Optimization of method for simultaneous multi-element determination of trace elements by Inductively Coupled Plasma-Optical Emission Spectrometry: Chemometric approach

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Abstract

Two objective functions for multi-element optimization in ICP-OES were used and compared using signal-to-background ratios as a figure of merit. Three dimensional response surfaces were generated for a number of elements (Fe, Zn, Cu, Se, Mn, Cr, Ni and Co) to evaluate the performance of both objective functions in locating the optimum compromise instrumental operating conditions in multi-element determinations. IEC technique was used for correction of spectral interferences. Validation of the applied method was carried out by determination of linearity (1 to 100 µg/l), accuracy, precision, detection and quantification limit for each element. Detection limit was calculated using SBR-RSD approach. Both objective functions gave the same set of instrumental operating conditions for simultaneous multi-element determination as the best compromise.

Key words: ICP-OES; multi-element determination; objective functions; interelement correction

Introduction

Inductively coupled plasma optical emission spectrometry (ICP-OES) is a powerful technique for multi-element analysis. ICP-OES is applicable to around 73 elements and provides fast multi-element analysis with superior detection limits to atomic absorption spectrometry (AAS) for many elements. The versatility of ICP-OES makes it a good analytical technique for a wide variety of applications. This versatility is due not only to the large number of elements that can be determined rapidly at trace levels but also to the wide variety of sample types that can be analyzed using the ICP-OES technique (1-4).

Optimization of instrumental operating conditions in simultaneous multi-element ICP-OES methods may improve analytical accuracy, precision and limit of detection. The instrumental operating conditions of an ICP that may be optimized are Rf power, nebulization gas flow rate and observation region in the plasma. Using the conventional lateral viewing mode of the ICP, the net signal, sensitivity (S) and signal-to-background ratio (SBR) are highly dependent on these parameters. It has already been demonstrated that Rf power, nebulization gas flow rate and the viewing height play a major role in both the energy transferred from the plasma to the analyte species and the residence time of the species in the plasma (2, 3). For most of the lines alteration of instrumental operating conditions lead not only to variable gross line signals but also to variable background values. Because the net signal and the background are not modified in a similar way, the SBR optimization does not correspond to that of S. The SBR is a good figure of merit since it can be correlated to detection limits (5-7).

Optimization of simultaneous multi element analysis requires a single value representing each set of operating conditions corresponding to the best results for each element. Since the parameters are often linked together, an unvaried search, which is the most common way, will sometimes fail to determine an optimum set of conditions. One of the most commonly used strategies for optimization of the plasma parameters is the simplex method. Numerous

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objective functions have been proposed for the simplex optimization procedures. We tested two approaches for satisfying the criteria required for obtaining optimum compromise conditions: (1) the maximization of the signal-background ratio; (2) the minimization of the relative standard deviation of the background; (3) the maximization of the ratio of atomic or ionic lines; (4) obtaining the maximum compromise SBRs for all the elements and (5) emphasizing the maximization of SBR of the elements close to their detection limits (2, 8-10). The first approach was Leary's objective function based on SBRs, which is represented by the sum of the reciprocals of the SBRs of elements studied, as follows:

$$F = n \left/ \sum_{i=1}^{n} (SBR)_i^{-1} \right. \tag{1}$$

where *n* is the number of the elements studied for the optimization and SBR*i* are the SBRs of each of the *i*th elements. This equitation generates a value, for each set of instrumental operating conditions using the SBR of all elements. The second tested approach was an objective function called Combinated Ratio Method (CRM), and it is given by:

$$F = \sum_{i=1}^{k} (SBR)_i \left/ \sum_{j=1}^{k} R_j \right. \tag{2}$$

where *n* is the number of studied elements, *k* is (n-1)+(n-2)+….+1, SBR*i* are the SBRs of each of the elements and *Rj* is the ratio of the SBRs of two given elements (*j*th combination), where the maximum SBR of the two is the numerator, so that Rj >1.The CRM performs a weighted average on the sum of the SBRs and maximizes the individual SBRs while minimizing the difference among these ratios.

ICP-OES is a powerful technique for multi-element analysis, but it can be affected by spectral interferences which limit the accuracy, repeatability and reproducibility of the method. Several methods for correction of spectral interferences have been applied (2,9,11) One of the most frequently used is the method of Interelement Correction Factor (IEC). According to this method, Eqn 3 was applied to obtain the corrected analyte concentration:

$$C_c = C_u - \sum(K_i \times I_{ic}) \tag{3}$$

where C_u, C_c F_i and I_{ic} are uncorrected analyte concentration, corrected analyte concentration, IEC factor and interfering concentration, respectively, for each interfering element *i*.

The aim of our work was optimization of the method for simultaneous multi-element determination of the following elements: Fe, Zn, Cu, Se, Mn, Cr, Ni and Co. In this work, we compeared Leary's objective function and CRM by examing the factors obtained by each function and by evaluating the performance of each function in determining the optimum instrument operating conditions. We have also determined IEC for all suspected elements.

Experimental

Instrumentation

Measurements were made on Perkin Elmer, Optima 2000 DV ICP emission spectrometer equipped with: Coupled Echelle monochromator; CCD (Charged coupled devise) detector with wavelength range 165-800 nm, Spectral band pass 0.009 nm on 200 nm, 0.,027 nm on 700 nm and radially and axially viewing on plasma; 40 MHz Rf generator with 750-1500W power. Three channel peristaltic pump with sample uptake rate of 0.2-1.5 ml/min and ultrasound nebuliser U 5000AT was used.

Chemicals and reagents

All working solutions were prepared from standard solutions of 1000 mg/l solutions of the element of interest (Merck) and ICP multi-element standard solution VIII 100 mg/l (Merck). Standards solutions were diluted with 0.1 mol/l HNO_3 (Merck, trace pure).

Methods

Optimization

All operating conditions were held constant except for the observation height and Rf power. Nebulisation gas flow, auxiliary gas flow and plasma gas flow were 0.75 l/min, 0.5 l/min, and 15 l/min respectively. The sample flow rate was 2.5 ml/min. Axially viewing on plasma and signal integration time of 1.0 s were used. The background for each line was selected at 0.05 nm on both sides of each spectral line peak. An average of the background was used for all readings.

The observation height varied from 9.0-24.0 mm above the top of the load coil (ATOLC) in steps of 3.0 mm and the Rf power varied from 900-1400 W in steps of 100 W.

The SBR were determined for all eight elements (Co, Cr, Cu, Fe, Mn, Ni, Zn and Se) at each set of operating conditions using 10 µg/l working solutions. Spectral lines of these eight elements studied are shown in Table 1 along with their excitation and ionization potentials (16).

Table 1. Selected analytical lines

Element (*)	λ (nm)	EP (eV)	IP(eV)
Co II	228.616	5.60	7.86
Cr II	267.716	6.18	6.76
Cu I	324.752	3.82	7.72
Fe II	259.940	4.77	7.87
Mn II	257.610	4.81	7.43
Ni II	231.604	6.39	7.63
ZnII	213.856	5.80	9.39
Se I	196.026	6.32	9.75

*(I-atomic line, II-ionic line)

Based on these SBRs, a set of operating conditions for determination of each of the elements was made. Using these values for the eight elements, two response surfaces were generated, one using Leary's objective function and the other using CRM. The single value representing each set of operating conditions corresponding to the best results for each element were determined from these surfaces and used in comparison of two objective functions.

Interelement correction(IEC)

Interelement correction factors for each of the suspected interfering elements were determined. Determinations were made using standard solution of each element (10.μg/l) in presence of interfering element in concentration of 1000 μg/l. Measurements were made on wavelength on analyte line of interest. The concentrations of the analyte and of the interfering element were determined. IEC factor was calculated by dividing the apparent analyte concentration at that particular wavelength by the interfering concentration. Eqn. 3 was applied to obtain the corrected analyte concentration.

Results and discussion

It has already been told that Rf power, the nebulization gas flow rate and viewing height play a major role in both the energy transferred from plasma to analyte species and in the residence time of the species in the plasma (1-4). The Rf power is directly linked to the amount of energy transferred to the species and then it has a direct influence on the net signal intensities and on SBR values. For most of the lines, increasing the Rf power lead not only to higher gross line signals but also to higher background values (12-14).The role of the nebulisation gas flow rate is more complex. An increase in this rate increases the amount of analyte and solvent introduced into the plasma, but leads to a decrease in the residence time and then in the energy transfer

efficiency. These two competitive effects usually result in an optimum value of the carrier gas flow rate, which is then a compromise between the amounts of aerosol introduced into the plasma and the residence time of the species. In line with the literature data, it was concluded that using ultrasound nebuliser, nebulisation gas flow rate of 0.75 l/min gave satisfactory sensitivity value of analytical signals (11,15,17). The effect on the location of the maximum intensity, i.e., the viewing height where the maximum intensity could be observed, was described by Boomans (2). The lines can be subdivided into two basic categories. One group, atomic and ionic lines with EP < 5.8 eV and IP < 8.0 eV (called "soft" lines after Boumans) have spatial emission behavior that is very dependent on power, aerosol flow and analyte excitation and ionization characteristics. The second group, ionic lines with EP > 5.8 eV and IP > 8.0 eV (called "hard" lines after Boumans) have spatial emission behavior that is relatively insensitive to all of the above parameters. In all cases ion lines have hard line behavior similar to majority atom lines. Under fixed ICP conditions all hard lines have their peak emission at essentially the same position in the discharge which is always higher in the discharge than it is for soft lines (1,2,4).

In our work, the Rf power and viewing height were studied simultaneously, i.e., for each value of viewing height, Rf power was studied in range 900-1400 W. The influence of Rf power and viewing height was studied on the SBR value. The SBRs of each element at each set of operating conditions were determined. The obtained SBRs values have revaled that all the behaviors of analytical lines were dependent on the Rf power and viewing height.

The maximum value of SBR for atomic lines (CuI) and ionic lines (CoII, FeII, MnII) with EP < 5.8 eV and IP < 8.0 eV was obtained in "thermal region" on plasma. Behaviors of these lines were strongly dependent on viewing height value. Atomic lines (Se I) and ionic lines (CrII, NiII, ZnII) with EP > 5.8 eV and IP > 8.0 eV had maximum SBR value in "non-thermal" region on plasma. Measurement of SBRs on different Rf power, has shown three different behaviors of the used analytical lines. For analytical line of CuI (324.752), the highest SBR values were obtained for a low Rf power (900 -1000 W); further increase of Rf power leads to a decrease of SBR value. For analytical lines of FeII (259.94) and MnII (257.610), the SBR values increase with increasing of Rf power in range of 900-1200 W; further increase of Rf power leads to a decrease of SBR values. For analytical lines of CoII (238.892), CrII (267.716), NiII (231.604), ZnII (213.856) and SeI (196.026), the highest SBR values were obtained for a high Rf power (1200-1300 W); further increase of Rf power leads to small changes of SBR value.

The optimum instrumental operating conditions, which mean the highest obtained value of SBR for each element, are presented in Table 2.

Table 2. Optimum operating conditions for each element

Selected analytical line (λnm)*	Observation height (mm)	Rf power (W)	SBR
CoII (228.616)	15	1200	13.02
Cr II (267.716)	18	1300	7.81
Cu I (324.752)	12	1000	38.44
Fe II (259.94)	15	1200	39.95
Mn II (257.610)	12	1200	41.05
Ni II (231.604)	15	1300	14.48
ZnII (213.856)	15	1200	17.73
Se I (196.026)	18	1300	10.32

*(I-atomic line, II-ionic line)

As it can be seen in Table 2, optimum instrumental operating values for Rf power and viewing height for each element have different values. For example, optimized parameters for CoII, FeII and ZnII lines have the same value, but the use of the optimum parameters for these lines would degrade SBR values of the MnII, CrII, CuI, NiII and SeI lines. Similarly, the use of the optimized parameters for the CrII and SeI lines, would degrade SBR values of other lines. Because of these reasons, using the obtained SBR values for each element for each set of operating conditions, the optimum compromise instrumental operating conditions for all elements were determined using Leary's function and CRM. The application of these two objective functions produces value of factors F (Leary's function) and CRM factors (Combinated Ratio Method). The highest generated value of factors indicates the best compromise instrumental operating conditions for determination of all of the elements. Values of factor F (Leary's function) and CRM factors are shown in Table 3 and Table 4 respectively.

Leary's objective function provides the best compromise instrumental operating conditions maximizing the total of the SBRs, but CRM puts the more emphasis on minimizing the difference between the SBRs of investigating elements. Instead of two different approaches of applied functions, values of obtained factors (factor F and CRM factor), shown in Tables 3 and 4, indicate that two functions provides the same set of operating conditions as the best compromise (Rf power of 1300 W and observation height of 15 mm).

Analyzing emission spectra of investigating elements (2,3,18-20), spectral interferences from analytical lines of Cu, Fe and Mn were expected. Interelement correction factors were determined for all analytical lines of interest. Values of IEC are presented in Table 5.

Table 3. Values of coefficient F (according to Leary's objective function)

Observation height (mm)	Rf power(W)					
		900	1000	1100	1200	1300	1400
	6	0.397	0.595	0.995	1.535	1.610	1.095
	9	0.550	0.908	1.639	2.880	3.420	2.896
	12	1.060	1.629	3.966	5.943	7.469	5.194
	15	2.023	3.611	6.541	9.770	10.973	7.670
	18	3.014	5.409	8.519	10.314	8.537	7.428
	21	3.012	5.063	7.575	8.213	6.134	5.453
	24	2.591	3.855	4.770	4.616	3.898	3.174

Table 4. Values of coefficient CRM (according to Combinated ratio method)

Observation height (mm)	Rf power (W)					
		900	1000	1100	1200	1300	1400
	6	0.050	0.076	0.130	0.236	0.226	0.156
	9	0.074	0.117	0.214	0.391	0.497	0.440
	12	0.136	0.210	0.538	0.829	1.187	0.857
	15	0.267	0.485	0.930	1.470	1.198	1.402
	18	0.405	0.762	1.291	1.693	1.527	1.388
	21	0.426	0.788	1.285	1.547	1.084	0.943
	24	0.379	0.524	0.810	0.763	0.620	0.486

Table 5. Magnitude of IEC factors used to correct spectroscopic interferences

Interfering element	*Cu*	*Fe*	*Mn*
	K_i	K_i	K_i
Analytical line(λ, nm)			
Co II (228.616)	1.08×10^{-4}	1.38×10^{-3}	2.45×10^{-4}
Cr II (267.716)	6.78×10^{-5}	5.45×10^{-3}	2.05×10^{-3}
Cu I (324.752)	/	1.47×10^{-5}	8.03×10^{-5}
Fe II (259.940)	2.95×10^{-5}	/	1.07×10^{-2}
Mn II (257.610)	1.37×10^{-5}	1.36×10^{-2}	/
Ni II (231.604)	2.23×10^{-5}	6.95×10^{-3}	7.32×10^{-3}
Zn II (213.856)	4.89×10^{-2}	8.75×10^{-4}	1.67×10^{-2}
Se I (196.026)	6.50×10^{-2}	9.90×10^{-2}	6.68×10^{-5}

Table 6. Calibration parameters (concentration range of all elements 1 -100 µg/l)

Element	$a \pm SD \times 10^{-3}$	$b \pm SD \times 10^{-3}$	R^2	LOD(µg/l)	LOQ(µg/l)
Co	0.2254±2.98	0.4845±5.67	0.9992	0.061	0.305
Cr	0.2553±3.41	0.6406±7.81	0.9979	0.045	0.225
Cu	0.1142±1.72	0.1471±2.56	0.9996	0.077	0.385
Fe	0.2008±2.32	0.1796±2.89	0.9960	0.056	0.280
Mn	0.8564±9.21	0.1644±3.14	0.9987	0.007	0.035
Ni	0.1106±1.75	0.4729±6.25	0.9996	0.080	0.400
Zn	0.8085±9.31	0.8290±9.71	0.9997	0.150	0.750
Se	-0,1183±2.32	0.31066±4.53	0.9979	1.050	5.250

a-intercept, b-slope, R-coeficient of correlation, LOD-limit of detection, LOQ-limit of quantification

The magnitude of the IEC factors varied considerably from 1.37×10^{-5} – 1.36×10^{-2}. Values of IEC factors have shown: spectral interference from emission spectra of Mn (259.373 nm, 257.610 nm and 260.568 nm emission lines) to analytical line of Fe II (259.940 nm); spectral interference from emission spectra of Fe (259.373 nm emission line) to analytical line of Mn II (257.610 nm); spectral interference from emission spectra of Cu (213.597 nm, 224.700 nm emission lines) and from Mn (spectral range 250-260 nm) to analytical line of Zn II (213.856); spectral interference from emission spectra of Cu (spectral range 217-220 nm) and from Fe (spectral range 234 - 239 nm) to analytical line of Se I (196.026 nm).

Concentrations of affected elements from spectral interferences, Fe II (259.940 nm), Mn II (257.610 nm) and Se I (196.026 nm), were corrected using values of IEC, according to Eqn 3.

Validation of the optimized method for simultaneous determination of Fe, Zn, Cu, Se, Mn, Cr, Ni and Co was carried out by determination of linearity (in concentration range 1-100 µg/l), accuracy, precision, detection and quantification limit for each element. Detection limit was calcu-

lated using signal-to-background ratio-relative standard deviation approach (SBR-RSD). Calibration parameters with obtained limits of detection and limits of quantification of each investigated element are diven in Table 6.

Conclusion

ICP-OES method for simultaneous determination of trace elements Fe, Zn, Cu, Se, Mn, Cr, Ni and Co was developed and validated. The obtained results of proposed ICP-OES method for simultaneous determination of trace elements have shown improved detection limits (Fe 0.056, Zn 0.15, Cu 0.077, Se 1.05, Mn 0.007, Cr 0.045, Ni 0.08 and Co 0.061 µg/l) which were in agreement with literature (5,6,9,15). Optimization was made using two factorial designs which gave the same set of instrumental operating conditions as the best compromise. Both objective functions, Leary's objective function and CRM method, could easily be applied to optimization of the other instrument parameters (e.g. gas flow rates, solution pump rate to the nebuliser) using any group of analyte elements.

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Резиме

Оптимизација на метод за симултано мултиелементарно определување на микроелементи со примена на индуктивно спрегната плазма-оптичка емисиона спектрометрија: хемометриски пристап

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Клучни зборови: ICP-OES, микроелементи, мултиелементарно определување, објективни функции, корекција на интерференции

Оптимизацијата на методот за симултана мултиелементна анализа на Fe, Zn, Cu, Se, Mn, Cr, Ni и Co со примена на ICP-OES беше извршена со примена на две објективни математички функции. Однесувањето на избраните аналитички линии при промена на моќноста на радиофрекфентниот генератор и висината на зоната над магнетниот калем беше определено преку утврдување на зависноста на односот сигнал-позадинско зрачење (SBR) за сите испитувани елементи. Утврдувањето на присуство на спектрални интерференции и проценката на нивната значајност беше извршено со примена на експериментално - математичкиот модел за пресметување на фактор за интерелементна корекција на спектрални интерференции (IEC). Методот беше валидиран преку определување на линеарност (во концентрациско подрачје од 1-100 µг/л), точност, прецизност, лимит на детекција и лимит на квантификација за секој елемент одделно. Лимитот на детекција за секој елемент беше определен користејќи го пристапот на проценка на односот меѓу сигнал/релативна стандардна девијација на задинско зрачење (SBR-RSD). Резултатите покажуваат дека лимитите на детекција на одделните елементи се во согласност со долните граници на лимитите на детекција познати во литературата (Fe 0.056, Zn 0.15, Cu 0.077, Se 1.05, Mn 0.007, Cr 0.045, Ni 0.08 и Co 0.061 µg/l).