MICROANALYSIS IN THE METALS RECYCLING INDUSTRY

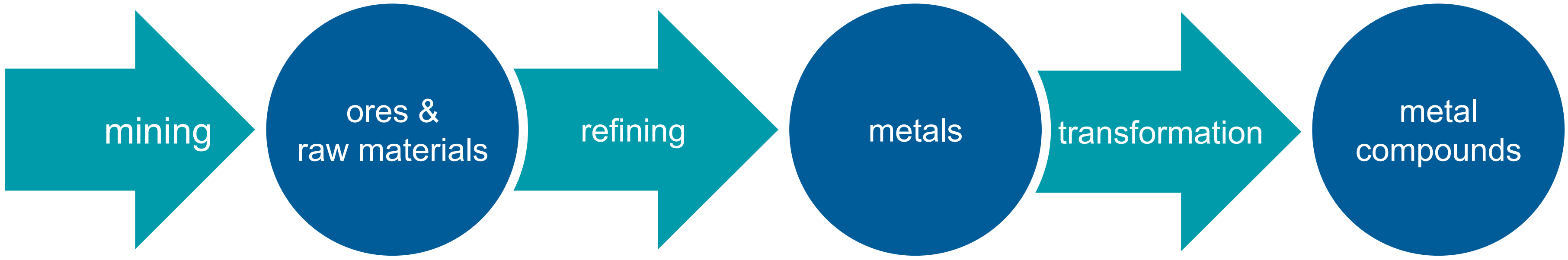
Eddy Boydens

Agenda

- Introduction
- X-ray diffraction analyses
- Optical microscopy & scanning electron microscopy
- Microanalyses EDS and WDS
- Area analysis by EDS
- Background calculation for WDS
- Interference corrections for WDS
- Element standards for WDS
- Microanalytical example for WDS
- Conclusions

Introduction

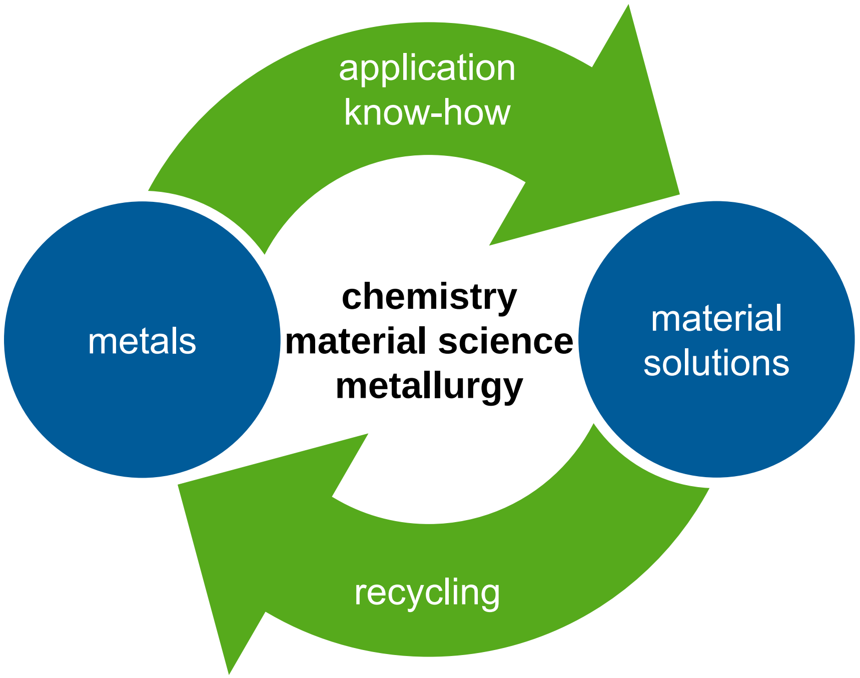
Umicore in the past - a bit of history …



Introduction
Umicore today- a materials technology group

"Less is more"

Metal related materials can be efficiently and infinitely recycled, which makes them the basis for sustainable products and services



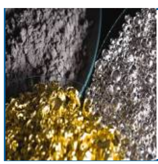
Introduction
Global market leadership in four divisions

Advanced Materials

#1	World	Cobalt & Germanium materials
Top 2	World	Rechargeable battery materials

Precious Metals Products & Catalysts

Top 3	World	Automotive catalysts
#1	World	Brazing alloys & contact materials



Precious Metals Services

#1	World	Precious metals recycling
#4	World	PGM refiner

Zinc Specialties

#1	World	Zinc specialty products

Introduction

Recycling solutions

Recovering scarce and valuable metals

- The majority of Umicore’s raw materials supply for its refining operations comes from secondary materials (end-of life materials and industrial by-products)
- Umicore operates the world’s largest precious metals recycling operation in Hoboken (Belgium)
- Hoboken processes some 350,000 tonnes every year from more than 200 different materials

Spent industrial catalysts

Electronic scrap

Spent automotive catalysts

Precious metal bearing raw materials

Non-ferrous byproducts

- “Above ground mining” means less energy and less waste → more value

Introduction

Recycling solutions

Recovering scarce metals from e-scrap

- Obsolete mobile phones contain valuable precious metals such as gold (Au), silver (Ag) or palladium (Pd) which Umicore is able to capture

- Currently, only 1-2% of all mobile phones are recycled worldwide, offering huge potential

- Batteries are also recycled

Introduction

Recycling mostly done by melting

resulting in four main different products that can be further treated

Well structured combination of:		Homogeneous mixture of :		Heterogeneous separation into:
Metals and alloys Salts Oxides Organic material Et cetera	→	Volatile elements Alloys Oxides Sulphides	→	Fumes Oxides Sulphides Alloys

Introduction

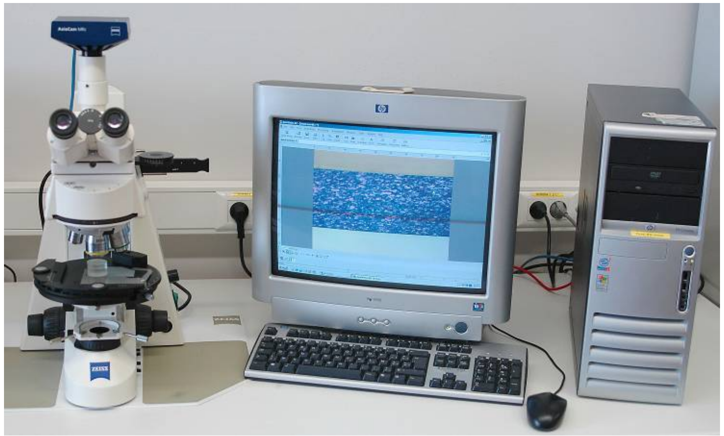
As separation happens on microscopic scale, microanalyses are needed to investigate which element is combined to which other one.

Minimum techniques needed to investigate the repartitioning of elements:

- chemical analyses to determine the sample composition
- X-ray diffraction analyses to identify compounds
- optical microscopy to see the microstructure and to see the compounds
- scanning electron microscopy to see the microstructure and the compounds
- microprobe analyses to determine the composition of the compounds with energy or with wave length dispersive spectrometry

A combination of all these techniques leads generally in the most efficient way to understand which phases are formed, how much and with which elements umicore Research

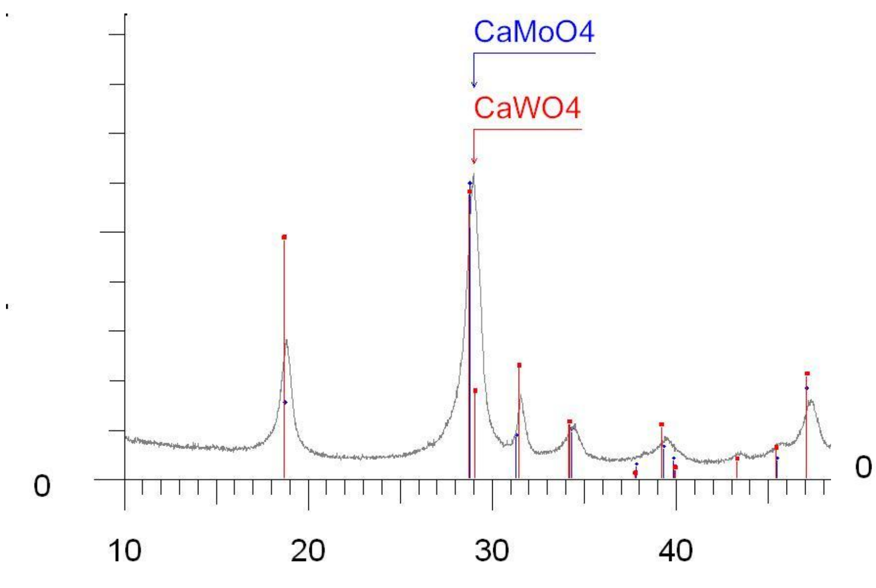
Introduction



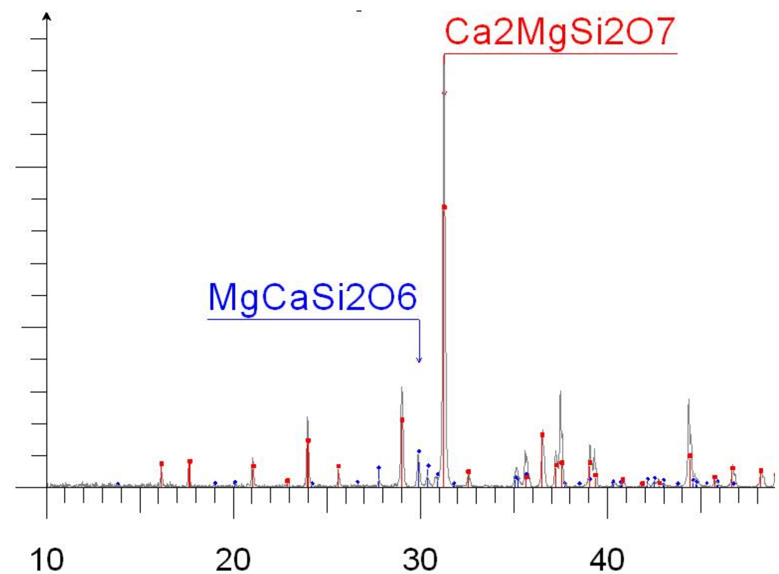
X-ray diffraction analyses

Easiness to identify - Difficulty to determine the real composition

Two or one compound ???



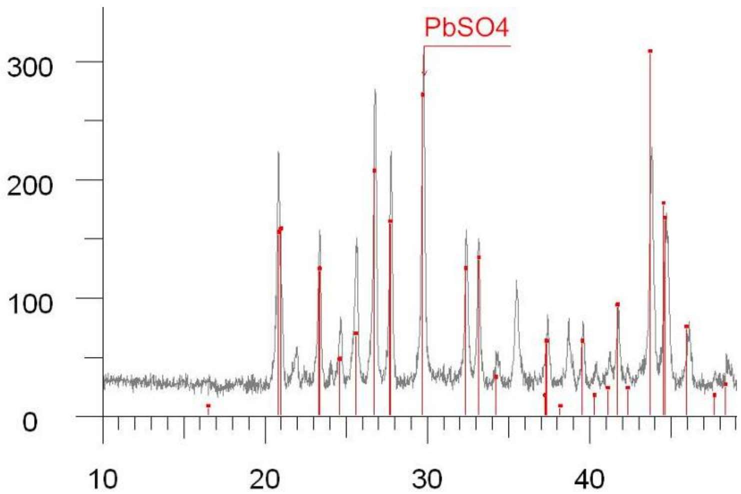
Al ???



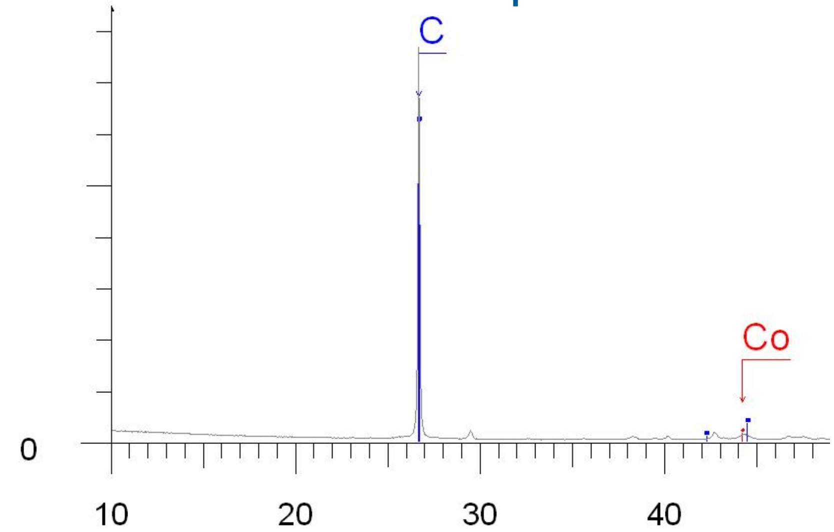
X-ray diffraction analyses

Easiness to identify - Difficulty to solve completely

Other compounds ???



%Co > 70 ???
Intermetallic phase ?



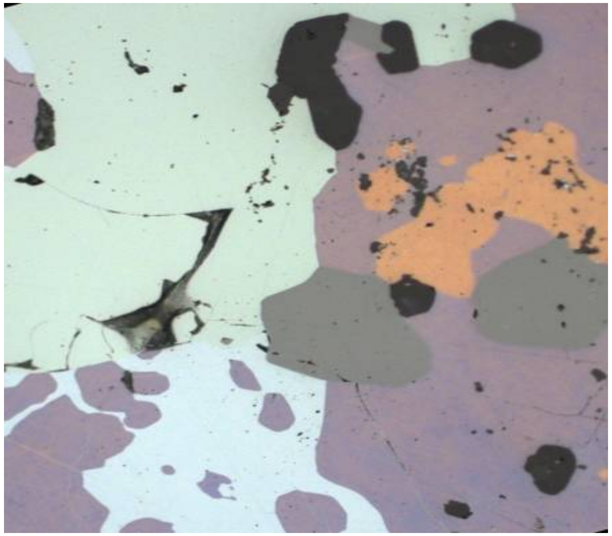
Optical and scanning electron microscopy

LM : Nice colors – SEM : Black & white contrasts

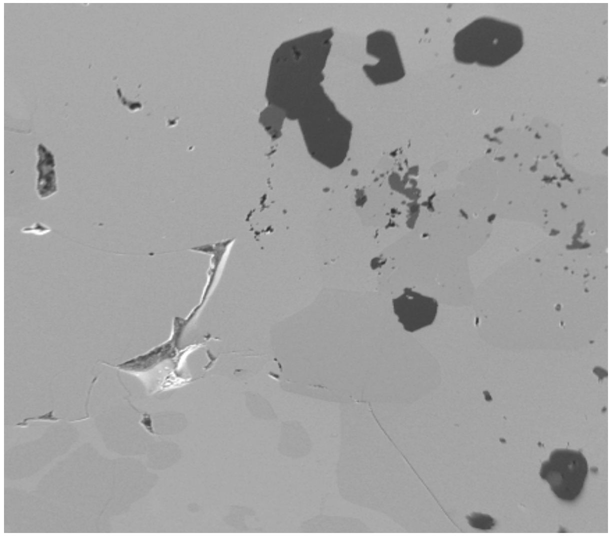
Amount of phases when combining both

Liberation possibility

LM



SEM



Optical and scanning electron microscopy

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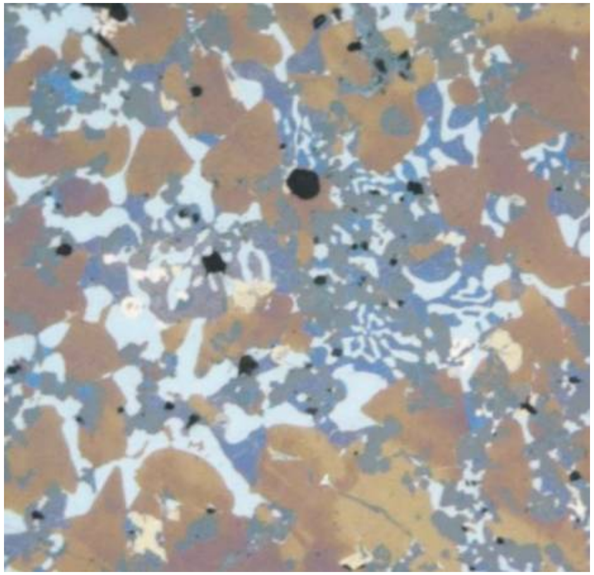
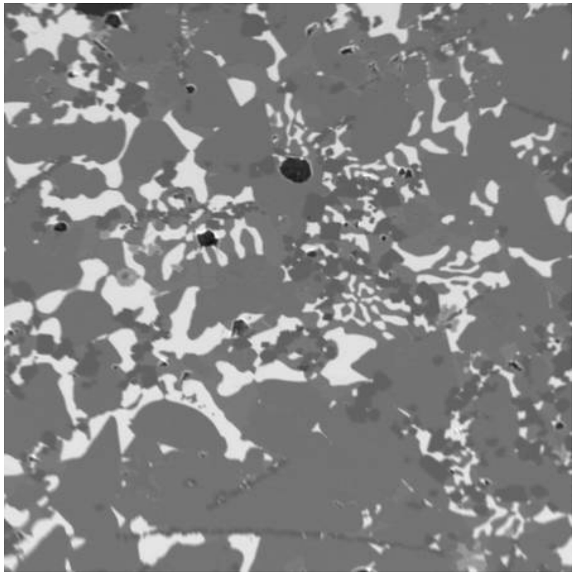


SEM



Microanalyses EDS - WDS

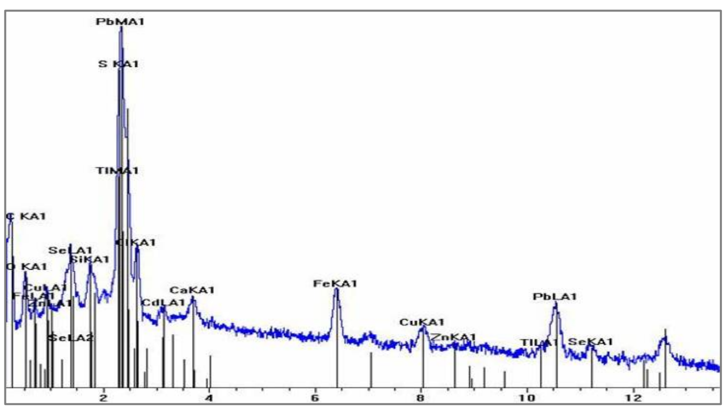
EDS: fast, multi-element, bad Peak/Background, multi Z, spot and area

WDS: slow, element by element, good Peak/Background, focused Z, spot

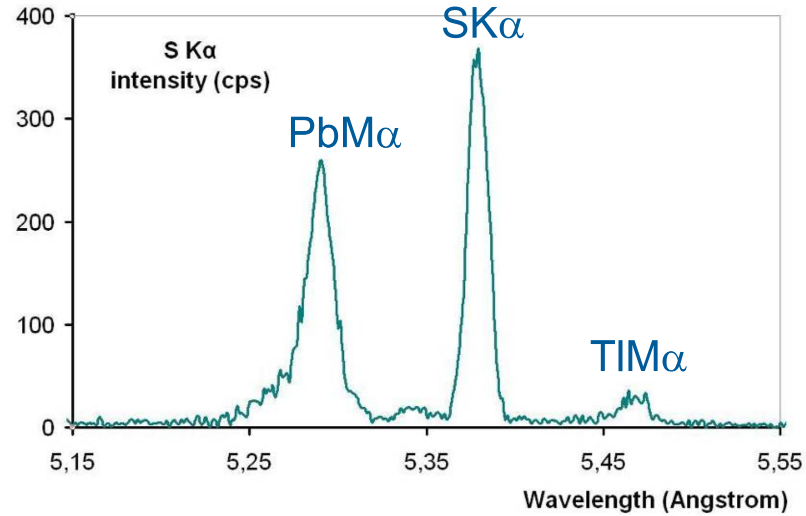
Composition of a phase

EDS

Pb&S&Tl



WDS



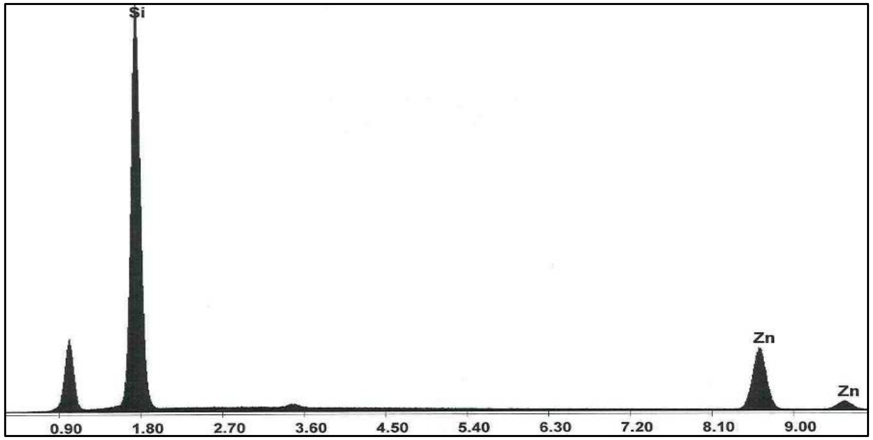
Area analyses by EDS

Composition of the sample ???

48.6% Zn – 51.4% Si

BSE

EDS



Area analyses by EDS

Composition of the sample ???

71.6 wt% Zn - 28.4 wt% S

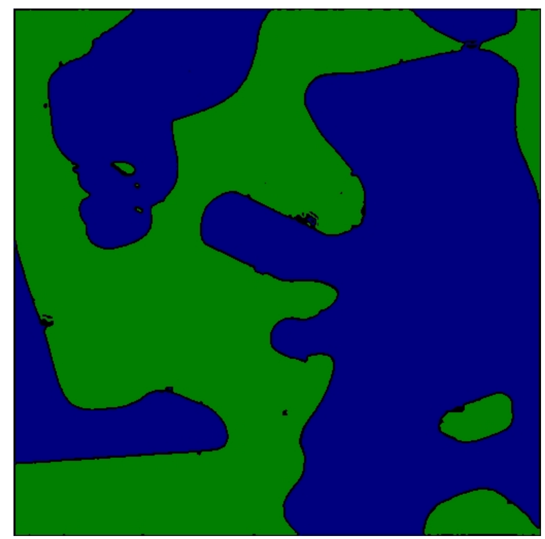
7.1 g/cc Zn
2.3 g/cc Si

48.6% Zn – 51.4% Si

45.0 vol% Zn - 55.0 vol% Si

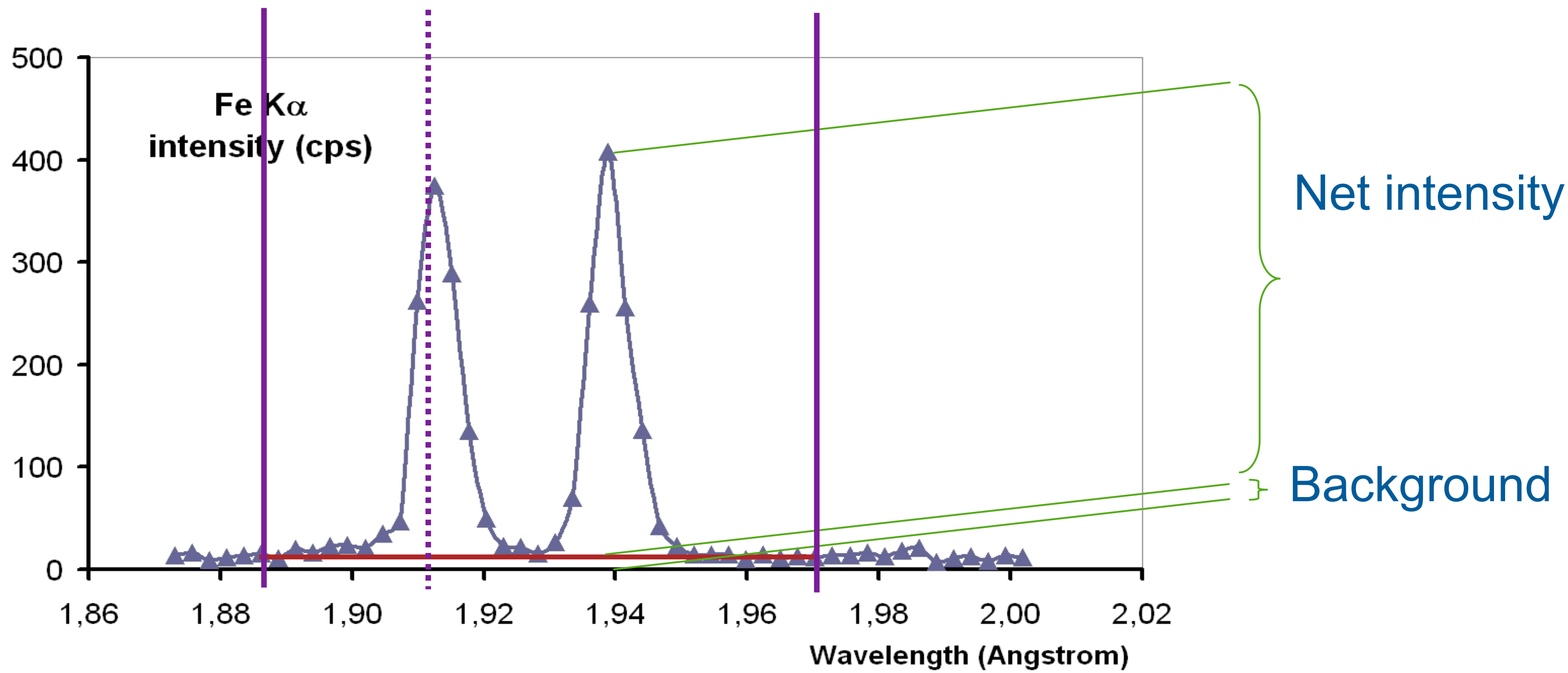
BSE

Treated image



Background calculations for WDS

Determining the net intensity – Influence of interfering elements !!



Background calculations for WDS

Mean atomic number MAN: MAN = Σ (wt%i x Z_i) / 100

SnO_2 78.8% Sn & 21.2% O

Z=50 for Sn and Z=8 for O

MAN SnO_2 = (78.8 x 50 + 21.2 x 8) / 100 = 41.1

Sn 100.0% Sn

Z=50 for Sn

MAN Sn = (100.0 x 50) / 100 = 50.0

Background calculations for WDS

Standard	MAN
C	6,0
Spinel MgAl2O4	10,6
Al2O3	10,6
SiO2	10,8
Anorthoclase (Na,K)AlSi3O8	11,0
Olivine (Mg,Fe)2SiO4	11,9
Glaverbel glass Al-Ca-Si	12,6
Fluor-apatite Ca5(PO4)3F	14,0
Si	14,0
Fluorite CaF2	14,6
Ardennite	14,9
TiO2	16,4
TiC	18,8
Hematite Fe2O3	20,6
Pyrite FeS2	20,7
Willemite Zn2SiO4	21,3
Ti	22,0
V	23,0
Chalcopyrite CuFeS2	23,5
Sulvanite Cu3VS4	23,7
Celestite SrSO4	23,7
NiO	23,7

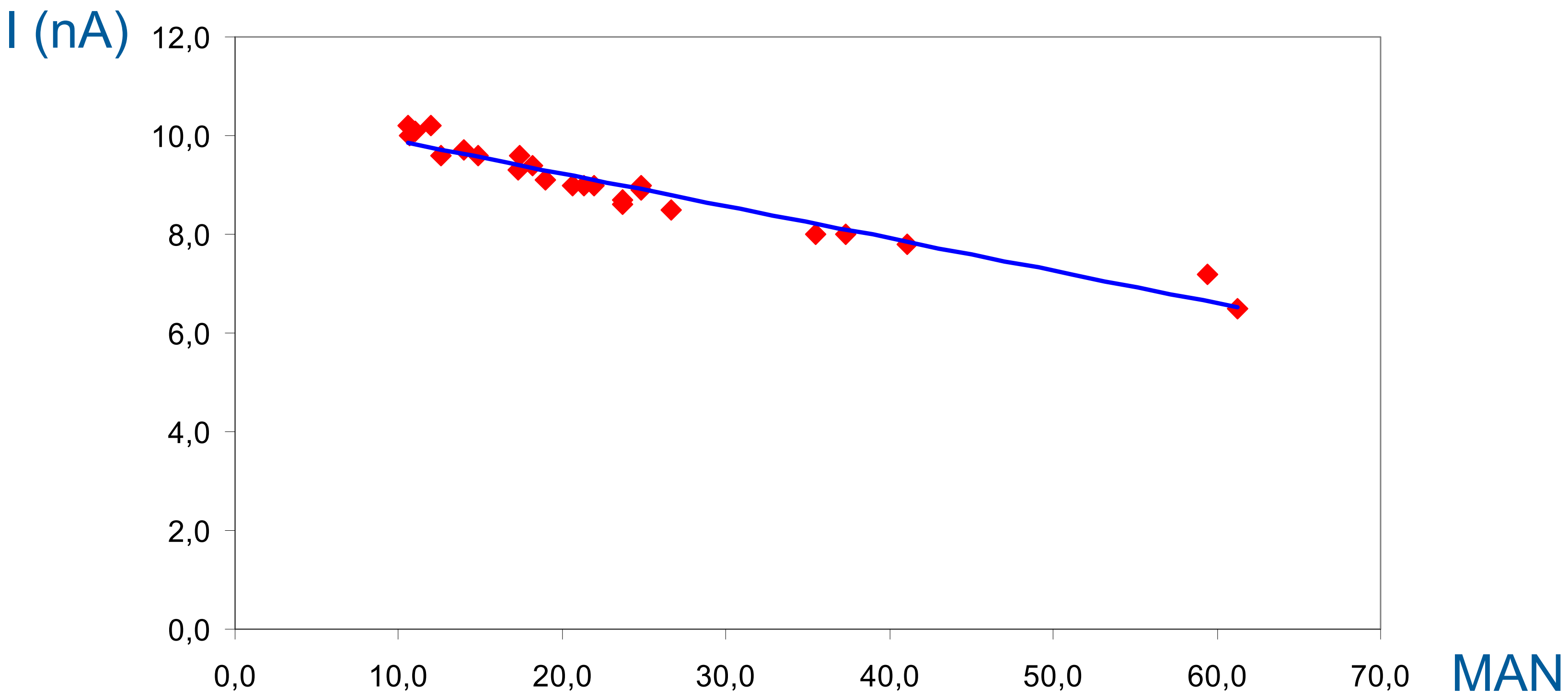
Standard	MAN
Cr	24,0
Mn	25,0
Sphalerite ZnS	25,4
Fe	26,0
Cuprite Cu2O	26,7
Co	27,0
Arsenopyrite FeAsS	27,3
Ni	28,0
Cu	29,0
Zn	30,0
Berzelianite Cu2Se	30,9
Nb2O5	31,1
Skutterudite CoAs3	31,3
Ge	32,0
Y2O3	32,4
BaSO4 Barite	37,3
Weissite Cu2Te	40,5
Nb	41,0
Cassiterite SnO2	41,1
Stibnite Sb2S3	41,1
Mo	42,0
Sb2Se3	42,6

Standard	MAN
Naumannite Ag2Se	43,5
GaSb	43,7
Ru	44,0
Rh	45,0
Pd	46,0
Ag	47,0
Cd	48,0
Hessite Ag2Te	48,9
Sn	50,0
CdTe	50,1
Sb	51,0
Te	52,0
Anglesite PbSO4	59,4
Ta2O5	61,2
Coloradoite HgTe	69,1
Bismuthinite Bi2S3	70,5
Ta	73,0
Galena PbS	73,2
W	74,0
Pt	78,0
Au	79,0
Bi	83,0

Background calculations for WDS

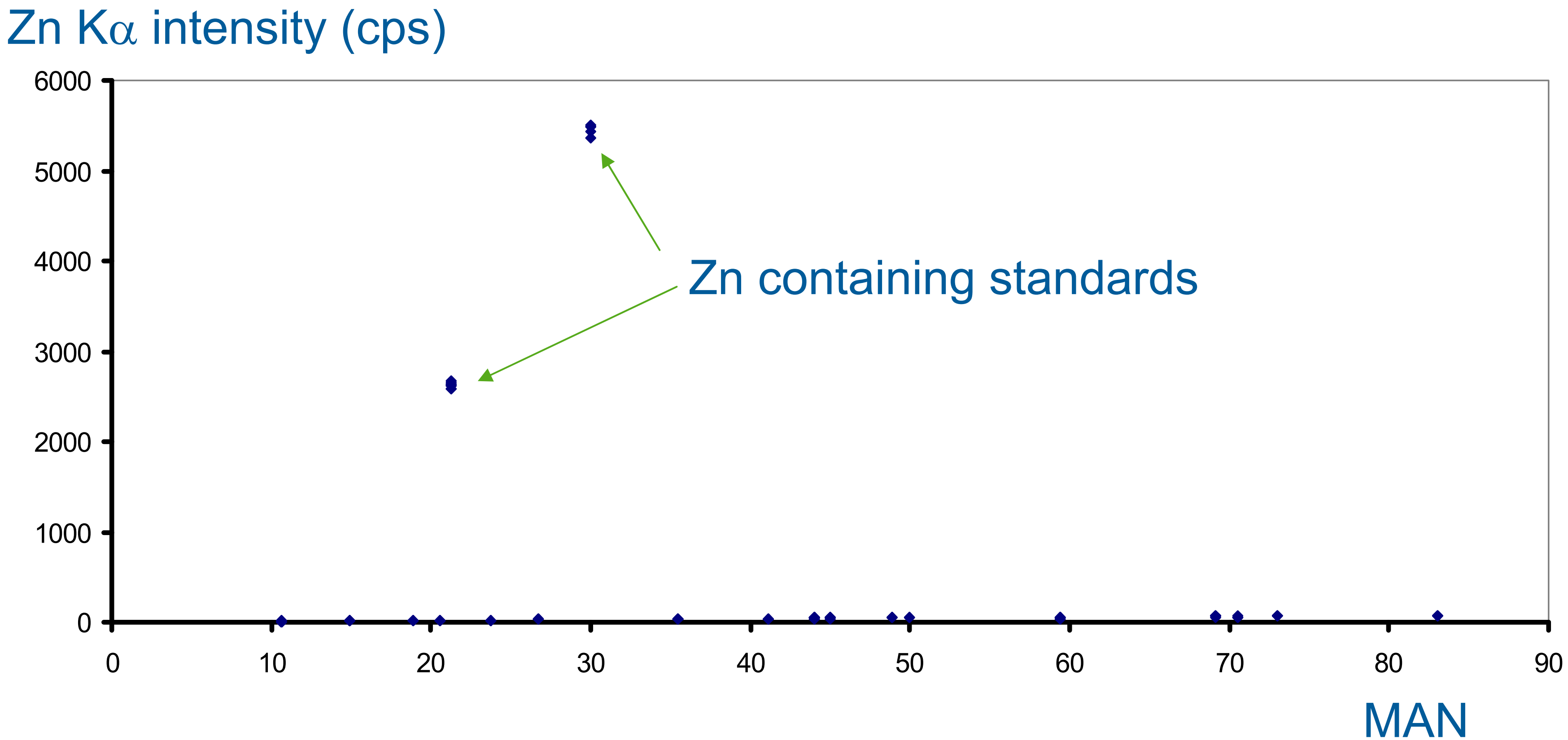
Specimen current (nA) as a function of Mean Atomic Number

Reference : 9.0 nA at 20 kV on Willemite



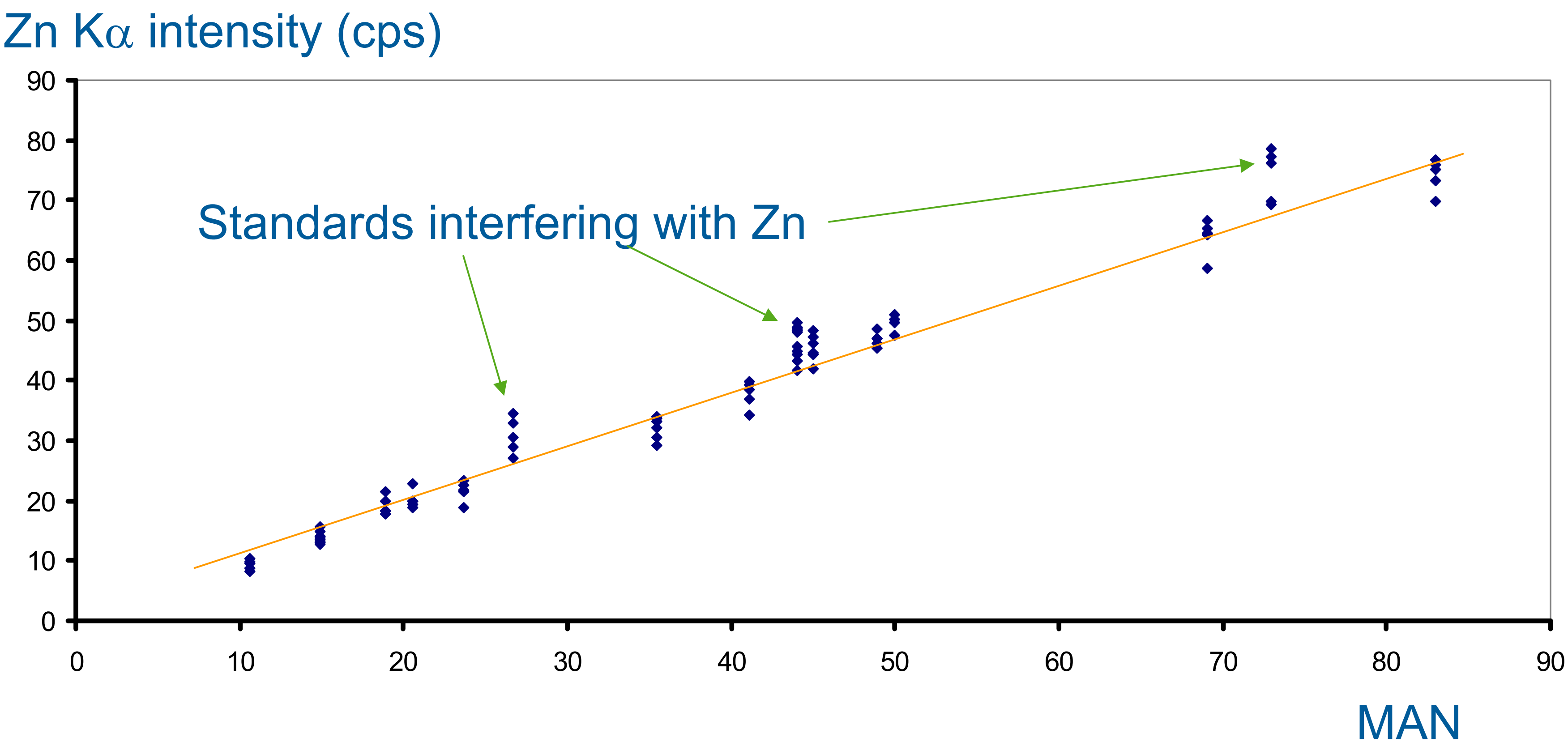
Background calculations for WDS

Background as a function of MAN: all standards



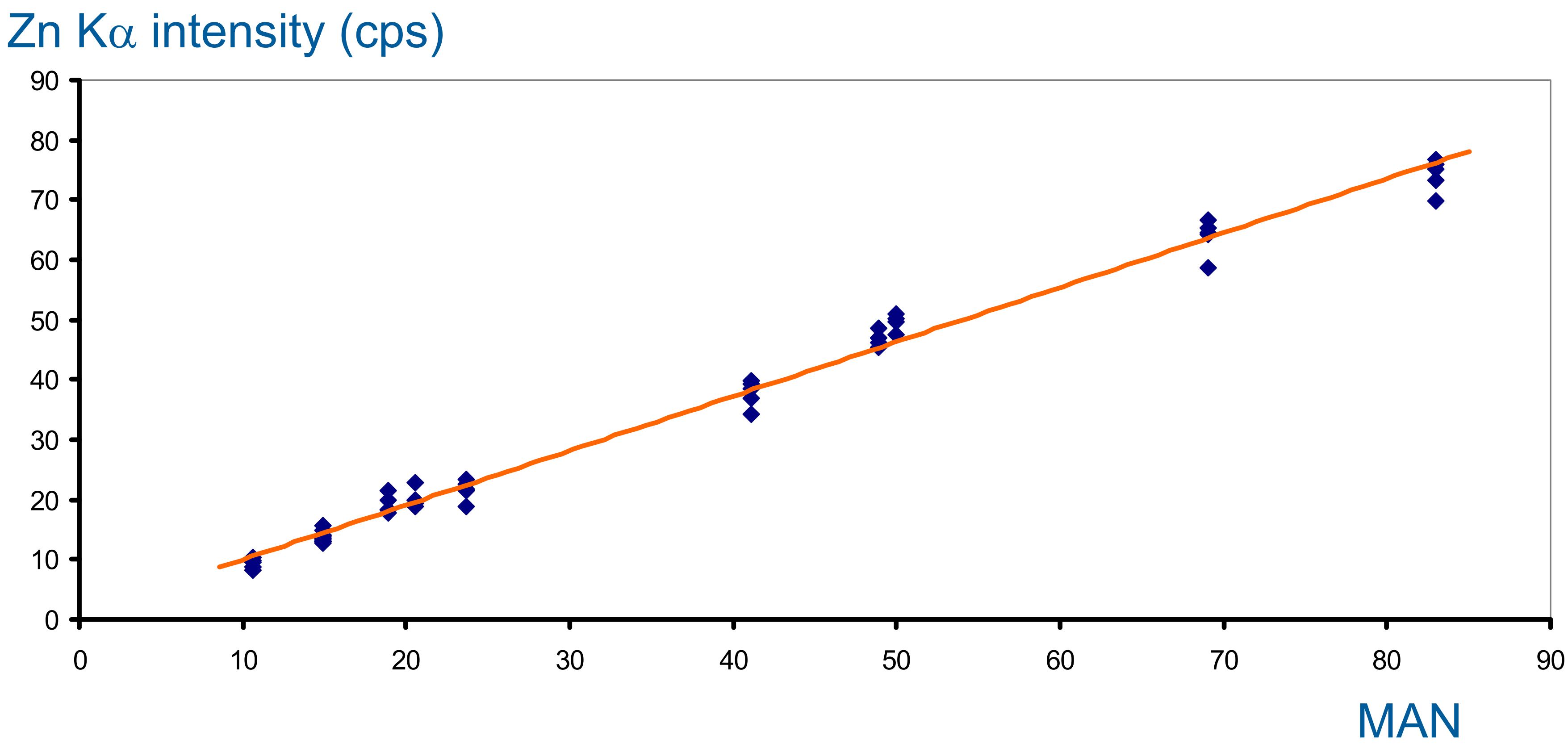
Background calculations for WDS

Background as a function of MAN: all standards not containing zinc



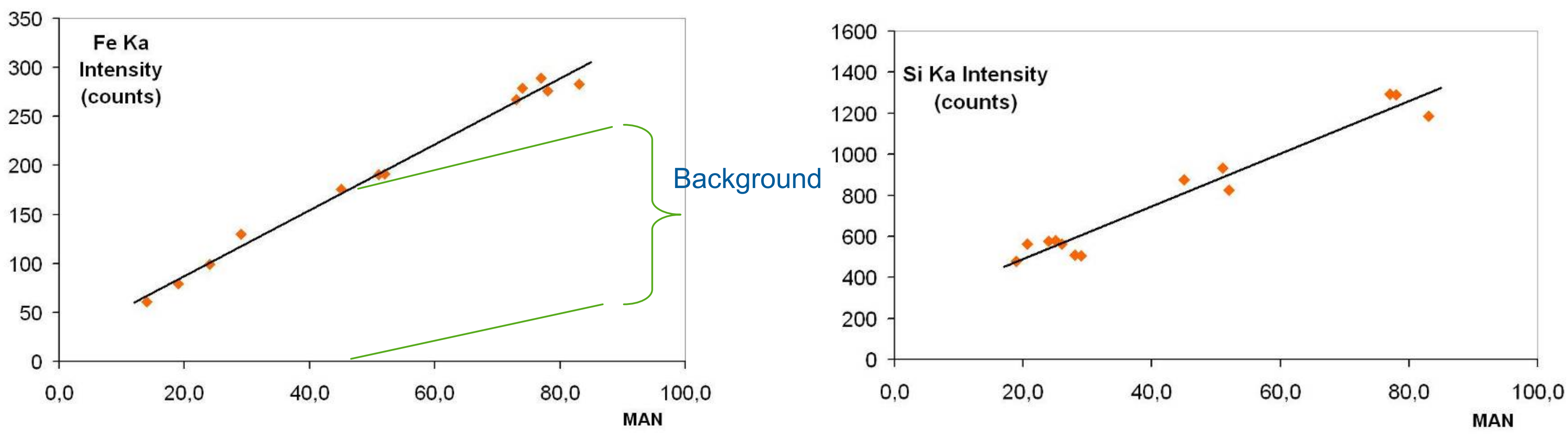
Background calculations for WDS

Background as a function of MAN: all real background standards



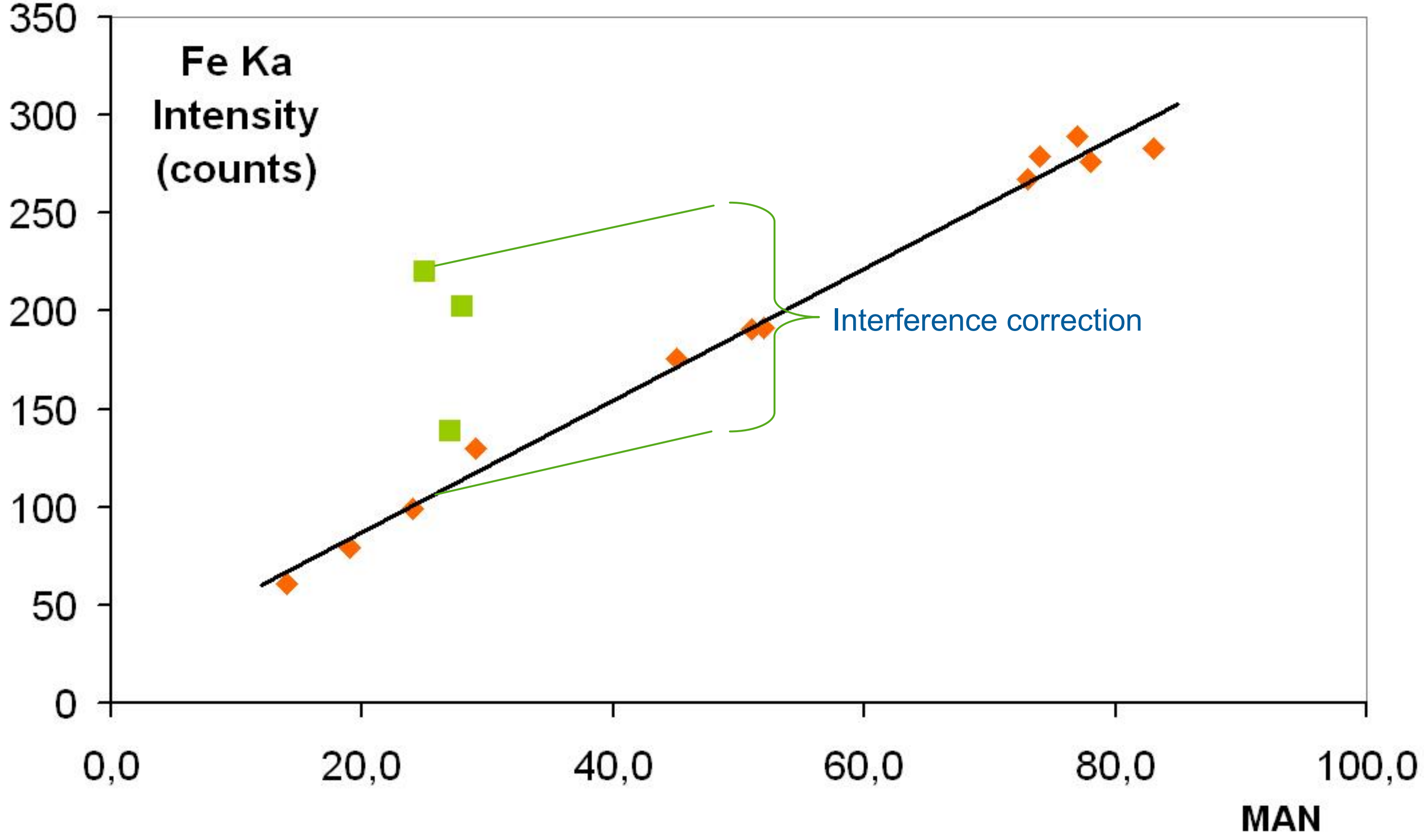
Background calculations for WDS

Standards for background correction



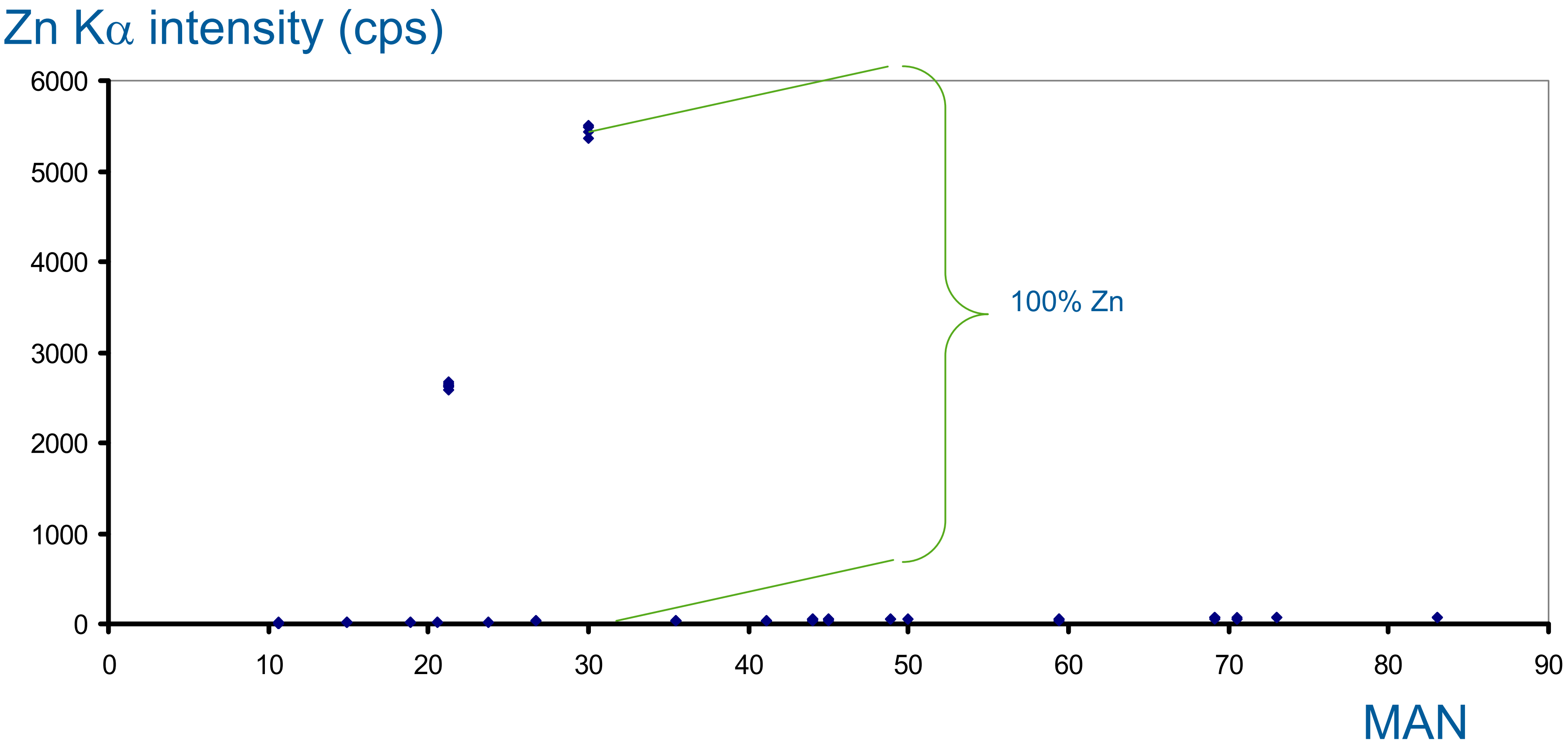
Interference corrections for WDS

Standards for interference corrections



Element standards for WDS

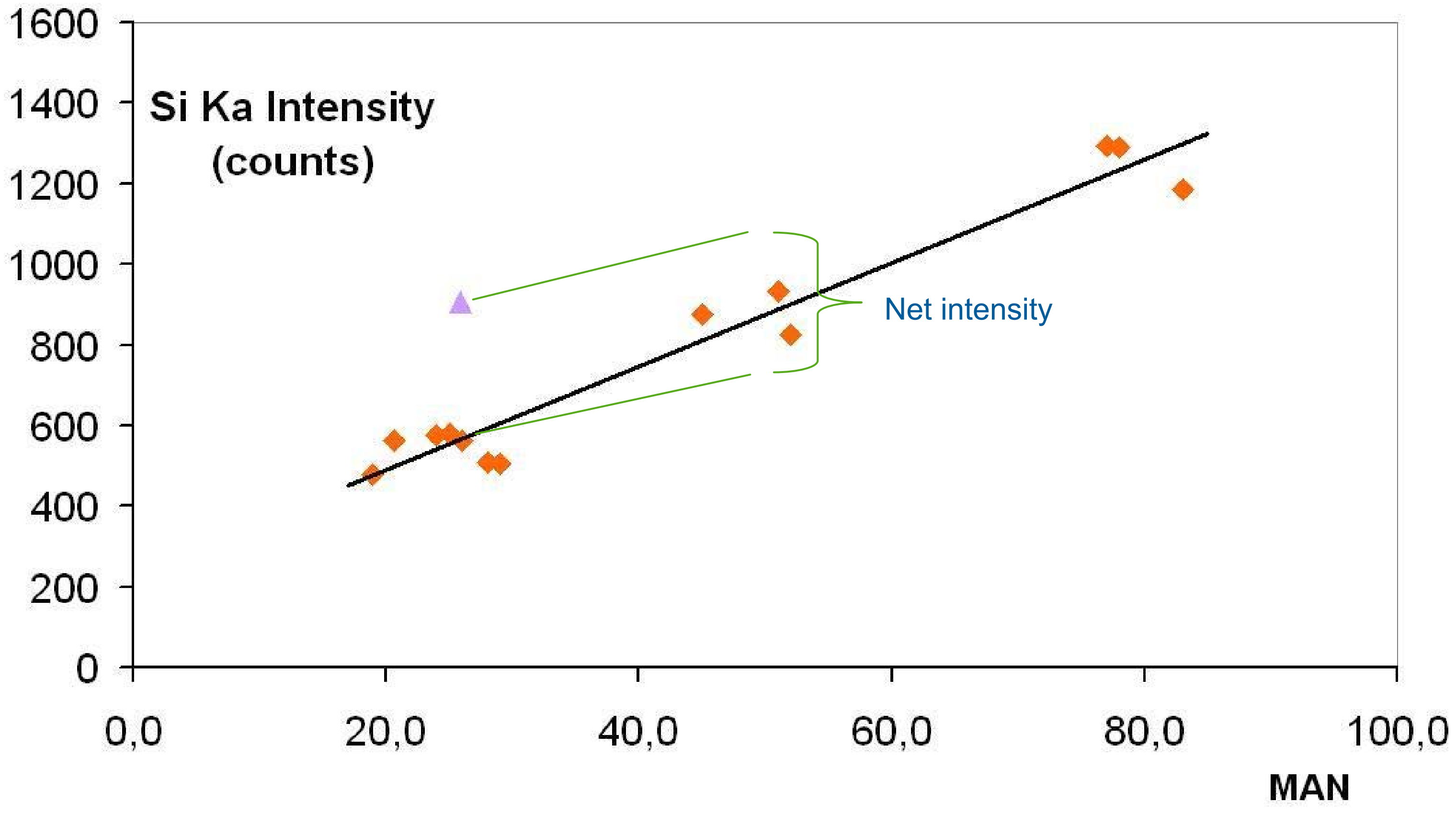
Standards for composition calibration



Element standards for WDS

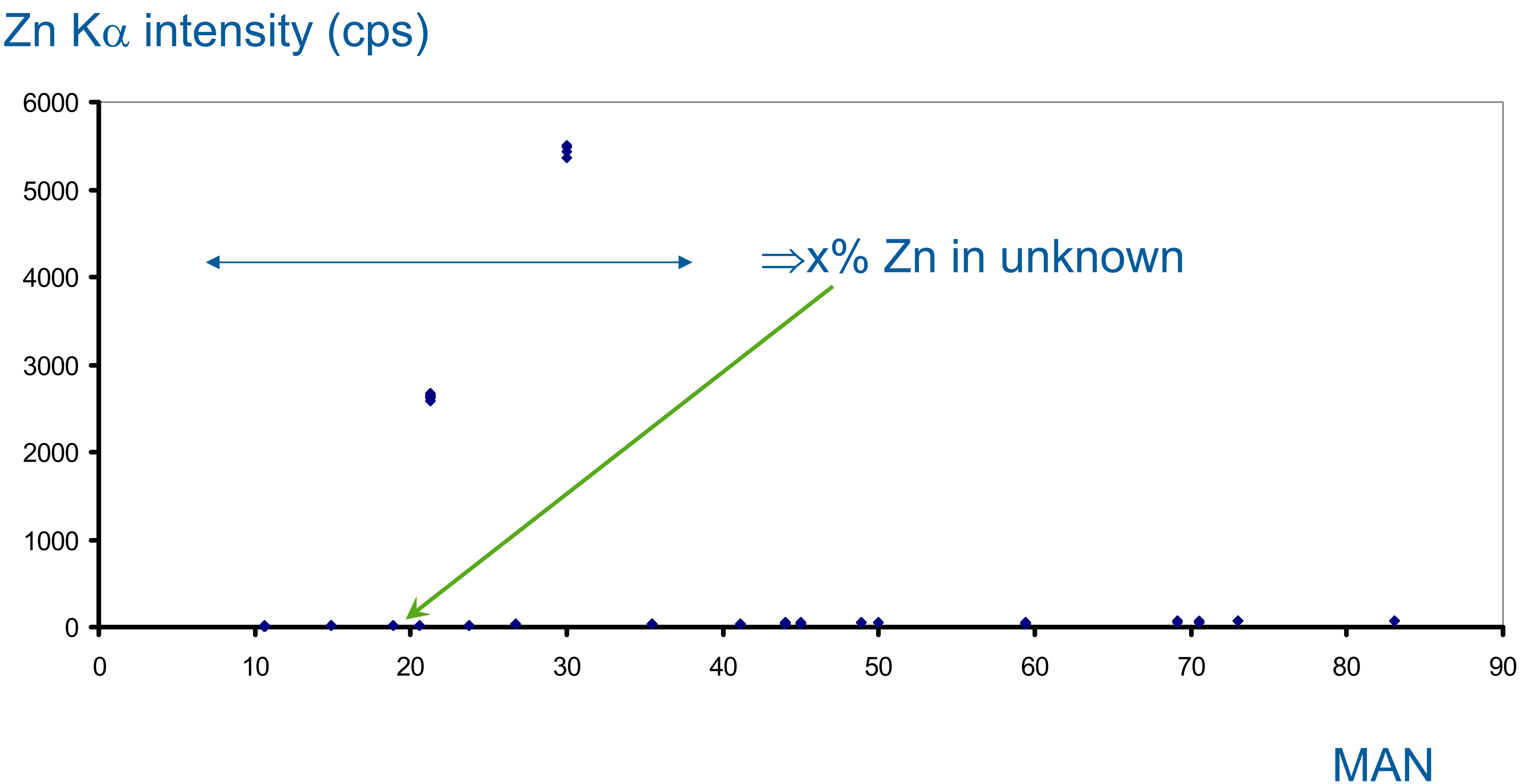
Standards for composition calibration

0,15% Si in steel



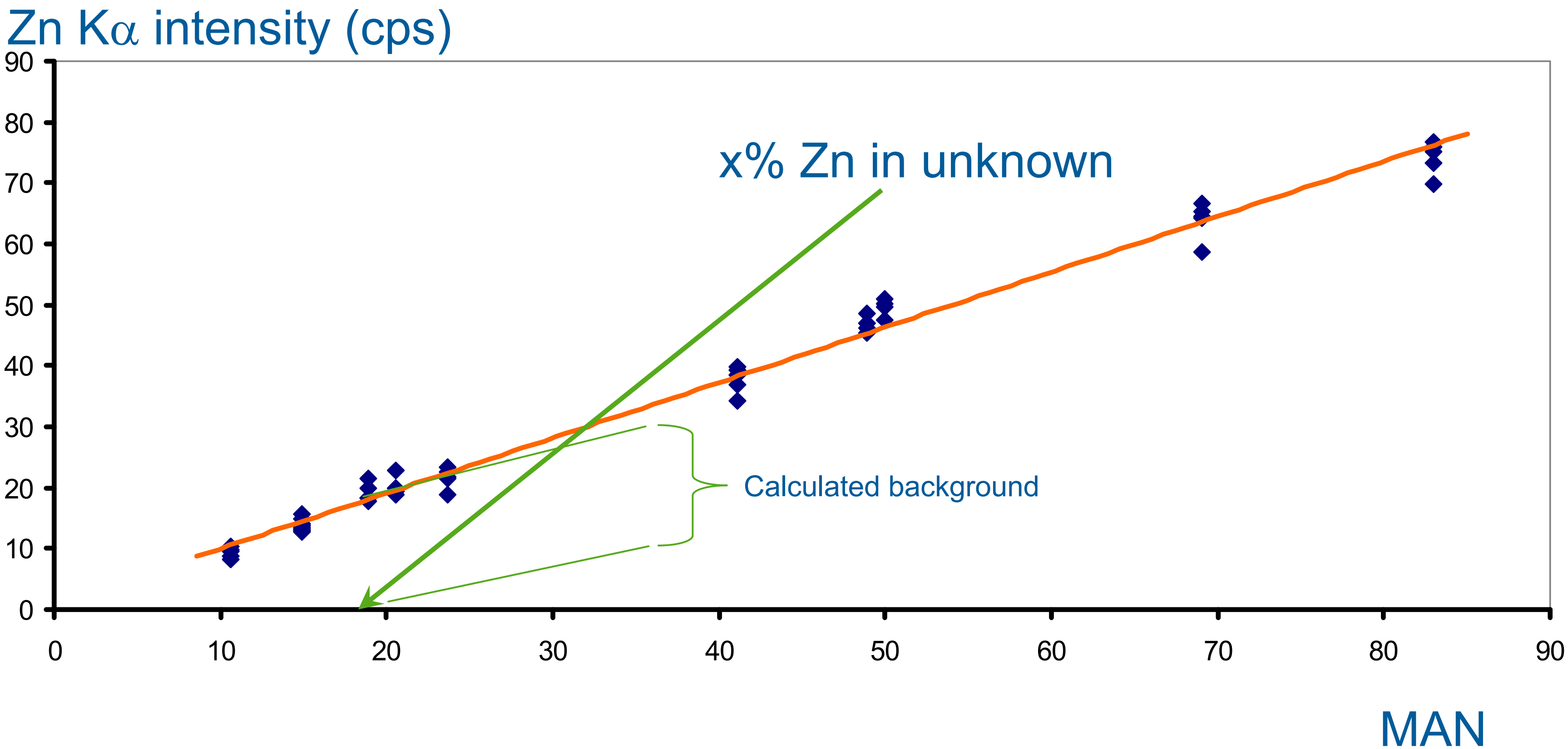
Analysis of unknown by WDS

Positioning the unknown



Analysis of unknown by WDS

Determining the background for the unknown



Microanalytical example for WDS

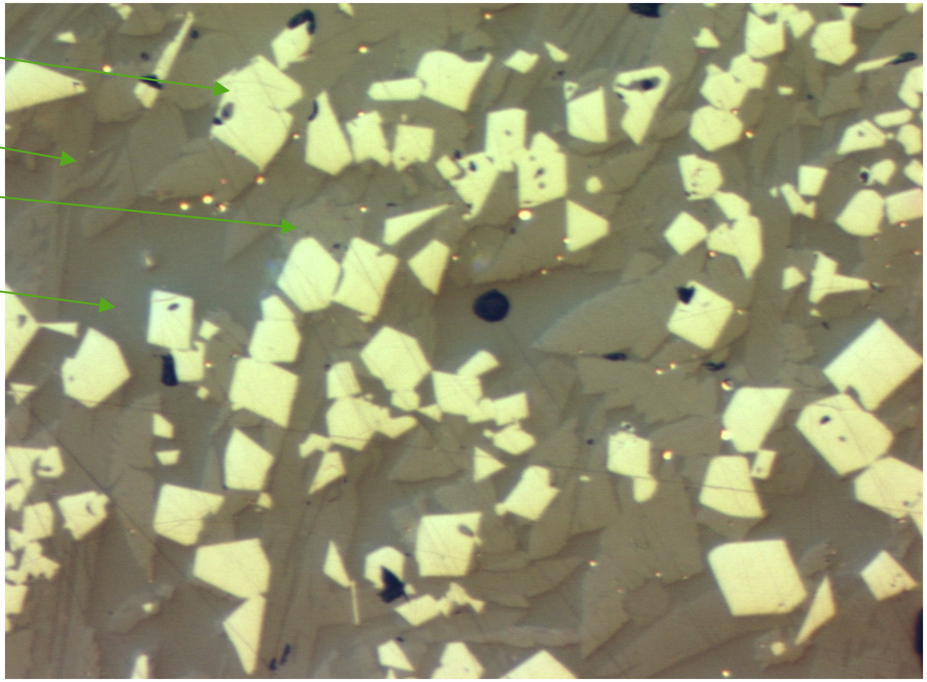
Four phases:

Spinel ZnFe204

Zinc silicate Zn_2SiO_4

Pyroxene $CaFeSi_2O_6$

Glassy silicate matrix



Microanalytical example for WDS

Composition of each phase (%) by WDS

	Total	SiO2	PbO	K2O	CaO	MnO	ZnO	FeO	Al2O3	Cr2O 3	MgO	Na2O
Spinel	94,3	0.1	0.2	0.0	0.2	2.6	17.9	67.2	1.9	2.1	2.1	0.0
Pyroxene	100.2	46.1	0.2	0.2	18.9	4.1	6.7	15.7	2.5	0.0	5.4	0.5
Zinc silicate	101.0	30.3	0.2	0.1	1.3	3.5	49.2	9.5	0.2	0.0	6.8	0.0
Matrix	99.3	42.0	3.7	1.6	14.6	4.6	12.0	11.6	2.5	0.0	1.8	4.8

Microanalytical example for WDS

Calculated amount of each phase (%)

	Phase	SiO2	PbO	K2O	CaO	MnO	ZnO	FeO	Al2O3	Cr2O3	MgO	Na2O
Spinel	38.2	0.0	0.1	0.0	0.1	1.0	6.8	25.7	0.7	0.8	0.8	0.0
Pyroxene	16.8	7.7	0.0	0.0	3.2	0.7	1.1	2.6	0.4	0.0	0.9	0.1
Zinc silicate	22.9	6.9	0.0	0.0	0.3	0.8	11.2	2.2	0.0	0.0	1.5	0.0
Matrix	19.8	8.3	0.7	0.3	2.9	0.9	2.4	2.3	0.5	0.0	0.4	1.0
Total :	97.7	23.0	0.9	0.4	6.4	3.4	21.6	32.8	1.7	0.8	3.6	1.0
Sample composition :		23.0	1.2	N.A.	6.9	3.4	21.6	32.8	2.0	0.3	2.8	N.A.

Microanalytical example for WDS

Calculated distribution over the phases for each element (%)

	Phase	SiO2	PbO	K2O	CaO	MnO	ZnO	FeO	Al2O3	Cr2O3	MgO	Na2O
Spinel	38.2	0.1	9.9	1.1	1.2	29.3	**<u>31.7</u>**	78.3	43.5	99.0	22.0	0.0
Pyroxene	16.8	33.6	4.0	8.4	49.4	20.2	5.2	8.1	24.8	0.4	25.1	7.5
Zinc silicate	22.9	30.1	3.9	3.8	4.7	23.5	52.1	6.6	2.7	0.3	43.0	0.2
Matrix	19.8	36.1	**82.2**	86.7	44.8	27.0	11.0	7.0	29.0	0.2	9.9	92.3
		100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Conclusions

Many products with lots of elements occur in non-ferrous recycling.

X-ray diffraction analyses alone often fail to identify the present compounds.

Microanalyses are essential to characterize the present phases, to know really their composition and their quantity.

Spot analyses have to be realized on many spots to obtain average compositions.

Wave length dispersive spectrometers are indispensable as many elements can not be treated by an energy dispersive spectrometer and as quantification with standards is often necessary.

A background calculating technique based on the mean atomic number enhances drastically the analytical speed of these wave length dispersive analyses.

Conclusions

Area analyses with an energy dispersive spectrometer are not done.

EDS is used for a qualitative check of the present elements in a phase.

Optical micrographs and back scattered electron images contribute moreover to see all present phases, their size and their bonding.

By knowing these analytical data, processes can be further optimized or developed.

Thank you for your attention