Application Note 41243

Ultra-fast analysis of micro inclusions in steel with Thermo Scientific ARL iSpark Metal Analyzers – Standard Inclusion Analysis

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Key Words

ARL iSpark, Micro inclusions in steel, Process control, Qualitative size distribution, Steel cleanness, Inclusion analysis

Goal

Perform ultra-fast analysis of micro inclusions in steel

Introduction

Optical emission spectrometry (OES) is a fast, easy-to-use and cost-effective analytical technique used for elemental analysis of solid iron and steel samples in various contexts, from production to recycling and from foundries to service laboratories. The Thermo Scientific™ ARL iSpark™ Series metals analyzer is a high-performance OES spectrometer platform delivering the ultimate precision and accuracy for the analysis of iron and steel from trace to alloying element levels.

The Spark-DAT (Spark Data Acquisition and Treatment) methods considerably extend its capability beyond the spectrochemical analysis by also enabling ultra-fast inclusion analysis. In the steel industry, these methods enjoy growing popularity, in particular for their ability to provide information about the inclusions during the steel elaboration process.

Benefits

The benefits of using the ARL iSpark 8860 or 8880 spectrometers with Spark-DAT methods are the following:

- Drastic reduction of investment costs for inclusion analysis. The spectrometer is capable of performing inclusion analysis in addition to analysis of elemental concentrations
- Information on inclusions is available shortly after sample taking. This offers unequalled perspectives for in-process control of the metal elaboration
- Extremely short time for inclusion analysis and related sample preparation. The sample and its preparation are the same as for standard OES analyses
- No additional cost and time for operations is required as compared to the standard OES spectrometer. Maintenance, service and sample preparation for inclusion analysis remain the same
- Inclusion analysis performed in parallel with the analysis of elemental concentrations possible for more than 30 samples per hour. Inclusion analysis can be performed on all samples analyzed by OES
- Detection of randomly distributed exogeneous inclusions is easier since it is possible to rapidly analyze very large surface areas.

Principles

With the Spark-DAT methods, different treatment principles are used compared to OES concentration analyses: instead of being integrated and translated into concentration, the light intensity values for all the single sparks are submitted to a special mathematical treatment.

The intensity of a single spark signal depends on the composition of the sample at the position struck by the corresponding single spark. If the concentration of an element in the ablated sample material is significantly higher than the concentration of its soluble form in the matrix, the outcome is an intensity peak. This is typically the case when a spark hits a sample area containing an Al based inclusion (e.g. Al_2O_3), because the Al concentration is much higher than in the metal matrix due to the contribution of the inclusion.

For a better understanding we can explain this with numbers: the concentration of Al in an Al_2O_3 particle is ~53%, and if a spherical inclusion with a diameter of 5µm is ablated together with the sample material, this gives an apparent rise in the concentration of 0.075%.

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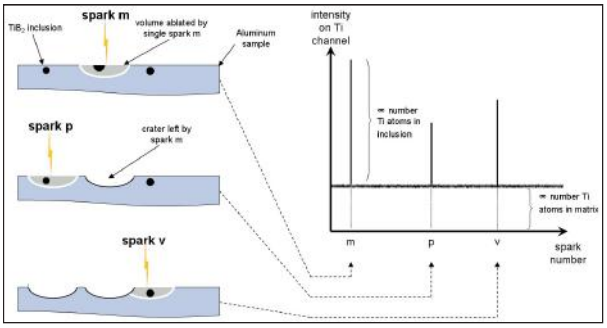
Graphically, this is illustrated by the following picture:



The intensity of the flat, noisy baseline signal is proportional to the concentration of Al atoms dissolved in the matrix and the intensity of a peak depends on the amount of Al atoms contained in the inclusion(s) ablated by a single spark. Consequently, the number of peaks is related to the number of such inclusions and their intensity to such factors as the inclusion size and the concentration of Al in the inclusion.

Practical aspects

The Spark-DAT methods include software and specialized algorithms and are available with PMTs only. The single spark intensities are used for inclusion analysis and traditional elemental concentration analysis, allowing the two types of analyses to be run simultaneously. Usually thousands of single intensity values are acquired on every channel, which makes the Spark-DAT raw dataset extremely large and complex. Because of this, fast dedicated algorithms are used to calculate the values corresponding to the information of interest.

The values calculated can then be handled like conventional OES results by the analytical software: they can be displayed, printed, stored, transmitted, used in pseudo-element calculations, checked against product specifications, etc.

Analysis time

The Spark-DAT analysis alone takes typically 7s for a single measurement (including 2s Ar flush). This mode is recommended only for quick counting and confirmation of inclusion types, and for obtaining raw data for off-line interpretation. However, the Spark-DAT analysis offers more possibilities when combined with the analysis in concentration. In this case, the analysis time taken between the start of the analysis and the display of the results is in average the following:

Application	Model	Time [s]
Low alloy steel (without N, O)	ARL iSpark 8880	20
	ARL iSpark 8860	16
Low alloy steel (with N, O)	ARL iSpark 8880	25
	ARL iSpark 8860	21
Additional time for free-cutting steel	ARL iSpark 8860/8880	30

These analysis times (unchanged compared to standard elemental analysis) make inclusion analysis possible in many contexts, in particular during steel production, where analysis times are extremely critical.

Sample preparation

The standard OES sample preparation can be used for Spark-DAT inclusion analysis. However, paper grinding should be used only if it is demonstrated that no contamination by paper influences the results obtained on inclusions of interest (paper material deposits can be in some cases difficult to distinguish from inclusions). Because aluminum oxide inclusions are generally critical in steel, it is recommended using Al_2O_3-free grinding papers.

Milling is more and more used for steel samples surfacing, because it guarantees a clean, unpolluted surface, ideal for inclusion analysis.

Contexts of use of Spark-DAT inclusion analysis

Spark-DAT inclusion analysis offers tremendous benefits for:

- Inclusion control for quality assurance. The most important application is inclusion analysis during steel elaboration. However, interesting applications exist also for incoming materials or intermediate and finished products
- Process control via on-line monitoring of inclusions. The inclusions are "process markers" that indicate a change in the process. With Spark-DAT analysis they are monitored online, providing a unique way to take rapid corrective actions
- Samples screening. Hundreds of samples can be screened for inclusions in a day. This may help solving critical quality problems very rapidly. In a preventive approach, archived samples can be screened to verify if a quality problem signaled by a customer also affects products manufactured for others
- Replacement of long or costly analysis techniques. Spark-DAT methods can replace traditional techniques of inclusion analysis. It also offers the possibility to replace a technique that measures a property of steel which depends on the inclusions it contains (e.g. fatigue resistance), if correlation may be established between Spark-DAT inclusion analysis and the results of the said technique.

Soluble/insoluble contents of elements

The soluble or insoluble part concentration of some elements such as Al, Ca, Ti, B are traditional indicators of the steel making process and are still widely used. The algorithm *Insoluble* is therefore one of the most commonly used Spark-DAT application. It consists in calculating the soluble or insoluble part of an element. With Insoluble, the ratio R_{insol} of the sum of the intensity signals due to the matrix insoluble part to the sum of all the intensity signals is calculated:

$$R_{insol} = \frac{\sum_{i=1}^{n} I_i \big| I_i > I_{threshold}}{\sum_{j=1}^{n} I_j}$$

In the case of Al, the concentrations of the soluble and insoluble parts are obtained in the following way:

$$Al_{insol} = Al_{tot} \times R_{insol}$$

$$Al_{sol} = Al_{tot} - Al_{insol}$$

where Al_{tot} is the concentration of total Al measured by OES.

The *Insoluble* Spark- DAT method does not need calibration samples for soluble/insoluble concentrations. The method is therefore also applicable to any partly insoluble element, like B, Ti and Ca, even in the case where

	Sample	180A	181A	182A	183A	184A
Certified values	Al tot	0.0001	0.016	0.023	0.15	0.022
	Al sol	0.0001	0.014	0.017	0.141	0.016
	Uncertainty U on Al sol	0.0001	0.001	0.002	0.006	0.002
Spark-DAT values	Al sol	0.0001	0.0156	0.0199	0.1491	0.0206
	Sample	185A	186A	187A	188A	189A
Certified values	Al tot	0.06	0.042	0.019	0.093	0.041
	Al sol	0.054	0.038	0.017	0.083	0.039
	Uncertainty U on Al sol	0.004	0.003	0.002	0.004	0.003
Spark-DAT values	Al sol	0.0591	0.0409	0.0189	0.0923	0.0409

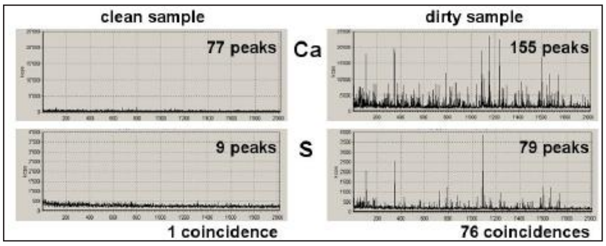
no certified reference material (CRM) exists. The above table illustrates the excellent accuracy obtained on CKD low alloy steel standards having certified Al_{sol} concentrations.

Evaluation of number and type of inclusions

The simplest application of the Spark-DAT methods consists in counting intensity peaks on the channel of a given element with the algorithm *Peaks*. A peak is defined as an intensity signal I_{peak} higher than a threshold situated at the mean intensity m of the element dissolved in the matrix plus three times its standard deviation SD:

$$I_{peak} > m + 3 \cdot SD_{Imatrix}$$

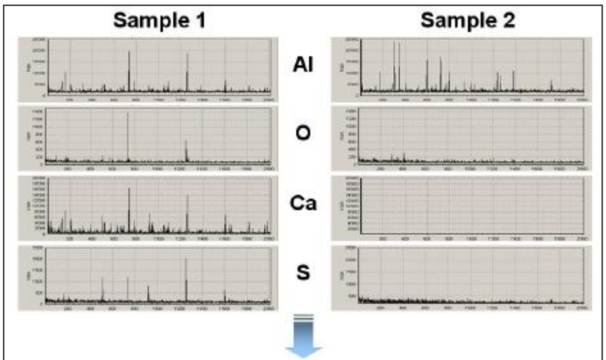
Counting intensity peaks enables the evaluation of the number of inclusions containing this element. As shown in the following figure, clean and dirty steel samples can easily be identified by comparing the number of peaks counted on the channels of the inclusion elements.



The algorithm *Composition* allows counting coincidental peaks, i.e. peaks appearing on the channels of several elements concurrently during the same single spark. The coincidence of a peak on Ca and S channels means that these two elements are part of the same inclusion, for instance a calcium sulfide (CaS) inclusion. In the previous example, one CaS coincidence was counted in the clean sample and 76 were counted in the dirty one.

Coincidences of up to four channels can be counted with the algorithm *Composition*. This enables the chemical formulation of complex inclusions or inclusion clusters. Furthermore, the possibility to check for non-coincidences in addition to coincidences helps remove ambiguities on the inclusion type. This is illustrated in the following example, where the number of Ca aluminate, Al oxide and Ca oxide inclusions were evaluated as follows:

- Al oxide (Al_2O_3): by counting Al peaks coincident with a peak on O channel and non-coincident with a peak of the Ca channel
- Ca aluminate inclusions (Al_2O_3-CaO): by counting Al peaks coincident with peaks of Ca and O channels
- Ca oxide (CaO): by counting Ca peaks coincident with a peak of the O channel and non-coincident with a peak of the Al channel

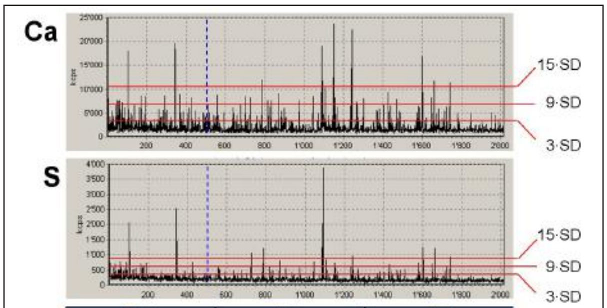


		Sample 1	Sample 2
Peaks	Al tot	40	36
	O tot	57	40
	Ca tot	124	53
	S tot	22	9
Composition	Al_2O_3	0	5
	Ca aluminate	10	2
	CaO	17	0
	CaS	20	0

Processing of intensities 500-2000

Qualitative size and size distribution

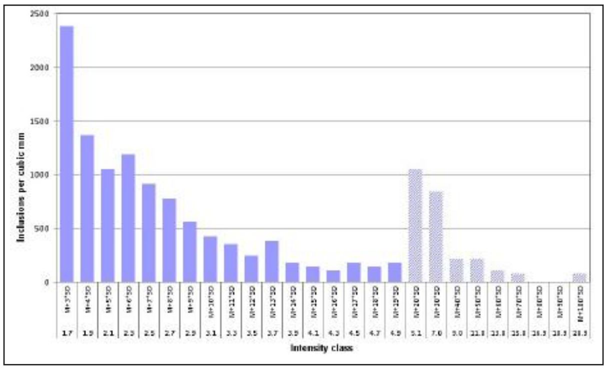
Knowing the size of the inclusions or, better, their size distribution is important, since large inclusions are normally the most detrimental to the metal quality. The two algorithms *Peaks* and *Composition* can also be used in order to count signals belonging to different intensity classes. Because the peak intensity is related to the volume of the inclusion, these classes can qualitatively be considered as size classes. Setting the threshold 3•SD above the intensity of the element in the matrix allows the counting of all visible peaks. Setting it higher, for example at 9 or 15•SD as in the following example, allows counting only the inclusions of larger size, above 9 or 15•SD respectively.



Ca tot			S tot			CaS		
3·SD	9·SD	15·SD	3·SD	9·SD	15·SD	3·SD	9·SD	15·SD
99	25	7	68	19	8	63	16	6
small	medium	large	small	medium	large	small	medium	large
74	18	7	49	11	8	47	10	6

Calculating the inclusions between consecutive threshold values provides the number of inclusions in the size class that they delimit. In the example, the number of peaks and coincidences between 3 and 9•SD correspond to small size inclusions, between 9 and 15•SD to medium size inclusions and higher than 15 to large size inclusions.

Such calculations allow generating qualitative inclusion size distributions. In the following example, the horizontal axis gives the intensity classes of inclusion signals of Ca, incremented in steps of 1•SD between m + 3•SD and m + 20•SD, and in steps of 10•SD afterwards. The vertical axis gives the number of inclusions per cubic millimeter of steel (obtained by multiplying the number of intensity peaks counted by a factor depending on the sparking conditions used). The resulting qualitative size distribution diagram can for example be used in order to compare inclusion distributions in samples of different heats.



The Spark-DAT methods also enable quantitative analysis of inclusions in terms of size and size distribution. They allow for example to calculate the average ESD (Equivalent Spherical Diameter) for size classes of various inclusions types. A separate application note (AN41244) is available with more information on the Advanced Inclusion Analysis option.

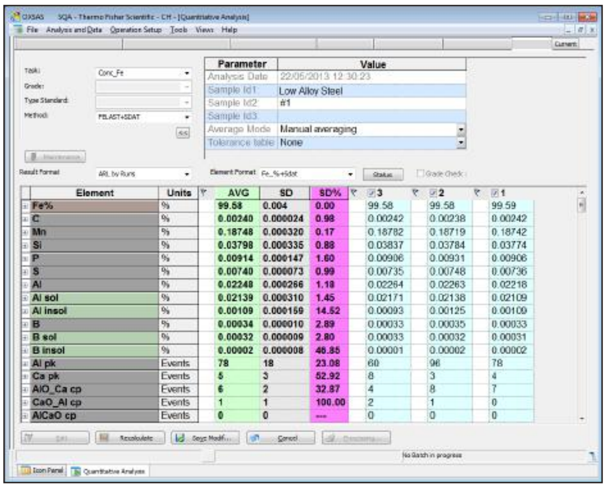
Inclusions detectable with Spark-DAT methods

Various types of endogenous and exogenous inclusions may be observed directly or indirectly in steel with the ARL iSpark spectrometer with Spark-DAT methods, e.g. oxides (Al_2O_3, MgO, CaO, MnO, TiO_2, SiO_2), spinels (Al_2O_3-CaO, Al_2O_3-MgO), sulfides (CaS, MnS, AlS) and others.

The detection of an inclusion is limited mainly by the sensitivity of the analytical lines used, by the size of the inclusion and by the concentration level of the inclusion elements as soluble elements in the matrix: higher line sensitivity and lower soluble content allow determining smaller inclusions. For example in a steel with 50ppm of Al, the smallest detectable Al_2O_3 inclusion is about 1µm diameter, while with 0.2% of Al it is about 4.5µm diameter.

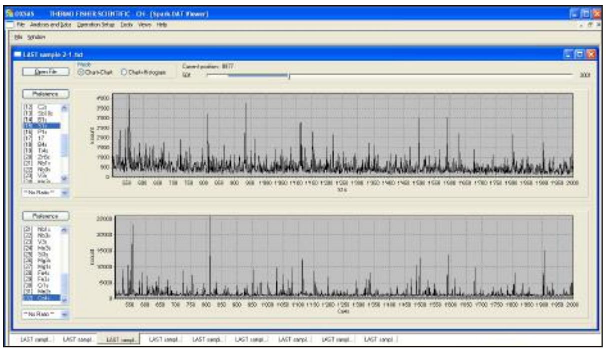
On-line analysis

The results of Spark-DAT analyzes, such as soluble or insoluble concentration, number of intensity peaks and number of coincidental peaks, can be monitored simultaneously with concentration values. The Spark-DAT results can be processed (for example used in order to calculate advanced parameters with so-called pseudo-elements), displayed, transmitted and stored like any standard OES result.



Off-line investigations

The Spark-DAT intensity data can be stored in standard text (.txt) or comma separated value (.csv) files. These files can then be used off-line for investigations on inclusions or for research and development of new methods or algorithms for instance.



They can be displayed graphically with the Spark-DAT viewer integrated in OXSAS, a very useful tool that shows sparks diagrams (pulsograms) and intensity distributions, and helps searching coincidental peaks, set-up your inclusion analysis program and refine its parameters. They can also be used as input for third party programs.

New algorithms

Our company continues to develop new and improve existing algorithms. These are available to the existing users together with OXSAS upgrades.

Conclusions

The optional Spark-DAT methods available with the ARL iSpark 8860 and ARL iSpark 8880 metals analyzer increase the versatility of the instrument. From routine use to research, Spark-DAT methods provide quick, simple and cost-effective solutions for inclusion analysis in the steel industry. Among all the inclusions analysis methods available today for the steel industry, the Spark-DAT methods are the fastest.

The simplest Spark-DAT methods allow soluble/insoluble determination, ultra-fast on-line counting of inclusions, identification of their composition and qualitative size classification in a time ranging from several seconds to a couple of minutes. This makes it highly effective for controlling inclusions and steel cleanness during production. Furthermore, the Advanced Inclusion Analysis option allows quantitative determinations of inclusion parameters, for instance size and total oxygen content (see details in AN41244).

The inclusion analysis can be combined with the standard analysis of elemental concentrations. The sample and its surface preparation, as well as the instrument maintenance and consumables, are equivalent compared to a standard OES instrument, milling being advisable in some situations. This means extremely low operation costs compared to the other inclusions analysis techniques that require dedicated instruments. In addition, the ability to obtain elemental analysis information and inclusion contents with a single OES instrument greatly reduces investment costs.

To know more on ARL iSpark Series, visit www.thermoscientific.com/ispark

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