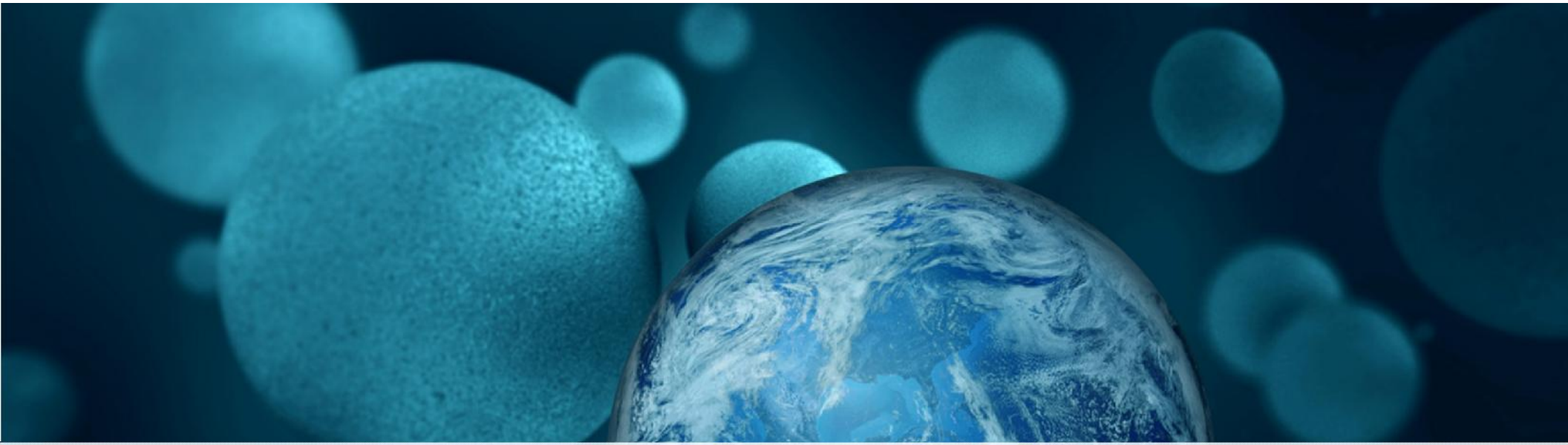

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Ultra-fast evaluation of inclusions with Spark OES – Principles and latest developments for the Thermo Scientific ARL iSpark

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Pragolab Discovery Week 2020
8 June 2020

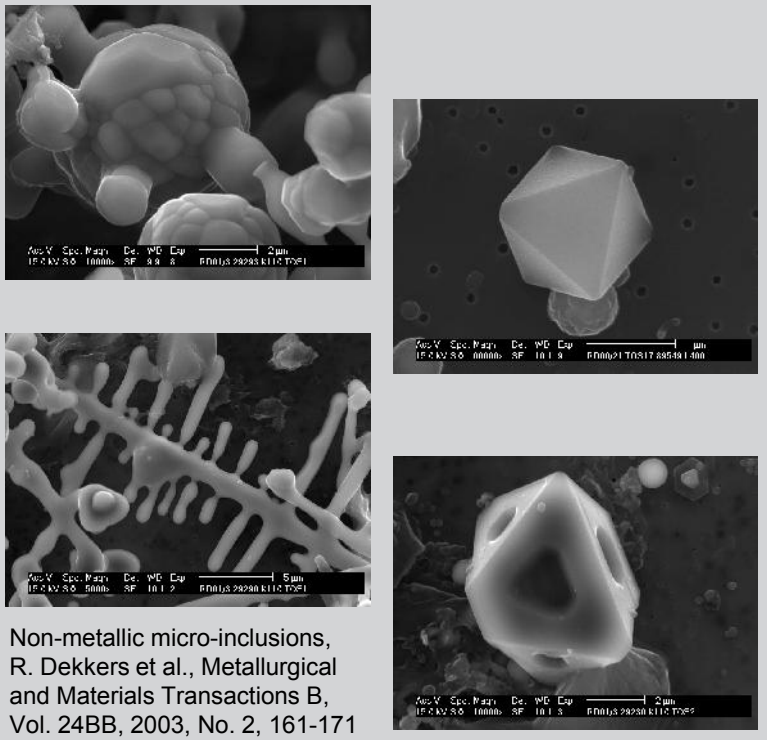
Contents

- Introduction
- Principles and examples of application
- Latest developments for inclusion analysis with the ARL iSpark
- Concluding remarks

Thermo Scientific ARL iSpark
with Spark-DAT inclusion analysis

Introduction

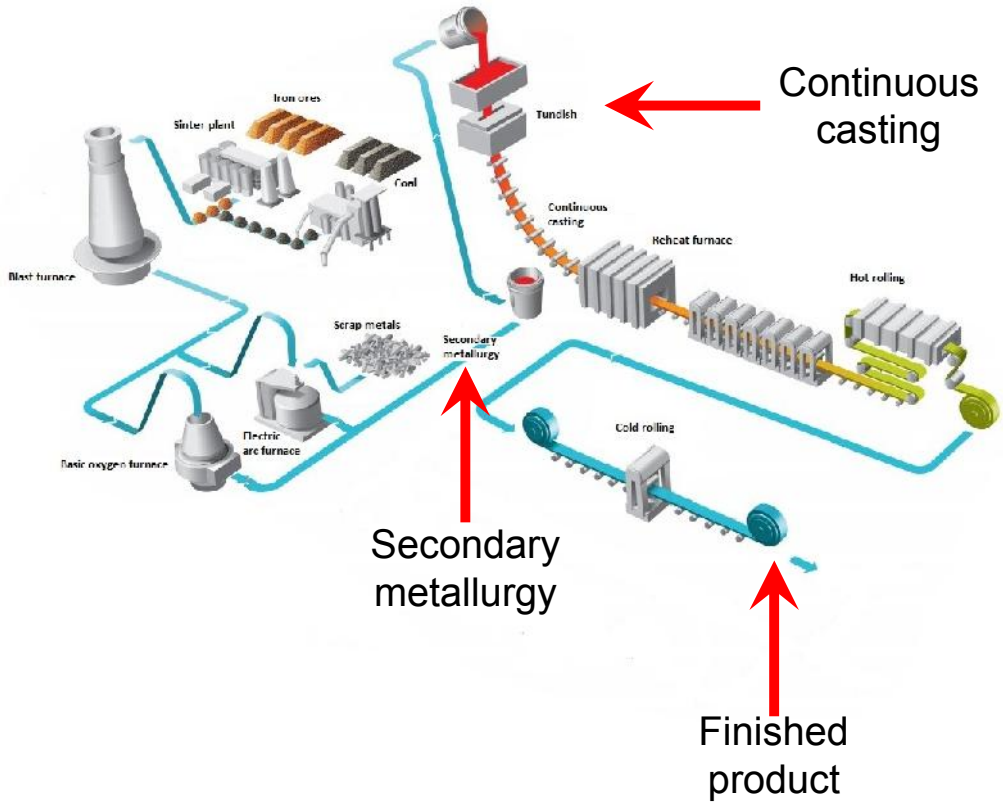
- Non-metallic inclusions in metals must be controlled
  - Strongly affect metals properties
  - Are responsible for failures of the metals products
  - Cause costly process issues
- Since more than 20 years steelmakers have been using our OES spectrometers to guarantee the metals quality and a smoothly running process
- Reasons for using spark OES
  - Unequalled speed – Can be used for control in the production process
    - Inclusions data available a few minutes after sample taking
  - Performed during the “normal” OES analysis
    - Up to hundreds of samples analyzed per day
    - No special preparation
    - No additional maintenance and cost of operation
  - Low additional investment cost compared to standard spark OES



Non-metallic micro-inclusions, R. Dekkers et al., Metallurgical and Materials Transactions B, Vol. 24BB, 2003, No. 2, 161-171

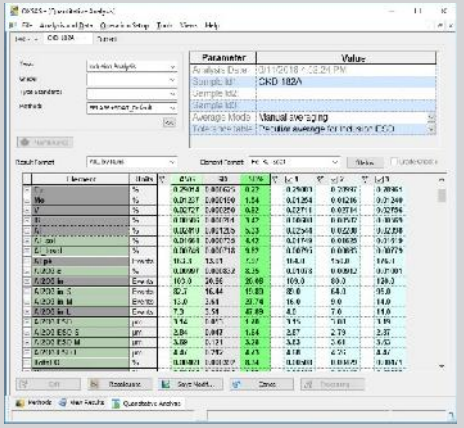
Introduction – Benefits of using spark OES in inclusion analysis

- In steel, highest benefit of using OES inclusion analysis is obtained
  - At secondary metallurgy
    - Where fast **corrective actions** can be taken
  - At continuous casting
    - With **early warning indicators** of problems like nozzle clogging
  - On the finished product
    - As a **fast and economical quality control**



Introduction – The ARL iSpark

- Top of range spark OES metals analyzer
  - Fast, high performance measurement of concentrations of all the elements needed
- Salient features
  - 1m vacuum optics with PMT detectors
  - Single Spark Acquisition on all the elements
  - OXSAS analytical software integrating inclusion analysis
- Inclusion analysis can be added to the normal bulk elemental analysis !

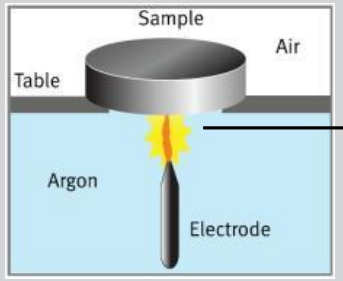


Principles and examples of application

Principles of inclusion analysis with the ARL iSpark

Short "single sparks"

Pulsed @ e.g. 500 Hz

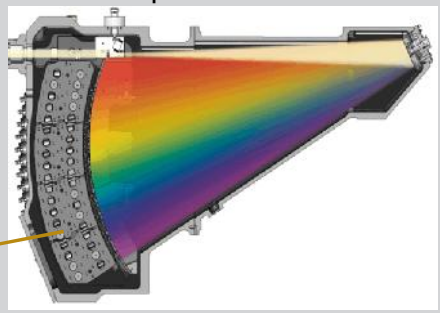


Analytical stand

Light pulses

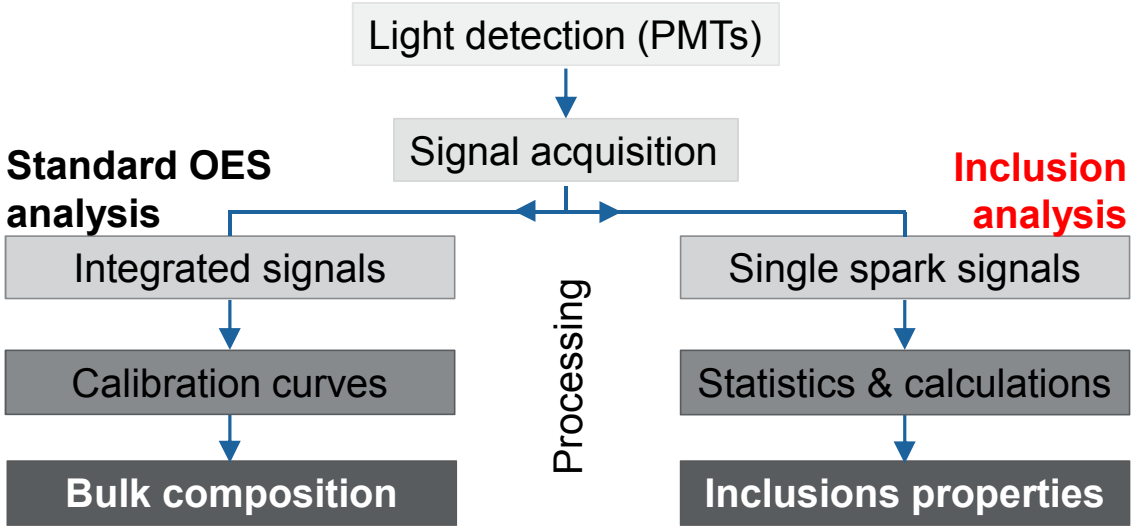
Information on elements and their concentration

1m vacuum spectrometer



Diffraction grating

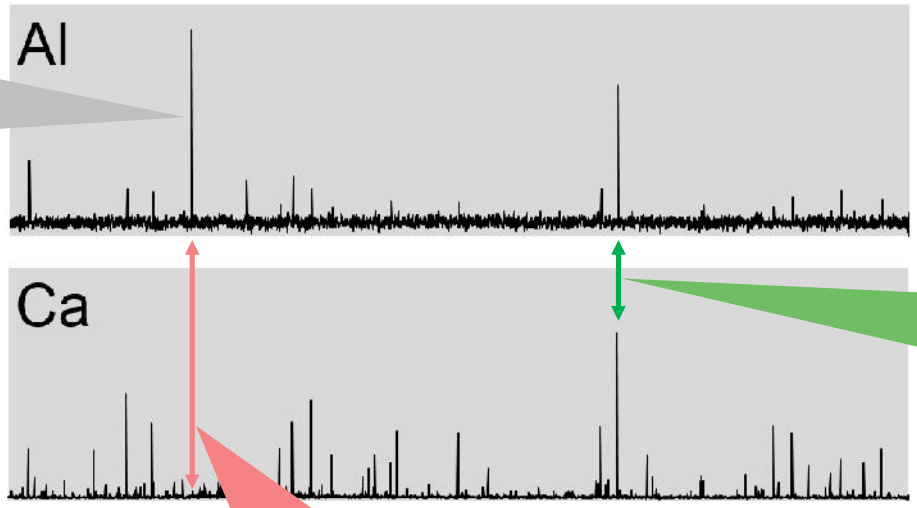
PMTs



Principles of inclusion analysis with the ARL iSpark

Al peak
⇒
Inclusion contains Al
⇒ **Al_2O_3, Al_2O_3-CaO…**

Run-charts of single spark signals

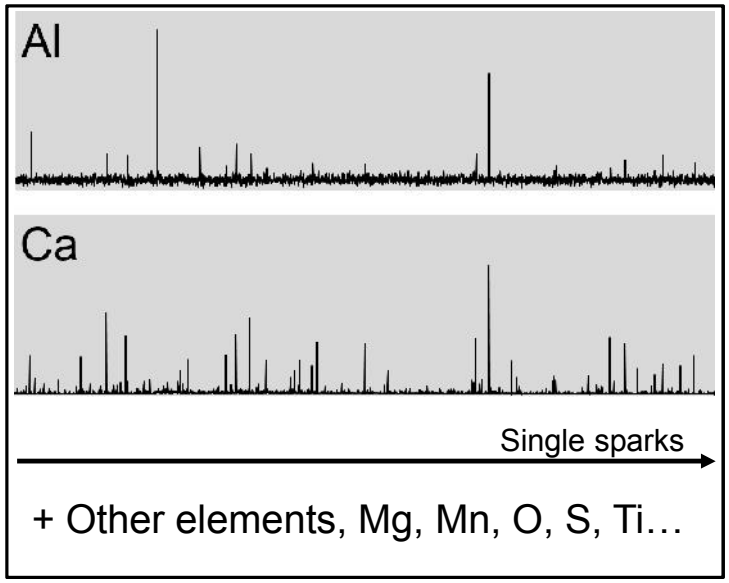


Ca peak coincident with Al peak
⇒
Inclusion contains Al & Ca
⇒ **Al_2O_3-CaO**

No Ca peak coincident with Al peak
⇒
Inclusion contains only Al
⇒ **Al_2O_3**

Principles of inclusion analysis with the ARL iSpark

Single spark signals
(intensity run charts)



Statistical processing

- Numbers of peaks
- Numbers of coincidences on multiple elements
- Peaks intensities

No or simple calculations → Standard "qualitative" inclusions properties

Advanced calculations → Advanced "quantitative" inclusions properties

Examples of qualitative and quantitative inclusion properties

Standard “qualitative” inclusions properties

Peaks

	S	M	L	Total
N	2865			2865
O	10408	215	24	10647
Mn	4225			4225
Si	7066			7066
Al	4178	573	764	5515
Ni	406			406
Cr	859			859
Cu	1695			1695
Mo	310			310
V	263			263
Nb	406			406
W	1050			1050
Sn	215			215
Co	48			48
Ca	4965	1027	836	6827
Pb	1194			1194
B	1122	48		1170
Sb	1337			1337
Zr	191			191
Bi	716			716
Se	1313			1313
Te	477			477
Zn	740			740
Ce	645			645
Mg	9740	1528	1981	13249
La	5443			5443
Sr	1767			1767
Ba	501	48	24	573
Pr	263			263
Cd	430			430
Ti	359	48	95	1003
S	9764	836	310	10910
C	72			72
P	48			48
Sum	75581	4323	4034	83938

Peaks coincidences

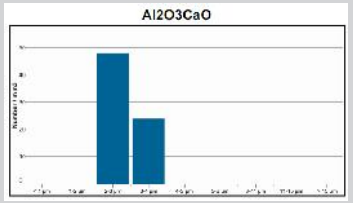
	S	M	L	Total
MnS	1337			1337
AlCaO	454		48	501
CaS	1408	286	358	2053
AlCaMg	1313	143	430	1886
AlCaMgS	525	95	95	716
AlO_Ca	454	119	24	597
CaO_Al	573	95	48	716
AlO	907	119	72	1098
CaO	955	143	119	1217
AlMgO	764	119	72	955
MgO	2125	191	501	2817
TiO	167		24	191
Sum	10982	1310	1791	14084

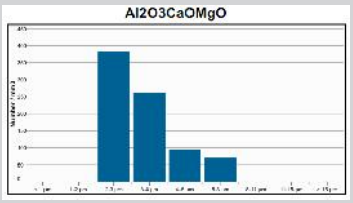
- Signal processing for advanced properties
  - Statistics
  - Advanced calculations
- All numerical standard and advanced properties available for fast on-line analysis

Advanced “quantitative” inclusions properties

Size Distribution (ESD in µm)

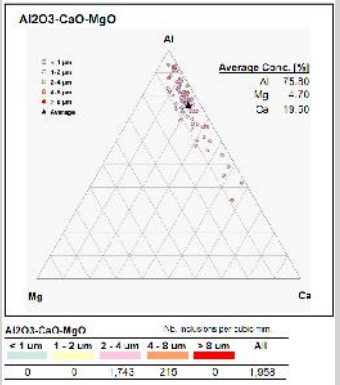
	< 1 µm	1 - 2 µm	2 - 4 µm	4 - 8 µm	> 8 µm	Total
Al2O3			454			454
Al2O3Ti(C,N)						
Al2O3Ti(C,N)TiS						
CaS	215	48				263
MnS			4727			4727
Al2O3CaO			72			72
Al2O3CaOMgO			645	167		812
Al2O3CaOMgOCaS			286	119		406
Al2O3CaOCaS			24			24
Al2O3CaOSiO2						
Al2O3MgO			1719	95		1814
Al2O3MnS			24			24
Al2O3SiO2			48			48
Sum	215	48	7999	381		8644





Inclusion Concentration in Sample [ppm]

Al2O3	Al2O3MgO	Al2O3MnS	Al2O3Ti(C,N)	Al2O3Ti(C,N)TiS
0.53	3.56	0.02	0.00	0.00
Al2O3SiO2	**CaS**	**Al2O3CaOMgO**	**Al2O3CaOSiO2**	**MnS**
0.05	0.01	2.18	0.00	3.57
Al2O3CaO	**Al2O3CaOMgOCaS**	**Al2O3CaOCaS**	**Al2O3CaO**	
0.10	0.86	0.02	0.10	



Inclusion Volume Fractions (*10e6)

	< 1 µm	1 - 2 µm	2 - 4 µm	4 - 8 µm	> 8 µm	Total
Al2O3			2.03			2.03
Al2O3CaOSiO2						
Al2O3SiO2			0.35			0.35
CaS	0.05	0.03				0.08
MnS			23.12			23.12
Al2O3CaO			0.64			0.64
Al2O3CaOCaS			0.24			0.24
Al2O3CaOMgO			7.86	9.71		17.57
Al2O3CaOMgOCaS			4.61	5.56		10.16
Al2O3MgO			15.15	4.59		19.74
Al2O3MnS			0.18			0.18
Al2O3Ti(C,N)						
Al2O3Ti(C,N)TiS						
Sum	0.05	0.03	54.18	19.86		74.11

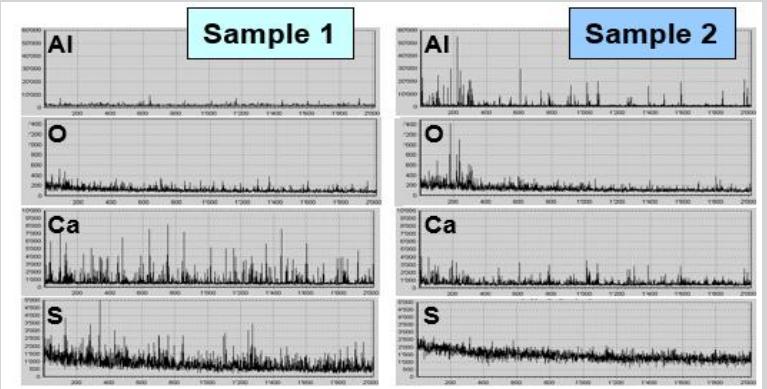
Standard inclusion analysis in steel

- Signal processing method
  - Statistics
  - No or very simple additional calculations

- **Quick proof of big differences in the inclusions content**

- Applications
  - Control inclusion modification during Ca treatment
  - On-line control of nozzle clogging
  - Steel cleanness index

Samples taken from 2 different steel heats



	Peaks			
	Al tot	O tot	Ca tot	S tot
Sample 1	60	87	192	61
Sample 2	132	78	117	11

	Coincident peaks			
	Al2O3	Ca alum.	CaO	CaS
Sample 1	0	8	17	32
Sample 2	9	14	4	4

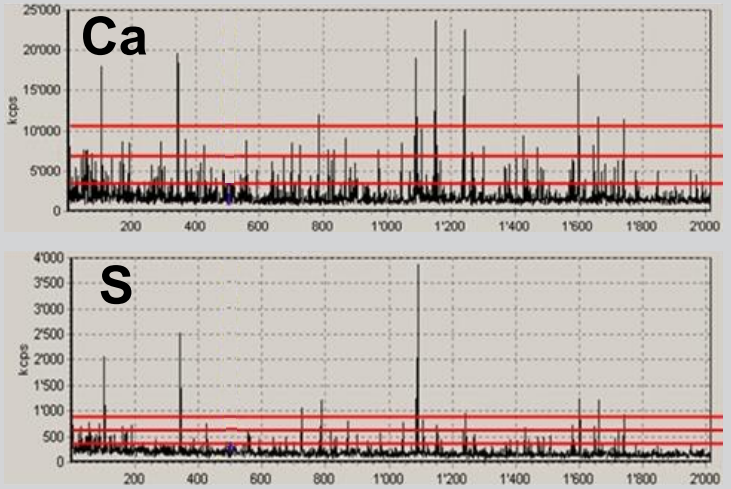
Results obtained with online algorithms processing intensities 500-2000 (average of 5 runs)

Standard inclusion analysis in steel

- "SML classification"
  - Classification as small, medium and large inclusions
- Inclusions **criticity** depends on the size

L > M > S

- Adjust inclusion control criteria to the need, e.g.
  - Count only L inclusions for less demanding grades or customer specification
  - Count S + M + L inclusions for very demanding grades or customer specification



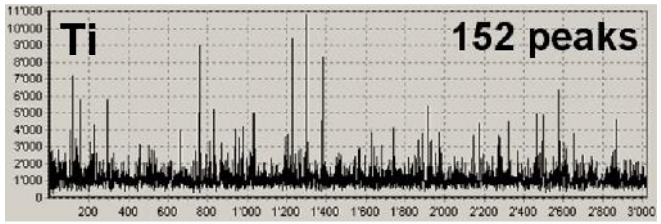
Ca peaks		S peaks		CaS coincidences	
S	74	S	49	S	47
M	18	M	11	M	10
L	7	L	8	L	8
Total	99	Total	68	Total	63

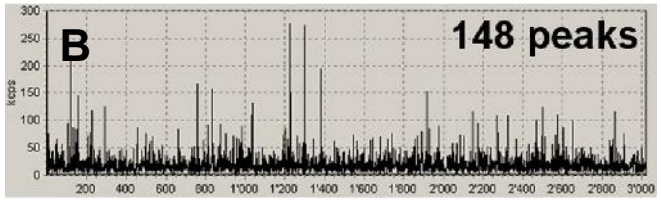
S
M
L

Standard inclusion analysis in aluminum (6000 series)

- Ti and B containing materials added to the melt for grain refinement to improve mechanical properties

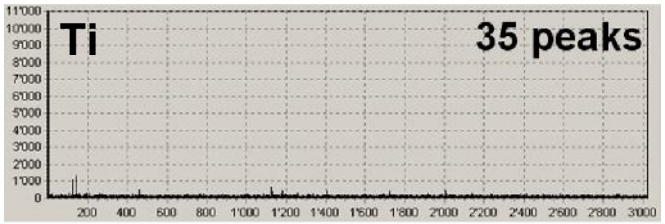
- May form TiB_2 particles
  - Detrimental to mechanical properties and surface aspect of the final product

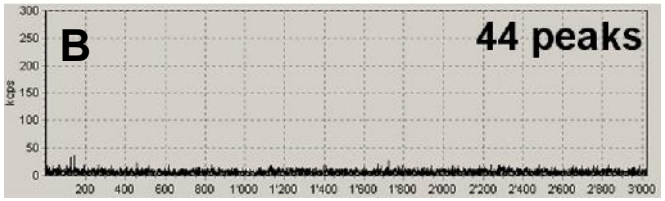




- Many TiB_2 inclusions
- Some of them very large

Product quality insufficient





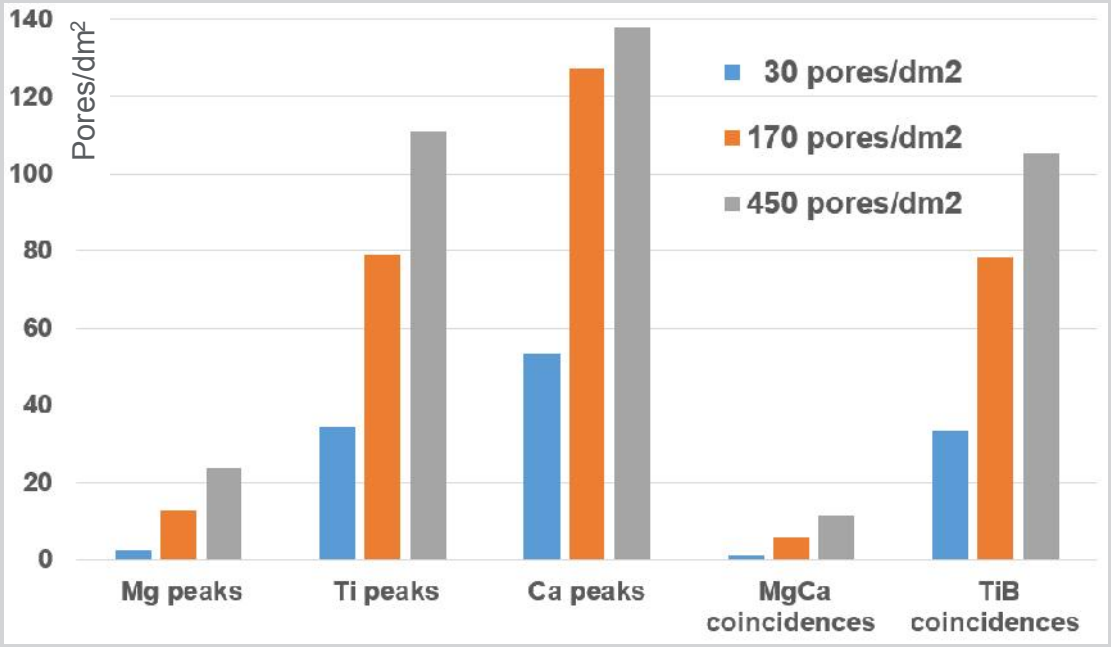
- Few small TiB_2 inclusions

Product is good

SML distribution and other standard inclusion analysis methods also available in aluminum and other non-ferrous matrices

Standard inclusion analysis in aluminum (6000 series)

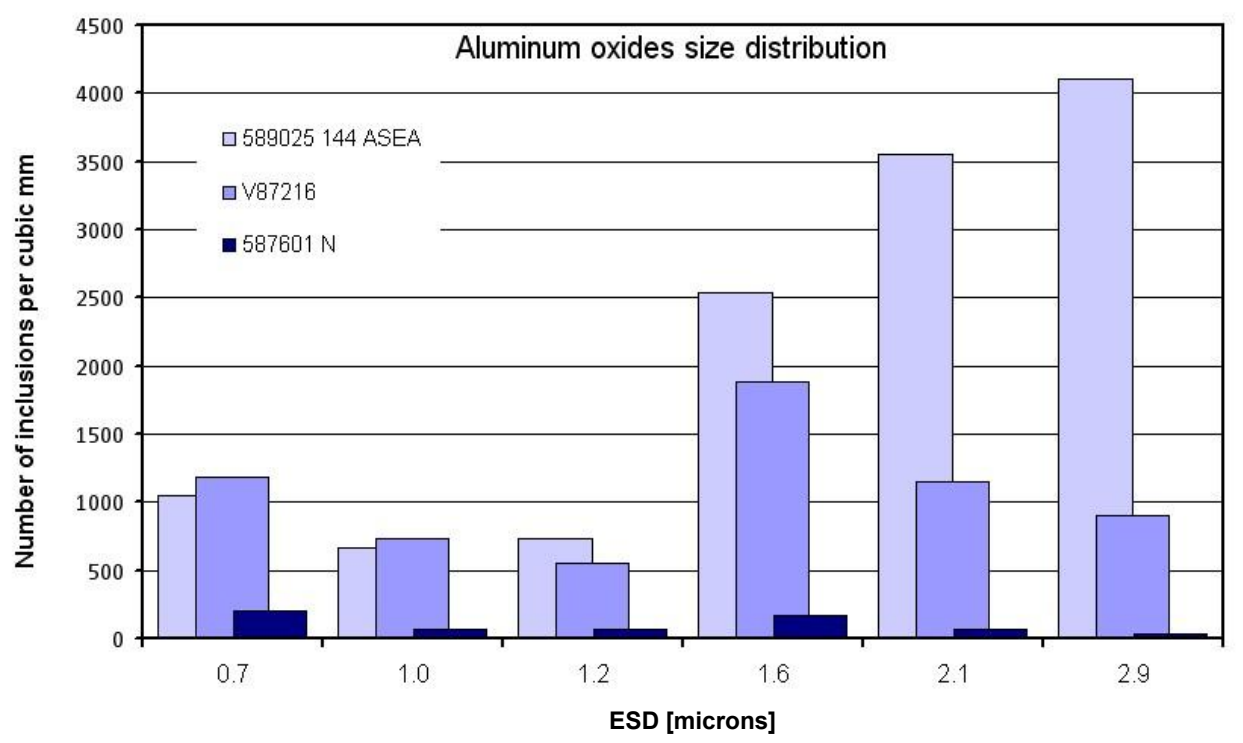
Porosity vs numbers of peaks and coincidence in 3 aluminum samples (6000 series)



- Relatively good correlation of porosity with numbers of peaks and coincidences
- Relation between inclusions and pores
  - Many inclusions are obviously located in the pores
  - The more pores, the more inclusions (or vice-versa)
- Spark OES used to control porosity in the production process

Advanced inclusion analysis in steel

Size distribution of Al_2O_3 in 3 low alloy steel samples

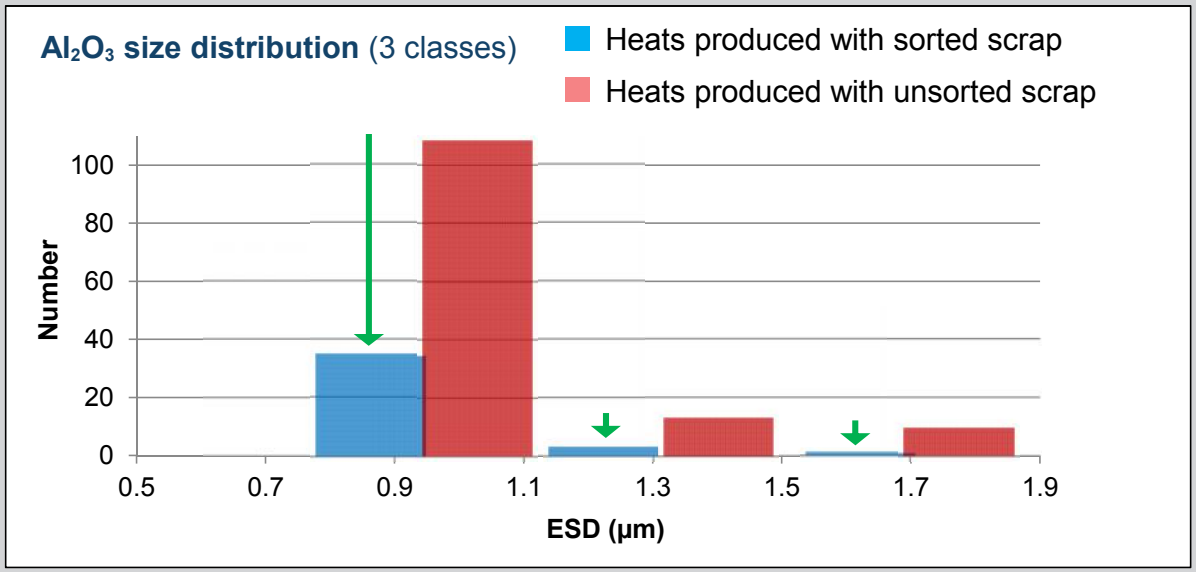


ESD = Equivalent Spherical Diameter

- Quantitative!
  - Size in microns
  - Number of inclusions per cubic mm

Advanced inclusion analysis in steel

Aluminum oxides in 2 samples
from heats produced using different scrap qualities



SiMn-killed steel with Al wire treatment - Samples taken at casting

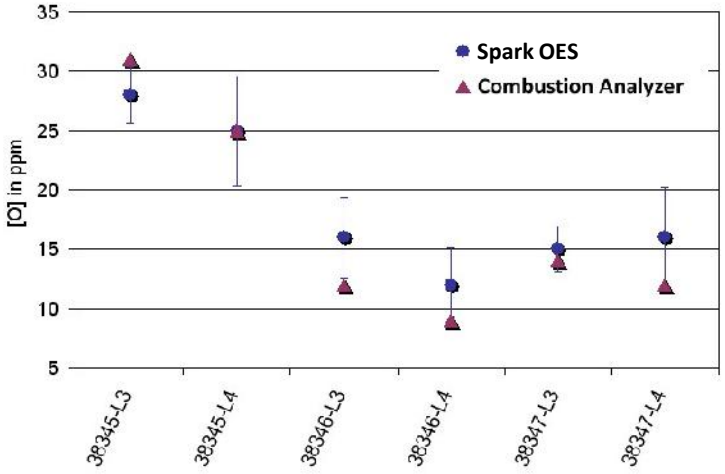
- Sorted scrap
  - Less inclusions
  - Mostly the smallest ones
- Sorted scrap allows producing cleaner steel
- Can be used in order to optimize supply and use of scrap according to requirements on the final product

Total oxygen content in killed low alloy steel

- Oxygen concentration needs to be known rapidly…
  - … but spark OES standard elemental analysis not suitable to control very low oxygen concentrations as required for high quality steels grades (< 40 ppm)
- Solution: recalculate oxygen content from the oxide inclusions

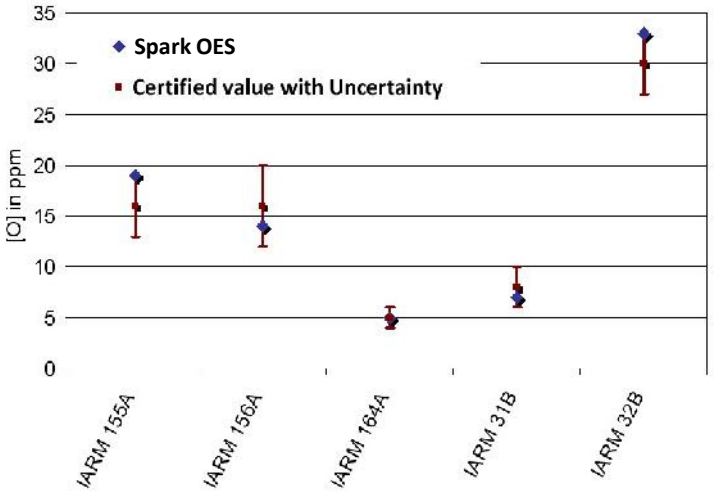
Steel product	Maximum allowed oxygen [ppm]
IF steel	40
Drawn and ironed cans	20
Alloy steel bars	10
Line pipes	30
Bearings	10
Tire cord	15
Heavy plate steels	20
Wires	30

Killed steel samples
from continuous casting mold



(With permission of ArcelorMittal, Ghent)

Low alloy steels CRMs

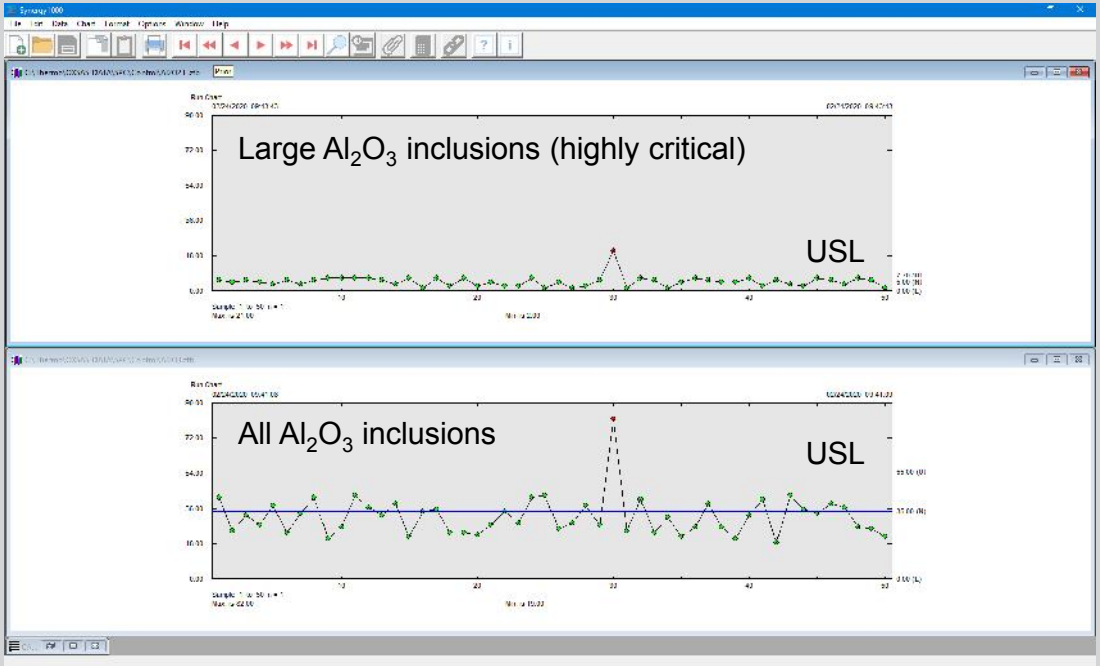


- Excellent match with references down to few ppm's
- Can replace combustion analysis

Use SPC software to control inclusions in the process !

- A simple way to control **metal quality** as well as **process stability**
  - Minimize non-compliant products, rework and scrap
  - Minimize very costly process problems due to inclusions (e.g. **nozzle clogging**)
- **Any numerical inclusion property** can be used !
- **Key features**
  - **USL**: user defined Upper Specification Limit
  - Trends and warnings

SPC run charts of numbers of Al peaks (Al_2O_3)



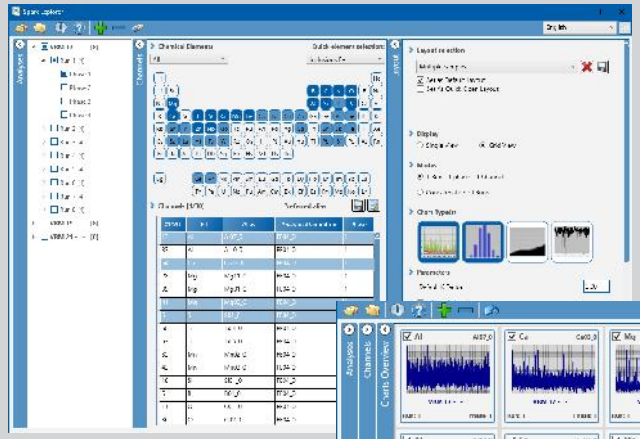
Sample #30 not compliant:
the number of Al peaks is > USL

Latest developments
for inclusion analysis with the ARL iSpark

Spark Explorer – New software module for off-line work

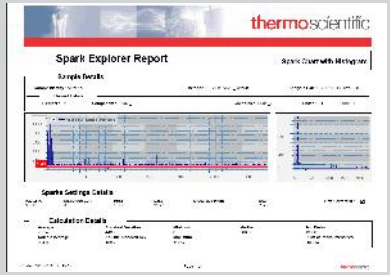
- **In-depth study** of single spark signals
  - Metal quality or process issue
  - Ambiguous inclusions results
- Optimization of methods
- Documentation of analysis results

- Highlights
  - Quick selection and preview of all chart types
  - Comparison of run charts of unlimited number of elements, runs and samples
  - Real-time computations
  - Reports and exports of charts to files

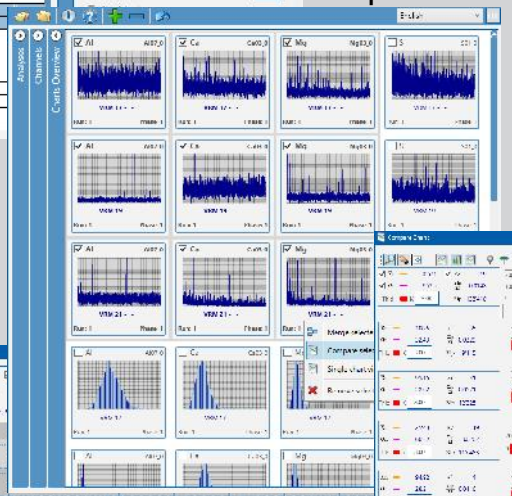


Quick selection

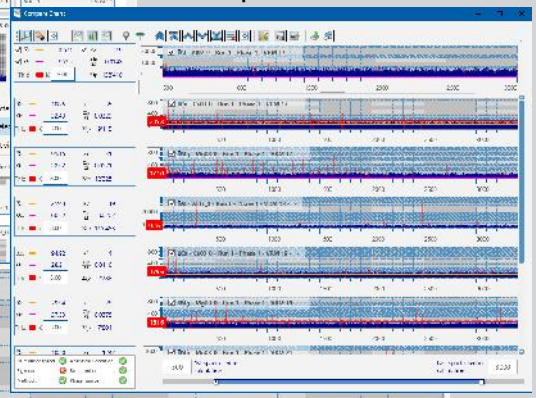
Report



Quick preview



Comparison of run charts



Histogram

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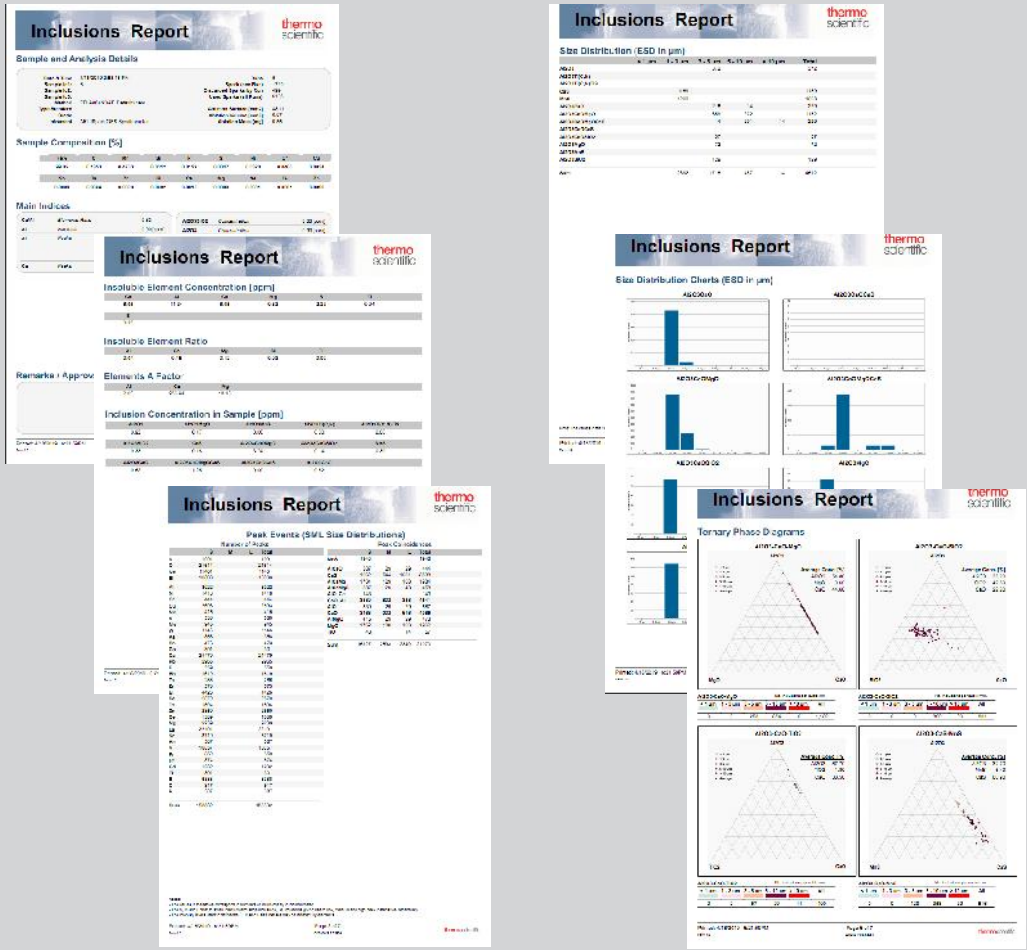
Inclusions Report – New software tool

- Compilation of all the inclusion properties available and more
  - Ideal for transmission to various services concerned with inclusions

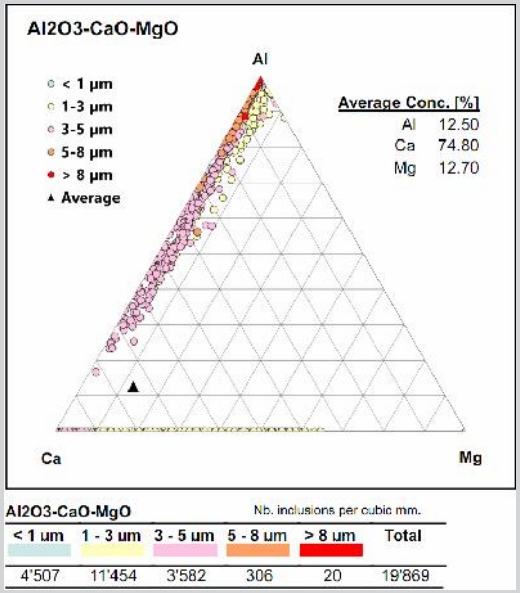
- **Customizable** information
  - Sample and analysis details
  - Bulk chemical concentrations
  - Special inclusion indices
  - Soluble/insoluble ratios and concentrations
  - Peaks and coincident peaks
  - …
  - **Advanced properties**, e.g.
    - Oxygen content
    - Inclusions concentrations
    - Inclusions sizes and size distributions
  - **Ternary diagrams**



Ternary Diagrams - New software tool

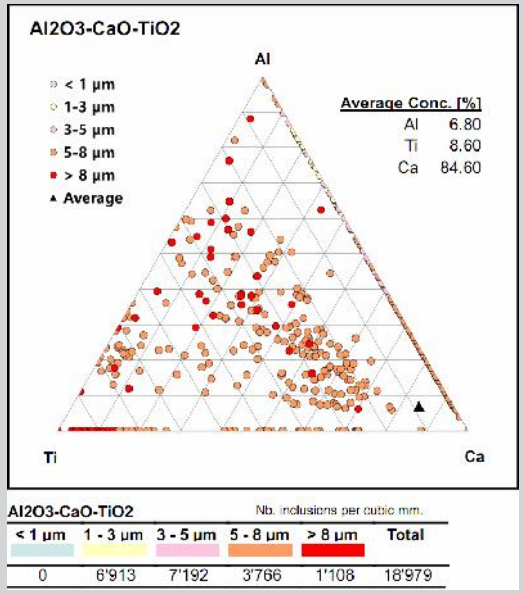
- Show the distribution of composition of inclusions systems based on three chemical components
  - Used typically to check inclusions modifications induced by steel treatments
- With
  - Customizable size classes in microns
    - Dots of different colors
  - Average composition on diagram and in %
  - Class frequency in inclusions per cubic mm
- Available with Inclusions Report

Ternary phase diagrams (low alloy steel sample)



Al2O3-CaO-MgO — Nb. inclusions per cubic mm.

< 1 µm	1 - 3 µm	3 - 5 µm	5 - 8 µm	> 8 µm	Total
4'507	11'454	3'582	306	20	19'869



Al2O3-CaO-TiO2 — Nb. inclusions per cubic mm.

< 1 µm	1 - 3 µm	3 - 5 µm	5 - 8 µm	> 8 µm	Total
0	6'913	7'192	3'766	1'108	18'979

Concluding remarks

Concluding remarks

- The ARL iSpark is the instrument steelmakers needed for inclusion analysis
  - Inclusion analysis performed during the usual bulk metal composition analysis
    - Evaluates inclusions in hundreds of samples per day, shortly after sample taking
    - Real-time control of the inclusions and a smoothly running process
- Other benefits
  - Investment cost low and no additional cost of ownership
  - Instrument easy to use and maintain
  - Normal OES sample preparation, i.e. fast and simple
- Available with manual and automated ARL iSpark
- Applications in other metals and industries, e.g.
  - Aluminum, lead, nickel, precious metals
  - Metals processing industries

ARL iSpark automated with ARL SMS-2300

- Spark OES is fast, but it does not replace the microscopy techniques of reference
  - Both are complementary and should be part of the company's inclusion analysis strategy

To learn more on ARL iSpark and ultra-fast inclusion analysis

Visit

www.thermofisher.com/oes

Or contact

jean-marc.bohlen@thermofisher.com

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