A COMPARATIVE STUDY OF INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY AND MICROWAVE PLASMA ATOMIC EMISSION SPECTROMETRY FOR THE DIRECT DETERMINATION OF LANTHANIDES IN WATER AND ENVIRONMENTAL SAMPLES

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Abstract

A new instrumental technique – Microwave Plasma Atomic Emission Spectrometry (MP-AES) is compared to conventional Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for direct determination of lanthanides. Estimation of both methods is done using standard measurement conditions. The present study includes spectral and non-spectral matrix effect evaluation. Tested analytical wavelengths of lanthanides are divided into three groups: 1) relatively free, 2) interfered by other lanthanides and 3) interfered by concomitant elements. Non spectral effect on analytes is examined in two typical real matrices – acidic plant digests and saline water. The capabilities of both plasma methods for quantitative determination of La, Ce, Sm, Eu, Gd and Er are compared. The interference-free emission lines are selected; appropriate background correction is proposed and the corresponding instrumental detection limits are calculated.

Key words: *lanthanides, ICP-OES, MP-AES, spectral and non-spectral interference*

INTRODUCTION

The aim of the study is to compare a new instrumental technique Microwave Plasma Atomic Emission Spectrometry (MP-AES) to conventional Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) for direct determination of lanthanides in water and environmental samples. As ICP-OES is one of the most frequently used methods for this task, it was considered as an appropriate referent (Li & Hu 2010) (De Jong et al. 2005) (Liang et al. 2005).The main limitation in determination of lanthanides by optical emission methods is their numerous absorption/emission wavelengths which are strongly interfered by other elements as well as lanthanides themselves. Different approaches have been applied for elimination or correction of spectral interferences as separation of analytes from sample matrix (Li & Hu 2010)(Liang et al. 2005) (Waqar et al. 2009) (Jia et al. 2008) or mathematical correction (Daskalova et al. 1996)(E.H. van Veen 1998)(Boumans & Vrakking 1986). Although many of these procedures lead to positive result, they are time consuming and complicated.

The new atomic emission method is based on stable magnetically excited microwave plasma source working in nitrogen atmosphere. Continuous nitrogen supply is provided by extraction from the air eliminates the need for ongoing supply of flammable (FAAS) or expensive gases (ICP) for plasma operation. The attractive combination of low operation costs; flexible liquid sample introduction via aerosol generation; high sample throughput and multielemental capability make the new method a promising alternative to classical atomic spectrometry equipment (Agilent Technologies 2014). Besides, the MP-AES provides a relatively good sensitivity for many elements (Karlsson et al. 2015) (Ozbek & Akman 2015)(Balaram et al. 2013). The lower energy of the microwave plasma source results in a slight increase in detection limits, but in the particular case of lanthanides determination, it can prevent the occurrence of interfering spectral lines. In the present study we compare the analytical characteristics of two plasma techniques for determination of lanthanides in pure model solutions and samples containing concomitant elements. The plasma stability and non-spectral matrix effect is tested in saline waters and plant digests. Appropriate calibration strategy is proposed and efficiency of non-spectral matrix effect correction is estimated as well. The main aim of this work is to evaluate the applicability of MP-AES for direct determination of lanthanides in real environmental samples.

INSTRUMENTATION AND REAGENTS

1. Reagents and standard solutions

Monoelemental solutions:

Ce, Er, Eu 1000 $mg.l^{-1}$, CPA-spectr™

Gd_2O_3, 99,9%, Sigma-Aldrich

$La(NO_3)_3$, 99%, Sigma-Aldrich

Sm_2O_3, 99,9% Fluka AG

Multielemental solution (MY), 100 $mg.l^{-1}$Spectracer Ref. № M001100

Initial multielemental solutions for measurements:

Ln - La, Ce, Gd, Eu, Sm, Er

Ln + MY - La, Ce, Gd, Eu, Sm, Er, Li, Be, B, Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Ta, Pb, BiY 1000 $mg.l^{-1}$ Merck

NaCl p.a. Valerus

HNO_3 for trace metal analysis, VWR Prolabo

Double distilled water was used for the preparation of all solutions.

Solutions for measurements were prepared by dissolving Gd_2O_3, $La(NO_3)_3$ and Sm_2O_3 in diluted nitric acid. Plants are digested in Microwave system (Milestone Ethos One) using standard procedure. Measurement solutions are prepared by diluting original solutions.

2. Instrumentation

a. ICP-OES iCap 6000 Thermo Scientific

	UV	VIS
Exposure time, s	15	5
RF power, kW	1,150	1,150
Nebulizer gas, $L.min^{-1}$	0,5	0,5
Auxiliary gas, $L.min^{-1}$	0,5	0,5
Pump speed, rpm	0,5	0,5
Nebulizer type	OneNeb®	
Measurement mode	axial	
Resolution at 200 nm, pm	7	

Table 1 ICP-OES operating conditions

b. MP-AES 4200 Agilent Technologies

Magnetron (fixed), MHz	2450
Plasma gas (fixed), $L.min^{-1}$	20
Auxiliary gas (fixed), $L.min^{-1}$	1.5

Nebulizer Flow, L.min^{-1}	0.7
Pump speed, rpm	15
Nebulizer type	OneNeb®
Resolution (full width at half maximum), pm	50

Table 2 MP-AES operating conditions

RESULTS AND DISCUSSION

Spectral interferences

At constant concentration of tested elements, the number and intensity of registered spectral lines strongly depend on the excitation power of the used specific emission source. ICP is well known as a highly efficient discharge, able to generate rich of lines spectra. In contrast, the excitation capability of nitrogen-MP is not well studied yet. On the other hand, the capability to separate a neighborhood lines depends on the spectral resolution of the optical system. Both effects reflect in spectral interferences of every particular method. Therefore, a comparison of MP-AES and ICP-OES is done in terms of the emission lines of lanthanides.

Evaluation of spectral interferences is done for the first three (or four, where possible), recommended emission lines for lanthanides, included in the spectral library of every instrument by the corresponding producer.

	Measured wavelengths, nm					
La	379.478[a,b]	412.323[a,b]	408.672[a]	433.374[a]	333.749[b]	
Ce	404.076[a,b]	456.236[a,b]	413.38[a]	413.765[a]	535.353[b]	785.754[b]
Sm	428.079[a,b]	442.434[a,b]	446.734[a]	359.26[b]	360.949[b]	
Eu	381.967[a,b]	412.973[a,b]	420.505[a,b]	397.196[a]	393.048[b]	
Gd	342.247[a,b]	376.839[a]	385.097[a]	310.050[b]	335.047[b]	336.223[b]
Er	323.058[a,b]	326.478[a,b]	337.271[a,b]	390.631[a]	369.265[b]	

Table 3 Measured wavelengths for lanthanides [a] - Recommended for MP-AES, [b] - recommended for ICP-OES

In order to investigate inter-element spectral interferences the signals obtained by ICP-OES in water solution of lanthanides 1 mg.l^{-1} (Ln) and multielemental solution - lanthanides 1 mg.l^{-1} + Li, Be, B, Na, Mg, Al, Ca, Ti, V, Cr, Mn, Fe, Ni, Co, Cu, Zn, As, Se, Mo, Ag, Cd, Sb, Ba, Ta, Pb, Bi 10 mg.l^{-1} (Ln +MY), were compared. All signals are normalized to the ones, measured in water solution of lanthanides only and presented on Figure 1.

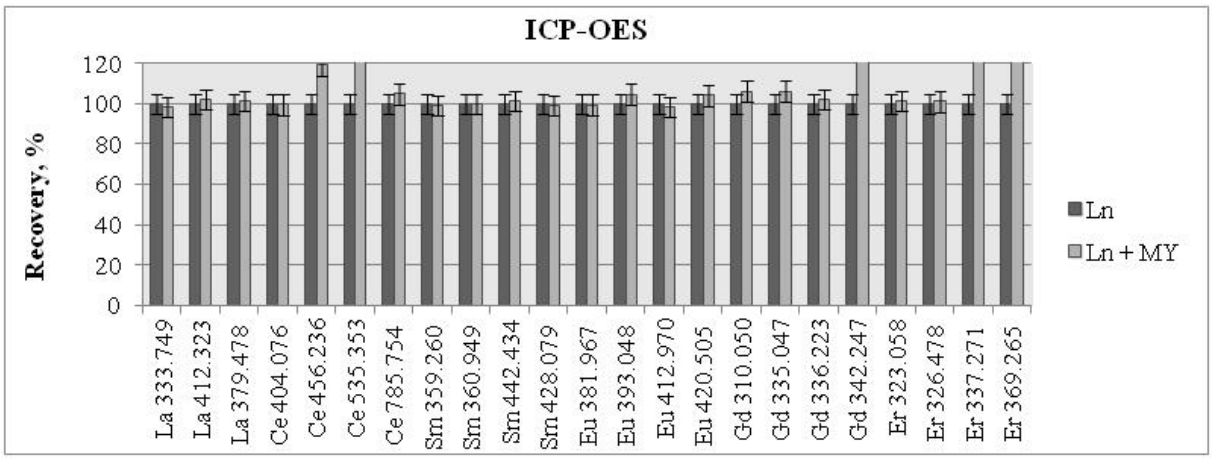


Figure 1 Spectral interferences on lanthanides (1 mg.l^{-1}) from metals in multielemental solution (10 mg.l^{-1}). Signals are normalized to signals for Ln only (at standard measurement conditions).

It could be seen that most of the emission lines remain free from spectral interference by the presence of concomitant metals. The higher resolution of the ICP instrument (4-20 pm) leads to moderately reduced spectral interferences, even though the higher temperature in the plasma. Serious spectral overlaps are observed for Ce 535.353 nm (Co, Fe), Ce 456.236 (Mg, Ti), Er 369.058nm (Mn, Mo), Gd 342.247 nm (Fe, Mo), Gd 310.050 nm (Fe, Mo). Slight increase of the signals for Gd 335.047 nm (Ca, Mn) and Eu 393.048 nm (Fe) was also registered.

Free spectral lines of studied lanthanides that could be directly measured by ICP-OES are as follows: La 333.749nm, Ce 404.076 nm, Sm 359.260 nm, Sm 428.079 nm, Sm 442.434 nm, Eu 381.967 nm, Eu 412.970 nm, Gd 336.223 nm, Er 326.478 nm, Er 323.058 nm. Lines that are not mentioned, but present in the graphics are interfered by lanthanides (inter-lanthanide interference). This type of overlap is not obvious from the figure, because analytes are in equal concentration in both solutions.

Figure 2 presents results for measurement of the same solutions with MP-AES. The spectral interferences from concomitant elements here are more pronounced. This could be ascribed by the lower resolution of the optical system (50 pm), rather than the excitation capability of MW plasma. It should be noted that some of the interferences caused by the occurrence of nearby lines could be significantly reduced by appropriate off peak background correction.

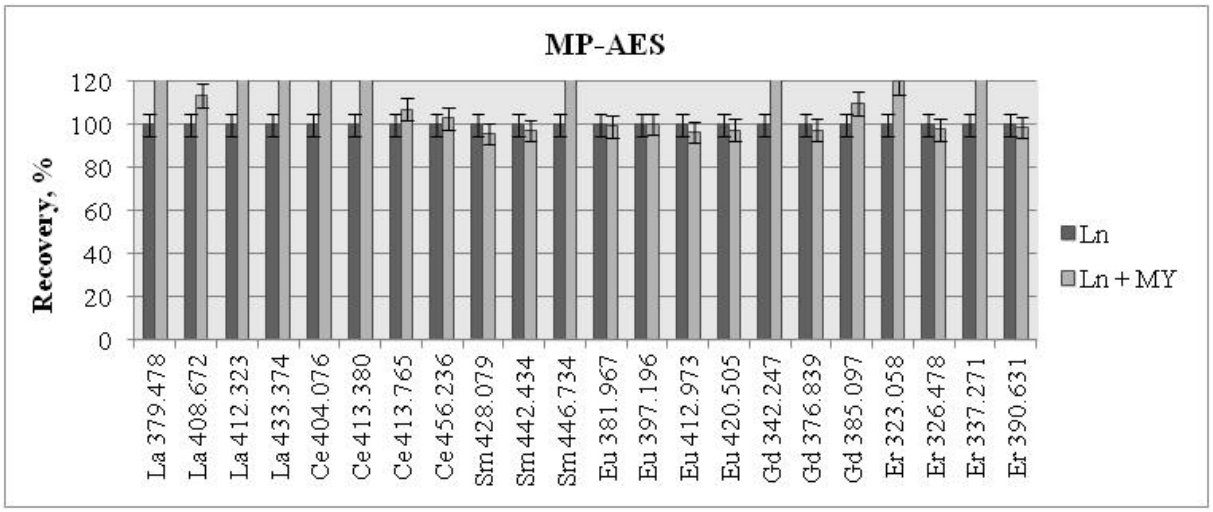


Figure 2 Spectral interferences on lanthanides (1 mg.l^{-1}) from metals in multielemental solution (10 mg.l^{-1}). Signals are normalized to signals for Ln only (at standard measurement conditions).

Free from multielemental interference emission lines that could be used for determination of lanthanides by MP-AES and corresponding background corrections and relative intensity, taken from the instrument library are summarized on Table 4. Since all tested lines for La are strongly interfered, a new one i.e. 442.99 nm, was included in the study.

Analyte	**Wave legth, nm**	**Relaive Intensity**	**Background correction**	**Possible Interference**
La	442,990	42828	Off peak left	-
Ce	413,765	18210	Off peak left	-
Er	326,478	42841	Standard	-
Eu	397,196	171802	Standard	-
Eu	412,973	278263	Off peak left	Ba, V
Eu	420,505	276641	Off peak left	background
Gd	376,839	35244	Off peak right	Fe
Gd	385,097	28984	Off peak right	Fe
Sm	442,434	45026	Off peak left	Ca, V
Sm	446,734	30877	Off peak left	Ti, V, Gd

Table 4 Free wavelengths for lanthanides in MP-AES with appropriate background correction and possible interferences.

Inter-lanthanide overlaps are also considered. The recommended emission lines are not interfered by other lanthanides in concentration below 1 mgl^{-1}. Very low intensive lines are observed in the nearby spectrum of selected wavelengths. In case of higher and variable concentrations of analytes in samples, possibility of inter-lanthanide interference should be kept in mind. Some of the inter-lanthanide interferences with corresponding Relative Intensity (RI) are shown on next figures:

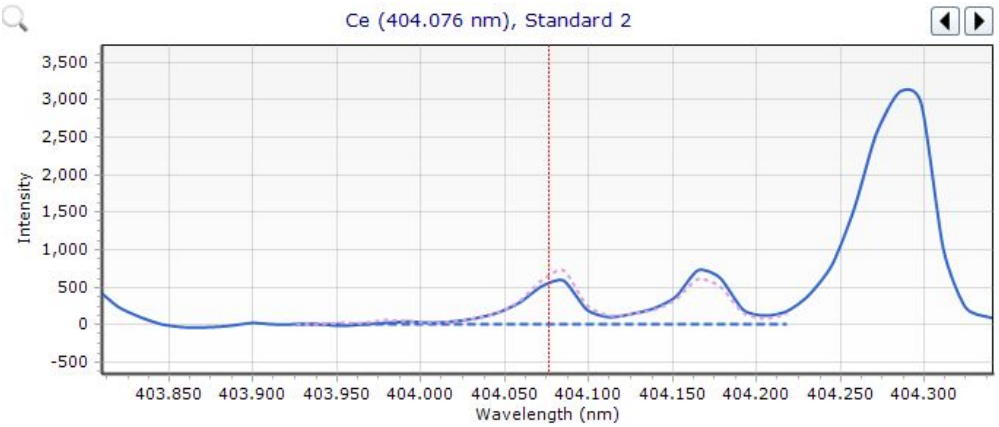


Figure 3.1 Interference of Sm 404.168 nm (RI=4512) on Ce 404.076 nm (RI=12183)

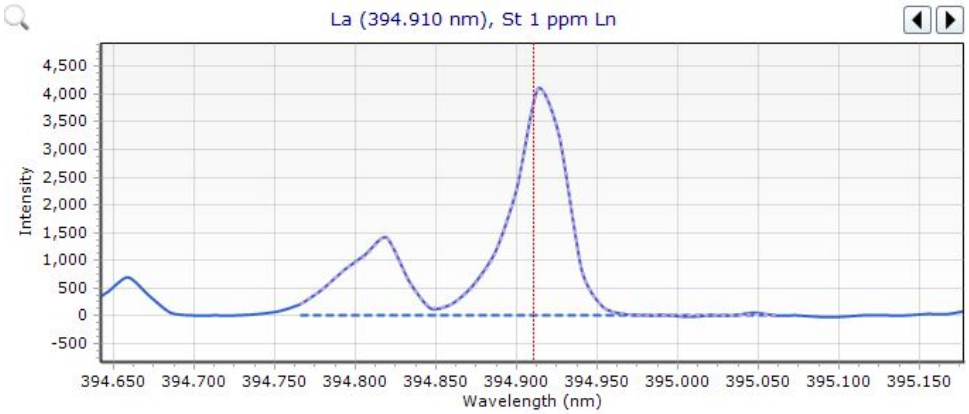


Figure 3.2 Interference of Sm 394.811nm (RI=7133) on La 393.910 nm (RI=112123)

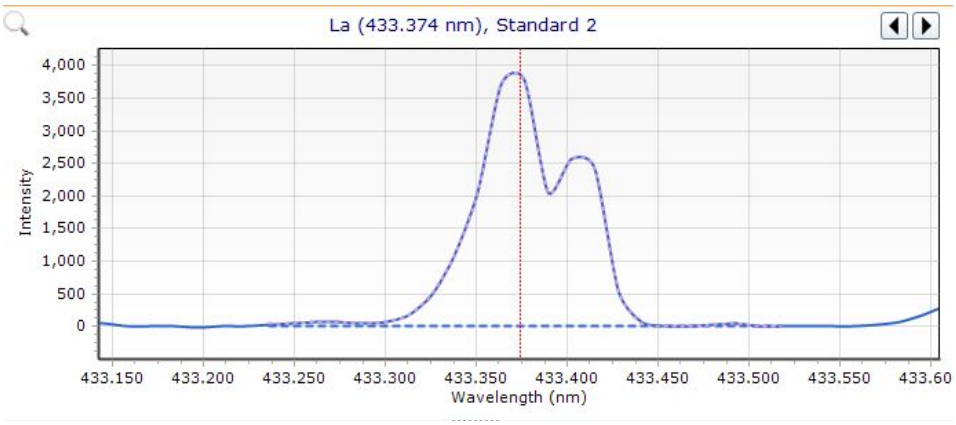


Figure 3.3 Interference of Sm 433.415nm (RI=15313) on La 433.374 nm (RI=90980)

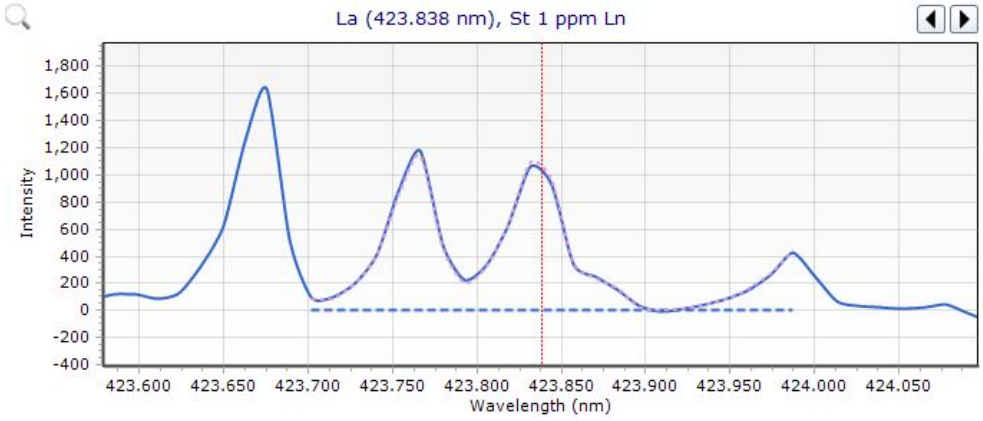


Figure 3.4 Interference of Sm 423.766 nm (RI=6551) and Gd 423.878 nm (RI=2371) on La 423.838 nm (int=30445)

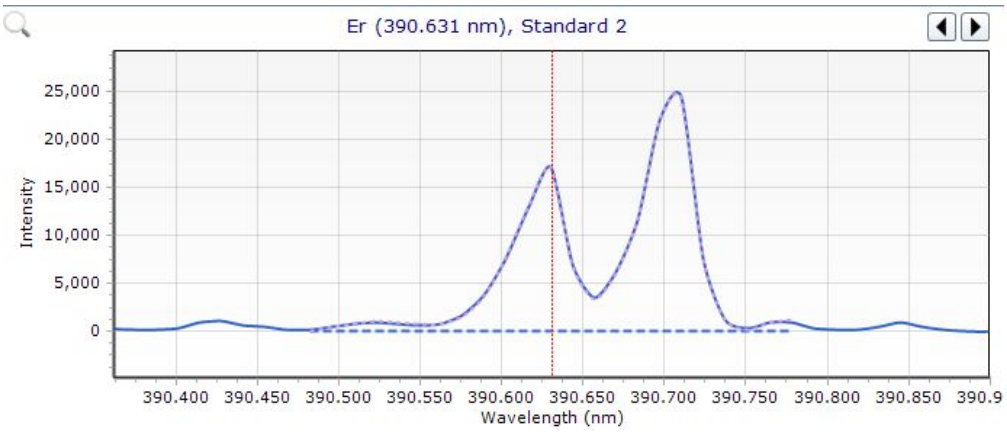


Figure 3.5 Interference of Eu 390.710 nm (RI=128814) on Er 390.631 nm (RI=103872)

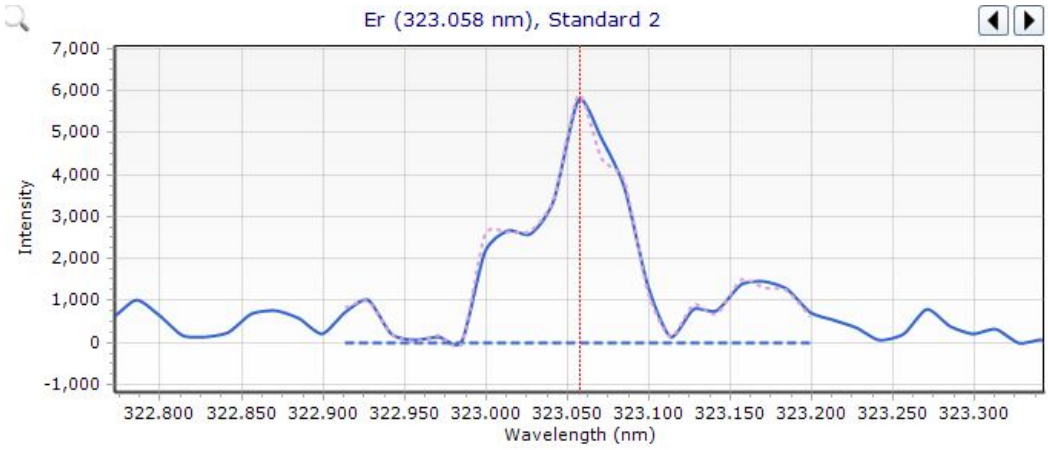


Figure 3.6 Interference of Sm 323.056 nm (RI=3123) on Er 323.058 nm (RI=40219)

Most appropriate analytical lines for MP-AES of tested elements are selected, in terms of minimizing the inter-lanthanide spectral interferences. In addition the "threshold concentration" for each interfering element above which the interference becomes statistically important (eq. 1) for selected analytical emission line is determined.

$$C_{Threshold} = \frac{3SD_0.C_I}{Sig_{A_i}} \qquad \text{(eq. 1)}$$

The "threshold concentration" corresponds to the interfering element concentration which generates a signal measured at a particular analytical line (Sig_{Ai}), equal to three times standard deviation of the blank sample ($3SD_0$). The threshold values were determined by consequently introducing into MP-AES a single element solution of each interfering element, with known concentration (C_I=10 mg.l^{-1}). The obtained values are presented in Table 5.

Analyte	Wavelength (nm)	Threshold concentration of interfering element, $mg.l^{-1}$					
		La	Ce	Sm	Eu	Gd	Er
La	**442.990**	-	No	**1.7**	No	No	No
Ce	**413.765**	No	-	No	No	**2.5**	No
Sm	**442.434**	No	No	-	No	No	No
Eu	**412.973**	No	No	No	-	No	No
Gd	**385.097**	No	No	**6.8**	No	-	**2.1**
Er	**326.478**	**2.8**	No	**2.8**	No	No	-

Table 5. Threshold concentrations of interfering element established for MP-AES

The results from the study of inter-lanthanide effects show that only two analytical lines (Sm and Eu) are completely free from spectral interference. For all other elements (i.e. La, Ce, Er and Gd) correction equations should be applied to ensure the accuracy of MP-AES measurement when the concentration of interfering element in the real matrix exceeds the presented above threshold levels.

Obviously the most pronounced effect is originated by Samarium, which overlaps the analytical lines of three other lanthanides. The strongest interference is detected for La line where only 1.7 $mg.l^{-1}$ Sm generates a statistically distinguishable signal.

Non spectral matrix effect

Non spectral interferences in both plasma techniques are examined in two common matrices, namely acidic plant digests and saline water. In order to evaluate the matrix effect on obtained signals, sensitivity for analytes in water solution is compared to sensitivity in real matrices, only for lines free from spectral interference. As Easy Ionized Elements (EIE) in real saline waters have dramatic effect on the plasma (Zhang & Wagatsuma 2002) and high total dissolved solids content of the sample may lead to problems with the nebulizer, model solutions containing up to 1 % NaCl (m/m) were analyzed.

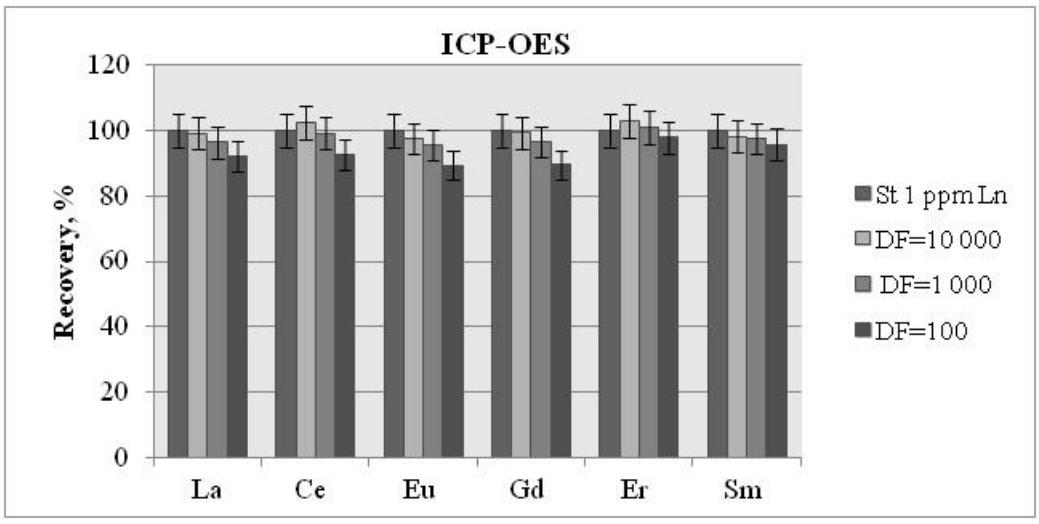


Figure 4 Signals for analytes measured in plant digest ICP-OES

Obtained signals for 1 mg.l^{-1} lanthanides spiked in plant digest with DF=10000, 1000 and 100 (the last is initial DF of plant sample after microwave mineralization) clearly showed that this matrix does not lead to dramatic change in plasma conditions for both instruments (Fig. 4-5). It should be noted that MW plasma demonstrated better stability of the excitation conditions towards plat matrix. Signals for the highest matrix concentration is statistically identical with signals obtained in model water solutions. The slight decrease of sensitivity for La, Ce, Sm and Eu in ICP-OES could be compensated via adequate calibration strategy. The obtained recoveries of the signals with the both techniques show that they could be applied for direct determination of lanthanides.

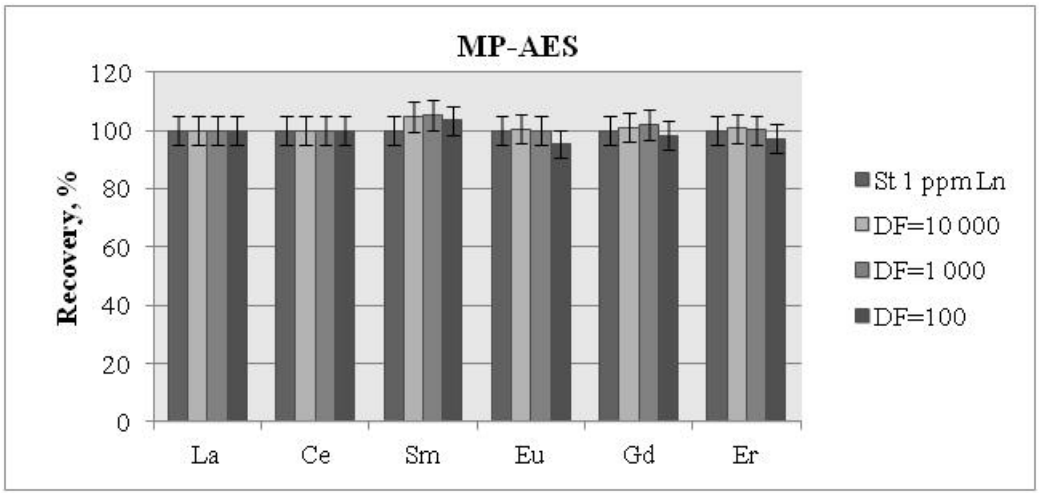


Figure 5 Signals for analytes measured in plant digest MP-AES

Similar experiments were carried out for evaluation of non-spectral matrix effect from dissolved solids in saline water - standard solution containing 1 mg.l^{-1} lanthanides and graduating concentration of NaCl were analyzed. Since saline water contains TDS≈3-5%, mainly NaCl, preliminary dilution should be done. The influence of NaCl concentration, % on analyte signals for both methods is presented on next Figures 6-7.

Here, ICP shows more stable behavior and higher tolerance as significant signal loss is observed for concentrations higher than 0,1 % NaCl. By increasing the concentration of NaCl, lanthanide signals are reduced and the yields reach to 60-70% in the 1% matrix.

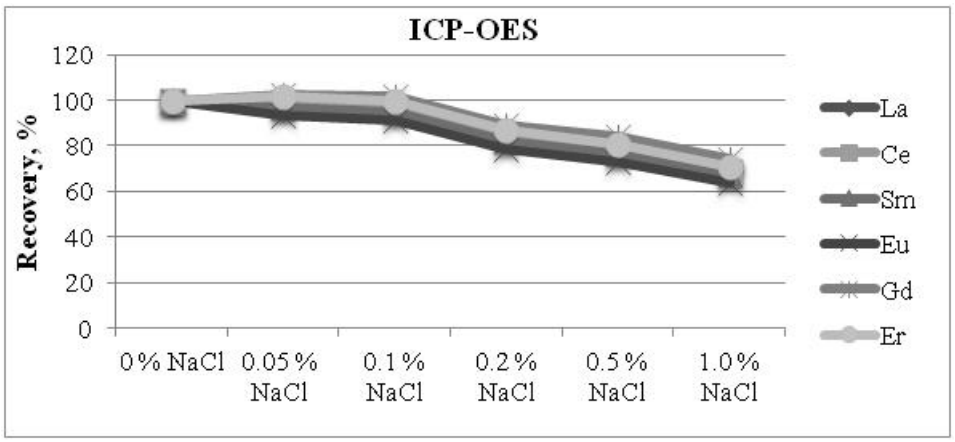


Figure 6 Effect on NaCl concentration, % (m/m) on analyte signals; C_{Ln}=1 mg.l^{-1} ICP-OES

Microwave plasma showed much lower tolerance for tested solutions. Concentrations of NaCl higher than 0,05 % lead to severe non-spectral effect. In NaCl 1% the approximate signal loss for all elements is up to ~80%.

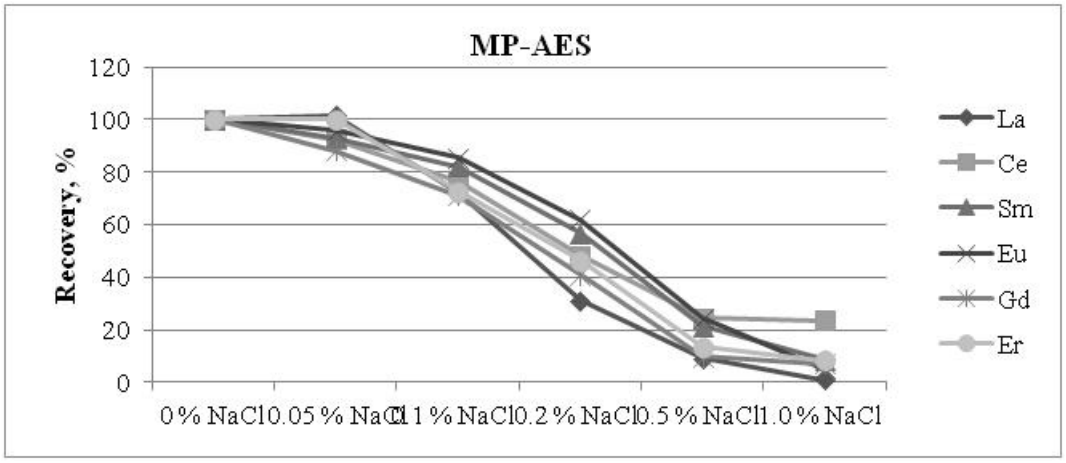


Figure 7 Effect on NaCl concentration, % (m/m) on analyte signals; C_{Ln}=1 mg.l^{-1} MP-AES

Although both instruments showed decrease of signals in presence of NaCl, ICP possesses relatively higher tolerance towards high salt content solutions, due to the higher temperature in the plasma.

Non-spectral matrix effect correction

In order to compensate the strong matrix effect in MP-AES determination of lanthanides, Y was tested as internal standard. Interference-free lines of Y were measured in 0.2 % NaCl on wavelengths 360.073 nm, 371.029 nm, 395.035 nm and 437.494 nm. Recovery (in percent) of signals for analytes (1 mg.l^{-1}) calculated with IS are in the range 97-103 with exception of Eu (R=89%) and Sm(R=92%). The elements were divided into three groups: 1) Er and Gd for which Y 371.029 completely compensates ~50% suppression, 2) Eu and Sm for which Y 395.035 nm is best internal and 3) La and Ce, for which the best correction is achieved with Y 437.494 nm.

Matrix suppression in ICP-OES was corrected by a single line of internal standard (Y 371.029 nm) which matched analyte behavior successfully and compensated signal loss for all analytes.

Analytical characteristics

The analytical characteristics of both optical emission methods for determination of lanthanides were compared at best line selected for every one of them and using the selected above internal standards. A statistical evaluation of calibration equations obtained using 4 calibration standards and blank, together with correlation coefficients and corresponding concentration range are presented on Tables 6-7.

ICP-OES Element	Intercept	SD	Slope	SD	Correlation coefficient
La 333.749 nm	0,01	0,003	218	0,4	1,000
Ce 404.076 nm	1,49	0,03	28	0,1	1,000
Sm 442.434 nm	0,55	0,05	93	0,1	1,000
Eu 381.967 nm	-0,22	0,38	1118	1,3	1,000
Gd 342.247 nm	0,41	0,11	123	0,3	1,000
Er 323.058 nm	0,36	0,05	91	0,1	1,000

Table 6 Analytical characteristics of the method obtained by measuring 4 standards and blank (0, 0.05, 0.0.1, 0.5, 1.0 µg.l^{-1}) ICP-OES

MP-AES Element	Intercept	SD	Slope	SD	Correlation coefficient
La 442.990 nm	0.2	1.1	42.2	0.2	1.000
Ce 413.765 nm	0.6	1.1	23.7	0.2	1.000
Sm 442.434 nm	7.7	7.0	185	1.5	1.000
Eu 412.973 nm	56	34	1643	7.4	1.000
Gd 385.097 nm	-1.85	3.2	88.2	0.68	1.000
Er 326.478 nm	-3.03	2.8	160	0.60	1.000

Table 7 Analytical characteristics of the method obtained by measuring 5 standards and blank (0, 0.5, 1, 2, 5 mg.l^{-1}) MP-AES

Limits of detection (LOD) for lanthanides are calculated for both methods in three matrices (model water solutions, plant digest and 0.2% NaCl). All calculations are based on 3xSD_0 deviation of the corresponding blank. Results are presented in Tables 8-9:

Limits of detection, µg.l^{-1} (3xSD_0)						
ICP-OES	**La**	**Ce**	**Sm**	**Eu**	**Gd**	**Er**
DL BDW	0. 4	3	0.5	0. 4	1	0. 4
DL NaCl (0.2%)	0. 6	8	0.6	0. 4	1	1.3
DL Plant (DF=100)	0. 4	7	0.6	0. 3	1	1.2

Table 8 Limits of detection for analytes in model solution, 0,2 % NaCl and plant digest DF=100. Values are calculated with IS - ICP-OES

Limits of detection, µg.l^{-1} (3xSD$_0$)						
MP-AES	**La**	**Ce**	**Sm**	**Eu**	**Gd**	**Er**
DL BDW	4	3	3	0.7	4	3
DL NaCl (0.2%)	6	9	3	0.9	4	9
DL Plant (DF=100)	5	3	4	0.8	4	4

Table 9 Limits of detection for analytes, in model solution, 0,2 % NaCl and plant digest DF=100. Values for NaCl solutions are calculated with appropriate IS – MP-AES

Calculated limits of detection are similar for the variety of studied matrices, which shows that both instruments could be used for measurement of lanthanides in different samples. Values for NaCl solutions are a little higher, because of the commented above matrix induced suppression.

The obtained limits of detection for MP-AES are definitely higher than the ones for ICP-OES, but the potential of new emission method to provide direct determination of lanthanides in environmental objects at trace levels (>10µg.l^{-1}), in combination with low running costs and high analysis throughput is promising. In order to check the applicability of MP-AES for determination of lanthanides solutions, containing sodium chloride and plant digests were spiked with lanthanides. The recovery of additions as well as corresponding uncertainty is given in Table 8

	La	**Ce**	**Gd**	**Eu**	**Sm**	**Er**
ICP-OES						
NaCl	1.000±0.070	0.965±0.030	1.030±0.020	0.978±0.080	1.010±0.040	0.999±0.070
Plant	1.004±0.003	1.004±0.002	0.987±0.010	0.994±0.001	1.010±0.010	1.040±0.020
MP-AES						
NaCl	1.03±0.04	0.96±0.03	0.98±0.03	0.99±0.01	1.02±0.03	0.98±0.02
Plant	1.01±0.02	1.04±0.06	1.01±0.02	1.02±0.02	0.95±0.02	1.02±0.02

Table 8 Recovery of spiked lanthanides, initial concentration 1 mg.l^{-1}

These values are indicative for the applicability of MP-AES for the direct determination of lanthanides in real samples.

CONCLUSIONS

MP-AES is an attractive alternative to ICP-OES as regards the determination of lanthanides in environmental objects. MW-nitrogen plasma shows good stability to plant matrices, but the suppression of signals in the presence of sodium chloride was more pronounced compared to the ICP. Non spectral matrix effect in both methods can be successfully corrected by internal standardization using appropriate analytical line of Yttrium. Examination of the spectral interferences showed that the most suitable for analysis of lanthanides lines differ in both emission methods. The obtained limits of detection by MP-AES are a little higher than the corresponding by ICP-OES. Despite this, the combination of lower instrument and running costs together with possibility of accurate simultaneous determination of lanthanides at µg/l levels makes the new MW-AES technique promising for large scale environmental studies.

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