



A Multi-line analysis by ICP/OES of cobalt in complex solutions at different instrument setting

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Received: 25th March, 2012 ; Accepted: 25th April, 2012

ABSTRACT

The determination of trace amount of cobalt ion has been investigated in different operating conditions of analysis. The analysis was performed by varian (induced coupled plasma - optical emission spectroscopy) ICP-OES vista instrument using three wavelength lines which provide interferences of several cations and anions. Throughout this work, Relative Standard Deviation values are determined and examined as a function of Argon flow (carrier, intermediate and outer), uptake time (intergration time in nebulizer), interferences of anions (chloride, nitrate and nitrite) and cations (Na, Pb and Ba). It has been found that, nitric acid may perform a good linearity with a minimum RSD compared to aqueous or other acidic medium (hydrochloric and phosphoric acids). Different time of uptake, residence and transportation of sample are investigated.

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KEYWORDS

ICP-OES;
Cobalt interferences;
Multiline analysis;
Argon gaz flow.

INTRODUCTION

Analysis of trace elements constitutes a real challenge in the analytical chemistry especially when the elements are found in complex matrix. Several works have been published in the field of speciation, digestion and treatment of materials containing cobalt in its different form in different media. Behaviour of this element in complex matrix did not fully investigate and some complementary research requires more attention.

On-line preconcentration and determination of nickel by flow injection has been followed by ICP-OES achieving 3% of RSD value when modified uptake of sample was realized. The flow rate was

investigated^[1].

Some authors have studied dissolution and determination by ICP-OES of cobalt among a serie of 8 heavy metals in aqua regia medium compared to HF/HCl/HNO₃ procedure using microwave assisted digestion. Two wavelengths have been chosen for cobalt determination: 230.786 and 228.616 in respectively both ICP instruments (sequential and simultaneous) and only simultaneous one instrument. A success of procedure has been confirmed by repeatability and reproducibility of results^[2].

Some work have established a subsequent growth in inhibitory against bacteria, such as staphylococcus aureus ATCC4533 using cobalt

ion chelated with chitosan macromolecules. This complex is reported to be an interesting antimicrobial agent^[3].

Fishes through respiration, adsorption, and ingestion can accumulate metals. This accumulation of metal depend on the water environment in which they are caught, season, and their trophic levels, sexes and sizes. For example 0.17mg/kg and 1.49 mg/kg of trace cobalt element were found respectively in skin and Liver of Rutilus and carpio species from Porsuk Dam Lake/Turkey^[4].

Analysis of cobalt ion among several trace elements by ICP-OES has been done after digestion of macroalga near Baltic Sea^[5]. Concentration of cobalt was found to be equal to 11.8 μ g/L using simultaneous spectroscopic method of analysis.

EXPERIMENTAL PART

The ICP / AES used in this work VARIAN Vista Pro 710 (Australia) equipped with axially viewed plasma was used throughout in this work. It has an Echelle optical system and a solid-state detector. The ICP instrumental conditions for analysis are depicted in TABLE 1.

TABLE 1 : Initial operating conditions.

Parameter	Value
Plasma gaz flow (L/min)	15,00
Auxiliary gaz flow (L/min)	1,50
Carrier gaz flow (L/min)	1.00
Reading time (sec)	1,00
Apparatus stabilising time (sec)	15,00
Drawing up time (s)	30,00
Rincing time(s)	10,00
Pump circulation flow (rpm)	15,00

This apparatus operates with a radio-frequency generator of 27MHz allowing the adjustment of power between 750 and 1700 and a simultaneous charge coupled device (CCD) solid-state detector that allows measurements from 120 to 820. The instrument was purged with argon. An end-on gas interface was used in the axially viewed configuration to minimize interference caused by self-absorption. This instrument provides a simultaneous determination of elements whatever the matrix constitution. The analysis focuses on the determination of cobalt at three

emission lines in the order to check the accuracy of results and possibility of interference between elements of the matrix.

Before measurements, alignment of the torch is required to ensure that the torch is properly aligned. So, a manganese 5 mg/L solution was employed cause the similarity of spectrum with the most elements. Figure 1 present torch alignment obtained using manganese solution.

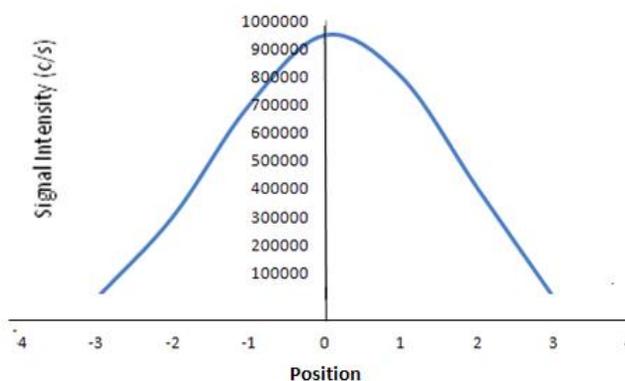


Figure 1 : Torch alignment of 5mg/L of mn solution.

Standard calibration wavelength is performed to ensure adjustment and orientation for different elements at the chosen wavelength. This step is required whenever the instrument is turn on using a standard solution that contains multiple elements (05 mg / L of Al, As, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, Se, Mo, Sr, Sn and 50 mg / L of K in 1% HNO₃).

Double distilled water is used for all preparation and dilution of solutions. All reagents used were of analytical grade quality and were purchased from commercial suppliers. A calculated amount of cobalt was weighed from mineral hydrated salts containing cobalt : cobalt nitrate hydrate Co (NO₃) 26H₂O (246.915 mg / L), cobalt chloride hydrate CoCl₂ 6H₂O (201.864 mg / L), natrium hexanitrocobaltat (III) Na₃Co (NO₂) 6 (342.710 mg / L). Then, dissolution by different studied acid was performed such as hydrochloric, nitric, phosphoric acid. All preparations are of 05, 10, 25 mg/L, and the standard solutions of known concentrations are 04, 15, and 30 mg/L.

Three fixed wavelength for cobalt measurements 236,379 nm, 238,636 nm, et 238,892 nm have been determined as furnished by the equipment with different interferences.

RESULTS AND DISCUSSIONS

In the Figure 2 are presented a multi line spectrum and interference of cobalt wave length at 238,892 nm. It is important to note that variation of wavelength is observed at the second decimal number. This result means that precision of measure is very high.

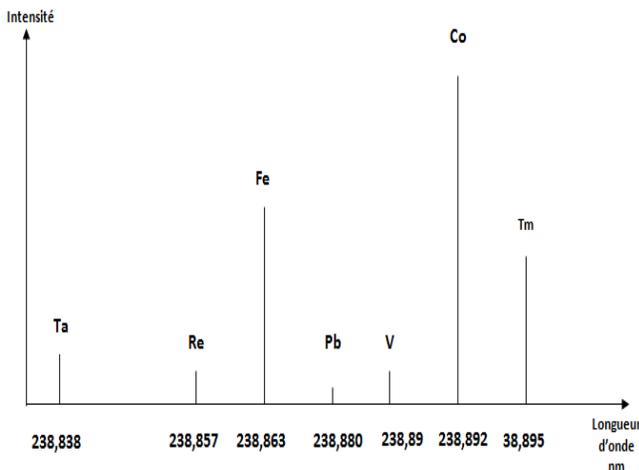


Figure 2 : Multiline spectrum and interference of cobalt at 238.892nm.

The main purpose of our work is to ensure that each variation of solution composition or parameters in the instrument may cause a change in the intensity of emission and also variation in the RSD values. The matrix effect is examined by using three different counter ion at each emission line.

TABLE 2 shows the effect of chloride, nitrate and sodium-nitrite ions on the concentration of standards initially fixed at 5, 10 and 25 mg/L and relative standard deviation (RSD) parameter in 1% nitric acid solution.

Anion interference is illustrated, the difference from standard values increase according $\text{NO}_3^- > \text{Cl}^- > \text{NO}_2^-$. This difference is not linked to the initial concentration of standard.

In the most cases low RSD values are obtained at 238.892nm except RSD = 0.2 for the wavelength 236.379nm. This may be explained by the presence of sodium ion which minimizes some spectral interferences.

It may be seen that the better values of relative standard deviation parameters are obtained at the wave length 238,892 except in the nitrite and sodium salt. Nitric salt shows the better result.

TABLE 2 : Counter ion effect on the cobalt analysis using 5, 10 and 25 mg/L standards in 1 % nitric acid.

	Co(NO ₃) ₂		CoCl ₂		Na ₂ Co(NO ₂) ₆	
	Concentration	% RSD	Concentration	% RSD	Concentration	% RSD
236.379nm	5,2850	0,1	5,8654	0,2	5,923	0,2
	10,533	0,4	10,662	0,4	10,810	2,9
	25,431	0,1	25,601	0,7	25,725	3,5
238.636nm	5,2267	0,5	5,5923	0,8	5,201	0,5
	10,952	0,3	10,769	0,9	10,991	1,5
	24,995	0,4	25,402	0,6	26,501	0,5
238.892nm	5,2426	0,2	5,9621	0,2	6,057	2,3
	10,225	0,1	11,052	0,3	11,115	0,7
	25,012	0,1	25,902	0,1	25,998	2,2

In the TABLE 3 are summarized the main results concerning nitric salt of cobalt ion at the three line emission in different solutions.

In all cases, the nitric acid medium give the low RSD values whatever is the emission line.

A higher RSD% is obtained when phosphoric media is employed. This anion is known to be strongly dependent on pH media and has important chelating properties^[6].

Effect of parameters linked to the apparatus and may be followed by the SBR indicator. The high value of SBR the high accurate value of measurements.

Such as:

$$\text{SBR} = (\text{signal intensity} - \text{noise background} / \text{noise background})$$

Effect of power generator

The power generator is also an important adjustable parameter in the analysis. Figure 3 shows the variation of the signal intensity of cobalt

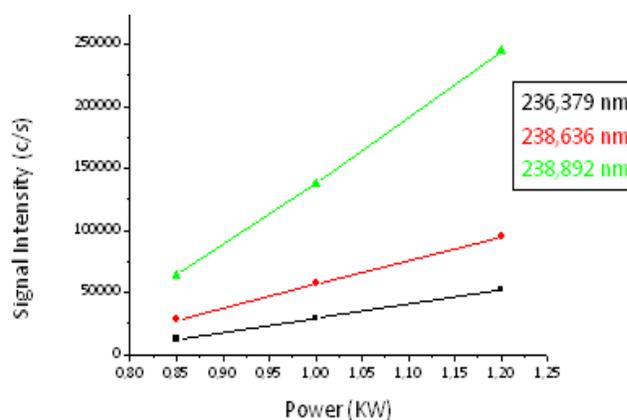


Figure 3 : Influence of the power generator on the analysis of cobalt.

TABLE 3 : Influence of aqueous and acidic medium on the RSD values at different wavelengths.

	Aqueous medium		Chlorhydrique medium		Nitrique medium		Phosphorique medium	
	Concentration	%RSD	Concentration	%RSD	Concentration	%RSD	Concentration	%RSD
236.379nm	4,8362	1,3	5,1590	1,5	5,2850	0,1	5,0371	1,7
	10,101	1,3	10,422	0,6	10,533	0,4	10,221	2,4
	23,297	0,9	25,092	0,5	25,431	0,1	25,112	8,7
238.636nm	4,7529	1,1	5,0168	0,9	5,2267	0,5	4,9424	1,2
	10,089	1,0	10,561	0,6	10,952	0,3	10,248	2,6
	23,431	0,9	24,523	1,5	24,995	0,4	24,799	2,5
238.892nm	4,6888	0,5	5,0120	0,4	5,2426	0,2	4,9913	0,6
	9,9296	0,5	9,9948	0,4	10,225	0,1	9,9923	0,4
	22,820	3,1	24,749	3,1	25,012	0,1	24,287	4,6

measurements according to three power values at the different wave length.

It appears that the signal intensity increases proportionally with the power of generator, however, our goal is to find values of SBR and RSD most satisfactory, in other words, a high SBR and an error report RSD very low. These conditions are provided to a power of 1 KW ($0,1 < \text{RSD} < 0,3$) and ($68 < \text{SBR} < 77$).

Effect of carrier gaz flow

Carrier Argon flow have been examined through nebulisation system. Gaz pressure has been examined from 50 to 250kPa at the three wavelengths. Signal intensity seems to be strongly dependent of carrier pressure. Results of signal intensity versus Ar pressure have been plotted in Figure 4.

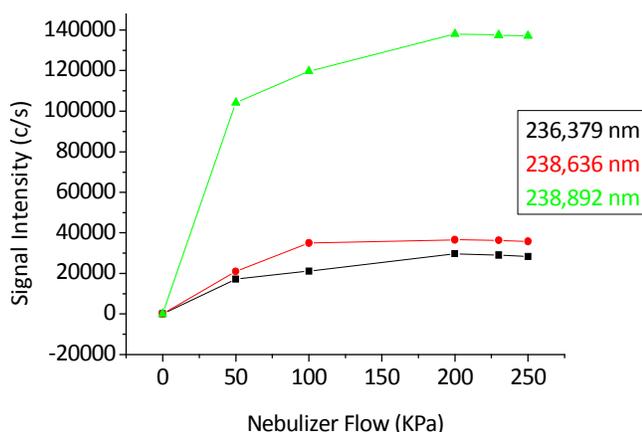


Figure 4 : Carrier gaz effect on the signal intensity of cobalt at the three wavelength.

Signal intensity increases when carrier Ar flow increase, a plateau is reached at about 100kPa. This may be explained by total transport

of solutions attained at about 200kPa. At this Ar pressure, results of analysis precision are very satisfactory ($0,1 < \text{RSD} < 0,3$) et ($66 < \text{SBR} < 67$). It also observed that this relationship between signal intensity and nebulizer flow is more pronounced at 238,892nm.

Auxiliary ar flow

Gaz circulation in the intermediate tube is used to facilitate aspiration and injection of sample in the torch. Variation in its flow may cause fluctuation in relative standard deviation and precision of instrument reading.

Figure 5 shows the variation of signal intensity as a function of auxiliary gaz flow. No significant change is observed when the wavelengths 236.372 and 238,636nm are used. In the case of 238.892nm, a gaz flow of $0.75 \text{ L}\cdot\text{min}^{-1}$ give a higher intensity signal.

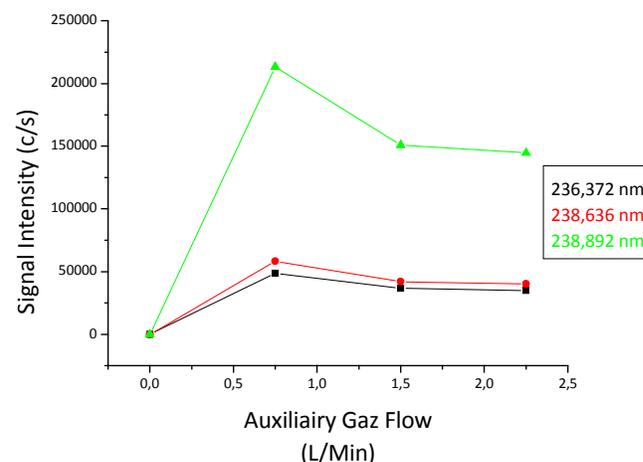


Figure 5 : Effect of auxiliary gaz pressure on the signal intensity of cobalt at 3 wavelengths.

However, stabilization is observed starting

TABLE 4 : Effect of reading time on the RSD and SBR values.

Concentration (mg/L)	1 s		5 s		10 s		30 s		50 s	
	%RSD	SBR								
5	3,0	45,491	0,3	66,615	2,1	43,691	1,9	39,551	3,8	24,661
10	3,2	45,071	0,2	66,219	1,7	43,101	2,4	38,501	4,8	23,901
25	3,0	46,171	0,1	63,718	1,8	42,221	2,5	35,212	3,9	23,221

from 1.5L. min⁻¹. At this Argon flow optimum parameters are obtained: 0,2<RSD<0,4 and 75<SBR<78.

Plasmagene Ar flow

Plasmagene gaz flow is also investigated from 5 to 23L.min⁻¹. Signal intensity decrease when gaz flow increase at 238.892nm. No effect is observed for other wavelengths. In these conditions optimum values are 0,4<RSD<0,7 and 76<SBR<78. Results are plotted in Figure 6.

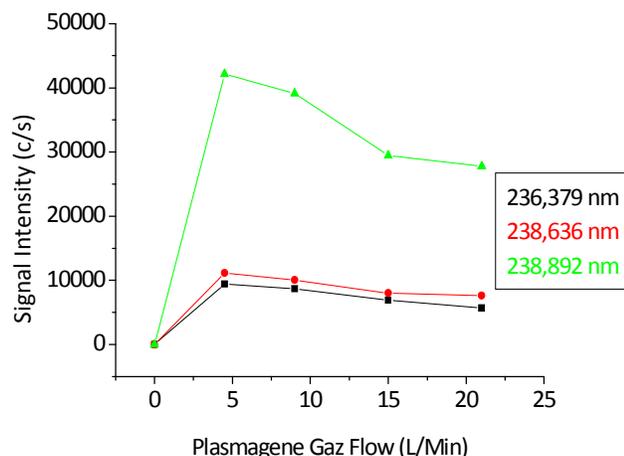


Figure 6 : Effect of Argon plasmagene flow on the signal intensity of cobalt at three wavelengths.

Effect of flow rate of peristaltic pump

The flow rate sample through the nebulizer and torch is strongly dependent on peristaltic pump ve-

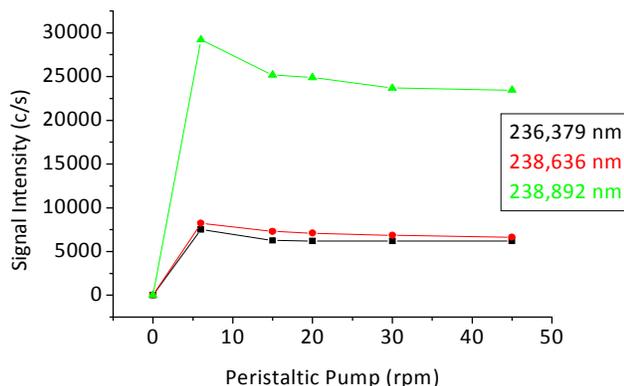


Figure 7 : Effect of circulation of solution on the signal intensity at different wavelengths.

locity. It is a very important parameter since it controls the analysis time. Figure 7 shows evolution.

Values are almost the same from 5 to 45 rpm in the case of both wavelength 236.379 nm and 238.636 nm the intensity decrease slightly when the rate of adsorption increase in the case of 238.892nm regarding RSD and SBR values from standardization a 15 rpm is selected for obtaining the best result 0,8<RSD<1 and 78,591<SBR<78,401.

Reading time

This parameter has been controlled in the order to examine the influence of the residence time of sample in the plasma. TABLE 4 give the values of SBR and RSD parameters for 3 certified concentrations when the reading time varying from 1 second to 50 seconds.

Regarding relative standard deviation values, a lower percentage is obtained at 5 sec of reading time. Considering result, a shorter or greater time is not recommended.

Effect of the aspiration time

This parameter should be distinguished from the rate of peristaltic pump. It concerns the amount of transported sample through spray chamber and constancy of solution homogeneity. TABLE 5 presents the aspiration time varied from 10 to 250 seconds for 3 standard concentrations.

In all domain of suction time, it could be considered that 30 seconds are sufficient to give a lower RSD percentage (0.4-0.5%) and higher SBR (70-71.5) equivalent to better signal reproducibility.

Spectral interferences. FACT (fast automated curve-fitting technique) correction

Analysis of cobalt ion has been realized in the presence of Pb, Ba individually and in the presence of mixture of the both ions and other ions as

TABLE 5 : Effect of aspiration time on RSD and SBR parameters.

Concentration (mg/L)	10 s		30 s		50 s		150 s		250 s	
	% RSD	SBR								
5	3,1	66,661	0,4	71,515	2,2	68,951	3,1	55,591	4,0	51,619
10	3,4	61,791	0,5	71,090	2,5	68,015	3,3	53,847	4,2	48,781
25	3,4	61,351	0,5	70,451	3,1	67,891	3,4	53,001	4,3	47,211

TABLE 6 : Interferences on cobalt analysis corrected by FACT method in the presence of Pb, Ba and others elements

	Co/Pb (241nm)		Co/Ba (221nm)		Co/ (Ba, Mo, Mn, Fe, Cr, Rh, Al)	
	Before	after	before	after	before	After
	Concentrations of cobalt before and after correction using FACT method.	0,6143	0,4954	0,6514	0,5101	0,7615
	1,3341	1,0101	1,4213	1,2018	1,3341	1,1941
	1,6756	1,4899	1,6671	1,600	1,7781	1,5716
	2,3413	2,0123	2,4451	2,0111	2,4919	2,0091
	2,5991	2,4999	2,451	2,5119	2,7870	2,4998
	3,351	3,0125	3,2231	3,016	3,3342	3,1001
	3,7615	3,5011	3,6651	3,4998	3,7835	3,5019
	4,2314	4,0532	4,1951	4,1022	4,3398	4,1001
	4,6415	4,5201	4,8891	4,4999	4,8712	4,5100
	5,3413	5,1443	5,8179	5,1124	5,4921	5,0191

mentioned in the TABLE 6.

Result of the application of FACT technique to reduce interferences at different wavelength show a decrease in the value red for each concentration.

Figures 8 and 9 show shifting the curve of the maximum intensity when lead and barium are employed as interfering element. Obtained results demonstrates a relationship between cobalt emission spectrum alone and in the pres-

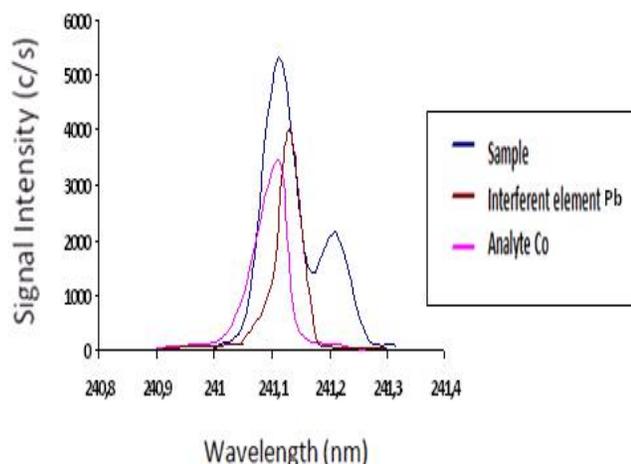


Figure 8 : Interferences cobalt-lead near 241nm.

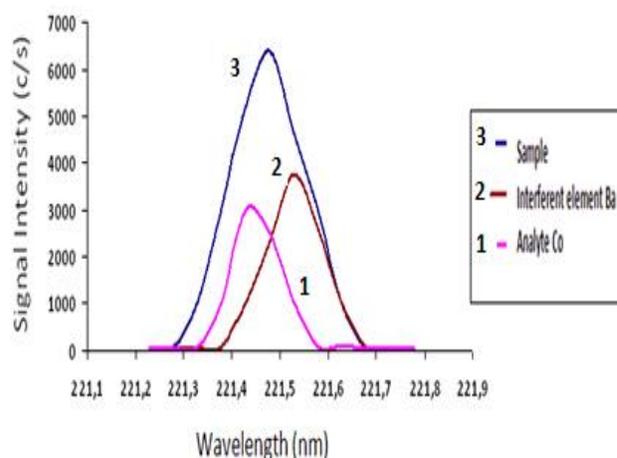


Figure 9 : Interferences Co/Ba near 221nm.

ence of common impurities.

CONCLUSION

In this work, the influence of some internal and external parameters affecting reproducibility of signal intensity of cobalt is examined. Throughout this study relative standard deviation for 3 standards solutions have been determined at 3 wavelengths in different conditions. Conditions are changed individually from those existing in the setup of the instruments. The influence of Argon flow as carrier, auxiliary and plasmagene permit us determination of optimum conditions at respectively 200kPa, 0.75 and 5 L.min⁻¹. Increasing in power generator deals to increasing signal intensity.

Residence solution in spray chamber and plasma including reading time and rate of peristaltic pump are investigated. Improvements in RSD and SBR values for reading time, time of aspiration are 5sec (0,1<%RSD<0,3 and 63<SBR<67), and 30sec (0,4<%RSD<0,5 and 70<SBR<71).

Interferences in the presence of lead and barium are investigated by shifting the curve of maximum intensity in both cases. FACT method correction was applied and satisfactory improvement are obtained.

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