

specified minimum requirements, the spectrometer system can be released for testing procedures.

Keeping mean-value control charts should also be regulated via an operating procedure. This should determine what must be done if the upper and lower warning threshold is exceeded (e.g., when cleaning the spark stand, cleaning the windows, during recalibration, etc.). Even if warning thresholds are not exceeded, corrective measures may be necessary.

Corrective measures are common, for example, if:

- Seven consecutive measurement values are above or below the mean value,

- Of 11 measurement values, 10 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 standard controls (CRM) must be available for every testing method used.

Used to inspect analysis devices, CRM (Certified Reference Materials) samples 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 be known only approximate-

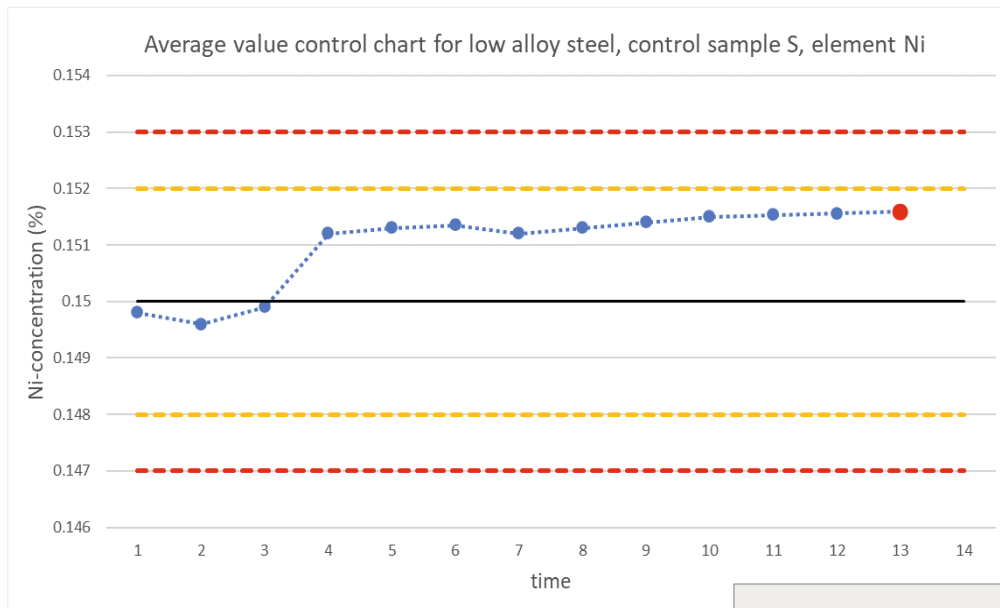


Figure 1: Example of an average value control chart

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

- Of the last 11 measurements, 10 were above the mean value line.
- Seven consecutive measurements were larger than their predecessors.

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

Average value and standard deviation determined in the preliminary period, prior to the utilization phase:

- Average value (Av): 0.15%
- Standard deviation: 0.01%

Calculated from this:

- Upper intervention limit (UCL, upper red line): 0.153%
- Upper warning limit (UWL, upper orange line): 0.152%
- Lower warning limit (LWL, lower orange line): 0.148%
- Lower intervention limit (LCL, lower red line): 0.147%

ly. As a rule, several samples of a batch are obtained from each control standard. These are used only to check whether the measured values remain constant. By comparison, CRMs are more expensive. They are usually used only at longer intervals, in cases of uncertainty, or in audits.

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

6. Proficiency tests

For an accreditation according to DIN EN 17025, participation in proficiency tests (round robin tests) is required. Samples from an external service provider are analyzed at regular intervals (for example, 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 — 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). Also included must be the name and address of the client and of the testing laboratory; a clear description of the materials tested; the testing date and date of entry for the test specimens; and place of employment and signature of the person approving the test report.

Requirements for the analysis device

The environmental requirements above show why users can't simply buy an "audit-proof spectrometer." No matter what model is chosen, certain organizational measures in the user's operational environment will remain unavoidable.

However, the user can — and must — take care to check whether their existing or prospective spectrometer system can cope with the testing tasks that regulators now require.

DAkkS document "71_sd_1_005" [4] differentiates between external basic calibration (done by a service provider or the device manufacturer) and internal basic calibration (done by the users themselves). Mobile spectrometers are usually not user-calibrated. 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 DAkkS documents. Of course, the aspects described should also be taken into account before purchasing equipment.

1. Requirements for detection and determination limits

For many analytical tasks, 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 nonalloyed steel, a pure iron (Fe) sample is used to determine the detection limit. This is relatively simple. In contrast to the DIN 32645, several device manufacturers indicate two times the standard deviation as the detection limit. Know-



ing this, the user can calculate the standard detection limit by multiplying by a factor of 1.5 to get a comparable value. DIN 32645 gives ten times the standard deviation of the zero sample as the determination threshold, which is the value from which quantitative analysis is possible.

It is important to note that the aim here is to perform detection or a quantitative determination in a high-purity material.

Example: The standard deviation for carbon is 60 ppm (0.006%). If you measure a pure sample and obtain a value above 0.018%, the pure sample contains carbon. For values above 0.06%, you may transmit the discovered 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 (carbon 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). Grade

1.4306 may contain a maximum of 0.03% carbon. To ensure this limit can be monitored 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. Grades 1.4301 and 1.4306 may both contain between 0 and 1% silicon (Si), and between 0 and 2% manganese (Mn). The elements chromium (Cr) and nickel (Ni) have allowable fluctuations of approximately 2%. Several tenths of a percent of other elements can occur.

Systematic errors can result, leading to a report of increased or reduced carbon content. These 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 concentration varies within a raw material. For our example, if a possible systematic error of 0.01% is determined, a measurement uncertainty of at least 0.01% must always be expected. Figure 2 illustrates this relationship. A zero sample reproducibility of well below 30 ppm (e.g., 15 ppm) should therefore be sought to minimize random errors.

So it is not sufficient that the detection limit lie 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 when purchasing a spectrometer. Analyses performed with a system that cannot sufficiently handle everyday tasks are useless. On the contrary, they may suggest that a user's obligations have been fulfilled — even though the conducted tests themselves are not meaningful. This can lead to difficulties if, in retrospect, users are trying to prove that work was done in accordance with the state of the art.

2. Calibration function requirements

Auditors often marvel at the calibration functions possible with advanced spec-

trometers today. The course of the calibration curve reveals the best achievable measurement uncertainty. From the dispersion of samples around the found calibration function, any 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 on a string. If the samples are far removed from the calibration curve, this distance is a measure of the expected systematic error.

Spectral lines for small contents are usually quite steep for higher concentrations. (In the accompanying image, the x-axis is the intensity; the y-axis is the concentration). 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.

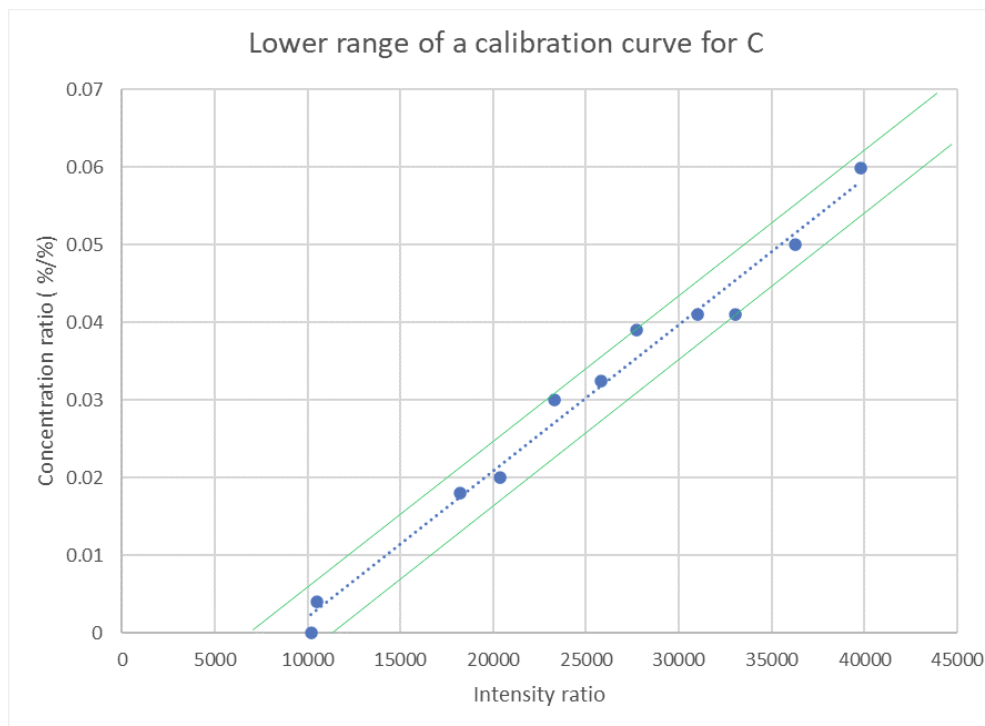


Figure 2: Illustration of expected systematic calibration errors

With the calibration function shown in Fig. 2, a systematic error must be expected that corresponds to the distance between one of the green lines and the curve (dotted line). In the example, this is approximately 0.004%. Other sources of systematic errors must of course also be considered.

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 calibration functions only be recorded using reference materials traceable to SI units. In practice, however, this is not possible; the availability of such standards is extremely limited. However, a calibration supported by only a few samples cannot accurately reflect reality. So instrument manufacturers make sure

that as many quasi-official samples as possible (from manufacturers such as BAM and NIST) are measured when starting calibration functions.

Not all mobile spectrometers work with classical empirical calibration, in which calibration functions are determined using reference materials. Instead, "fingerprints" of so-called master samples may be taken. After measuring an unknown sample, the system finds the best-fitting master sample and displays its analysis. Usually the contents of the unknown sample are determined by interpolation based on its intensity differences with the master sample.

Caution: if one uses systems that work according to this principle, often no calibration curve can be shown to the auditor. It is advisable to obtain precise information from the manufacturer on how the corresponding fingerprint algorithms work, to be able to answer questions if necessary (as when an audit occurs in case of damage) and to gain clarity about possible pitfalls before using such systems.

The problems of the nontransparency of fingerprint algorithms can be shown by the example of a fingerprint algorithm where no interpolation takes place:

A master sample of grade 1.4306 steel with a manganese content of 0.8%, and a master sample of 1.4301 steel with a manganese content of 1.5%, are both stored in a device's fingerprint database. If an unknown sample of grade 1.4306 is then measured that shows approximately 0.8% manganese, this kind of system reliably finds the master sample of the 1.4306 and outputs its analysis exactly.



This may give the impression that the device has very good repeatability. But now another sample of the alloy 1.4306 is measured — one which has a manganese content of about 1.5%. In this case, due to the higher manganese content, the system may find the 1.4301 master sample instead, and (mistakenly) output its analysis. This result may then be repeated with multiple other measurements. Obviously, unexpected errors can then occur.

It must be noted that the determination of contents by means of fingerprint identification is always more difficult to understand than is the case with classical empirical calibration. If fingerprint algorithms are used, a concentration interpolation should be conducted.

Using a device that offers calibration curves, you can see the concentration ranges within which it makes sense to use the spectral line. The curves also make it easy to estimate the size of systematic errors, and to approximate them separately for small, medium, and high contents. This is not possible when using fingerprint algorithms.

Fingerprint algorithms are not always contraindicated. Excitation sources such as arcs and lasers are strongly influenced by third elements. During empirical calibration, large systematic errors occur (due to temperature changes in third elements in the arc, or non-constant energy coupling in the laser). If laser excitation is used, the analysis of Cr/Ni steels for the elements chromium and nickel, for example, can lead to misdeterminations in percent ranges. In these kinds of situations, fingerprint algorithms can be used instead.

There are also applications, e.g. in the presorting of scrap, where the problems men-

tioned above hardly matter. Many mobile and handheld devices are manufactured for the scrap presort market. The use of fingerprint algorithms is less critical here.

3. Stability requirements

Prudent analytical work also includes getting an idea of the stability of the spectrometer system. This is necessary if only to determine 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. This may also require a time-consuming recalibration of several methods, associated with dozens of measurements. Not all operating spectrometers work with modern algorithms whereby all methods can be recalibrated by measuring only one or two samples.

To determine the stability of a spectrometer, users may work with it over a period of several days. The number of measurements carried out should be similar to those that would be performed in practice. Over this period, a set of control standards would be measured at regular intervals (e.g., every 2 hours). Plotting contents against time, the user can quickly gain an impression of the system’s stability.

As far as spark or laser systems are concerned, no significant maintenance work should be required during a test run that lasts 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 requires dismantling components, is not. With arc systems, combustion of the electrodes can occur. Here it is inevitable that the electrode be readjusted or replaced from time to time.

CONCLUSION

We live in a complex age, when our work is increasingly regulated by standards. This may have its costs — but it is also indispensable in preventing damage, ensuring safety, and enabling efficiency. For our own assurance as much as for regulatory compliance, our analytical work should be performed according to the state of the art.

So our operational environment must be organized in such a way that work in conformity with standards is possible. And that work must be performed by sufficiently capable, efficient analytical equipment.

Device manufacturers design their spectrometers to perform a wide variety of analytical tasks. Users should remain cognizant of this, and must show due diligence in checking whether a spectrometer system is actually capable of handling the inspection tasks for which the user will apply it.

Manufacturers may promote their attractive designs, modern software, low price, or low weight. These are important for a variety of applications. But the decisive question for each user must remain: Does this spectrometer system meet today's requirements for my inspection tasks?

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