

Background Correction In AAS – Can You Really Trust It As Much As You Do?

Oliver Büttel, Product Manager Optical Spectroscopy

Analytik Jena AG

Background Correction (BGC) is an essential part of any spectrometric analysis. Typically a non-specific signal, the spectral background, is superimposed on the analyte-specific signal and needs to be excluded to obtain the net analyte signal. Different techniques have been developed to distinguish specific from non-specific signals. In ICP OES with an array detector for example, the spectral background can be calculated from the emission spectrum of a sample by evaluating the baseline on both sides of the analyte emission line.

In traditional Atomic Absorption Spectrometry however, sample spectra cannot be used for this purpose because of the line emission profile of the light source used and the detection system, which make it impossible to record wavelength-resolved signals. For this reason the spectral background must be measured in a separate measurement. Practically, total (specific and non-specific) and background (non-specific only) absorbance are measured alternatingly and automatically subtracted from each other.

Traditionally three different methods are used in AAS: Deuterium-, Zeeman- and Self-Reversal-BGC. In all three cases the instrument software only shows numeric values for Atomic Absorption (AA) and Background (BG). As we will see, these numeric values are sometimes not sufficient because no information is available where they actually come from, and the user must have a certain level of trust in these values without being able to verify them.

It should also be mentioned that all three BGC methods increase the noise level of the signal to a certain extent because of the differential measurement of AA and BG. The fact that AA and BG are not measured exactly at the same time is an additional error source, particularly in Graphite Furnace AAS with its fast-changing signals. Each of the traditional BGC methods has its typical correction limitations and additional disadvantages.

Traditional Correction Methods

Deuterium Background Correction

Nowadays commonly used in Flame and low-cost Graphite Furnace AAS instruments, Deuterium-BGC is the oldest one of the traditional methods. It uses the continuous radiation of a Deuterium lamp to measure the average background absorption over the slit width monitored. An inherent limitation of this method is the Deuterium lamp itself, which only emits in the UV-range. At wavelengths higher than about 350nm Deuterium-BGC cannot be used. In addition to this, any noise or drift of the Deuterium lamp will directly be added to the AAS signal.

As this method can only measure the average background over the spectral range monitored, it only works correctly if the baseline is horizontal. In case of a structured baseline, for example if molecule absorption bands or other atomic absorption lines are present, it will calculate a false value. The Graphite Furnace signal shown in Figure 1 shows an over-correction leading to a negative AA signal for Arsenic in presence of Phosphate molecule absorption bands.

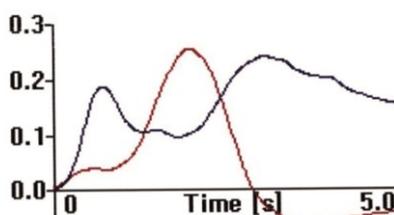


Fig.1: Over-correction of BG (blue) leads to negative AA-signal (red)

Zeeman Background Correction

Born in the 1980s, Zeeman-BGC uses a strong magnetic field to make the specific Atomic Absorption “invisible” to the spectrometer. This way the Background alone can be measured exactly on the analyte wavelength using the hollow cathode lamp of the analyte element. Zeeman-BGC is almost exclusively used in Graphite Furnace

AAS, where the correction performance of the Deuterium method is often not sufficient.

Zeeman-BGC shows a better correction performance than Deuterium-BGC because it measures the atomic and background absorbance on exactly the same wavelength and with the same light source. Thus it can handle structured background in a much better way – given that the background does not change in the magnetic field. This fundamental requirement is fulfilled by most background structures.

However, certain molecule bands and all atomic lines show the Zeeman effect, i.e. a spectral background of molecular or atomic absorption by matrix constituents can be changed by the magnetic field. These will not be corrected accurately if they are close to the analyte wavelength. Some examples have been described in the literature, and a particular one many AAS users may face is the interference on the primary Nickel line by Iron (Figure 2). The absorption spectrum shows the interference of a high Iron signal on the relatively small Nickel line. The Nickel

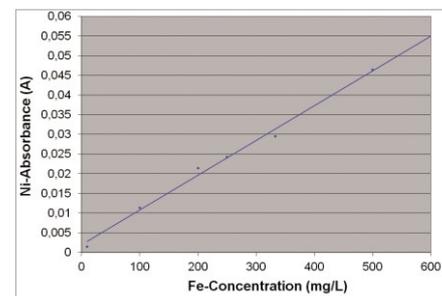
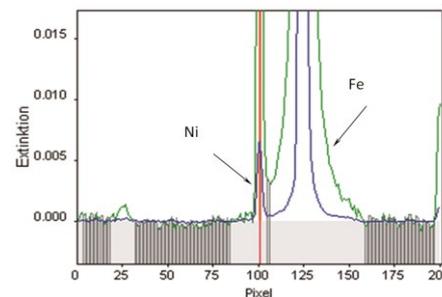


Fig. 2: Interference of Fe on Ni-line (above), False Ni-signal produced by high Fe-concentrations

result measured with Zeeman-BGC will be falsely high with increasing Iron concentrations. This case will occur whenever traces of Nickel are determined next to a high Iron content.

Self-Reversal Background Correction

Self-Reversal-BGC (SR-BGC) is the least common one of the three techniques described here. It is also often referred to as Smith-Hieftje-BGC, according to the names of its inventors. A self-reversal condition is created in the analyte HCL by applying a high-current pulse, during which the background is measured.

SR-BGC has not been very successful commercially, currently only one major instrument manufacturer uses this technology. SR-BGC has certain disadvantages that originate in the function principle. The high current applied to the light sources used reduces their lifetime and requires suitable lamps. Self reversal in the lamp is not complete, resulting in sensitivity being reduced by up to 70% and non-linear calibration curves. Background showing molecular or atomic absorption structures close to the analyte wavelength cannot be corrected. Additionally, the lamp needs a certain relaxation time after a high-current pulse, which limits the frequency of alternating AA- and BG-measurements and thus the capability of following the fast signals in Graphite Furnace AAS.

The better way of Background Correction

With the introduction of the High-Resolution Continuum Source AAS (HR-CS AAS) in the contrAA® instrument series in 2004 a new method of Background Correction became available. With a light source emitting a continuous spectrum, a high-resolution Echelle spectrometer and a CCD array detector, these instruments routinely display sample absorbance spectra – for the first time in AAS!

The spectral background is corrected directly and simultaneously in the spectrum by automatically fixing the baseline at Zero Absorbance. At the same time fluctuations of the lamp intensity are corrected the same way – double-beam functionality in a single-beam instrument.

The sample spectrum contains valuable information – in the simplest case it proves that the background is corrected properly and there are no spectral interferences. It gives the user the confidence that the analyte element is measured correctly (Figure 3).

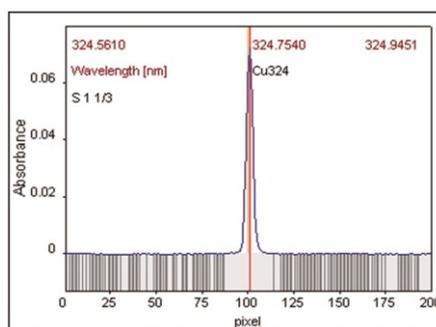


Fig. 3: Background corrected, interference-free Absorbance spectrum

Besides giving the analyst trust in his results, the spectrum contains much more useful information. Additional lines in the spectrum give qualitative information about other elements present in the sample (Figure 4) – and can be quantified simultaneously if required.

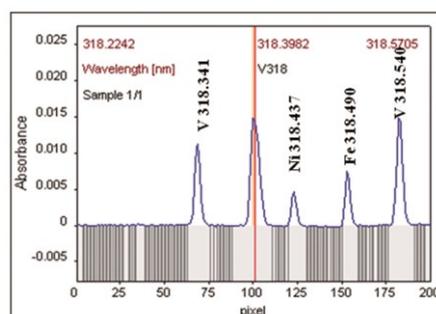


Fig. 4: Vanadium analysis reveals additional elements

As mentioned before, structured background and spectral interferences can often not be corrected using the classical BGC techniques. In fact, with these techniques an interference can easily remain undetected if the results are not carefully examined. Here the High-Resolution Continuum Source AAS instruments and their specific software are clearly ahead. The high spectral resolution avoids almost any interference in the first place. To be sure, the spectrum of each sample is displayed and can be printed in the report. So even in the rare case of spectral interferences they can be detected, identified and corrected easily. The typical spectral structures that might appear in AAS are stored in a reference library in the operating software for identification. Then it is enough to record a matrix spectrum of the interfering substance and implement it in the method. Now the interference will automatically be subtracted from each sample spectrum (Figure 5), always ensuring correct results.

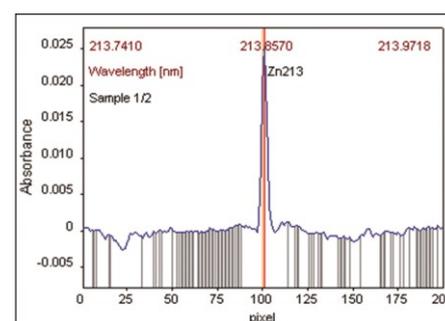
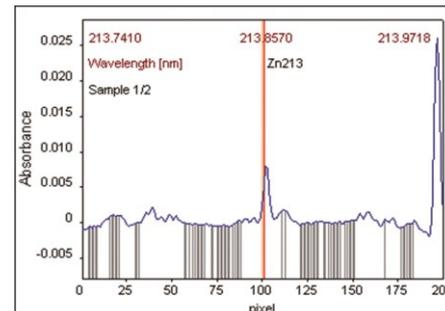
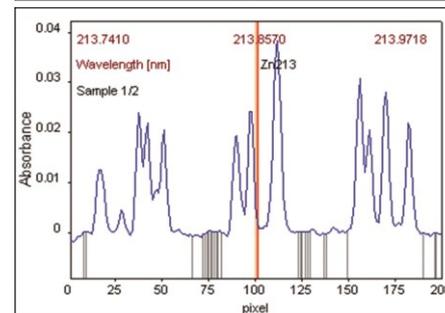
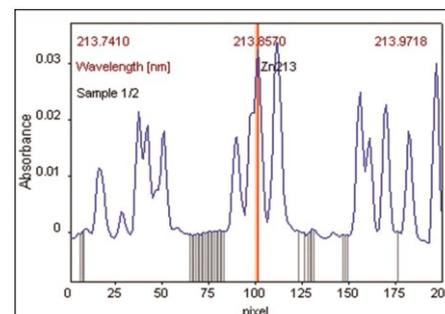


Fig. 5: (a) Absorbance spectrum of Zn 213.857 nm in a matrix containing Nitrate and Fe; (b) Nitrate matrix spectrum; (c) Fe 213.859 nm matrix spectrum; (d) Corrected Zn spectrum after subtraction of Nitrate and Fe spectra

Summary

Traditional methods of background correction have limited capabilities, particularly in case of structured background or matrix wavelengths directly overlapping with the analyte wavelength. Often enough, correction errors remain undetected or unidentified because of the limited information provided by the instrument. As a result, erroneous analysis values are produced and complicated method development becomes necessary to minimize the error.

HR-CS AAS in the contraAA® series has clear advantages because of its revolutionary optical design. All corrections can be done simultaneously, directly in the sample spectrum. Thanks to the spectrum display any interference, including the one between Ni and Fe mentioned above, is obvious at first glance and can be corrected with a few

mouse-clicks. In addition to this, it is the ideal instrument for multielement analysis. The continuous light source makes lamp exchange a matter of the past, the possibility of simultaneous evaluation of multiple wavelengths further increases the sample throughput. Even non-metals like the halogens or sulfur can be analyzed – a completely new application field for an AAS! The 10 years approved HR-CS AAS technology can drastically increase the productivity and the quality of results of any analytical lab.