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A simple method for the multi-elemental analysis of organic fertilizer by slurry sampling and total reflection X-ray fluorescence

Luciene V. Resende, Clésia C. Nascentes *

Department of Chemistry, Federal University of Minas Gerais, PO Box 702, 31270-901 Belo Horizonte, Minas Gerais, Brazil

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ABSTRACT

A simple and fast method for the multi-elemental determination of 18 inorganic constituents (P, S, Cl, K, Ca, Ti, Cr, V, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Ba and Pb) in organic fertilizers employing slurry sampling and total reflection X-ray fluorescence (TXRF) is presented. A 2^3 factorial design with a central point was employed to optimize the slurry sampling procedure. The internal standard and instrumental conditions were optimized by univariate studies. The selectivity of the method to determining Se, As, Pb, Cr, Ni and Cd was assessed. The accuracy was evaluated by the analysis of four standard reference materials (SRM). The recoveries varied from 72% to 114%. For most of the elements, good agreement was achieved between the certified value and the value measured in the SRM. The relative standard deviation (RSD %) ranged from 0.5% to 14%. The evaluated method was applied to the determination of analytes in the press cake of palm, castor, curcas, sunflower, fodder turnip, white lupin, rapeseed and pequi, and their potential to be used as organic fertilizer was evaluated in accordance with Brazilian legislation.

1. Introduction

Biodiesel has attracted considerable attention as a renewable, biodegradable, and nontoxic fuel and can contribute to solving energy problems and reducing the emissions of gases that cause global warming [1]. The most used process for the production of biodiesel is transesterification, which is the chemical reaction between oil or vegetable or animal fat and an alcohol in the presence of a catalyst [2]. Several types of oilseed plant have been used as raw materials for the production of biodiesel worldwide. Atabani et al. [3] reported that there are more than 350 oil-bearing crops that have been identified as potential sources for biodiesel production, including edible vegetable oils such as rapeseed, soybean, peanut, sunflower, palm and coconut oils and non-edible vegetable oils from jatropha, karanja, sea mango, algae and halophytes.

The technique of oil extraction by mechanically pressing the plant seeds is the most conventional method and generates the press cake as a by-product of the production of biodiesel. According to the literature [3,4], it has been found that the feedstock alone represents 75% of the overall biodiesel production cost. Biodiesel is currently not economically feasible, so selecting the cheapest feedstock and utilization of the by-products are vital to ensuring the economic viability of biofuel production. Some oil-bearing crop press cakes have been investigated for their potential to be used as animal feed [5–10], organic fertilizer [11] and activated carbons [12,13].

The use of organic byproducts to improve the yield of agricultural crops is a traditional alternative to the disposal of agricultural and industrial waste, with additional advantages of avoiding environmental impact and generating income for industry and for farmers. Organic waste is used not only as fertilizer, but also as a growth substrate in horticulture and vegetable seedlings. Organic fertilizers can supply macro and micronutrients, improve the soil's physical properties, immobilize toxic elements such as aluminum and promote the activity of microorganisms [11].

According to Brazilian law, the mineral composition of organic waste has to be known to evaluate their use as organic fertilizer [14,15]. In this sense, the development of faster and more accurate analytical methods is needed to enable the use of different agricultural wastes as organic fertilizers. These methods can also contribute to the biodiesel production chain, adding value and ensuring an appropriate environmental fate for the large amount of by-products generated.

Inductively coupled plasma optical emission spectrometry (ICP OES) is a well-established method for multi-elemental analysis. However, this technique requires the introduction of the sample as a solution, which makes a sample preparation step necessary. On the other hand, using total reflection X-ray fluorescence (TXRF), sample digestion can be avoided for most analytical tasks, and sample preparation can thereby be reduced to a few simple steps.

* Corresponding author. Fax: +55 31 3409 5700.
E-mail address: clesia@qui.ufmg.br (C.C. Nascentes).

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Sample preparation is frequently the most time consuming step of an analytical procedure and the bottleneck of the whole analytical process when elements are determined in solid samples [16–19].

Total reflection X-ray fluorescence analysis is a powerful analytical multielemental tool with respect to its detectable elemental range and simplicity of quantification and detection [20]. The total reflection of primary X-ray photons on the carrier plates causes the excitation efficiency to be higher, thereby resulting in lower detection limits. The formation of a thin layer from liquid or solid samples makes the elimination of matrix effects and the application of internal standardization possible [21,22].

Liquids and digested solid samples can be analyzed directly by TXRF. For solid samples, different types of preparation are possible. The slurry sampling technique stands out because it reduces the sample preparation time, decreases the possibility of the loss of analyte, and minimizes the risk of contamination [23]. For slurry sampling, a powdered sample is suspended in a liquid diluent containing an internal standard. After homogenization, a microvolume (10–20 μL) is deposited onto the sample carrier.

Based on the necessity to know the mineral composition of the seed press cakes to evaluate their use as organic fertilizer, the aim of this work is to develop a fast and accurate method for the simultaneous determination of P, S, Cl, K, Ca, Ti, Cr, V, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Ba and Pb in press cake samples employing slurry sampling and the TXRF technique.

2. Experimental

2.1. Instrumentation

Measurements were performed using a benchtop S2 PICOFOXTM TXRF – spectrometer (Bruker Nano GmbH, Karlsruhe, Germany). The TXRF spectrometer is equipped with a Mo tube – Kα 17.5 keV excitation source (600 μA, 50 kV, 50 W), a multi-layer monochromator and a silicon drift detector with an active area of 10 mm^2. The resolution of the detector was better than 160 eV at 10 kpcs (Mn Kα). The X-ray tube is provided with a primary radiation protection made of 5 mm-brass, a thin Beryllium window (100 μm) by which the X-rays escape to the outside. In the direction towards the monochromator a 3 mm-opening for the emission of the useful beam is provided. The beam shaping is performed by means of an aperture system and results in a beam shape in the sample area of about 7×0.1 mm^2. The monochromatization of the tube radiation is done via the Bragg reflection on a multilayer. Multilayers are made of alternating layers of light and heavy elements or their compounds. A typical example for this type of structures is a layer system made of 100 Nickel/Carbon duplicate layers with a spacing of 2.88 nm.

The measurement times (live time) ranged from 250 s to 1000 per sample. The processing of the X-ray spectra and the accounting for fluorescence peak overlaps were performed using the software SPECTRA version 7.0 (Bruker Nano GmbH, Karlsruhe, Germany).

A VCX 550 model ultrasonic processor (Sonics, Newtown, CT, EUA) (50 W, 20 kHz frequency) type cup horn was used for slurry preparation. A Shimadzu (AUW220 D – UniBloc) balance was employed for weighing samples. A cryogenic mill (Spex model 6800, Metuchen, NJ, USA) was used to ground the press cake samples. The determination of the particle size distribution of the comminuted press cakes was performed by low-angle laser light scattering using a CILAS 1190 particle size analyzer (CILAS, Orleans, France).

2.2. Reagents and materials

All chemical were of analytical reagent grade. Yttrium and gallium standard solutions with concentrations of 1000 mg L^{-1} (Fluka Analytical, Buchs, Switzerland) were used as internal standards (IS). Nickel, arsenic, lead, selenium and cadmium standard solutions with concentrations of 1000 mg L^{-1} (Fluka Analytical, Buchs, Switzerland) were used to prepare the spikes. Ultrapure water from a Millipore purification system (Milli-Q, Millipore, Billerica, MA, USA) and the non-ionic detergent Triton X 114 (Merck, Darmstadt, Germany) were used for the dilution of the samples analyzed.

Quartz glass disks of 30 mm diameter and a thickness of 3.0 ± 0.1 mm were applied as TXRF sample carriers. Acetone (Vetec, Rio de Janeiro, Brazil) and RBS non-ionic detergent (Sigma-Aldrich GmbH, Seelze, Germany) were also used for cleaning the quartz sample carriers. Sample carriers were previously siliconized by 10 μL of a silicon solution in isopropanol (Serva™, Heidlberg, Germany) to make the surface of the quartz reflector hydrophobic and to prevent the spreading of the sample drop prior to analysis.

2.3. Standard reference materials and samples

SRM Spinach Leaves (NIST 1570a) (National Institute of Standards & Technology, NIST, Gaithersburg, USA) were used to optimize the method. For testing the performance of the analytical method, the following standard materials were evaluated: Tomato Leaves (NIST 1573a), Peach Leaves (NIST 1547), Wheat Flour (NIST 1567a) and Sewage Sludge 2 (CRM029-50 FLUKA).

The analyzed press cakes were palm (*Ellaeis guineensis*), castor (*Ricinus communis L.*), curcas (*Jatropha curcas L.*), sunflower (*Helianthus annuus*), fodder turnip (*Raphanus sativus L.*), white lupin (*Lupinus albus*), rapeseed (*Brassica napus*) and pequi (*Caryocar brasiliense*), all furnished by the Federal University of Lavras, Minas Gerais, Brazil.

2.4. Method optimization

Factorial design allows evaluating all possible interactions by using all combinations of levels of the variables investigated. In this way, a 2^3 factorial design with a central point was employed, in two levels (minimum and maximum), to evaluate the effect of the variables of time of slurry mixing (4 and 12 min), mass of sample suspended (10 and 50 mg), and concentration of Triton X 114 solution (0.1 and 1.0% v v^{-1}) on the recovery and lowest limit of detection (LLD) of the certificated elements in SRM NIST 1570a to optimize the slurry sampling (Table 1). In this context, recovery can be defined as the fraction of the analyte determined in the certified material. Replicates of the central point were performed to evaluate the pure error (i.e. a measure of the random error).

To obtain the conditions that simultaneously satisfy the recovery and LLD of the elements investigated, the overall response (OR) equation was adopted (Eq. (1)) [24]:

$$OR = \frac{R(Ca)}{HR(Ca)} + \frac{R(K)}{HR(K)} + \ldots \frac{R(i)}{HR(i)} \quad (1)$$

where R(element) is the recovery or LLD for that element in a particular experiment and HR(element) is the high recovery or LLD in the set of experiments for that element.

The effects and significance of the variables in the sample pretreatment were evaluated using analysis of variance (ANOVA) and Pareto charts using STATISTICA® software, version 7.0 (StatSoft, Brazil).

A mass of 10–50 mg was accurately weighed in a propylene tube with a capacity of 5 mL and then suspended in 2.5 mL of