AutoMax — Fast, automated method optimization

Technical Overview

700 Series ICP-OES

Introduction

AutoMax eliminates manual optimization and provides fast, automated method development. A major advantage of the Agilent 720/730 Series ICP-OES is its ability to measure many elements in a sample at once. No matter how many elements (or emission lines) are selected for measurement, the speed at which data is collected and reported by the system is the same. As a consequence of this greater measuring capacity, the determination of optimum operating conditions for a full suite of elements can become a daunting task. The optimum conditions for one element and its associated emission lines do not necessarily suit those of another. Even the optimum conditions for different emission lines of the same element can vary significantly. As a result, a compromised set of conditions is typically used. Achieving the lowest possible detection limits on critical elements is the main consideration in the optimization of the system. With an ever-increasing demand being placed on laboratories to measure more elements in less time, the need for a powerful, yet easy-to-use automatic optimization program has never been more important.

AutoMax is a powerful optimization program in the ICP Expert II software that provides fast and accurate optimization of instrument parameters, without time-consuming method development. AutoMax intelligently determines the optimum set of parameters for all elements of interest without sacrificing the performance of one element for another. During the optimization process, emphasis is given to less sensitive emission lines and to elements present in samples in low concentration without sacrificing performance for other elements. In short, AutoMax finds the best operating conditions for your application.

Of the many instrument parameters that can be changed, only a few have a significant effect on the sensitivity, and therefore on the detection limits. They are RF plasma power, plasma viewing position and nebulizer gas flow.

Earlier forms of automatic method optimization were considered cumbersome and time-consuming. AutoMax has been designed to obtain optimum conditions for a suite of elements in the least amount of time.

Response hypersurface

The multi-dimensional plot of the optimization criterion against the full set of values of each variable parameter is termed the 'response hypersurface'. The optimum can be defined as 'a region on the hypersurface in which there is no appreciable improvement in the optimization criterion when the value of any variable is changed.'[1]

Instrumentation

An Agilent 725 system with radially-viewed plasma was used in this study. Table 1 shows the instrument conditions used to construct the optimization hypersurface for the Cu 327.395 nm emission line.

Instrument parameter	Settings
Plasma gas flow	15 L/min
Auxiliary gas flow	1.5 L/min
Pump rate	15 rpm
Stabilization time (s)	15 s
Read time (s)	1 s
Background correction	Fitted
Nebulizer type	V Groove
Spraychamber type	Sturman-Masters
Torch type	Standard one-piece quartz

Table 1. Experimental conditions for the Cu 327.395 nm hypersurface.

Results and discussion

1. Speed of Optimization

The time required for AutoMax to determine the optimum operating conditions will vary depending on the number of parameters selected for automization. The parameter options are as follows:

- RF power
- Viewing height (Radial only)
- Nebulizer flow (MFC only)

The time required for optimization was found to be independent of the number of elements selected.
Table 2 lists the typical time required for AutomMax to determine the optimum parameters when optimizing on the viewing height only, a combination of viewing height and RF power and the combination of all three parameters in viewing height, RF power and nebulizer flow. The experimental conditions listed in Table 1 were used.

Viewing height (mm)	Viewing height (mm), Power (kW)	Viewing height (mm), Power (kW), Nebulizer flow (L/min)
<1.5 min	4 - 8 min	< 10 min

Table 2. Typical time required for AutoMax to determine the optimum conditions (minutes). The optimization criterion used was signal-to-background ratio (SBR).

2. Cu 327.395 nm hypersurface

Historically, parameter optimization routines have been slow, particularly if they test every possible combination of parameters. Such a process creates a full definition of the hypersurface but is exceedingly time consuming. To speed the optimization process, AutoMax starts at the mid-point of the parameter range and searches outwards from that point. The user can specify the parameter range to exclude unnecessary parameter values from the search range. For example, the range for plasma RF power could be reduced to 1.3 to 1.5 kW in the analysis of organic solvents.

Figure 1 shows the signal-to-background ratio (SBR) optimization hypersurface for the Cu 327.395 nm emission line in the optimization of RF power and viewing height. The mid-point of each parameter range is selected as the starting point, in this case, 1.2 kW for RF power and 10 mm for viewing height. At first, AutoMax fixes the viewing height position and increments the RF power in predetermined steps. If the initial search to 1.25 kW and 10 mm, does not improve the result, AutoMax searches in the opposite direction (red arrows in Figure 1).

When the optimization criterion (in this case SBR) passes through a maximum or reaches the upper boundary of the selected RF power range, the RF power is set to that level and the viewing height is optimized. Once the optimum parameters are established (represented in Figure 1 at coordinates 0.9 kW, 12 mm), there is a final check to ensure that the parameters are in fact the optimum. AutoMax remeasures each neighboring point comparing the new data with the previously acquired results. This prevents the search locking onto noise-induced maxima. If AutoMax confirms that the values of the optimization criterion at neighboring points are still below the optimum, then the optimization routine is complete. If not, optimization will continue.

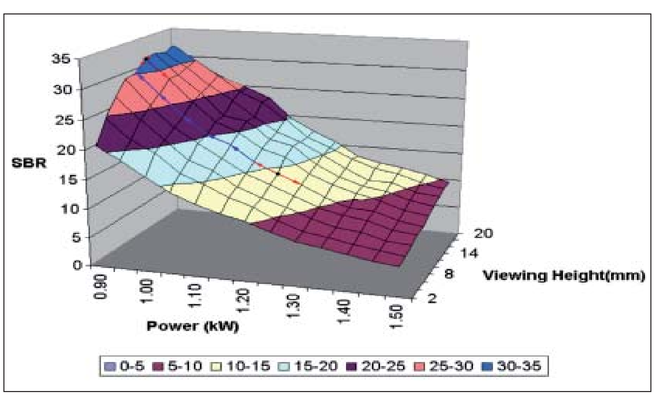

Figure 1. Optimization surface for Cu 327.395 nm showing SBR response versus the two parameters – RF Power and Viewing Height.

3. Figure of Merit

An auto-optimization program such as AutoMax must be able to manage data from multiple emission lines. Changing one parameter may improve the optimization criterion for one line while reducing that at another. A simple averaging of the optimization criterion values could be used but this would be biased in favour of more sensitive emission lines of elements present in higher concentrations.

For example, if we use the average (arithmetic mean) of all the net signals, then a 1% improvement in an element signal of 10000 counts would outweigh a 50% degradation in an element signal of 100 counts.

If a geometric mean is used, the optimization criterion for each wavelength receives equal weighting in the equation. For example, the doubling of the net signal for one emission line would exactly compensate for a 50% degradation in another, regardless of signal intensity. The only disadvantage is that one equally weak signal might be sacrificed in favour of another. To compensate for this, AutoMax uses an algorithm that includes both a geometric mean component and an equally weighted factor for the emission line showing the lowest value of the optimization criterion.

The algorithm calculates a Figure of Merit (FoM), which is recalculated for each set of conditions. An increase in the FoM is regarded as an overall improvement. In this way AutoMax searches for an overall improvement in the value of the optimization criterion, while attempting to improve the result for the emission line that shows the lowest value of the optimization criterion. Once the optimum conditions have been found, the relevant method conditions are automatically changed to the optimum settings.

Figure of Merit 1(FoM_1) = SUM(LOG(R_i)/N) (geometric mean component)

Figure of Merit 2(FoM_2) = MIN(LOG(R_i)) (minimum component)

Figure of Merit(FoM) = $a*FoM_1 + b*FoM_2$

Where:

R_i = optimization criterion result for emission line i

N = number of emission lines

a = b = 0.5

4. Optimization criteria for best detection limit

Figures 2-5 are two-dimensional contour plots that represent the performance of Mn at the 257.610 nm line at various nebulizer flow and viewing height positions, based on the following optimization criteria:

- Signal to background ratio (SBR)
- Signal to Root Background Ratio (SRBR)
- Net Signal (NS)

The detection limit for Mn at the 257.610 nm line was also measured at each parameter and a two-dimensional contour plot was created. Comparing the maxima of the SBR, SRBR and NS plots with the minimum of the detection limit plot shows which optimization criterion is best for Mn 257.610 in determining the optimum conditions for lowest detection limits (Figure 6).

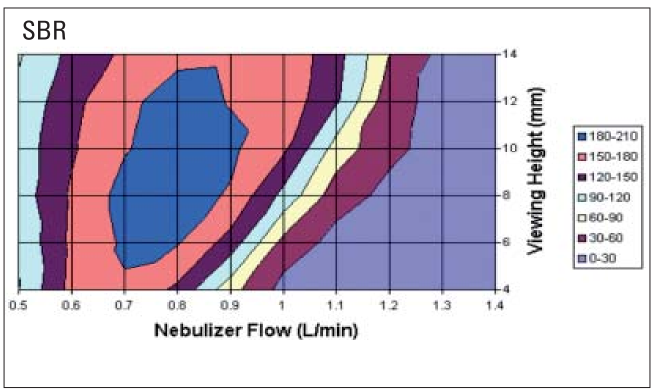

Figure 2. Two dimensional contour plot of SBR for Mn 257.610 nm.

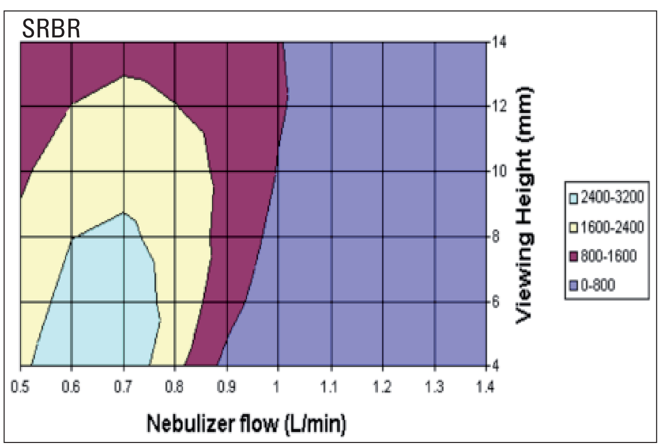

Figure 3. Two dimensional contour plot of SRBR for Mn 257.610 nm

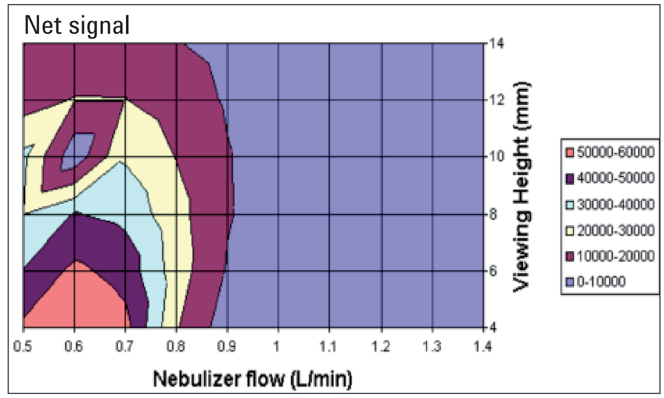

Figure 4. Two dimensional contour plot of Net Signal for Mn 257.610 nm

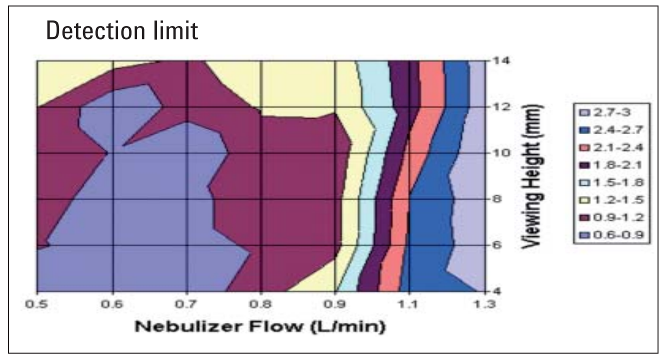

Figure 5. Two dimensional contour plot of detection limit for Mn 257.610 nm

As shown in Figure 6, the region of optimal (maximum) SBR for Mn 257.610 only partially overlaps with the region where detection limits are lowest. This suggests that SBR is not the best criterion with which to optimize for best detection limits for the Mn 257.610 nm emission line. The optimization criteria of SRBR and NS show greater overlap indicating that either SRBR or NS is suitable for optimization of the Mn 257.610 nm line.

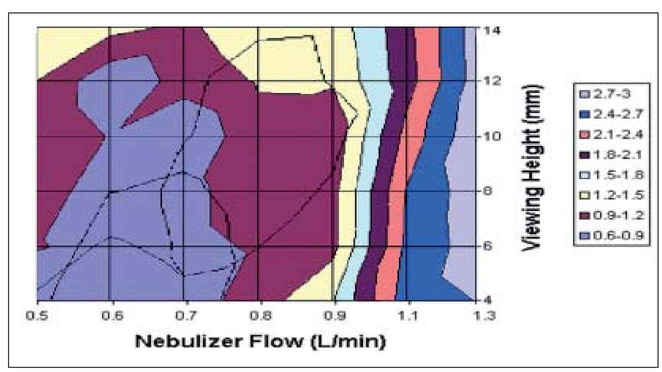

Figure 6. The two dimensional contour map shows the measured detection limit for Mn 257.610 nm. Superimposed are the optimum regions of SBR, SRBR and NS.

5. Optimization criteria vs wavelength

Figure 7 shows the detection limit performance of various elements across the wavelength range that have been optimized using AutoMax for each optimization criteria.

The data shows that the best optimization criterion for achieving instrument conditions that produce best detection limits for a given element can vary according to wavelength. Wavelengths below 200 nm, are best served by optimizing for NS while those in the range 200-400 are best optimized using SRBR. For wavelengths > 400 nm, SBR is best. This is summarized in Table 3.

Wavelength range (nm)	Optimization criterion
<200	NS
200-400	SRBR
400-800	SBR

Table 3. Optimization criteria achieving best detection limits across the wavelength range.

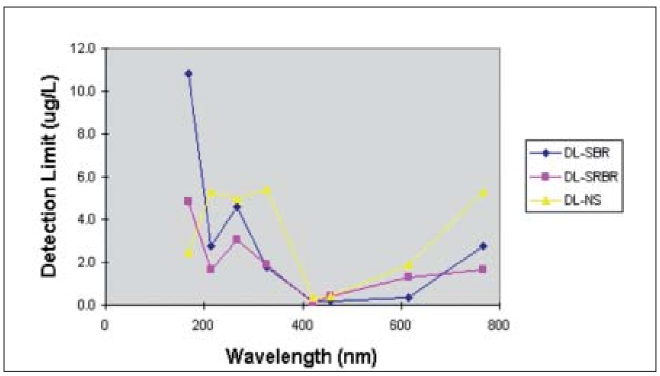

Figure 7. Detection limits acquired for various emission lines when the operating conditions have been optimized using the following criteria, SBR, SRBR and NS.

The relationships between optimization criteria, detection limits and wavelengths indicated in Figure 7 and Table 3 can be explained as follows:

The detection limit depends ultimately on two factors[4]:

1. The intensity for a given concentration of analyte and
2. The magnitude of the random fluctuation in the intensity of the background, i.e. the background noise.

The best detection limit is achieved when the ratio of the signal for a given concentration of an element to the background noise is as large as possible. This signal-to-background-noise ratio is not to be confused with the ratio of the signal to the background intensity, commonly called the signal-to-background ratio or SBR.

The background noise is made up of several essentially independent components including electronic noise, readout noise, dark current noise, photon shot noise and source flicker noise. The total background noise is given by the square root of the sum of the squares of each noise component[4]. For this reason, one noise component usually dominates. The dominant noise component depends on the optical background, i.e. that part of the background that arises from light reaching the detector. The optical background from the argon ICP comes mostly from continuum emission. The intensity of this continuum varies with wavelength, and consequently the relationship between background noise and background intensity also varies with wavelength.

1. At very low wavelengths, there is almost no optical background. The background noise is dominated by readout noise and electronic noise. These do not change with instrument operating conditions, so at these wavelengths the best signal-to-background-noise ratio, and therefore the best detection limit, is obtained when the operating conditions are optimized to give the greatest NS.

2. At higher wavelengths, the optical background intensity is such that the dominant component of the background noise is photon shot noise arising from the random emission of electrons from the photon detector in ICP-OES. This varies with the square root of the background intensity. The best detection limit is obtained when the operating conditions are optimized to give the greatest ratio of the net signal to the square root of the background, i.e. the best SRBR.

3. At still higher wavelengths, the optical background intensity is so high that photon shot noise is insignificant compared to flicker noise. The flicker noise is proportional to the background intensity, and the best detection limit is obtained when the operating conditions are optimized to give the greatest ratio of the net signal to the background intensity, i.e. the best SBR.

This broadly accounts for the relationship between optimization criterion and wavelength shown in Figure 7. As would be expected, there is overlap between the three wavelength regions just discussed. This is evident from Table 3. In addition, the relationship between wavelength and dominant noise breaks down when molecular emission bands make the optical background at a low wavelength much higher than would be expected from the general consideration of the argon continuum just presented.

Conclusion

This work describes the advantages of AutoMax, an auto-optimization program that is available for the Agilent 720 and 730 series. AutoMax is a unique tool that is suited to CCD-based simultaneous ICP where the optimum settings of the instrument parameters need to be determined quickly and efficiently in the measurement of multiple elements in samples.

This work has shown that the choice of optimization criterion (SBR, SRBR or NS) plays a major role in the successful optimization of a method for analysis.

References

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