Analysis of Iron, Steel, Nickel and Cobalt Alloys with Thermo Scientific ARL iSpark 8820 FeNiCo2 Optical Emission Spectrometer

Dr Jean-Marc Böhlen, Thermo Fisher Scientific, Ecublens, Switzerland

Key Words

ARL iSpark, iron, steel, nickel, cobalt, superalloys, optical emission, OES, metal analyzer, dual CCD/PMT optics

Goal

Perform reliable and fast quantitative determination of trace and alloying elements in solid iron and steel, nickel and cobalt alloy samples

Introduction

For over 80 years, our company has set the standard of quality for spectrochemical analysis of metals. Throughout these years, performance, stability, reliability and longevity have been the key attributes of our optical emission spectrometers. The Thermo Scientific™ ARL iSpark™ 8820 metals analyzer combines these guiding principles with our experience and technical innovation to bring our customers the complete value based solution they have come to expect from our company.

The ARL iSpark 8820 will determine all the elements necessary in your current and future applications, in all possible qualities of iron and steel, nickel and cobalt alloys.

It is the answer to your analytical needs, whether for incoming goods control, metal sorting, process QC, final product QC, certification or investigation. Working 24 hours a day and 7 days a week, the ARL iSpark 8820 Metals Analyzer delivers dependable performance year after year. Specific performance is detailed in this application note.

ARL iSpark 8820 - Experience and innovation

The ARL iSpark 8820 is based on Thermo Scientific famous one-meter PMT spectrometer in Paschen-Runge mounting operated under vacuum. The spectrometer offers optimal resolution and stability, and ensures outstanding performance for all the critical elements. The instrument is equipped with an additional spectrometer with a high performance, scientific grade tri-linear CCD (Charge Coupled Device) detector.

Together the two spectrometers compose a unique dual PMT/CCD optics that significantly increases the analytical capability of the instrument.

Other highly innovative features and technologies characterize further the instrument, among which:

- Advanced PMT and CCD signal acquisition and processing for improved performance and accuracy
- IntelliSource, a digital spark source with increased flexibility and efficiency
- Spark stand with improved design to reduce maintenance and minimize argon consumption during the analysis
- ECOmode and super ECOmode allowing significant argon savings when the instrument is idle
- Optimal design increasing the instrument functionality

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ARL iSpark 8820 FeNiCo2 - Detection limits (3 σ) and precision values (1 σ) for iron matrix

ELEMENT	Al	As	B	Bi	C	Ca	Ce	Co	Cr	Cu	Mg	Mn	Mo	N
Typical DL	1	0.9	0.2	1.4	3	0.2	2	7	8	7	0.3	8	19	5
Guaranteed DL	1.3	1.3	0.4	1.8	5	0.4	3	9	11	9	0.4	11	25	8
Level %	Precision													
0.001	0.00006	0.00005	0.00003	0.00006	0.00006	0.00006	0.00012				0.00005			0.00012
0.002	0.0001	0.00006	0.00004	0.0001	0.00008	0.0001	0.00015	0.0002		0.00015	0.00008			0.00015
0.005	0.00018	0.00008	0.00006	0.00015	0.00015	0.0002	0.00025	0.0003	0.0003	0.00015	0.0002	0.0004		0.0002
0.01	0.00028	0.0001	0.00008	0.0002	0.0002	0.0003	0.0004	0.0004	0.00035	0.00025	0.0003	0.0005	0.0005	0.00025
0.02	0.0004	0.00016	0.00012	0.00035	0.0004	0.00045	0.0005	0.0005	0.0004	0.00035	0.0007	0.0006	0.0009	0.00035
0.05	0.0007	0.0003	0.0002	0.0006	0.0007		0.001	0.0006	0.0005	0.0006	0.0015	0.001	0.0013	0.0007
0.1	0.001	0.00045	0.00026	0.0009	0.001		0.007	0.0008	0.0007	0.001	0.0025	0.0012	0.002	0.0012
0.2	0.002	0.0005			0.0014			0.002	0.0014	0.0015	0.004	0.002	0.0022	0.002
0.3	0.0025				0.002			0.0023	0.0017	0.002		0.003	0.003	0.003
0.5	0.004				0.003			0.0025	0.0025	0.003		0.0035	0.004	0.004
1	0.008				0.004			0.005	0.0035	0.0045		0.006	0.006	0.006
2	0.013				0.008			0.01	0.005	0.007		0.01	0.008	
3					0.012			0.012	0.006	0.01		0.015	0.014	
4					0.014			0.015	0.007	0.011		0.018	0.022	
5					0.016			0.02	0.01	0.012		0.02	0.026	
10								0.03	0.02			0.035	0.04	
20									0.035			0.05		
30									0.045					
40									0.06					

ELEMENT	Nb	Ni	P	Pb	S	Sb	Si	Sn	Ti	V	W	Zn	Zr
Typical DL	8	20	0.6	1.4	0.5	2	17	1.1	2	12	5	1	6
Guaranteed DL	10	25	1	1.8	1	3.5	25	1.5	4	15	8	1.5	8
Level %	Precision												
0.001			0.00003	0.00005	0.00004	0.00005		0.00005	0.00012			0.0001	
0.002			0.00006	0.00008	0.00008	0.00008		0.00006	0.0002		0.0003	0.00015	0.0002
0.005	0.0004		0.0001	0.00015	0.00015	0.00012	0.0004	0.0001	0.0003	0.0004	0.0003	0.0002	0.00035
0.01	0.0005	0.0004	0.00015	0.0003	0.0003	0.0002	0.0005	0.00015	0.0005	0.0005	0.0003	0.0003	0.0005
0.02	0.001	0.0005	0.0002	0.0005	0.0005	0.0003	0.0007	0.00022	0.0007	0.0006	0.0003	0.0004	0.0007
0.05	0.0013	0.0006	0.0005	0.001	0.001	0.0006	0.0012	0.00035	0.0013	0.001	0.0004	0.0007	0.0012
0.1	0.002	0.0008	0.0009	0.002	0.002	0.0008	0.0014	0.0005	0.0017	0.0012	0.0006	0.001	0.0025
0.2	0.003	0.0012	0.0015	0.008	0.004	0.002	0.002	0.001	0.0025	0.0015	0.001		0.004
0.3	0.0035	0.0015	0.002	0.012	0.006	0.003	0.0025	0.002	0.0035	0.002	0.0015		
0.5	0.006	0.0021	0.005				0.003		0.005	0.0025	0.0025		
1	0.01	0.0033	0.008				0.005		0.01	0.005	0.005		
2	0.03	0.007					0.009		0.02	0.01	0.01		
3	0.035	0.01					0.013			0.012	0.015		
4	0.042	0.013					0.018			0.015	0.02		
5		0.014					0.02			0.02	0.023		
10		0.03								0.035	0.04		
20		0.06									0.07		
30		0.08									0.09		
40		0.10											

- Homogeneity of the elements depends on the metallurgical structure obtained through the sampling procedure (cast, forged or rolled) and on the metallurgical history including mechanical deformation by forging or rolling and heat treatments. These values apply when homogeneously distributed elements are present in samples which are prepared by recommended sample preparation methods. A measured precision higher than the guaranteed precision indicates, with a probability higher than 95%, that the element is segregated or has an inhomogeneous distribution over the sample's surface.
- The precision values (given in percent) are typical instrumental repeatability. The guaranteed precision values are 1.5 times higher.
- The detection limits (given in ppm) and the precision values are based on ten repeated measurements.
- Guaranteed DLs are calculated at 95% confidence limit.
- The values are valid for ARL iSpark 8880 instruments with the same configuration. For ARL iSpark 8880 instruments, with different PMT lines and grating, the performance may vary slightly.

ARL iSpark 8820 FeNiCo2 - Detection limits (3 σ) and precision values (1 σ) for nickel matrix

ELEMENT	Al	B	C	Co	Cr	Cu	Fe	Mg	Mn	Mo	Nb
Typical DL	5	0.1	4	6	2.5	2.5	15	0.1	0.4	12	2.5
Guaranteed DL	10	0.15	6	10	4	4	20	0.3	0.9	16	4
Level %	Precision										
0.001		0.000025									
0.002		0.000042						0.000091			
0.005		0.000084	0.000093	0.00049				0.0002			0.00077
0.01	0.00011	0.00014	0.00017	0.00061				0.00035	0.00041		0.0012
0.02	0.00022	0.00024	0.00033	0.00077	0.0016	0.00054		0.00063	0.00063	0.0015	0.0018
0.05	0.00053	0.00048	0.00076	0.001	0.0024	0.00089		0.0014	0.0011	0.0021	0.003
0.1	0.001		0.0014	0.0013	0.0034	0.0013	0.0042	0.0024	0.0017	0.0027	0.0046
0.2	0.002		0.0027	0.0016	0.0048	0.0019	0.0059	0.0044	0.0027	0.0035	0.0069
0.5	0.0049		0.0063	0.0022	0.0076	0.0031	0.0092		0.0048	0.0049	0.012
1	0.0097		0.012	0.0027	0.011	0.0045	0.013		0.0075	0.0086	0.018
2	0.019			0.0071	0.012	0.0066	0.018		0.012	0.016	0.027
5	0.046			0.016	0.029	0.018	0.028		0.021	0.035	0.047
10				0.03	0.056	0.032	0.039			0.065	0.071
20				0.055	0.11	0.057	0.054			0.12	
30					0.16	0.079	0.065			0.17	
40						0.1	0.075			0.22	

ELEMENT	P	Pb	S	Si	Sn	Ta	Ti	V	W	Zr
Typical DL	0.4	0.6	0.7	2.5	0.5	6	1.7	3.5	15	6
Guaranteed DL	0.6	1	1.2	5	1	10	3	5	18	8
Level %	Precision									
0.001										
0.002	0.000038				0.000042					0.00055
0.005	0.000098	0.00024	0.00024		0.000065					0.00079
0.01	0.00018	0.00041	0.00043		0.00012	0.00011	0.00069			0.001
0.02	0.00033	0.00069	0.00078	0.00073	0.00018	0.00021	0.00088	0.00063	0.00077	0.0014
0.05	0.00074		0.0017	0.00097	0.00036	0.0005	0.0012	0.001	0.00094	0.002
0.1			0.0031	0.0012		0.00098	0.0016	0.0015	0.0011	0.0026
0.2			0.0056	0.0022		0.0019	0.003	0.0022	0.0013	0.0033
0.5			0.012	0.0047		0.0046	0.0068	0.0037	0.0015	0.0047
1				0.0083		0.009	0.013	0.0054	0.0018	
2				0.015		0.018	0.023		0.01	
5				0.031			0.053		0.027	
10										
20										
30										
40										

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- The precision values (given in percent) are typical instrumental repeatability. The guaranteed precision values are 1.5 times higher.
- The detection limits (given in ppm) and the precision values are based on ten repeated measurements.
- Guaranteed DLs are calculated at 95 % confidence limit.
- The values are valid for ARL iSpark 8880 instruments with the same configuration. For ARL iSpark 8880 instruments, with different PMT lines and grating, the performance may vary slightly.
- The limit of detection for Fe can be improved if another brush than steel brush is used.
- The concentration range covered in this table represent the overal range of our specific calibrations. It should be noted that a specific calibration may exhibit a narrower range.

ARL iSpark 8820 FeNiCo2 - Typical detection limits (3 σ) and precision values (1 σ) for cobalt matrix

ELEMENT	Al	B	C	Cr	Cu	Fe	Mn	Mo	Nb
Typical DL	2	0.2	2.4	7.5	4	6	3	16	4
Level %	Precision								
0.001		0.000026							
0.002		0.000036							
0.005		0.000055							
0.01		0.000075							
0.02	0.00077				0.00071			0.0015	0.0013
0.05	0.0011		0.0021		0.00097		0.00096	0.0018	0.0015
0.1	0.0015		0.0028		0.0012	0.0042	0.0013	0.0021	0.0017
0.2	0.002		0.0036			0.0054	0.0018	0.0024	0.0032
0.5	0.003		0.005			0.0074	0.0028	0.003	0.0077
1	0.004		0.0064			0.0095	0.0038	0.0075	0.015
2	0.0053		0.0083			0.035	0.0052	0.015	0.03
5						0.05		0.037	0.072
10								0.073	
20				0.055					
30				0.082					
40				0.11					

ELEMENT	Ni	P	Pb	S	Si	Sn	Ti	V	W
Typical DL	7	0.5	0.2	0.35	8	0.4	6	11	6
Level %	Precision								
0.001			0.000042						
0.002		0.000071	0.000066			0.000071			
0.005		0.00017	0.00012	0.00014		0.00011			
0.01		0.00033	0.00019	0.00028		0.00015	0.00038	0.00065	
0.02		0.00064	0.00029	0.00057		0.0002	0.0005	0.00087	
0.05		0.0015	0.00053	0.0014		0.0003	0.00072	0.0013	0.00081
0.1					0.0019	0.00041		0.0017	0.001
0.2	0.0025				0.0025			0.0023	0.0013
0.5	0.0041				0.0036			0.0033	0.0018
1	0.0058				0.0048				0.0023
2	0.018				0.0064				0.028
5	0.032								0.044
10	0.05								0.063
20	0.077								0.089
30	0.099								
40									

- Homogeneity of the elements depends on the metallurgical structure obtained through the sampling procedure (cast, forged or rolled) and on the metallurgical history including mechanical deformation by forging or rolling and heat treatments. These values apply when homogeneously distributed elements are present in samples which are prepared by recommended sample preparation methods. A measured precision higher than the guaranteed precision indicates, with a probability higher than 95%, that the element is segregated or has an inhomogeneous distribution over the sample's surface.
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- The limit of detection for Fe can be improved if another brush than steel brush is used.
- The concentration range covered in this table represent the overal range of our specific calibrations. It should be noted that a specific calibration may exhibit a narrower range.

Dual CCD/PMT optical system

On the ARL iSpark 8820, selection of PMT or CCD type of detectors is made for each element according to the principle "best of both technologies" in order to guarantee optimal performance for every element. For example, PMTs are used for the most critical elements, which allows their determination down to low trace levels.

In addition, the CCD spectrometer offers flexibility for extension of analysis capabilities.

Finally, the CCD spectrometer has a continuous spectral coverage that offers unique capability for spectral investigations, making it a precious tool for metal research.

IntelliSource digital spark source

The Thermo Scientific intelliSource is a double current controlled source (CCS), the most innovative excitation source for Spark-OES. More flexible than the other digital sources, it allows discharge shapes to be tailored for most efficient control of the sample surface preparation, material ablation and light emission in various metal matrices. Matrix-optimized pre-integration sparks significantly reduce the effects of matrix and metallurgical structure (in re-melting the sample surface before the integration spark), which improves the accuracy of the analysis.

Other innovative features contribute to the performance of the intelliSource, e.g. DISC (Discharge Interrupt by Short-Circuit) that improves the repeatability in trace analysis.

Time Gated Acquisition (TGA) for PMT channels

TGA is a high precision version of the TRS (Time Resolved Spectroscopy). The acquisition is performed during TGA windows, i.e. very short time windows synchronized with the single sparks. Optimized start and duration of the window allow collecting the signal of interest when unwanted signals (e.g. noise, high background emission or spectral interference) have minimal deleterious effect. This results in lower detection limits and better precision values. In some cases, TGA also reduces the need for interference correction, therefore improving accuracy.

PTM signal processing

The signals integrated during the TGA windows are digitized for each individual spark. Several signal processing methods contribute to the performance with the PMTs:

- The algorithm FAST (Flexible Acquisition STart/stop) allows acquiring an optimal subset of single spark intensities - the most steady part of the signal - for each channel
- The algorithm DISIRE (DIffuse Spark Intensities REmoval) improves precision by discarding abnormally low intensity signals

CCD signal acquisition and processing

Different techniques and methods are applied in order to improve performance with the CCD of the ARL iSpark 8820. Simultaneous read-out of the 3 lines of the CCD (binning) and dynamic dark current subtraction enhance the signal to noise ratio. Spectrum alignment and digital resolution enhancement are performed automatically during every acquisition to maximize precision, accuracy and long-term stability.

Sample preparation

The sample is generally prepared by using a grinding machine (e.g. stone grinding for cast irons and paper for steels, nickel and cobalt alloys). Milling machines are also recommended for some critical qualities in order to avoid any residual contamination by the abrasive material of the grinding machine.

Sample analysis time

The analysis time taken between the start of the analysis and the display of its result is in average the following:

Material analyzed / Type of analysis	Time [s]
Steels (without N)	21
Steels (with N)	26
Cast iron and high alloy cast iron	29
Free-cutting steel	58
Ni alloys without N	26
Stellites	26

Performance guarantee

Our company guarantees the precision and the detection limit (DL) as shown on pages 2 to 4.

The precision expresses the closeness of the concentration values of the individual runs of an analysis. The lowest the precision value, the smallest the number of runs needed for high confidence in the average result.

The DL is the smallest concentration that can be distinguished from a blank value with a given probability. It is defined as three times the standard deviation of the background expressed in concentration units. For quantitative analysis, however the lower limit of quantification (LLQ ≈ 3•DL) must be considered. The LLQ is also the lowest possible value in our calibration menu, when calibration standards availability allows calibrating down to this point.

Accuracy and factory calibration

The accuracy is the most important figure of merit of a spectrometer. It expresses the agreement between the result and the reference value. It depends on the quality of the reference materials used for calibration, on some instrumental attributes and parameters (e.g. the optical resolution, the spark source condition or the TGA window) and on the mathematical model used to calculate the calibration curves. The ARL iSpark 8820 is individually calibrated in our factory. The calibrations are performed by using thoroughly tested and well accepted certified reference materials (CRM's) and reference materials (RM's). The calibration curves are established utilizing CARL (Calibration ARL), a very sophisticated multi-variable regression (MVR) software tool that corrects for matrix effects as well as spectral interferences and ensure the highest possible accuracy. The same MVR is included in OXSAS analytical software for on-site calibration.

Calibration summary

- For iron and steel, our company provides a Global Iron calibration (including all qualities except for Free Cutting Steel), as well as calibrations for the analysis of Low Alloy Steel, Free Cutting Steel, Chrome Steel (ferritic stainless steel), Chrome-Nickel Steel (austenitic stainless steel), Manganese Steel, High Speed Steel, Cast Iron (including Nodular Iron and Ni-hard), High Alloy Cast Iron and Nickel Resist.

- For nickel alloys analysis, a general sorting Ni calibration that covers the analysis of Hastelloy, Incoloy, Inconel, Nimonic and Monel alloys, as well as the specific calibrations for the analysis of these alloys are available
- For cobalt alloys analysis, a Stellite calibration is available.

Our calibrations are delivered as turn-key, fully parameterized applications. Setting-up samples (SUS) are delivered with the instrument to maintain the accuracy of the calibration. Please contact your nearest Thermo Fisher Scientific office for more specific information on our calibrations.

Based on the calibration curves and the repeatability of the measurements, the measurement uncertainty can be displayed for each sample. A specific Product Specification is available.

Insoluble

The optional Insoluble Spark-DAT method is used to determine the concentration of the insoluble or soluble fraction of Al and B in low alloy steel. It does not need special skills from the operator and it advantageously replaces costly wet chemistry.

Stability

Stability of the instrument is of the utmost importance when performing routine analysis. High stability reduces the frequency for maintenance and drift correction operations.

Mid-term stability tests over 2-5 days show typical standard deviation below two times the guaranteed precision value, which is excellent.

Memory effects

The memory effect is defined as the number of runs necessary to reduce the apparent concentrations of elements after measuring high alloyed samples, such as stainless steels. For the ARL iSpark 8820 the electrode is completely cleaned and the instrument will measure very low concentration of the alloying elements after 5 runs.

Conclusion

The ARL iSpark 8820 provides not only state-of-the-art technology, but also has all the total system features which meet the critical needs of the metals analysis markets:

- Unmatched hardware for stability and reliability
- Exceptional performance in detection limits, precision, accuracy, stability and memory effects, all this in minimum analysis time
- Most advanced software technology
- Potential to cover your future analytical needs
- Easy operation by unskilled worker or research scientist
- Widest range of metals analysis
- Advanced technical/service support.

All these features allow you to optimize your productivity and to achieve the shortest payback times:

- Your investment costs are reduced by:
  - Exceptional instrument lifetime and continuous upgrade possibilities (software and hardware)
  - Instrument capability to cover your future needs
- Your production costs are reduced by:
  - More accurate and reproducible analyses made available faster
  - Increased instrument availability thanks to its high stability and less frequently required drift corrections
- Your operating and maintenance costs are reduced by:
  - Low consumption of drift correction samples and simple maintenance
  - Significant argon savings during analysis and in stand-by
- Your overall cost management is reduced by:
  - Optimum utilization of materials
  - Extremely low running costs compared to other methods

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

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Africa-Other +27 11 570 1840
Australia +61 2 8844 9500
Austria +43 1 333 50 34 0
Belgium +32 53 73 42 41
Canada +1 800 530 8447
China +86 10 8419 3588
Denmark +45 70 23 62 60
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Finland /Norway/Sweden +46 8 556 468 00
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India +91 22 6742 9434
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Middle East +43 1 333 50 34 0
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South Africa +27 11 570 1840
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Switzerland +41 21 694 71 11
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