A WHITE PAPER BY
SPECTRO ANALYTICAL INSTRUMENTS

Standards-Compliant Elemental Analysis: Does Your Testing Meet Today's Requirements?

INTRODUCTION

Many users are currently being audited for the first time according to the new versions of ISO 9001 [1] and IATF 16949 [2]. These are IATF 16949:2016 and ISO 9001:2015. The deadlines up to which work could be carried out according to the previous versions of the standards elapsed almost simultaneously on September 14th, 2018 (ISO 9001) and September 16th, 2018 (IATF16949). Both standards are characterized by the fact that, compared with their predecessors, they place increased demands on the performance of measurements and tests. These intensifications are reasonable. By following these rules, the risk of giving "incorrect" results is significantly decreased. Such errors can have considerable consequences such as accidents resulting in damage to material and personnel, product recalls, etc. A logical system for avoiding incorrect results must therefore be welcomed.

The key points of the standard requirements are outlined in this paper. If one complies with the current standard versions then one is working according to the state of the art. It is beneficial to be able to prove this in the event of damage or loss.

Accredited testing laboratories usually adhere to the standard DIN EN 17025 [3]. General competence requirements for testing and calibration laboratories are defined therein. By adapting to the rules outlined in this standard, you will have a good foundation regarding compliance with ISO 9001 or IATF16949.

The DAkkS (German Accreditation Body) is the national accreditation body for the Federal Republic of Germany. In Germany, the Accreditation Act stipulates that only the DAkkS is allowed to conduct accreditations. An accreditation by the German Accreditation Body is, in general terms, a quasi-official confirmation that work is carried out correctly, i.e., in conformity with DIN EN 17025.

When auditing the analytics according to the new versions of ISO 9001 or IATF16949, similar requirements are set as for an audit to obtain an accreditation according to DIN EN 17025 by the DAkkS. It is therefore reasonable to work with the accreditation requirements of the DAkkS.

In the paper, "71_sd_1_005" [4], the DAkkS lists the conditions which must be fulfilled for proper operation of a stationary spark spectrometer. By complying wih the points described therein, one can expect an audit of the analytics in accordance with DIN EN 9001 and IATF 16949. The document, "71_sd_1_005" can be downloaded from the DAkkS home page. It is only a few pages long, clearly formulated, and is absolutely worth reading. You only need to work through this list point by point.

Only the most important requirements should be mentioned and annotated here. They can be summarized under two generic terms (classes):

- The environment must be organized in such a way so that work in conformity with standards is possible.
- The measuring equipment, in this case the spark spectrometer, must meet minimum requirements.

Both previously mentioned requirement classes will now be examined in more detail.

Environmental requirements

1. Definitions of conducted tests
Elements and content ranges of the methods available in the spectrometer systems used can be listed here, provided they are actually used. Not all tests are analyses. If, for example, sorting verifications are performed, the parameters used should also be described for these. Such parameters are, for example, the wavelengths of the spectral lines used and the associated tolerance limits.

2. Determination of measurement uncertainties
The measurement uncertainties for each element of every method used should be determined. To this end, it may be necessary to dismantle the content ranges of an element into several parts. A subdivision of content ranges into two or three ranges (traces, medium, high content) has proven to be valuable. Of course, the measurement uncertainty can not be better than the analysis system allows. The section "Requirements for the analysis device" describes what must be observed here. The measurement uncertainty is not only dependent upon the properties of the device but also on the sample preparation and the knowledge of the personnel. Example: If the carbon content is to be determined on a hardened prefabricated part, the surface may contain a higher carbon content. If the carburized layer is not sufficiently polished down, an excessively high carbon value will result.

How measurement uncertainties are to be estimated can be found in the relevant technical literature (e.g. [6]-[12]).

3. Documentation of qualifications and Competencies of the Personnel Responsible for Conducting the Analytics
The minimum here is a list with the personnel, their training, and their authorizations. Persons performing routine analysis are not necessarily authorized to take corrective measures when warning thresholds are exceeded. In addition, suitable technical literature should be made available to personnel.

4. Operating instructions
Standard operating procedures should be in place for performing routine analyses. These must contain the methods which define the elements to be determined and their content ranges. They should also include provisions on sample preparation and test procedure, and there should also be rules on how to ensure that the analytical equipment can be released for testing. In order to be able to carry out this assessment, control samples are measured, and the results are recorded in mean value control charts. The control charts have the following structure:

There is a chart for each control standard and for each element. The mean value of the control standard content and the expected fluctuations is investigated during the preliminary phase. Based on this observation, limits are set above and below the mean value, indicating the expected range of variation. In addition, an upper and lower warning threshold is defined. If the narrower panel is left between the warning thresholds, actions are necessary to correct systematic measurement errors.
If the measurement values of all control standards are within the allowed fluctuations and satisfy repetitive accuracy of specified minimum requirements, the spectrometer system can be released for testing procedures.
The keeping of mean value control charts should also be regulated in an operating procedure. It should regulate what has to be done if the upper and lower warning thresh-

old is exceeded (e.g. cleaning the spark stand, cleaning the windows, recalibration, etc.). Even if the warning thresholds are not exceeded, corrective measures can be necessary.

Corrective measures are common, for example, if:

- seven consecutive measurement values are above or below the mean value,
- 10 of 11 measurement values are on one side of the mean value line,
- seven consecutive measurement values are steadily increasing or decreasing

Figure 1 shows an annotated example of a mean-value control chart.

5. Certified Reference Materials (CRM) must be available for every testing method used. These samples can be used to inspect the analysis devices. These CRMs are not identical to the control standards mentioned under point 4. Control standards are measured relatively frequently and are therefore consumed quite quickly. Although they must be homogeneous, their element contents need only be known approximately. As a rule, several pieces of a batch are obtained from each control standard. These are only used to check whether the measured values remain constant. CRMs are comparatively expensive. They are used at longer intervals, in cases of uncertainty, or in audits.

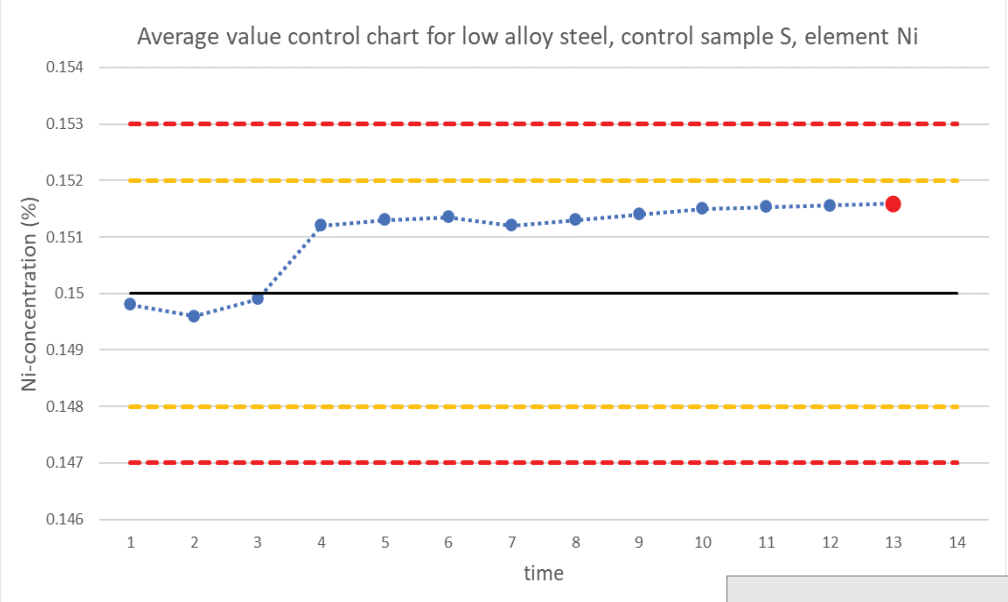

Figure 1: Example of a mean-value control chart

After the last measurement (red marked point) an intervention is necessary for two reasons:

- *10 of the 11 previous measurements were above the mean value line.*
- *7 consecutive measurements were larger than their predecessors.*

Of course, measures are also required when intervention limits are exceeded.

Mean value and standard deviation determined in a preliminary phase:

- *Mean value (black line in the graphic): 0.15%*
- *Standard deviation: 0.01%*

Calculated from this:

- *Upper control limit (UCL, upper red line): 0,153%*
- *Upper warning threshold (UWT, upper orange line): 0,152%*
- *Lower warning threshold (LWT, lower orange line): 0,148%*
- *Lower control limit (LCL, lower red line): 0,147%*

For CRMs, auditors usually require that the values stated on the corresponding certificates are traceable to SI units[1] (see [13]). This is only the case for very few of the CRMs available on the market. However, if one procures quasi-official standards, e.g. from the Federal Institute for Material Testing (BAM) or NIST, one avoids this annoying pitfall.

6. Suitability tests

For an accreditation according to DIN EN 17025, participation in suitability tests (ring tests) is required. Samples from an external service provider are analyzed at regular intervals such as annually. If the values differ from those of another participant in a statistically significant way, corrective measures must be taken (see also [14]).

7. Test reports must satisfy minimal requirements

In addition to the test result, this includes an indication that the document is a test report, together with a unique identifier (e.g. a sequential number). In addition, the name and address of the client and of the testing laboratory, a clear description of the materials tested, testing date, and date of entry for the test specimens as well as place of employment and signature of the person who approved the test report must be included.

Requirements for a Spark Spectrometer

The section "Environmental Requirements" was written to show that it is not readily possible to order "an audit-proof spectrometer". Certain organizational measures in the operational environment of the user are unfortunately unavoidable.

1 Tracable to the basic units: second (s), meter (m), kilogram (kg), ampere (A), kelvin (K), mole (mol) and candela (cd) as defined in the International System of Quantities ISQ)

However, it must be checked just as carefully whether the existing spectrometer system or spectrometer system to be purchased can cope with the testing tasks to be performed. The DAkkS document, "71_sd_1_005" [4] differentiates between external basic calibration (done by an external service provider or by device manufacturer) and internal basic calibration (done by the users themselves). Stationary spark spectrometers are not usually calibrated by the users themselves. Nevertheless, in audit situations or in case of disputes on test results, the user should be able to answer questions on the parameters mentioned in these DAkkS documents.

1. Requirements for detection and determination limits

For many analytical tasks, the detection sensitivity is of central importance. The detection limit is defined in DIN 32645 [5] as three times the standard deviation of a zero sample. In spark spectrometry, the zero sample is a pure sample of the base metal. Example: In a method for unalloyed steel, a pure iron sample is used to determine the detection limit. This is a relatively simple thing. In contrast to the DIN 32645, several device manufacturers indicate two times the standard deviation as the detection threshold. Knowing this, you can calculate the standard detection threshold through multiplication with a factor of 1.5. DIN 32645 gives ten times the standard deviation of the zero sample as the determination threshold which is the value above which the quantitative analysis is possible.
It is important to note that the aim here is to perform a detection or a quantitative determination in a high-purity metal.

Example: Let the standard deviation for the element C be 10 ppm. If a pure sample is measured and gives a value of > 0.003%, then carbon is indeed present in

the pure sample. For values > 0.01%, one can be confident in passing on the found value as a quantitative result.

The same logic can be applied within grades of alloyed metals, if a) the range of all alloying elements of the grade to be considered is narrow and b) the standard deviation is determined with a grade that does not contain the considered analytes (element C in our example). Unfortunately, neither a) nor b) usually apply for steels.

Example: One is often faced with the problem of separating grades such as 1.4301 (USA: 304) and 1.4306 (USA: 304L). 1.4306 may contain a maximum of 0.03% carbon. To ensure that you are able to monitor this

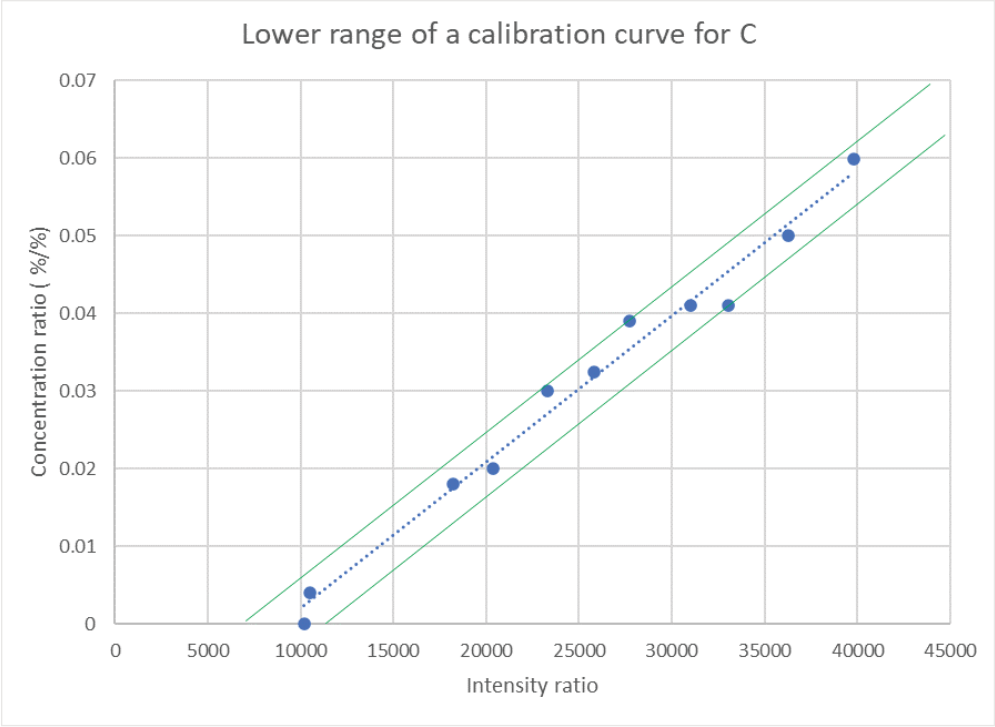

Figure 2: Illustration of expected systematic calibration error

With the calibration function shown in Fig. 2, a systematic error must be expected which corresponds to the distance of one of the green lines to the curve (dotted line). This is around 0.004% in this example. Other sources for systematic errors must also be taken into account.

limit reliably, it must lie within the quantitative measuring range. The standard deviation of a sample without carbon must not exceed 30 ppm.
But that's not all. The grades 1.4301 and 1.4306 may both contain between 0 and 1% silicon and between 0 and 2% manganese. The elements Cr and Ni have allowable fluctuations of ca. 2%. Several tenths of a percent of other elements can occur. Systematic errors can result which lead to a report of increased or reduced carbon content. The systematic errors can only be recognized through a critical examination of the calibration function. However, they are always present to a greater or lesser extent when the concentration varies within a raw material. If a possible systematic error of 0.005%, is determined for our example, a measurement uncertainty of at least 0.005% must always be expected. Figure 2 illustrates this relationship. One will therefore aim for a zero sample reproducibility well below 30 ppm (e.g., 10 ppm) to at least keep the random error fraction small.

It is therefore insufficient if the detection limit lies below the lowest concentration limit to be monitored. Our example shows that a detection limit of 45 ppm, 0.0045%, can be necessary if a limit of 0.03% is to be monitored.

The observations expressed here must be taken into consideration prior to purchasing a spectrometer. Examinations which are done with a system that can not sufficiently handle everyday tasks are useless. On the contrary, they suggest that one's obligations have been fulfilled even though the conducted tests themselves are not very meaningful. This can lead to difficulties if, in retrospect, work has to be proven to be in accordance with the state of the art.

2. Calibration Function Requirements

The auditors often marvel at the calibration functions. There is a reason for that. The course of the calibration curve reveals the best possible measurement uncertainty which can be achieved. From the dispersion of the samples around the found calibration function, the systematic errors in the content determinations can be read. In the ideal scenario, the number pairs, formed from the intensity and concentration ratios of the individual standards, lie on the determined calibration curve, like beads strung on a string. If the samples are far removed from the calibration curve, this distance is a measure for the systematic error to be expected.

Spectral lines for small contents are usually quite steep for higher concentrations. (In this image, the x-axis is the intensity, the y-axis is the concentration axis). With increasing contents, the line is no longer suitable for analysis since a large difference in concentration only corresponds to a small difference in intensity.

The calibration function also provides information about the contents from which a determination is possible. An example of the importance of dispersion for concentrations close to zero has already been given under point 1. This dispersion limits detection and quantitative determination.

So let us note that the calibration function and the position of the samples in relation to the calculated calibration function provide information about the usable range of the spectral line. If, as an additional parameter, the reproducibility for measurements with the spectral line under consideration is included, its analytical performance capability is completely known.

Auditors often insist that the calibration functions are only recorded using reference materials traceable to SI units. In practice, however, this is not possible because the availability of such standards is very limited. A calibration supported by only a few samples cannot accurately reflect reality. The instrument manufacturers make sure that as many of the quasi-official samples (from manufacturers such as BAM and NIST) as possible are measured when starting the calibration functions.

From the calibration curves, you can see the concentration ranges within which it makes sense to use the spectral line. The calibration curves also make it easy to estimate the size of the systematic errors and to estimate them separately for small, medium, and high contents.

Spark spectrometers are usually supplied with a basic calibration performed by the manufacturer. For standard-compliant work, this basic calibration must be checked before commissioning and at regular intervals thereafter. Previously, these tasks had to be carried out by the users themselves or by the instrument manufacturer. The device manufacturer issued a factory calibration certificate after the check.

3. Stability requirements

Prudent analytical work also includes getting an idea of the stability of the spectrometer system. This is necessary if only to deter-

mine appropriate time periods after which control standards must be measured. If the device is unstable, i.e. "drifting", this check must be carried out at short intervals. It may also require a time-consuming recalibration of several methods, associated with dozens of measurements.

Not all spark spectrometers work with modern algorithms where all methods can be recalibrated by measuring only one or two samples. To determine the stability of a spectrometer, it is possible to work with the spectrometer over a period of several days. A similar number of measurements should be carried out, as would later be the case in practice. Over this period, a set of control standards is measured at regular intervals (e.g. every two hours). If the contents are plotted against time, one quickly gains an impression of the stability of the system.

No significant maintenance work should be required during a test operation lasting several days. Significant maintenance work means anything that takes longer than a few seconds. For example, brushing off the electrode is acceptable, but compulsory standardization or cleaning work that involves dismantling components are not.

CONCLUSION

We live in an age when our work is increasingly regulated by standards. This is costly, but it is also indispensable in order to prevent damage in our increasingly complex world. For our own assurance, our analytical work should be performed according to the state of the art. On the one hand, the operational environment must be organized in such a way that work in conformity with standards is possible. On the other hand, efficient analytical equipment must also be available.

Device manufacturers make their spectrometers for a variety of purposes. Therefore, the user is not spared the trouble of checking whether a spectrometer system is actually capable of handling his/her inspection tasks.

It is often the case that device manufacturers focus on aspects such as an attractive design, modern software, a low price, low argon consumption, or a compact design. These points are unquestionably important. But the decisive question is whether the system is up to the user's testing tasks.

Literature

[1] DIN EN ISO 9001:2015-11, Qualitätsmanagementsysteme - Anforderungen (ISO 9001:2015). Berlin, Beuth Verlag, 2015

[2] International Automotive Taskforce: IATF 16949:2016 Anforderungen an Qualitätsmanagementsysteme für die Serien- und Ersatzteilproduktion in der Automobilindustrie, 1st Edition, October 2016. Available via the online store of the German Association of the Automotive Industry (VDA), http://webshop.vda.de/QMC/de/IATF-169492016

[3] DIN EN ISO/IEC 17025:2017-02 – Draft: Allgemeine Anforderungen an die Kompetenz von Prüf- und Kalibrierlaboratorien (ISO/IEC DIS 17025:2016). Berlin, Beuth Verlag, 2017

4] Mindestanforderungen zur Akkreditierung der optischen Funkenemissionsspektrometrie (OES), Document 71 SD 1 005, Revision 1.1, February 24th, 2014 http://www.dakks.de/sites/default/files/dokumente/71_sd_1_005_funkenemissionsspektrometrie_20140224_v1.1.pdf, Viewed on 9.10.2017

[5] DIN 32645:2008; Chemische Analytik – Nachweis-, Erfassungs- und Bestimmungsgrenze unter Wiederholbedingungen – Begriffe, Verfahren, Auswertung. Berlin, Beuth-Verlag

[6] DIN V ENV 13005 Leitfaden zur Angabe der Unsicherheit beim Messen (Deutsche Fassung, 06-1999)

[7] EURACHEM CITAC GUIDE Ermittlung der Messunsicherheit bei analytischen Messungen 2004

[8] EUROLAB Leitfaden zur Ermittlung von Messunsicherheiten bei quantitativen Prüfergebnissen (TB_2_2006)

[9] GUM Evaluation of measurement data - Guide to the expression of uncertainty in measurement 2008

[10] Nordtest Report TR 537 HANDBOOK FOR CALCULATION OF UNCERTAINTY IN ENVIRONMENTAL LABORATORIES 2004-02

[11] DIN ISO 11352 EN DE Wasserbeschaffenheit - Bestimmung der Messunsicherheit basierend auf Validierungsdaten (03-2011)

[12] Deutsches Einheitsverfahren DEV AO-4 Leitfaden zur Abschätzung der Messunsicherheit aus Validierungsdaten (2006)

[13] Merkblatt zur messtechnischen Rückführung im Rahmen von Akkreditierungsverfahren, Document 71 SD 0 005, Revision 0. www.dakks.de/userfiles/71%20SD%200%20005_merkblatt_r%C3%BCckf%C3%BChrung.pdf, Viewed on 9.20.2017

[14] Einbeziehung von Eignungsprüfungen in die Akkreditierung, Document 71 SD 0 010, Revision 1.2 , April, 14th, 2016. www.dakks.de/sites/default/files/dokumente/71_sd_0_010_eignungspruefungen_20160414_v1.2.pdf, Viewed on 9.20.2017

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