Optical emission spectrometry for control of cleanness during steelmaking

Thermo Electron's ARL 4460 optical emission spectrometer offers the highest performance and the broadest capabilities in the field of OES. It analyses trace elements and inclusions simultaneously, thus enhancing the steelmakers' capability for on-line steel cleanness assessments.

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There is increasing demand for special steels that have better mechanical performance or have longer life under critical conditions. Such steels are especially useful to industries dealing with demanding applications such as the automotive, aerospace, nuclear, off-shore and pipeline industries. A common concern of the industries that produce or use these steel products is the cleanness that helps guarantee these special properties. Early knowledge of cleanness during steelmaking is, therefore, of great importance to steel producers.

Fig.1 The ARL 4460 automated with the SMS-2000

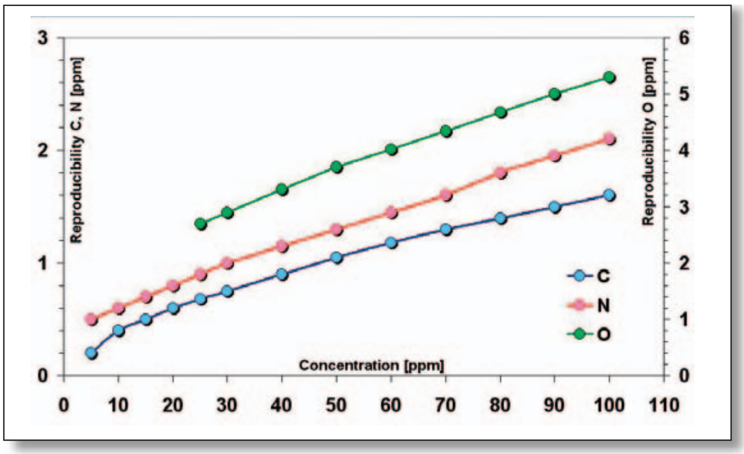
STEEL CLEANNESS

Traditionally only steels that had low levels of oxide and sulphide inclusions were considered to be clean. Nowadays, the definition of clean steel depends on the steel grade and its end use. Cleanness has generally a much wider significance, including control of many unwanted trace elements and inclusions. The concentration of impurity elements such as C, H, N, O, P and S should be reduced or controlled, as they have, individually or together, dramatic effects on steel mechanical properties, such as strength, formability, toughness, weldability, cracking resistance, corrosion resistance and fatigue resistance. In the case of car body sheet, for instance, C, N and O must be typically lower than 20ppm each. Increasingly, limits are being set for other trace elements such as As, Sn, Sb, Se, Cu, Pb, Nb and Bi.

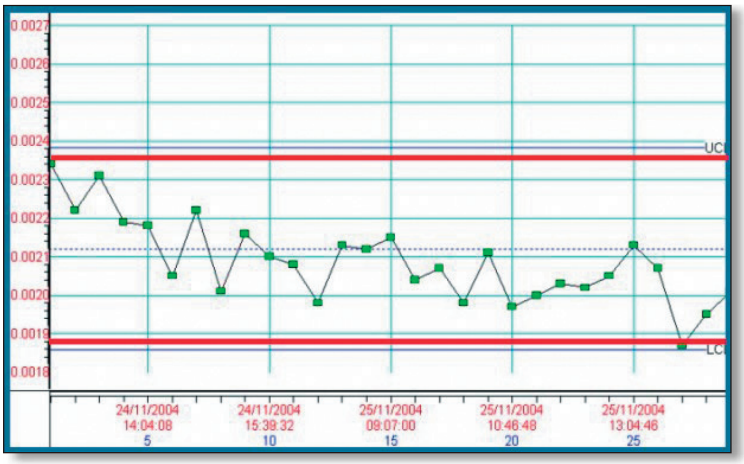
While the presence of inclusions with a well-defined composition can sometimes be beneficial (eg, MnS inclusions improve the machinability of steels and TiC inclusions allow precipitation strengthening of low carbon steels), for most steel grades the presence of inclusions increases the number of defects and has a deleterious effect on their physical and mechanical properties. For instance, inclusions like aluminium oxides are often initiation points of fatigue cracks, therefore, size, distribution, morphology and composition of the inclusions have to be controlled. In general, the fewer the number of inclusions the better, and large macro-inclusions must not be present as they are the most harmful to mechanical properties and can also affect casting and rolling. In practice each steel product has its cleanness standard defined by the requirements on its properties and economic arguments.

OPTICAL EMISSION SPECTROMETRY (OES)

OES is a standard method, traditionally used during steel manufacture, to determine elemental concentrations. It is robust, simple to use, cost-effective and can accurately measure the concentration in steels of more than 30 alloying and trace elements in less than a minute. This includes most of the elements relevant to cleanness. For low concentrations of C, N and O, however, other methods such as combustion analysis were often preferred to OES thereby resulting in higher analysis costs. The Thermo Electron ARL 4460 high performance OES is particularly ▷



Ⓐ **Fig.2 Typical reproducibility values (1σ) of C, N and O below 100ppm**



Ⓐ **Fig.3 Stability over 24 hours of N at 21ppm for sample SUS B6**

Detection limit ppm	C	N	O	P	S
ARL 4460 typical	0.4	1.5	8	0.3	0.7
ARL 4460 guaranteed	<1	<3	<25	0.8	1.3
ARL 3460 typical	5	3	40	1.9	1.5

Table 1 Typical and guaranteed DL of some elements important to cleanness

well adapted for cleanness control during the steelmaking process, following significant progress in its capability for analysis of C, N and O.

The ARL 4460 This spectrometer (see *Figure 1*) is equipped with special features ensuring fast elemental analysis with high analytical performance. The patented Current Control Source (CCS) and Time Resolved Spectrometry (TRS) provide significant advantages compared to other OESs. The CCS is the only spark source on the market that allows the shape of the discharge to be tailored according to the specifics of the matrix and of the elements to be analysed. TRS allows integration of the signals during the best time window of the individual sparks, hence this time-gated acquisition makes it possible to optimise sensitivity, precision and accuracy, and reduce interference on the analytical lines.

The ARL 4460 can be further equipped with the Spark-DAT (Spark Data Acquisition and Treatment device), sometimes referred to as Pulse Discriminated Analysis (OES-PDA), and which allows the acquisition of the signal spark by spark. Signals from the individual sparks are not integrated as with conventional acquisition, but are stored separately for special processing. With the Spark-DAT, the ARL 4460 has the ability to simultaneously conduct inclusion detection and bulk analysis.

ELEMENTAL ANALYSIS

The new Detection Limits (DL) and reproducibility values obtained with the ARL 4460 fulfill the latest analytical requirements of the most demanding steel producers. The precision and accuracy of C and N analysis are at least as good as that obtained with other reference techniques. *Table 1* presents the DL of C, N, O and some other elements important to cleanness, as measured on the ARL 4460. The values are between 2 and 10 times better than those of a standard ARL 3460 OES. These results show that fully quantitative analysis, ie, above the lower limit of quantification (LLQ), typically defined as about 5 times the DL, can be performed as low as typically 2ppm for C and 7.5ppm for N. This is excellent, considering the numerous potential sources of contamination such as impurities in argon (traces of O_2, H_2O, N_2, H_2, CO, CO_2 and organic molecules), and massive presence of these elements in the air (about 78% N_2 and 21% O_2).

The reproducibility values of C, N and O below 100ppm are displayed in *Figure 2*. The lowest concentration is the LLQ, so that only quantitative analysis is considered. Guaranteed values are 1.5 times higher. Reproducibility values of 0.6ppm for C and 0.8 for N at concentration of 20ppm or 1.1ppm for C and 1.3 for N at 50ppm are excellent and fulfill the current demands of steel producers. The improved reproducibility and DL also have a positive effect on the accuracy of the analysis of low concentrations, as illustrated in *Table 2* for N analyses performed on certified reference samples. In this table, the accuracy is illustrated by the Delta parameter – the difference between certified and average concentrations – which is always smaller than u, the uncertainty value of the sample certificate.

Instrument stability is excellent, a prerequisite for the utilisation of this method in steel production, and is demonstrated in *Figure 3*. All the values are within the interval of ±2 times the guaranteed reproducibility value (between the red lines).

Sample	NBS 1765	NBS 1762	NBS 1764	NBS 1761	NBS 1763	BAS 404/1	BAS 405/1
Individual runs	0.0011	0.0023	0.0021	0.0046	0.0046	0.0103	0.0112
	0.0010	0.0022	0.0023	0.0047	0.0045	0.0103	0.0110
	0.0010	0.0020	0.0024	0.0045	0.0047	0.0107	0.0111
	0.0010	0.0023	0.0024	0.0045	0.0045	0.0102	0.0107
	0.0009	0.0020	0.0024	0.0047	0.0048	0.0102	0.0113
						0.0102	0.0113
Ave conc'n	0.0010	0.0022	0.0023	0.0046	0.0046	0.0103	0.0111
SD	0.00007	0.00013	0.00012	0.00011	0.00013	0.0002	0.0002
RSD	6.7	6.2	5.2	2.4	2.7	2.0	2.2
Certified conc'n	0.0010	0.0022	0.0023	0.0044	0.0044	-	-
U certificate	0.0003	0.0003	0.0004	0.0003	0.0003	-	-
Delta	0.00001	0.00004	-0.00002	-0.0002	-0.0002	-	-

Table 2 Results of N analyses in reference samples covering the range shown in *Figure 2*

INCLUSION ANALYSIS

Non-metallic inclusions have many origins and can be endogenous or exogenous. The first type corresponds to inclusions produced by chemical reactions such as alumina (Al_2O_3) that are formed when aluminium is added for deoxidation. The second type are typified by slag particles carried along with steel during transfer between steelmaking vessels, and loose dirt or refractory brickwork. Different sorts of inclusions can appear all through the steelmaking process, hence several techniques are needed to control or characterise these inclusions. Scanning Electron Microscopy (SEM), metallographic microscope observation, ultrasonic scanning and Liquid Metal Cleanness Analyser (LIMCA) are some of the techniques available. Their main drawbacks are that analysis takes a long time and they are costly.

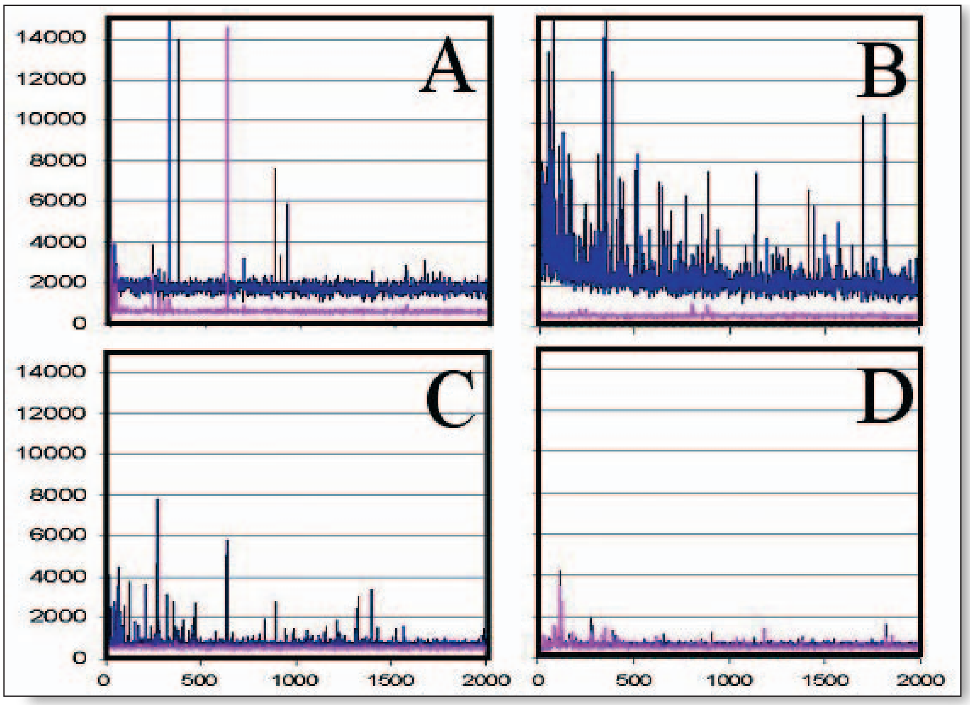


Fig.4 Spark-DAT acquisition of Al and Ca in a low alloy steel sample

Spark-DAT, although not as exhaustive as some other methods, enables fast on-line evaluation of micro inclusions only a few minutes after sample taking. Compared to most other methods it scans a large surface in a short time, which is particularly important when inclusions are not homogeneously spread throughout the sample, or when rare inclusions have to be detected. The evaluation is performed on the same instrument as the one already used for quality control, so providing cost savings. The ARL 4460 also offers simple and efficient automation possibilities, when coupled with the ARL SMS-2000 (sample manipulation system).

An example of how Spark-DAT can be used in production is shown in *Figure 4*. The spark diagrams of Al (blue) and Ca (red) channels were measured on samples taken at different stages of the deoxidation process of a low alloy steel. Each diagram shows the 2,000 individual intensities measured during sparking. Intensity is proportional to the concentration of Al or Ca at the place hit by the corresponding spark. The ground signal is proportional to the concentration of the element in the matrix, whereas a peak corresponds to a place where the elemental concentration is higher, typically a place where an inclusion is located. The number of peaks, related to the ▷

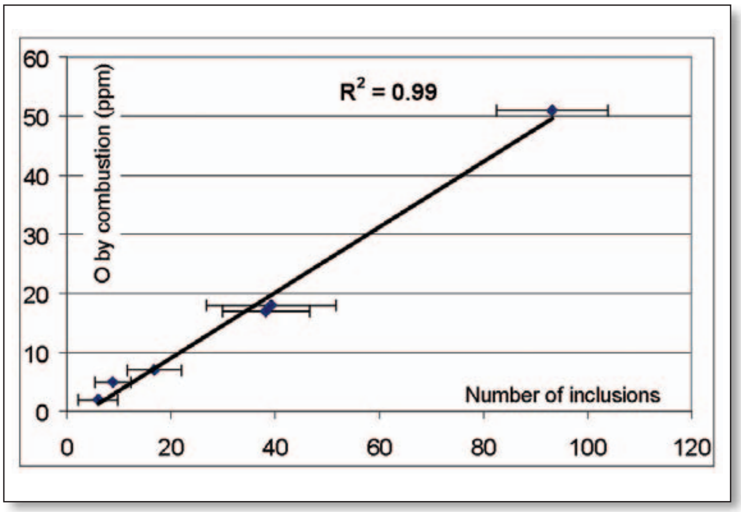


Fig.5 Correlation of oxygen concentration measured by combustion analysis with number of Spark-DAT oxide inclusions

number of inclusions, and their height related to factors such as the inclusion size and the stoichiometry of Al in the inclusion, are used in a comparative method for cleanness assessment.

In sample A, taken before any addition of metallic Al, 22 Al peaks were counted. In sample B, taken just after the first addition, the count reported 171 Al peaks. Al was added to remove the oxygen dissolved in the steel by forming Al_2O_3 particles and, as expected, more inclusions were detected in B than in A. These inclusions were then eliminated by migration into the slag. Sample C was taken just after a second addition of Al. In this sample, 97 Al peaks were counted, which were also smaller than after the first treatment due to less soluble oxygen being present at this stage. In the final product D, only 41 peaks were found because most of the newly formed Al oxides had migrated into the slag. Again, the peaks are smaller than in the previous sample, because most of the soluble oxygen was removed. The final product is considered clean, with the smallest oxygen content and the least and smallest Al inclusions.

Spark-DAT analyses allows the count of inclusion peaks or correlations of peaks appearing simultaneously on two to four element channels. (*Figure 4D* illustrates this. In this case correlations between Al and Ca peaks can be observed – strong evidence of the presence of Ca aluminate inclusions.) These simple numbers can often be correlated with other techniques normally used to determine characteristics or properties that are affected by the presence of inclusions (eg, fatigue tests).

Thus, Spark-DAT offers the potential to replace on-line complex, expensive or time-consuming techniques. An interesting example is the use of Spark-DAT for the indirect analysis of oxygen.

INDIRECT DETERMINATION OF OXYGEN BY SPARK-DAT

Most of the oxygen in solid steel is in the form of oxide inclusions such as oxides of aluminum, calcium and magnesium. Its concentration is thus related to the amount of such inclusions present in the sample. By counting these oxide inclusions, Spark-DAT can lead to excellent correlations between the oxygen concentration measured by combustion and the number of oxide inclusions found. This is illustrated in *Figure 5*.

The success of this method depends on several factors such as how the sample is taken and the uniformity of the distribution of oxide inclusions. Good correlations are naturally obtained when inclusion types and relative population distributions are similar in all the samples. In *Figure 5* only bearing steel samples from the same production were considered. Since the samples were inhomogeneous regarding inclusion distribution, eight runs had to be performed to obtain this excellent correlation. The method clearly allows oxygen determinations lower than the limit of quantification obtained with the standard OE analysis.

CONCLUSIONS

The ARL 4460 is extremely well suited for cleanness assessments during steel manufacture. The combination of three state-of-the-art technologies (Spark-DAT, CCS and TRS) provides the ARL 4460 spectrometer with the highest performance and the broadest capabilities in the field of OES. Most of the elements that are critical to cleanness, including low C and N, can be quickly, accurately and reproducibly analysed. The Spark-DAT provides the ARL 4460 with the unique ability to perform fast evaluations of non-metallic inclusions during steel production. Spark-DAT results may be considered as comparative, or additionally, may be correlations of Spark-DAT results with the results of other techniques, measuring properties or characteristics of steel that depend on the inclusion contents can be attempted. This allows the replacement of long and costly analysis techniques by a method performed simultaneously with traditional optical emission analysis.

The ARL 4460 equipped with Spark-DAT has also a wide range of applications outside of the production environment, making it an extremely interesting tool for research and development. **MS**

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