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Evaluation of inductively coupled plasma optical emission spectrometers with axially and radially viewed configurations[☆]

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Abstract

The analytical performance of two inductively coupled plasma optical emission spectrometers with axially and radially viewed configurations, equipped with charge coupled device solid-state detectors was evaluated using Ar, Ba, Mg, and Ni as test elements. Both instruments have similar Echelle optical arrangements and radio-frequency generators, differing only in the viewing mode and in the diameter of the central injector tube, i.e. 2.3 for the axially and 1.4 mm for the radially viewed ICP. The figures of merit evaluated were: warm-up time, short- and long-term stabilities, UV and VIS spectral resolution and limit of detection (LOD) for Ni in 0.14 $\mathrm{mol\,l^{-1}}$ HNO_3 and 1000 $\mathrm{mg\,l^{-1}}$ Cr media, respectively. The influence of residual carbon content on background equivalent concentration (BEC) and sensitivity attained for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Se and Zn was also investigated in both viewing modes. The robustness, short- and long-term stabilities, and UV and VIS spectral resolutions were similar for both configurations. For the radially viewed equipment, the warm-up time was at least a factor of 2 shorter than that for the axially viewed configuration. On the other hand, the sensitivity attained for Ni with the axially viewed arrangement was approximately 20 times better than that with the radially viewed. In both viewing modes, and for most of the evaluated elements, the values of BEC and LOD were similar for all studied carbon concentrations (from 10 to 10 000 $\mathrm{mg\,l^{-1}}$ C) when working with robust plasma conditions. The Mg II/Mg I ratio at an applied power of 1.3 kW and a nebulizer gas flow-rate of 0.90 and 0.70 $\mathrm{l\,min^{-1}}$ for axially and radially viewed configurations were 10.6 and 13.7, respectively. Quantitative determinations were successfully performed using both systems.

Keywords: Figures of merit; Axial viewing; Radial viewing; ICP OES

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1. Introduction

Inductively coupled plasma optical emission spectrometry (ICP OES) is a well established method for multielemental analysis. This method had a rebirth in the last decade due to the development of equipments with axially viewed configuration and solid-state detectors that improved flexibility and sensitivity [1]. The incorporation of segmented charged device or charge coupled device (CCD) solid-state detectors enabled to reach spectral resolution, linear response range and simultaneous reading of a wide range of electromagnetic spectrum, required by an ICP OES. The use of this kind of detector became possible after development of new materials in the semi-conductors technology [2,3]. The idea of axially viewed measurements was proposed in the 1970s [4], however, in spite of an improvement in sensitivity, the system performance was degraded due to increased interferences. After two decades this proposal becomes viable due to the development of proper interface systems based on shear gas or end-on gas [1]. However, common sense in this area still recommends ICP OES with axially viewed configuration for applications requiring better sensitivity, but without a complex matrix. For samples with complex matrices, the best option appears to be to use an ICP OES with radially viewed configuration. This general opinion needs a more critical evaluation. Dubuisson et al. [5] showed that neither the effect caused by easily ionizable elements, nor the gain in sensitivity was so impressive in an ICP OES with axially viewed configuration. These authors employed three ICP OES systems with different configurations. Ivaldi and Tyson [6] presented similar conclusions and pointed out that an axially viewed plasma might be successfully used when lower detection limits are desired, but reduced plasma robustness could be a problem.

In a recent comprehensive review, Brenner and Zander [1] pointed out that the interfaces used in ICP OES with axially viewed configuration should be critically compared to gain better understanding of the performance of each arrangement. Similarly, ICP OES with the same optical arrangement and solid-state detector, but with different torch positions should also be compared to generate critical data about the performance of each system. The work here described dealt with this evaluation using plasma diagnostics according experiments proposed by Mermet [7], Poussel et al. [8], and Mermet and Poussel [9].

2. Experimental

2.1. Instrumentation

Two simultaneous ICP OES instruments with axially and radially viewed configurations Vista AX-CCD and RL-CCD (Varian, Mulgrave, Australia) were used in this investigation. Both systems are equipped with a simultaneous CCD solid-state detector that allows measurements from 167 to 785 nm. The pre-optical systems are purged with argon in order to enable readings below 180 nm. The polychromator was thermostated at 34 °C and purged with argon. An end-on gas interface was used in the axially viewed configuration to minimize interferences caused by self-absorption and recombination, to provide a wide linear dynamic range and low background. In the radially viewed ICP OES, a snout was used to purge the environment around the plasma with argon. The same sample introduction system, composed by a cyclonic spray chamber and a concentric nebulizer, was employed in both systems in order to obtain comparable results. However, the injector tube diameter of the torch used in each equipment was different; i.e. 2.3 mm in the axially and 1.4 mm in the radially viewed configuration. The observation height used in the radially viewed configuration was adjusted in order to reach the highest signal-to-background ratio (SBR) for most elements. The observation zone in the axially viewed system was automatically set by the program supplied with the Vista AX control software using the Mn II 257.610 nm emission line. The detailed description of both spectrometers is presented in Table 1 and operational parameters are listed in Table 2. All emission signals were integrated using the automated adaptative integration time that is performed in VISTA equipments according to line intensities and analyte concentrations. All meas-

Table 1
Characteristics of Vista AX and RL ICP OES

Characteristic	Vista AX and RL
Generator frequency	40 MHz
Optical sytem	
Polycromator	Echelle-grating + CaF_2 cross dispersing prism
Grating density groove	95 grooves mm^{-1}
Focal length	400 mm
Entrance slit	Height = 0.029 mm and width = 0.051 mm
Sample introduction system	
Nebulizer	Concentric
Spray chamber	Cyclonic
Detector	Peltier cooled CCD 70 908 pixels spread across 70 non-linear arrays Wavelength range = 167–785 nm
Torch injector tube diameter	2.3 (axially viewed) and 1.4 mm (radially viewed)

urements were performed using two pixels for each wavelength.

Microwave-assisted acid digestion of two certified reference materials was performed using a cavity-type oven (ETHOS 1600, Milestone, Sorisole, Italy) equipped with ten closed perfluoralkoxy Teflon vessels with pressure relief mechanism. The power applied was controlled by monitoring the temperature in a single vessel using a fiber optical sensor.

2.2. Solutions

A multielement solution containing 5.0 mg l^{-1} Ba and Mg, and 10 mg l^{-1} Ni in 0.14 mol l^{-1} HNO_3 medium was used to evaluate warm-up time, short and long-term stabilities, robustness, UV and VIS spectral resolutions and the limit of detection (LOD) for Ni II 231 nm attained by each configuration. In order to check matrix effects on sensitivity and selectivity a solution containing

Table 2
Operational parameters used in axially and radially viewed ICP OES

Operational parameter		
RF power (kW)	1.2	
Plasma gas-flow rate (l min^{-1})	15.0	
Auxiliary gas-flow rate (l min^{-1})	1.5	
Nebulizer gas-flow rate (l min^{-1})	0.8	
Sample flow-rate (ml min^{-1})	0.8	
Observation height (mm)[a]	13	
Emission lines (nm)	Al I 396.152	Cr II 267.716
	Ar I 404.442	Cu I 324.760
	Ar I 404.597	Fe II 238.204
	As I 188.980	Mg II 280.264
	Ba II 230.424	Mg I 285.208
	Ba II 455.403	Mn II 257.610
	Ca II 317.937	Ni II 231.604
	Cd II 226.502	Se I 196.026
	Co II 228.619	Zn II 206.204

[a] Only for radially viewed configuration.

Table 3
Summary of diagnostic procedure used for evaluation of axially- and radially-viewed ICP OES [5–7]

Figure of merit	Parameter
UV spectral resolution	Profile of Ba II 230 nm line
VIS spectral resolution	Profile of Ba II 455 nm line
Robustness	Mg II 280 /Mg I 285 nm ratio
Short-term stability	R.S.D. for Mg I 285 nm emission signal ($n=15$)
Long-term stability	R.S.D. for Mg I 285 nm emission signal ($n=8$; $t=2$ h)
Sensitivity	LOD for Ni II 231 nm line
Warm-up time	R.S.D. for Ar, Ba and Mg emission signals

10 mg l^{-1} Ni in 1000 mg l^{-1} Cr medium and multielement solutions containing 20 mg l^{-1} of Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Se and Zn in 10, 100, 1000 and 10 000 mg l^{-1} C medium, respectively, were employed. All solutions were prepared by suitable dilution of 1000 or 5000 mg l^{-1} stock solutions of each element (Spex Sample Preparation, Metuchen, NJ) with Milli-Q® distilled and deionized water (Millipore, Bedford, MA) and sub-boiling distilled nitric acid (Milestone). Urea (CH_4N_2O, Reagen, Brazil) was used as carbon source for investigation of residual carbon content effects on sensitivity. The use of this compound was based on a previously described study [10].

An analytical curve—Blank: 0.14 mol l^{-1} of HNO_3; Reference Solution 1: 2.0 mg l^{-1} of Cu, Fe, Mn and Zn + 20 mg l^{-1} Mg + 50 mg l^{-1} Ca, and Reference Solution 2: 4.0 mg l^{-1} of Cu, Fe, Mn and Zn + 40 mg l^{-1} Mg + 100 mg l^{-1} Ca—was used to assess the precision and accuracy of measurements performed in both axially and radially viewed configurations.

2.3. Procedure

Diagnostic tests performed were based on experiments proposed by Mermet [7], Poussel et al. [8] and Mermet and Poussel [9] and they are summarized in Table 3.

The background equivalent concentration (BEC) and LOD were calculated according to IUPAC [11].

$$\mathrm{BEC}=\frac{C_{\mathrm{rs}}}{\mathrm{SBR}},\quad \mathrm{SBR}=\frac{I_{\mathrm{rs}}-I_{\mathrm{blank}}}{I_{\mathrm{blank}}},$$

$$\mathrm{LOD}=\frac{3\times\mathrm{BEC}\times\mathrm{R.S.D.}}{100}$$

where, C_{rs}, concentration of multielemental reference solution (20 mg l^{-1}); SBR, signal-to-background ratio; I_{rs} and I_{blank}, emission intensities for multielemental reference and blank solutions, respectively, and R.S.D., relative standard deviation for 10 measurements of blank solution.

2.4. Sample preparation

A mass of 250 mg of two certified reference materials, NIST 1577b Bovine liver and NIST 1515 Apple leaves (National Institute of Standards and Technology, Gaithersburg, MD), was digested using 2 ml of concentrated sub-boiling distilled HNO_3 plus 1 ml of H_2O_2 30% v/v. The heating program used is shown in Table 4.

3. Results and discussion

All measurements were carried out using instrumental parameters according to Tables 1 and 2. The performance of axially and radially viewed ICP OES configurations was evaluated using simple experiments proposed by Mermet and Poussel [9]. The emission lines of Ar I 404.442 and

Table 4
Heating program used to perform closed-vessel microwave-assisted acid digestions

Step	Time (min)	Power (W)	T (°C)
1	2.0	250	100
2	2.0	0	100
3	5.0	250	120
4	4.5	400	180
5	4.5	650	220

A sixth step was implemented to perform 5 min of ventilation without heating.

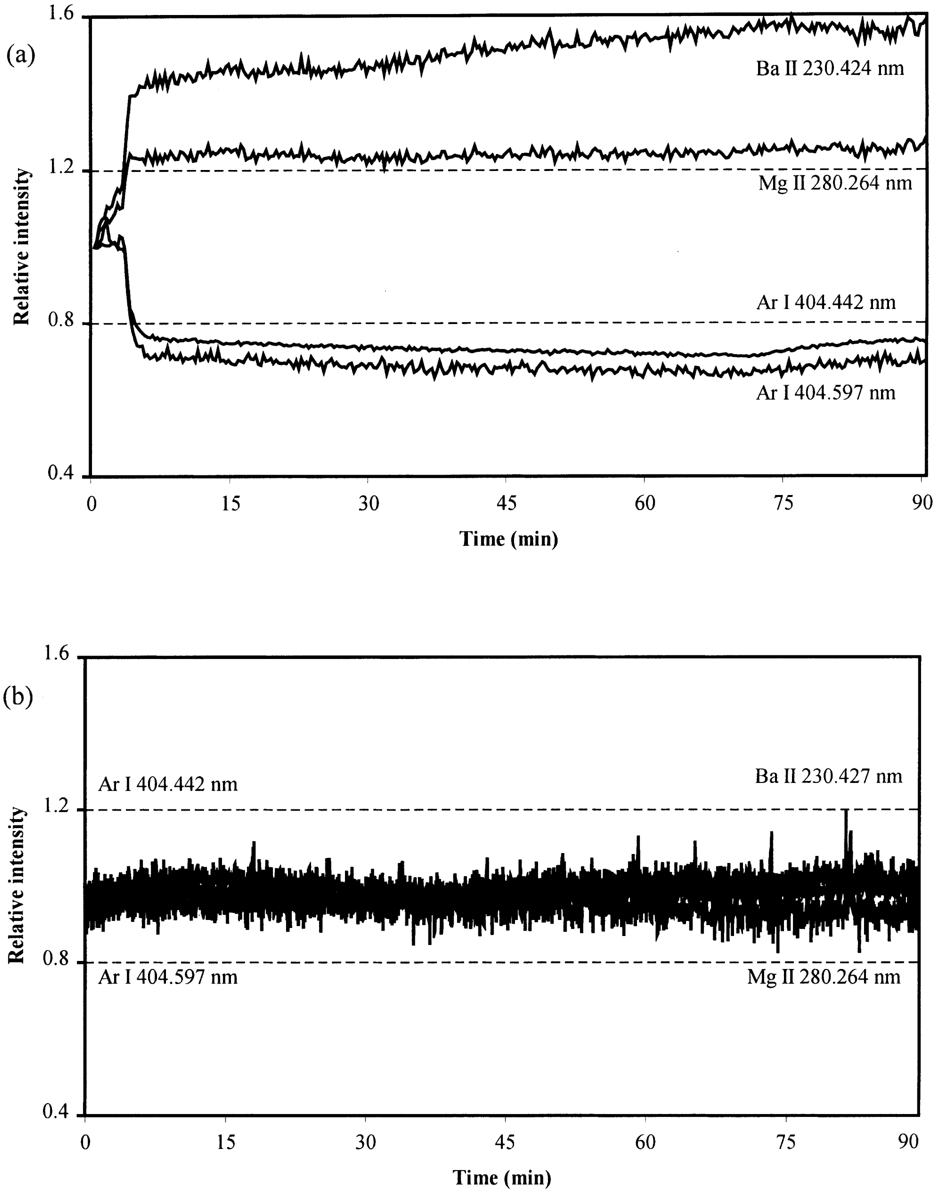

Fig. 1. Warm-up time for axially and radially viewed ICP OES. (a) Axially and (b) radially viewed configurations.

404.597 nm, Ba II 230.424 nm and Mg II 280.264 nm were used for evaluation of warm-up time. The relative intensity observed for both equipment used is shown in Fig. 1.

In the ICP OES with axially viewed configuration, a high variation of emission signals was observed during the initial 5 min. Ar I emission intensities decreased while Ba II and Mg II intensities increased. This behavior was not observed when using radially viewed ICP OES configuration. In this case, emission signals were practically stable during the entire measurement time (90 min). According to Fig. 1, warm-up times for axially and radially viewed configurations were 20

Table 5
Emission intensities and Mg II/Mg I ratios for axially and radially viewed configurations

Configuration	Mg I 285.208 nm	Mg II 280.265 nm	Mg II/Mg I[a]
Axially viewed	151 075	890 419	10.6
Radially viewed	2643	20 139	13.7

[a] Multiplied by 1.8 according to Ref. [12].

and 10 min, respectively. These times were established by considering emission intensity deviations less than 5%.

The short-term stability was determined by performing 15 consecutive measurements of emission intensity at the Mg II 280.265 nm line. For axially and radially viewed configurations, R.S.D. were 0.70 and 0.60%, respectively. When the emission signal was monitored during a 2-h period ($n=8$, i.e. measurements at time intervals of 15 min), R.S.D. observed for radially and axially viewed configurations were 1.5 and 1.4%, respectively.

The Mg II/Mg I ratio is a practical criterion to evaluate plasma robustness and analytical performance. The term robustness was proposed to represent the efficiency of energy transfer and response of the plasma to changes in atomization and excitation conditions and chemical composition of the aspirated solution [7]. This experiment was made by applying a radio-frequency power of 1.3 kW in both ICP, and afterwards by adjusting the nebulizer gas flow-rate in each one to reach the highest Mg II/Mg I ratio. This parameter was set at 0.90 and 0.70 $\mathrm{l\,min^{-1}}$ for axially and radially viewed ICP OES, respectively. The obtained ratios were multiplied by 1.8 to correct response intensities taking into account the use of an Echelle grating and a solid-state detector. This value was previously established by Dennaud et al. [12], also working with a Vista ICP; according to these authors this value can vary from 1.5 to 1.8. As expected, the results showed a higher Mg II/Mg I ratio for the radially viewed configuration (Table 5). The elevated ratios obtained indicate that both instruments were operated at robust conditions [1]. It should also be mentioned that robust conditions are effective to alleviate matrix effects but the sensitivity is slightly degraded [6].

Spectral resolution was similar in both Echelle polychromators. Using Ba II 230.424 and Ba II 455.403 nm emission lines, spectral resolution values of 8 and 30 pm were measured, respectively. It should be mentioned that the selected Ba lines are positioned at the center of the order in the CCD detector that is characterized by a better resolution.

LOD in each configuration were evaluated using Ni II 231.604 nm line. The LODs were calculated based on BEC. The effect of matrix on the LODs was evaluated determining this parameter in 0.14 $\mathrm{mol\,l^{-1}}$ HNO_3 and 1000 $\mathrm{mg\,l^{-1}}$ Cr media. Results are presented in Table 6. LOD were approximately 16–24-fold better when the axially viewed configuration was employed. These data are in agreement with Brenner and Zander [1] that the mean detection limit improvement factor for axially viewed, compared to radially viewed configurations, varied from 2 to 20, using conventional nebulization [1]. The deterioration of detection power was slightly higher in the medium containing Cr, particularly

Table 6
LOD and BEC for Ni II (231.604 nm) in 0.14 $\mathrm{mol\,l^{-1}}$ HNO_3 and 1000 $\mathrm{mg\,l^{-1}}$ of Cr media for axially and radially viewed configurations

Sample medium	Axially viewed		Radially viewed	
	BEC ($\mu g\,l^{-1}$)	LOD ($\mu g\,l^{-1}$)	BEC ($\mu g\,l^{-1}$)	LOD ($\mu g\,l^{-1}$)
0.14 $\mathrm{mol\,l^{-1}}$ HNO_3	11	0.23	301	3.8
1000 $\mathrm{mg\,l^{-1}}$ of Cr	4	0.31	741	7.6

Table 7
LOD and BEC for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Se and Zn in solutions containing different carbon concentrations in axially viewed ICP OES

Element	Carbon concentration (mg l^{-1})									
	0.14 mol l^{-1} HNO_3		10		100		1000		10 000	
	BEC	LOD	BEC	LOD	BEC	LOD	BEC	LOD	BEC	LOD
Al I 396.152	0.11	0.072	0.12	0.077	0.11	0.073	0.11	0.074	0.13	0.086
As I 188.980	2.2	2.4	2.4	2.6	2.3	2.5	2.3	2.5	2.5	2.7
Ca II 317.937	0.091	0.067	0.097	0.071	0.091	0.067	0.092	0.067	0.097	0.071
Cd II 226.502	0.34	0.40	0.36	0.44	0.34	0.41	0.35	0.42	0.38	0.46
Co II 228.619	0.73	0.84	0.78	0.90	0.74	0.85	0.74	0.86	0.79	0.91
Cr II 267.716	0.18	0.28	0.19	0.30	0.18	0.29	0.18	0.29	0.19	0.30
Cu I 324.760	0.064	0.048	0.069	0.051	0.065	0.048	0.064	0.048	0.068	0.051
Fe II 238.204	0.45	0.54	0.48	0.59	0.46	0.56	0.46	0.56	0.49	0.60
Mg II 280.264	0.022	0.039	0.024	0.041	0.023	0.039	0.023	0.039	0.024	0.042
Mn II 257.610	0.038	0.082	0.040	0.087	0.038	0.082	0.038	0.083	0.040	0.087
Se I 196.026	4.8	4.2	5.3	4.7	5.0	4.5	5.2	4.6	5.6	5.0
Zn II 206.204	0.42	0.22	0.45	0.24	0.42	0.22	0.43	0.23	0.47	0.25

Values of BEC and LOD are expressed in μg l^{-1}.

in the radially viewed configuration. These results seem to indicate that the end-on gas interface used to eliminate the plasma tail recombination zone in the axially viewed configuration was efficient. The performance of the end-on gas interface can even proportionate lower matrix interferences in axially viewed compared to the radially viewed configuration, as recently demonstrated for Dy, Eu and Yb determination in sheep faeces [13]. Results obtained for the influence of the carbon content on the sensitivity of measurements also confirms this observation (Tables 7 and 8).

The axially viewed configuration did not present significant variations in BEC and LOD values,

Table 8
LOD and BEC for Al, As, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Se and Zn in solutions containing different carbon concentrations in radially viewed ICP OES

Element	Carbon concentration (mg l^{-1})									
	0.14 mol l^{-1} HNO_3		10		100		1000		10 000	
	BEC	LOD	BEC	LOD	BEC	LOD	BEC	LOD	BEC	LOD
Al I 396.152	8.6	5.2	8.9	5.4	8.4	5.1	8.3	5.0	9.5	5.7
As I 188.980	40	98	40	98	37	92	37	89	37	90
Ca II 317.937	10	9.8	11	10	10	9.5	9.9	9.5	11	10
Cd II 226.502	19	26	18	23	17	22	16	21	18	23
Co II 228.619	27	34	26	32	25	31	24	30	26	32
Cr II 267.716	34	30	31	28	29	26	29	25	29	26
Cu I 324.760	4.3	1.9	4.4	2.0	4.2	1.9	4.2	1.8	4.3	1.9
Fe II 238.204	16	14	14	13	13	12	13	12	14	13
Mg II 280.264	0.50	0.79	0.50	0.80	0.47	0.75	0.47	0.75	0.48	0.77
Mn II 257.610	4.2	2.8	4.2	2.8	3.9	2.7	3.9	2.6	4.0	2.7
Se I 196.026	66	148	63	142	60	135	57	127	49	111
Zn II 206.204	17	37	17	37	16	35	16	35	17	38

Values of BEC and LOD are expressed in μg l^{-1}.

Table 9
Results for Ca, Cu, Fe, Mg, Mn and Zn determination based on dry matter, using axially and radially viewed ICP OES

Sample	Ca (% m m^{-1})	Cu (mg kg^{-1})	Fe (mg kg^{-1})	Mg (% mg kg^{-1})	Mn (mg kg^{-1})	Zn (mg kg^{-1})
NIST 1577b Bovine liver						
Axially viewed	146[a] ± 12	142 ± 1	164 ± 4	546 ± 5	7.20 ± 0.58	114 ± 1
Radially viewed	107 ± 5	148 ± 1	156 ± 4	523 ± 4	9.14 ± 0.75	110 ± 3
Certified value	116 ± 4	160 ± 8	184 ± 15	601 ± 28	10.5 ± 0.17	127 ± 16
NIST 1515 Apple leaves						
Axially viewed	1.32 ± 0.06	4.98 ± 0.23	61.9 ± 1.4	0.241[a] ± 0.010	44.5 ± 1.1	10.9 ± 0.3
Radially viewed	1.46 ± 0.03	6.14 ± 0.06	66.5 ± 4.3	0.247 ± 0.003	48.5 ± 2.5	19.6 ± 2.7
Certified value	1.526 ± 0.015	5.64 ± 0.24	(80)[b]	0.271 ± 0.008	54 ± 3	12.5 ± 0.3

[a] Concentration expressed in mg kg^{-1} for Ca and % m m^{-1} for Mg.

[b] Estimated value.

when the carbon concentration of a multielement solution varied from 10 to 10 000 mg l^{-1}. In general, the deviation of results was less than 15%. The suitable performance presented by this configuration can be associated to the efficiency of the end-on gas interface to eliminate the plasma tail recombination zone. The increase of carbon concentration could produce non-specific emission and deteriorate the power of detection due to the increase of background radiation (BEC). It is expected that this drawback could be more pronounced for the axially viewed configuration. However, this undesirable effect was not observed in the evaluated carbon concentration range using the ICP OES with an end-on gas interface. Similar behavior was observed using radially viewed configuration when operating the ICP at robust conditions. In this case the presence of carbon in multielement solutions only affected the BEC and LOD for Se I 196.025 nm, for which a variation approximately 30% was observed over the carbon concentration range evaluated. The matrix effect caused by residual carbon on ICP OES measurements of Se was previously described by Knapp et al. [14], and it can also cause problems in inductively coupled plasma mass spectrometry [15,16].

Recovery experiments were performed using both instruments to assess the accuracy and precision of measurements. All results for Ca, Cu, Fe, Mg, Mn and Zn were in agreement with certified values at a 95% confidence level (Table 9). Other elements, such as Al, As, Cd, Co, Cr and Se, were not determined because their concentration in digestates were below the detection limit, even when using ICP OES with axially viewed configuration.

4. Conclusion

Axially and radially viewed configurations presented similar figures of merit. Despite differences in warm-up time and LODs, analytical performance of both configurations was not significantly compromised. It can be inferred that quantitative determinations can be carried out with suitable precision and accuracy using any viewing configuration. Taking into account the obtained results, the axially viewed configuration presented higher detection power than that achieved by the radially viewed configuration, independent of the complexity of the sample medium. In spite of some particularities, such as the longer warm-up time observed for the axially-viewed configuration, it could be supposed that the efficiency of the end-on gas interface improved the performance of this arrangement. It can also be supposed that most applications could perfectly be performed using an ICP OES with this arrangement without any serious degradation of analytical performance, as previously suggested by Brenner and Zander [1].

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