'Fitted' — Fast, accurate and fully-automated background correction

Technical overview

Introduction

It's commonplace in ICP-OES for background (baseline) correction to be applied on the total signal observed for an analyte emission line. This is because many factors influence the background signal at a specific wavelength. Some of these are constant, while others can cause the background to change from sample-to-sample.

A major source of constant background in ICP-OES originates from the argon plasma in what is termed the 'background continuum'. The background continuum is radiation distributed continuously over the wavelength range of a spectrometer. In the wavelength range of 160–800 nm, the range typically covered in ICP-OES, the background signal is small for lower UV wavelengths and gradually increases with increasing wavelength. Another form of background is 'dark current', which is the contribution of background signal arising from the ICP detector. Dark current related background is often corrected for prior to sample analysis, by measuring the signal from the detector when it is not exposed to the emission source (argon plasma). The type, design and overall quality of the optical system will also define the relative background observed on a particular ICP-OES system.

The magnitude of background signal observed at a specific wavelength is influenced by key plasma parameters including plasma configuration, power and gas flows, nebulizer gas flow and plasma viewing position. The signal intensity of an analyte emission line is also affected by these key plasma parameters. As the intensity of an emission line and the adjacent background directly impacts on the detection limit of an analyte, optimization of the plasma parameters is important. The same element can have different optimal plasma conditions depending on the selected wavelength. For example, the plasma conditions for the aluminum 167 nm ionic emission line will differ from those required for the 396 nm atomic emission line in order to achieve lowest possible detection limits. Once plasma parameters are set, the background from the argon plasma is fairly constant and background correction is usually straightforward.

The presence of high concentrations of elements in samples contributes to background and can make correction far more complex. These may include:

- Stray light resulting from very intense emission lines. For example, calcium 393.366 nm and 396.847 nm emission lines.
- Electron-ion recombination effects. For example, elevated aluminum levels in the background between 193–210 nm.
- Spectral line-broadening. For example, Ca 396.847 nm emission line on Al 396.152 nm, and Al 220.467 nm emission line on Pb 220.353 nm.
- Molecular bands. For example, OH bands from dissociated water molecules, and carbon-based molecular bands from organic solvents.

As the matrix from sample-to-sample can often vary, so too can the background signal in both intensity and structure. This application challenge has created a need for a sophisticated, yet simple, fast, and accurate means of background correction, independent of the sample matrix.

Off-peak background correction (OPBC)

Off-peak background correction is the oldest and most traditional form of background correction used in ICP-OES. In the simplest case, the continuum background adjacent to the analyte peak is flat, and the measurement of a single background point is sufficient for calculating the net intensity. Sample-to-sample variation in the background level is also easily accounted for. A suitable background correction point is determined by scanning a representative sample during method development.

In situations where the analyte emission line is close to a broadened interferent, resulting in a linear but sloping background, two points measured either side of the analyte peak are necessary for an accurate determination of the background.

For curved or more complex background structures adjacent to the analyte peak, OPBC is unsuitable due to greater inaccuracy. Sample-to-sample variation of matrix elements also makes it extremely difficult to find suitable background points that can cater to all background variations that may be observed during an analysis.

‘Fitted’ background correction (FBC)

In addition to OPBC, the Agilent 700 Series ICP-OES offers the unique fitted background correction — a powerful, yet easy to use background correction technique, utilizing a sophisticated mathematical algorithm to model the background signal under the analyte peak. FBC not only provides accurate correction of both simple and complex background structures, it requires no method development. Just ‘set and forget’ and FBC does the rest, no matter what the sample matrix.

FBC works by mathematically modeling the measured spectrum by:

1. Determining the offset component to model the unstructured continuum background.

2. Determining the slope component to model the wings of large distant peaks.

3. Applying three Gaussian peak components to model:

a. The analyte peak.
b. Any potential interference peak to the left of the analyte peak.
c. Any potential interference peak to the right of the analyte peak.

4. Using an iterative procedure to estimate the width and position of the peaks.

5. Using a method of least squares to determine the magnitude of the offset, slope and peak heights.

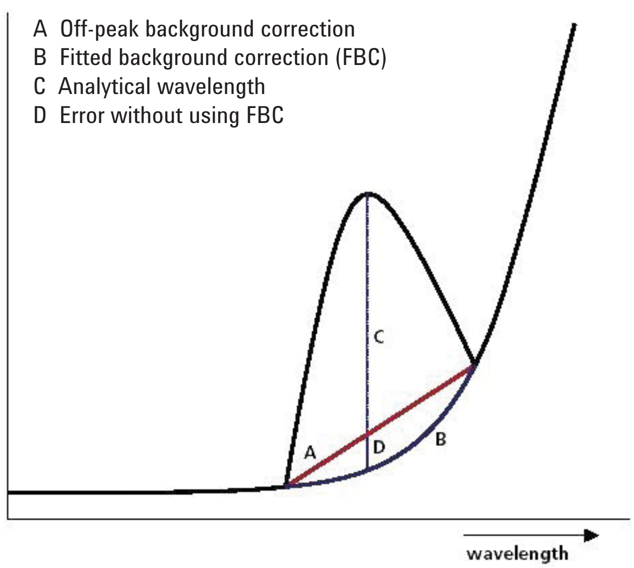

Figure 1. Fitted background correction calculates the true background signal, improving accuracy

Once the model has been fitted, the analyte peak component is removed from the equation, leaving only the model for the background. FBC is applied simultaneously upon measurement of the analyte peak, and provides fast and accurate background correction.

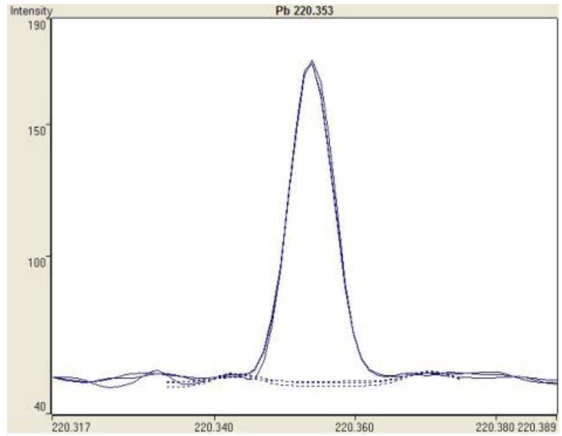

Figure 2a. Pb 220.353 nm emission line in deionized water. Simple background spectrum with either OPBC or FBC being suitable.

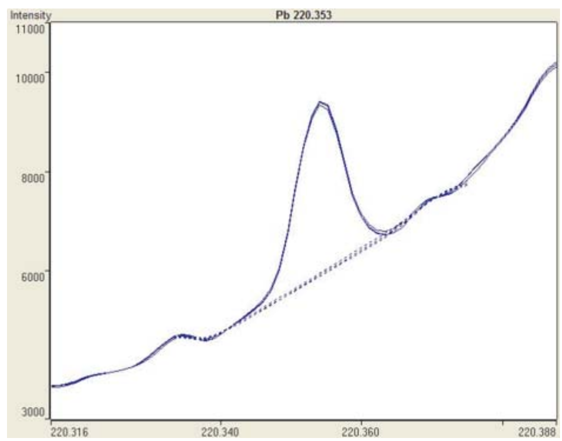

Figure 2b. Pb 220.353 nm emission line in 2000 mg/L aluminum. Wing overlap from spectral-line broadening of Al 220.467 nm has resulted in a higher background signal with a curved profile at Pb 220.353 nm, which FBC successfully corrects for.

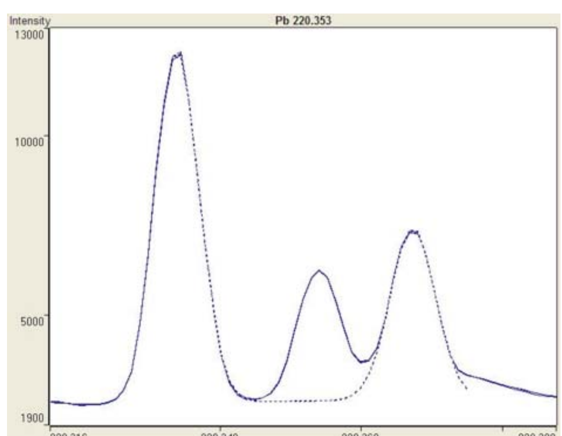

Figure 2c. Pb 220.353 nm emission line in 1000 mg/L molybdenum. Nearby interfering emission lines of Mo make using OPBC near impossible. Again, this is no problem for Agilent's fitted background correction.

Summary

Agilent's FBC takes the guesswork out of background correction. No matter what your sample challenge may be, FBC easily adapts to background structures that off-peak background correction cannot. This powerful, yet easy to use technique also requires no method development, meaning you'll never have to waste time trying to find suitable background correction points for all your samples.

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