



# Additivity of optical emissions applied to neodymium and praseodymium quantification in metallic didymium and (Nd,Pr)-Fe-B alloy samples by low-resolution atomic emission spectrometry: An evaluation of the mathematical approach used to solve spectral interferences

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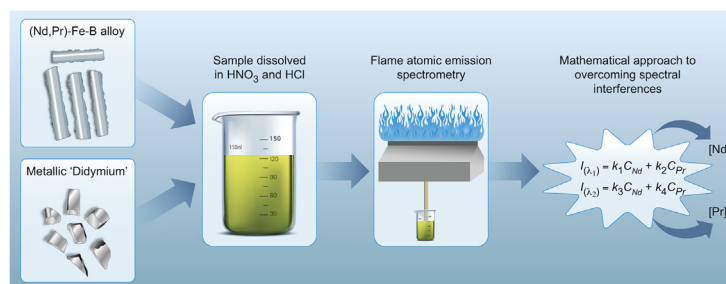
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## HIGHLIGHTS

- Spectral interferences of Nd and Pr in atomic spectrometry surpassed by math approach.
- Quantification of Nd and Pr in metal alloys intended to super-magnets production.
- Good recoveries for spiked in metallic didymium and (Nd,Pr)-Fe-B alloy samples.
- Agreement achieved between F-AES low-resolution and ICP-OES with greater resolution.
- A method for quality control of Nd and Pr employing accessible atomic spectrometer.

## GRAPHICAL ABSTRACT



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## ABSTRACT

In this work, the effectiveness of a mathematical approach to solve the spectral interferences involved in the optical emission of two chemical species (neodymium and praseodymium) when using monochromators with low-resolution in atomic spectrometry is evaluated. Although recent technological advances have promoted spectrometers equipped with high-resolution monochromators, which have a great instrumental capability in the separation of nearby lines and consequently avoid spectral interferences, many laboratories still have old spectrometers installed with insufficient resolution to

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overcome such interferences. In order to evaluate a mathematical approach based on Lambert-Beer's Law, the optical emissions of neodymium and praseodymium were monitored on a low-resolution (200 pm) flame atomic emission spectrometry (F-AES). These two elements were strategically chosen as an application model because they exhibit similar physicochemical properties, joint occurrence in nature and because they are increasingly used in the manufacture of super-magnets, a material increasingly required by the high technology industry. The effectiveness of the mathematical approach was evaluated in three different ways: (i) by recovery of the analytes in synthetic mixtures containing known quantities of the species; (ii) by spike and recovery trials on a representative blend of dissolved samples and (iii) by comparing the results obtained with another analytical method: Inductively coupled plasma optical emission spectrometry (ICP-OES) with a higher spectral resolution. The results indicate the effectiveness of this simple mathematical approach, allow the "survival" of instruments equipped with low-resolution monochromators and demonstrate the applicability of this approach to spectral correction. In addition, this work contributes an analytical method for the quantification of neodymium and praseodymium in metallic alloy samples involved in the production of super-magnets, aiding in the strict quality control of these materials.

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## 1. Introduction

When someone desires to determine the elemental composition of some samples, one of the first analytical techniques tried is atomic spectrometry. Undoubtedly, it is a reference technique in elemental analysis [1–5].

Flame atomic absorption spectrometry (F-AAS) [6,7], flame atomic emission spectrometry (F-AES) [6], inductively coupled plasma optical emission spectrometry (ICP-OES) [8,9], graphite furnace atomic absorption spectrometry (GF-AAS) [10–13], microwave plasma atomic emission spectrometry (MP-AES) [14–16] and laser-induced breakdown spectroscopy (LIBS) [17,18] are some optical methods commonly reported in the scientific literature. Their numerous applications stand out atomic spectrometry methods and make them an indispensable tool in making decisions about various analytical problems.

The success of these methods in the scientific community is primarily due to: (i) the convenience of measuring non-ionizing electromagnetic radiation [19]; (ii) the satisfactory precision of results [20–22], with the exception of LIBS measurements that often require sample preparation strategies to ensure the desired precision [23–26]; (iii) the flexibility of operating conditions, allowing the analytical performance characteristics to be adapted according to the samples [27]; (iv) the linear relationships that are easily found between the concentration of chemical species and the radiation intensities absorbed or emitted by free atoms and/or ions in the gaseous phase, which allows traditional approaches of calibration [28] and (v) the achievement of accurate results, reaching the real concentration of the analyte in the sample.

The mathematical basis for the quantitative evaluation of the atomic absorption spectrum is a linear function that connects analyte concentration with absorbance [29] (a dimensionless parameter), calculated by:  $A = \log\left(\frac{P_0}{P}\right) = k_\lambda N_0 l$ , where  $P_0$  is the radiant energy of light, power per unit area, focusing on one side of the sample,  $P$  is the radiant energy emerging from the other side,  $k_\lambda$  is an absorption coefficient specific for a wavelength,  $N_0$  is the number of atoms contained in the absorption volume and  $l$  corresponds to the length of the absorption layer. This function is described by Lambert-Beer's Law [30], which is widely known and used in chemical analyses.

In atomic emission, the emission intensity is often linearly proportional to the analyte concentration and this is useful for quantifying these emitting species. Although no "atomic emission law" is known, that is, no historical record about the origin of the mathematical function that connects the intensity emitted with the

concentration of the emitting species has been found in the scientific literature. The equation  $I = kC$  is widely used as a linear relationship between the emission intensity ( $I$ ) at a given wavelength and the analyte concentration ( $C$ ). The  $k$  constant is dependent on several experimental factors, such as: (i) the nature of the emitting chemical species; (ii) the medium temperature; (iii) the atomization mechanism; (iv) the wavelength measured; and (v) the matrix, which may cause interferences, that can either increase the  $k$  value due to other emissions or decrease the  $k$  value by suppressing the emission of the analyte.

Although electronic transitions in atoms occur at very specific wavelengths, interference may occur in absorption and in atomic emission. As much as these atomic or ionic transitions require a quantized energy, a "single" energy for every possible transition, the observed spectral interferences are almost always consequences of the instrumental limitation in separating the wavelengths in their tenths, hundredths, or even thousandths of nanometres, so that it is difficult to distinguish the spectral lines because in the "view" of the monochromator they overlap.

The accelerated technological development in this century has allowed several advances in the instrumentation used in atomic spectrometry. One of the most notable was the incorporation of high resolution optical monochromators into absorption and emission atomic spectrometers [31–34], which are able to separate down to 2 pm [35]. This is an extremely useful feature to avoid the spectral interference commonly observed in other monochromators. However, because they are high-value-added instruments, their acquisition requires significant financial investment and is often an impediment to most laboratories. This fact creates a "resistance" to obsolescence, and it is very common to find absorption and/or atomic emission spectrometers that are technologically lagged in full operation in chemistry labs. Conventionally, spectral interferences in chemical analysis are overcome in two ways: (i) by changing a spectrometer, looking for another with higher spectral resolution which has the advantage of a simultaneous correction of the background near the analytical line [36] or (ii) by using chemical strategies, such as extraction procedures that have the ability to eliminate interfering species [37].

In this context, aiming at the widest possible use of spectrometers considered technologically "lagged" but still present in several laboratories, this article evaluates a simple mathematical approach to solve the spectral interference problem caused by the emission of a chemical species in the measurement of another species. This approach was inspired by the additivity of the Lambert-Beer's Law

[38–40], a property commonly demonstrated in practical laboratory activities during university chemistry teaching [41,42], widely exploited for molecular absorption measurements in UV–Vis spectrophotometry when different colored species absorb at the same wavelength [43] and rarely exploited in atomic spectroscopy [44]. As an application, the neodymium (Nd) and praseodymium (Pr) elements were quantified by flame atomic emission spectrometry in an instrumental condition that where spectral interferences occur, and whose concentrations were determined by a system of linear equations.

The Nd and Pr elements were strategically chosen because they present: (i) similarity in their electronic structure, a fact that results in electronic transitions occurring at very near wavelengths [45]; (ii) joint occurrence in nature, commonly found as a mixture called “didymium” [46,47]; (iii) growing interest of the scientific community in the rare earth elements properties and in their quantification [48], and (iv) extensive use of these metals by industry [49], as they are applied in modern electronic components, for example: as dopant in ultrapure crystals for the production of lasers and as permanent magnets [50] present in electric motors, wind turbines, speakers, hard disks [51] and in other products closely related to the high technology industry.

Inspired by the same logic present in the additivity of absorbance [39], in this work, the additivity of the optical emission intensities of Nd and Pr was evaluated with the objective of correcting spectral interferences and providing reliable measurements using spectrometers equipped with low-resolution monochromators. For this, the Nd and Pr contents were determined in samples of metallic “didymium” (a solid solution containing Nd and Pr) and in metal alloys composed of neodymium, praseodymium, iron and boron - (Nd,Pr)-Fe-B, a base material for the production of super-magnets [52–55].

## 2. Experimental

### 2.1. Reagents and solutions

All solutions were prepared with analytical grade chemicals and ultra-pure type I deionized water, obtained from a Milli-Q system (Millipore™). Potassium nitrate (Merck™) solution 0.5% w/v was evaluated as ionization buffer. Analytical solutions containing the ions of interest were prepared by appropriate dilution of commercially available reference standards: Nd – 100,000 mg L<sup>-1</sup> (Specsol™) and Pr – 100,000 mg L<sup>-1</sup> (Specsol™), using 1% w/v nitric acid (Merck™) as the diluent. The solutions were prepared and stored in a 50 mL conical-shaped polypropylene tube (Falcon, Corning™).

### 2.2. Samples and preparation

The metallic didymium samples were produced in our laboratory by igneous electrolytic reduction, using molten salts from didymium oxides concentrates. The (Nd,Pr)-Fe-B alloys were prepared by the incorporation of iron and boron into the previously produced metallic didymium.

Each solid sample was fractionated in four distinct portions, the mass was varied from 0.25 to 0.68 g for each test portion. After weighing, 10 mL of 15% (w/v) nitric acid (Merck™) and 5 mL of 15% (w/v) hydrochloric acid (Merck™) were slowly added into a falcon tube containing the solid sample.

After about 20 min, another 10 mL of 15% nitric acid (w/v) was added to complete the dissolution reaction, obtaining a clear solution. The contents were diluted to 50 mL and subsequently diluted 15–45 times for the determinations by F-AES and up to 150 times for determinations by ICP-OES (comparative method). Blank

solutions were performed by adding all the reagents described above in the absence of samples. All solutions were produced in triplicate (n = 3).

### 2.3. F-AES analysis

A flame atomic absorption/emission spectrometer (AA240FS, Varian Inc™) equipped with a: (i) Nebulization chamber (Mark 7, Agilent™) adjusted in 7.0 mL min<sup>-1</sup> increments; (ii) Burner for mixing nitrous oxide (N<sub>2</sub>O)/acetylene (C<sub>2</sub>H<sub>2</sub>) (Mark 7, Agilent™) and (iii) Czerny-Turner monochromator with software-controlled wavelength selection (SpectraAA, Varian Inc™) with 0.2 nm of slit (resolution) was used for the determination of Nd and Pr in emission mode.

The wavelengths used for the measurement step were selected by monitoring the injection of mono-elemental standard solutions. Instrumental blank (zero) was performed with continuous injection of deionized water. The general operating conditions are shown in Table 1.

### 2.4. ICP-OES analysis

An inductively coupled plasma optical emission spectrometer (iCap 7400 Duo, Thermo Scientific®) equipped with an Echelle monochromator, simultaneous readout, 52.91 grooves/mm ruled grating, 383 mm effective focal length and 9.5° UV fused silica cross-dispersion prism and with spectral resolution of 0.007 nm was also used for analysis of the same samples. The main conditions used during the ICP-OES analysis are summarized in Table 2.

### 2.5. Mathematical approach

The atomic emissions observed in a mixture containing Nd and Pr at a given wavelength are the sum of the individual Nd and Pr emissions, under the same conditions. By observing at least 2 wavelengths ( $\lambda_1$  and  $\lambda_2$ ) it is possible to formulate a system of linear equations with two variables and two equations [39,42], as follows:

$$\begin{cases} I_{(\lambda_1)} = k_1 C_{Nd} + k_2 C_{Pr} \\ I_{(\lambda_2)} = k_3 C_{Nd} + k_4 C_{Pr} \end{cases} \quad [39]$$

where  $I_{(\lambda)}$  corresponds to the emission intensity measured at a specific wavelength ( $\lambda$ ) and ( $k_1$ ,  $k_2$ ,  $k_3$  and  $k_4$ ) correspond to the emission constants for Nd and Pr, obtained from the slopes of the individual calibration curves for these elements.  $C_{Nd}$  and  $C_{Pr}$  correspond to the concentrations of Nd and Pr in solution, respectively. The concentrations of Nd and Pr in a sample was found

**Table 1**  
Operational conditions for F-AES.

Parameter	Condition
Flame type	N <sub>2</sub> O/C <sub>2</sub> H <sub>2</sub>
Gases flow	11.00/7.15 L min <sup>-1</sup>
Observation height	10 mm
Top standard <sup>a</sup>	500 mg L <sup>-1</sup>
Slit	0.2 nm
Wavelengths	660.8 nm and 495.1 nm
Measure mode	Emission/Peak height
Read time	4 s

<sup>a</sup> Top Standard refers to a high concentration solution used for the equipment to identify spectral emissions and establish a maximum signal. Individual solutions of Nd and Pr containing 500 mg L<sup>-1</sup> were prepared for this purpose.

**Table 2**  
Operational conditions for ICP-OES.

Parameter	Condition
RF generator power	27.12 MHz solid state, operated at 1150 W
Plasma gas (Ar) flow rate	12 L min <sup>-1</sup>
Auxiliary gas flow rate	0.50 L min <sup>-1</sup>
Nebulizer type	Concentric (glass)
Spray chamber	Glass Cyclonic
Nebulizer gas flow	0.50 L min <sup>-1</sup>
Peristaltic pump rate	50 rpm
View mode	Axial
Exposure time	15 s
Replicates	3
Analytical lines	Nd II 401.225 nm and Pr II 414.311 nm

by solving the system, such that:

$$C_{Nd} = \frac{k_4 \cdot I_{(\lambda_1)} - k_2 \cdot I_{(\lambda_2)}}{k_1 k_4 - k_2 k_3}$$

and

$$C_{Pr} = \frac{k_1 \cdot I_{(\lambda_2)} - k_3 \cdot I_{(\lambda_1)}}{k_1 k_4 - k_2 k_3}$$

An extension of this reasoning can be applied to cases of interference with more than two elements, according to previous studies in the literature [44]. In these cases, the use of a matrix and solving the linear system by Cramer's rule is an interesting alternative.

The associated deviations ( $\sigma_{C_{Nd}}$  and  $\sigma_{C_{Pr}}$ ) were estimated by propagation of uncertainties, detailed in the supplementary material.

### 3. Results and Discussion

#### 3.1. Flame condition and measurement mode

The first attempt was to use F-AAS for quantitative measurements of Nd and Pr, since the atomic absorption is less subject to interference than atomic emission. However, F-AAS was relatively difficult because a flame produced by an air/acetylene mixture (the standard mixture used in F-AAS) does not have a high enough temperature to atomize both elements and is unable to provide free atoms in the gaseous phase to absorb radiation from the hollow cathode lamps. A flame produced from a mixture of nitrous oxide (N<sub>2</sub>O) with acetylene (C<sub>2</sub>H<sub>2</sub>) was evaluated. Although the flame results in higher temperatures than the standard air/acetylene mixture, in this flame condition the temperature increases sharply, providing a chemical environment capable not only of atomizing the Nd and Pr elements but also ionizing them (loss of electrons), a process that hinders quantification by atomic absorption. To avoid this ionization process, a solution of potassium nitrate (KNO<sub>3</sub>) was used as an ionization buffer at a concentration of up to 0.5% w/v. The addition of this salt aims to suppress the ionization of the analytes, so that potassium is ionized preferentially in relation to Nd and Pr, keeping both elements in a form suitable to absorb radiation.

However, this approach showed some limitations due to: (i) the need for high potassium concentration to prevent Nd and Pr ionization, which causes great instability in the flame and (ii) the high concentration required to obtain an appreciable signal (about of 10,000 mg L<sup>-1</sup>). In this experimental context, our investigations suggested that the determination of both species is preferable by atomic emission with the flame produced by acetylene and nitrous

oxide. The acetylene/nitrous oxide ratio and the burner height were optimized [56] for flame stability and the maximum intensity emitted by the analytes together. The optimum conditions (Table 1) were used for next studies.

#### 3.2. Wavelengths selection

Nd solutions at different concentrations (100–500 mg L<sup>-1</sup>) were injected into the flame and nine different wavelengths (commonly used for the quantification of Nd and Pr) were evaluated in relation to the optical emission, 660.8, 513.3, 495.1, 492.5, 491.4, 489.7, 473.7, 463.4 and 284.0 nm.

All wavelengths showed a linear trend between emission intensity and Nd concentration, except for 284.0 nm whose behaviour was random. The same behaviour was observed when inserting solutions with different concentrations of Pr, revealing a situation of spectral interference in which the monochromator used was unable to separate the wavelengths satisfactorily, thus not allowing the selection of a specific wavelength for one of the elements. The selected slit (resolution) was set as small as possible to obtain the best separation of wavelengths in this spectrometer.

Linear regression by the least squares method provided different slopes ( $k$ ) for the equation  $I = k \cdot C$  at different wavelengths, as shown in Table 3.

To choose the ideal wavelengths for the quantification of Nd and Pr, in which spectral interference was the smallest possible, the ratio between the calibration sensitivities obtained for the two elements at each monitored wavelength was evaluated. The closer this ratio is to 1 (100%), the longer the wavelength will be susceptible to significant spectral interference.

Based on the results in Table 3, the highest and the lowest sensitivity ratio obtained were found at 660.8 and 495.1 nm, respectively. These wavelengths were more selective for the quantification of Nd and Pr, allowing better discrimination between these elements. Consequently, 660.8 and 495.1 nm were selected for the next studies.

#### 3.3. Calibration, precision and limits

Fig. 1 shows the calibration curves, constructed using manual injection of solutions for each of the elements in isolation (mono-elemental calibration).

The individual calibration curve is extremely important for obtaining the characteristic calibration sensitivities for each element at the monitored wavelengths. All the mathematical parameters obtained after linear regression by the least squares method and forcing a null intercept are shown in Table 4. The good linear adjustment is confirmed by the high coefficient of determination ( $R^2$ ) achieved (ranging from 0.9961 to 0.9999) and by the random distribution on the residual plot.

Within the linear range explored, the calibration sensitivity and analytical sensitivity were estimated [57]. While the calibration sensitivity ( $k$ ) reflects the variation of the instrumental signal as a function of concentration (slope of the calibration curve), the analytical sensitivity ( $\gamma$ ) indicates the minimum difference in analyte concentration that can be distinguished with the method.

Table 4 also reports the main figures of merit associated with the proposed method. The injection precision [58] (also called instrumental precision [59]) was estimated using the standard deviation from repetitive and sequential injections of the same sample (a standard solution of intermediate concentration in the calibration curve = 250 mg L<sup>-1</sup>) and reached a maximum of 1.1% variation, indicating adequate stability to obtain precision results in the evaluated concentration range [60].

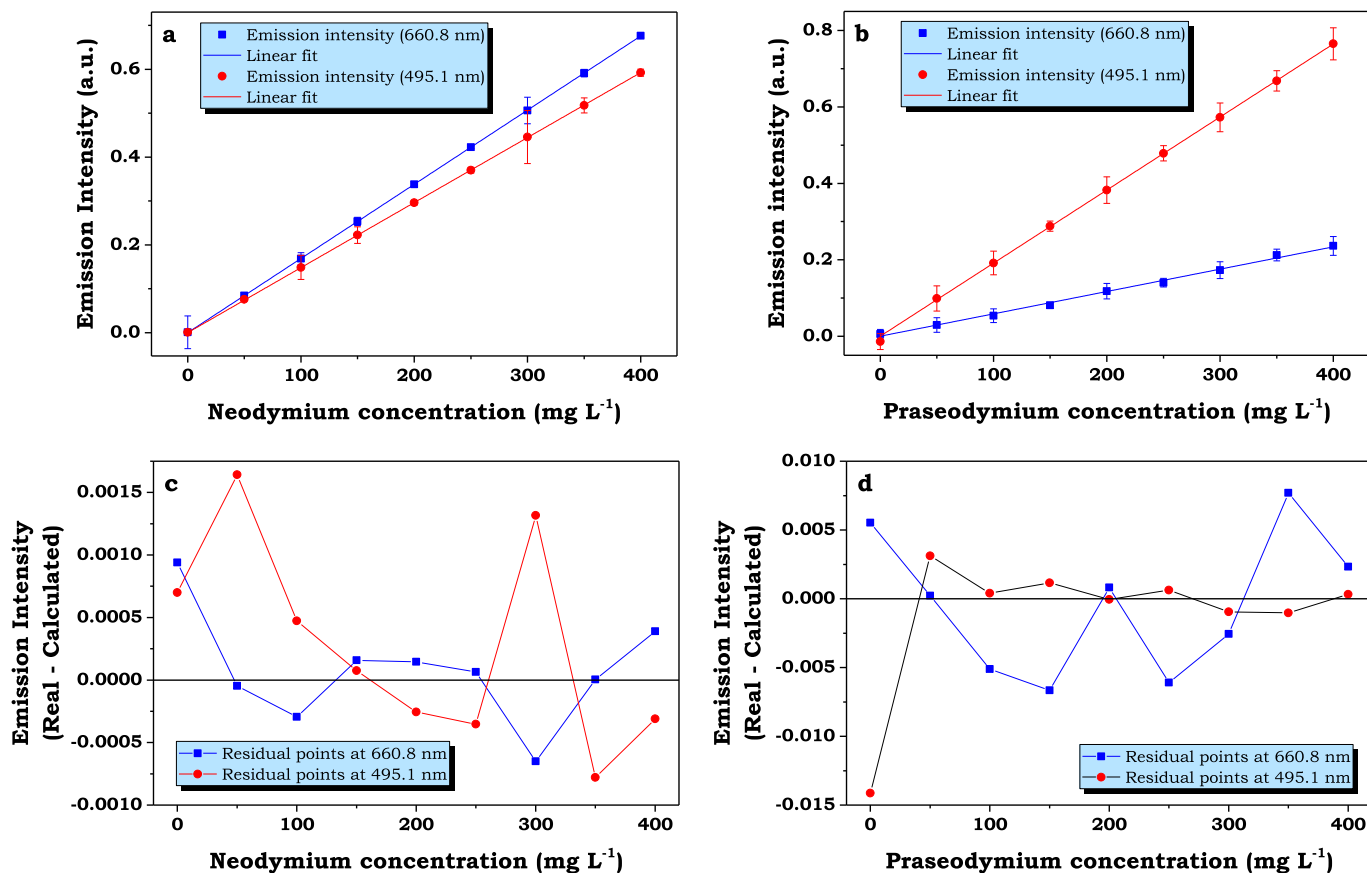
The lower limits of detection and quantitation (LLOD and LLOQ,

**Table 3**  
Sensitivities for Nd and Pr at different wavelengths by F-AES.

Wavelength (nm)	660.8	513.3	495.1	492.5	491.4	489.7	473.7	463.4
Calibration sensitivity <sup>a</sup> for Nd ( $\times 10^{-3}$ ) L mg <sup>-1</sup>	1.6	1.4	1.4	2.7	2.2	2.2	1.5	2.1
Calibration sensitivity <sup>a</sup> for Pr ( $\times 10^{-3}$ ) L mg <sup>-1</sup>	0.59	1.5	1.9	0.99	1.8	1.1	1.4	0.88
Sensitivity ratio <sup>b</sup> Nd/Pr (%)	281	94	76	271	123	193	106	236

<sup>a</sup> Slope of the calibration curve calculated by linear regression.

<sup>b</sup> Percentage ratio calculated by:  $100 \times (\text{Nd Sensitivity}) / (\text{Pr Sensitivity})$ .



**Fig. 1.** Calibration curves constructed for (a) neodymium and (b) praseodymium at both wavelengths (660.8 and 495.1 nm). Below the calibration curves are the residual graphs obtained after linear regression for (c) neodymium and (d) praseodymium (a.u. = arbitrary units).

**Table 4**  
Figures of merit of the mono-elemental calibration.

Wavelength (nm)	Metal	Linear regression equation	R <sup>2</sup>	LLOD (mg L <sup>-1</sup> )	LLOQ (mg L <sup>-1</sup> )	Injection precision (%)	Analytical sensitivity <sup>a</sup> (L mg <sup>-1</sup> )
660.8	Nd	$I = 1.66 \times 10^{-3} \times C$	0.9994	3.1	10.4	0.4	6.6
	Pr	$I = 5.90 \times 10^{-4} \times C$	0.9961	8.8	29.2	1.1	1.7
495.1	Nd	$I = 1.47 \times 10^{-3} \times C$	0.9999	4.7	15.6	0.8	2.6
	Pr	$I = 1.93 \times 10^{-4} \times C$	0.9997	3.6	11.9	0.5	3.8

<sup>a</sup> Estimated value by the slope of the calibration curve divided by the lowest standard deviation of the obtained analytical signal.

respectively) were estimated using the standard deviations obtained from 10 consecutive measurements of the blank solution and was calculated in two different ways: (i) considering the direct quantifications without mathematical correction - whose values are reported in Table 4, and (ii) considering the quantification in the joint presence of these elements, using the mathematical correction by the linear system of equations - whose values (LLOD; LLOQ) were respectively (2.5; 8.4) mg L<sup>-1</sup> for Nd and (1.6; 5.4) mg L<sup>-1</sup> for

Pr. These values show that the minimum concentrations that can be measured at an acceptable level of precision are adequate for the quantification of both elements in the super-magnets samples whose majority composition is Nd, Pr, Fe and B. Smallest limits are reached when the linear system is used, since the emission signals in two wavelengths are added, the tendency is to improve the detectability.



### 3.4. Accuracy and interference correction evaluation

The mathematical correction to overcome interferences was applied to the results obtained using a F-AES with 0.2 nm resolution, categorized in this article as “low-resolution”, due to its poor capability for separating wavelengths in relation to the most modern instruments. The effectiveness of this mathematical approach to correct spectral interference was evaluated in three different ways: (i) recovering the analytes in synthetic mixtures containing known quantities of the analytes (Nd and Pr); (ii) recovery in a representative mixture of the samples that have undergone a spike of the analytes at different levels of concentration, and (iii) comparison of the results obtained with another analytical method (ICP-OES), which has sufficient spectral resolution to overcome the interference.

When possible, the results obtained were compared to those in the absence of the mathematical correction to demonstrate the extension of the spectral interference effect. For this, the quantification of these elements was performed through the mono-elemental calibration curves without applying the system of equations and directly using the most selective wavelengths for Nd (660.8 nm) and Pr (495.1 nm). The recovery values obtained with the synthetic mixtures are shown in Table 5 and ranged from 95 to 104%, which are acceptable for the species concentration level, in accordance with the maximum acceptance criteria established by the Official Association of Analytical Chemists [60].

In the absence of the mathematical correction and in the joint presence of Nd and Pr, the recovery values ranged from 120 to 249%, revealing significant interferences between the two elements. Such behaviour could lead to inadequate results when both elements are present in the sample. These results reinforce the importance of using a mathematical approach to overcome spectral interferences. On the other hand, the recoveries of the isolated standards show that these wavelengths may be adequate when only one of them is present in the sample.

Although the results expressed in Table 5 already demonstrate

the effectiveness of the spectral correction, it should be emphasized that these synthetic mixtures represent an ideal condition in which only the combined Nd and Pr elements exist. In a real sample, other chemicals could intensify spectral interference (especially other rare earth elements or the high iron content in some samples). Thus, spike and recovery trials of the analytes were carried out in the matrix medium.

Table 5 also shows the results obtained after spike and recovery trials on a representative mixture of the dissolved samples (blend). The recoveries obtained (94–106%) indicate the feasibility of using this correction method to overcome spectral interferences in a matrix medium composed mainly of Nd, Pr, Fe and B. Table 5 also reports recovery values obtained in the absence of the mathematical correction. When the two species are together in solution, the recoveries ranged from 131 to 176%, inadequate values that indicate the inapplicability of the analytical method under these conditions.

For comparison purposes, ten different samples were analysed by this method with mathematical correction and the results obtained were compared with another optical method of higher resolution. In the “high-resolution” method used in this work, the monochromator was efficient in separating the wavelengths involved in the quantification of Nd and Pr. It should be noted that the wavelengths used for the ICP-OES measurement were different from those used by F-AES, since the atomization and temperature conditions of the plasma compared to the flame differ significantly, with different electronic transitions occurring in these media. Fig. 2 shows spectral fragments for Nd and Pr emissions recorded at their characteristic wavelengths, evidencing the absence of interferences from one species to the other.

The results obtained by both methods were compared using a paired Student's t-test with a confidence level of 95%, the results indicated that the methods provide results that are not significantly different ( $t_{\text{calculated Nd}} = 0.12$ ;  $t_{\text{calculated Pr}} = 1.27$  and  $t_{\text{critical}} = 2.26$ ). The results were also compared individually, as shown in Table 6. The results allow to state that the mathematical

**Table 5**  
Recovery of Nd and Pr from synthetic mixtures with and without mathematical correction.

Solutions	Reference value		Value without mathematical correction				Value with mathematical correction			
	Nd (mg L <sup>-1</sup> )	Pr (mg L <sup>-1</sup> )	Nd (mg L <sup>-1</sup> )	Pr (mg L <sup>-1</sup> )	Rec. Nd (%)	Rec. Pr (%)	Nd (mg L <sup>-1</sup> )	Pr (mg L <sup>-1</sup> )	Rec. Nd (%)	Rec. Pr (%)
Synthetic mixture 1	100	100	137 ± 2	182 ± 2	137	182	99 ± 2	97 ± 4	99	97
Synthetic mixture 2	100	200	170 ± 2	269 ± 2	170	135	96 ± 4	205 ± 6	96	102
Synthetic mixture 3	200	100	239 ± 2	249 ± 2	120	249	208 ± 4	95 ± 7	104	95
Only Nd	250	0	254 ± 2	199 ± 2	102	–	252 ± 2	<LLOD	101	–
Only Pr	0	250	83 ± 2	248 ± 2	–	99	<LLOD	254 ± 2	–	101
Blend of samples	–	–	173 ± 1	147 ± 3	–	–	166 ± 2	20 ± 4	–	–
Spiked in blend of dissolved samples <sup>a</sup>	10	0	183 ± 1	154 ± 2	99	105	176 ± 1	20 ± 3	101	96
	0	10	176 ± 1	157 ± 2	102	95	166 ± 1	30 ± 2	100	99
	10	10	187 ± 4	164 ± 1	133	170	176 ± 1	30 ± 1	100	94
	20	0	193 ± 2	166 ± 1	100	110	187 ± 1	19 ± 1	102	95
	0	20	181 ± 2	166 ± 1	104	95	167 ± 1	39 ± 1	100	94
	20	20	200 ± 1	182 ± 1	131	172	185 ± 1	40 ± 1	96	99
	40	0	213 ± 1	177 ± 1	99	120	206 ± 1	20 ± 1	100	97
	0	40	187 ± 1	187 ± 1	108	98	167 ± 1	59 ± 2	100	98
	40	40	228 ± 1	218 ± 1	136	176	206 ± 1	60 ± 1	100	100
	60	0	234 ± 1	192 ± 1	100	131	227 ± 1	20 ± 1	101	96
	0	60	194 ± 1	209 ± 2	112	104	165 ± 1	84 ± 3	99	106
	60	60	253 ± 2	253 ± 3	133	176	224 ± 1	83 ± 4	96	103
	80	0	253 ± 3	208 ± 1	100	141	246 ± 1	20 ± 2	100	97
	0	80	203 ± 1	231 ± 2	117	105	166 ± 7	105 ± 2	100	106
	80	80	282 ± 1	287 ± 1	136	175	247 ± 1	99 ± 1	101	98
	100	0	274 ± 1	223 ± 1	100	152	267 ± 1	20 ± 1	100	98
	0	100	209 ± 1	247 ± 3	120	100	166 ± 1	120 ± 4	100	100
	100	100	308 ± 1	322 ± 2	135	175	266 ± 1	119 ± 2	100	99

<sup>a</sup> Considering the dilution factors, the addition of 10 mg L<sup>-1</sup> of Nd or Pr in the solution corresponds to 1.5% (mass fraction) in the original sample.

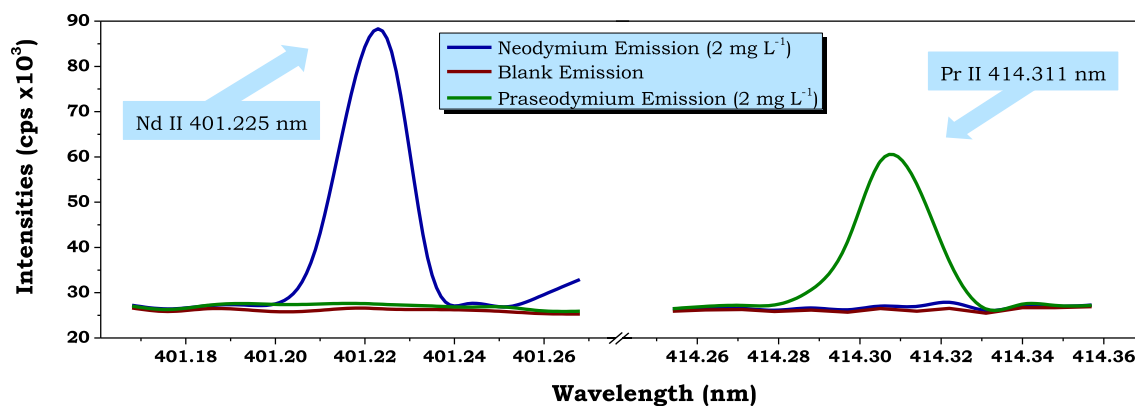


Fig. 2. Fragment spectra obtained by ICP-OES in the range of 401.17–414.36 nm with the range from 401.27 to 414.25 nm removed.

**Table 6**

Results of the analyses of (Nd,Pr)-Fe-B alloys (samples 1–4) and metallic didymium (samples 5–10) by F-AES method with mathematical correction and ICP-OES method. Values expressed as percentage mass fractions.

Sample	Neodymium results			Praseodymium results		
	F-AES method (%)	ICP-OES method (%)	Agreement (%)	F-AES method (%)	ICP-OES method (%)	Agreement (%)
1	27.7 ± 0.3	27.5 ± 0.2	101	4.2 ± 0.8	4.0 ± 0.1	104
2	27.1 ± 0.2	26.9 ± 1.4	101	5.4 ± 0.5	5.1 ± 0.1	106
3	31.7 ± 0.2	31.5 ± 1.9	101	1.1 ± 0.5	0.8 ± 0.1	129
4	17.5 ± 0.1	17.6 ± 2.5	99	14.5 ± 0.4	14.0 ± 0.3	103
5	79.2 ± 0.5	79.2 ± 1.7	100	18.9 ± 1.4	21.0 ± 0.4	90
6	79.6 ± 0.9	79.6 ± 1.4	100	21.8 ± 2.4	20.0 ± 0.5	109
7	81.8 ± 0.3	81.4 ± 1.1	101	20.5 ± 0.7	19.8 ± 0.8	103
8	80.3 ± 0.3	80.4 ± 0.6	100	21.4 ± 0.8	20.3 ± 0.4	105
9	83.3 ± 0.6	82.9 ± 1.5	100	22.0 ± 1.7	21.5 ± 0.7	103
10	82.5 ± 0.9	83.5 ± 1.6	99	22.4 ± 2.5	21.6 ± 0.5	104

approach applied in F-AES analysis with low-resolution monochromator is effective at overcoming the existing spectral interferences, since ICP-OES analysis obtained equal concentration values.

#### 4. Conclusions and outlooks

The mathematical approach with the purpose of correcting spectral interferences in the optical emissions of Nd and Pr proved to be effective at overcoming intrinsic adversities in the use of low-resolution monochromators in atomic spectrometry. The evaluation reported in this paper contributes to a “survival” of the various spectrometers found in several laboratories that still have low-resolution monochromators, allowing the use of these instruments for applications with spectral interference between Nd and Pr.

In addition to confirming the effectiveness of this approach, we also provide an analytical method for determining Nd and Pr in alloy metal samples destined for the production of super-magnets, which is a sample type of growing interest in the high technology industry. Since the rare earth content affects the magnetic performance of these materials, the analytical method developed is important to assist in quality control. Although this sample type does not require complex preparation, the whole challenge in quantifying the chemical elements present in this sample consists of overcoming the spectral interferences between Nd and Pr.

We hope that this analytical methodology will allow the secondary standardization of these alloys containing Nd and Pr for future calibration of these elements in other instrumental techniques, such as x-ray fluorescence spectroscopy (XRF), since the shortage of suitable calibrating materials often makes it impossible

to use for analytes determination in these alloys.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.aca.2019.07.049>.

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