



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 2³ 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.

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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 micro-nutrients, 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).

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 micro-volume (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 PICO-FOXTM TXRF – spectrometer (Bruker Nano GmbH, Karlsruhe, Germany). The TXRF spectrometer is equipped with a Mo tube – $K\alpha$ 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 kpcps (Mn $K\alpha$). 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 $7 \times 0.1 \text{ mm}^2$. 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 $3.0 \pm 0.1 \text{ mm}$ 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 (ServaTM, Heidelberg, 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 (*Elaeis 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]:

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

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 (Stat-Soft, 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

Table 1

Two-level factorial design and responses (recovery and lowest limit detection) for screening of factors studied.

Factors			Low level (−1)			Center point (0)			High level (+1)			
V1, mass of sample (mg)			10			30			50			
V2, TX 114 (% v v ^{−1})			0.1			0.55			1.0			
V2, sonication time (min)			4.0			8.0			12			
V1	V2	V2	Recovery (%)			Ca	Mn	Ni	Cu	Zn	Rb	OR
2 ³ factorial design with a central point			P	S	K							
−1	−1	−1	96	104	94	116	104	86	113	104	78	8.75
+1	−1	−1	62	63	81	69	86	92	86	86	73	6.87
−1	+1	−1	86	87	92	95	95	81	93	95	75	7.86
+1	+1	−1	66	75	86	89	98	111	97	99	76	7.78
−1	−1	+1	84	86	88	96	91	75	95	91	71	7.61
+1	−1	+1	70	71	88	78	91	103	93	92	76	7.48
−1	+1	+1	82	83	89	94	94	81	106	92	72	7.77
+1	+1	+1	68	72	90	77	91	95	94	95	80	7.49
0	0	0	77	83	88	92	93	86	98	91	76	7.69
0	0	0	78	85	88	93	98	101	101	97	75	7.91
0	0	0	77	85	87	95	99	97	97	96	75	7.99
V1	V2	V2	LLD (mg kg ^{−1})			Ca	Mn	Ni	Cu	Zn	Rb	OR
2 ³ factorial design with a central point			P	S	K							
−1	−1	−1	55.5	29.3	8.9	4.5	0.8	0.5	0.4	0.3	0.4	8.98
+1	−1	−1	32.4	18.5	4.0	3.0	0.4	0.2	0.2	0.2	0.1	8.68
−1	+1	−1	62.4	34.8	8.7	5.4	1.1	0.7	0.5	0.4	0.5	7.61
+1	+1	−1	35.6	17.8	4.3	2.6	0.4	0.2	0.2	0.2	0.2	7.11
−1	−1	+1	58.7	32.9	8.8	5.1	0.8	0.6	0.4	0.4	0.4	4.69
+1	−1	+1	28.4	16.2	3.6	2.6	0.3	0.2	0.2	0.1	0.1	4.53
−1	+1	+1	66.1	36.6	9.0	5.5	1.1	0.7	0.5	0.5	0.5	4.29
+1	+1	+1	34.9	18.8	4.1	3.1	0.4	0.2	0.2	0.2	0.2	3.78
0	0	0	38.4	20.6	5.3	3.2	0.5	0.3	0.2	0.2	0.2	3.91
0	0	0	36.2	19.1	5.0	2.9	0.5	0.3	0.2	0.2	0.2	3.62
0	0	0	38.3	20.4	5.3	3.2	0.5	0.3	0.2	0.2	0.2	3.22

aqueous (0.1–1.0% v v^{−1}) Triton X – 114 solution. A volume of 10–50 µL of Ga standard solution with a concentration of 100 mg L^{−1} was added to the mixture as the internal standard, so that the final concentration of Ga in the sample would be 100 mg kg^{−1}. The mixture was subjected to stirring by ultrasound for 4–12 min. An aliquot of 10 µL of the suspension was transferred onto a siliconized quartz glass sample carrier and vacuum dried for 15 min. After drying, a thin film remains on the surface of the sample carriers. The measurements were conducted at a 50 kV operating voltage and 600 µA current. The measurement time was 1000 s per sample.

Another study on the mass influence on the recovery of the elements studied was also performed on Spinach Leaves NIST 1570a. A sample powder mass of 5–30 mg was suspended in 2.5 mL of aqueous 0.1% v v^{−1} Triton X – 114 solution followed by the addition of Ga standard solution. The mixture was sonicated for 4 min before the analysis by TXRF employing the procedure described above.

The influence of the gallium and yttrium internal standards (IS) was evaluated as well. For that, 20 mg of Spinach Leaves NIST 1570a was accurately weighed and suspended in 2.5 mL of aqueous 0.1% v v^{−1} Triton X – 114 solution, followed by the addition of 20 µL of the Ga and Y standard solutions with concentrations of 100 mg L^{−1}. The measurement time was 1000 s per sample.

The mixtures, in both studies, were sonicated for 4 min and analyzed by TXRF according to the procedure described above. Three replicates were prepared in each experiment.

The effective time of measurement (i.e., integration time) was investigated using 250, 500, 750, and 1000 s, when applying Ga as IS.

2.5. General procedure

After optimization, 20 mg portions of standards NIST 1573a, NIST 1547, NIST 1567a and CRM029-50 and press cakes of palm,

castor, sunflower, fodder, turnip, white lupin, rapeseed and pequi were accurately weighed in propylene tubes with a capacity of 5 mL. Then, 2.5 mL of aqueous 0.1% v v^{−1} Triton X – 114 solution was added to the tubes, followed by the addition of 20 µL of Ga standard solution. The mixtures were subjected to stirring by ultrasound for 4 min. An aliquot of 10 µL of the suspension was transferred onto a siliconized quartz glass sample carrier and vacuum dried for 15 min. The measurement time was 250 s per sample.

2.6. Method performance

To evaluate the matrix effect, 10 g portions of white lupin and pequi press cakes were spiked with 1000 mg L^{−1} solutions of Se, As, Pb, Cr, Ni and Cd so that their final concentrations in the sample would be in 80; 20; 150; 200; 70, and 3 mg kg^{−1}, respectively (Brazilian legislation values for contaminants in organic fertilizers). The samples were dried at 50 °C for 24 h and ground and homogenized in an agate mortar. Prior to the TXRF analyses, the samples were treated by the proposed method.

To evaluate the accuracy, precision and limits of detection (LD) and quantification (LQ), four SRM (NIST 1573a, NIST 1547, NIST 1567a and CRM029-50) were analyzed according to the general procedure.

2.7. Analysis of press cake samples

Samples of press cake were dried at 60 °C until constant weight and ground in a cryogenic mill (Spex model 6800) with a 5 min pre-cooling step, followed by 15 grinding cycles of 2 min each to guarantee homogeneity. The milled samples were analyzed by the proposed method.

3. Results and discussion

3.1. Method optimization

3.1.1. Optimization of slurry procedure for elemental determination

As pointed out by Market [25], the comminution of sample materials is one of the most important steps in the overall analytical procedure. Comminution usually refers to the grinding of solid samples made up of large particles into a powder consisting of small particles. This process improves the analyte micro-homogeneity and prevents the segregation of the material as a result of the wide particle size distribution. 30 min of cryogenic grinding of the press cakes resulted in 90% of the particles having a size in the range of 59–182 μm .

A 2^3 factorial design with a central point was applied to optimize the slurry procedure. Table 1 shows the experimental design matrix, the results of the recovery and limits of detection obtained for P, S, K, Ca, Mn, Ni, Cu, Zn and Rb, and the overall response, which represents the sum of the normalized results for each element. Considering an analysis of variance (ANOVA), the results demonstrate that the mass of the sample and an interaction of third order ($V1*V2*V3$) are statistically significant (95% confidence level) on the recovery of the elements investigated in SRM NIST 1570a. A Pareto chart (Supplementary material – S1a) shows the negative effect of the sample mass, namely, when the mass is increased from 10 to 50 mg, there is a decrease in the recovery. We also observed a negative effect in the interaction of the third order, indicating that a lower mass of the sample combined with a smaller concentration of Triton X and a shorter time of ultrasound increase the recovery. The other two factors showed no significant influence on the recovery in the experimental domain investigated.

When the LLD was employed as a response, the sample mass presented a negative effect and the concentration of Triton X 114a positive effect, both statistically significant (95% confidence level). (Pareto chart, Supplementary material – S1b). As can be noted, increasing the sample amount and diminishing the Triton X 114 concentration promote the enhancement of the LLD of the elements. The detection limit of the elements determined for the slurries was estimated according to the 3-sigma approach. As a general rule, it is considered that an element can be detected if the peak area is statically more than three times the background, and it can be quantified accurately when the intensity of the peak exceeds 10 times the background level [22,26,27]. The following formula is commonly accepted to define the detection limit in TXRF techniques (Eq. (2)):

$$\text{LLD} = \frac{3 \cdot \text{Ci} \cdot \sqrt{\text{Nbg}}}{\text{Ni}} \quad (2)$$

where LLD is the lowest limit of detection of the element, Ci is the concentration of element i, Ni is the area of the fluorescence peak in counts and Nbg is the background area subjacent to the fluorescence peak.

The values of the background radiation for the tests using 10 mg and 50 mg of sample with 0.1 and 1% v v⁻¹ Triton X 114 indicate that higher concentrations of this surfactant resulted in an increased background radiation signal (Fig. 1) and therefore a higher LLD. This effect was more pronounced when 10 mg of sample was used.

As smaller masses of samples resulted in higher recoveries and lower concentrations of Triton X 114 provide lower LLDs, the following investigations evaluated the effect of the sample mass (5–30 mg) on the recovery of the elements in a 0.1% v v⁻¹ solution of Triton X 114. As shown in Fig. 2, the recovery values for the trace and major elements P, S, K, Ca, Mn, Ni, Cu, Zn and Rb slightly

depend on the sample amount. The recoveries varied in the range of 85–109%, except for Rb, which showed a recovery in the range of 67.5–78%. The low recoveries observed for Rb can be attributed to spectral interferences, since Rb L α (1.691 keV) line overlaps with Si K α (1.739 keV) due to the sample support. The best recoveries were observed when 5 mg of sample was used in the slurry. However, in this condition, the standard deviations associated with the measurements were higher as well. Taking into account the recovery and standard deviation between measurements, we chose to work with 20 mg of sample for the slurry preparation.

3.1.2. Internal standard evaluation

For the internal standardization, a defined amount of a mono-element standard solution is added. The element to be selected depends on the element content of the samples. An element must be selected that is not already present in the sample itself, and the fluorescence lines of the internal standard should not interfere with those of the important elements in the sample. In this way, the influence of the Ga and Y internal standards were evaluated and the results were compared by significance testing or hypothesis testing (i.e., a process by which we determine the probability that there is a significant difference between two results) If the t experimental (t_{exp} – calculated t value) is higher than the t critic (t_{crit} – tabulated t value, obtained from a two-tailed Student's t distribution) there is significant difference between two results at a confidential level. It can be noted (Table 2) that there were significant differences between the recovery values of P, S, K, Mn, Cu, Zn and Rb on NIST 1570a when employing Ga and Y as IS (i.e., $t_{\text{exp}} > t_{\text{crit}}$ for a 95% confidence level, $n=4$, in a two-tailed Student's t distribution). Even the results showed significant differences, those are smaller, as can be noted by lower t_{exp} value, both Y as Ga showed satisfactory recoveries. Since, in the conditions that the experiments were conducted, the recoveries using Ga as IS showed a little bit higher recoveries values than Y, Ga was chosen as IS for following experiments.

3.1.3. Measurement time evaluation

Concerning the choice of measurement time, it is a difficult task to find a compromise between sensitivity and productivity. It does not make sense to spend a measurement time of 1000 s if the analytical task is an analysis of the main elements in the percentage range. A general rule for selecting the measurement time cannot be given. Thus, in many cases, a test measurement for the evaluation of the lowest limits of detection and for the optimization of the measurement times is necessary. Beside the measurement time, the sample matrix is of primary importance for the obtainable lowest limits of detection [28].

The effective time of measurement (i.e., integration time) was investigated at 250, 500, 750, and 1000 s when applying Ga as an IS. The LLD decreased with the increasing measurement time (Table 3). Increasing the measurement time from 250 s to 1000 s decreases the LLD by a factor of two. However, the estimated LLD obtained with the 250 s measurement is suitable for the determination of contaminants and nutrients in the press cake, and its time was defined in the proposed method. In this way, the analytical frequency will be increased by a factor of 4.

3.2. Method evaluation

The selectivity and accuracy (trueness and precision) of the proposed method were checked with the four standard reference materials, three of which are botanical materials (Tomato Leaves NIST 1573a, Peach Leaves NIST 1547, Wheat Flour NIST 1567a) and another Sewage Sludge (CRM029-50 FLUKA). Three replicates of each were performed. A set of 18 elements was chosen for the

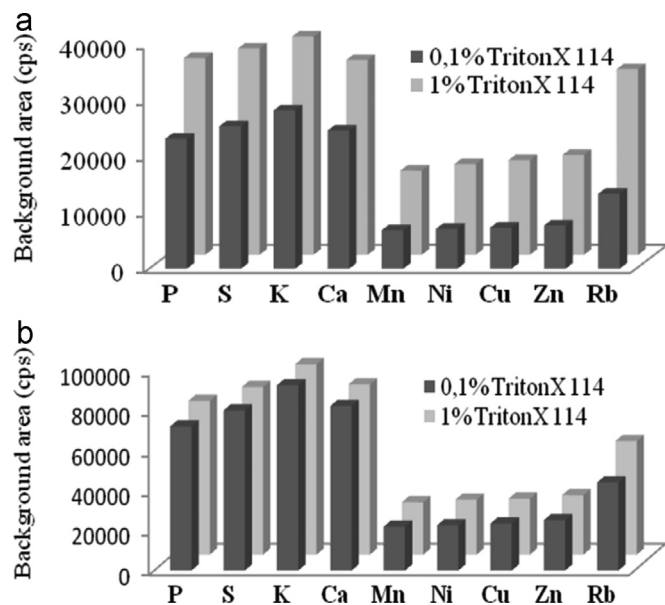


Fig. 1. Effect of concentration of Triton X 114 solution on the background area results: (a) 10 mg of NIST 1570a suspended in 2.5 mL of surfactant; (b) 50 mg of NIST 1570a suspended in 2.5 mL of surfactant.

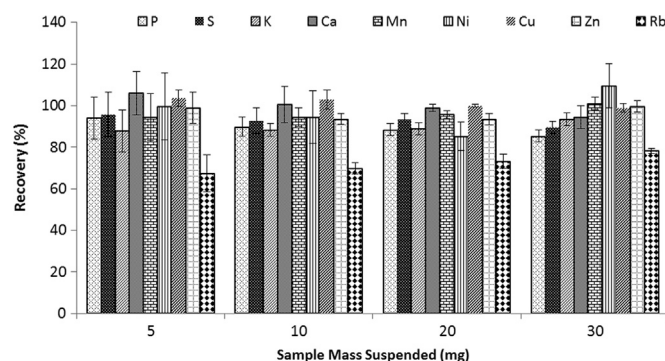


Fig. 2. Effect of sample mass of NIST 1570a on the TXRF results (errors bars represent the standard deviations of three replicates).

Table 2

Experimental results for recovery in the SRM NIST 1570a, employing Ga and Y as internal standards, and Student's test (tabulated t value for $n=4$ and $\alpha=0.05$ is 2.78).

Element	Recovery (%) Ga (100 mg kg ⁻¹)	Recovery (%) Y (100 mg kg ⁻¹)	Calculated t - Value
P	96.0 ± 2.6	86.0 ± 0.74	6.3
S	95.0 ± 3.2	85.0 ± 1.3	4.8
K	86.0 ± 1.8	78.0 ± 3.1	4.2
Ca	109 ± 7	98.0 ± 4.4	2.3
Mn	97.0 ± 1.9	87.0 ± 3.1	4.6
Ni	115 ± 23	103 ± 19	0.7
Cu	101 ± 1	91.0 ± 1.6	8.8
Zn	93.0 ± 2.7	84.0 ± 4.0	3.3
Rb	86.0 ± 2.6	78.0 ± 3.5	3.4

study (P, Cl, S, K, Ca, Cr, Mn, Rb, Se, Fe, Ni, Cu, Zn, Sr, Ba, Tl, Pb and Br). Two criteria were used to verify the suitability of the method: (i) a recovery in the range of 80–120% and (ii) a maximum relative standard deviation (RSD%) of 15%.

3.2.1. Evaluation of TXRF method selectivity

Selectivity is the degree to which a method can accurately quantify an analyte in the presence of interferences. Interferences

Table 3

Effect of measurement time on the lowest limit of detection for Ca, K, Rb, Cl, S, P, Br, Rb, Zn, Sr, Cu, Ni, Fe, Mn, Cr, Ti on SRM NIST 1570a.

Element	Measurement time (s)			
	250	500	750	1000
	LLD (mg kg ⁻¹)			
P	77.3	54.5	44.7	38.8
S	44.6	31.4	25.7	22.4
Cl	28.7	20.3	16.5	14.3
K	12.2	8.67	6.99	6.06
Ti	2.27	1.62	1.29	1.14
Ca	7.69	5.45	4.40	3.81
Cr	1.40	0.98	0.79	0.70
Mn	1.16	0.83	0.67	0.58
Fe	0.94	0.66	0.54	0.47
Ni	0.64	0.45	0.37	0.32
Cu	0.58	0.41	0.34	0.29
Zn	0.51	0.37	0.30	0.26
Br	0.35	0.25	0.20	0.18
Rb	0.41	0.29	0.23	0.20
Sr	0.50	0.36	0.29	0.25

present in the sample matrix may increase or decrease the signal, and the magnitude of the effect may also depend on the concentration. Especially for complex samples, strong overlaps of the individual fluorescence peaks in the spectrum occur because of the line diversity and the finite detector resolution. To allocate the correct intensities to the individual elements, the spectrum must be separated into individual element lines by a complex mathematical process (deconvolution). The result is the peak area (intensity) for each element of the individual, not overlapped, fluorescence peaks. For the quantification in TXRF analysis, the SPECTRA software applies a deconvolution routine (SuperBayes) that uses measured mono-element profiles for the evaluation of peak intensities [28]. This mathematical approach has shown satisfactory results.

Fig. 3 displays the X-ray spectrum obtained from Sewage Sludge (CRM029-50) in the Cd L α (3.126 keV) to Y K α (14.882 keV) energy range. As can be seen, the Fe K β (7.059 keV) line overlaps with the Co K α (6.930 keV) line, and the Pb L α (10.551 keV) line overlaps with the As K α (10.543 keV) line. Co was not detected in CRM029-50, despite their value being certificated (5.70 mg kg⁻¹), probably due to the overlaps mentioned before. As can be seen in Fig. 3 any possible peak of Cd L α (3.126 keV) line is strongly suppressed by K K α (3.313 keV) peak to the background level. This can be attributed to a huge disproportion between the concentration of K in CRM 029-50 (3370 mg kg⁻¹) and Cd (487 mg kg⁻¹). Additionally, the production of Cd L α line with Mo anode (17.5 keV) has very low excitation efficiency. Because of this limitation Cd could not be determined by TXRF [29].

In accordance with Brazilian legislation [14], the concentrations of Se, As, Pb, Cr, Ni and Cd in organic waste to be used as organic fertilizer cannot exceed 80; 20; 150; 200; 70 and 3 mg kg⁻¹, respectively, because those elements are considered contaminants. In this way, press cakes of white lupin and pequi were spiked with solutions of those elements so that the final concentration in the dry sample would be within those levels. As expected, Cd was not detected in either of the samples analyzed. This is characteristic of a sample with high amount of potassium, as noted before. Therefore, this method is not appropriate to determine Cd in compliance with Brazilian regulations. The low recoveries and high deviations (Table 4) observed for Ni and Se in pequi press cake and for Ni, As and Pb in white lupin press cake could be

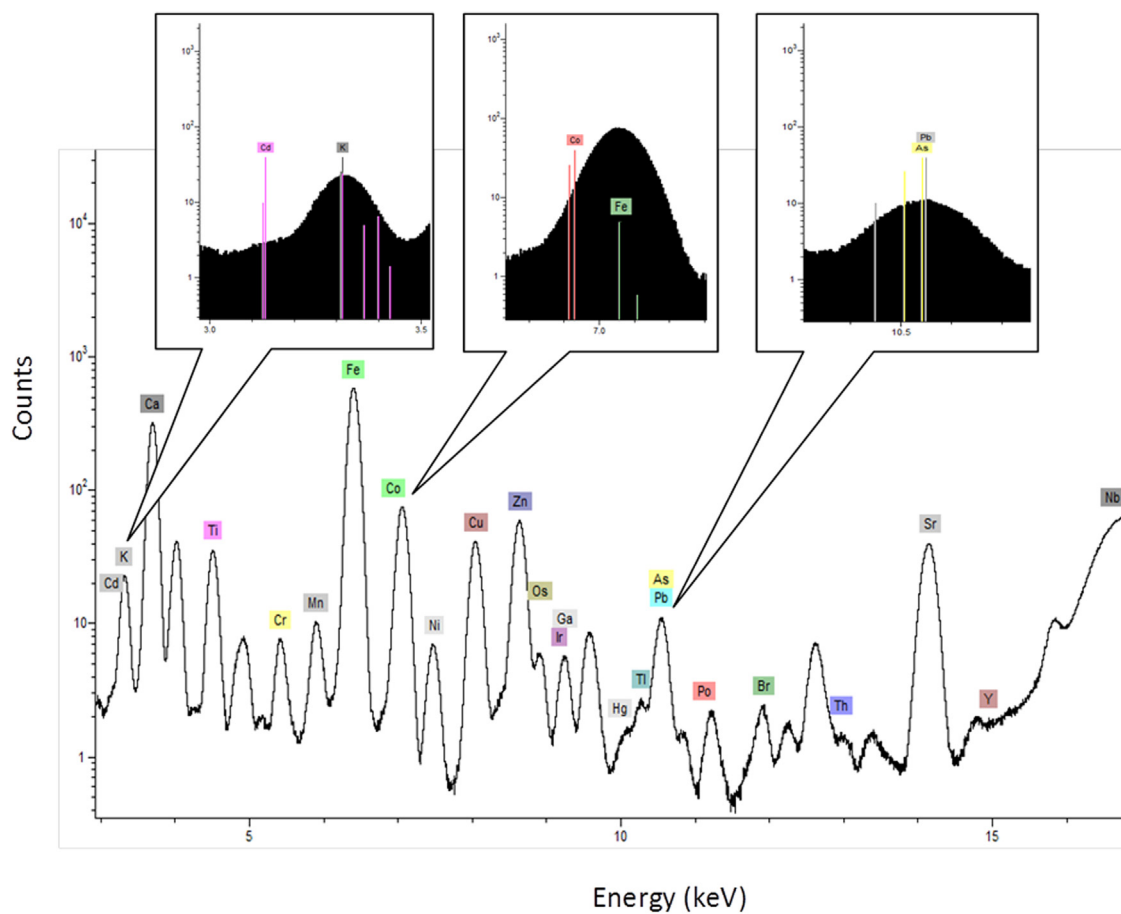


Fig. 3. X-ray spectrum obtained from Sewage Sludge (CRM029-50) in the Cd $L\alpha$ (3.126 keV) to Y $K\alpha$ (14.882 keV) energy range.

attributed to the lack of homogeneity in the spiked sample. However, it has been found that it is possible to quantify these analytes in press cakes.

3.2.2. Evaluation of method accuracy

Table 5 displays a summary of the analytical characteristics obtained for the analysis of SRMs: concentration interval (lowest and highest certified values concentration in SRMs), intervals of recoveries in the four SRMs, repeatability expressed as relative standard deviation (RSD%), lower limit of detection (LLD) and limit of quantification (LQ).

To provide a quantitative estimate of the analytical precision for the proposed method, the relative standard deviation (RSD%) based on a triplicate analysis of each sample was calculated. The RSD values for the three replicates of all the SRMs evaluated indicate a good precision (Table 5) for most of the elements investigated, varying from 0.5% to 14%. There seems to be a trend that the highest RSD is associated with the lowest concentration of analytes in the samples studied, mainly concentrations close to their estimated LLDs. For example, the certified value of Cr in NIST 1573a is 1.99 mg kg^{-1} , close to the estimated LLD (1.8 mg kg^{-1}) and below the estimated LQ (5.9 mg kg^{-1}). The triplicate analysis of that sample showed an RSD of 14%, while the triplicate analysis of Cr in CRM029-50 (certified value of 345 mg kg^{-1}) presented an RSD of 1.5%. Another source of variation in the repeatability can be associated with disturbances by overlaps between elements with high and comparatively low concentrations (Ca $K\alpha$ 3.688 keV line overlaps K $K\beta$ 3.590 keV line) and also variation due to sample drying on the sample holder.

Table 4

Experimental results for recovery of Cr, Ni, As, Se and Pb in spiked press cakes of pequi and white lupin.

Element	Pequi		White lupin	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Cr	84.0	7.6	86.4	6.2
Ni	64.3	11.9	72.2	14.4
As	81.1	12.5	72.4	16.4
Se	70.8	11.7	88.8	10.3
Pb	96.4	5.1	74.2	21.7

The trueness of the major and trace element determinations by the proposed method was checked using the SRM (Table 5). Most recovery values ranged between 72–114%. Discrepant recoveries were obtained for Ni, whose certified values in the SRM investigated are close to the estimated limit of quantification. The certified value of Ni in NIST 1547 is 0.69 mg kg^{-1} (recovery of 189% – $LQ=1.96 \text{ mg kg}^{-1}$), and the certified value in NIST 1573a is 1.59 mg kg^{-1} (recovery of 256% – $LQ=2.5 \text{ mg kg}^{-1}$). However the recovery of Ni in CRM029-50 was 103%, compared to a certified value of 172 mg kg^{-1} , and the estimated LQ is 5.3 mg kg^{-1} . Discrepant recovery values were also observed for the determination of Ba in Peach Leaves (NIST 1547) and As in Sewage Sludge (CRM029-50). In spite of the estimated LQ (16.5 and 3.12 mg kg^{-1} , respectively) being lower than the certificated values in these materials (124 and 27.4 mg kg^{-1} , respectively), the recovery was underestimated. Only chlorine and sulfur showed recoveries under

Table 5

Experimental results obtained from method evaluation. Concentration range in reference material (NIST 1567a, NIST 1547, NIST 1573a and CRM 029-50), recovery, relative standard deviation (RSD%), lower limit of detection (LLD) and quantification (LD).

Element	Range (mg kg ⁻¹)	Recovery (%)	RSD (%)	LLD (mg kg ⁻¹)	LQ (mg g ⁻¹)
P	1370–21,700	88–99.7	3.7–5.0	52–129	173–429
Cl	360–6600	72–84	8.8–9.7	23–36	76–120
S	1650–13,600	76–99	2.7–4.2	27–71	90–238
K	1330–27,000	82–106	1.3–9.1	6.5–19.2	37–53
Ca	15,600–50,500	87–114	1.4–1.6	7–13.3	23–34
Cr	1.99–345	99.5–103	1.5–14	1.8–3.9	5.9–12.9
Mn	9.4–246	85–100	0.5–7.6	1.2–3.3	3.6–11.1
Fe	218–20,700	105–112	2.5–7.0	0.9–2.6	2.9–8.5
Ni	0.7–172	103–256	4.4–9.6	0.6–1.6	2.5–19.6
Cu	2.1–1100	84–96	3.1–11.4	0.5–1.3	1.7–4.5
Zn	17.9–1400	87–106.1	1.1–7.3	0.5–1.3	1.5–4.4
Sr	53–647	95–110	2.1–2.2	0.5–0.7	1.5–2.4
Ba	124–1080	99.2–181	2.6–9.5	4.9–29.4	16.5–98.1
Tl	44.9	99.4	10.7	5.5	18.2
Pb	0.87–300	106–113	5.5–8.9	0.4–1.1	1.5–3.6
Br	6.02–11.5	100–104	0.9–8.8	0.32–0.35	1.06–1.16
Rb	19.7	73.9	4.2	0.37	1.24
Se	1.1	84.2	10.7	0.38	1.26
Br ^a	6.0–11	104–105	0.9–8.8	0.32–0.35	1.1–1.2
As	27.4	136.2	0.6	0.93	3.12

^a Not certified value.

80%, and for most of the other elements, good agreement was achieved between the certified value and the observed value.

3.3. Application of the proposed method to multi-elemental determination in press cakes

The proposed method was applied to the determination of P, S, Cl, K, Ca, Ti, Cr, V, Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Ba and Pb in the press cakes of palm, castor, curcas, sunflower, fodder turnip, white lupin, rapeseed and pequi.

The results are presented in Table 6. The metal concentrations in the press cakes varied widely. One factor that may have contributed to this variation in the element composition is different plants presenting a variation in nutrient uptake. The availability of the element in the soil for uptake by the plants is another important factor to be considered. The availability depends on the soil cation exchange capacity, which may vary considerably with the type of soil, pH, and mineral composition. Other factors, such as the region of planting and harvesting of the crop, fertilization, irrigation water, and mycorrhizal fungi in the root zone must also be considered [30,31]. Certainly, all those factors are responsible for the concentration of the elements in the press cakes.

As noted before, the contents of some elements such Se, As, Pb, Cr, Ni and Cd in press cakes is an important factor for the assessment of the use of these by-products of biodiesel as organic fertilizer. In accordance with Brazilian regulation [15], the maximum

Table 6

TXRF mean elemental concentrations (mg kg⁻¹), standard deviation (mg kg⁻¹) and RSD (%) in press cakes.

Element	Palm		Sunflower		Fodder Turnip		Castor	
	Concent.(mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)
P	1038 ± 124	12	6339 ± 159	2.5	7853 ± 327	4.2	6524 ± 157	2.4
S	8933 ± 503	5.6	2717 ± 211	7.8	14,915 ± 479	3.2	2432 ± 283	12
Cl	45.0 ± 4.1	9.2	770 ± 10	1.2	442 ± 21	4.8	747 ± 30	4.0
K	5474 ± 854	16	11,315 ± 383	3.4	8891 ± 752	8.5	10,816 ± 703	6.5
Ca	12,394 ± 388	3.1	2104 ± 88	4.2	2549 ± 89	3.5	2344 ± 152	6.5
Ti	718 ± 159	22	17.3 ± 1.8	10	60.6 ± 12.1	20	10.6 ± 1.0	9.6
Cr	15.2 ± 2.0	13	5.9 ± 0.4	7.0	Nd		14.8 ± 1.0	7.1
V	Nd ^a		Nd		5.6 ± 0.7	12	Nd	
Mn	583 ± 27	4.6	28.7 ± 1.6	5.4	26.2 ± 1.2	4.7	18.9 ± 0.8	4.3
Fe	10,796 ± 1968	18	130 ± 9	7.2	690 ± 38.4	5.6	214 ± 8	3.6
Ni	6.20 ± 0.40	6.9	2.1 ± 0.1	5.0	10.1 ± 0.3	2.5	4.30 ± 0.50	11
Cu	12.7 ± 1.0	7.9	23.4 ± 1.3	5.5	4.50 ± 0.50	10	21.1 ± 0.9	4.1
Zn	29.5 ± 4.1	14	94.1 ± 4.3	4.6	48.9 ± 6.4	13	68.2 ± 3.9	5.7
Br	0.80 ± 0.10	15	1.40 ± 0.10	11	1.7 ± 0.4	24	Nd	
Rb	37.0 ± 7.7	21	15.4 ± 1.0	6.3	17.3 ± 0.5	3.0	23.2 ± 0.9	4.1
Sr	73.6 ± 2.4	3.3	8.40 ± 0.40	5.0	21.0 ± 1.0	4.8	5.80 ± 0.20	3.8
Ba	127 ± 43	34	Nd		Nd		Nd	
Pb	5.20 ± 2.60	49	Nd		Nd		Nd	
Element	Pequi		Curcas		White Lupin		Rapeseed	
	Concent. (mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)	Concent. (mg kg ⁻¹)	RSD (%)
P	758 ± 40	5.3	7828 ± 682	8.7	3586 ± 341	9.5	7785 ± 347	4.5
S	744 ± 58	7.8	3372 ± 188	5.6	2627 ± 339	13	4652 ± 253	5.4
Cl	982 ± 94	9.6	677 ± 30	4.5	386 ± 52	14	173 ± 7	4.2
K	6438 ± 716	11	9383 ± 390	4.2	9244 ± 862	9.3	7928 ± 480	6.1
Ca	706 ± 36	5.1	3486 ± 170	4.9	1614 ± 119	7.3	3897 ± 300	7.7
Ti	8.9 ± 0.6	6.5	11.1 ± 0.4	4.1	Nd		Nd	
Cr	4.1 ± 1.1	27	1.48 ± 0.04	3.1	Nd		Nd	
Mn	12.3 ± 0.6	5.2	21.3 ± 1.2	5.6	493 ± 12	2.5	53.0 ± 2.7	5.0
Fe	57.6 ± 8.3	14	207 ± 8	4.0	95.4 ± 14.2	15	68.7 ± 4.6	6.7
Ni	0.9 ± 0.1	8.1	2.7 ± 0.3	10	2.20 ± 0.20	9.2	1.20 ± 0.03	2.9
Cu	7.4 ± 0.4	4.7	19.1 ± 0.7	3.6	9.30 ± 1.00	11	4.10 ± 0.40	8.9
Zn	10.7 ± 0.9	8.5	129 ± 9.7	7.6	62.1 ± 0.7	1.1	54.3 ± 1.9	3.6
Br	2.22 ± 0.01	0.7	0.8 ± 0.2	26	0.90 ± 0.1	14	10.7 ± 0.6	6.0
Rb	13.3 ± 0.9	6.8	11.2 ± 1.0	9.3	8.5 ± 0.7	8.3	17.9 ± 2.1	12
Sr	2.3 ± 0.5	19	14.8 ± 0.9	6.1	15.0 ± 1.2	8.1	17.1 ± 1.0	6.0

^a Not detected.

values allowed for those elements are 80, 20, 150, 200, 70, and 3 mg kg⁻¹, respectively. The developed method is not selective to Cd in the presence of a high amount of K, so we cannot confirm its presence or absence in the analyzed press cakes only by TXRF. Selenium and arsenic were not detected. The concentrations of Ni and Cr were lower than the maximum allowed by regulation, and the same is true for Pb, as quantified in palm press cake.

The macro(Ca) and micronutrients (Mn, Fe Cu and Zn) have minimum concentration limits in organic fertilizer established by Brazilian legislation [14] of 10 g kg⁻¹, 0.5 g kg⁻¹, 2 g kg⁻¹, 0.5 g kg⁻¹, and 1 g kg⁻¹, respectively. The palm press cake presents concentrations of Ca, Mn and Fe and white lupin press cake presents a concentration of Mn above the minimum recommended for these nutrients. The other press cakes investigated present concentrations of these nutrients below the minima recommended by Brazilian legislation. Although no sample contains all micronutrients with the established minimum levels, this is no impediment to their use as organic fertilizers, as it just means that they cannot be considered sources of these nutrients. Thus, with respect to their nutrient content and low concentrations of contaminants, these press cakes could be used as fertilizers.

4. Conclusions

A method for the simultaneous determination of macro and trace elements in press cakes employing slurry sampling and TXRF was developed and evaluated. The ability of TXRF to quantify 18 analytes, including P, S, Cl and Br, for which the determination by other spectrometric techniques is more difficult, applying only a simple method of sample preparation, makes the technique very attractive and useful. The method is fast, consumes fewer reagents and takes place at room temperature, preventing analyte losses due to volatilization.

Limitations of the method such as overlaps of the Fe K β (7.059 keV) line with the Co K α (6.930 keV) and Pb L α (10.551 keV) line with As K α (10.543 keV) line and the necessity of very homogeneous samples must be overcome to ensure the analytical quality of the determinations. Another important limitation is the impossibility of determination of Cd at trace level in matrix with presence of K using Mo K α (17.5 keV) excitation source.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.talanta.2015.10.007>.

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