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# Multielemental inductively coupled plasma optical emission spectrometry analysis of nickeliferous minerals



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## ABSTRACT

An inductively coupled plasma optical emission spectrometry method for the quantitative simultaneous determination of Al, Ca, Co, Cu, Cr, Fe, K, Mg, Mn, Na, Ni, P and Zn in Cuban laterite and serpentine minerals has been developed. Additionally, V and Ti can be quantitatively determined in laterite mineral; Li, Sr, and Zr can be detected in both mineral types and Pb can be detected just in laterite mineral. The microwave-assisted total acid digestion of samples was achieved with HCl+HNO<sub>3</sub>+HF and HNO<sub>3</sub>+HClO<sub>4</sub>+HF acid mixtures for laterite and serpentine samples, respectively. In non-robust plasma operating conditions, the matrix effect characteristics of the laterite sample were dictated by the principal component Fe; while the character of the Mg principal component matrix effect was some how modified by the concomitants Fe and Ni in serpentine sample. The selection of robust conditions decreased the matrix effect. Additionally, the simulation of the matrix samples by introducing the principal component Fe or Mg, correspondingly, in calibration dissolutions was needed to overcome completely the matrix effect over the analysis accuracy. Precision of analysis was very near or lower than 10% for most elements, except Sr (15%) in L-1; and K (15%) and Li (15%) in SNI sample. Accuracy of analysis was around or lower than 10% for most elements, except K (15%), Na (19%), P (19%) and V (19%) in L-1 sample; and Ca (14%) and P (20%) in SNI sample.

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## 1. Introduction

The export of iron and cooper minerals from the west zone of Cuba began since 1902 by some foreigners companies such as the Bethlehem Steel Corporation. The deepest geological study on the presence of nickel in those ferruginous mineral deposits was carried out by researchers of the Padners Corporation (1939–1940). As result, the mineral body was characterized and the processing and extraction of nickel like matter has been prevailed since 1941 [1,2].

At present, the Cuban nickel deposits are recognized as one of the biggest in the world with, approximately, 37% of the nickel planet reserves. On the other hand, nickel industry represents one of the most important sectors of Cuban economy [3]. Seventy five thousand

annual tons of nickel and cobalt mixture are currently produced from Cuban lateritic ores at three national hydrometallurgical plants. In connection with the prospecting and processing of this mineral, the determination of Ni, Co and Fe has been carried out at the geological chemical laboratories of the Republic of Cuba for more than forty years.

As known, inductively coupled plasma optical emission spectroscopy (ICP OES) is worldwide employed in geological studies [4,5]. Also, ICP OES has been routinely used for determination of Al, Co, Cr, Fe, Mg, Mn, Ni and Si in Cuban lateritic minerals since 1996, according to developed appropriate laboratory guidelines [6,7]. However, this mineral contains other elements, which should be determined as well because of several reasons. Particularly, the monitoring of Ca, Cu, K, Na, and Zn concentration is important in order to prevent their possible negative influence on the extraction metallurgical process of Ni plus Co concentrated product [8,9]. Additionally, the extension of the characterization of lateritic minerals to others elements, such as Cu, P and V, can contribute to a better evaluation of the mineral body [10].

According to the currently employed ICP OES methodology in Cuban laboratories [6,7], the sample test portion is digested by a

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fusion technique with lithium metaborate. Then, it is dissolved in hydrochloric or nitric acid dissolution. The addition of a significant amount of reagent to sample (sample:lithium metaborate=1:10) and the inherent laboriousness of the digestion procedure increases the risk of sample contamination and simultaneously reduces the net amount of sample to be analyzed. Consequently, an improvement of the limits of detections of determined analytes is not practically favoured.

In general, several alternative acid digestion procedures have been used instead of the fusion technique, prior to ICP OES elemental quantification of geological samples [11–16]. Among them, the microwave-assisted acid digestion has showed certain relevant characteristics such as, a shorter acid digestion time; better recovery of volatile elements and compounds, lower contamination levels, minimal volumes of reagents, more reproducible procedures and a better working environment. Generally, the proposed digestion methodologies involve two different acids combinations. In some reports [11–14], a mixture of nitric plus perchloric acids with a further addition of hydrofluoric acid, for the complete lixiviation of metals strongly linked to the crystalline lattice, has been employed. Also, a starting sample treatment with aqua regia (HCl:HNO<sub>3</sub>=3:1), followed by the addition of hydrofluoric acid has been used [14,15]. The advantages or disadvantages of the both acid mixtures employed are not totally clear. In any case, the study and selection of an appropriate alternative acid digestion method of Cuban nickeliferous mineral for further ICP OES multielemental determination, including analytes at low concentration, is an important and necessary analytical task to be done.

On the other hand, an international recognized guideline standard method for the ICP OES analysis of nickeliferous minerals was not found in the reviewed literature. Moreover, ICP OES techniques have been relatively little reported [16–18] for the analysis of these minerals. Thus, the increment of the background intensity of the element spectral lines, caused by the high concentration of Fe, was compensated by matching Fe concentration in sample and calibration dissolutions [16]. In other work [17], ICP OES matrix effect was observed and further avoided by using the internal standard method. Finally, a simultaneous testing method for determination of few elements Ni, Co, Fe, Mg in laterite type Ni deposit was reported [18].

In this context, the aim of the current work was to carry out an analytical study for the determination of Al, Ca, Co, Cu, Cr, Fe, K, Li, Mg, Mn, Na, Ni, P, Pb, Sr, Ti, V, Zn and Zr in Cuban nickeliferous minerals by ICP OES. A special attention to the digestion of sample and matrix effect is given.

## 2. Materials and methods

### 2.1. Nickeliferous mineral samples

This work was focused on two types of Cuban nickeliferous minerals represented by the two reference materials (RMs), “Nickeliferous Laterite (L-1)” [19,20] and “Nickeliferous Serpentine (SNi)”. Both RMs were manufactured at the Central Laboratory of Minerals José Isaac del Corral (LACEMI), as part of an international project with the participation of twenty eight laboratories from ten different countries. Eight diverse analytical techniques, Atomic Absorption Spectrometry, Inductively Coupled Plasma-Optical Emission Spectrometry, Colorimetry, Volumetry, Gravimetry, X-Ray Fluorescence, Potentiometry and DC Arc Atomic Emission Spectrography were employed in the certification process. The both types of selected minerals are the most important because they represent the 60% of the Cuban nickeliferous minerals with economical interest. On the other hand, the content of major

elements of these two samples is extreme within the concentration interval of elements of the minerals that they represent. Thus, L-1 reference material is principally composed by 82% of goethite-FeO(OH), 6% of clay minerals, 5% of chromite-FeCr<sub>2</sub>O<sub>4</sub> and 3% of serpentine-Mg<sub>3</sub>[Si<sub>2</sub>O<sub>5</sub>](OH)<sub>4</sub>; while SNi reference material is composed by 88% of serpentine-Mg<sub>3</sub>[Si<sub>2</sub>O<sub>5</sub>](OH)<sub>4</sub>, 7.5% of goethite-FeO(OH) and 2% of clay minerals. Concentrations of Ca, Cu, K, Na and P in SNi; and of Ca, K, Na, P and V in L-1 reference material, are given as approximated values, because of the high dispersion among concentrations reported by the participating laboratories. Nevertheless, they are still the best available reference concentrations that can be used for sake of statistical comparison with found concentrations.

### 2.2. Instrumentation

Microwave-assisted digestion of samples was carried out by using a Milestone ethos 1600 microwave lab station (Sorisolet, Italy), which was operated at 2450 MHz and output energy of 900 W. Maximum temperature and pressure were of 300 °C and 100 bar, respectively. The microwave system is equipped with ten closed reaction vessels (100 mL capacity) made from polytetrafluoroethylene. The temperature inside the vessels was monitored by using a 300 Automatic Temperature Control Probe.

Measurements of the emission lines intensity were made in an axial view mode ICP OES SpectroArcos spectrometer (SPECTRO Analytical Instruments, Kleve, Germany) at operating parameters listed in Table 1.

### 2.3. Reagents and calibration dissolutions

65% Suprapur-grade Nitric acid (Merck, Darmstadt, Germany), 25% Suprapur-grade Hydrochloric acid (Panreac, Barcelona, Spain), 60% Suprapur-grade Perchloric acid (Merck, Darmstadt, Germany) and 48% Suprapur-grade Hydrofluoric acid (Panreac, Barcelona, Spain) were employed for sample digestion and/or dissolutions preparation; while the used deionised water of 18 MΩ cm<sup>-1</sup> of resistivity was obtained with a Mili-Q system (Millipore, Bedford, MA, USA). Unielemental 10,000 mg L<sup>-1</sup> CertiPURs standard dissolutions of Al, Ca, Fe, K, Mg, Mn Na, Ni, P, Ti, Zr; and 1000 mg L<sup>-1</sup> of Co, Cu, Cr, Sr, Li, Zn, Pb, V (Merck, Darmstadt, Germany) were used for the preparation of calibration dissolutions and dissolutions used in the interference study.

For calibration purposes, two groups of multielemental dissolutions were prepared. The first group of five dissolutions contained six analytes, at the following concentration intervals: Al and Ni: 1–6 mg L<sup>-1</sup>; Cr: 1.4–4 mg L<sup>-1</sup>; Fe: 10–100 mg L<sup>-1</sup>; Mg: 4–40 mg L<sup>-1</sup>; Mn: 0.6–3 mg L<sup>-1</sup>. The second group included three calibration dissolution subgroups. The first one, did not contain

**Table 1**  
Operating conditions for Spectro ARCOS ICP optical emission spectrometer.

Parameter	Value
Nebulizer model	Modified Lichte
Spray chamber type	Glass, cyclonic
Injector ceramic tube internal diameter	2.5 mm
Read time	28 s
Radiofrequency incident power:	
• Highest MgII/Mg I	1400 W
• Lowest MgII/Mg I	900 W
Plasma argon flow rate	12 L min <sup>-1</sup>
Nebulizer argon flow rate:	
• Highest MgII/Mg I	0.8 L min <sup>-1</sup>
• Lowest MgII/Mg I	1.3 L min <sup>-1</sup>
Auxiliary argon flow rate	1 L min <sup>-1</sup>
Sample uptake rate	2 mL min <sup>-1</sup>

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