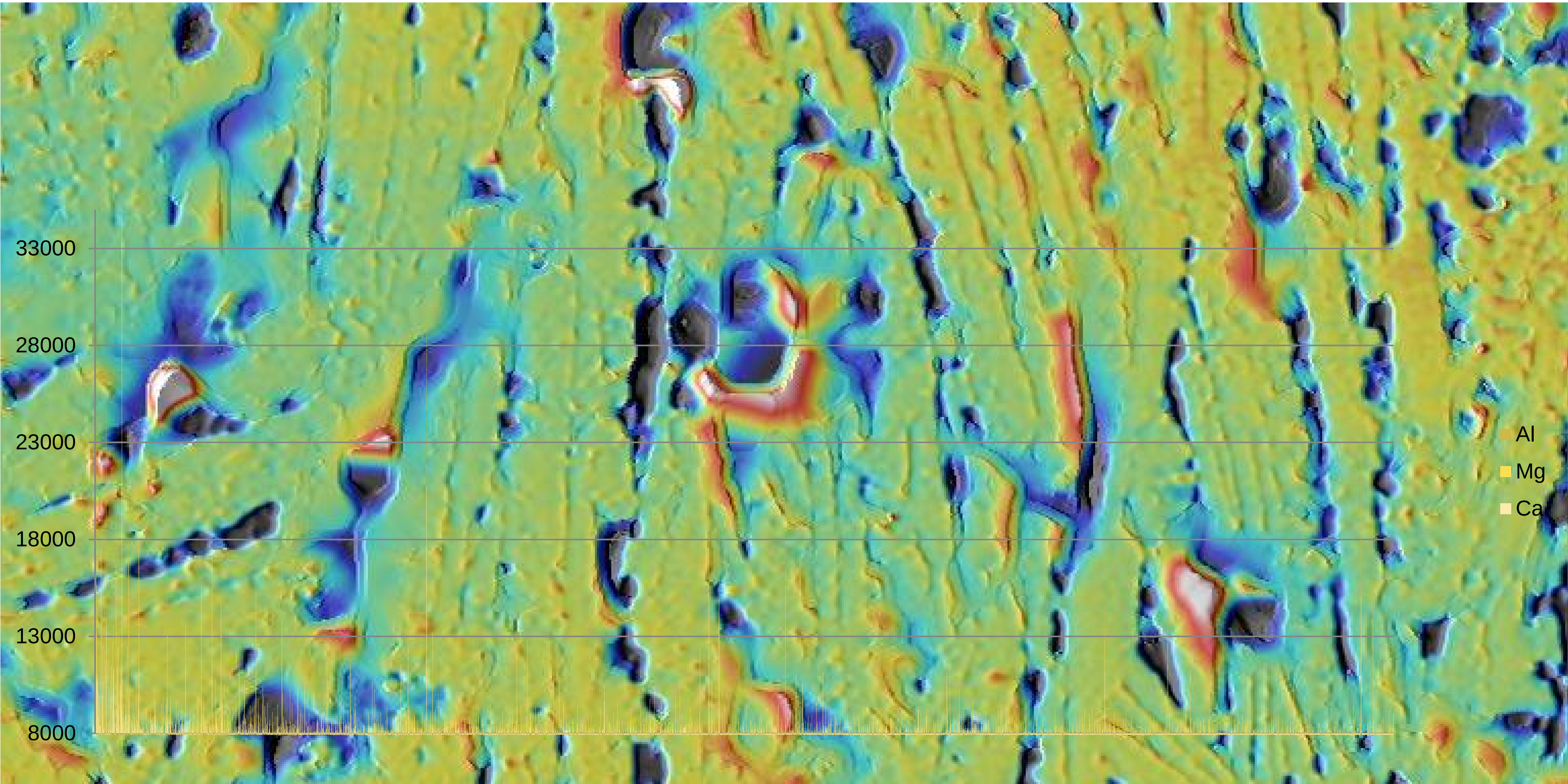
Q8 MAGELLAN
Metal Cleanliness Inspection (MCI)

Characterization of inclusions in steel by
OES Pulse Discrimination Measurement (OES-PDM)



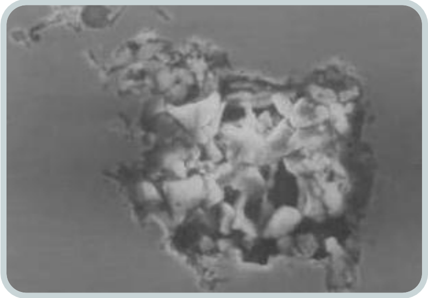
Demands & Goals of MCI

Increasing demand for higher cleanliness in steels by customers in the metal processing industries.

- Production of high purity steels
  - Process monitoring of production steps
  - Final inspection of outgoing material
- Optimisation of production process
  - Improving Slagging Practices
  - Fast determination of oxide inclusions during the process
  - Calculation of oxygen content
- Determination of parameters that define Steel Cleanliness

Why analyze inclusions?

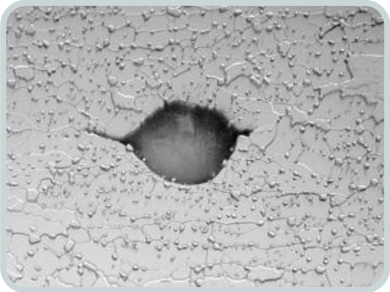
- After Aluminum addition (eg killed steels), aluminum bonds to oxygen, making Al_2O_3
- Al_2O_3 crystallizes and clogs nozzles in turndish
- To prevent this, addition of Ca-Si is necessary
- But then, Al_2O_3-CaO and CaS are produced
- CaS increases steel viscosity, making cast difficult



What inclusions?

- Al_2O_3-CaO inclusions are globular, and inoffensive, but they reduce clogging and increase nozzle lifespan

- Al_2O_3 are big, and create multiple problems, from casting to rolling. Steel containing excess of these inclusions will be of poor quality.



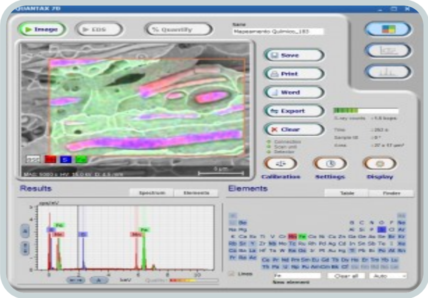
- CaS increases steel viscosity, therefore needs to be monitored, also to control level of CaSi addition

- Many others can be monitored, like Ti and Mg oxides

Reference Method for Inclusion Analysis: SEM/EDS with Bruker QUANTAX 400 EDS

Scanning electron microscope with energy dispersive x-ray spectroscopy

- Universal method: differentiation of carbides, oxides, nitrides, sulfides
- Larger observation area
- Imaging method
- Highest accuracy
- Surface method, low penetration depth (~1 µm)
- Costly, long measurement time (~10 h)
- Highly educated operating staff



SEM/EDX QUANTAX Steel Package

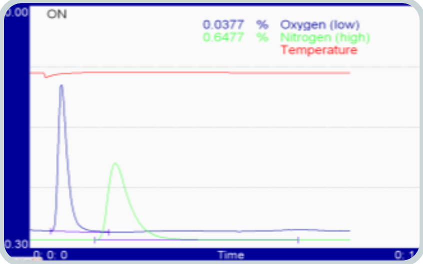
Overview

- Steel Cleanliness Analysis Package
- Measurement of steel cleanliness and quality for Quality Assurance and Control
- Classification according to international standards: ISO 4967, DIN 50602, **EN 10247**, ASTM E45, ASTM E2142, **JIS G 0555**
- Generic reports, Ternary Charts (Pirelli and general Metallurgy) and others
- Fully automatic particle analysis with possible false positive rejection

Reference Method for oxygen analysis: melt extraction with G8 GALILEO

Melt extraction with carrier gas method for the determination of oxygen

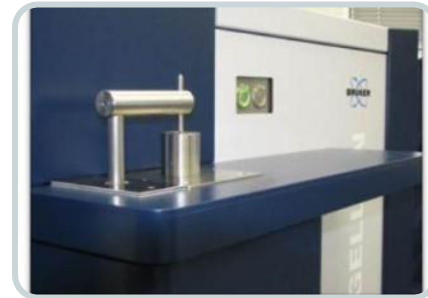
- Accurate analysis of total oxygen
- Fast measurement (~80 s)
- High analysed sample mass (~1000 mg)
- Demanding sample preparation
- Limited to oxygen only



Alternative method for inclusions & oxygen: OES-MCI with Q8 MAGELLAN

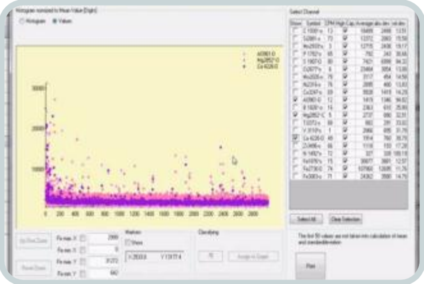
Inclusion characterisation & oxygen determination by Optical Emission Spectrometry with Pulse Discrimination Analysis

- Complete elemental analysis
- Determination of various oxide inclusion parameters
- Calculation of total oxygen
- Simple sample preparation (grinding w/ SiC paper or milling)
- Fast measurement (~20s/burn, multiple burns recommended, e.g. 5x)
- User-friendly software for normal OES operator
- Feasibility study advisable



Q8 MAGELLAN
Main Instrument Features for MCI

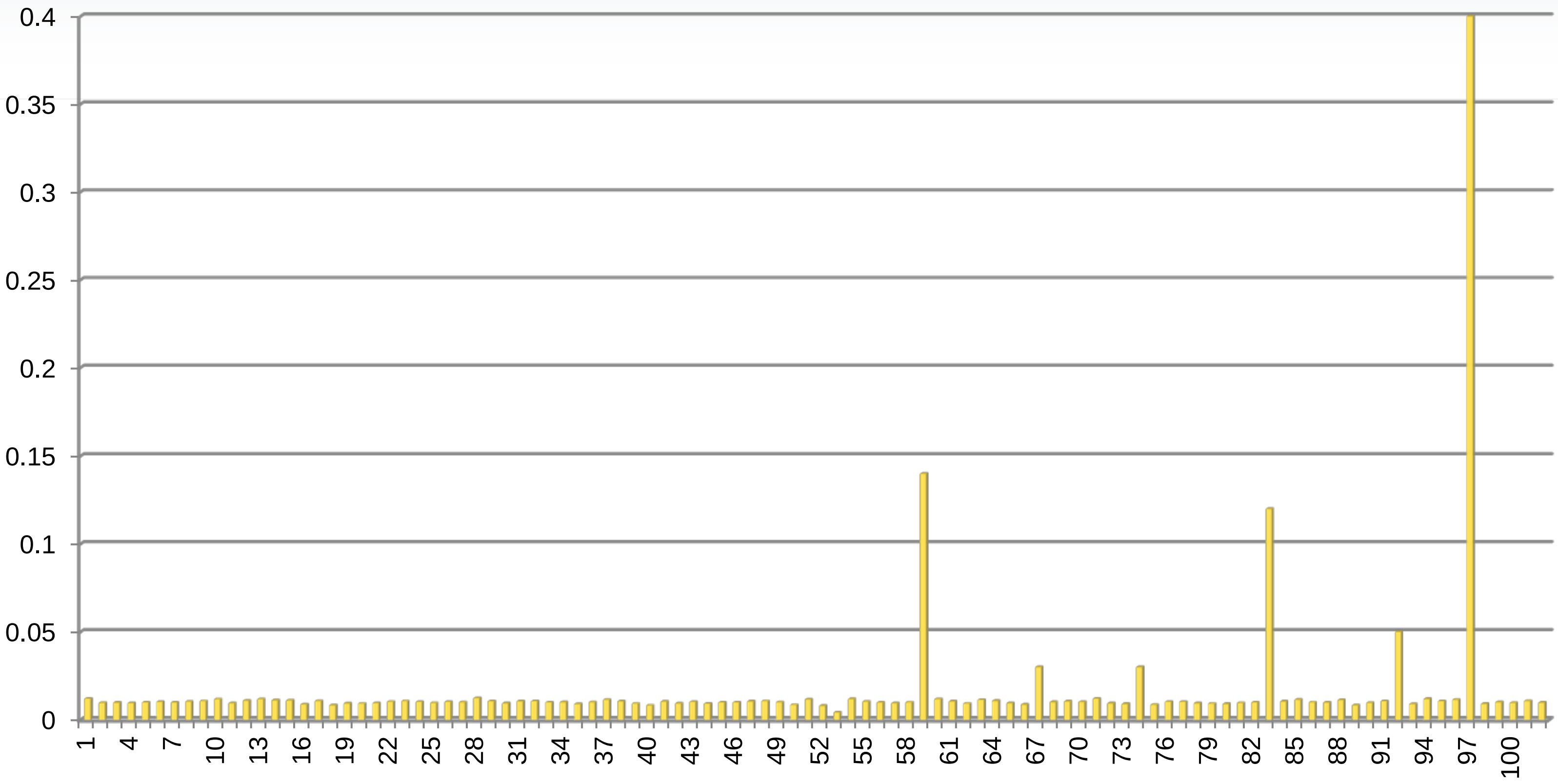
- Single Spark Detection (SSD) with visualisation
- Unlimited parameters
  - Any frequency up to 1 kHZ
  - All channels available for SSD
  - Free source curve design
- Highest spectral sensitivity, lowest detection limits
- Lowest dark current Channel Photomultipliers



PDA-OES - Principles

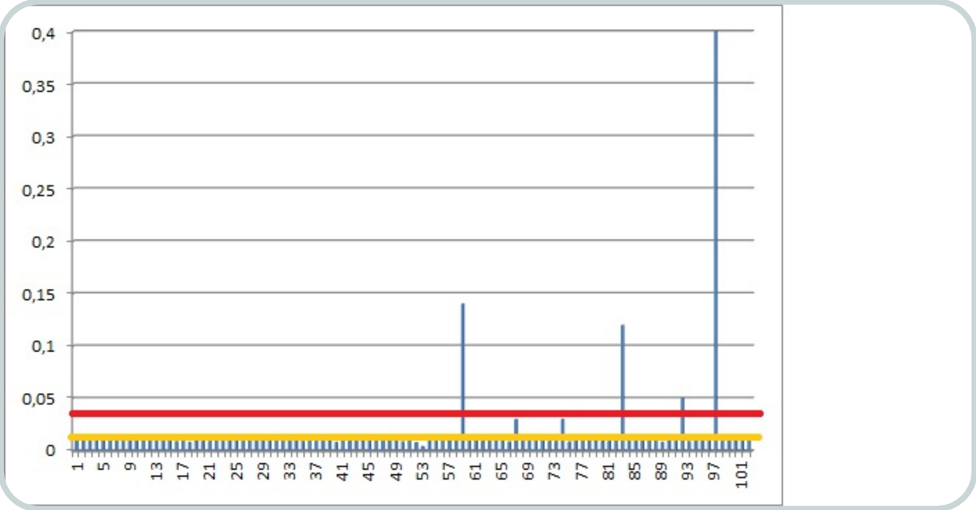
- We need to establish correlations between raw data acquired by each spark, for each element, to determine:
  - The number of inclusions
  - The nature of the inclusions and composition of non metallic
  - The size of inclusion
- Equations are required!

Number of inclusions

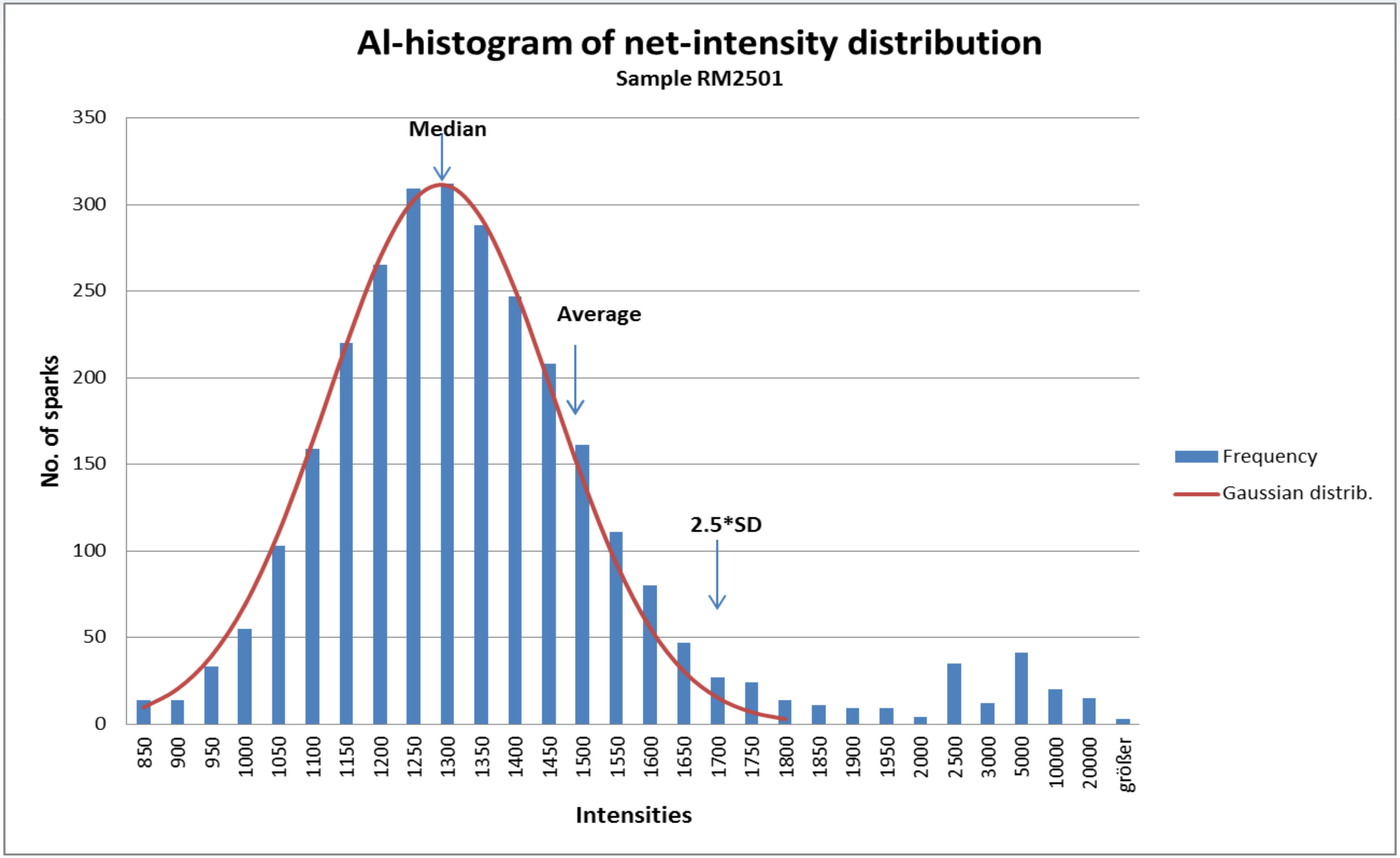


Determination of threshold

	Ca
1	0,011715373
2	0,009471482
3	0,011199334
990	0,008988848
991	0,011858899
992	0,010627056
993	0,011412163
994	0,4
995	0,009065761
996	0,010050017
997	0,009644071
998	0,010710132
999	0,009782549
mean	0,010680617
SD	0,01357857
Threshold x+3	0,051416325
x+6s	0,092152034
x+10s	0,146466312



Bruker Elemental PDA Software

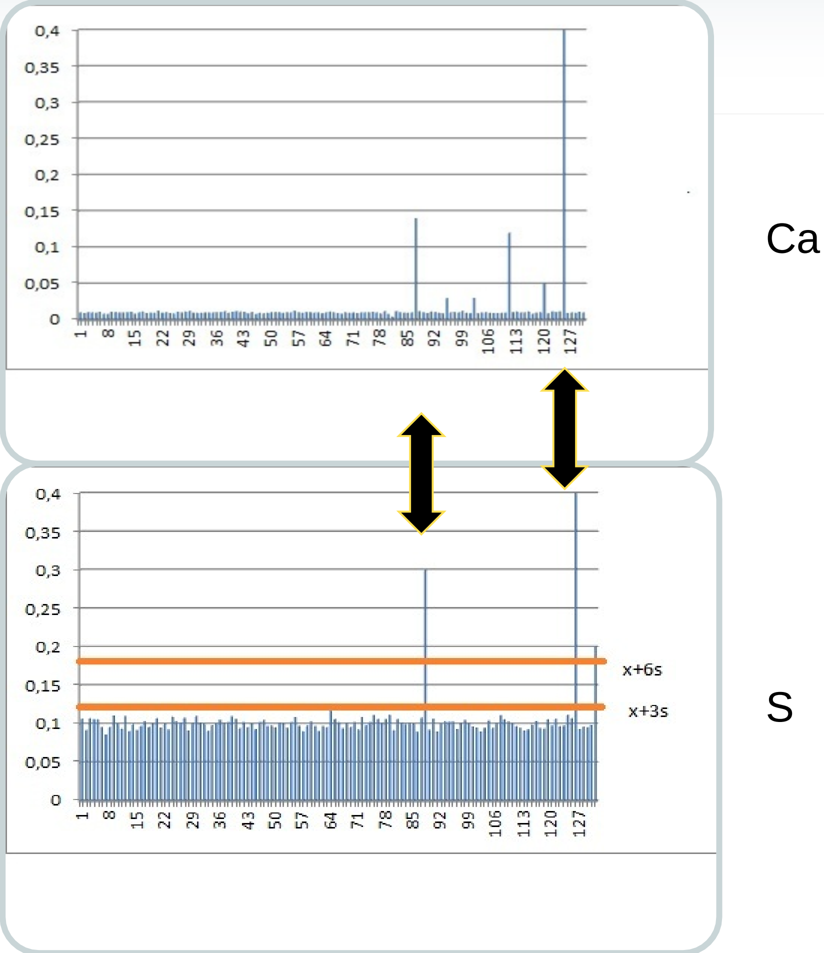


Threshold usage

- Graph cps = f(spark#) considered as a « spectrum »
- Peak considered as such if intensity I> x+3*s (x=mean, s=SD)
- Threshold defined as above
- Classes can be established: x+3; x+6; x+9, for example
- Inclusion SIZE falls into the different class levels
- Because the bigger the inclusion, the higher the signal

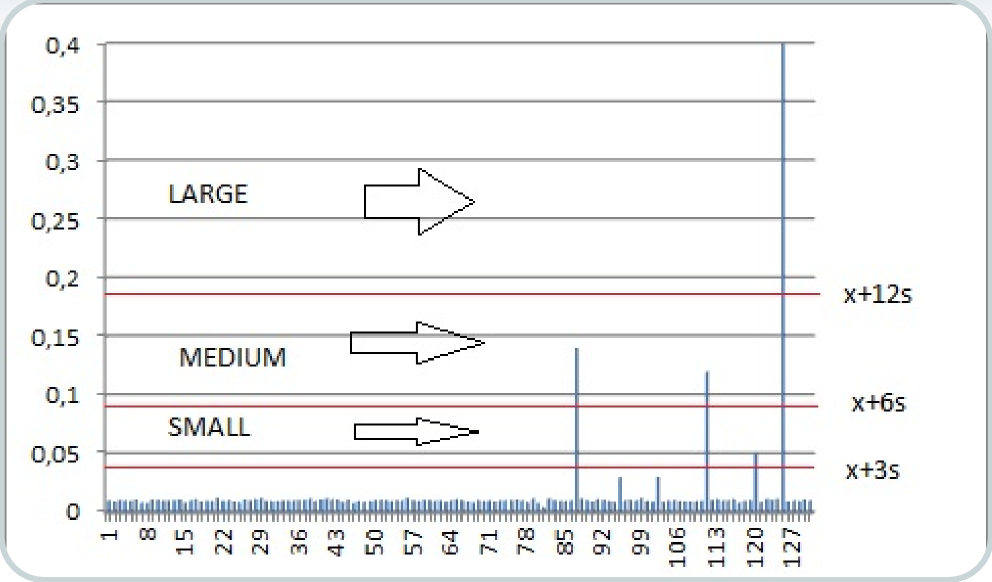
Nature of inclusions

- 2 common peaks
- Means CaS inclusion
- Other correlations are made
- With Oxygen channel
- With Sulfur channel



Inclusion size

- In this example
- 3 classes are defined
- Small, Medium and Large
- Large inclusions are harmful
- More classes might be defined



Inclusion size quantification

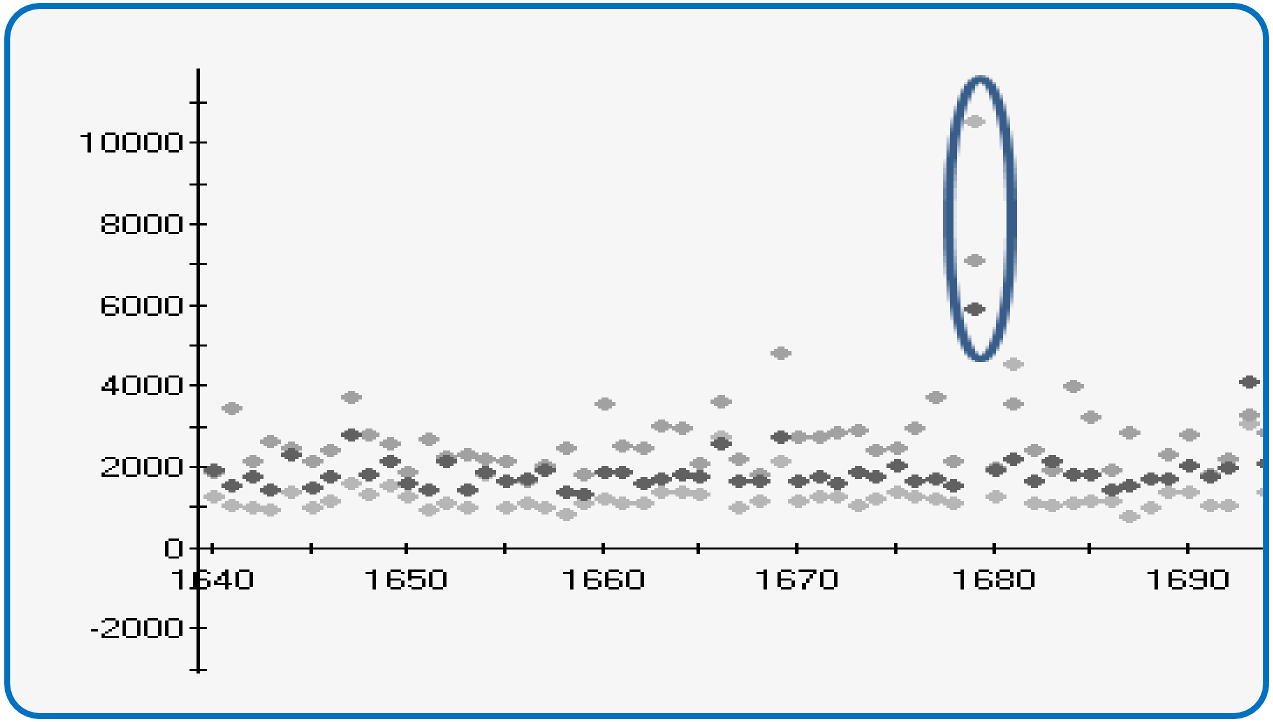
- Assumptions:
  - Inclusion is a **sphere**
  - It is **homogeneous**
  - Mass ablated is 200 - 400 ng
  - 1 spark = 1 inclusion (crater is re-melted after several sparks)

- Volume V=M/C, M is mass, C is concentration
  - 4/3*ΠR3=M/C, so R is defined
  - Inclusion size is calculated, in microns

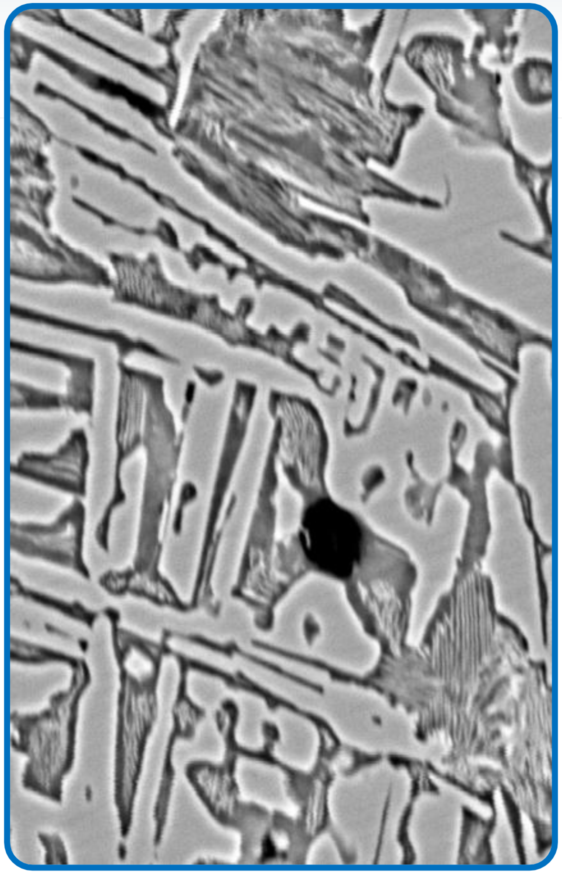
- Sizes measurable down to sub-micron

Single Spark Evaluation - the basis for MCI

Demonstration of Q8 MAGELLAN's Single Spark Detection:



Bruker Elemental MCI Software



MCI-Inclusion Software

- Intuitive
- Flexible (customized methods adjustable)
- Structured
- Fast calculation (two mouse clicks)

Principles of MCI method

Application field:

- Low and mild alloyed steels with aluminium desoxidation

Workflow MCI calibration & measurement

- Development of inclusion method with definition of spark parameters
- Calibration of method
- Sparking samples / generating data files (CSV format)
- Import data into MCI software
- Execute MCI software
- Print out (PDF) and export (CSV) and transfer results to other databases

Principles of MCI method

MCI Calculation steps

- Exclusion of sparks in the instable starting phase
- Detect and remove unenergetic sparks
- SD-Calculation of normalized Gaussian distribution
- Selection of oxide outliers (e.g. >3 SD)
- Calculation of element concentrations
- Identification of Ca as CaS, removing from oxide examination
- Identification of different oxides (correlation of outliers, e.g. Al to Ca)
- Stoichiometric calculation of oxide compounds
- Calculation of total oxygen
- Classification of inclusions and grain size distribution

Results of MCI method

PDF Print out

Analysis of a ball bearing steel (Standard quality)

Bruker Elemental

Q8 MAGELLAN PDA-Inclusion 22.05.2012

Sample name	B140.2
No. of ignored sparks (Fe)	0
No. of ignored sparks (CaS)	35
PDA code	78343,36
No. of inclusions (per 1000mm²)	4152,20
Cleanlinless value (app. K4-SEP)	4,21
PDA-Oxygen (ppm)	13,69

Statistic of single sparks	Al	Ca	Mg
Average	1219,60	992,66	1098,66
Standard deviation	1074,64	333,76	316,90
Median	1081,68	968,68	1069,96
Median std. deviation	139,50	134,99	225,63
Outlier (No.)	163	42	82

Concentration [ppm]			
Sum (Intensity)	557547,86	159686,29	176822,52
Outlier / Insoluble	13,84	1,13	1,42
Oxygen / equivalent	12,30	0,45	0,93
app. total	53,52	4,74	5,24

Inclusion analysis	Al2O3	CaO	MgO	Ca-Al-O	Mg-Al-O	Mg-Ca-Al-O
No.	148	41	67	0	14	1
Grain size [µm]						
Klasse 1 (<1)		38	38			
Klasse 2 (1-2)	110	3	29		12	1
Klasse 3 (2-3)	31				2	
Klasse 4 (3-5)	7					
Klasse 5 (5-8)						
Klasse 6 (>8)						

Results of MCI method

PDF Print out

Analysis of a ball bearing steel (Premium Quality)

Bruker Elemental

Q8 MAGELLAN PDA-Einschlussanalytik 15.05.2012

Probenname	A107.4
Anzahl ignorierter Abfunkungen (Fe)	0
Anzahl ignorierter Abfunkungen (CaS)	1
PDA Kennzahl	20825,12
Einschlussdichte (je 1000mm²)	1103,73
Reinheitsgradkennwert (ca.K1 SEP)	1,12
Schätzwert Sauerstoff (ppm)	3,50

Statistik	Al	Ca	Mg
Mittelwert	2905,29	941,69	1031,24
Standardabweichung	414,07	151,65	240,40
Median	2865,41	931,30	1021,11
Median Standardabw.	357,33	133,11	223,71
Ausreißer (Anzahl)	86	53	39

Konzentration [ppm]			
Summe (Intensität)	341709,23	76028,78	67258,62
Ausreißer / Insoluble	3,46	0,34	0,44
Sauerstoff	3,07	0,14	0,29
Schätzwert Gesamt	218,72	2,90	2,34

Einschlussanalyse	Al2O3	CaO	MgO	Ca-Al-O	Mg-Al-O	Mg-Ca-Al-O
Anzahl	83	53	36	0	3	0
Korngrößen [µm]						
Klasse 1 (<1)		52	30			
Klasse 2 (1-2)	82	1	6		3	
Klasse 3 (2-3)	1					
Klasse 4 (3-5)						
Klasse 5 (5-8)						
Klasse 6 (>8)						

Results of MCI method

Software screenshot

Analysis of a ball bearing steel

PDA-Inclusion - Calculation result

Spark	Al	Ca	Mg	Ca-S	Al2O3	CaO	MgO	Ca-Al-O	Mg-Al-O	Mg-Ca-Al-O
301	25,21	8,11	26,56	-	-	-	44,04	-	-	-
322	372,70	3,25	-17,03	-	704,03	-	-	-	-	-
326	86,42	8,52	11,12	-	163,25	-	-	-	-	-
343	84,62	5,27	17,94	-	159,85	-	-	-	-	-
359	88,22	13,39	21,57	-	166,65	18,74	-	-	-	-
371	27,91	2,84	23,39	-	-	-	38,77	-	-	-
373	125,13	6,49	3,86	-	236,38	-	-	-	-	-
390	114,33	13,39	14,76	-	215,97	18,74	-	-	-	-
399	125,13	-	76,51	232,99	-	-	-	-	363,23	-
418	8,10	51,12	0,68	-	-	71,57	-	-	-	-
424	86,42	11,77	13,85	-	163,25	-	-	-	-	-
472	87,32	6,49	-0,23	-	164,95	-	-	-	-	-
476	114,33	6,90	9,31	-	215,97	-	-	-	-	-

	Al	Ca	Mg	Ca-S	Al2O3	CaO	MgO	Ca-Al-O	Mg-Al-O	Mg-Ca-Al-O
Statistics										
Average	2978,18	895,09	852,66							
Standard deviation	547,06	197,83	264,49							
Median	2935,05	888,97	842,03							
Median std. deviation	363,87	144,31	213,00							
Outlier	79	35	43	9	75	35	39	0	4	0
Concentration [ppm]										
Sum (Intensity)	355617,91	74198,06	75907,70							
Outlier	4,26	0,47	0,63							
Oxygen	3,79	0,19	0,42							
Approximate total	220,97	2,22	1,66							
Grain size [µm]										
Klasse 1 (<1µm)						32	30			
Klasse 2 (1-2 µm)					70	3	9		2	
Klasse 3 (2-3 µm)					4				2	
Klasse 4 (3-4 µm)					1					
Klasse 5 (5-8 µm)										
Klasse 6 (>8 µm)										

Count of ignored sparks (Fe): 0
Count of ignored sparks (CaS): 9
Approximate sum oxygen: 4,39

PDA code: 25529,07
Degree of purity: -
Dense inclusion (per 1000mm²): -

Sample name A107-1

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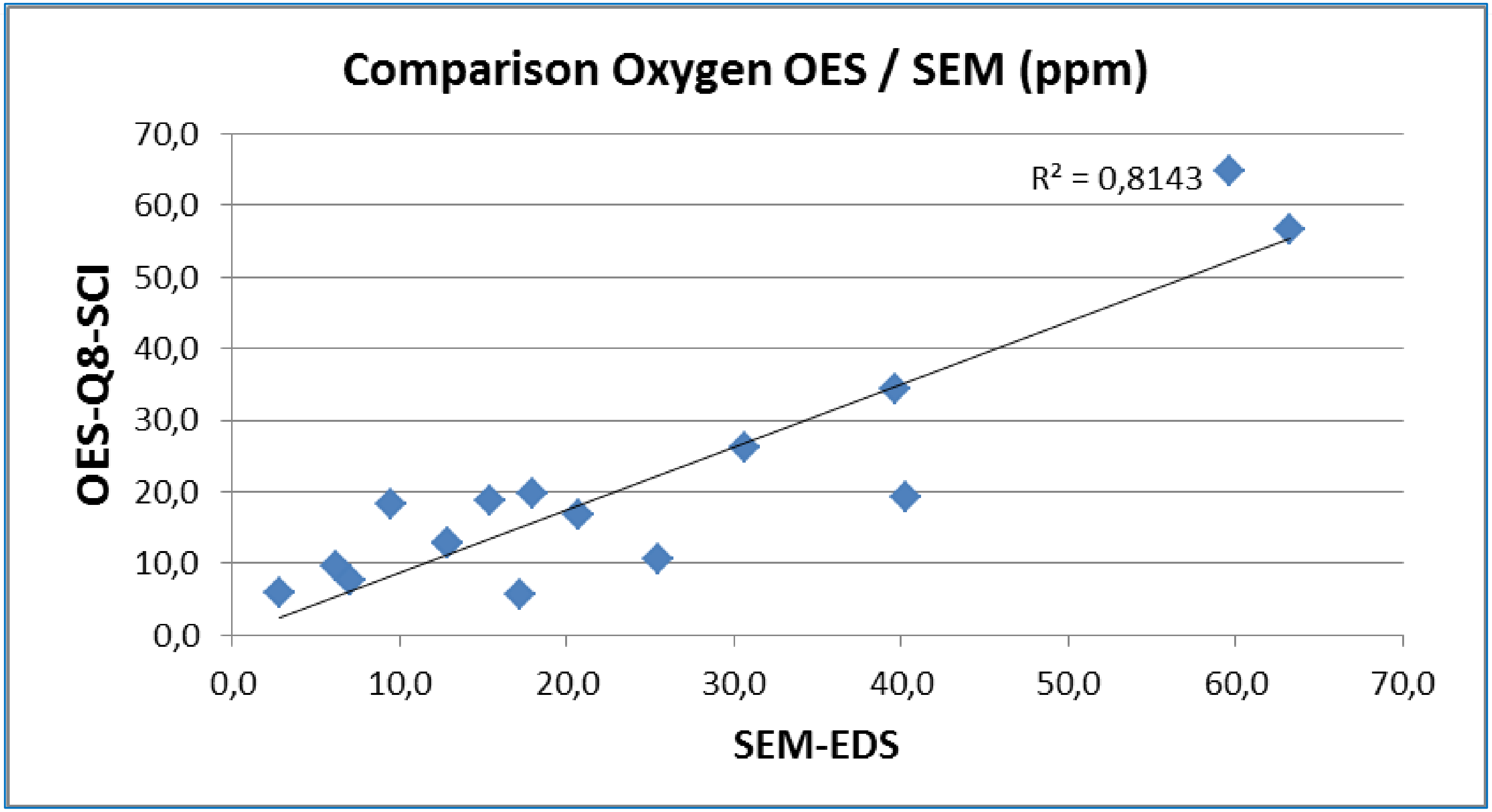
- Statistics
- Grain size distribution
- Total oxygen

Results of MCI Method

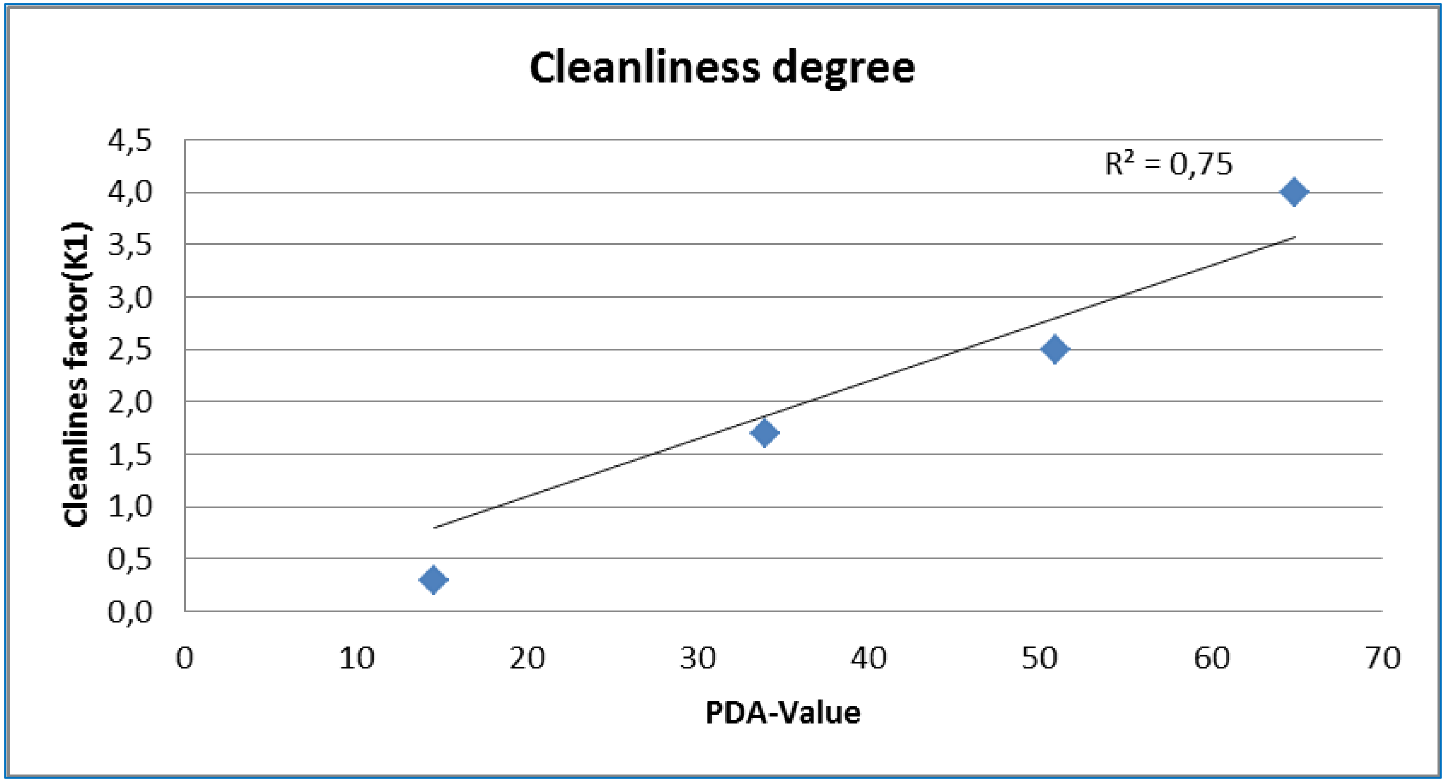
Validation of MCI-method by comparison with SEM/EDS



Results of MCI Method

Assessment of cleanliness degree

Example of calibration based on customer samples (acc. EN 10247)



Results of MCI Method

Reproducibility - Example ball bearing steel

Sample	Analyse No	O-total (ppm)	Al-total (ppm)	Al-insoluble (ppm)	app. K1 value (EN 10247)	PDA-value
72 - BBS O_{REF} = 7 ppm	1	5,9	88	5,5	1,9	35100
	2	6,4	88	6,1	2,0	37527
	3	5,4	86	5,1	1,7	31491
	4	6,3	87	6,1	1,9	36122
	5	7,9	89	7,6	2,5	45566
	Mean	**6,4**	**88**	**6,1**	**2,0**	**37161**
	SD or RSD (PDA)	**0,9**	**1,1**	**0,9**	**0,3**	**14**
N14 - BBS O_{REF} = 12 ppm	1	13,1	54	13,3	4,2	77534
	2	13,7	53	13,8	4,2	78343
	3	10,3	50	10,2	3,2	60312
	4	12,9	55	12,8	4,0	73774
	5	13,5	57	13,4	4,2	77671
	Mean	**12,7**	**54**	**12,7**	**4,0**	**73527**
	SD or RSD (PDA)	**1,4**	**2,6**	**1,4**	**0,4**	**10**

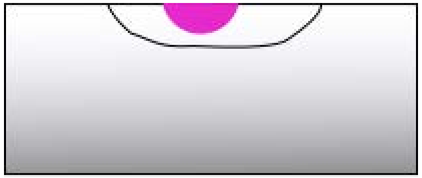
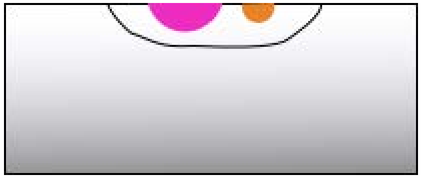
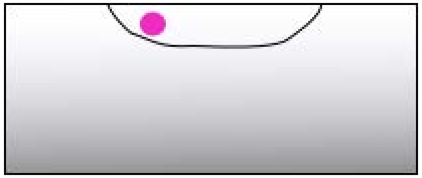
Results of MCI Method

Reproducibility - Example reference material, low alloy steel

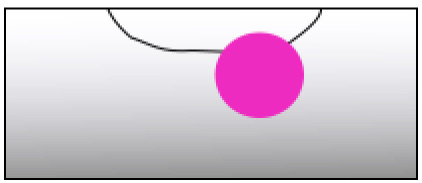
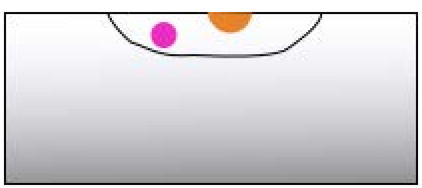
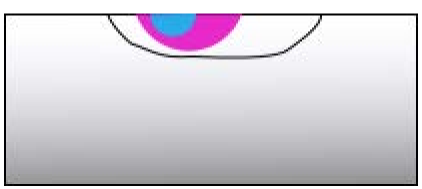
Sample	Analyse No	O-total (ppm)	Al-total (ppm)	Al-insoluble (ppm)	app. K1 value (EN 10247)	PDA-value
RM - V1 *) O_{REF} = 19 ppm	1	26,8	312	26,4	8,8	163033
	2	17,7	311	15,3	5,7	106909
	3	44,7	364	44,0	14,7	273353
	4	46,0	349	45,3	15,1	280605
	5	15,1	310	14,6	4,9	91548
	Mean	**30,1**	**329**	**29,1**	**9,8**	**183090**
	SD or RSD (PDA)	**14,6**	**25,5**	**14,9**	**4,8**	**49**
RM - V3 O_{REF} = 17 ppm	1	19,4	1059	21,1	6,1	113989
	2	17,9	1062	19,6	5,6	103371
	3	19,3	1043	19,3	6,0	111988
	4	19,8	1061	21,3	6,2	114449
	5	17,6	1052	19,1	5,5	102769
	Mean	**18,8**	**1055**	**20,1**	**5,9**	**109313**
	SD or RSD (PDA)	**1,0**	**8,0**	**1,0**	**0,3**	**5**

***)** Inhomogeneous inclusion distribution!

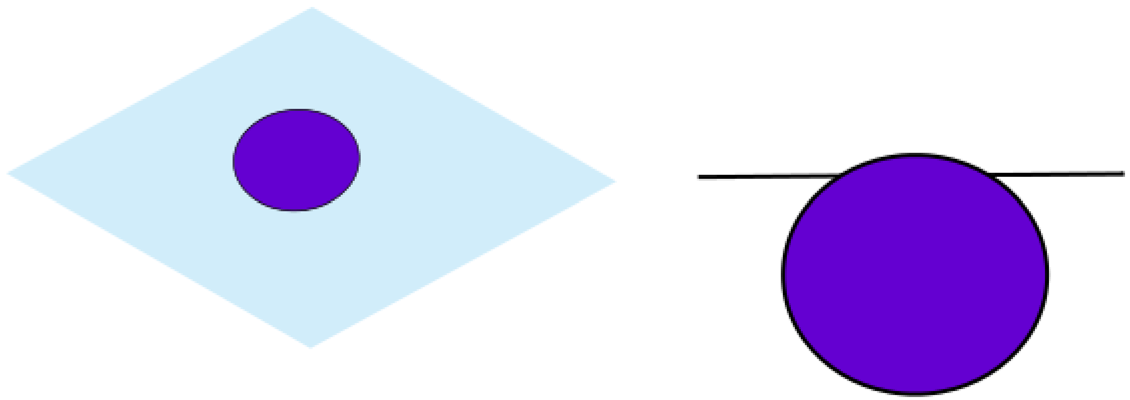
Reasons for discrepancies

	PDA	SEM/EDX	Reality
	1	1	**1**
	1	2	**2**
	1	0	**1**

Reasons for discrepancies

	PDA	SEM/EDX	Reality
	(2)	0	**1**
	1	2	**2**
	1	2	**2**

Reasons for discrepancies SEM / EDX



If section < diameter, size is always underestimated

Comparison of methods

	SEM/EDS	ON/(H)	OES-MCI
Capital investment (approx. K$)	720	80	110
Operating Costs	High	Medium	Low
Reference Method / norm compliance	Yes	Partly	No
Penetration Depth (of sample), approx.	1-3 µm	Complete	10 µm
Tested area (of sample), approx.	200 mm^2	Complete	6 mm^2)*
Measurement time, approx.	10h	80s)*	20s)*
Ease-of-use (instrument)	Complex	Easy	Easy
Sample Preparation	Medium	Complex	Easy

)* values given for single reading, multiple measurements may be necessary

Conclusion & Outlook

Conclusion

- OES-MCI reduces effort and cost
- Quick scanning method for material inspection
- Allows process control
- Final product assessment for steelworks and processing plants
- Easy extension of typical OES analysis

Outlook and future developments of analytical methods for

- Carbo Nitrides in low alloyed steel
- Sulfides in Ca-alloyed and free cutting steel
- Graphite in cast iron
- Non-ferrous applications, e.g. Al-base

Successful further developments have to be based on a good cooperation of OES– and steel-producer and chemical metallurgical experts!!!

BRUKER

Innovation with Integrity