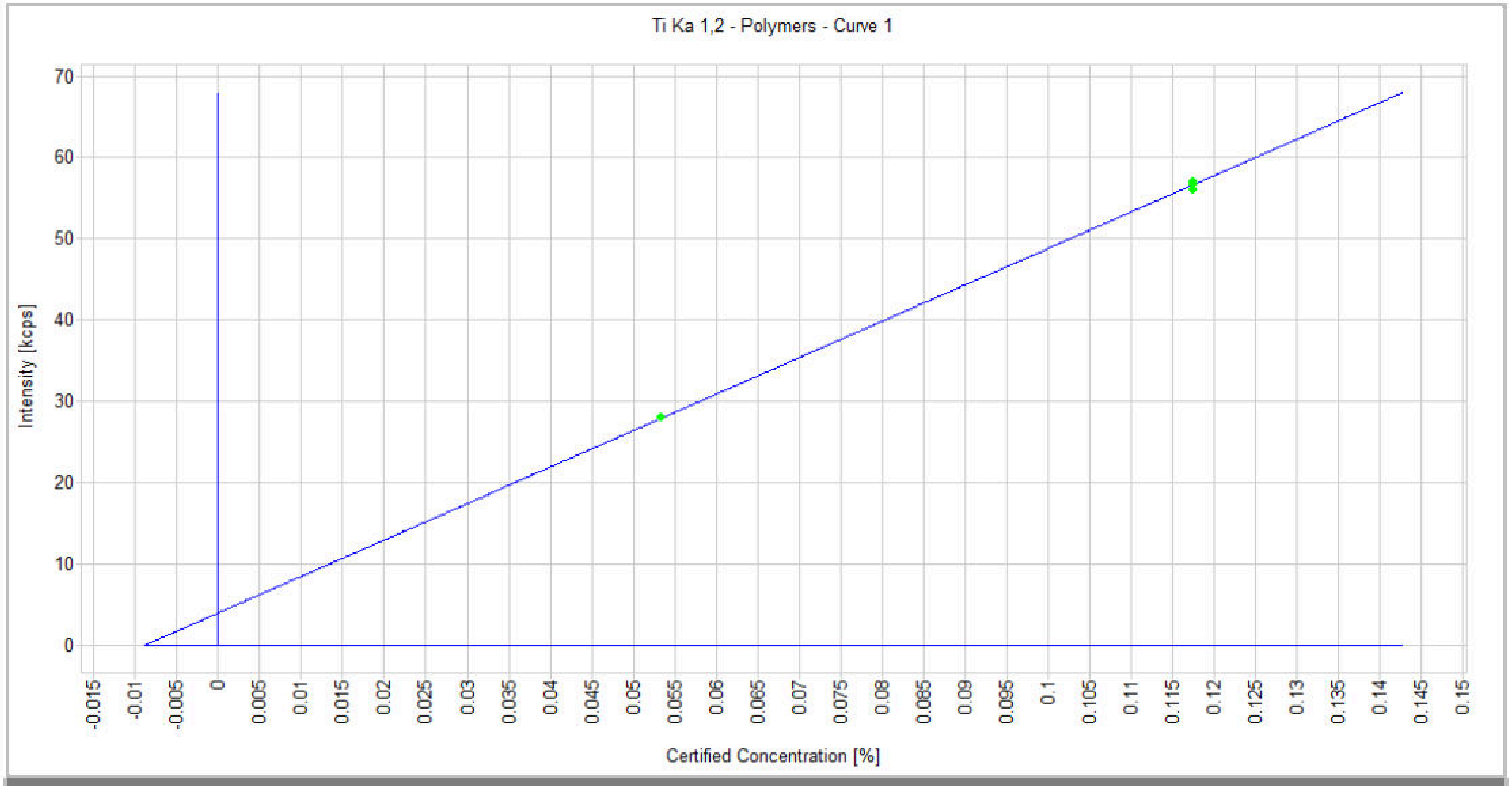
# Zinc in polymer – calibration curve

- Zn up to 0.05% – SEE = 0.00024%



# Titanium in polymer – high levels calibration curve

- Ti up to 0.12% – SEE = 0.001%



# Conclusion

- Latest sequential XRF instrument permit to achieve limits of detection from 0.1ppm for some elements
- Use of primary beam filters permit improved limits of detection
- Dedicated sets of certified standard samples for polymers are now available
  - Allow calibrating the XRF instrument according to your specific customer needs
  - An excellent accuracy can be obtained

# 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..**

# Repeatability on a blank polymer sample

| Channel | *As Kb 1,3* | *Cd Ka 1* | *Cl Ka 1,2* | *Hg La 1* | *S Ka 1,2* | *Ti Ka 1,2* | *Pb Lb 1* | *Zn Ka 1,2* | *Cr Ka 1* | *Cu Ka 1* | *Ni Ka 1* | *Br Ka 1* | *Ba La 1* |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Unit** | ppm | ppm | ppm | ppm | % | % | ppm | ppm | ppm | ppm | ppm | ppm | ppm |
| **Run 1** | 0.54 | 2.41 | -3.87 | 1.4 | 0.0034 | 0.0001 | 4.01 | 1.67 | 0.71 | 1.11 | 4.34 | 3.5 | -1.08 |
| **Run 2** | 0.7 | 0.25 | -2.61 | 2.36 | 0.0036 | 0.0001 | 4.28 | 1.65 | 0.66 | 1.13 | 4.47 | 3.64 | -0.83 |
| **Run 3** | 2.02 | 1.1 | -2.57 | 2.06 | 0.0038 | 0.0001 | 4.06 | 1.77 | 0.8 | 1.16 | 4.46 | 3.49 | -0.88 |
| **Run 4** | 1.98 | 2.1 | -1.89 | 2.42 | 0.0038 | 0.0001 | 3.51 | 1.83 | 0.7 | 1.2 | 4.33 | 3.53 | -0.71 |
| **Run 5** | 0.22 | 0.93 | -2.55 | 2.33 | 0.0038 | 0.0001 | 3.69 | 1.68 | 0.92 | 1.19 | 4.29 | 3.72 | -1.79 |
| **Run 6** | 0.54 | -0.31 | -2.43 | 2.52 | 0.0038 | 0.0001 | 3.65 | 1.92 | 0.91 | 1.36 | 4.56 | 3.39 | -1.13 |
| **Run 7** | 0.47 | 1.3 | -3.01 | 2.46 | 0.0038 | 0.0001 | 3.09 | 1.73 | 0.79 | 1.11 | 4.34 | 3.59 | -1.17 |
| **Run 8** | 0.74 | -0.69 | -2.22 | 2.63 | 0.0038 | 0.0001 | 3.09 | 1.86 | 0.83 | 1.15 | 4.4 | 3.66 | -0.6 |
| **Run 9** | -0.15 | 0.89 | -2.48 | 3.57 | 0.0038 | 0.0001 | 3.01 | 1.73 | 0.94 | 1.34 | 4.44 | 3.56 | -1.22 |
| **Run 10** | 1.15 | 2.21 | -3.76 | 3.26 | 0.0039 | 0.0001 | 2.64 | 1.71 | 0.91 | 1.27 | 4.4 | 3.53 | -1.23 |
| **Run 11** | -0.07 | -0.28 | -2.79 | 3.74 | 0.0039 | 0.0001 | 2.93 | 1.78 | 0.94 | 1.21 | 4.43 | 3.6 | -0.49 |
| **Average** | **0.74** | **0.9** | **-2.74** | **2.61** | **0.0038** | **0.0001** | **3.45** | **1.76** | **0.83** | **1.2** | **4.41** | **3.57** | **-1.01** |
| **Std Dev** | 0.723 | 1.069 | 0.602 | 0.679 | 0.00014 | 0.00001 | 0.533 | 0.085 | 0.105 | 0.085 | 0.077 | 0.092 | 0.364 |
| | | | | | | | | | | | | | |
| kV/mA | 60/60 | 60/60 | 30/120 | 60/60 | 30/120 | 30/120 | 60/60 | 60/60 | 60/60 | 60/60 | 60/60 | 60/60 | 30/120 |
| Peak [s] | 32 | 60 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 | 32 |
| Bgd [s] | 16 | 30 | 16 | 16 | 16 | 16 | 16 | 16 | 16 | 16 | 16 | 16 | 16 |
| PBF | Yes | Yes | | Yes | | Yes | Yes | Yes | Yes | Yes | Yes | Yes | Yes |