A sponsored Dedicated Dialogue

Method development for ICP-OES

Matthew Cassap, ICP-OES Product Manager, Thermo Fisher Scientific

To learn more about Method development for ICP-OES, Spectroscopy Magazine talked with Matthew Cassap, Product Manager ICP-OES and AA, at Thermo Fisher Scientific. After graduating in chemistry, Matthew worked at the British Standards Institute and later for the Centre for Environment, Fisheries and Aquaculture Science (a British government laboratory), supporting a number of National and European marine monitoring programs. In 2006 Matthew joined Thermo as an applications specialist becoming an expert in trace element analysis across a broad range of industry segments. In 2012 Matthew assumed responsibility for the Thermo ICP-OES product line in Cambridge, UK and since 2014 has been based at the Thermo Center of Excellence in Bremen, Germany as AA and ICP-OES Product Manager.

Spectroscopy Magazine: Can you provide a short description of ICP-OES and some of the typical applications?

Matthew Cassap: ICP-OES is a multi-element technique used for the identification and quantification of elements. A liquid sample is converted to an aerosol and transported to the plasma using a nebulizer and spray chamber ensuring only small droplets are transferred to the plasma. In the plasma the sample undergoes desolvation, vaporization, atomization and ionization. The atoms and ions then absorb energy from the plasma which causes electrons within them to move from one energy level to another. When the electrons fall back to ground state a photon of light is emitted at a specific energy or wavelength. The amount of light is directly proportional to the concentration of the element in the sample. Typical applications include the analysis of drinking, ground and sea water, quality control of products like alloys, and monitoring of food and supplements for nutritional elements.

Spectroscopy Magazine: What are the first steps in the process of developing a method for ICP-OES that should be considered?

Matthew Cassap: The initial selection of the sample introduction system such as the combination of nebulizer and spray chamber is critical and dependent on the sample type. The aerosol produced from the samples travels thru the spray chamber where large droplets are removed and smaller droplets are transported to the plasma. As the amount of dissolved solids in a sample increase (e.g. drinking water versus sea water) the tolerance of the plasma will decrease so a slightly less efficient sample introduction system is required. Once the correct sample introduction system is selected parameters including plasma settings and analysis wavelengths are selected. The plasma conditions depend on the matrix and the wavelength's to be measured; the combination of matrix and wavelengths are critical factors in setting the plasma power. The same is true with gas flows within the plasma.

Spectroscopy Magazine: For more advanced applications or matrices what different or additional steps would you take?

Matthew Cassap: An example of a more advanced application is the analysis of volatile organic samples. As the volatility of the sample increases much more of the sample is transported to the plasma causing instability and conversion of the organic solvent into an aerosol or gas. Since at room temperature and pressure one mole of a gas is 24L in volume, changing the solvent into a gas suddenly increases the flow into the plasma. To compensate for the extra volume the spray chamber is cooled to condense the gas back to a liquid for removal. In addition, when organic matrices are introduced, a high concentration of elements that emit light (e.g. carbon) not only at discreet wavelengths but also in large molecular emission bands across the spectrum can also be introduced, and these interferences have also to be taken into account when selecting method parameters.

Spectroscopy Magazine: Are there any steps that can be taken during the method development process to mitigate interferences?

Matthew Cassap: There are three main types of interferences in ICP-OES analyses: physical, chemical and spectral. Physical in-

terferences are characterized as a difference between the samples and calibration standards affecting the sample transport or nebulization. These differences can be viscosity, density, and matrix differences, either from the sample itself or the digestion/preservation procedure and can usually be alleviated by dilution. Care must be taken not to dilute a sample below the analytical range of the instrument. Matrix-matching is the process of closely matching the constituents of the calibration solutions and the samples. Matrix-matching is an ideal solution to negate physical interference and is the preferred analysis technique for most applications. The method of standard addition is also an excellent way of negating matrix effects, as the sample acts as its own calibration matrix. The Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES software automatically calculates the sample concentration for standard addition methods. Where full matrix matching is not possible acid matching is generally accepted, although it is not a substitute for complete matrix-matching. Internal standard addition is also a popular method used to overcome sample transport effects. The internal standard (normally aspirated continuously via a Y-piece and mixing loop) acts as dynamic drift correction and Thermo Scientific™ iCAP™ 7000 Plus Series ICP-OES Qtegra ISDS automatically corrects either during or post-analysis for any enhancement or suppression of the sample response.

Chemical interferences can also occur due to differences between the sample and calibration standard reactions to ionization, molecular formation and plasma loading. Chemical interferences can be caused by ionization or molecular formation in the plasma and can either suppress or enhance a signal. Dilution, matrix matching and internal standardization, along with plasma optimization and sample doping can all be used to mitigate chemical interferences. Plasma optimization can also be used to vary the energy available in the plasma and also increase or decrease the sensitivity of specific wavelengths by altering the RF power, and the auxiliary and nebulizer gas flow. These adjustments are normally done during method development and often alleviate plasma loading and ionization problems simply by optimizing the method parameters. Ionization problems are common with samples that contain high concentrations of easily ionized elements (EIEs) such as sodium, potassium and calcium. These elements take energy from the plasma and can result in poor results for wavelengths below 235 nm which require high energy to reach excitation and an emission state. The use of an ionization buffer can often alleviate this problem; plasma optimization techniques also commonly involve doping the samples (normally by continuous aspiration via a Y-piece and mixing loop) with EIEs like cesium or lithium.

Spectral interferences are characterized by either partial or direct overlap of the analyte of interest by an interfering element. They are normally apparent during method development and can lead to suppression or enhancement of signals, and false-negative or positive results which ultimately degrade the accuracy and precision of the method. Spectral interferences are sometimes severe in ICP-OES due to the effectiveness of the plasma as an excitation source and the complexity of the emission spectrum of the elements and their ions. These interferences can be a shoulder on a peak, or a partial or full spectral overlap. It is a challenge to analytically correct for a full spectral interference, so a wavelength experiencing this uncommon phenomenon would be eliminated at the early stages of method development. Partial and peak overlaps are dealt with by either off-peak background correction or with the use of an experimentally derived mathematical correction, or the use of wavelengths that are free from interferences in the first place.

Spectroscopy Magazine: What other tools are available during the method development process?

Matthew Cassap: There are a number of plasma optimization software tools available within the Qtegra ISDS software. With Qtegra ISDS there is a plasma optimization tool that uses multi-variant optimization which has significant advantages over univariate optimization. This tool can be used to optimize the analysis of all elements in a method, or only for those required. For elements such as potassium and calcium, sensitivity is not usually an issue and they are normally not included in the optimization in favor of other more critical elements like lead or arsenic. For spectral interferences, the Element Finder plug-in for the Qtegra ISDS software is a method development tool that allows the selection of wavelengths that are free from spectral interferences taking into account the analytes present in the sample and the sample matrix. This tool uses the "full frame" of the sample (a full frame is an image of the entire sample spectrum within the wavelength range of the instrument) and intelligently selects the wavelengths that are suited to analysis of the elements selected, saving considerable time through automation.

Spectroscopy Magazine: Once developed what steps can be taken to ensure that the method is accurate and precise?

Matthew Cassap: The most important items to check are the linear range of the method from the detection limit to the top standard level. If there are interferences, the proposed USP elemental impurity chapters describes a lengthy spiking method. A faster approach is to analyze range-certified reference materials over the range concentrations to be analyzed, followed by further validation with the USP spiking method.

Spectroscopy Magazine: Does that complete method development or is it an ongoing process?

Matthew Cassap: Since the long term stability and robustness of the method is important it is an ongoing process. Methods need to ensure that detection limits are achievable over long periods of time, with different operators and a range of samples. Samples containing a different set of elements compared to the samples that were used for method development may require wavelengths to be revisited. Instrument maintenance should be written into SOPs forming an integral part of any method. The frequency of these checks should be refined as the method is used for daily analysis.