FINISHING PROCESSES

Ultra-fast quantitative analysis of non-metallic inclusions in steel

The Thermo Scientific ARL 4460 metals analyzer is a high-end Optical Emission Spectrometer delivering ultimate performance in the analysis of steel from trace elements to alloying elements. The Spark-DAT (Spark Data Acquisition and Treatment) option considerably extends its capability beyond the analysis of elemental concentrations by enabling ultra-fast inclusion analysis.

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Optical emission spectrometry (OES) is a fast, easy to use and cost-effective analytical technique used for elemental analysis of solid steel samples in various contexts, from production to recycling, and from foundries to service laboratories. The Thermo Scientific ARL 4460 metals analyzer (see *Figure 1*) is a high-end OE spectrometer, delivering ultimate performance in the analysis of steel from trace elements to alloying elements.

The Spark-DAT (Spark Data Acquisition and Treatment) option considerably extends its capability beyond the analysis of elemental concentrations by enabling ultra-fast inclusion analysis. In the past decade, Spark-DAT enjoyed growing popularity, in particular for its ability to provide soluble or insoluble contents of elements (typically Al, B, Ca and Ti) and information on number and type of inclusions [1] during the steel production process. Recent developments further increase its attractiveness, making Spark-DAT based methods faster, higher in performance and even capable of performing quantitative determination of size or size distribution of inclusions and quantitative analysis of oxygen at concentrations even lower than 30ppm.

⊕ **Fig 1** ARL 4460 metals analyzer

PRINCIPLES

Spark-DAT is a package comprising acquisition hardware, software and algorithms included with OXSAS analytical software. The Spark-DAT acquisition is performed in parallel with the conventional one. Typically two thousands single intensity values are acquired on every channel. However, unlike the standard OES acquisition principle, where the single intensity values are integrated and transformed into a concentration, the light intensity values due to each single spark are acquired separately and submitted to special mathematical treatment. Because typically 2,000 single intensity values are acquired on every channel, the Spark-DAT raw dataset is extremely complex. Therefore, fast dedicated algorithms are used to calculate values corresponding to the information of interest. The values calculated are then supplied to the analytical

software which can handle them like conventional OES results (eg, display, print, storage and transmission).

The intensity of a Spark-DAT 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 (eg, Al_2O_3), because the Al concentration is much higher than in the metal matrix due to the contribution of the inclusion. For example, the concentration of Al in an Al_2O_3 particle is ~53%, and if an inclusion with the size of 5μm ESD (Equivalent Spherical Diameter) is contained in the ablated sample material, an apparent rise of the ▷
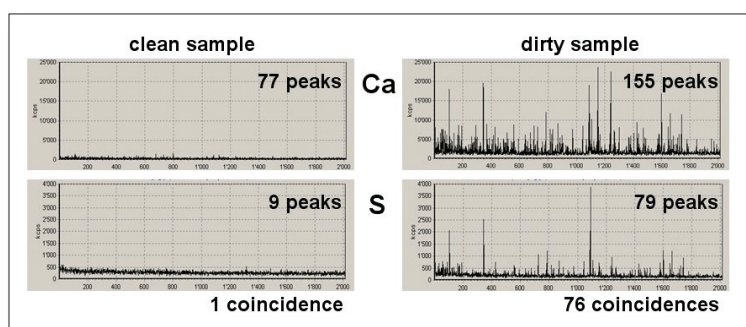
Fig 2 Illustration of Spark-DAT principles

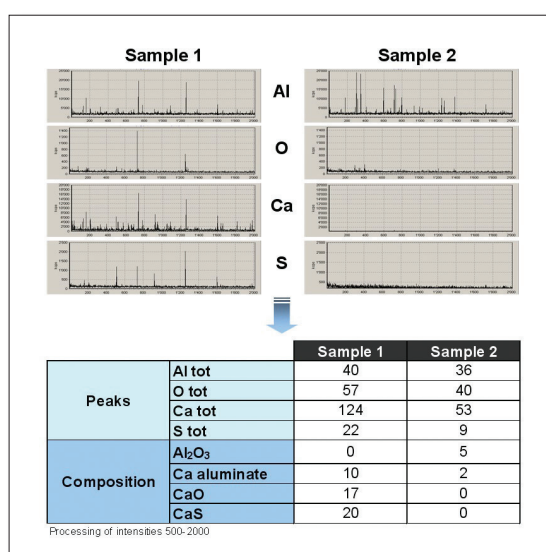Fig 3 Comparison of clean and dirty steel samples

		Sample 1	Sample 2
Peaks	Al tot	40	36
	O tot	57	40
	Ca tot	124	53
	S tot	22	9
Composition	Al₂O₃	0	5
	Ca aluminate	10	2
	CaO	17	0
	CaS	20	0

Processing of intensities 500-2000

Fig 4 Example of inclusion counting with the algorithms *Peaks* and *Composition*

concentration of 0.075% is observed. This is illustrated in *Figure 2* for Al_2O_3 inclusions in an Fe matrix.

The intensity of the 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. As a consequence, the number of peaks is related to the number of such inclusions and their intensity to factors such as the inclusion size and the concentration of Al in the inclusion.

PRACTICAL DETAILS AND BENEFITS
Inclusion analysis can be performed stand-alone in about 7secs for a single measurement. However, combined with elemental concentration analysis, it offers more possibilities, while increasing the time necessary for a single measurement to about 22secs only (against 19secs for the standard OES analysis).

The main benefits of such a short combined analysis are:

❑ Inclusion analysis during steel elaboration on most of the samples analysed normally by OES
❑ Quantitative inclusion size determinations
❑ Quantitative determination of the total oxygen content in killed steels

The standard, quick OES sample preparation can be used for Spark-DAT inclusion analysis. However, with paper grinding, the paper should be chosen in order to avoid any influence on the analysis of the inclusions of interest (eg, using SiC paper when Al_2O_3 inclusions have to be analysed). For advanced Spark-DAT, milling is necessary to guarantee quantitative results.

Other benefits of using Spark-DAT inclusion analysis are:

❑ Low investment costs, the spectrometer being sufficient for performing inclusion analysis in addition to analysis of elemental concentrations
❑ No additional cost and time for operations compared to the standard OE spectrometer. Maintenance, service and sample preparation for inclusion analysis are equivalent

EVALUATION OF NUMBER AND TYPE OF INCLUSIONS
The algorithm *Peaks* allows evaluating the number of inclusions counting intensity peaks on the channels of element present in inclusions. 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:

$$I_{peak} > m + 3 \cdot SD_{I\,matrix}$$

As shown in *Figure 3*, steel samples can easily be classified as clean or dirty according to the number of peaks counted on the channels of the inclusion elements.

The algorithm *Composition* allows counting coincidences of peaks, ie, peaks appearing on the channels of several elements consecutively to the same single spark, as illustrated in *Figure 4*. The coincidence of a peak on Ca and S channels signifies that these two elements are part of the same inclusion, very often a calcium sulfide (CaS) inclusion. Coincidences of up to four channels can be counted with this algorithm. This enables the chemical formulation of complex inclusions or inclusion clusters. Furthermore, the possibility to check for non-coincidences on top of coincidences helps removing ambiguities between inclusions that share elements, like Al_2O_3 and Al_2O_3-CaO or CaO and Al_2O_3-CaO as shown in *Figure 4*.

QUALITATIVE INCLUSION SIZE ANALYSIS

Knowing the size of the inclusions and in particular their size distribution is important because large inclusions are normally the most detrimental to metal quality. The algorithms *Peaks* and *Composition* can be used to count inclusions (signals) belonging to different size (intensity) classes. Setting the threshold 3·SD above the intensity of the element in the matrix allows us to count all the inclusions that are large enough to be detected. Setting it higher, for example at 9 or 15·SD, as in *Figure 5*, allows us to count inclusions with a larger size.

Calculating the inclusions between consecutive threshold values gives the number of inclusions in their specific size class. 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 are possible with more than three size classes. This allows generating inclusion size distribution diagrams that are qualitative, but can be extremely useful for example in order to compare the inclusion distributions in samples of different heats.

QUANTITATIVE INCLUSION SIZE ANALYSIS

Nowadays, measurements of inclusion size and size distribution are normally performed by techniques such as optical microscopy and scanning electron microscopy (SEM/EDX). However, the methods are time-consuming, taking typically 2-4hrs per analysis in a very competent laboratory.

The algorithm QuIC (Quantification of Inclusion Content) enables quantitative analysis of inclusions in term of size and size distribution. With it, average ESD of inclusions belonging to several size classes can be calculated.

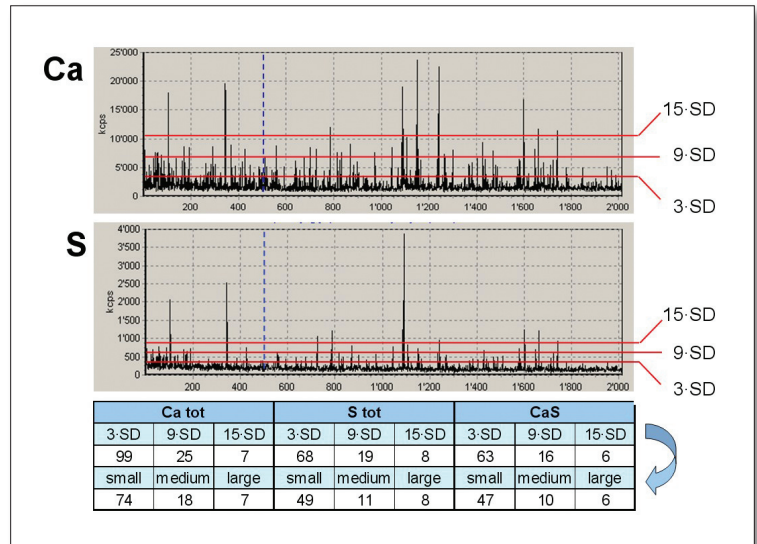*Figure 6* presents an example of size distribution

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

⊕ **Fig 5** **Example of inclusion counting using different threshold values**

diagram, based on the application of the QuIC algorithm and size calculation method for several production samples.

Other parameters, such as the surface fraction Sf (see *Figure 7*), of a given inclusion type and the total oxygen content, can also be calculated from the results of the algorithm QuIC.

QUANTITATIVE ANALYSIS OF OXYGEN

Due to the relatively low sensitivity of the analytical line, the standard routine quantitative analysis of total oxygen by OES is currently semi-quantitative below 60ppm and very limited below 30ppm. In the steel industry, oxygen at very low concentration is therefore normally analysed by dedicated combustion analysers.

For killed steels treated with the typical deoxidisers (Al, FeSi, FeMn and Ca, etc.) this type of size determination is quantitative, because most of the oxygen is insoluble, more precisely, in the form of oxide inclusions. With Spark-DAT the total oxygen concentration can therefore be calculated directly from the amount of oxygen contained in the oxide inclusions obtained with QuIC.

The method is quantitative and determines the oxygen concentration by OES well below 30ppm, as demonstrated in *Figure 8*, which compares results obtained with those of a combustion analyser for low alloy steel samples taken from the casting mold (*samples and combustion results with permission of R Dumarey and F Medina, ArcelorMittal, Gent, Belgium*). ▷
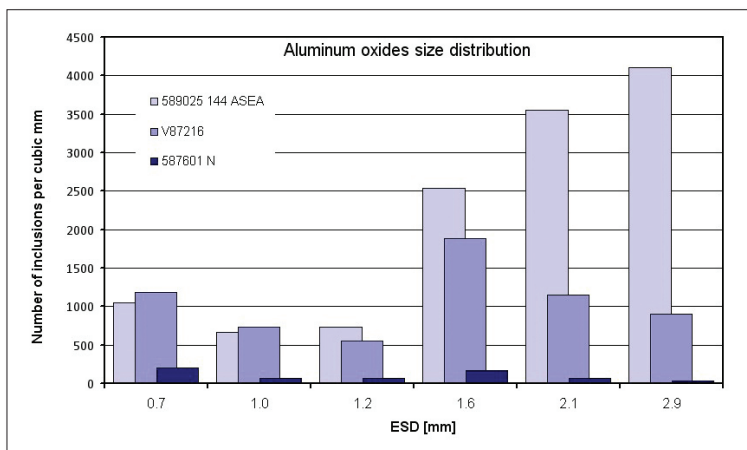
Fig 6 Example of size distribution of Al_2O_3 for three alloy steel samples
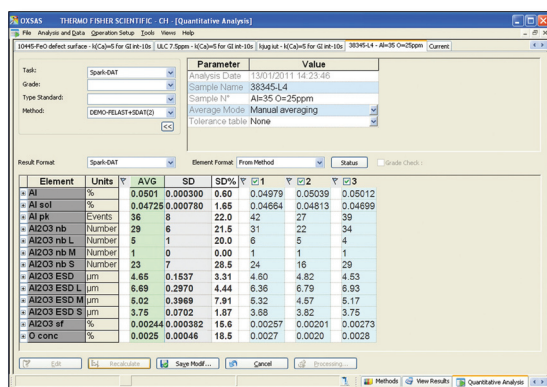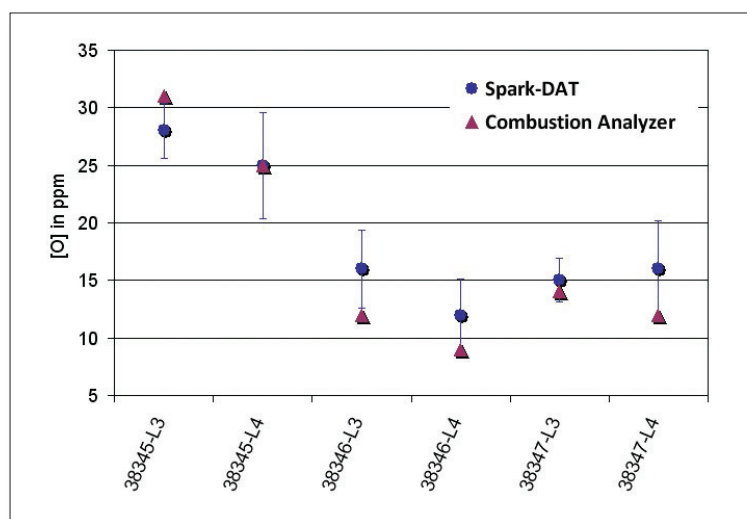

Fig 7 Example screen display

Fig 8 Comparison of Spark-DAT and combustion analysis results for samples coming from the casting mold

INCLUSIONS QUANTIFIABLE WITH SPARK-DAT

Various endogenous and exogenous inclusions can be observed directly or indirectly in steel using the ARL 4460 with Spark-DAT, eg, oxides (Al_2O_3, MgO, CaO, MnO, TiO_2, SiO_2), spinels (Al_2O_3-CaO, Al_2O_3-MgO) and sulfides (CaS, MnS, AlS). Detection of an inclusion type is limited mainly by the sensitivity of the analytical lines used, the size of the inclusion and the concentration of the inclusion elements as soluble elements in the matrix: higher line sensitivity and lower soluble content determine smaller inclusion ESDs. For example, for a steel containing 50ppm of Al the minimum detectable ESD is about 1μm, while for 0.2% of Al the minimum is 4.5μm.

CONCLUSIONS

The Spark-DAT option of the ARL 4460 metals analyzer increases the versatility of the OE spectrometer. From routine use to research, Spark-DAT provides quick, simple and cost-effective solutions for inclusion analysis in the steel industry. Among all the inclusion analysis techniques available today, the Spark-DAT based methods are the fastest. It allows ultra-fast online counting and identification of inclusions, determining their size and total oxygen content, ranging from several seconds to a few minutes, making it highly effective for controlling inclusions and steel cleanness during production. The sample and its surface preparation, as well as instrument maintenance and consumables, are equivalent to a standard OES instrument, milling being required for quantitative analysis. This signifies extremely low operating costs compared to other techniques that need dedicated instruments. Also, the ability to obtain elemental analysis information and inclusion contents with a single OES drastically reduces investment and operating costs.

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REFERENCE

[1] J-M Böhlen & R Yellepeddi, "Combined quantitative analysis and ultra-fast analysis of non-metallic inclusions by optical emission spectrometry", *Millennium Steel 2009*, pp167-171

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