

FACT spectral deconvolution

Technical overview



Introduction

In a perfect world, ICP-OES instruments would have infinite spectral resolution, with the most sensitive emission lines for each element always being free from spectral interference, regardless of the sample. For complex sample matrices, this is not always possible, but Agilent's proprietary Fast Automated Curve-fitting Technique (FACT) makes this ideal situation a reality. It does this by applying a highly sophisticated, yet easy-to-use spectral modeling technique to accurately model complex analytical spectra often observed when analyzing challenging sample matrices by ICP-OES.

The advantages of FACT lie in its ability to accurately correct for strongly overlapping peaks near the analyte wavelength. FACT models are easily created either before or after the collection of analytical data, giving you the confidence to handle any challenge your samples may present. FACT also saves valuable time by eliminating further sample preparation, re-analysis of samples, or the need to churn through vast quantities of results in search of erroneous data.



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FACT is a simpler and more powerful alternative to inter-element correction (IEC). It also offers the capability of accurate background correction, particularly useful when highly-complex background structure is observed and more traditional background correction techniques are unsuitable.

How does FACT work?

FACT provides real-time spectral correction by using an advanced spectral modelling technique to mathematically deconvolute (or separate) the analyte signal from the raw spectrum. Models are built by measuring the expected components separately and the response for each. This typically includes measuring these solutions:

1. A blank solution
2. A pure analyte solution
3. Pure interferent solutions.

Each spectral component model is analyzed and fitted to a Gaussian curve to obtain a mathematical description of the peak. The residuals are inspected for remaining structures, and if large enough, may be fitted to additional Gaussians. The model component is then represented as a sum of Gaussian peaks and relatively small residuals. Any minor wavelength offset or drift that may occur between model creation and application in an analysis is accounted for by monitoring six plasma-based emissions lines across the wavelength range. This maintains the wavelength accuracy of the models for long-term use.

Unlike IEC, the known concentration of the analyte and interferent in the respective solutions is not required. The solution concentration only needs to be high enough for the signal peak to be easily distinguishable from the background (typically 50 times the detection limit).

The example in Figure 1 demonstrates model building for the prominent cadmium 214.439 nm emission line that is partially interfered by the significantly less sensitive 214.445 nm iron emission line. A common occurrence in the analysis of soils samples, the accurate determination of trace-level cadmium can be compromised by the presence of high iron concentrations.

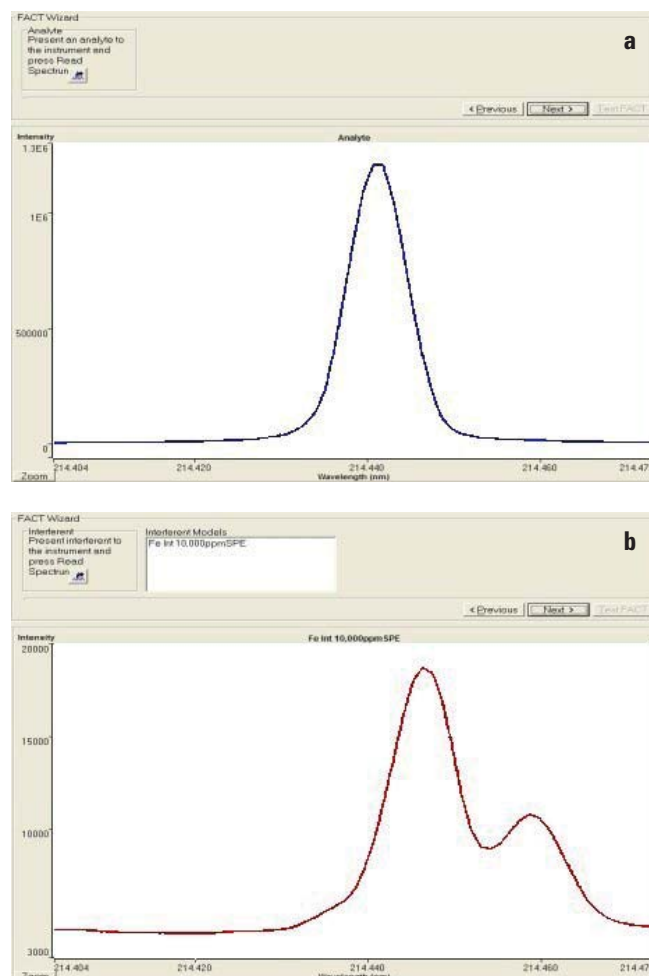


Figure 1. a) FACT model of 10 mg/L cadmium analyte solution. b) FACT model of 10,000 mg/L iron interferent solution.

Once models have been created, all sample results are immediately updated. Up to seven interference models can be applied to an analyte, and all models are transferrable between methods for future analyses.

Peak separation <1 pm

The optical resolution of an ICP-OES is characterized by the physical attributes of the optical system and is defined as the full-width at half maximum (FWHM). This represents the width of the analyte peak at half the peak signal intensity. The distance separating the Cd and Fe peaks in Figure 2 is approximately 6 pm, which an ICP-OES optical system is typically unable to completely resolve. In the Figure 2 example, FACT is able to mathematically separate the two peaks with a precision and accuracy of <2% RSD. Even at 0.6 pm, FACT can determine the analyte concentration to a precision (and accuracy) of <5% RSD, providing more than 10 times improvement on the instrument optical resolution (Figure 3a).

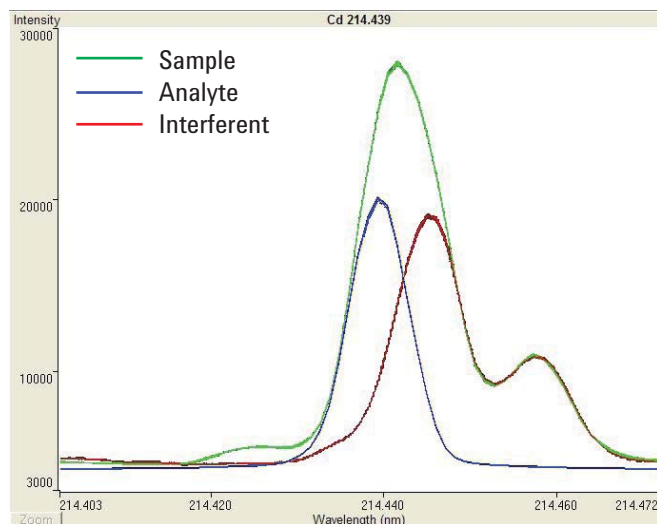


Figure 2. Example of a FACT model being applied to Cd 214.439 nm interfered by Fe. A solution containing ~100 µg/L Cd in 10,000 mg/L Fe was analyzed on an Agilent 720 ICP-OES.

When analyte and interference peaks directly overlap at exactly the same wavelength, the selection of an alternative line is typically preferred. However, FACT can accurately correct for directly overlapping interference peaks when additional spectral information relating to the interferent is available nearby. In Figure 1b, although the overlapping peak of Fe 214.445 nm only partially overlaps with Cd 214.439 nm, the second Fe peak at 214.457 nm would make it possible to accurately correct for directly overlapping analyte and interference peaks.

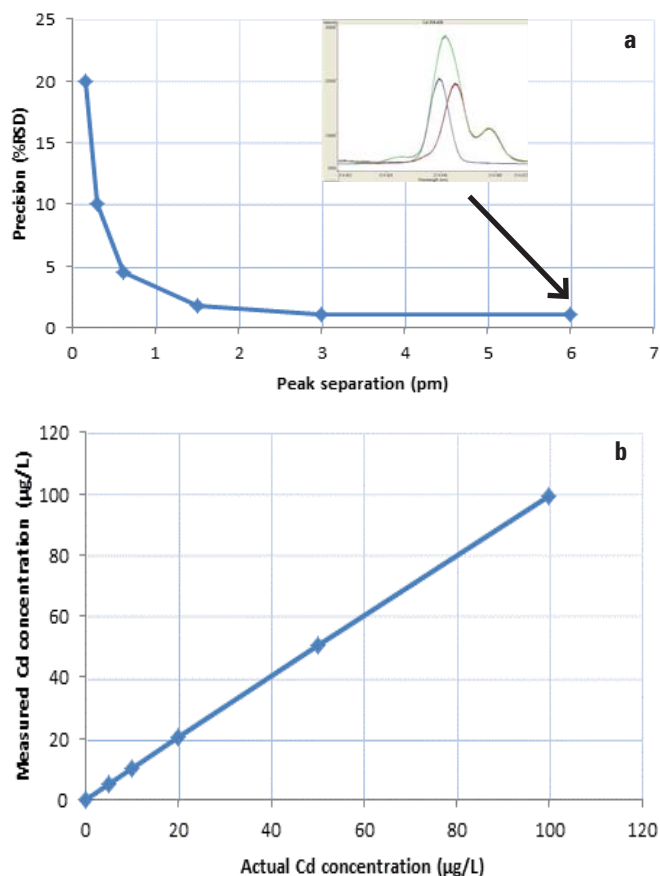


Figure 3. a) Precision of the measured Cd concentration (50 replicates) following FACT correction as a function of peak separation. b) Accuracy of the measured Cd concentration at various levels relative to the Fe interference.

Using FACT for background correction

Spectral interference on an analyte peak can also result from the solvent itself, particularly non-aqueous solvents. Emissions from carbon when analyzing samples diluted in organic solvents are widely known to interfere with important elements. For example, in the analysis of wear metals in oils, complex background structures compromise detection limits for sodium and potassium. Traditional background correction techniques cannot effectively determine the background signal under the analyte peak with adequate accuracy or precision. By using FACT to model this complex background structure, a far more accurate measurement of the analyte signal is possible. In the determination of sodium in oil dissolved in a kerosene-based solvent like Jet-A, FACT can lower the quantitative limit by an order of magnitude.

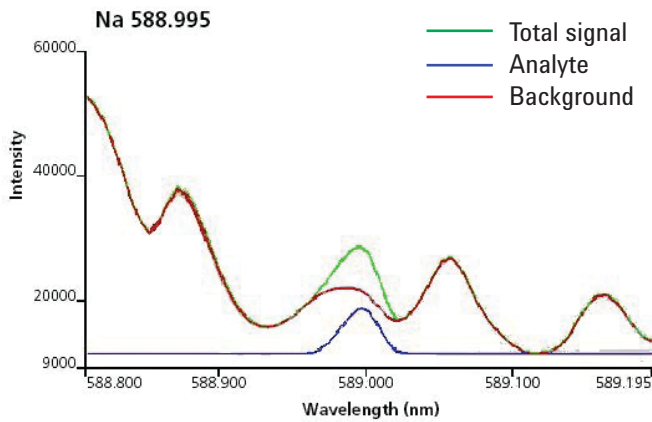


Figure 4. Accurate background correction of low level Na in oil (diluted in Jet A) using FACT

Precious metal analysis

In the mining and refining of precious metals, samples containing very high concentrations of gold and platinum group metals (PGMs) in platinum, palladium, rhodium, iridium, ruthenium and osmium, and base metals including copper, chromium, nickel, cobalt, copper, iron and zinc are often analyzed by ICP-OES. IEC is typically employed to correct for possible spectral interferences, and involves analyzing single-element solutions of all elements at known concentrations to determine interference factors for each analyte/interferent combination. With good wavelength selection, most elements will be free from spectral interference, although it can be difficult to avoid all interferences in such highly concentrated samples.

Iridium, with its main emission lines at 224.268 nm and 212.681 nm, is an important precious metal where FACT has shown to be of advantage. While these two wavelengths offer the lowest detection limits for iridium, they are susceptible to spectral interference. Without correction, the presence of other precious and base metals in samples at high concentrations, including copper, gold and rhodium, can potentially lead to erroneous results being reported.

Ir 224.268 nm

The Ir 224.268 nm line is interfered by a reasonably strong copper emission line at 224.262 nm (Figure 5a). With a peak separation of 6 pm, without correction, even a moderate concentration of copper relative to iridium will produce incorrect results. While significantly weaker than the copper interference, the more closely overlapping emission lines of gold and nickel are also identifiable at concentrations >1000 mg/L. By modeling the Ir analyte and Cu interferent, FACT can accurately correct for the copper interference. With only 2 pm peak separation, FACT successfully corrects for the gold interference (Figure 5b).

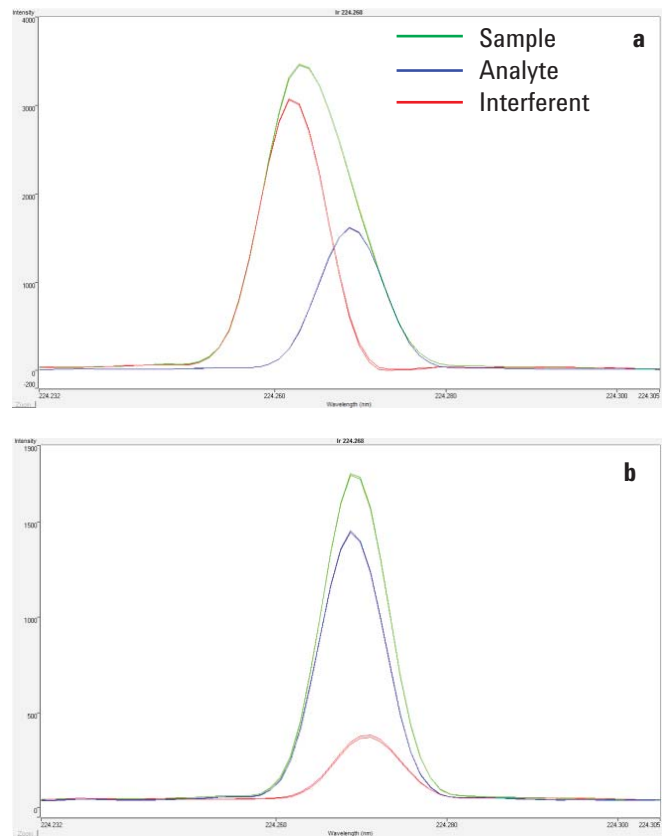


Figure 5. a) FACT model of 2.5 ppm Ir in 25 ppm Cu. b) FACT model of 2.5 ppm Ir in 1000 ppm Au.

Ir 212.681 nm

While free of spectral interference from copper, a moderately strong gold emission line lies near the 212.681 nm line of iridium (Figure 6a). While the Ir analyte and Au interferent peaks are fully resolved, the intensity of the gold signal can still degrade accuracy when measuring low concentrations of iridium. A significantly weaker emission line of Rh 212.675 nm also partially overlaps with the Ir 212.681 line as shown in Figure 6b.

Figure 6c shows FACT correction of both Au and Rh interferences on Ir and demonstrates the advantages of FACT in providing accurate correction of multiple interferences. While the interfering Au peak is essentially resolved from the Ir analyte, peak-tailing from a strong interference signal can lead to inaccurate background correction on the analyte. FACT easily accounts for such events and is a powerful software tool that provides peace of mind in the analysis of difficult and complex sample matrices.

Summary

Agilent's FACT provides real-time spectral correction by using an advanced spectral modelling technique to mathematically separate the analyte signal from the raw spectrum. A simpler and more powerful alternative to inter-element correction, FACT provides accurate background correction, enabling you to analyze spectrally complex samples with confidence.

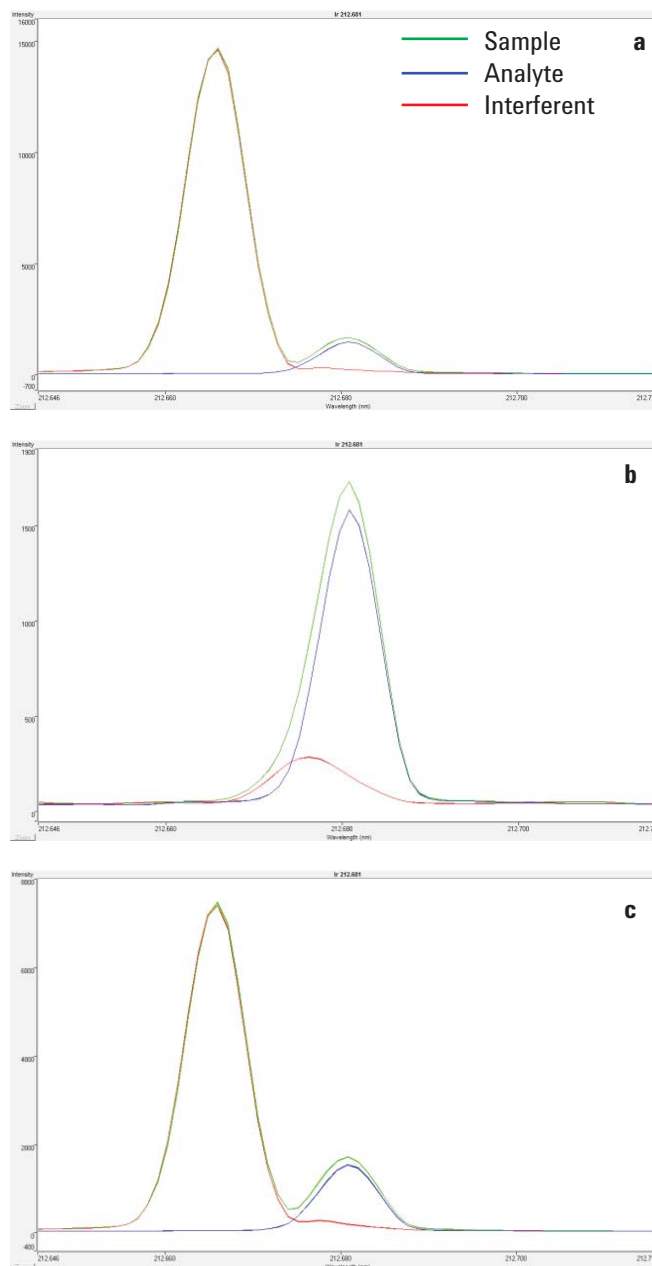


Figure 6. a) FACT model of 2.5 ppm Ir in 1000 ppm Au. b) FACT model of 2.5 ppm Ir in 1000 ppm Rh. c) FACT model of 2.5 ppm Ir in 500 ppm Rh and Au.

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