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Fast Assessment of Mineral Constituents in Grass by Inductively Coupled Plasma Optical Emission Spectrometry

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ABSTRACT

A method for evaluating inorganic constituents in the grass by ICP OES is proposed. The samples were digested with nitric acid plus hydrogen peroxide in a microwave system. Seventeen samples were collected in the metropolitan area of Curitiba and Castro in the Paraná State, Brazil. The following elements were studied: Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se and Zn. The linear coefficients of the curves were higher than 0.999 and the precision, expressed as the relative standard deviation, which was below 10%, being considered adequate. The accuracy was validated by using the recovery test (recoveries from 80 to 107%) and by the analysis of botanical certified materials. For one sample, two other digestion procedures, using two different mixtures of nitric and hydrochloric acids, produced results in agreement with the adopted procedure. Eleven out of the twenty studied elements could be quantified in real samples. High concentrations of Ca, K, Mg and P, the essential elements for bovines and other animals, were found. The results were evaluated using the principal component analysis that gathered the samples in three groups, according to the areas where the plants were grown.

Key words: ICP OES, Inorganic constituents, Acid digestion, PCA

INTRODUCTION

Grass plants are among the main fodder sources for bovines, being considered as a voluminous feed, growing rapidly in favorable conditions and presenting high contents of fibers and water. They also can provide the majority of the required nutrients, depending on the animal species, soil quality, plant fertility and age, among other factors. Efficient pasture management is required to guarantee the availability of the nutrients. Brazil has the biggest cattle herd in the world, with more than 95% of the animals being grown in pastures. Certainly, the milk and meet quality will depend on the grass composition, which should be known (Martuscelo et al. 2009; Souza et al. 2007).

For an adequate animal feed, inorganic nutrients or mineral compounds are required. Some of the nutrients are present in the grass as an inorganic salt, for example as $CaCO_3$ or as part of an organic compound, for example P in caseine. Usually, the nutrients are classified as macro constituents, such as Ca, K, Mg, Na and P and as micro constituents, such as Cu, Co, Fe, Mn, Mo, Se and Zn. The macro constituents are required in levels from 0.2% to 1% of the animal corporal mass, while the micro constituents are required from 0.001% to 0.05% of the corporal mass. Some of the mineral constituents are stored in the organism, such as Fe in the liver or Ca in the bones, while the nutrients that are readily soluble in water, such as Na and K, are not stored and must be supplemented

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continuously by the food. However, deficiency or toxicity symptoms can be verified for low or high constituent concentration, respectively. Selenium, Mo and Cu toxicity can lead to problematic feeding situations. Elements such as As, Cd and Pb can be present in the grass due to environmental pollution. The knowledge of the chemical composition of the grass certainly is very important for the producer and also for the consumer (Azevedo and Chasin 2003; Da silva et al. 2006; Euclides and Medeiros 2003; Nicodemo and Laura 2001; Trevizan et al. 2007). Inductively coupled plasma optical emission spectrometry (ICP OES), in comparison to other atomic spectrometric techniques, can be employed for the determination of a relatively large groups of elements in high or low levels of concentration. Specifically for grass, ICP OES was recommended for analyte detection and quantification (Li and Thornton 1993; Madejón et al. 2002; Alexander et al. 2006; Farfel et al. 2005; Melo et al. 2009). In this way, As, Bi and Sb were determined, after sample calcination at 450 °C for 6 h in the presence of $Mg(NO_3)_2$, using hydride generation (Li and Thornton 1993). Digestion with nitric acid in a microwave oven (Madejón et al. 2002) or in digestion blocks with controlled temperature were used for the determination of As, Cd, Cu, Ca, Fe, K, Mn, Mg, Ni, Pb, P, Tl and Zn (Alexander et al. 2006; Farfel et al. 2005). Nitric plus perchloric acids in digestion block were used for the determination of As (Melo et al. 2009). The goal of this work is the development of a method for the simultaneous determination of 20 elements in grass from the metropolitan area of Curitiba and Castro, in the State of Paraná, Brazil. The samples will be acid digested in a focused microwave system, prior to the analysis. The principal components analysis (PCA) will used for data interpretation.

MATERIALS AND METHODS

Instrumentation

The emission intensity signals, in peak height, were measured in an ICP OES instrument, model Vista Pro from Varian (Mulgrave, Australia), using the experimental conditions shown in Table 1. A focused microwave system, *Star* System 2 from CEM (Matthews, NC, USA) was employed for sample digestion. A mechanical Mill, model 3600 from Perten (Huddinge, Switzerland) was used to grind the samples previously dried in a drying oven model 400 ND from Nova Ética (Vargem Grande Paulista, SP, Brazil).

Table 1 – Instrumental parameters of the ICP OES.

Radiofrequency	40 MHz
Forward power	1.2 kW
Plasma gas flow rate	15.0 L min^{-1}
Auxiliary gas flow rate	1.5 L min^{-1}
Measurement mode	Peak height
Replicate read time	3 s
Instrument stabilization delay	35 s
Replicates	3
Torch	Quartz, axial view
Nebulizer type	Concentric glass K

Reagents and materials

All chemicals were of analytical grade, unless otherwise specified. High purity water (resistivity of 18.2 MΩ cm) was de-ionized in a Milli-Q system (Bedford, MA, USA). The following reagents were used: 65% v/v HNO_3 Suprapur® (Part nº 1.00441.1000); 30% v/v H_2O_2 (Part nº 1.07210.1000) and 30% v/v HCl Suprapur® (Part nº 1.00318.0250), all from Merck (Darmstadt, Germany). Aqua regia (HCl + HNO_3 3:1 molar ratio) and inverse aqua regia (HCl + HNO_3 1:3 molar ratio) were prepared by mixing the concentrated acids. Mono-elemental stock standard solutions containing 1000 mg L^{-1} of the analytes, from AccuStandard (New Haven, USA) were used to compose the multi-elemental standard solutions used for calibration, in the concentration range from 0.1 to 2 mg L^{-1} of the analytes in 10% v/v HNO_3.

Samples and reference certified materials

Seventeen samples of fodder grass were collected from April to May, 2010 in pastures in the metropolitan area of Curitiba (Campo Magro, Campo Largo and Bateias) and in Castro in the State of Paraná, Brazil. Among the samples, the following varieties were found: *Avena strigosa Schreb*, *Lolium perenne* and *Cynodon sp* and from the *brachiaria* gender. In the field, about 50 g of the plant was cut close to the root with an inox knife and kept in a plastic bag. In the lab, the plant samples were washed with de-ionized water and dried at 25 ± 2ºC until constant weigh (Li and Thornton 1993). The samples were then cut into small pieces, ground in a mechanical mill and stored in plastic bags, under the names G1 to G17, being G1 to G10 from the Curitiba area and G11 to G17 from the Castro area.

The following reference certified materials were analyzed: SRM 1515 (Apple Leaves) from the National Institute of Standards and Technology (NIST, Gaithersburg, MD, USA) and SRM 1573 (Tomato Leaves) from the National Bureau of Standards (NBS, Washington, DC, USA).

Sample preparation

An aliquot of about 0.5 g of the ground sample was weighed and transferred to the glass tube of the focused microwave system. Then, 5 mL of concentrated HNO_3 and 4 mL of concentrated H_2O_2 were added to the flask that was left standing for 12 h, before being digested in the focused microwave system under reflux, for 5 min at 110 ºC. The resulting solution was filtrated through a filter paper from JProlab, (No JP41, Curitiba, Brazil) and transferred to a 50 ml volumetric flask, before completing the volume with water. For comparison purpose, the G1 sample was also digested using 10 mL of aqua regia or inverse aqua regia.

Statistical program

The statistical program Statgraphics Plus 5.0 (Statgraphics Graphics Corp.,ST.SC., USA) was used for the principal component analysis (PCA).

RESULTS AND DISCUSSION

Sample digestion

Table 2 shows the obtained results for the analytes concentrations in G1 sample using the three mixtures, above mentioned, in the digestion. According to the pared *t-test*, at a 95% confidence level, the three results for each analyte are in agreement. The method using nitric acid plus hydrogen peroxide was adopted, only because the precision, expressed by the relative standard deviation, was somewhat better than for the other two mixtures. This experiment also indicates that the proposed method is accurate.

Table 2 - Obtained concentrations (average ± standard deviation) for the sample G1, mg kg^{-1} (minor and trace elements) and g/100g (major elements) in different media, n=3, dry weigh basis.

Analyte	**$HNO_3 + H_2O_2$**	**$HCl + HNO_3$ (3:1)**	**$HCl + HNO_3$ (1:3)**
Al	16 ± 1	16 ± 3	16 ± 2
As	< 2	< 2	< 2
Ba	1.7 ± 0.1	1.7 ± 0.2	1.8 ± 0.2
Ca (g/100g)	0.36 ± 0.01	0.36 ± 0.04	0.36 ± 0.01
Cd	< 0.1	< 0.1	< 0.1
Co	< 0.1	< 0.1	< 0.1
Cr	< 0.5	< 0.5	< 0.5
Cu	10.4 ± 0.9	9.9 ± 1.4	9.9 ± 0.1
Fe	181± 8	183 ± 7	176 ± 5
K (g/100g)	2.61 ± 0.02	2.64 ± 0.24	2.70 ±0.04
Mg (g/100g)	0.21 ± 0.01	0.21 ± 0.02	0.21± 0.01
Mn	74 ± 1	73 ± 1	73 ± 2
Mo	< 0.5	< 0.5	< 0.5
Na (g/100g)	0.046 ± 0.004	0.047 ± 0.004	0.041 ± 0.001
Ni	< 0.5	< 0.5	< 0.5
P (g/100g)	0.28 ± 0.01	0.27±0.01	0.28 ± 0.01
Pb	< 1	< 1	< 1
Sb	< 1	< 1	< 1
Se	< 3	< 3	< 3
Zn	38 ± 2	37 ± 2	38 ± 4
RSD, %	0.8-8.7%	1.4-18.8%	1-13%

Figures of merit

The figures of merit obtained for sample G1 are shown in Table 3, together with the analytical lines used for the intensity signal measurements. The intensity peaks for the G1 sample, not shown in this paper, were very similar to the intensity peaks for the standard solutions for the different analytes, also indicating absence of interference. Absence of interference was verified also for sample G2, by applying the recovery test and by the analysis of two certified reference materials, as described below. Certainly, the sample digestion and dilution allowed the interference free analysis of grass samples. The linear correlation coefficients of the calibration curves in 10% v/v HNO_3 were higher than 0.999, demonstrating good and adequate linearity. The limit of detection (LOD) and the limit of quantification (LOQ) were defined as the ratios 3s/b and 10s/b, respectively, where s is the standard deviation of 10 measurements of the blank and b is the slope of the calibration curve (Nolte 2003; Miller et al. 2000). The obtained limits, shown in Table 3, demonstrate that the proposed method is adequate for the determination of Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn in grass, with LOQ values going from 0.05 (Mg and Mn) to 1 mg kg^{-1} (Al, Fe and K). The linear range for all analytes was from the LOQ values up to 200 mg kg^{-1}. However, the proposed method is not enough sensitive for trace elements such as As, Cd, Co, Cr, Mo, Ni, Pb, Sb and Se, for which the concentrations were below the LOQ values (from 0.1 mg kg^{-1} for Cd to 3 mg kg^{-1} for Se), as it will be shown later, in the analytical application.

Table 3 - Figures of merit: slope of calibration curve, correlation coefficient (R), limit of detection (LOD) and quantification (LOQ) for 0.5 g of the sample in a final volume of 50 mL. Linear range up to 200 mg kg^{-1}.

Analyte	Lines, nm	Slope, (kg mg^{-1}s^{-1})	R	LOD, (mg kg^{-1})	LOQ, (mg kg^{-1})
Al	396.152	44500	0.99996	0.25	1
As	193.696	700	0.99998	0.5	2
Ba	455.403	193000	0.99999	0.03	0.1
Ca	422.673	125000	0.99959	0.02	0.1
Cd	226.502	37000	0.99999	0.02	0.1
Co	230.786	14200	0.99998	0.03	0.1
Cr	267.716	50400	0.99991	0.10	0.5
Cu	327.395	52600	0.99993	0.05	0.2
Fe	238.204	40100	0.99992	0.3	1
K	769.897	28100	0.99953	0.2	1
Mg	280.270	231000	0.99998	002	0.05
Mn	257.610	227000	0.99998	0.02	0.05
Mo	202.032	5900	0.99997	0.12	0.5
Na	589.592	274000	0.99987	0.2	1
Ni	231.604	5790	0.99997	0.1	0.5
P	213.618	1260	0.99996	0.8	0.5
Pb	220.353	2700	0.99995	0.3	1
Sb	217.582	850	0.9999	0.3	1
Se	196.026	381	0.99999	0.8	3
Zn	213.857	34000	0.99996	0.02	0.1

Precision and accuracy were evaluated for the G2 sample, which was enriched with 1% m/m of Ca, K, Mg, Na and P and 100 mg kg^{-1} of the minor components elements. The obtained concentrations are shown in Table 4. The relative standard deviations (RSD) were below 10%, indicating an adequate precision. The recovery values were from 80% to 107%, demonstrating a good accuracy (Miller and Miller 2000; Okada et al. 2007; Rosecrance 2005). The accuracy was further demonstrated by the analysis of botanical certified reference materials and the results are shown in Table 5. The recoveries of the certified values were between 83% and 119%, confirming the adequate accuracy of the proposed method. The obtained precision in the analysis of the certified materials was also adequate, confirming RSD values lower than 10%.

Table 4 - Recovery and RSD values for sample G2, enriched with 1% m/m of Ca, K, Mg, Na and P and 100 mg kg^{-1} of the minor component elements, n=7.

Analyte	Sample (n=3)	Enriched sample (n=7)	Recovery (%)	RSD, %
Al	6.0 ± 0.1	106 ± 1	100	0.9
As	< 2	97 ± 2	97	2.1
Ba	18.4 ± 0.4	113 ± 1	94	1.0
Ca (g/100g)	0.58 ± 0.02	1.56 ± 0.03	98	1.9
Cd	< 0.1	97.5 ± 1.2	98	1.2
Co	< 0.1	93.0 ± 1.3	93	1.4
Cr	< 0.5	96.5 ± 0.8	97	0.8
Cu	8.3 ± 0.3	103.0 ± 0.6	95	0.6
Fe	218 ± 5	298 ± 19	80	6.4
K (g/100g)	2.59 ± 0.02	3.67 ± 0.05	107	1.4
Mg (g/100g)	0.36 ± 0.01	1.35 ± 0.02	99	1.5
Mn	79 ± 3	168 ± 3	89	1.8
Mo	< 0.5	96.3 ± 1.0	96	1.0
Na (g/100g)	0.101 ± 0.001	1.110 ± 0.010	101	0.9
Ni	< 0.5	94.0 ± 1.1	94	1.2
P (g/100g)	0.33 ± 0.01	1.33 ± 0.014	100	1.1
Pb	< 1	93 ± 2	93	2.2
Sb	< 1	100 ± 1	100	1.0
Se	< 3	106 ± 2	106	1.9
Zn	29	130 ± 10	101	7.7

Table 5 - Analysis of botanical certified reference materials, mg kg^{-1} (minor and trace elements) and g/100g (major elements), n=3.

Analytes	SRM 1515		SRM 1573	
	Certified	Found	Certified	Found
Al	286 ± 9	321 ± 5	(1200)[a]	1100 ± 50
As	0.038 ± 0.007	< 2	0.27 ± 0.05	< 2
Ba	49 ± 2	48.1 ± 0.3	-----	48.9 ± 0.8
Ca (g/100g)	1.526 ± 0.015	1.55 ± 0.02	3.00 ± 0.03	2.97 ± 0.05
Cd	0.013 ± 0.002	< 0.1	(3)[a]	3.4 ± 0.1
Co	(0.09)[a]	0.1	(0.6)[a]	0.5
Cr	(0.3)[a]	<0.5	4.5 ± 0.5	3.8 ± 0.2
Cu	5.64 ± 0.24	5.5 ± 0.1	11 ± 1	9.4 ± 0.4
Fe	83 ± 5	81 ± 6	690 ± 25	678 ± 25
K (g/100g)	1.61 ± 0.02	1.44 ± 0.05	4.46 ± 0.03	4.62 ± 0.05
Mg (g/100g)	0.271 ± 0.008	0.26 ± 0.01	(0.7)[a]	0.61 ± 0.01
Mn	54 ± 3	50 ± 1	238 ± 7	235 ± 4
Mo	0.094 ± 0.013	< 0.5	-----	<0.5
Na	24.4 ± 1.2	29.0 ± 1.2	-----	479 ± 10
Ni	0.91 ± 0.12	0.94 ± 0.05	-----	0.77 ± 0.07
P (g/100g)	0.159 ± 0.011	0.16 ± 0.01	0.34 ± 0.02	0.35 ± 0.01
Pb	0.470 ± 0.024	< 1	6.3 ± 0.3	6.9 ± 0.1
Sb	(0.013)[a]	<1	-----	<1
Se	0.050 ± 0.009	< 3	-----	< 3
Zn	12.5 ± 0.3	12.9 ± 0.3	62 ± 6	64 ± 4
RSD, %		0.6-7.4%		1.1-9.1%
Recovery, %		89-119%		83-113%

[a] non-certified concentration.

Analytical application

Table 6 shows the obtained concentrations for the seventeen samples, after digestion using nitric acid and hydrogen peroxide under microwaves. For nine analytes (the non-essential elements As, Cd, Cr, Ni, Pb, Sb, Co, Mo and Se), the concentrations were below the quantification limits that could indicate that they were grown in non-contaminated environments. Usually, contaminants are more concentrated in the roots than in other parts of the plants, indicating poor translocation (Trevizam et al. 2007; Lamego and Vidal 2007).

Table 6 - Obtained concentrations (average ± standard deviation) for the seventeen samples, after digestion using nitric acid and hydrogen peroxide under microwaves, n=3.

Samples	***Al mg kg^{-1}***	***Ba mg kg^{-1}***	***Ca g/100g***	***Cu mg kg^{-1}***	***Fe mg kg^{-1}***	***K g/100g***	***Mg g/100g***	***Mn mg kg^{-1}***	***Na g/100g***	***P g/100g***	***Zn mg kg^{-1}***
G1	16 ± 1	1.7 ± 0.1	0.36 ± 0.01	10.4 ± 0.9	181 ± 8	2.61 ± 0.02	0.21 ± 0.01	74 ± 1	0.046 ± 0.004	0.28 ± 0.01	38 ± 2
G2	6.0±0.1	18.4 ± 0.4	0.58 ± 0.02	8.3 ± 0.3	218 ± 5	2.59 ± 0.02	0.36 ± 0.01	79 ± 3	0.101± 0.001	0.33 ± 0.01	29
G3	63 ± 6	8.3 ± 0.3	0.66 ± 0.01	7.0 ± 0.1	149 ± 8	1.35 ± 0.01	0.27 ± 0.01	38 ± 3	0.013 ± 0.001	0.37 ± 0.01	31 ± 1
G4	26.0±0.1	3.4 ± 0.3	0.49 ± 0.02	7.4 ± 0.7	111 ± 11	1.28 ± 0.03	0.40 ± 0.01	19.0±0.1	0.019 ± 0.001	0.31 ± 0.01	40 ± 4
G5	7.0 ± 0.1	1.0 ± 0.1	0.50 ± 0.01	8.5 ± 0.7	100 ± 6	0.87 ± 0.01	0.32 ± 0.01	72 ± 1	0.225 ± 0.002	0.31 ± 0.01	29 ± 1
G6	15.0 ± 0.1	11.4 ± 0.3	0.52 ± 0.02	7.4 ± 0.7	155 ± 3	1.51 ±0.02	0.34 ± 0.01	31.0±0.4	0.010± 0.001	0.32 ± 0.01	28 ± 1
G7	439 ± 45	9.4 ± 0.6	0.44 ± 0.02	7.4 ± 0.7	646 ± 52	3.38 ± 0.01	0.29 ± 0.01	140 ± 9	0.032± 0.002	0.370±0.011	24 ± 2
G8	137 ± 13	41.2 ± 0.1	0.28 ± 0.01	6.9 ± 0.1	456 ± 22	1.43 ± 0.07	0.33 ± 0.01	88 ± 9	0.011± 0.001	0.16 ± 0.01	42 ± 1
G9	274 ± 26	8.5 ± 0.2	0.55 ± 0.01	10.4 ± 0.7	617 ± 60	1.01 ± 0.01	0.40 ± 0.01	67 ± 2	0.0017	0.310±0.001	30 ± 2
G10	30 ± 1	3.7 ± 0.1	0.56 ± 0.01	7.9 ± 0.1	145 ± 2	3.72 ± 0.02	0.260±0.002	23 ± 1	0.008	0.300±0.002	28 ± 1
G11	145 ± 2	4.2 ± 0.2	0.55 ± 0.01	7.9 ± 0.1	154±1	2.98 ± 0.01	0.380±0.001	51 ± 1	0.022± 0.001	0.47 ± 0.02	26 ± 2
G12	265 ± 1	14.8 ± 0.3	0.62 ± 0.01	6.0 ± 0.1	203 ± 1	3.48 ± 0.04	0.57±0.01	29.0±0.3	0.012± 0.001	0.32 ± 0.01	28 ± 2
G13	57 ± 3	2.8 ± 0.2	0.25 ± 0.01	3.90±0.01	91 ± 1	2.16 ± 0.02	0. 370 ± 0.001	120 ± 2	0.0070±0.0001	0.050±0.001	17 ± 1
G14	83 ± 2	5.0 ± 0.2	0.34 ± 0.02	3.9 ± 0.1	114 ± 6	1.89 ± 0.04	0.42 ± 0.02	158 ± 4	0.0080±0.0002	0.060±0.001	18 ± 1
G15	61 ± 4	4.6 ± 0.1	0.39 ± 0.01	4.8 ± 0.3	112 ± 6	3.22± 0.01	0.43 ± 0.01	153 ± 6	0.010± 0.001	0.100±0.001	23 ± 1
G16	146 ± 5	1.80 ± 0.01	0.26 ± 0.01	6.9 ± 0.1	210 ± 12	1.81 ± 0.01	0.29 ± 0.01	88 ± 5	0.020± 0.001	0.090±0.002	38 ±4
G17	72±1	7.9 ± 0.4	0.60±0.01	6.6 ± 0.3	77 ± 3	6.94 ± 0.21	0.30 ± 0.01	19.0±0.1	0.019± 0.001	0.49 ± 0.01	26 ± 2

Eleven elements could be measured: Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, P and Zn. Certainly, Ca, K, Mg and P are the most important constituents. The PCA for the concentrations of these analytes is represented in Figure 1, where PC1 is the first principal component and PC2 is the second principal component (Dos Santos et al. 2008; Morgano et al. 1999; Yabe and Oliveira 1998). The PC1 is related mainly with Ca, Cu and P, while the PC2 is related to Al, Fe and Mn. As shown in the Figure, the samples are distributed in three groups. One of them gathers the majority of the samples (G1-G6 and G10-G12), being characterized by relative high concentrations of Ca and P, which are essential elements for the living being, and of Cu, important for the immunologic system. The samples from this group, except G11 and G12, were grown in the same Curitiba area, what explains its similarity concerning the elemental composition. The second group contains G7-G9 samples with relatively high concentrations of Al, Fe and Mn. They were grown in Campo Magro. The Al concentrations in all samples showed a great variability going from 6 to 439 mg kg^{-1}, indicating differences in acid of the soil (Wenzl et al. 2003). In the third group, involving samples G13-G15, they have a relatively high concentration of Mn, which in conjunction with P and Zn activate the animal enzymatic system. The samples of this group come from the Castro area, what could explain their similarity. Two samples, G16 and G17 from the Castro area, do not belong to any of the three groups. Samples G11 and G12 were also collected in Castro, but they were similar to the samples from the Curitiba area. Certainly, the PCA statistical tool can be very useful for understanding the elemental composition of plants, gathering the samples that show similarity in the concentrations of the constituents (Rocha et al. 2000; Schunke 2001).

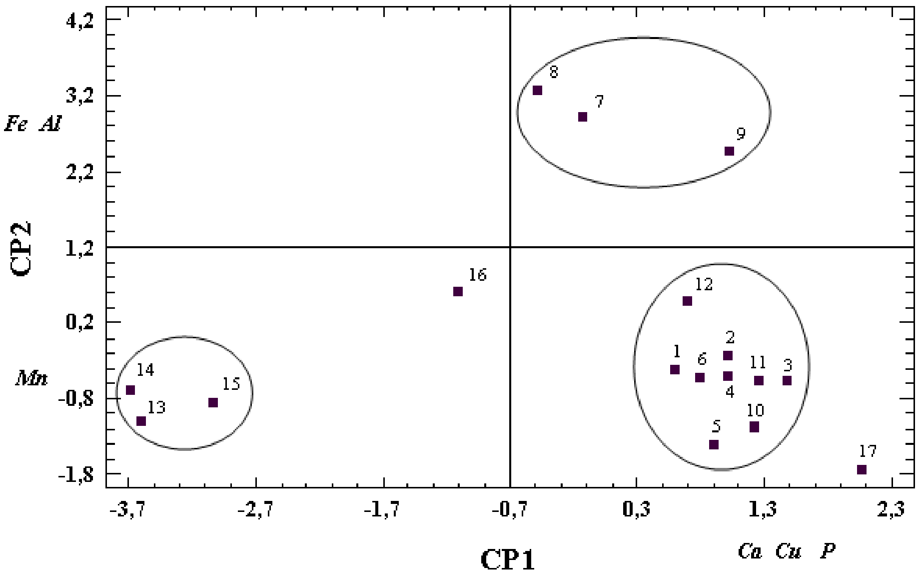

Figure 1 - Principal component analysis applied to the obtained concentrations for the seventeen fodder grass samples from the Curitiba and Castro areas.

CONCLUSIONS

The simultaneous determination of several elements in grass by ICP OES, following microwave-assisted sample digestion is proposed. Three different acid digestion mixtures produce results in agreement for a grass sample. The precision of the proposed method, measured by the relative standard deviation, is adequate. The method is accurate, as verified by the analysis of certified reference materials, by the recovery test and also by comparing different acid mixtures in the digestion. Eleven out of 20 studied elements could be determined, including the most important ones, concerning nutrition, such as Ca, K, Mg and P. The concentration of 6 non-essential plus 3 trace elements were below their quantification limits. The principal component analysis, applied to the concentration results for 17 grass samples, gather the samples in 3 groups according to their composition. The groups could be associated to different areas of plant culture. Most probably, the proposed method can be used for the analysis of other botanical samples.

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