

# Multicomponent Spectral Fitting

## ICP-Optical Emission Spectroscopy

### Introduction

Baseline and interfering element correction (IEC) techniques are used with ICP optical emission spectroscopy to correct analytical signals for contributions from the plasma, the matrix, or elements other than the analyte. If the contributions from these components are not corrected accurately, the analytical result will be erroneous. Yet both correction techniques rely on interpolated or extrapolated correction factors.

Baseline correction measurements typically are made at one or two wavelengths adjacent to the analyte wavelength with the assumption that the baseline at the analyte wavelength can be interpolated from the baseline correction measurement. IEC correction relies on the validity of single-point measurements made on each interfering element, assuming that the IEC measurements can be extrapolated accurately to correspond to different concentrations of the interferent. Both techniques rely on the validity of the interpolation or extrapolation. Although the two techniques can improve performance with some types of samples, they are not universally applicable.

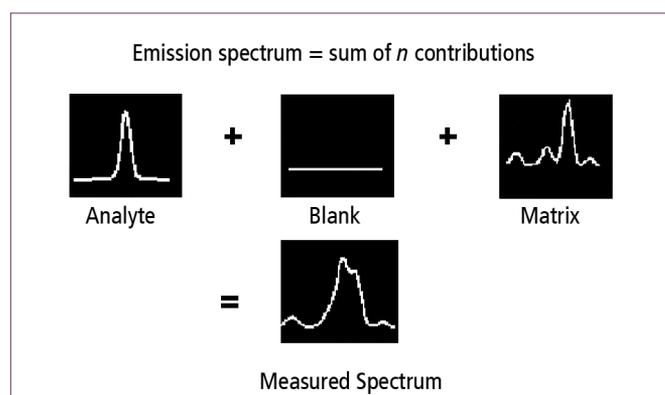


Figure 1. The measured spectrum consists of several components, demonstrating the need for improved spectral fitting techniques like MSF.

### Multicomponent Spectral Fitting

For greater accuracy, using a full segment of the spectrum around the analyte wavelength is preferred to using just one or two points. To achieve that goal and to provide superior correction capabilities, PerkinElmer developed Multicomponent Spectral Fitting (MSF). Mathematically, MSF uses a multiple linear least squares model based on an analysis of the pure analyte, the matrix, and the blank (Figure 1). It sounds complicated, but it isn't. Think of it as automatic simultaneous multi-point background correction. Using MSF for spectral overlap correction requires only that a minimum of three solutions are analyzed: the blank, a pure solution of the element being determined, and pure solutions for each of the potentially interfering elements in the matrix. MSF and the computer do the rest – automatically. There are no limits on the number of interfering elements that can be included in a model. In addition, once models are developed for an element, they can be used in many different analytical methods.

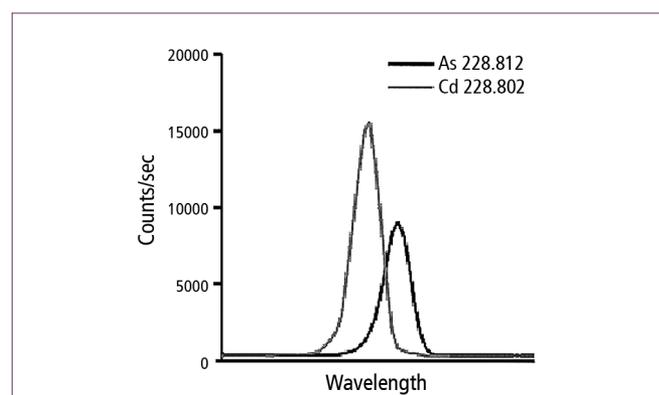


Figure 2. Running the Cd and As standards separately demonstrates the spectral overlap.

As an example, let's look at the determination of arsenic in the presence of cadmium at the 228.812-nm emission line. The sample spectra for solutions containing 1.1 mg/L Cd and 31 mg/L As are shown in Figure 2.

After creating an MSF model using these spectra, the combined spectrum of the complex matrix can be measured, as shown in Figure 3. Applying MSF, the corrected spectrum for arsenic (Figure 4) shows no evidence of the interfering sample matrix and is easily quantifiable. It's that simple.

Because MSF uses all of the spectral information available, both the analytical accuracy and the detection limits are improved. Figure 5 shows that the detection limits for this group of elements are improved significantly with MSF over those obtained with no background correction, with sequential off-peak background correction, or with simultaneous background correction.

### Why does MSF improve detection limits more at longer wavelengths?

Detection limits in the lower UV with a low-noise detector are usually limited by photon shot noise, caused by the random arrival times of the photons as they reach the detector. In contrast, detection limits at higher wavelengths are limited by noise due to the sample introduction system, often called "flicker" noise. Simultaneous background correction (including MSF) can compensate for flicker noise automatically, so the performance improvements are more pronounced at higher wavelengths.

MSF can significantly improve your analytical results – detection limits, accuracy, and precision. Even better, it's included as a standard feature with all PerkinElmer Avio® ICP-OES spectrometers.

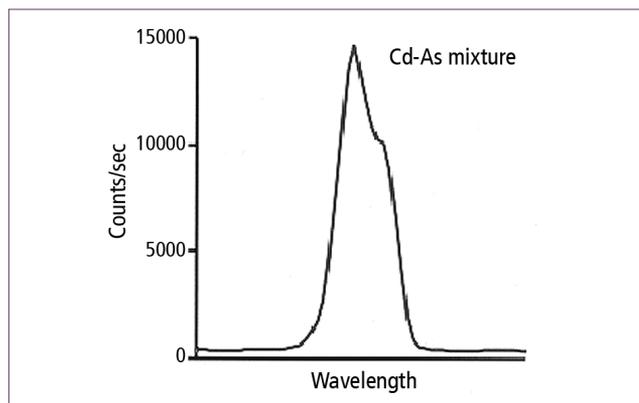


Figure 3. The Cd overlaps the As peak, making it difficult to measure As with conventional background correction techniques and necessitating the selection of an alternate wavelength.

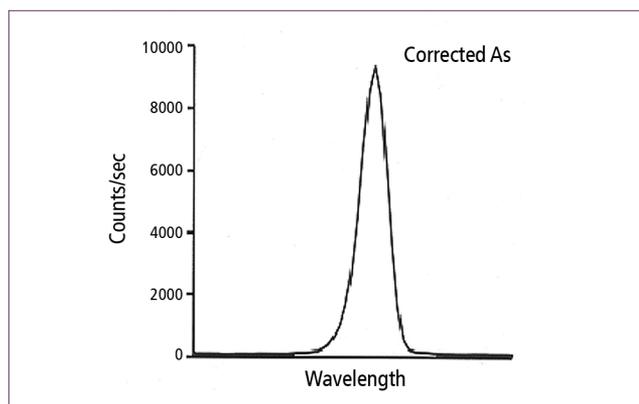


Figure 4. The correct As concentration is determined despite the Cd overlap, making it easier to develop methods using MSF.

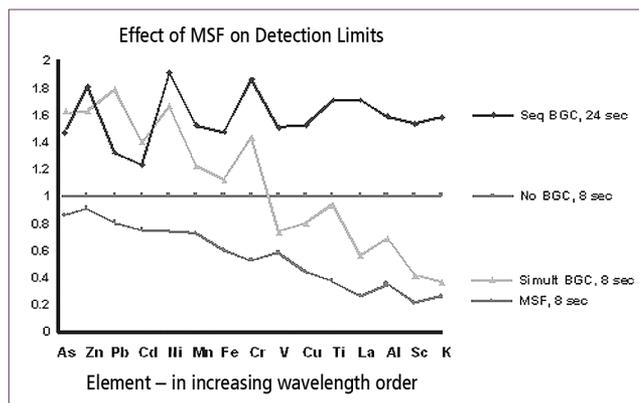


Figure 5. MSF improves detection limits over sequential and simultaneous background correction techniques.