OPTIMAL CAST IRON MELT CONTROL WITH OES



HITACHI

Inspire the Next

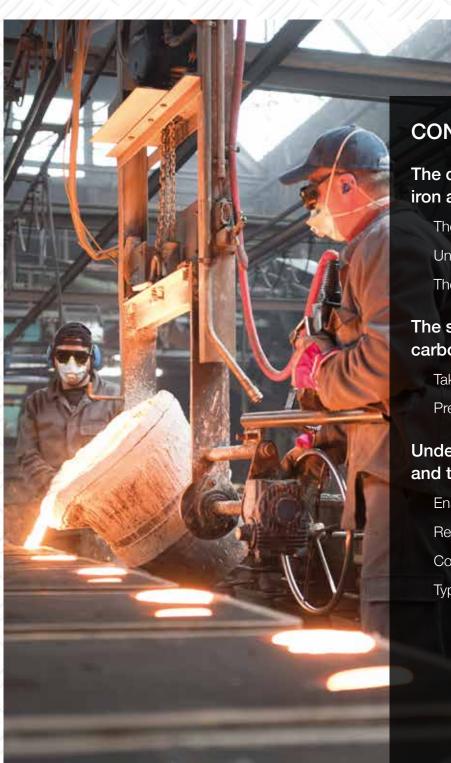
HOW TO ACHIEVE OPTIMAL MELT CONTROL IN CAST IRON WITH OES ANALYSIS INTRODUCTION

2016 saw global casting production hit around 104,4 million tonnes. Malleable iron makes up 70% of all castings, with the remaining 30% comprising steel castings and non-ferrous metal castings, such as aluminium, copper, zinc, magnesium and others.

Of the roughly 50,000 foundries around the world, approximately 20,000 produce cast iron.

These foundries rely on optical emission spectrometry (OES) in production control throughout the melting process. The exact chemical composition of the alloy being manufactured needs to be checked throughout the melt process to ensure the quality of the finished product meets specification.

In cast iron production, this has traditionally been a costly undertaking requiring multiple processes. However today's OES technology is primed to deliver accurate and reliable one-step quality control throughout the process. Here Hitachi High-Tech product manager Wilhelm Sanders explains how this can be achieved.



CONTENTS

The challenges of cast iron analysis	04	Maintaining your OES analyser
The problem		Verifying burn spots
Understanding the issue		Analysing your sample: top tips
The solution		Control samples
The secret to perfect OES carbon analysis: sample prep	07	Type standardisation
Taking the perfect sample Preparing your sample		Editing the sample identification dialogue
Understanding calibration and type standardisation Ensuring stability	10	Grade verification/identification Optional charge correction Report generator
Recalibration Control samples		Making process control audits safe
Type standardisation		Making spark OES your first choice
		Contact us

03

18

22

25

27

28



THE CHALLENGES OF CAST IRON ANALYSIS

THE PROBLEM

While OES technology is an effective way of analysing elements at low limits of detection, such as sulphur, boron and carbon, cast iron presents more of a challenge.

Operators often struggle to get the required results quickly and in a cost effective manner.

I UNDERSTANDING THE ISSUE

Ductile cast iron requires carbon formation in special grain forms in order to get the right mechanical properties (such as ductility, tensile and yield strength, and impact resistance). Ductile cast iron needs a nodular formation of free graphite, which is typically achieved by the addition of nodulising elements such as magnesium, cerium or tellurium.

However, this desired grain formation of nodular free carbon flakes is what creates the challenge for analysis.

Gray cast iron (laminar carbon formation)*

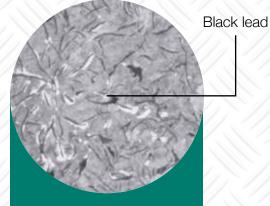


Photo one Stereo microscope photo of gray cast iron (X100)

Ductile cast iron (Nodular carbon formation)**

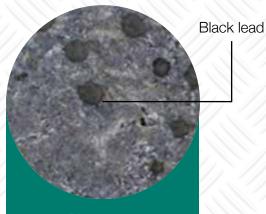


Photo two Stereo microscope photo of ductile cast iron (X100)

OES uses a high-energy pre-spark sequence to excite the metal sample properly and create a stable, accurate and homogenised sample surface.

This pre-spark sequence is necessary in order to condition the plasma and to ensure that the emitted light of the atoms in the sample can be read out consistently at a stable level.

Without this sequence, reproducible results cannot be achieved. However, the pre-spark method also makes the accurate determination of the carbon content in ductile, gray and malleable cast iron much more difficult by burning away some of the free carbon. This could lead the OES system to record the carbon content as being lower than it is. To combat this problem, bigger iron foundries turn to additional methods to accurately determine the total amount of carbon in the sample, such as combustion and thermal analysis. However, these methods tend to add operational costs. The ideal solution would be to use one analysis method.

Ductile cast iron needs a

formation of free graphite

**Microstructure and mechanical properties of CuNiMo austempered ductile iron / Erić O., Jovanović M., Šidjanin L., Rajnović D. / 2004 / Journal of Mining and Metallurgy, 40B, (1), p. 11-19

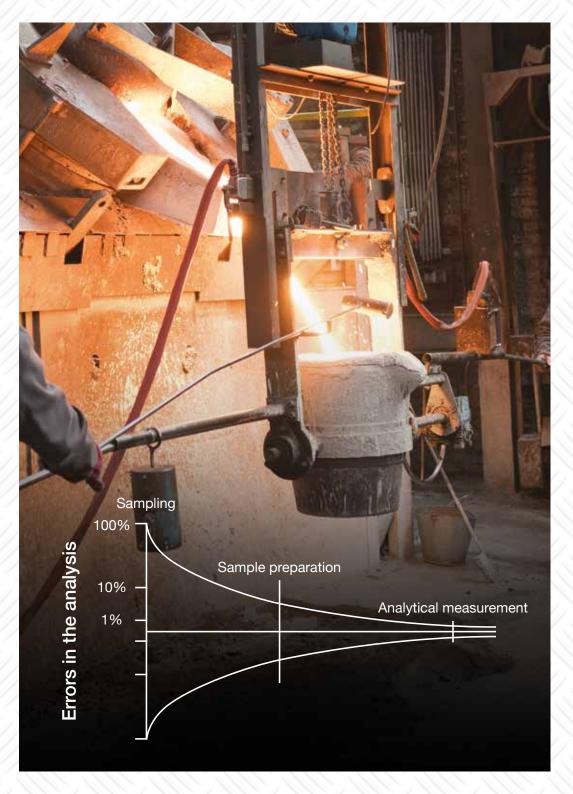
THE SOLUTION

OES is capable of accurately determining carbon, as well as other elements, such as manganese, phosphorus, sulphur, chromium and nickel, and nodulising or inoculating elements. Operators can achieve one step quality control, while streamlining costs in a few simple steps.

Here is a guide to achieving trustable and accurate results by avoiding errors during sample taking and preparation and optimising the way you work with your OES analytical equipment.

The sample stage

is most important for accurate results





THE SECRET OF PERFECT OES CARBON ANALYSIS: SAMPLE PREP

TAKING THE PERFECT SAMPLE

White solidification (where carbon is dissolved in as homogenous a fashion as possible) is a necessity for OES.

Gray solidification, where nodules form in the casted sample, must be avoided to achieve the best homogeneity for carbon.

To get the best sample:

- Avoid catching any slag when taking the sample.
- Cool the sample quickly (up to 50°C/s).
- Make sure the moulds are completely made of thermal conductive material (e.g. copper).
- Keep the moulds clean so that crust formations from previous samples do not slow the cooling process.
- Keep the sample diameter and height to a minimum (remember to leave enough space for a minimum four focal spots: Ø: 25–30 mm, height: few mm).

Alternatively, you could use an immersion probe. Commonly used in steel production, immersion probes expose the sample taker to less risk and can eliminate common traditional spoon sampling problems, such as:

- Cold shuts due to interrupted sample casting.
- Catching slag.
- Partial gray solidification due to contaminated material.
- immersion probes also drastically reduce sample preparation time.
- The most important factor here is the cooling time. Taking too long is likely to cause the formation of nodules that prevent accurate carbon reading. You can see these with the naked eye as cloudy darker shadows on the sample surface.

PREPARING YOUR SAMPLE

If your metal to be

analysed is steel, nickel, cobalt or titanium based, grinding machines with grinding paper are the right choice for sample preparation.

Typically, aluminium oxide (corundum) is used, but if low aluminium concentrations have to be determined, zirconium oxide or silicon carbide is a good alternative. The grain size should always be in the 40–80 µm range. Another common mistake is not changing the grinding paper regularly enough. Ideally, you should do this after every 5–10 samples. If you are changing to a different alloy, you must replace the grinding paper in order to avoid cross-contamination.

Today, steel is often milled to eliminate contamination and to determine gases such as oxygen and nitrogen. Cast and pig iron samples are typically prepared with grindstones or cup wheels. In these instances, grinding wheels that are not self-dressing need to be dressed periodically in order to achieve optimum surface results for samples.

Nonferrous materials like aluminium, copper, zinc as well as those with lower melting points such as lead and tin need to be prepared with a milling machine or a turning lathe. It is important to ensure that the

sample's surface is completely metallic without any remaining oxides or other inclusions.

Avoid cross contamination left from previous samples.

Heat input should be minimised too in order to keep the effects of chemistry from tarnishing your sample too badly.

UNDERSTANDING CALIBRATION AND TYPE STANDARDISATION

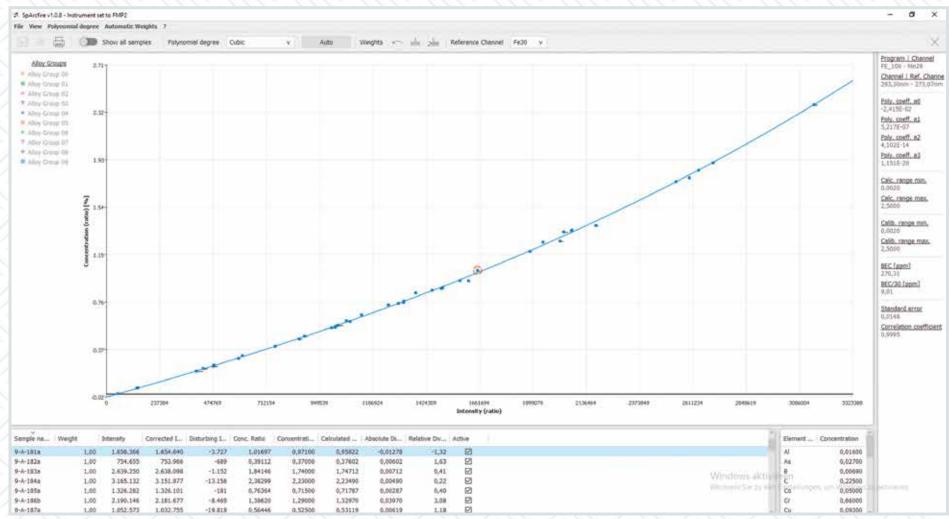
OES is a fast and accurate analysis method but also very sensitive.

There are a few essential verification, maintenance and recalibration tasks that can help you to make sure that your analyser is performing at its optimum level.

OES uses a relative measurement instead of an absolute measurement, meaning that the parameters (absorption, voltage, etc.) are dependent on the concentration or quantity of the analysed substance. The value of the measurement parameter to the concentration or quantity is set through a calibration with the certified reference materials (CRMs). Without this calibration, OES would only measure light intensity, instead of performing any kind of quantitative chemical analysis.

CRMs are huge databases of credited reference materials and are obligatory for accredited and certified test and calibration laboratories in quality assurance. Based on a huge number of samples and tests, CRMs create calibration curves for the elements that the OES user wants to determine. Example of a certificate of analysis:





Example of a calibration curve:

ENSURING STABILITY

The sensitivity of your spark spectrometers to environmental parameters means that instruments are often not stable over the long term and may be subject to drift.

The primary causes of instrument instability are:

- Ageing components affecting sensitivity.
- Contaminated optical planes (lenses and windows of the spectral system).
- Dependence on fluctuating external factors, such as air pressure and temperature, or the composition of the supplied gas (min. argon 4.8), which may fluctuate.
- A modification of the transmission depending on the construction type (change of purging gas or vacuum level).
- Shocks caused by the position of the instruments and its robustness.

Efforts to minimise these effects typically fall into two main camps. Some manufacturers opt to select materials that are less likely to suffer elongation due to temperature changes, while others focus on trying to stabilise temperature and pressure.

Total wavelength coverage between 130-800 nm Hitachi High-Tech take a different route. Our OES systems use a more efficient, more cost-effective and smarter approach. Our optics have total wavelength coverage between 130 and 800 nm. This makes it possible to

monitor and correct any drift occurring due to a change in dispersion caused by a temperature or pressure change by using the unique peak positioning alignment system.

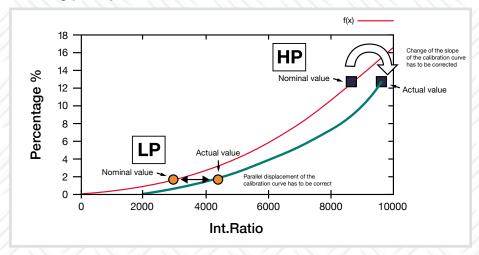
This smart algorithm determines and monitors the spectral positions of all relevant channels, automatically and directly correcting them if necessary during each analysis.

RECALIBRATION

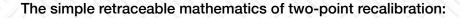
While our smart system elongates the long-term stability of our systems significantly, it does not eliminate the need for regular recalibration to combat the loss of transparency of optical planes over time due to contamination.

Recalibration is a valuable correction method to restore stability in your OES system. The spectrometer data undergoes changes over time as the additive and/or multiplicative changes impact instrument sensitivity and begins to alter the calibration curve in the linear scale of the coordination system.

These changes are corrected through normalisation, so as to always use the original calibration. The OES system also needs to be standardised on a regular basis to re-establish the status of the calibration. Accuracy is of paramount importance here, as the reliability of future analysis will be influenced.



Working principle of recalibration:



$$IntLP_{nominal} = Faktor * IntLP_{actual} + Offset$$

$$IntHP_{nominal} = Faktor * IntHP_{actual} + Offset$$

$$Faktor = \frac{IntLP_{nominal} - IntHP_{nominal}}{IntLP_{actual} - IntHP_{actual}}$$

$$Offset = \frac{IntLP_{nominal} * IntHP_{actual} - IntHP_{nominal} * IntLP_{actual}}{IntHP_{actual} - IntLP_{actual}}$$

CONTROL SAMPLES

In the past, recalibration was often carried out after a predefined time interval or after a predefined number of measurements. This practice is still used by some operators today. Set of control samples:

SUS

In fact, the only truly reliable method of ensuring the reliability of your OES system is to analyse control samples.

Control samples should be similar in their composition to the material you will be analysing, homogeneous and verified by different chemical methods regarding their accuracy.

Using control samples verifies the analysis of a similar unknown sample. It also checks that the spectrometer's performance is still holding up after defined periods or after a certain number of measured samples.

When preparing your control samples, make sure that:

- Vou have sufficient quantity to avoid fundamentally modifying the analysis method.
- They are easy to measure with the spectrometer in their shape and manageability (Ø: ca. 40–60 mm; height: 40–60 mm).
- You only use recently prepared samples (grind iron and similar material; non-ferrous material milling sample preparation).
- The samples match the material property of the analytical sample.

Once you have checked the accuracy and functionality of the system with CRMs, enter the recently prepared new control sample into the spectrometer's database for control samples. The sample should be measured at least ten times and the standard deviations recorded.

If you need to, you can repeat this precision test on different days. Use the average value of the established twofold and threefold standard deviation to determine the tolerance.

With this method, you will not only determine if your spectrometer needs recalibration but will also ensure (for audits) that it is working at the desired level of performance and delivering good, trustable results.



Statistical process control (SPC) chart of a control sample

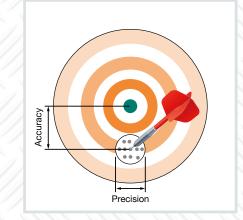
TYPE STANDARDISATION

If your analyser is not meeting the required level of accuracy for any unknown materials, type standardisation may be necessary.

There are a number of reasons you could be seeing deviations in accuracy, despite your OES system being calibrated with a large number of CRMs. CRMs are mostly synthetically manufactured, so they might not correspond to the matrix of the analytical sample, in terms of either composition or sample structure. Alternatively, the material to be analysed might deviate in its composition strongly from the matrix's basic material.

Other common reasons include the accuracy requirements being higher than the calibration of the instrument can deliver and spectrometer drift.

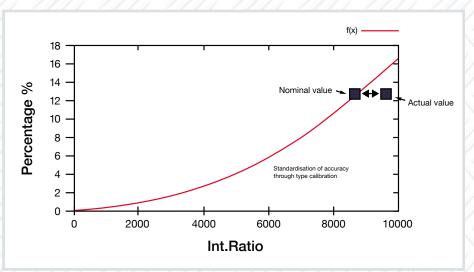
In these scenarios, type standardisation can improve the accuracy of your analytical results. Based on the determination of correcting quantities, this method can compensate faults originating from deviations in the calibration curves for the elements to be standardised.



Important:

Type standardisation is only valid for the correction of unknown material that is similar to the composition of the type standardisation sample. Never use this method as a global correction method to analyse different materials.

Principle of the effect of type standardisation:



The samples you use for type standardisation need to correspond to the composition of the material that is to be analysed and standardised. It is important to check the optimal accuracy of the basic calibration with CRMs before usage. Just like control samples for recalibration, you are going to need sufficient quantity of recently prepared, easy to measure materials.

After choosing suitable type samples, these have to be entered into the corresponding library of the analyser software as type recalibration samples with their desired concentrations.

	TAXABLE INCOME.		C. Bernetter					2 214	-	1000			2.1		
	Measurin	ng			1000		Rece	a land	1948		100.0	Part.		24	1
	and the second	a contract of the second	-		- marine			Earlufe 1			10000			1	
or a robe	Winser	ward a second	Maria 9	EPE A	Sum 2	Bern A	Sart 7	Average	. 8	Seemit .	Bern 1	Bren d. 1	Bern, A.	Bode: 4	Berte
84.7	Fr 4	94.5						94.1	1		94.2	94.2			
8.246	e +	0.346						. 8.1			0.324	6.338		_	
8.534	85 A	0.528						8.4	24 8	4.4	8-332	9.138			
8.556	80. 9	0.804						4.5	147 18	n 1	8.528	0.714			
8.824		1.0344						8.6	1248 \$	108	5.8243	0.0273			
6.051	1 8 4	0.0115						8.4	13.3 8		0.8190	8.0145			
1.94	Cr +	1.99	ex	pecte	ed Ni va	lue: 2.2	5 %	- 8.0	19 10	x +	1.98	1.99			
8.399	80.8	6.300								a (a)	8-244	8.312			
3.57	#5 F	4.47	foi	und: :	2.17 %			3.1		67.5	4.43	9.48			
8.823	AL N	0.8234						3.1	10.50 4	8. A.	8.5214	8.0028			
6.905	7 Ex 4	0.6279						8.4	1070 0	s).	9.5243	0.0275			
6.057	6 Ga. 4	0.8824						8,8	witt (d	5 B	0.0842	8-0403			
0.000	1 AD 1	0.0035						8,4	123.9 8		8.0043	0.0008			
0.004	1 T1 8	0.0048					00	5 8.4	1048 2	5.8	1.0108	8.0028			
0.000	E 17 . W.	8.0218						8.8	N41 [4	5 J.K.	1.0010	8.5548			
6.011	w +	< 1.4110						4	111.4	10 ()	4 0.2100	4 8-1009			
E-515	100 W	× 0.0210						W 0.0	1055 8	6 B	5 4 1 4,000	4. 0.4210			
8.000	a 36 A	0.6324						8.4	nn 9	a. 4	0.5597	0.0104			
6.000	2 4	4. 0.0004						4 8.4	1111 2			< 8.1014			
8.000	t Ca b	8.0001						8.6	10.00 (2		8.0003	6.0008			
6.000	Sr . 6	4 0.0000						8 . 8.4	ant 1	ir, H	1 0.5403	4 8,0008			
6.003	5 SH +	0.0013						8.4	01.5	6.9.	0.0053	8.0019			
6.027		0.8253						8.4	1238 8	1. A	8-3247	0.0256			
0.008	4. 4	0.0039						8.4	1040 A	a: 14	8.0012	0.0049			

There are a few important points to remember:

- The elements you are using for the standardisation need to be highlighted.
- If in doubt, use additive standardisation.
- Vou can switch the standardisation on or off at any time.

- Two standardisation methods are possible:
 - Additive (or offset): should be used for low contents.
 - Multiplicative (or factor): for larger contents.

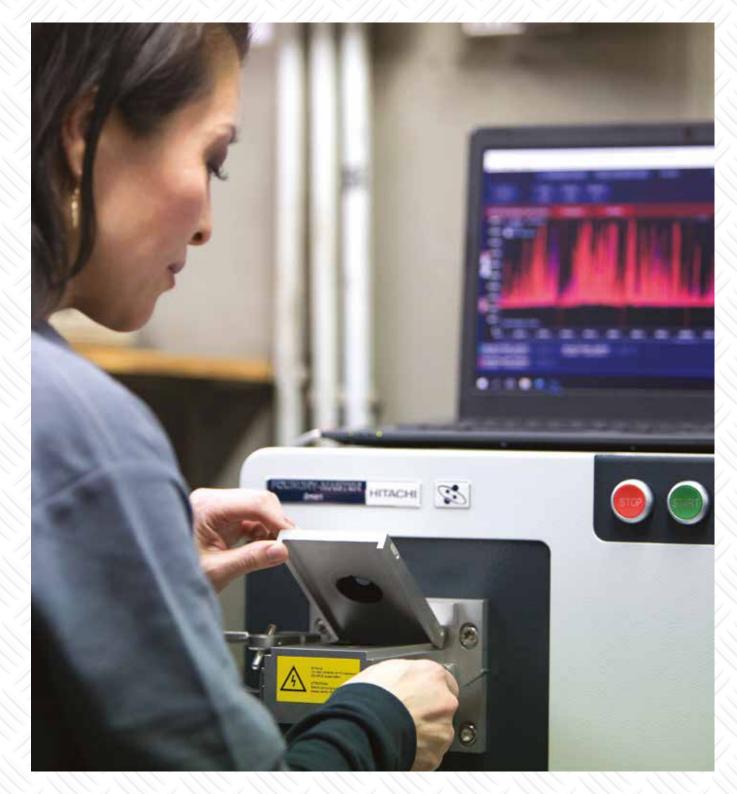
MAINTAINING YOUR OES ANALYSER

Maintaining your device properly is extremely important for getting effective analysis out of your OES system in the long term.

Checking the quality and quantity of the inert gases you will be using is an important starting point.

Argon requires a purity level of 99.998%

Nitrogen analysis requires an Argon purity level of 99.999%



I VERIFYING BURN SPOTS

A bad burn spot indicates diffuse discharge and means that your analysis will be useless, so it is important to be able to identify a burn spot quickly. If the centre of the burn spot has not re-melted or the edge of the burn spot looks milky white, it is likely that you have a bad burn. A good burn spot has a clear re-melted centre and a dark black circle of black deposit around it.

Prepare the instrument according to the manufacturer's instructions, especially regarding periodical maintenance procedures.



Bad burn spot

If you are getting bad burn spots, you need to check:

- The material (inclusions, blow holes and cracks).
- The sample preparation.
- Your argon quality and the tightness of the argon system and supply.

Assembly	Maintenance activity	N	- Further information				
	Maintenance activity	m	у ОН		Further mormation		
Entire	replacement of all loaded parts and analytical check of the instrument		1		by customer service		
instrument	check of filters and replacement, if required	3			chapter 9.5, page 49		
	cleaning the instrument	1			chapter 9.7, page 51		
	cleaning and filling the washing bottle	when dirty or filled to	chapter 9.6, page 49				
	replacing the argon bottle	cing the argon bottle as necessary			chapter 9.8, page 51		
Spark stand	replacing the electrode	at every change of n	chapter 9.4.1, page 45				
	adjusting the electrode	after every change of electrode					
	cleaning of the electrode with a brush	after every measurer	chapter 9.4.3, page 48				
	cleaning of the spark stand	after 300 sparkings at every change of n	chapter 9.3, page 43				

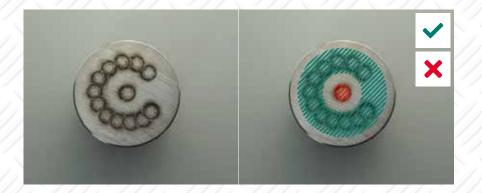
ANALYSING YOUR SAMPLE: TOP TIPS

- Verify that you have selected the correct matrix and/or subprogram for the material to be analysed. If you do not know the perfect matching subprogram, select the global program of the matrix. The global program switches automatically to best match the analytical subprogram.
- 2. Make sure that you have entered correct sample identification information and that your system is set up correctly for the data transfer and storage of your analysis.
- **3.** Use an argon pre-flush before the analysis and position the sample on the spark stand in order to minimise the influence of air and oxygen.
- **4.** Use a cloth to remove particles and dust from the previous sample of the spark stand plate to avoid cross-contamination.
- 5. Ensure that you have cleaned the electrode correctly (refer to the user manual).
- 6. If the current sample differs notably in composition from the previous sample, use a burn sample. The composition of this burn sample should ideally have a pure matrix (so a pure iron sample in case of analysing iron or steel). Measure this sample several times

- (e.g. five times). You can use the repeat spark sequence function if the software of your equipment provides this feature. This sequence makes sure that possible particles within the spark chamber do not contaminate your results.
- 7. Make sure that your sample has been prepared in the same way that your standardisation and control samples were. When grinding, use different paper for high-alloyed and low-alloyed materials in order to prevent cross-contamination from the sample preparation. Change the paper frequently (refer to the section on sample preparation for details).
- **8.** The sample's surface should be flat; cover the spark stand gap completely in order to prevent air from entering.



9. Solidification most strongly affects the sample's homogeneity at the outer circle. Spark your samples as near to the edge as possible, as it is likely that the centre of the sample will contain segregations.



- 10. If the sample's surface has a crack, inclusion or any other visible defect, do not spark the sample on this position. The excitation will not be centric and the results will likely not be useful.
- **11.** Never touch the prepared surface of your sample. Your fingertips contain sweat and oil, which could destroy the validity of your analytical result.
- **12.** Carry out all these steps before analysing another sample.
- 13. Do at least three burns in order to fulfil the minimum for statistics. Please consider that your sample is only a few milligrams that represent the composition of tonnes of material in your furnace/melt shop.
- **14.** Verify the repeatability/precision of your burns. If you identify any outliers for an important element, repeat the measurements.





IDENTIFYING THE GRADE

For sample identification and printing, reporting, storing and transferring your results, our spectrometers come with the control software packages WASlab and SpAcrfire. Based on the latest Windows operating system, our software offers state-of-the-art tools and connectivity. Our analysers are flexible enough to communicate with the latest 2nd level, LIMS or ERP systems.

Connectivity:

- Network connection via RJ45 jack;
 Wi-Fi optional.
- Several USB ports.

Database:

- SpArfire uses an SQLite-based database.
- Soon: Connectivity to our cloud based system ExTOPE Connect.

Printing:

- To network or local printer.
- To PDF.

Storage formats:

- CSV.
- PDF.
- Text file for importing the analysis into an Office application simply via drag and drop (e.g. Word or Excel) for easy certificate creation.

EDITING THE SAMPLE IDENTIFICATION DIALOGUE

Properly identifying your samples is mandatory. The sample ID dialogue can be adapted to your needs with some automated features:

Date/time.

- Increments (e.g. for the charge number).
- Predefined lists for easy operation via a selection field (operator names, furnace names or numbers, and customer/supplier lists).
- Grades for a comparison of the analysis regarding meeting the limits and tolerances of the preselected grade.
- Mandatory ID fields.

Previous IDs are kept as default to make it as easy as possible in case a new ID does not differ much.

GRADE VERIFICATION/IDENTIFICATION

The Hitachi High-Tech Analytical Science Stationary OES System comes with the most comprehensive GRADE Database on the market. Users can not only make tailor-made spectrometer software internal-grade libraries but can also access a database containing >340,000 grades in 12,000,000 records from 69 designations/countries.

Operators can check at a glance if the material of the melt meets the specified grade or if the melt needs to be treated with additional material.



OPTIONAL CHARGE CORRECTION

If your melt material is not matching the targeted grade for one or more elements, working out what adjustments need to be made can be a complex and time-consuming process. We can provide you with charge correction software package that automatically calculates the most cost effective way to produce the desired grade.

The system database provides full inventory control and automatically updates during charging, to provide further time savings.

REPORT GENERATOR

Both WASIab and SpArcfire offer strong tools for the creation of report or certificate templates including your company's logo, sample ID details and result details. This adaptability allows you to present data how you want, with only average or single results (or both) and with statistical values such as relative standard deviation (RSD) and standard deviation (SD).





MAKING PROCESS CONTROL AUDITS SAFE

To make your process control audit safe regarding the melt analysis, we offer optional statistical process control (SPC) packages.

SPC is a method of quality control that uses statistical methods to monitor and control a process. Monitoring and controlling the process ensures that it operates at its full potential, with a minimum of waste. SPC can be applied to any process where the 'conforming product' output can be measured. Widely used in manufacturing lines, SPC focuses on continuous improvement and the design of experiments.

The application of SPC involves three main phases of activity:

- Understanding the process and the specification limits.
- Eliminating assignable (special) sources of variation so that the process is stable.
- Monitoring the ongoing production process, assisted by the use of control charts, to detect significant changes in the mean or variation.

The data from measurements of variations at points on the process map is monitored using control charts. Control charts attempt to differentiate assignable (special) sources of variation from common ones.

When the process does not trigger any of the control chart 'detection rules' for the control chart, it is said to be 'stable'. Process capability analysis may be performed on a stable process to predict the ability of the process to produce a 'conforming product' in the future.

When the process triggers any of the control chart detection rules (or, alternatively, the process capability is low), other activities may be performed to identify the source of the excessive variation. The tools used in these extra activities include Ishikawa diagrams, designed experiments and Pareto charts.

Designed experiments are a means of objectively quantifying the relative importance (strength) of sources of variation. Once the sources of variation have been quantified, actions may be taken to reduce or eliminate them. Common methods of eliminating variation sources are the development of standards, staff training, error proofing and changes to the process itself or its inputs.¹

It allows you to be 100% prepared for audits

SPC software enables you to collect, maintain, evaluate and archive your measurement data for production and control samples. It allows you to be 100% prepared for audits by monitoring your process at every stage and by filtering,

sorting and preparing analytical data for reports and certificates.



MAKING SPARK OES YOUR FIRST CHOICE

When considering all these measures, spark spectrometers should not only be your first choice for analysing main and auxiliary elements but is also a suitable tool for achieving good, reliable results for carbon.

ABOUT HITACHI HIGH-TECH

With over 45 years experience in providing cutting-edge analysis solutions to companies all around the globe, Hitachi High-Tech has a full range of metals analysers. This means we never have to compromise for our clients and can always provide a solution that is tailored to their needs. We provide reliable, robust and fast metals analysers so that you can have powerful materials analysis.

To explore the Hitachi High-Tech complete range of spectrometers for foundries further, book a demo or to talk to a member of our team, contact us today.

Visit: www.hhtas.net/master-every-melt or Email: contact@hitachi-hightech-as.com

@Hitachi High-Tech Analytical Science

This publication is the copyright of Hitachi High-Tech Analytical Science and provides outline information only, which (unless agreed by the company in writing) may not be used, applied or reproduced for any purpose or form part of any order or contract or regarded as the representation relating to the products or services concerned. Hitachi High-Tech Analytical Science's policy is one of continued improvement. The company reserves the right to alter, without notice the specification, design or conditions of supply of any product or service.

Hitachi High-Tech Analytical Science acknowledges all trademarks and registrations.

© Hitachi High-Tech Analytical Science, 2018. All rights reserved.

Part number: 63*156/1118







348399 QM08 CERT #3