

OPTIMAL NON-FERROUS MELT CONTROL WITH SPARK OES

HITACHI
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A GUIDE

HOW TO ACHIEVE OPTIMAL MELT CONTROL IN NON-FERROUS WITH OES ANALYSIS

INTRODUCTION

2016 saw global casting production hit around 104,4 million tonnes. Grey, ductile and 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 12,000 produce non-ferrous metal.

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 non-ferrous 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 our OES expert Wilhelm Sanders explains how this can be achieved.



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THE CHALLENGES OF NON-FERROUS ANALYSIS

THE PROBLEM

While OES technology is an effective way of analyzing elements at low limits of detection in various types of metal, important elements in non-ferrous casting such as phosphorus, antimony and bismuth present a greater challenge to measure.

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

UNDERSTANDING THE ISSUE

Aluminium alloy and other non ferrous based materials melts have a tendency to segregate as they solidify. This results in uneven concentrations of elements within casted products. You are likely to see segregation profiles in all directions, which makes it difficult to get representative sampling from melts, casted products or samples for the lab. For direct measurements of solid samples, (e.g. spark optical emission analysis) measuring signals are influenced by the morphology of the solidification and cast structure of the sample.

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

Spark OES is well-established as the workhorse for elemental analysis of melt samples within foundries. Thanks to low detection limits for almost all elements, this method is highly sensitive and offers excellent accuracy and precision. However, sample condition greatly affects the results. To achieve reliable and meaningful results, the sample must be homogeneous. To a certain extent, small inconsistencies in homogeneity can be overcome during the high energy pre-spark sequence.

The pre-spark sequence is necessary for reproducible results – it conditions the plasma and ensures that emitted light from the atoms in the sample can be detected consistently at a stable level. Unfortunately, it cannot overcome the kinds of inhomogeneity seen in aluminum alloys due to large segregations. To overcome this problem, you need to pay close attention to the methods of sample taking and sample preparation.

**OES requires
homogeneous
samples
from the melt**

Please refer to EN 14726 "Aluminium and aluminium alloys – Determination of the chemical composition of aluminium and aluminium alloys by spark optical emission spectrometry"

Die-cast aluminium sample

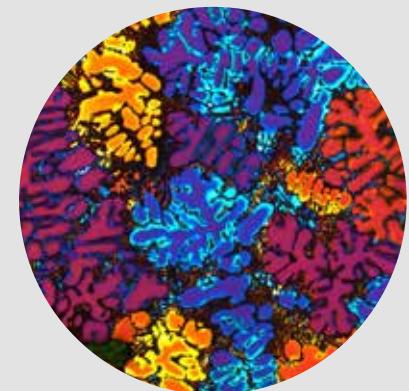
Macro photograph of an etched sample



Large inhomogeneous areas caused by partial solidification

AISi8Cu3

Barker etched sample in scanning electron microscope



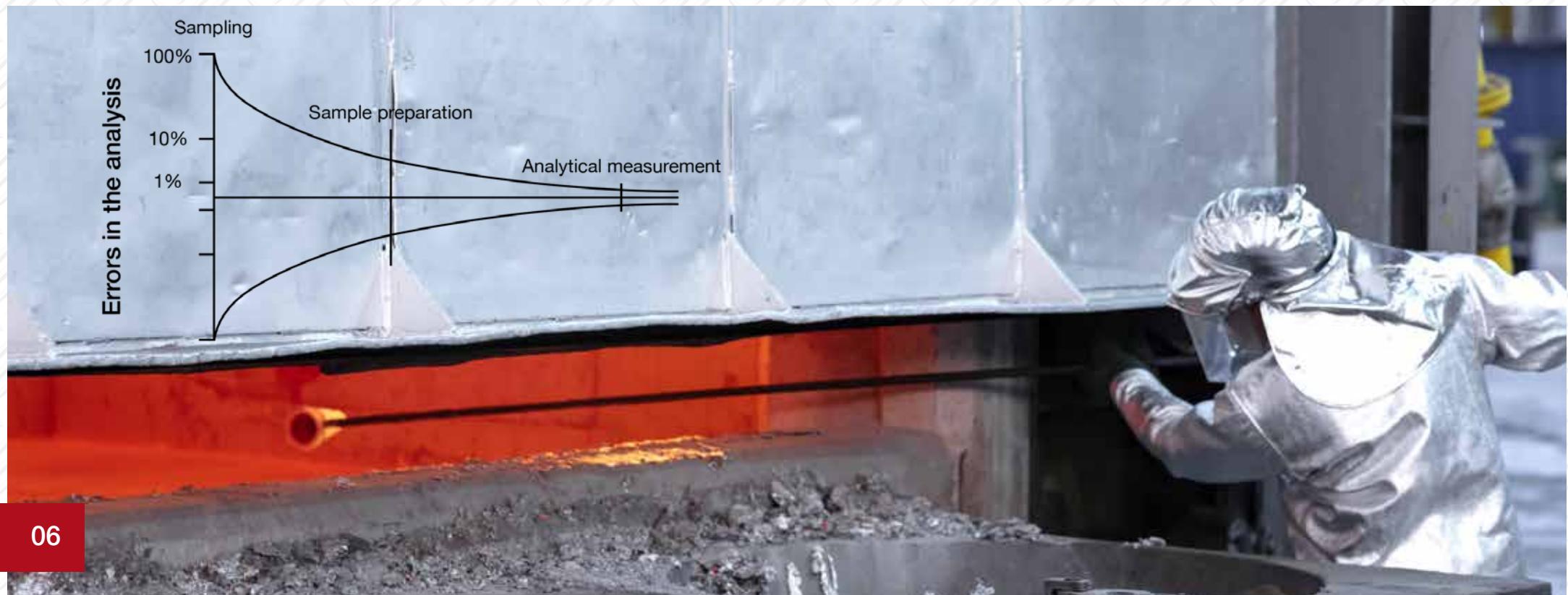
Segregation within dendrites

THE SOLUTION

OES is capable of accurately determining all main, trace, tramp and treatment elements within non-ferrous melts and casted products. Operators can achieve excellent quality control while streamlining costs in a few simple steps.

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

Sampling
is most important
for accurate results





THE SECRET OF PERFECT OES ANALYSIS: SAMPLE PREP

TAKING THE PERFECT SAMPLE

As the risk of segregation is high in non-ferrous melts, such as aluminium or copper, you need to be especially careful when taking samples, and the analysis area must be sufficient to give a homogeneous result.

You'll need to be aware of systematic deviations that could occur due to structural differences between the sample and the reference material; ideally the metallographic structure in both should be similar.

To get the best sample:

- Avoid catching any slag when taking the sample
- Pour the sample with a single drawing process
- Ensure the sample cools down quickly to minimize segregation
- Keep your molds clean so that crusts from previous samples do not slow the cooling
- After solidification, the sample should be free from cracks and irregularities
- Keep the sample diameter and height to a minimum. A good size is 40 mm × 30 mm (55 mm × 30 mm) for cylindrical samples
- Maintain your sample tools properly

You must ensure that the liquid metal only comes into contact with non-reactive materials. In practice, this means ensuring it doesn't come into contact with any moisture, iron or dust, so the sample taking tools must be clean.

Any metal that sticks to the tools after solidification could show that a chemical reaction has occurred.

The optimal sample shape, form and mold should allow for rapid solidification with no irregularities. Preliminary testing to establish this, and to determine the ideal distance from the analytical face and edge of the sample, must be carried out prior to routine testing. These measures are essential to ensure that segregation is minimized and results are reproducible.

PREPARING YOUR SAMPLE

Spark-OES requires a flat, level surface at the analysis site. The best way of preparing non-ferrous materials is with lathes and milling machines. It's preferable to analyze at the edge of the sample, as segregation is more likely towards the center.

Machining parameters, such as cutting speed, angle and type of tool, should be chosen to ensure no sample material extends beyond the machined surfaces and no single hard grains are torn from the soft microstructure. The surface roughness must not be too fine, as a certain degree of roughness helps to create a

focused, concentrated discharge onto the surface. You should avoid touching the prepared surface and ensure it doesn't come into contact with any other contaminants as this has an adverse effect on the results, especially for sensitive elements, such as calcium, sodium and phosphorous in aluminium alloys.

For control samples and reference materials, similar parameters should be used for each alloy type from the melt.





Non-ferrous 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.

Sample heat throughout the preparation process should be minimized in order to keep the potential for surface chemical interactions as low as possible.

UNDERSTANDING CALIBRATION AND TYPE STANDARDIZATION

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 analyzer is performing at its optimum level.

OES is a relative analysis technique as opposed to an absolute measurement technique, meaning that the parameters (absorption, voltage, etc.) are dependent on the concentration or quantity of the analyzed substance. The value of the measurement parameter to the concentration or quantity created by a calibration with certified reference materials (CRMs).

Without this calibration, OES would only measure light intensity, instead of performing any kind of quantitative chemical analysis.

Calibration with CRMs is required for accredited and certified quality control testing. CRMs are created by cross-referencing multiple measurement techniques and lab results to gain as much information about a sample as possible. This is advantageous to calibrating OES equipment as one CRM can help calibrate for a wide range of elements.

Example of a certificate of analysis

SIL G77J1
Page 1 of 4
Date 2000

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ANALYTICAL LTD

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Email: info@mbh.co.uk Website: <http://www.mbh.co.uk>

CERTIFICATE OF ANALYSIS

59X G77J1 (batch F)

Certified Reference Material Information

Type:	ALUMINIUM / MAGNESIUM / COPPER (CAST)
Form and Size:	Disc 40-50mm diameter x 15-20mm thick
Supplied by:	MBH Analytical Limited
Produced by:	Coleshill Laboratories Limited

Certified Analysis

Percentage element by weight						
Element	Cu	Mg	Si	Fe	Min	Ni
%	2.41	4.83	0.15	0.21	0.46	0.17
Zn					1.91	
Element	Pb	Sn	Tl	Cr	V	Co
%	0.125	0.126	0.178	0.24	0.005	0.018
Element	Zr	Cd	Ga	Mo	Bi	As
%	0.01	0.004	(0.013)	0.004	0.05	0.004

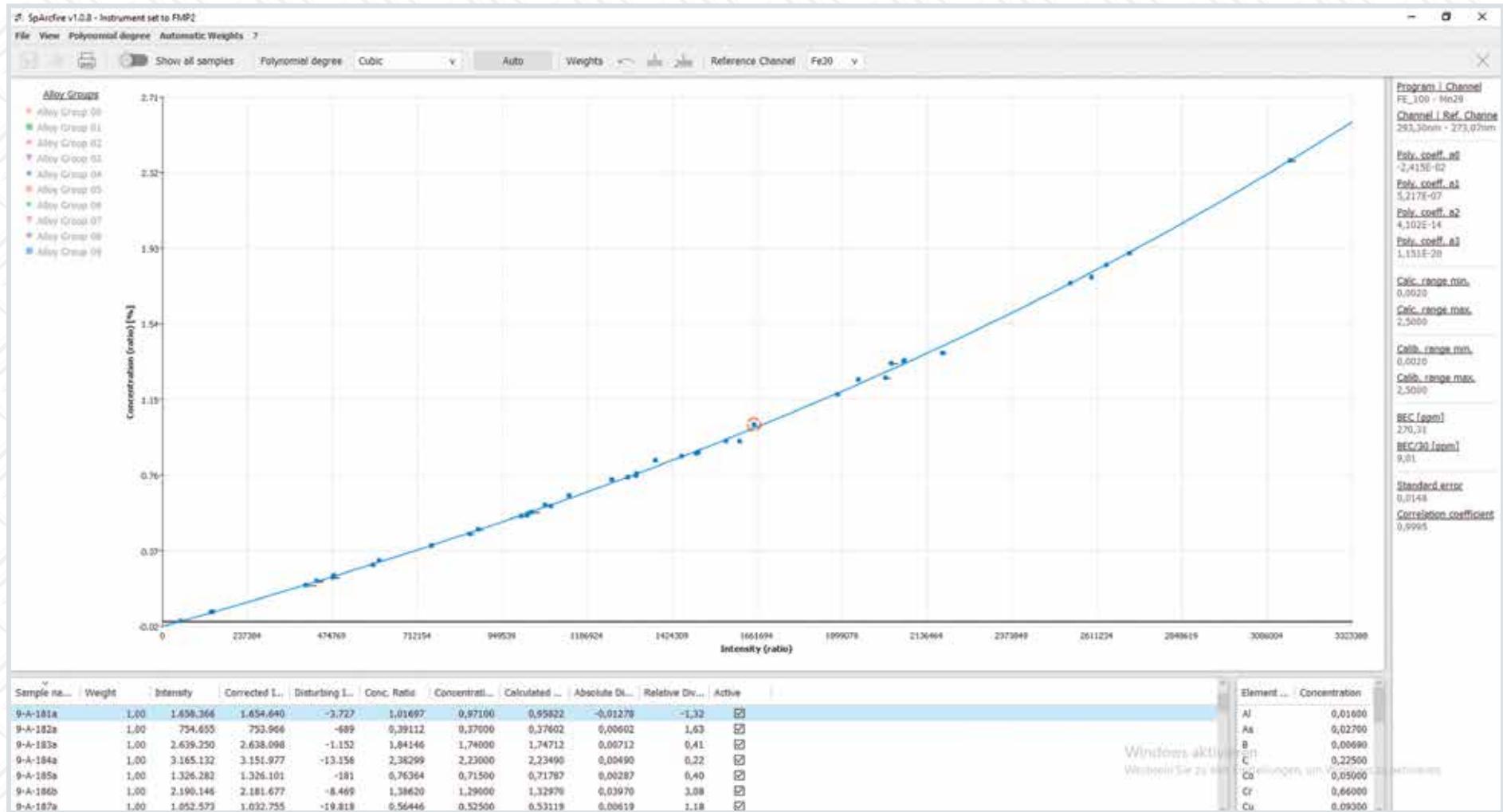
Usage

Intended use: With optical emission and X-ray fluorescence spectrometers.
Recommended method of use: Aluminium and aluminium alloys are generally prepared by machining on a lathe. However, users are recommended to follow the calibration and sample preparation procedures specified by the relevant instrument manufacturer.
Preparation should be the same for reference materials and the samples for test.
A minimum of three consistent replicate analyses is recommended to optimise precision and accuracy. Users are advised to check against possible bias between reference materials and production samples due to differences in metallurgical history, and be aware of possible inter-element effects.

Certified by: _____
on 06 June 2000

MBH ANALYTICAL LIMITED
Dawson 21, Herts, UK
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ISO 9001 Registered
Cert. No. 534

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 minimize 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

119-766

nm

Hitachi High-Tech takes a different route. Our OES systems use a more efficient, more cost-effective and smarter approach. Our optics have total wavelength coverage between 119 and 766 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.

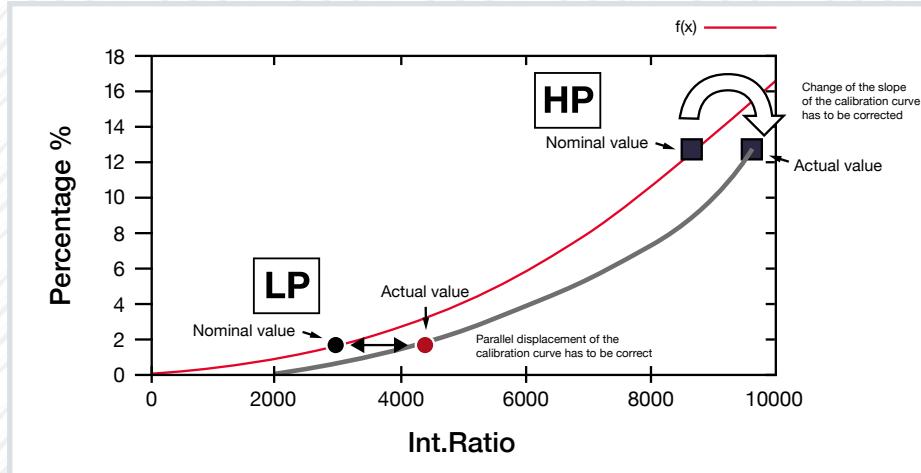
RECALIBRATION

While our Peak Position Alignment system significantly improves the long-term stability of our spectrometers, 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 normalization, so as to always use the original calibration. The OES system also needs to be standardized 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:



The simple retraceable mathematics of two-point recalibration:

$$\text{IntLP}_{\text{nominal}} = \text{Factor} * \text{IntLP}_{\text{actual}} + \text{Offset}$$

$$\text{IntHP}_{\text{nominal}} = \text{Factor} * \text{IntHP}_{\text{actual}} + \text{Offset}$$

$$\text{Factor} = \frac{\text{IntLP}_{\text{nominal}} - \text{IntHP}_{\text{nominal}}}{\text{IntLP}_{\text{actual}} - \text{IntHP}_{\text{actual}}}$$

$$\text{Offset} = \frac{\text{IntLP}_{\text{nominal}} * \text{IntHP}_{\text{actual}} - \text{IntHP}_{\text{nominal}} * \text{IntLP}_{\text{actual}}}{\text{IntHP}_{\text{actual}} - \text{IntLP}_{\text{actual}}}$$

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.

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

Control samples should be similar in their composition to the material you will be analyzing, 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.

Set of control samples



When preparing your control samples, make sure that:

- You have sufficient quantity to avoid fundamentally modifying the analysis method.
- They are easy to measure with the spectrometer in their shape and manageability (\varnothing : ca. 40–60 mm; height: 40–60 mm).
- You only use recently prepared samples (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, reliable results.

**Statistical process control (SPC)
chart of a control sample**

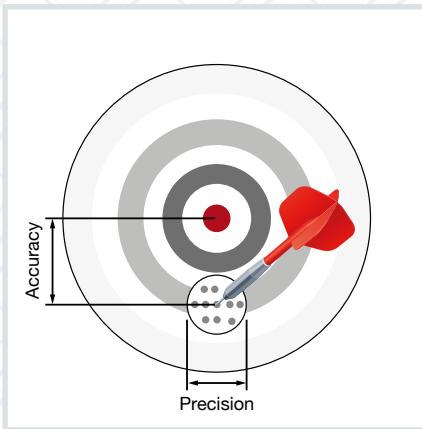
TYPE STANDARDIZATION

If your analyzer is not meeting the required level of accuracy for any unknown materials, type standardization 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 analyzed 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.

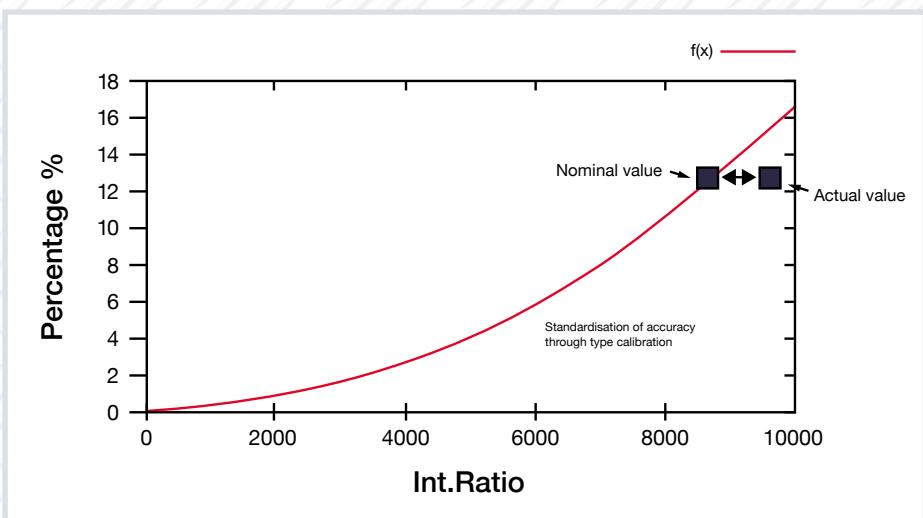
In these scenarios, type standardization can improve the accuracy of your analytical results. Based on the determination of correcting quantities, this method can compensate faults originating from deviations in the calibration curves for the elements to be standardized.



Important:

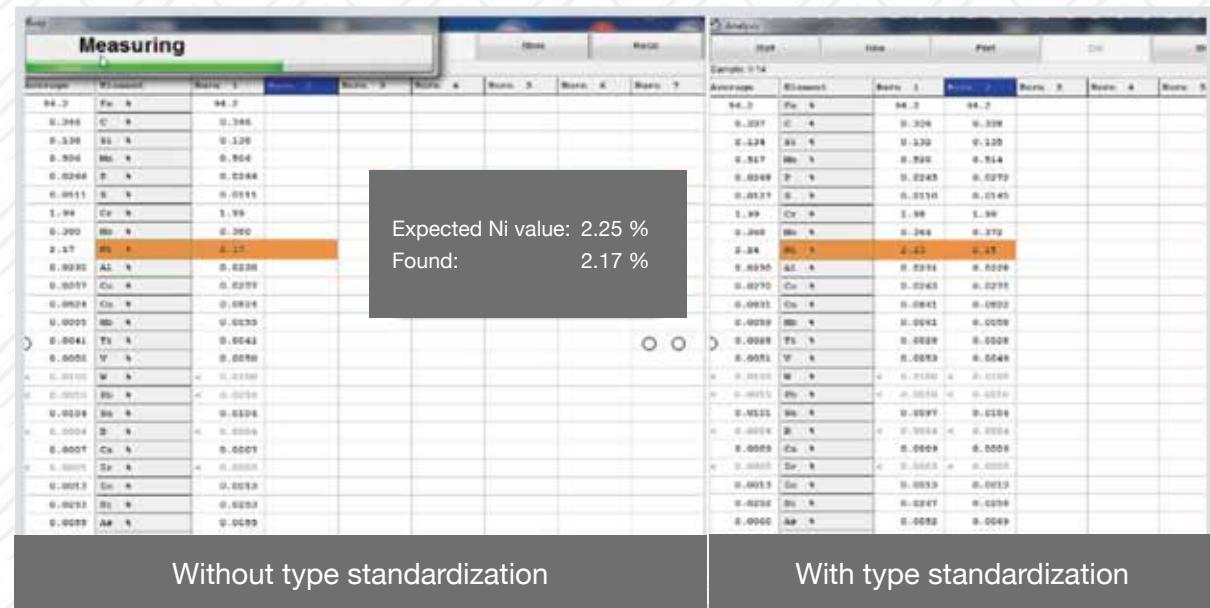
Type standardization is only valid for the correction of unknown material that is similar to the composition of the type standardization sample. Never use this method as a global correction method to analyze different materials.

Principle of the effect of type standardisation



The samples you use for type standardization need to correspond to the composition of the material that is to be analyzed and standardized. 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.



There are a few important points to remember

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

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

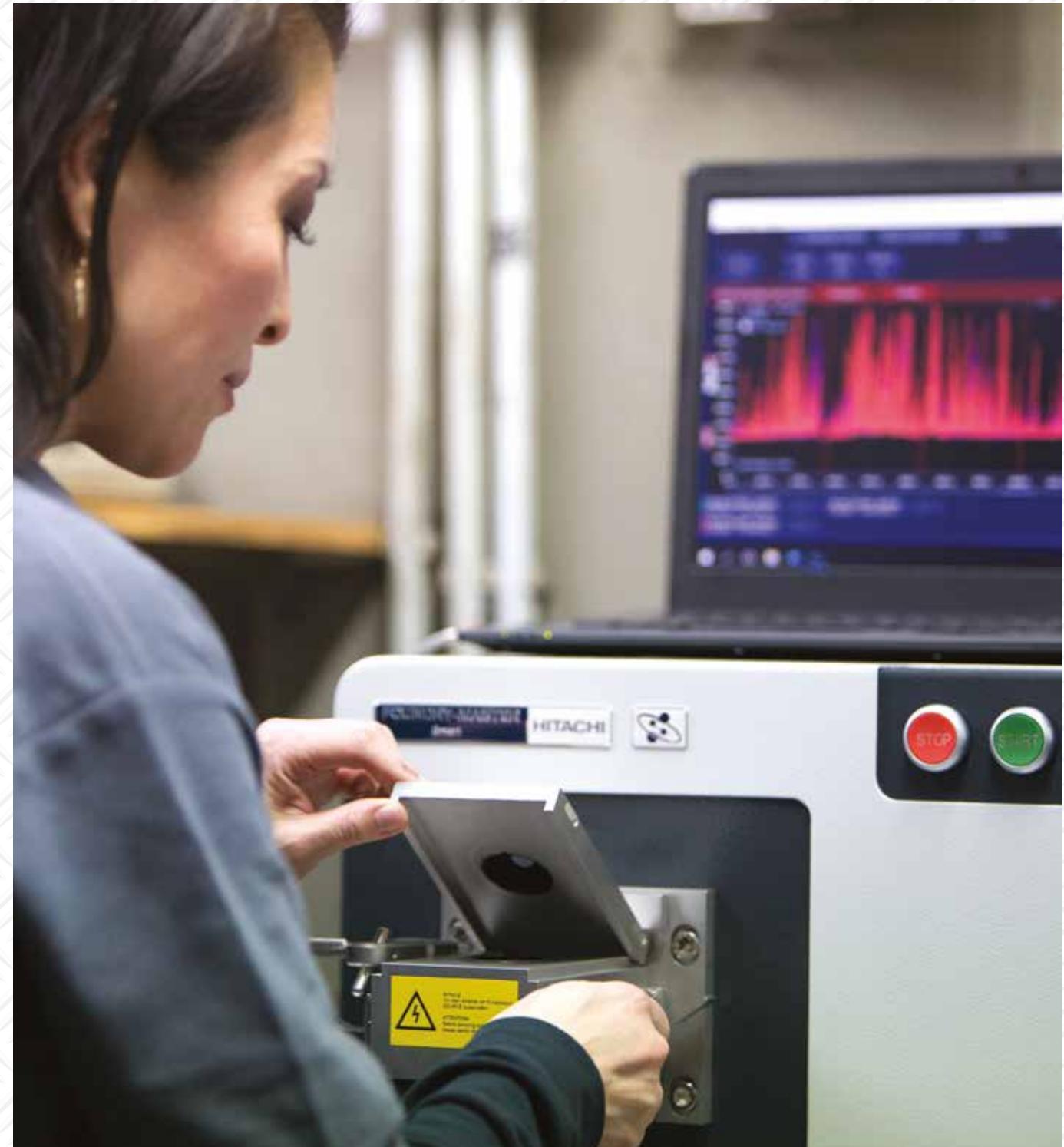
MAINTAINING YOUR OES ANALYZER

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%

Gas analysis
(e.g. O₂ in Cu, Ti, Fe matrix)
requires argon purity level of
99.999%



VERIFYING BURN SPOTS

A bad burn spot indicates diffuse discharge and means that your analysis is not valid, so it is important to be able to identify a burn spot quickly. If the center 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 center 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:

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

Assembly	Maintenance activity	Maintenance interval		
		m	y	OH
Entire instrument	replacement of all loaded parts and analytical check of the instrument		1	
	check of filters and replacement, if required	3		
	cleaning the instrument	1		
	cleaning and filling the washing bottle	when dirty or filled to a low level		
	replacing the argon bottle	as necessary		
Spark stand	replacing the electrode	at every change of matrix		
	adjusting the electrode	after every change of electrode		
	cleaning of the electrode with a brush	after every measurement and at every change of the sample		
	cleaning of the spark stand	after 300 sparkings each; upon notification; at every change of matrix		

ANALYZING YOUR SAMPLE: EXPERT TIPS

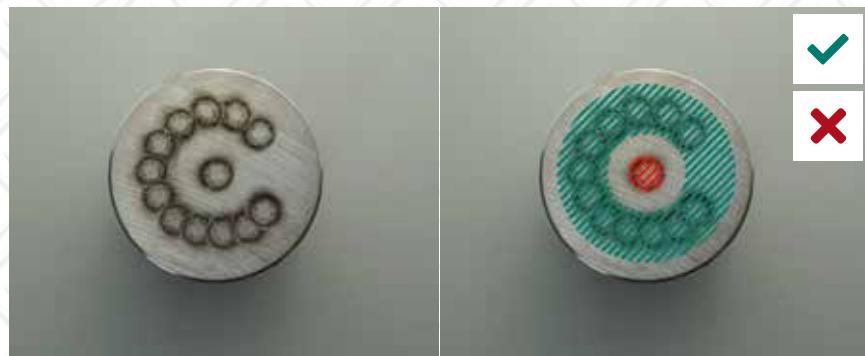
1. Verify that you have selected the correct matrix and/or subprogram for the material to be analyzed. If you do not know the perfect matching subprogram, select the global program of the matrix. The global program switches automatically to best match the analytical subprogram.
2. Make sure that you 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 minimize 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 standardization 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 analyzing 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 package SpArcfire. Based on the latest Windows operating system, our software offers state-of-the-art tools and connectivity.

Our analyzers 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:

- SpArcfire 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 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 >350,000 grades in 15,000,000 records from 74 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

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.

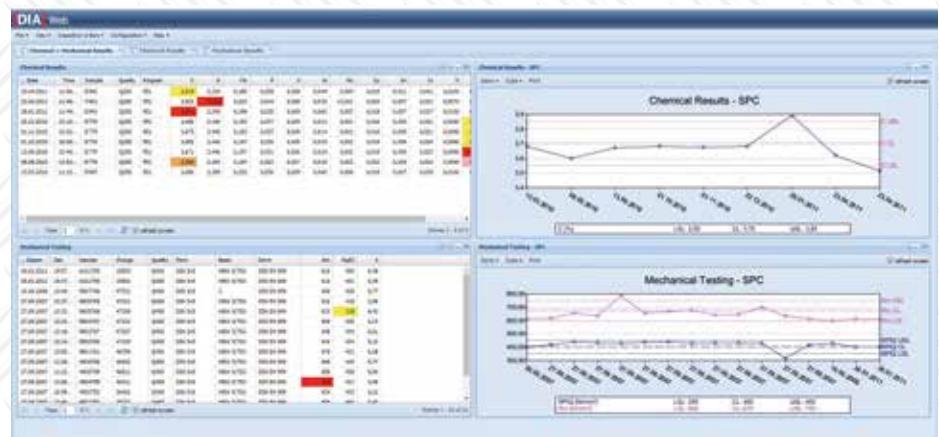
When the process triggers any of the control chart detection rules (or, alternatively, the process capability is low), other activities may be performed to identify the source of the excessive variation. The tools used in these extra activities include Ishikawa diagrams, designed experiments and Pareto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

Our range of stationary OES is ideal for efficient control of the melt process, ensuring you comply with material specification limits, avoid undesirable elements and control inoculation elements in the melt.

We also offer a broad range of analytical tools designed specifically for metal production. With Hitachi not only can you optimize your melt but also ensure quality throughout your entire process.

Explore our complete metals analyzer range at

hhtas.net/master-every-melt

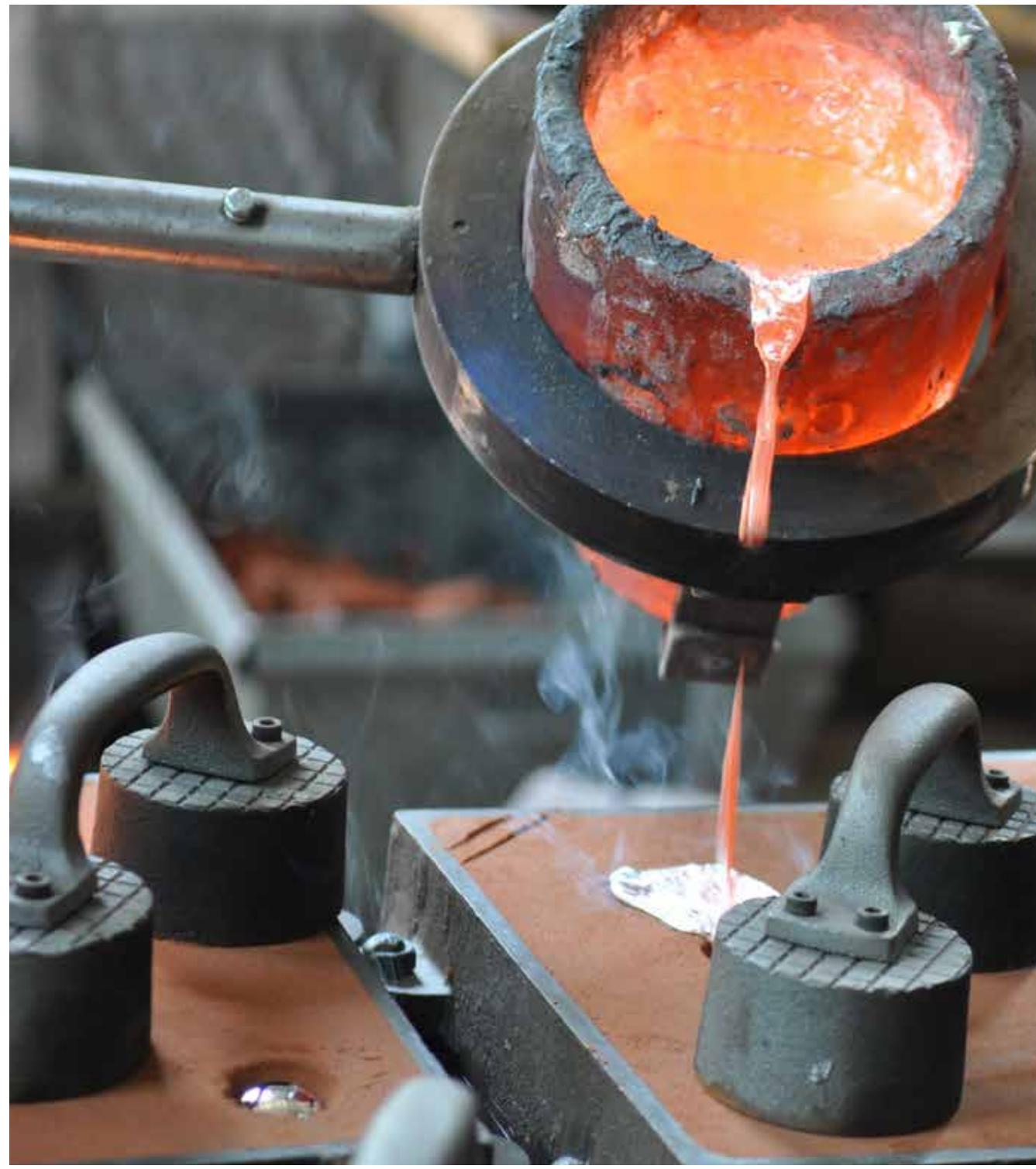


Stationary OES



Handheld LIBS / XRF

Mobile OES



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

Visit: hha.hitachi-hightech.com
or email: contact@hitachi-hightech.com

Hitachi High-Tech Analytical Science

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