Processing of short transient signals in multi-element analysis using an ICP-OES instrument equipped with a CCD-based detection system in Paschen-Runge mount

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ABSTRACT

A general protocol for the processing of short transient signals in multi-element analysis using an ICP-OES instrument equipped with a CCD detector system was developed. The performance of the optical system and the line setting position were accomplished by means of pneumatic nebulization sample introduction, and the resulting settings were afterwards applied for the acquisition of transient signals, generated via electrothermal vaporization (ETV). The influence of the most important data acquisition parameters, sampling rate and integration time, was evaluated for a wide spectral range. Subsequently, a MATLAB-based method was used for off-line generation of the 3D analyte spectrum, off-line BG correction and integration of the transient signals. The applicability of the developed approach was demonstrated via the determination of Al in two certified reference samples, one with low and another with high Ca concentration, using ETV-ICP-OES. Accurate results were obtained for Al, despite the significant overlap of the Al analytical line and the 'wing' of the matrix-related Ca line.

Keywords: Transient signal, ICP-OES, Background correction, CCD detector

1 Introduction

Inductively coupled plasma optical emission spectrometry (ICP-OES) is one of the most common techniques for multi-elemental analysis.[1] Both ICP-OES and inductively coupled plasma mass spectrometry (ICP-MS) instruments were initially designed for analysis of solutions and, at present, still the large majority of the samples analyzed are liquids or digests.[2] As a result, pneumatic nebulization is the traditional means of sample introduction into the ICP. However, also alternative sample introduction techniques, such as flow injection (FI), laser ablation (LA), electrothermal vaporization (ETV) or chromatographic separation techniques, are quite often used in combination with ICP-MS or ICP-OES.[2-6] In contrast to conventional pneumatic nebulization, these introduction systems do not produce a constant sample flow. In fact, their use results in a sample introduction rate that varies as a function of time and thus, in a transient signal. With such transient signals, larger efforts are required to ensure an adequate signal acquisition and handling, which might be especially challenging for short transient signals, such as those generated by an ETV system (typical signal duration expressed as FWHM-full width at half maximum- of a few s only) or, to a lesser extent, an LA unit. In these cases, wide linear dynamic ranges and the capability for fast multi-element detection are absolute musts if several analyte signals, varying in intensity from zero to millions of counts per second (cps), need to be recorded within a short time span (2-20 s).[2]

For a long time, the instrumental design of ICP-OES instruments (e.g., scanning devices) was such that it was simply impossible to fulfill these requirements. Nowadays, however, this limitation has been partially solved as a result of the introduction of later generation charged-coupled device (CCD) detector systems, enabling the simultaneous acquisition of almost the entire UV-VIS-NIR emission spectrum.[7,8] Such instruments are equipped with an Echelle grating and a 2-dimensional arrangement of CCDs or with a polychromator and linear CCD arrays. Although CCD detectors are capable of extremely fast data acquisition, they are typically characterized by a relatively slow rate of data transfer. As a result, even though the integration time can be as short as a few milliseconds, the system needs much longer times (up to 30 s) to process and transfer the data before a subsequent integration period can be started, which obviously hampers the use of these instruments for a proper characterization of transient signals. [9,10]

Even when the instrumental limitation mentioned above is (partially) overcome, the development of an adequate analytical approach, ensuring the best possible results to be obtained, is still a challenge wen dealing with short transient signals. With a proper approach, the signal-to-noise (S/N) ratio should be optimized for reaching the best limits of detection

(LODs) and allowing the widest dynamic ranges possible; and the close spectral environment of the analytical line should be monitored for proper background (BG) correction and for revealing spectral interferences and thus avoiding them from affecting the final result. Unfortunately, the tools for accomplishing all of this are not readily available in most present-date instrument hard- and software. Although several papers on the handling of short transients by means of ICP-OES systems have been published already,[6, 11-14] the influence of several important factors has not been sufficiently addressed in these works to render the approaches described generally applicable.

This paper focuses on optimization of the data aquisistion and background correction when dealing with short transient signals using an ICP-OES instrument equipped with CCD-based detection system in Paschen-Runge mount. However, the authors believe that the working protocol developed is also suited for dealing with such transient signals in other modern ICP-OES instruments based on simultaneous detection via CCD detectors. Transient signals of short duration were generated using an ETV system. Although the shape of the transient signal and thus also the performance of the analytical method (e.g., the possibility of temporal separation of the volatilization of analyte elements, thus creating the possibility of avoiding spectral overlap) depend on a proper optimization of the ETV parameters, these aspects are beyond the purpose of this work and are, therefore, not described.

2 Experimental

2.1 Instrumentation

All measurements were carried out using a Spectro Arcos ICP-OES instrument (SPECTRO, Germany) with radial plasma observation. The Spectro Arcos is outfitted with a Paschen-Runge mount, equipped with 32 linear CCD detector arrays, providing the capability of simultaneous monitoring of element emission lines in the wavelength region between 130 and 770 nm. The spectral resolution is 8.5 pm in the range from 130 to 340 nm and 15 pm for wavelengths > 340 nm.[15] Throughout the experiments, a plasma RF power of 1400 W, a cool gas flow rate of 12 L min^{-1}, an auxiliary gas flow rate of 1 L min^{-1} and a carrier gas flow rate of 1 L min^{-1} were used. Pneumatic nebulization was accomplished using a cross-flow nebulizer mounted onto a Scott-type double-pass spray chamber. Generation of transient signals was accomplished with a HGA- 600 MS electrothermal vaporizer (Perkin Elmer, USA), equipped with an AS-60 autosampler. Pyrolytic graphite - coated tubes with L'vov platform were used. The HGA 600 MS ETV unit was coupled to the ICP-OES instrument via a 80 cm length Tygon® flexible tube (6 mm internal diameter). The ICP-OES and ETV units were independently controlled using separate software programs. A set of general ETV program settings, typically suited for aqueous solutions, was used throughout the experiments and is summarized in Table 1. As all of the standard solutions used contained a total amount of at least 0.46 μg of target elements, no carrier (matrix modifier) was used as such amounts provide sufficient nucleation centers for optimum nucleation and analyte transport by themselves.[10] For evaluating the performance of the BG correction protocol proposed in section 3.2, the determination of Al in two reference materials was accomplished. Since Al mono-elemental standard solutions were used for calibration, 0.5 μg of Pd was added to the calibration standards and the samples to act as a carrier agent, normalizing the analyte transport efficiency. The signal profiles (intensity as a function of time transient) generated by the ETV system were recorded via ICP-OES monitoring and the data obtained were exported for off-line treatment with the software program developed, allowing BG correction and signal integration.

Table 1. HGA-600MS ETV temperature program.

Temperature (°C)	Ramp (s)	Hold time (s)	ETV internal gas flow rate (L min^{-1})
120	10	10	0.3
400	10	20	0.3
2500	1	10	0.3
20	5	1	0.3
2700	5	5	0.3
20	5	5	0.3

2.2 Standards and samples

Aqueous standard solutions containing appropriate concentrations of the analyte elements were prepared from a multi-elemental ICP standard solution 'ICP IV' available from Merck (Germany) and from single element 1000 mg L^{-1} standard solutions of Ca (Perkin Elmer, USA) and of Al (SCP Science, Canada). All dilutions were made with 2% v/v nitric acid, obtained by dilution of analytical grade HNO_3, also available from Merck, with ultra-pure water obtained via a Milli-Q system (Millipore, USA). Two certified reference materials from the National

Institute of Standards and Technology (NIST, USA) – “Bone ash” SRM 1400 and “Rice flour” SRM 1568a – were analyzed for their Al content in order to evaluate the performance of the BG correction methodology proposed. For sample preparation, 20 mg of the bone ash or 110 mg of the rice flour were accurately weighed directly in polypropylene tubes and 0.5 mL of concentrated nitric acid was added in both cases. Subsequently, the samples were diluted with ultra-pure water to 15 mL for the bone ash sample and to 3 mL for the rice flour sample. The bone ash was completely dissolved in the nitric acid medium. The rice flour sample, on the other hand, was analyzed as slurry. The Pd carrier solution used for these determinations was prepared from a $Pd(NO_3)_2$ stock solution containing 10 g/L of Pd, also available from Merck.

2.3 Data acquisition

In the Spectro Arcos software, the approach for data collection when using continuous sample introduction (*i.e.* via pneumatic nebulization) is termed ‘method mode’. The ‘transient mode’, on the other hand, is intended for processing transient signals. These data acquisition modes show significant differences. In ‘method mode’, signal collection by the CCD detectors and the corresponding read-out occur in different, consecutive phases, as illustrated in Table 2. Every phase consists of sequences of integration (time during which the detector is collecting the signal) and read-out intervals. The number of integration (and thus also read-out) intervals depends on the integration time selected. The duration of the integration interval defines the maximum measurable intensity during this phase, as the absolute intensity that can be determined by a CCD detector is limited. If the integration interval is too long, the detector becomes saturated for highly intense signals, resulting in an underestimation of their intensities expressed as counts per second (cps). Thus, the shorter the integration interval, the higher the maximum signal intensities that can be adequately processed. Several pre-defined integration methods (with different durations for each phase and the corresponding integration interval) are provided by the software, and can be selected depending on the needs of the analysis (e.g., best signal-to-noise ratio, high speed, high sensitivity, …), while additional ones can be created by the user. When carryng out a measurement, the detection system starts acquiring the signal with the set of parameters including the longest integration interval, corresponding to phase 5. Step by step, the system moves to phase 1, during which the shortest integration interval is used. Once the 5 phases are accomplished, the software automatically selects the most suitable phase for each wavelength and the resulting signal intensity is calculated correspondingly. Data acquired in ‘method mode’ can be reported as raw intensities, background-corrected intensities (after application of different BG correction algorithms that can be chosen by the user), interference-corrected intensities (if an adequate solution for BG correction has been previously measured), standardized intensities (if an internal standard has been used), intensity ratios or element concentrations (if a set of calibration standards has been previously measured).

For analysis of transient signals on the other hand, the Spectro Arcos software offers two different strategies, which are termed ‘method transient’ and ‘fast transient’. When using the first strategy, all measurements are as described in the previous paragraph. This acquisition mode has the advantage of providing background and/or interference correction possibilities, but the required immediate data processing after each acquisition increases the time interval between two successive data points from 1-2 s (when only a single wavelength is monitored) up to 30 s (depending on the number of wavelengths monitored), even if the acquisition time is as short as possible for each of the 5 phases. Obviously, this acquisition mode cannot be used for the monitoring of fast transient signals, such as those generated by ETV (FWHM = 1 - 3 s).

In the second strategy for transient analysis (‘fast transient’), on the other hand, the user is provided with the raw intensities (without any further data handling) and data acquisition can be done with frequencies up to 10 Hz (depending on the integration interval selected). An example of a set of data acquisition parameters for this fast transient mode is also given in Table 2. Acquisition is done in one phase this time, and the integration interval (time during which the system collects data points), the sampling rate (frequency at which data is read out) and total run time are selected by the user. The value for maximum intensity is governed by the integration interval selected. This working method is suited to deal with short transient signals, but only raw intensities are available, while visualization of the full spectrum is also not possible in a straightforward way.

A similar situation characterizes all ICP-OES instruments offering simultaneous detection via CCD-based array detectors: while the detector units themselves are capable of very fast, quasi-simultaneous data collection, the limited speed of data handling hampers their use for monitoring fast transient signals. As a result, ICP-OES has been used only seldom in such contexts, especially if complicated matrices generating a complicated background needed to be analyzed. In this paper, a combination of a general method for adequate collection of raw intensities in a fast way (“fast transient mode”) and subsequent off-line data handling is proposed, so that the capability of these simultaneous ICP-OES spectrometers can be fully exploited.

Table 2. Example of acquisition parameters for the ’method’ and ’fast transient‘ acquisition modes of the Spectro Arcos.

Method mode, total time 24 s				**Fast transient mode**	
Phase	Time (s)	Integration interval (ms)	Maximum Intensity (cps)	Run time, (s)	20
1	3	1	120000000	Sampling rate, (Hz)	10
2	3	10	12000000	Integration Interval, (ms)	100
3	3	100	1200000	Maximum intensity, (cps)	1200000
4	5	1000	120000		
5	10	10000	12000		

2.4 Optics calibration and wavelength selection

As the Spectro Arcos cannot display the full spectrum when transient signals are monitored, optimization of the instrument settings and data acquisition parameters need to be accomplished before changing to transient mode. For the Spectro Arcos system, calibration of the optics system is accomplished by means of the ICAL protocol (Intelligent Calibration And Logic), a patented calibration procedure, which relies on wavelength monitoring upon nebulization of a solution containing a set of 22 analyte elements (Be, Ca, Ce, Cu, Eu, Fe, In, K, Li, Mn, Mo, Na, Ni, P, S, Sc, Si, Sr, Ti, V, Zr and Y). Generally, every ICP-OES instrument will use a similar procedure for the alignment of its optical system.

Before switching to ETV, the exact positions of the emission lines of interest were located using the standard operating mode of the ICP-OES instrument (method mode), while using pneumatic nebulization for the introduction of a standard solution containing the elements of interest and the matrix components (if the composition of the sample is sufficiently known). In this work, 12 wavelengths for 8 different analyte elements covering a wide spectral range and showing different sensitivities were selected for the evaluation of the acquisition parameters (sampling rate and integration time) as will be discussed in section 3.1. The wavelengths selected were: Al (167.078 nm), Al (396.152 nm), Cr (267.716 nm), Cu (324.754 nm), Fe (275.573 nm), Fe (259.941 nm), Li (670.780 nm), Mg (279.553 nm), Mg (280.270 nm), Mg (285.213 nm), Na (589.592 nm) and Zn (213.856 nm). Additionally, one argon emission line

(404.442 nm) was monitored for diagnostic purposes. In another experiment, background monitoring and correction possibilities were evaluated by monitoring the Al 396.152 nm emission line in the presence of Ca. The influence of the wings of Ca lines on Al lines at 394.401 and 396.152 nm is a typical example of spectral interference (wing overlap) that cannot be solved by means of ETV temperature programming[16], and was therefore selected as a worst-case scenario for modeling the BG correction methodology. More details on the development of this BG correction methodology are included in section 3.2.

3 Results and discussion

3.1. Selection of data acquisition parameters: sampling rate and integration time

As already discussed in section 2.3, the most important acquisition parameters for multi-elemental ICP-OES analysis of short transient signals are the sampling rate and the integration time. These parameters are directly influencing the method performance properties, such as precision, limits of detection and maximum intensity that can be recorded before detector saturation.

First, the influence of the sampling rate on the signal intensities and precision was evaluated for several analytical lines covering a wide spectral range (Al 167.078 nm to Li 670.780 nm). As seen in Figure 1B, the number of data points describing the transient signal increases at increasing sampling rates, which results in better peak characterization. As could be expected, this has a direct effect on the analyte signals recorded: as shown in Figure 1A, slightly overestimated integrated intensities are obtained for sampling rates between 0.1 Hz and 0.5 Hz, as, under these conditions, part of the areas before and after the occurrence of the actual peak are integrated with the signal. For sampling rates between 0.5 to 10 Hz, however, no significant differences in analyte intensities were observed. As a consequence of this fact, on the other hand, also signal precision is improved for faster sampling rates. The RSD values, calculated based on 5 replicate measurements, were significantly reduced upon increasing the sampling rate, from values around 14% when using a sampling rate of 0.1 Hz to values lower than 5% for sampling rates higher than 0.5 Hz. According to these results, a minimal sampling rate of 2 Hz is recommended for monitoring a typical transient signal produced via ETV (duration: 1.5 – 3 s) with good precision (RSD < 5%). Under these conditions, at least 3 data points can be acquired per peak, which results in good transient signal characterization as shown by Resano *et al.* in their work on ETV-ICP-MS.[17] In contrast to single-collector quadrupole-based and sector field ICP-MS instruments, the acquisition of data for one target element or spectral line is not affected by the monitoring of additional lines, and there is no virtual limit for simultaneous ICP-OES systems in this regard.

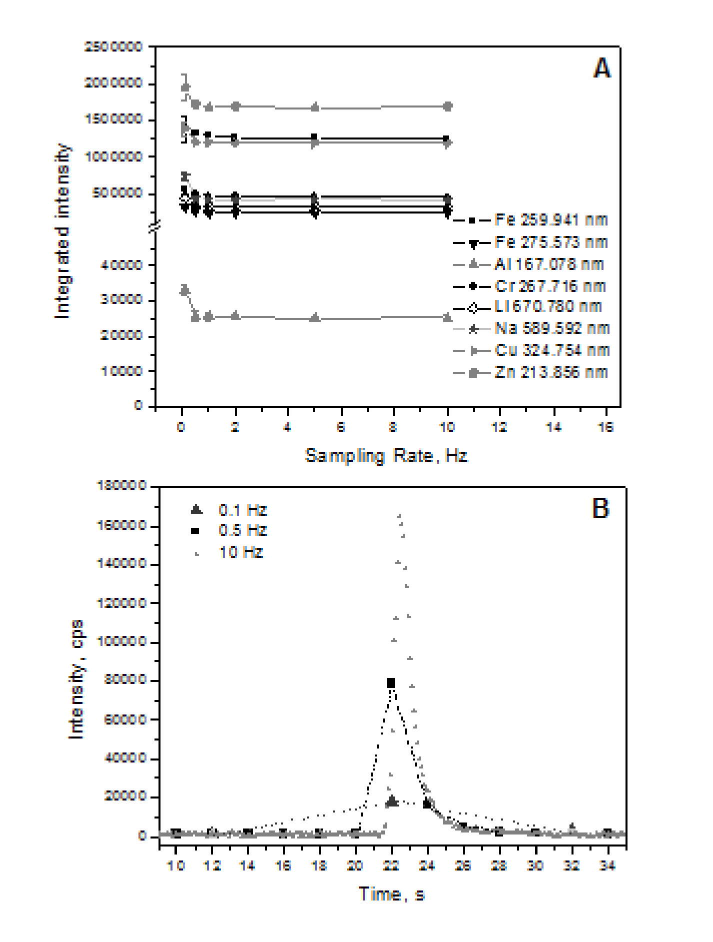

Figure 1. Influence of sampling rate on (A) integrated signal intensities and (B) recorded transient signal shapes. Signals were generated by vaporization of a multi-element sample solution containing 20 ng of each analyte and using the ETV program given in Table 1.

As described in section 2.3, the integration interval is the time during which the CCD detection system is collecting pulses. Depending on the analyte concentration, too short an integration time can result in poor precision; but, on the other hand, and due to the limited dynamic range shown by CCD detectors[8], too long an integration time can result in saturation of the CCD detector for more intense emission lines. As previously discussed, the maximum intensity that can be monitored before the detector becomes saturated is governed by the integration time selected. While with continuous nebulization, for every individual analytical line, the optimum set of parameters is selected among the 5 pre-selected phases (“method mode”), a single set of parameters needs to be used when dealing with short transient signals. As a result, there is always a compromise to be reached between line sensitivity and integration time.

This influence of the integration time is illustrated in Figure 2. The influence of the integration time on the sensitivities obtained for different Mg emission lines is presented in Figure 2A. As seen in the figure, detector saturation for the most intense emission lines is reached for values higher than 30 ms (Mg 279.553 nm) and 40 ms (Mg 280.270 nm), respectively. On the other hand, no significant influence can be observed for the weakest line (Mg 285.213 nm) with increasing integration times. On the contrary, for those situations where signal intensities are too low to cause detector saturation, a beneficial effect on the S/N ratio and LODs can be seen for increasing integration times. This effect is illustrated in figures 2B to 2D for the vaporization of 20 ng of Fe and selecting the weaker emission line at 275.573 nm. As seen in these figures, it is clear that the longer the integration time, the higher the S/N ratio and, consequently, the lower the limit of detection attainable.

As a result of all of the above, it is clear that selecting the best conditions for data acquisition when dealing with unknown samples might be difficult, as compromise conditions are needed. If the sample availability permits it, a preliminary evaluation before analysis using short integration times combined with sampling rates higher than 2 Hz is recommended to give a general idea of the analyte concentrations in the sample. If, on the other hand, sample availability is restricted, shorter integration times guaranteeing wide linear ranges are preferred, as it is always better to obtain valid analytical results with a rather poor precision than no results at all because the signal has saturated the detector. These deleterious effects of detector saturation can be alleviated by i) monitoring two or more emission lines with different sensitivities for each analyte of interest whenever possible and/or ii) monitoring the full spectral peak with sufficient resolution, thus enabling the possibility of wing integration, an approach that was already proven successful in continuous source atomic absorption spectrometry (CSAAS).[18] As will be shown in detail in section 3.2, a working protocol together with a post-acquisition data processing tool enabling wing integration (among other features) have been developed in this work. This enhances the versatility of the technique to a level much higher than normally available.

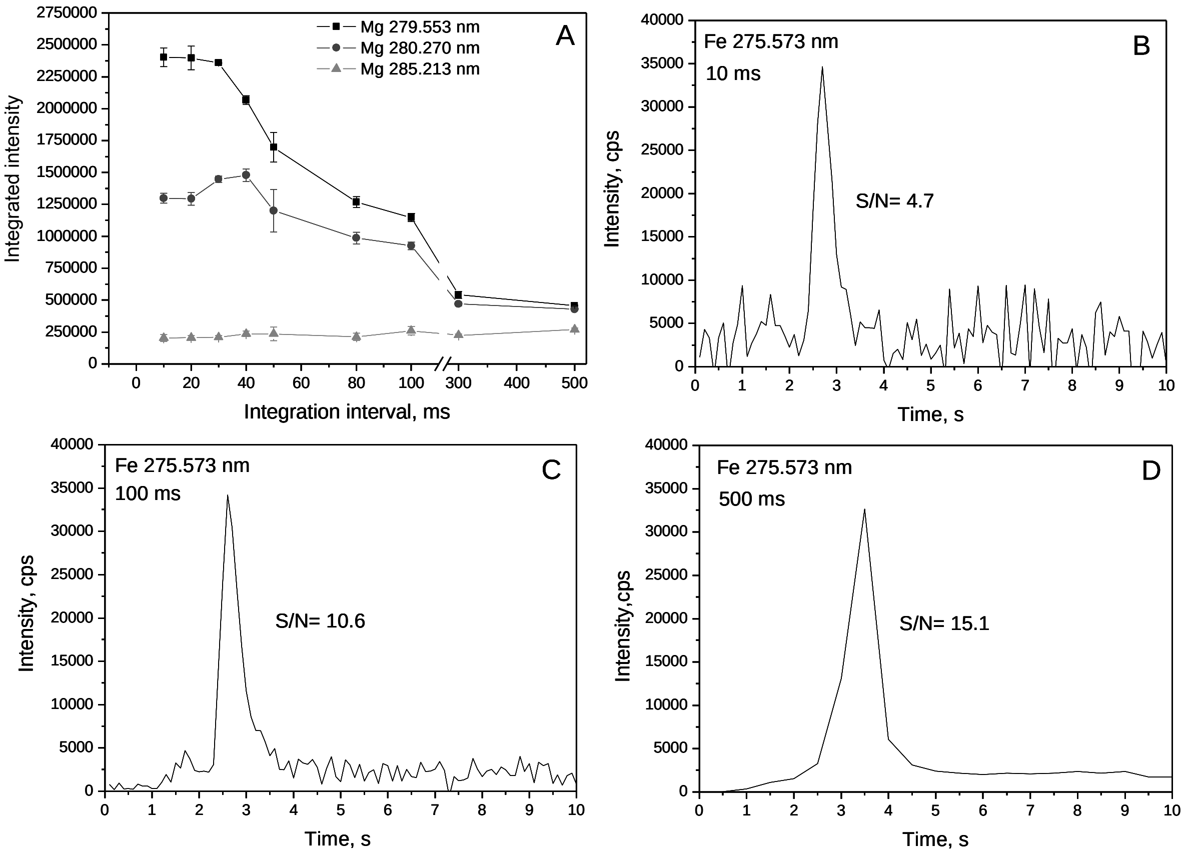

Figure 2. Influence of the integration time on (i) analyte sensitivity for Mg emission lines with different relative intensities (2A) and (ii) S/N ratios for a weak Fe emission line (2B to 2D). Signals were generated via ETV of a multi-element sample solution containing 20 ng of each analyte and using the ETV program given in Table 1.

3.2 Evaluation and correction of the background signal

Background (BG) can originate from two main sources in ICP-OES: (i) the continuous emission spectrum from the plasma itself, and (ii) the occurrence of a matrix-dependent, structured atomic and/or molecular background emission.[19] This situation, which is relatively easy to solve when using PN, is aggravated for sample introduction systems providing transient signals (such as ETV), as in this case, also the BG can change substantially during the measurement.[20] For this kind of situations, background monitoring together with signal monitoring is crucial in many cases in order to detect potential problems and correct for their contribution if necessary.[21] Unfortunately, to the best of the authors' knowledge, "automatic" BG monitoring and correction is not possible for measurements carried out in "transient mode" for every commercially available instrument as a result of the low data handling speed. This limitation can, however, be overcome if the data collected by the CCD detectors are treated off-line using an adequate software package.

In order to generate a 3D plot showing the entire spectral region around the analytical line and its evolution with time, several wavelengths at both sides of the maximum can be monitored in the transient mode and the data thus obtained can then be plotted off-line for their subsequent evaluation. The visual analysis of the 3D graphs thus obtained [intensity x wavelength=f(time)], will permit the design and application of mathematical algorithms for BG modeling and correction, leading to the net analytical signal. To show the potential of this methodology, the atomic emission line of Al at 396.152 nm, which is interfered by the presence of Ca, was selected as a model. First, an aqueous standard solution containing 1 mg L^{-1} Al and 100 mg L^{-1} Ca was analyzed using the standard operating mode of the ICP-OES instrument (sample introduction via PN and analysis via the “method mode” previously described). This operating mode, which allows the visualization of the emission spectrum showing the analyte and the potentially interfering emission lines, was used for the identification of the regions of interest and location of the exact positions of the wavelengths of interest (analytical line and surrounding). The signal generated with the ETV was subsequently monitored at these wavelengths using the transient mode of acquisition. As is the case for most modern ICP-OES instruments, selection of the desired wavelengths cannot be done directly with the instrument used in this work. With the Arcos software, an analyte of interest must be selected first and subsequently, a particular wavelength can be selected from a pre-defined list available for each element (this list can be edited by the user). As a result, selection of the surrounding wavelengths in the method was accomplished by selection of 50 times the same line for Al (396.15nm) in the instrument software, and de-centralization of the peak maximum to be coincident with the wavelengths desired, located at intervals of 0.01 nm from one another and covering the spectral range from 395.900 to 396.400 nm.

The resulting spectrum obtained using ETV for introduction of 10 µL of the Al/Ca solution is shown in Figure 3. As seen in the graph, it is evident that BG evaluation and proper correction would in this particular case certainly help improving the LOD for the determination of Al in presence of Ca using the 396.15 nm line.

Figure 3. 3D visualization of the spectral range around the Al 396.152 nm line during the vaporization step. Experimental conditions: 10 ng of Al and 1 µg of Ca, no modifier/carrier and and using the ETV program given in Table 1.

Several mathematical procedures for BG correction in ICP-OES have been reported in the literature. [20, 22] One of the possibilities most often included in ICP-OES software package consists of BG signal modeling by interpolation between two regions selected at each side of the analytical line, with its subsequent subtraction from the raw intensity signal. Different modeling algorithms, such as linear or cubic splines interpolation, can be used for this purpose. Selection of the best mathematical model can be done by analyzing a solution containing both the analyte(s) of interest and the interfering species, and comparing the values obtained for each correction method with the values expected for the sample.

With this aim, a post-acquisition data processing tool has been developed in Matlab, which relies on linear and cubic interpolation methods in order to BG-correct the matrix of acquired data [wavelength x intensity = f(time)](see Figure 3). The user must specify the significant range of wavelengths and the time for calculating the BG signal, subsequently used for correction. In order to aid the selection of this significant range, the 3D spectrum (Fig. 3) can be also visualized in the software interface. Once the interpolation range and method are chosen, the program provides the net signal intensity graph and the area below the curve "net intensity vs. time" for each wavelength under consideration, computed applying the trapezoidal method. The program also displays the raw intensity and BG contribution graphs. Screenshots of the correction program are included as additional online material.

In order to test the performance of this tool, two reference materials containing high and low amounts of Ca were analyzed for their Al content. A 3D plot intensity *vs.* analysis time for all the wavelengths of interest is shown in Figure 4A for the bone ash sample, which contains the higher Ca concentration. The wavelength and time intervals for BG characterization were selected according to this graph and comprised the wavelength values from 396.00 nm to 396.10 nm and from 396.20 nm to 396.30 nm. As for the time, the interval comprised between 1 to 6 s was considered in this case. Since the BG intensity is not the same at both sides of the analytical signal, the cubic splines interpolation was found to provide better results in this particular case, returning the BG-corrected 3-D representation shown in Figure 4B.

For quantification, an Al calibration curve was constructed based upon the results obtained for vaporization of 10 µL aliquots of mono-elemental standard solutions with Al concentrations ranging from 0.2 mg L^{-1} to 2.0 mg L^{-1} and 5µg of Pd as modifier/carrier. Integrated intensity values at the peak top, providing the highest sensitivity, were used for the determinations. Results obtained for the analysis of both reference materials with and without BG correction are gathered in Table 3. As can be seen in this table, results obtained after BG correction are in good agreement with the certified values, while clearly overestimated values are obtained if no BG correction is applied.

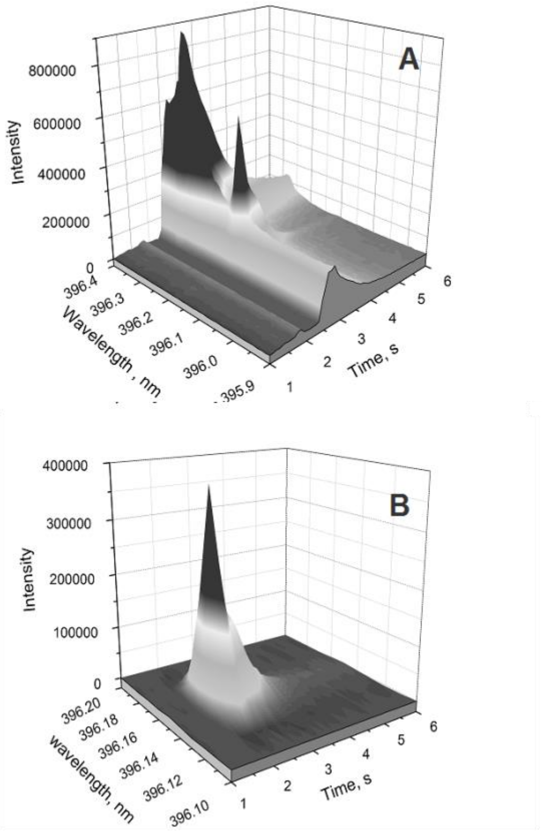

Figure 4. 3D spectrum obtained upon ETV of 10 µL of bone ash sample solution, based on the output of the mathematical correction program. Both raw data (A) without BG correction and

(B) with BG correction are shown. 5 µg of Pd as modifier/carrier and and using the ETV program given in Table 1.

For quantification, an Al calibration curve was constructed based upon the results obtained for vaporization of 10 µL aliquots of mono-elemental standard solutions with Al concentrations ranging from 0.2 mg L^{-1} to 2.0 mg L^{-1} and 5 µg of Pd as modifier/carrier. Integrated intensity values at the peak top, providing the highest sensitivity, were used for the determinations. Results obtained for the analysis of both reference materials with and without BG correction are gathered in Table 3. As can be seen in this table, results obtained after BG correction are in good agreement with the certified values, while clearly overestimated values are obtained if no BG correction is applied.

Table 3. Al determination in SRM 1400 and SRM 1568a by means of ETV-ICPOES, with and without BG correction, using 0.5 µg of Pd as carrier and the ETV program settings shown in Table 1. (n=3, Uncertainties indicated as standard deviation)

Sample	Reference value (µg g^{-1})	Experimental result with BG Correction (µg g^{-1})	Experimental result without BG Correction (µg g^{-1})
NIST 1400 Bone Ash *	530	587 ± 42	1354 ± 150
NIST 1568 a Rice Flour **	4.4 ± 1.0	4.5 ± 0.5	6.4 ± 0.2

* 38.18 ± 13 % of Ca; ** 0.0118 ± 0.0006% of Ca

The calibration curves and the determination of Al in the bone ash sample were also calculated using intensities obtained at wavelengths located in the wings of the Al signal (396.13 nm, 396.14 nm, 396.16 nm and 396.17 nm) and by applying the described BG correction algorithm. This quantification strategy is straightforward, since the software program developed integrates all the wavelengths inside the analytical range without the need for further optimization. The calibration curves obtained using this strategy show a good linearity within the range analyzed (2.0 ng to 20 ng). As for the Al concentration values, recovery percentages between 80% and 113% were obtained for the determination of Al in the bone ash sample for the different wing-wavelengths considered: 425 ± 42 µg g^{-1} (396.17 nm), 469 ± 44 µg g^{-1} (396.13 nm), 586 ± 53 µg g^{-1} (396.16 nm) and 602 ± 56 µg g^{-1} (396.14 nm). As a result, it can be concluded that quantification using the signal of the analytical wings is a powerful tool for extending the linear range and for avoiding detector saturation for highly intense emission lines

4 Conclusions

In this paper, a general working protocol for analysis of fast transient signals with modern, simultaneous ICP-OES instruments was developed. Additionally, a method for off-line generation of the analyte spectrum was developed and a program for off-line BG correction and integration of the transient signals was designed.

Calibration of the optical system as well as line selection was realized with pneumatic nebulization of a standard solution. The most important parameters affecting data acquisition of transient signals are the sampling rate and the integration time. A sampling rate of at least 2 Hz must be used in order to obtain a representative signal for a short transient signal as generated by ETV. Also the selection of the integration time should be done with great care, as too long integration times can result in saturation of the CCD detectors for the most intensive lines, while too short ones will lead to deterioration in the S/N ratio and, consequently, limits of detection for the less sensitive lines. Subsequently, off-line generation and evaluation of the entire spectral region around the analytical wavelength allows evaluation of the BG and potential interferences. The resulting spectrum enables the design and application of mathematical algorithms for background modeling and correction, leading to the net analytical signal.

All the conclusions drawn here, including the background correction strategy, could easily be applied to other emission lines and other sample introduction systems providing a transient signal (FI, LA, GC, HPLC) coupled to a simultaneous CCD-detection based ICP-OES instruments.

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5 References

1 N. H. Bings, A. Bogaerts, and J. A. C. Broekaert, *Anal. Chem.* 2010***, 82,*** 4653.

2 M.Tanner and D. Günther, *Anal. Chim. Acta*, 2009, **633**, 19.

3 M. Aramendía, M. Resano and F. Vanhaecke, *Anal. Chim. Acta*, 2009, **648**, 23.

4 C. Dubois, N. Gilon, C. P. Lienemann, S. Morin and J. M. Mermet, *J. Anal. At. Spectrom*., 2005, **20,** 950.

5 A. A. Menegário and M. F. Giné, *Spectrochim. Acta, Part B*, 2001, **56**, 1917.

6 C. Shizhong, L. Dengbo, H. Zhixiong and W. Zhan, *Int. J. Environ. Anal. Chem.*, 2005, **85**, 493.

7 A. F. Lagalante, *Appl. Spectrosc. Reviews*, 1999, **34**, 191.

8 T. Pettke, C. A. Heinrich, A. C. Ciocan and Detlef Günther, *J. Anal. At. Spectrom*., 2000, **15**, 1149.

9 S. Maestre and M.T.C. de Loos-Vollebregt, *Spectrochim. Acta, Part B*, 2001, **56** 1209.

10 L. Gras and M.T.C. de Loos-Vollebregt, *Spectrochim. Acta, Part B*, 2000, **55**, 37.

11 P. Masson, M. Dauthieu, F. Trolard and L. Denaix, *Spectrochim. Acta, Part B*, 2007, **62**, 224.

12 Y. Okamoto, K. Kanda, S. Kishiwada, and T. Fujiwara, *Appl. Spectrosc.*, 2004, **58**, 105.

13 Z. Fan, B. Hu and Z. Jiang, *Talanta*, 2006, **68**, 1359.

14 P. Masson, *J. Anal. At. Spectrom*., 2011, DOI: 10.1039/c0ja00156b

15 Spectro arcos, High Resolution ICP-CCD spectrometer for the Most Demanding Elemental Analysis Requirements in Industry, Environmental Protection and academia. Available on http://www.spectro.com/pages/e/p010312_arcos165_overview.htm, last accessed on 02/12/2011

16 H. Yinhui, Z. Zhanxia, Q. Haowen and L. Wenchong, Anal. Sci. 1991, **7**, 553.

17 M. Resano, M. Verstraete, F. Vanhaecke and L. Moens, *J. Anal. At. Spectrom*., 2001, **16**, 1018.

18 I. M. Dittert, J. S. A. Silva, R. G. O. Araujo, A. J. Curtius, B. Welz and H. Becker-Ross, *J. Anal. At. Spectrom*., 2010, **25**, 590.

19 Inductively coupled plasmas in analytical atomic spectrometry, ed A. Montaser and D.W. Golightly, VCH Publishers, Inc., New York, 2nd edn., 1992, ch. 5, pp. 262-293 and ch. 6, pp. 299-335.

20 George C.-Y. Chan and Wing-Tat Chan, *Spectrochim. Acta, Part B*, 2002, **57**, 1771.

21 L. Moens, P. Verrept, S. Boonen, F. Vanhaecke and R. Dams, *Spectrochim. Acta*, 1995, **50B**, 463.

22 E.H. van Veen and M.T.C. de Loos-Vollebregt, *Spectrochim. Acta, Part B*, 1998, **53**, 639.