

Quantification and characterization of Si in *Pinus Insignis Dougl* by TXRF

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Abstract A simple quantification of silicon is described, in woods such as *Pinus Insigne Dougl* obtained from the 8th region of Bío-Bío, 37°15" South-73°19" West, Chile. The samples were prepared through fractional calcination, and the ashes were directly analyzed by total reflection X-ray fluorescence (TXRF) technique. The analysis of 16 samples that were calcined is presented. The samples were weighed on plastic reflectors in a microbalance with sensitivity of 0.1 µg. Later, the samples were irradiated in a TXRF PICOFOX spectrometer, for 350 and 700 s. To each sample, cobalt was added as an internal standard. Concentrations of silicon over the 1 % in each sample and the self-absorption effect on the quantification were observed, in masses higher than 100 µg.

1 Introduction

The silicon (Si), which in woods is present as SiO₂ [1], is a material not deeply studied in this matrix, but it has a great importance due to the fact that it affects its properties and uses. The amount of Si, mainly owing to its crystalline structure, and the chemical components of the trees play an important role in determining the wear of the cutting tools [2, 3]. A specific study on the implications of the Si in the cutting tools concluded that the higher the concentration of silica (silicon oxide, SiO₂) in the woods, the greater the

wear rate of the cutting material [4, 5]. Silicon also affects the materials used as fodder in a negative way [6]. Therefore, its determination in quality control of the processes associated with agricultural and forest supplies is very important. In improvement programs in which the analysis of a large number of samples is necessary, the introduction of parameters such as chemical composition of wood leads to the expeditious development of characterization methods that are reliable, reproducible and inexpensive.

The increasing search for high-quality wood, with less variability of its properties and higher performance, placed great pressure on the studies for the sustainable forest development, which involves the qualitative improvement of the wood and its production. In this sense, there are genetic improvement projects, primarily directed to obtain the best-quality raw material for paper pulp industry and its derivatives, in different countries that promote forest plantations [7].

In this research, an atomic method for the simple characterization of silicon in woods is performed. The results could be applied to commercial plantations of *Pinus Insigne Dougl* (scientific name: *Pinus Radiata Don* [8]) which are the bases of the forest industry in Chile. This species was introduced around 1881, and they were initially used for stabilizing the dunes. *Pinus Radiata* was settled in different places with adverse weather conditions. In 1973, this tree occupied an area of only 158,000 hectares; however, with the Forestry Law Decree 701 of 1974, *P. Radiata* plantings dramatically increased. In 2009, there were 1.5 million hectares of *P. Radiata* plantings in Chile.

The *Pinus Insignis Dougl* belongs to the *Pinaceae* family [9]. Its wood is versatile and widely applied to an ample range of structural and decorative uses such as frames, linings, laminated wood beams, veneers and plywood. With

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adequate treatment, it can be used for many exposed structural and non-structural applications. It is a low-density and very soft wood, often presenting large annual growth rings. The duramen is yellow to light brown, and the laburnum is pale yellow to white, but the distinction is often blurry. The grain is generally straight, with a common appearance of knots. *Radiata pine* is very easy to work using standard tools, despite its knotty quality and resinous canals which can prematurely blunt the blades (anticipated steel wear-down). Its open grain structure easily accepts preservation and fast exploitation treatments [10]. Because of its importance, *Pinus Insigne* is a very interesting tree species to analyze, mainly due to the chemical composition, particularly chemical elements that have an impact on its extraction, such as silicon.

In the process of chemical characterization of woods, silica is insoluble in acid after the calcination [11]. This process presents difficulties in the analysis through techniques requiring sample dissolution. For this reason, a direct method of characterization is presented using total reflection X-ray fluorescence (TXRF). It must be noted that there is no previous register in the literature for quantification of Si in woods by TXRF, but this element was quantified by this technique in other types of materials such as ceramics [12] and in catalytic converters [13].

In 1971, Yoneda and Horiuchi in Japan introduced a technique of characterization for TXRF [14], and some years later, this idea was taken by Aiginger and Wobrauschek in Austria in 1975 [15]. TXRF spectroscopy is a variant of conventional energy-dispersive X-ray fluorescence (ED-XRF) spectroscopy. In the case of TXRF, the exciting beam hits the sample at a very small glancing angle so that the beam is totally reflected. If the sample is a thin layer on a flat sample-holder surface, the background originating from the scattering of the exciting beam will be extremely small compared to the conventional XRF. The second main aspect of TXRF is the excitation by the incident as well as the totally reflected beams. As a result and in comparison with XRF, TXRF background is decreased, while the intensity of atomic fluorescence signals is increased.

In the TXRF analysis of liquids, the specimen is prepared as a residue of dried drop (5–50 μl) on a pre-cleaned proper sample carrier. The absolute amount of this film-like deposit is usually below 1 μg , and the experiment is usually performed in air. The drying process must be performed in a clean environment, taking a few minutes to avoid contamination. Applying a hot plate or an infrared lamp can reduce the drying time. The residue formed normally has a size of 2–6 mm in diameter depending on two main factors: the volume and composition of the droplet and the type of reflector used. In some cases, the size can be reduced by suitable surface preconditioning. Uniform distribution and minimum height of the residue

are the two main prerequisites for an optimal TXRF analysis. This mature technique [17, 18] is used more often in scientific field; particularly in catalytic processes [16], the biochemistry or studies of cellular toxicity [19], physics of materials [20], archaeometry [21], among others. In this way, this technique of characterization and quantification is presented as a tool of getting quick information, for its application in industrial timber uses.

2 Theory

2.1 Total reflection X-ray fluorescence

If the prerequisites of uniform distribution and minimum height of the residue are fulfilled, the basic equation for TXRF [22] can be expressed as:

$$I_i = K_i I_0 N_0 \sigma_i \omega_i m_i / A_i \quad (1)$$

where I_i is the intensity of the signal produced by any element i . This is described based on the following parameters: K_i , a constant that depends on the geometric factors and the efficiency in the detection of the energy of the considered line; I_0 , the intensity of the excitement source; N_0 , the Avogadro's number; m_i , the superficial density of the i element with the atomic number Z_i and the atomic mass A_i ; σ_i , the excitation of the transversal section (scattering); and ω_i , the fluorescence performance.

The sample is not homogeneously deposited in the reflector, so m_i shows variations in its distributions. The measurements of the same sample in different sample holders show significant variations in the total counts acquired in different spectra. To avoid this uncertainty, an internal pattern is added to the solution. It must be an element that originally is not present in the solution and whose concentration is well defined. In the processing of data, the concentrations of the original elements are referred to the concentration of the included standard. If a small known quantity of the STD element is added as an internal standard to the original sample, the relationship between the relative intensity of the element STD with respect to each one of the elements i in the sample can be expressed as:

$$\frac{I_{\text{STD}}}{I_i} = \frac{K_{\text{STD}} I_0 N_0 \sigma_{\text{STD}} \omega_{\text{STD}} A_{\text{STD}}}{K_i I_0 N_0 \sigma_i \omega_i A_i} \cdot \frac{m_{\text{STD}}}{m_i} \quad (2)$$

Since the relation of m_{STD}/m_i is the same as the relation between the concentrations of these elements in the solution (C_{STD}/C_i), the previous equation can be written as [23]:

$$\frac{I_{\text{STD}}}{I_i} = S_{\text{STD}/i} \cdot \frac{m_{\text{STD}}}{m_i} = S_{\text{STD}/i} \cdot \frac{C_{\text{STD}}}{C_i} \quad (3)$$

where $S_{\text{STD}/i}$ is the relative sensitivity of the element i related to the internal pattern, STD. This relationship that is

obtained from the sensitivity of detection of an element i contained in the main equation as:

$$S_i = K_i I_0 N_0 \sigma_i \omega_i / A_i \quad (4)$$

This factor represents the quantity of counts per second, for unit of sample masses (for the element i). This sensitivity is different for each element and only depends on the fundamental parameters (σ_i and ω_i) and the conditions of measurement (K_i) that generally can be supposed as constant. Generally, this curve is obtained measuring certificated multi-elemental samples of equal concentrations and, in recent works, measuring the answer when analyzing the relative intensities of known stoichiometry compounds [24].

In summary, the conversion of the intensities measured into the concentrations is one of the most important steps in the XRF analysis. The addition of an internal pattern, with known concentration, leads to a procedure of simple quantification, in the following way:

- To choose or add multiple elements, an element as an internal pattern, that will be the reference for the calibration of the spectrometer.
- To establish the curve of concentration vs intensity as the curve of regression with reference to the internal pattern to determine the sensibility S_{STD}/S_i , from the multi-element standard.
- To add the internal pattern of known concentration of C_{STD} to the unknown sample.
- To measure the intensity of the element I_i and the intensity of the internal pattern I_{STD} .
- To determine the concentration of unknown element C_i using the relation that is deduced from the Eq. 2

$$C_i = \frac{I_i}{I_{STD}} \cdot \frac{C_{STD}}{S_{STD/i}} \quad (5)$$

3 Methodology

Samples were taken from pieces of *Pinus Insigne Globulus*, in the 8th Region of Bío-Bío, Chile, in the forest sector of Arauco (37°15" South-73°19" West). The trees were planted approximately in 2003. The pieces have a number of rings according to their growth [25]. The pieces

considered had well-differentiated rings among them, which do not correspond to particular series of the tree.

From the extracted piece, 507.6 ± 0.1 mg of sawdust using a steel coal rasp was obtained. This tool contains significant amounts of chromium, wolfram, molybdenum and vanadium; but silicon is not included in its composition.

The mass was dried on a heater at 60 °C for 1 h to eliminate the dampness presents on it; later, it was exposed to a gradient of temperature (fractional calcination), which consisted on four phases:

1. Phase: The dust wood was put on to 120 °C for 30 min.
2. Phase: The temperature was increased to 300 °C for 30 min.
3. Phase: The temperature was increased to 550 °C for 30 min.
4. Phase: The temperature was increased to 750 °C for 60 min.

The ashes obtained were 3.7 ± 0.1 mg in weight; the loss of mass due to calcination was in the order of 99.27 %. Once the ash is obtained from the oven, 16 samples of ashes were weighed in the microbalance (Perkin-Elmer AD2), with sensitivity of 1 µg (Table 1). These samples were put into the polyethylene sample holder or reflector (plastic CH₂n). Quartz reflectors cannot be used in this kind of experiments, since they have silicon in its composition (SiO₂). An internal standard of 3.03 ± 0.01 µg of cobalt (Co) in solution was added to the weighed samples onto the reflector and dried under an infrared lamp. The dried samples with internal standard were irradiated for 350 and 700 s of live counting time in the TXRF spectrometer.

It was necessary to make sure that small amounts of ash samples were measured due to TXRF requirement of thin films. But, it is important to measure the sample in different times, in order to evaluate the limit of detection for Si quantification in the studied system and the dependence of the results with respect to the counting time and the precision.

The TXRF analytical system used in this study is an S2 PICOFOX Bruker spectrometer, which is located within a

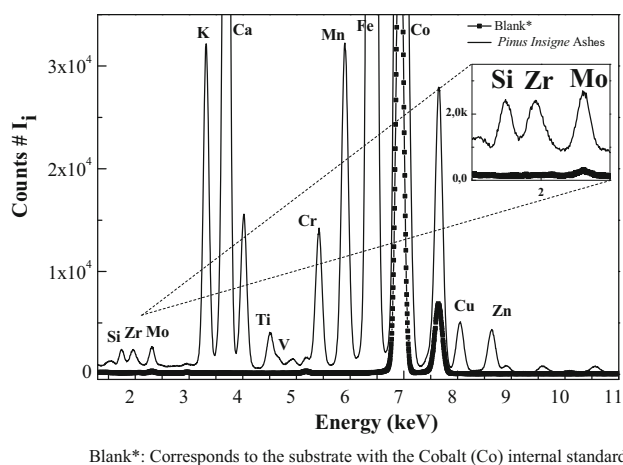
Table 1 Masses of each sample, measured at different times in TXRF. To each sample, 3 µg of Co as an internal standard was added

Time TXRF (s)	Sample 1 (µg)	Sample 2 (µg)	Sample 3 (µg)	Sample 4 (µg)	Sample 5 (µg)	Sample 6 (µg)	Sample 7 (µg)	Sample 8 (µg)
350 (s)	25(1)	26 (1)	38 (1)	44 (1)	49 (1)	76 (1)	112 (1)	170 (1)
Time TXRF (s)	Sample 9 (µg)	Sample 10 (µg)	Sample 11 (µg)	Sample 12(µg)	Sample 13 (µg)	Sample 14 (µg)	Sample 15 (µg)	Sample 16 (µg)
750 (s)	48 (1)	69 (1)	78 (1)	83 (1)	101 (1)	107 (1)	120 (1)	163 (1)

suitably designed X-ray biological shield. The system includes (a) an air-cooled X-ray metal–ceramic tube, with a molybdenum target, working at 50 W of maximum power, with 50 kV and 1 mA ; (b) a multi-layer monochromator; (c) a Peltier-cooled high-resolution XFlash[®] Silicon Drift Detector, with 30 mm² active area, and energy resolution <140 eV at 100 kcps (Mn K α line, 135.9 keV).

The interpretation of X-ray spectra and the composition determination was performed by the X-ray analysis software program SPECTRA 5.3, released by Bruker and included with the S2 PICOFOX 6. Elements are identified in an interactive procedure contrasting operator experience with X-ray library suggestions. Element abundances in each specimen were derived from X-ray signal intensities by a TXRF quantification sequence

The masses of the samples were measured with a microbalance; the obtained results are shown in Table 1, according to the measurement time. The first eight samples correspond to 350 s of live counting time, and the eight remaining samples were measured for 750 s.



Blank*: Corresponds to the substrate with the Cobalt (Co) internal standard

Fig. 1 Presence of a characteristic peak in the Si K α line of emission, from a sample of *Pinus Insigne* analyzed through TXRF

4 Analysis and results

From the analysis of each sample by TXRF, a spectrum was obtained (as shown in Fig. 1), where the silicon characteristic peak can be clearly seen around the energy of 1.74 keV, showing an adequate number of counts. The results are shown in Tables 2 and 3. The net Si counts increased as the sample mass increased in both counting times. In the same way, the $I_{\text{Si}}/I_{\text{Co}}$ ratio normalized to the internal standard counts. This behavior is maintained even at a sample mass of about 100 μm . After this point, the ratio decreases and the self-absorption becomes important. A part of the Si photons are being absorbed in the matrix and in consequence are not detected. The concentration values thus obtained decrease. The critical sample mass for the appropriate quantification should be less than 100 μm . This behavior is also observed for the other parameters in the tables, as detection limit (g/kg) and concentration (g/kg). The relative standard deviation as a measurement of the analysis precision is relatively low (<3 %) for both counting times tested. It is observed that duplication of the counting time implies an enhancement of the precision, from about 2.5 % RSD for 350 s. to 1.3 % RSD for 700 s. A significant improvement in the detection limit (calculated as the concentration corresponding to three times of the background square root) was observed when a counting time of 700 s is used.

The effect of self-absorption for masses higher than 100 μg is shown in Fig. 2, where the maximum ratio of the normalized intensity of silicon is reached at this mass value. Higher masses will induce a decrease in counts and $I_{\text{Si}}/I_{\text{Co}}$ ratio, as the mass and the thickness of the sample increase.

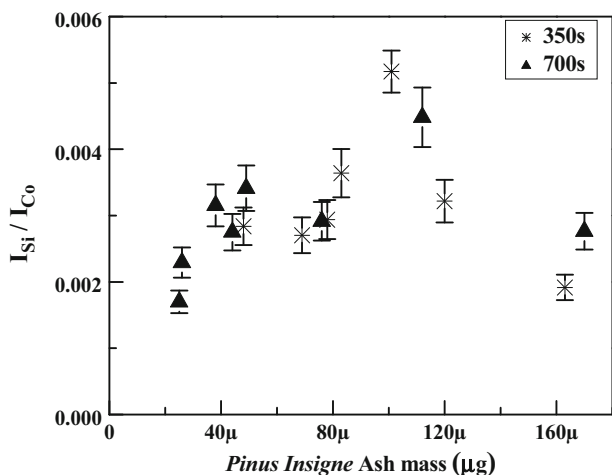
For acquisition data time of 350 s, an average of $I_i = 7,713$ counts in the range of masses up to 100 μg was allowed, which represented the average silicon concentration of 15 ± 3 g/kg. For the time of acquisition of 700 s, an average of $I_i = 21,790$ counts was allowed, which represents more than double the acquired value, and the

Table 2 Determination of silicon in wood ashes by TXRF for a counting time of 700 s and an internal standard (Co) mass of 3 μg

Sample mass (μg)	Net counts Si	Net counts Co	$I_{\text{Si}}/I_{\text{Co}}$	Concentration g/kg	Relative standard deviation (%)	Detection limit (g/kg)
48	20,300	7,150,935	0.0028	15.9	0.9	0.083
69	22,847	8,450,696	0.0027	11.1	1.2	0.072
78	21,067	7,166,126	0.0029	10.8	1.3	0.064
83	25,174	6,913,503	0.0036	12.7	1.1	0.060
101	23,975	4,635,659	0.0052	15.1	1.1	0.039
107	17,258	4,834,969	0.0042	10.5	1.5	0.037
120	20,417	6,345,686	0.0032	7.9	1.3	0.033
163	27,273	14,229,316	0.0019	3.6	1.2	0.037

Table 3 Determination of silicon in wood ashes by TXRF for a counting time of 350 s and an internal standard (Co) mass of 3 μg

Sample mass (μg)	Net counts Si	Net Counts Co	$I_{\text{Si}}/I_{\text{Co}}$	Concentration g/kg	Relative standard deviation (%)	Detection limit (g/kg)
25	6,587	3,874,744	0.0017	15.9	2.8	0.24
38	8,019	3,107,798	0.0026	17.5	2.5	0.15
44	7,065	2,567,104	0.0028	16.6	2.4	0.14
49	9,119	2,671,435	0.0034	18.8	2.2	0.12
76	8,362	2,868,344	0.0029	10.9	2.5	0.05
112	6,990	1,559,460	0.0045	11.9	2.8	0.08
170	4,672	1,689,958	0.0028	4.9	5.0	0.112

**Fig. 2** Effect of the sample mass on the $I_{\text{Si}}/I_{\text{Co}}$ ratio for counting times of 350 and 700 s. To each sample, an internal standard of Co with mass of 3 μg was added

concentration value found was 13 ± 3 g/kg of Si. Both values are close, showing in this way a good agreement with the results for both times of data acquisition, verified with the Student's t test at the confidence level of 95 %.

5 Conclusions

The TXRF is a simple and reliable technique for the quantification of silicon in woods. A direct method was developed for the analysis of wood ashes, avoiding the complex step of silicon mineralization. The proposed method does not require the manipulation of chemical products, and eliminates the uncertainty associated with the problem of Si recovery in woods after the acid digestion of ashes. The method requires very small amounts of sample and has an appropriate detection limit for the determination of the element in the wood matrix, which result in concentrations in the range of the micrograms for the studied element. The counting time of 700 s offers optimal analytical results in terms of precision as relative standard

deviation and detection limit. The superior limit of mass to be analyzed should be less than 100 μg of sample ashes. Above that limit, the data will not be reliable due to the self-absorption.

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