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Quantification of silicon concentration in sugarcane ash using the neutron activation technique with an isotopic source

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Abstract

In the realm of agronomic research, the neutron activation technique has gained traction, particularly in regions such as Paraguay, for its capability to deploy an isotopic source for the quantification and identification of agriculturally pertinent minerals. Within the ambit of sugarcane cultivation, both silicon (Si) and silica (SiO2) emerge as paramount, owing to their efficacy in fortifying the sugarcane plant's resistance to phytopathogens and pests, as well as their role in mitigating lodging phenomena. Notably, an uptick in silica accumulation has been correlated with amplified biomass and sucrose production metrics. This underscores the imperative for a meticulous quantification of Si and SiO2 within sugarcane derivatives, catering to both agronomic and industrial directives. Addressing the extant lacuna in regional datasets, this investigation endeavored to elucidate the inherent concentrations of Si and SiO2 within distinct anatomical segments of sugarcane, viz., leaves, entire stems, bark, and bagasse. A total of eight sugarcane cohorts, each encompassing 10 specimens, were subjected to the experimental paradigm. Adhering to a fully randomized design, each cohort was trialed in triplicate. Post desiccation at 105°C, the resultant specimens underwent calcination in a muffle furnace at an approximation of 500°C for a sextet of hours. The experimental variables under scrutiny encompassed mass (in grams), Si concentration (in percentage), and SiO2 content. Subsequent quantifications of Si and SiO2 within the ash specimens were operationalized using a nuclear analytical modality coupled with an isotopic neutron source. Post-acquisition, the data were subjected to a unidirectional analysis of variance, with an ensuing post-hoc DMS comparative analysis. Empirical findings highlighted that ash derived from integral sugarcane stems registered a preeminent mass juxtaposed against other segments. Intriguingly, leaf-derived ash manifested the zenith of Si and SiO2 concentrations, quantified at 24% for Si and 51.5% for SiO2. In summation, the neutron activation technique, undergirded by an isotopic source, has manifested its robustness in pinpointing Si concentrations within sugarcane ash, thereby accentuating the potential of leaf ash as a quintessential fount for silica extraction. Such insights bear salient implications for nations, such as Paraguay, where the evolution of agronomic modalities remains an ongoing endeavor.

Keywords: *Saccharum officinarum,* Silica, Neutron activation technique, Silicon and silica content, Silica extraction, Nuclear analytical technique.

Introduction

Brazil is the largest producer of sugarcane, accounting for 39% of the global production, followed by India, which is expected to experience a growth of 4.4 million tons by 2029 (Quiroz et al., 2021). In the 2020/2021 harvest, Paraguay cultivated sugarcane in an area of 105,000 hectares, yielding 68,772 kilograms per hectare and producing a total of 7,221,100 tons (MAG, 2021). The export of processed sugar witnessed a significant increase of 346% between 2000 and 2018, rising from 22.6 thousand tons to 72.7 thousand tons (Enciso, 2020).

The rapid industrial advancement at the national level leads to the generation of substantial amounts of waste, posing potential environmental challenges. Bagasse, an abundant by-product of the sugar-alcohol industry, is commonly employed as a fertilizer or inappropriately disposed of (Xu et al., 2018). Additionally, other waste by-products such as dry leaves and bark are also present. It is estimated that the incineration of each ton of bagasse yields approximately 25 to 40 kilograms of ash (Sales & Lima, 2010).

Amorphous silica, also known as residual ash, derived from various agricultural by-products, particularly grasses, has demonstrated successful utilization in agriculture, resulting in benefits for both plants and the environment (Monzón et al., 2021). The agricultural effectiveness of amorphous silica has sparked significant interest among researchers. Silicon, obtained from the ash of amorphous silica, is considered both an essential and non-essential element for plants. While not essential for their survival, there is evidence of its beneficial impact on plant adaptation to various biotic and abiotic conditions (Luyckx et al., 2017; Hussain et al., 2021).

In the Poaceae family, silicon exists in the form of silica, a chemical compound found in high concentrations. This compound accumulates in the tissues of leaves and inflorescences, with its concentration significantly increasing during plant development until reaching maturity (Herrera-Giraldo, 2009). The response to silicon application is typically evaluated in terms of yield (Pérez et al., 2016).

The ash obtained from bagasse typically exhibits a high silica content (Chindaprasirt and Rattanasak, 2020). However, data regarding other parts of the sugarcane plant, such as dry leaves, stems, and bark, are still limited at the national level. Therefore, there is a need to establish techniques capable of determining silicon concentrations in various parts of sugarcane for agricultural purposes.

The neutron activation analytical technique, utilizing an isotopic source, is a highly sensitive method applicable across diverse research fields (Morán et al., 2010). This technique involves the excitation of samples by neutrons, followed by the emission of gamma rays, enabling precise identification and quantification of elements present in the sample (Greenberg et al., 2011). The exceptional sensitivity offered by this technique provides an advantage over other analytical methods, while also being non-destructive (Fan et al., 2020).

Until recently, there was limited evidence of using this technique for quantifying silicon in ash derived from plant materials. Therefore, Michajluk et al. (2019) conducted a pioneering study to accurately determine the silicon content in sugarcane leaves and stems using neutron activation analysis. In line with this, the objective of the present study was to quantify the silicon content in sugarcane ash from different plant parts using the neutron activation analytical technique with an isotopic source.

Results and discussion

Table 1 displays the outcomes of the analysis of variance conducted on weight (g), silicon (Si), and silica (SiO2) variables in four representative samples of the sugarcane plant. The results reveal significant differences across all three variables, with silicon and silica variables demonstrating highly significant differences.

Table 1 here

The findings of the present study align with the research conducted by Chindaprasirt & Rattanasak (2020), which asserts that the silica content is influenced by the availability of silicon in soils. This observation further supports the outcomes reported by Michajluk et al. (2019), who investigated the silicon content in sugarcane across eight cities characterized by Rhodic paleuult and Rhodic Kandiudalf soil classifications. Their investigation revealed higher concentrations of silicon in sugarcane stems grown in clayey soils.

Figure 1 illustrates the sample weights of each sugarcane by-product. It can be observed that there were no significant differences in the ash obtained from the whole stems, bark, and leaves. However, the ash derived from bagasse exhibited a statistically significant difference compared to the other samples in this study.

Residual bagasse, which remains after the extraction of sugarcane juice, typically yields only 2 to 3% of its volume as ash (Loh et al., 2013), indicating a relatively small proportion. This finding supports the obtained data, where the highest amounts of ash were obtained from the entire stems.

Analyzing the percentage of silicon (Figure 2A) in the sugarcane by-products, a significant statistical difference is observed. The ash from the leaves exhibited the highest silicon content (24%) compared to the other by-products. The bark and bagasse contained 19.2% and 18.7% of silicon, respectively, with no significant differences observed between them. Similar findings were reported by Fox et al. (1969), who noted that the silicon content in sugarcane leaf sheaths was higher (93 µg/g) than in other sugarcane by-products. This is because silicon tends to be deposited in stems, leaves, and other plant parts, ranging from 0.1% to 10% by weight (Norsuraya et al., 2016). An experiment conducted by Korndörfer et al. (2002) found that sugarcane leaves contained high concentrations of silicon, ranging from 0.14% in younger leaves to 6.7% in older leaves.

Whole stems exhibited the lowest silicon content (12.8%), which was also the lowest value statistically. When examining the percentage of SiO2 (Figure 2B), the leaves displayed the highest values (51.5%), significantly standing out from the other samples. In a study conducted by Le Blond et al. (2010), the average SiO2 content in unprocessed sugarcane leaves was estimated using an Enraf-Nonuys diffractometer with a sensitive detector, quantifying 1.50% and 0.50% of SiO2. The results obtained by Teixeira et al. (2020), who performed thermogravimetric analysis, indicated a silica content in sugarcane leaves ranging from 43.60% to 52.71%, which aligns with the findings of this

Table 1. Average square obtained from the analysis of variance of different samples of leaves, whole stems, bark and bagasse, to determine weight, concentration of silicon and amorphous silica by the nuclear analysis technique.

	Average square			
	Df	Weight (g)*	Si**	SiO_2**
Sample	3	3.15	63.69	291.53
Wase	8	0.19	0.23	1.04
VC (%)	-	11.62	2.55	2.55

(**) Significant at 1%, (*) Significant at 5% and (ns) not significant.

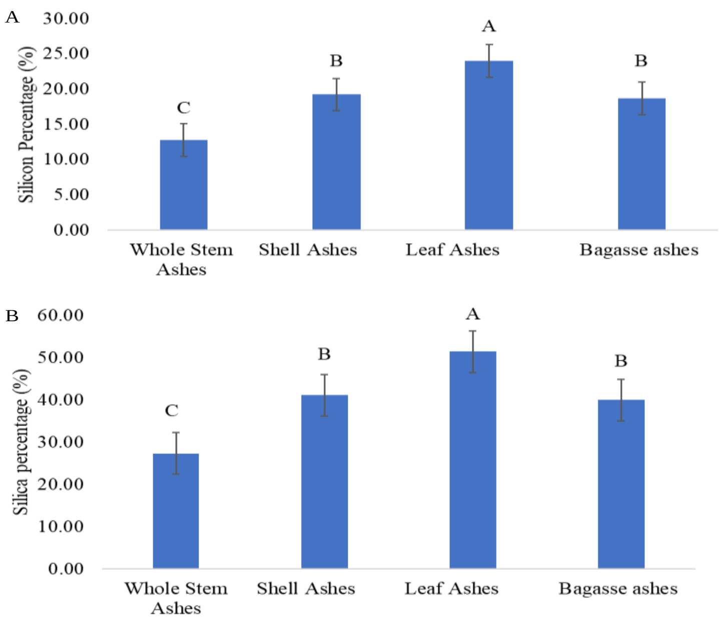

Figure 1. A. Percentage of Silicon (Si) and B. Percentage of Silica (SiO2) obtained from by-products of leaves, whole stalks, bark and bagasse of sugarcane.

investigation. However, Arumugam et al. (2013) reported a silica content of 80.1%. These variations in silica content can be attributed to different soil types.

The SiO2 results obtained from the bark ash and bagasse ash were statistically similar to each other, with values of 41.15% and 40.01%, respectively, but statistically different from the other by-products. Embong et al. (2016) analyzed bagasse ash using the Rigaku Miniflez X-Ray Defractometer and reported that bagasse ash, obtained from sugarcane, gained less popularity than leaf ash due to its relatively low amorphous silica content (<50% silica) after the incineration process to obtain ash. In contrast, Chindaprasirt & Rattanasak (2020) characterized silica using XRD and Fourier-transform infrared spectroscopy (ATR-FTIR, Perkin Elmer Frontier) and obtained a SiO2 composition of 54.9%. This increase in content can be attributed to the process of obtaining bagasse ash, which involved a prior treatment with acid and suspension of the obtained ash in 600 ml of HCl until reaching a pH of 7.

In relation to the ash obtained from the stems, the percentage of silica was statistically lower compared to all other by-products, measuring 27.4%. This finding aligns with the results reported by Michajluk et al. (2019), who also observed lower concentrations of silica in sugarcane stems at various locations, ranging from 0.360% to 0.464%.

The presented data clearly demonstrate that the ash derived from sugarcane by-products can serve as a viable source of silicon to produce foliar fertilizers. This assertion is supported by Tashima et al. (2012), who achieved silica values of 83.5% in rice husk ash for use as foliar fertilizer. Ongoing research in this field is of paramount importance, particularly with regards to the reuse of residual by-products generated during the industrialization of sugarcane.

Materials and methods

Plant materials

The study was conducted at the Laboratory of Nuclear Techniques, Faculty of Chemical Sciences, National University of Asunción (UNA). Eight batches of sugarcane samples were collected from the cities of Villa Hayes, San Lorenzo, Guarambaré, and Nueva Italia, in the month of March 2019. These samples were obtained from small rural properties. Soil classifications in these regions correspond to clayey soils (textural classification) and Alfisols (USDA classification). After collection, samples from these cities were mixed to form bulks. These plants, which were being harvested for animal consumption, had been cultivated for a period of 3 years. Ten plants per batch were harvested by cutting the stems approximately 10 cm above the soil surface. The samples were then separated into four sugarcane by-products: leaves, whole stems, bark, and bagasse.

Sample treatment and silicon and silica determination

For the purpose of determining the silicon and silica concentration, sugarcane samples underwent a comprehensive preparation and analytical procedure. Initially, samples were dried in an oven at 105ºC. Once dried, they were ground using a blade mill. The ground samples were then subjected to calcination in a muffle furnace at approximately 500ºC for six hours. The resulting ash was sieved using a 2 mm mesh and stored in airtight containers.

The ash's analytical procedure began by weighing three grams of each sample in triplicate, which were then placed in airtight plastic flasks. These flasks were positioned in a cadmium sample holder and underwent irradiation for ten minutes with an isotopic neutron source. This step allowed neutrons to interact with the sample, transforming non-radioactive nuclides into their radioactive counterparts. During the subsequent de-excitation, the radionuclides emitted gamma radiation. The signals from this radiation, each characteristic of a specific radionuclide, were identified using a scintillation detector (Morán et al., 2010; Moranchel et al., 2012).

The gamma radiation detection employed a 2" x 2" NaI scintillation detector paired with a multichannel PC board. To ensure accuracy in measurements, a silicon (Si) standard with 97.5% purity, prepared under conditions mirroring those of the samples, was used for calibration.

To determine the percentage of silica (SiO_2) based on the silicon content in a sample, the relationship between the molar masses of silicon (Si) and silica (SiO_2) is employed. The calculation is represented by the following formula:

$$\%\ SiO_2 = \frac{\%\ \text{Si x Molar mass of SiO2}}{\text{Molar mass of Si}}$$

To determine the percentage of silicon (Si) in a given sample, the calculation utilizes the sample's activity, control weight, and purity in relation to the control activity and the weight of the sample itself. The formula for this calculation is:

$$\%\ Si = \frac{Sample\ activity\ x\ Control\ Weight\ x\ Purity}{Control\ Activity\ x\ Sample\ Weight}$$

Statistical analysis

The study employed a completely randomized experimental design (CRD) with three repetitions for each sample. The statistical analysis conducted in this study involved the application of a one-way analysis of variance (ANOVA) to assess the variation among different samples (plant parts). Post-hoc analysis was performed using the DMS (Duncan's Multiple Range Test) comparison method. The statistical analysis was carried out using the R software, specifically the R Core Team program.

Conclusion

In conclusion, the application of neutron activation analysis using an isotopic source proved to be an effective technique for quantifying the silicon content in various sugarcane by-products. The results emphasize that ash derived from sugarcane leaves holds significant potential as a valuable source for silica extraction. This finding underscores the importance of exploring the utilization of sugarcane leaf ash as a sustainable resource for silica extraction in various applications.

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