

CNO Option - Analysis of Low C, N and O in Steels by Optical Emission

ARL 4460 Metals Analyzer

Key Words

- ARL 4460
- C, N, O
- Optical Emission
- Steels

Introduction

Significant progress has been realized in the analysis of low concentration C, N and O in steels by optical emission spectrometry. The concentration of these elements, as well as those of P, S and H should be reduced to obtain so-called “clean steels”, or controlled, as they have - individually or together - dramatic effects on steel properties, such as strength, formability, toughness, weldability, fatigue resistance, etc. For car body sheets for instance, C, N and O must be typically lower than 20 ppm each. The constant amelioration of steel cleanness being necessary to produce always improved and more competitive steel products, there is a demand for quantitative analysis at lower and lower levels. The new performance obtained with the ARL 4460 fulfills the latest analytical requirements of steel producers regarding C, N and O.

ARL 4460 Metals Analyzer

The patented Thermo's Current Control Source (CCS) of the ARL 4460 presents significant advantages in comparison to any other spark generator used in OES (Optical Emission Spectrometry). The computer controlled current waveform provides a high degree of flexibility in selection of parameters that enables optimization of the sensitivity.



Thermo's Time Resolved Spectrometry (TRS) offers important features in comparison to other acquisition systems. Selecting the appropriate time window for integrating the light emitted by the individual sparks allows data acquisition with the best sensitivity, precision and reduction of spectral interference.

The ARL 4460 Metals Analyzer can quantitatively determine about 40 elements in irons and steels. With the

CNO option, a typical analysis is performed in less than fifty seconds. Analytical performance of low C, N and O obtained with this option is detailed in this application note. Performance of these elements at higher levels and on the other elements can be found in application summary AN 41220 “Analysis of Iron and Steel by Optical Emission – ARL 4460 Metals Analyzer”. It is the case also for P and S that are now offered in the standard analysis as they were in the former “CNOPS option”. H still cannot be measured satisfactorily in steels by OES.

CNO option

The CNO option includes:

- A mechanically improved analysis stand minimizing the various contaminations that are critical for these three elements
- The most sensitive analytical lines
- Special photomultiplier tubes

Sample preparation

Paper grinding is possible in most of the cases, but for lowest C and O levels, milling is recommended. Simple and reasonable care must be taken during and after sample preparation, e.g.:

- The prepared surface must be flat in order to avoid air penetrating in the stand during the analysis
- Grinding paper change at well defined time intervals
- Exposure of sample surface to dust must be avoided
- Avoid touching the prepared surface

Sample analysis time

The analysis time, from the start of the analysis to the display of the result, is 22 s.

Factory calibration

The ARL 4460 equipped with the CNO option can be factory calibrated for micro-alloyed steels with the best reference samples available on the market. For C, N and O, the following calibration ranges are given:

- C from 4.5 to 900 ppm
- N from 9 to 200 ppm
- O from 75 to 1000 ppm

Improved performance obtained with the CNO option is also beneficial for the standard low alloy steel calibration, where downwards extensions of C, N and O calibrations are possible. Please contact your nearest Thermo office for more details on the calibrations with the CNO option.

Performance guarantee

The precision values shown in the graphs of the next sections are typical values. Values guaranteed by Thermo when using homogeneous samples and recommended sample preparation are 1.5 times higher.

The precision is calculated from the formula:

$$SD (1\sigma) = \pm \sqrt{\frac{\sum_{i=1}^{i=n} (X_i - \bar{X})^2}{n - 1}}$$

where:

- X_i the individual readings
- \bar{X} the arithmetic mean of the individual values
- n the number of determinations

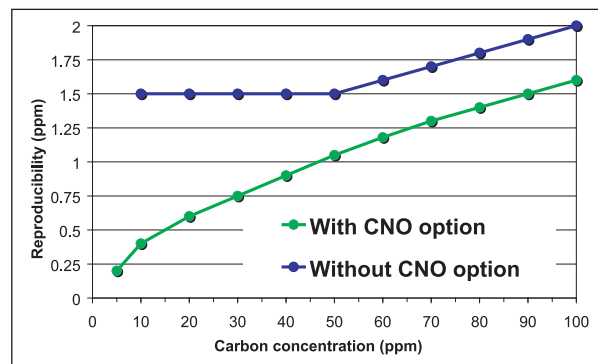
The DL (Detection Limit) is defined as three times the standard deviation of the background of a pure iron sample expressed in concentration units. The guaranteed DL (Detection Limits) is calculated at the 95% confidence limit.

The values will be updated as improvements are announced. Please contact your nearest Thermo office or consult our web site at www.thermo.com/elemental for the most recent values.

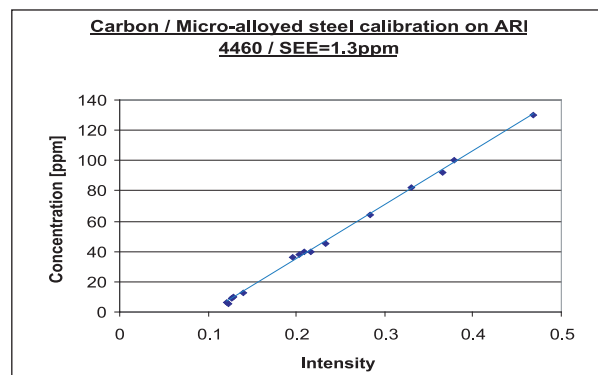
Precision is only one part of providing accurate analyses. Other factors include the accuracy and the quality of the calibration standards. These are achieved through the development of the calibration curve relative to a specific analytical task.

Carbon analysis

The typical DL is 0.4 ppm (2 ppm without CNO option) and the guaranteed DL 1 ppm (5 ppm without CNO option). The figure below shows the improvement in precision obtained for C below 100 ppm with the CNO option:



The next example illustrates the accuracy of the factory calibration:

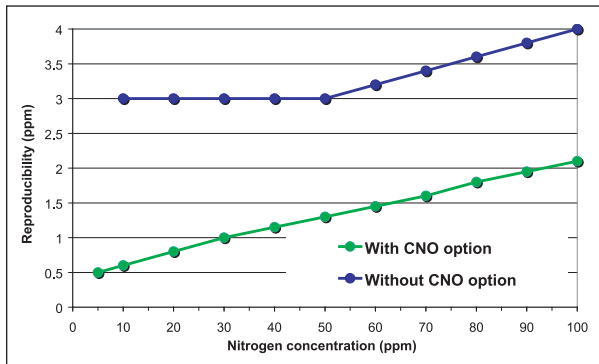


Excellence of the accuracy is also demonstrated in the following table, where the residual (difference between measured and certified concentration) is always smaller than 3 times u .

REFERENCE MATERIAL	CERTIF. CONC. [PPM]	UNCERTAINTY u [PPM]	MEASURED CONC. [PPM]	ABS. VAL. RESIDUAL [PPM]
JSS 1005	9.6	0.3	8.8	0.8
BS 50E	10	3	6.5	3.5
BS 50C	12	4	6.7	5.3
JSS 1007	23.6	0.3	23.9	0.3
JSS 1001	37.4	0.2	37.4	0
BS LC5	108	6	104	4
BAS 431	190	9	192	2
BS 250	220	10	203	17
BS XAAS	410	11	426	16
BS 233	710	17	723	13
BS 3972	1950	19	1898	52
BS 4971	2510	21	2465	45

Nitrogen analysis

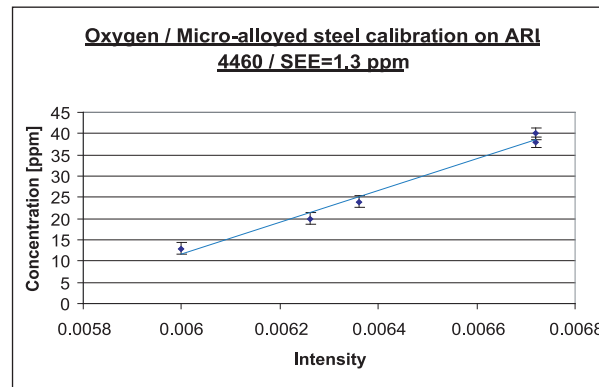
The typical DL is 1.5 ppm (2.7 ppm without CNO) and the guaranteed DL 3 ppm (4.5 ppm without CNO option). The next figure shows the improvement in precision obtained for N below 100 ppm with CNO option.



The example shown below illustrates the accuracy of the factory calibration. In this case also the residual is always smaller than 3 times u.

REFERENCE MATERIAL	CERTIF. CONC. [PPM]	UNCERTAINTY u [PPM]	MEASURE D CONC. [PPM]	ABS. VAL. RESIDUAL [PPM]
BS 234	13	2.1	13.2	0.2
BS 50C	19	4	13.2	5.8
BS 250	24	2.1	24.8	0.8
BS XAAS	37	2	38.5	1.5
BS231	45	1.9	41.9	3.1
BS230	48	3	42.6	5.4
BS232	56	3.7	50.9	5.1
BS3972	65	2.2	63.8	1.2
BS2932	80	3	78.0	2.0
BS50E	92	10	89.0	3.0
BS4971	99	5.4	97.6	1.4
BS233	107	4.3	107.6	0.6

The example shown below illustrates the accuracy of the factory calibration:



The next table illustrates it numerically:

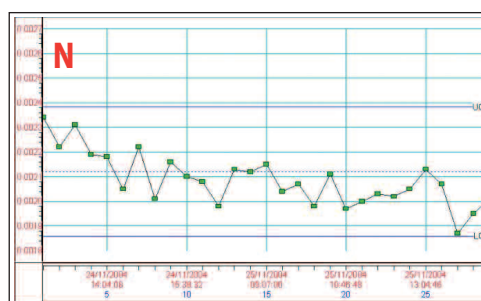
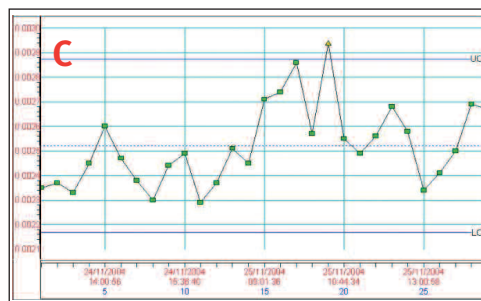
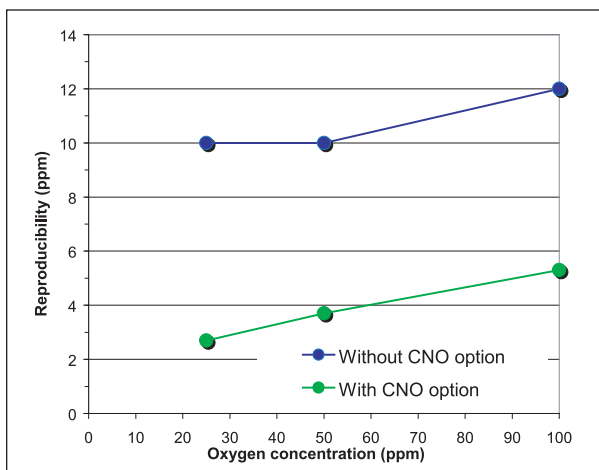
REFERENCE MATERIAL	CERTIF. CONC. [PPM]	UNCERTAINTY u [PPM]	MEASURE D CONC. [PPM]	ABS. VAL. RESIDUAL [PPM]
BS 230	24	3.1	21.1	2.9
BS 231	38	7.8	34.0	4.0
BS 3972	38	3.6	30.6	7.4
BS 4971	40	4	27.5	12.5
BS XAAS	235	20	176	59
BS 50E	239	10	183	56
BS 50C	540	15	555	15
BS 250	570	14	551	19

Stability

Stability of the instrument is of the utmost importance when performing routine analysis. Mid-term stability measured over one day shows that the standard deviation achieved is below two times the guaranteed precision value, which is excellent. The following examples show the typical stability over 24 hours of carbon at 25 ppm and nitrogen at 21 ppm. The values almost never went outside the 95 % confidence interval (delimited by red lines) which is ± 2.1 ppm for C and ± 2.4 ppm for N.

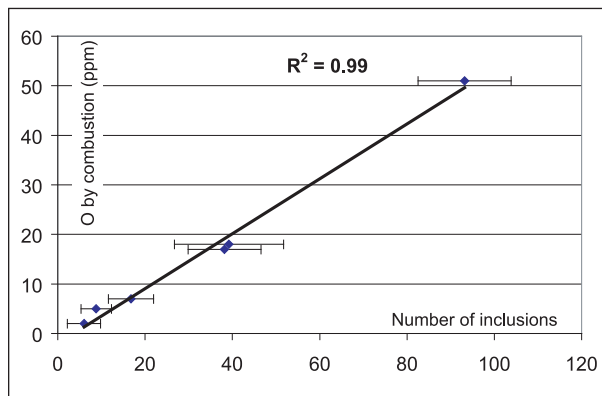
Oxygen analysis

Oxygen is the most difficult element to measure due to contamination. The typical DL is 8 ppm (20 ppm without CNO option) and the guaranteed value 25 ppm (30 ppm without CNO option). The figure below shows the improvement in precision obtained for O with CNO option:



Oxygen analysis with Spark-DAT

The CNO option can be combined with the Spark-DAT option (see application note 41232 “Spark-DAT option – On-Line Single Spark Acquisition and Treatment - ARL 4460 Metals Analyzer”). In steel oxygen is mainly present in the form of oxides (of Al, Mg, Ca, Si...). Therefore it is possible to quantify the oxygen content in a steel sample by evaluating the number of oxygen-containing inclusions it contains. For some bearing steels for example, an excellent correlation was found between the oxygen measured by combustion and by Spark-DAT (see graph below).



In this case, the preparation of the samples and the decontamination of the spectrometer are greatly simplified. Potentially lower levels of oxygen can also be measured than with the traditional method. Please contact your nearest Thermo office if you are interested in oxygen detection at lower levels than those described in this application note.

Benefits

Thanks to the CNO option and to the best possible use of digital excitation and acquisition technologies of the ARL 4460, the main requirements of the steel market regarding the analysis of the elements C, N and O at low concentrations are met:

- A high level of repeatability
- A very accurate analysis
- A short analysis time

The CNO option is the best opportunity to provide a more efficient control of steel production:

- The analysis is faster than with traditional combustion analyzers
- Time is saved, as all the elements, even ultra-low C and N, are analyzed on a single instrument
- Necessary investments and operating costs are reduced compared to combustion analysis
- Optical emission spectrometers are easier and cheaper to automate

In addition to these offices, Thermo Electron Corporation maintains a network of representative organizations throughout the world.

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