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Multielemental analysis of agroindustrial by-products employed in animal feeding by INAA

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Instrumental neutron activation analysis (INAA) with gamma-ray spectrometry was applied to determine As, Ca, Cd, Cl, Co, Cu, Cr, Fe, Hg, K, Mg, Mn, Mo, Na, Sb, Se and Zn in the Brazilian agroindustrial by-products. These materials are widely used in ruminant feeding. The results obtained were compared with requirement and maximum tolerable concentrations. The general conclusions from the data obtained were: (1) many by-products presented concentrations of some essential elements lower than the requirement concentrations, while in some samples the concentrations of Cr, Fe, Mg and Se exceeded by a little the maximum tolerable concentrations, (2) the elements As, Cd, Hg and Sb, generally considered toxic, showed concentrations lower than maximum tolerable values.

Introduction

Agricultural and agroindustrial by-products are residues whose commercial prices are maintained by strong market demand. In Brazil, a great quantity of residues and by-products from both, agricultural and agroindustry are widely used in ruminant feeding.

Therefore, it is important to measure the mineral composition of these by-products because minerals are essential for growth, reproduction and health. In the last years, there has been much discussion that mineral deficiences or imbalances are involved in great economic damage. On the other hand, the greater part of fruits that produce the by-products are treated with insecticides to combat insects and diseases. These chemical products, in many cases, contain toxic elements in their molecular structure that may be absorbed by plants. Moreover, informations about mineral composition of most Brazilian agroindustrial by-products are scarce.

Monitoring for mineral composition of the following by-products was carried out by means of INAA: hulls of cotton, rice, soybean and wheat; fish meal; feather meal, meat meal, feather plus viscera meal; rinds of cotton, rice, orange; citrus pulp and tomato residue. INAA is a method particularly attractive for analyzing this kind of materials, because it involves a minimum of sample handling and it is, therefore, less prone to errors. This method has continually been applied to the analysis of biological materials, by a few researchers[1–3] during the recent years, for instance.

Experimental

Sample collection and preparation

Samples of agroindustrial by-products were collected in several sites of production. Most of the samples presented suitable granules for analysis (>80 mesh), except for citrus pulp and rind of orange that had to be ground. These samples were ground in a domestic mill that was composed of a polyethylene cup, titanium blades and metallic parts covered with PTFE, to avoid any kind of contamination from this process. Aliquots of these agroindustrial by-product samples weighing about 200 mg were sealed in clean polyethylene bags for irradiation.

Preparation of standards

Standard solutions of the elements were prepared by dissolution of the high purity metals, oxides or salt of the elements in suitable reagents such as HCl, HNO_3, HF or H_2SO_4. Alíquots of 25, 50 or 100 µl, depending on the solution concentration, were pippeted onto analytical filter paper (Whatman No. 41), of 1.5 cm^2 in surface area. After drying, these filter papers were placed into clean polyethylene bags. For the preparation of Hg standard, 100 µl aliquots of 2.0 $mg \cdot l^{-1}$ thioacetamide solution were pippeted onto filter paper before transferring the Hg solution. The thioacetamide and Hg form a stable compound, avoiding losses of Hg during the irradiation due to volatilization. The standards contained the elements and their masses as follows: As (7.6 µg), Ca (1735 µg), Cd (47 µg), Cl (252 µg), Co (1.1 µg), Cr (2.5 µg), Cu (53 µg), Fe (181 µg), Hg (1.0 µg), K (1000 µg), Mg (827 µg), Mn (3.2 µg), Mo (50 µg), Na (163 µg), Se (9.9 µg) and Zn (25 µg).

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Irradiation and gamma-radiation measurements

All irradiations were carried out at the IEA-R1m nuclear research reactor. The determination of the samples consisted of two parts.

(1) Determination of Ca, Cl, Cu, K, Mg, Mn and Na. Samples and standards were irradiated together in Nylon containers for 3 minutes. After irradiation, samples and standards were transferred to stainless steel planchets for gamma-ray measurement. Each sample was measured twice. In the first counting, the sample was measured for 4 minutes after a decay time of 2 minutes for the following radionuclides: ^{49}Ca (3083 keV), ^{66}Cu (1039 keV) and ^{27}Mg (1013 keV). The second measurement was carried out after a decay time of 90 minutes, to measure the gamma photopeaks emitted by ^{38}Cl (1643 keV), ^{42}K (1525 keV), ^{56}Mn (846 keV) and ^{24}Na (1368 keV).

(2) Determination of As, Cd, Co, Cr, Fe, Hg, Mo, Sb, Se and Zn. Samples and standards were irradiated together in an aluminum container for 8 hours. After 3 days of decay time, each sample and standards were transferred to proper containers for the first gamma-activity measurement. Each sample was measured for 3 hours to detect the following radionuclides: ^{76}As (559 keV), ^{115}Cd (336 keV), ^{197}Hg (77 keV), ^{99}Mo (140 keV) and ^{122}Sb (564 keV). A second measurement was carried out after 15 days decay time to detect the photopeaks of following radionuclides: ^{60}Co (1332 keV), ^{51}Cr (320 keV), ^{59}Fe (1098 keV), ^{203}Hg (279 keV), ^{75}Se (264 keV) and ^{65}Zn (1115 keV). The measuring time was about 8 hours. In the case of the ^{203}Hg activity, the contribution of ^{75}Se activity at the 279 keV photopeak was subtracted.

Measurements were performed using an EG&G Ortec POP TOP high resolution solid state Ge detector (Model 20190 P) with an energy resolution of 0.80 keV FWHM for the 122 keV peak of ^{57}Co and 1.80 keV for the peak of 1332 keV of ^{60}Co. The detector was connected to an ACE card, model 916A MCB, 8192-channel analyser. Data reduction was carried out using an IBM/PC microcomputer, and VISPECT 2 software in Turb Basic language was used for spectral analysis.

Results and discussion

The certified reference materials Rice Flour (NIES CRM 10C)[4] and Oyster Tissue (NIST SRM 1566a)[5] were analyzed to verify accuracy of the method. The precision of the results varied between 1 and 20% using the arithmetic means of four determinations. The accuracy in general was found to be approximately 5%, meaning that the results obtained are in agreement with the certified values.

Tables 1, 2 and 3 present the concentrations of essential macroelements, essential microelements and toxic elements, respectively, in the samples of agroindustrial by-products. The results presented are arithmetic means of three determinations followed by standard deviations.

Table 1. Analytical results for essential macroelements, as compared to the requirement and maximum tolerable concentrations (in mg·kg^{-1})

By-products	Ca	Cl	K	Mg	Na
Fish meal	69106 ± 3999	7544 ± 757	4071 ± 163	1818 ± 147	6829 ± 682
Feather meal	2967 ± 344	2581 ± 308	3436 ± 211	512 ± 17	169 ± 16
Meat meal	211725 ± 13188	3231 ± 21	2418 ± 328	3751 ± 160	7493 ± 207
Feat. plus viscer.	5738 ± 152	2386 ± 138	2900 ± 151	868 ± 176	1776 ± 25
Rinds of cotton	875 ± 148	288 ± 63	13532 ± 2090	1247 ± 252	22 ± 3
Hulls of cotton	1474 ± 80	478 ± 27	19043 ± 1764	4207 ± 733	30 ± 3
Rinds of rice	678 ± 52	597 ± 78	2749 ± 69	797 ± 116	26 ± 4
Hulls of rice	979 ± 136	96 ± 1	5556 ± 201	6684 ± 405	17 ± 1
Rinds of soybean	2731 ± 114	67 ± 3	23832 ± 1554	3341 ± 119	603 ± 15
Hulls of soybean	2185 ± 127	64 ± 2	27628 ± 2427	3306 ± 291	5 ± 1
Rinds of orange	7872 ± 503	503 ± 16	10965 ± 155	1295 ± 28	344 ± 2
Citrus pulp	14075 ± 252	133 ± 20	11813 ± 187	1332 ± 26	84 ± 5
Residue tomato	2601 ± 182	2208 ± 62	15404 ± 1508	2964 ± 143	265 ± 10
Requirement*	1800–10400	1000–1800	5000–7000	1000–2000	600–1000
Max. toler. conc*	–	40000–90000	30000	4000	90000

* Ref. 6.

Table 2. Analytical results for essential microelements, as compared to the requirement and maximum tolerable concentrations (in $\mu g \cdot kg^{-1}$)

By-products	Co	Cr	Cu	Fe	Mn	Mo	Se	Zn
Fish meal	119 ± 4	703 ± 144	<18	525 ± 7	24 ± 2	1.6 ± 0.2	2640 ± 386	168 ± 11
Feather meal	139 ± 18	1282 ± 8	27 ± 9	560 ± 22	18 ± 2	1.0 ± 0.1	557 ± 18	148 ± 5
Meat meal	88 ± 9	863 ± 18	<54	525 ± 10	4.9 ± 0.3	1.0 ± 0.1	<32	65 ± 4
Feat. plus viscer.	41 ± 1	764 ± 99	19 ± 1	254 ± 45	26 ± 1	1.0 ± 0.1	762 ± 43	97 ± 3
Rinds of cotton	61 ± 3	84 ± 18	2.3 ± 0.1	12 ± 2	11 ± 2	0.28 ± 0.03	42 ± 8	4.2 ± 0.3
Hulls of cotton	227 ± 17	150 ± 38	9 ± 2	110 ± 11	23 ± 4	0.53 ± 0.04	120 ± 2	45 ± 3
Rinds of rice	544 ± 12	293 ± 75	<11	31 ± 4	439 ± 51	0.31 ± 0.06	21 ± 2	12 ± 2
Hulls of rice	86 ± 6	315 ± 6	26 ± 3	170 ± 22	210 ± 13	1.4 ± 0.4	<74	138 ± 3
Rinds of soybean	188 ± 4	341 ± 37	21 ± 2	228 ± 26	44 ± 1	2.5 ± 0.1	<53	45 ± 1
Hulls of soybean	192 ± 5	81 ± 18	13 ± 1	157 ± 13	36 ± 3	2.5 ± 0.3	<0.2	45 ± 3
Rinds of orange	60 ± 1	1081 ± 82	41 ± 3	159 ± 13	8.5 ± 0.1	0.43 ± 0.01	69 ± 11	16 ± 1
Citrus pulp	391 ± 49	2196 ± 167	<8	2113 ± 154	35 ± 1	0.43 ± 0.04	154 ± 11	14 ± 1
Residue tomato	522 ± 23	1588 ± 239	8 ± 3	927 ± 78	51 ± 4	0.74 ± 0.03	53 ± 13	25 ± 1
Requirement*	100	–	10	50	20–40	–	100	30
Max. toler. conc*	1000	1000	100	1000	1000	5	2000	500

* Ref. 6.

Table 3. Analytical results for toxic elements as compared to the maximum tolerable concentrations (in $\mu g \cdot kg^{-1}$)

By-products	As	Cd	Hg	Sb
Fish meal	1846 ± 169	<900	128 ± 4	17 ± 3
Feather meal	434 ± 6	<400	15 ± 1	28 ± 1
Meat meal	1383 ± 130	<600	<390	40 ± 5
Feat. plus viscer.	1036 ± 21	<700	160 ± 4	16 ± 1
Rinds of cotton	31 ± 4	<300	45 ± 1	0.9 ± 0.5
Hulls of cotton	12 ± 2	<200	175 ± 6	5.5 ± 1.4
Rinds of rice	256 ± 14	<200	91 ± 14	15 ± 3
Hulls of rice	13 ± 0	<200	507	11 ± 3
Rinds of soybean	<0.3	<200	372 ± 76	<6.7
Hulls of soybean	<3.0	<100	186 ± 113	16 ± 7
Rinds of orange	8.2 ± 1.9	<100	155 ± 7	40 ± 1
Citrus pulp	128 ± 18	<100	196 ± 5	207 ± 31
Residue tomato	28 ± 3	<100	61 ± 2	16 ± 1
Max. toler. conc*	50000	500	2000	–

* Ref. 6.

Many agroindustrial by-products analyzed showed concentrations of Ca, Cl, K, Mg and Na lower than the required concentrations to maintain important vital functions of domestic animals (Table 1). Only the hulls of cotton and hulls of rice samples exibited higher concentrations of Mg than their maximum tolerable values.

The knowledge of the mineral composition in ration is important since deficiency and excess of macroelements in the cattle feed can be harmful to the animal growth. It can be considered that the agroindustrial by-products analyzed here generally satisfy the requirements of macrominerals for domestic animals. These by-products are important sources of feed the cattle mainly in dry season, when the forage become scarce.

Table 2 shows that elements Cu, Mo and Se are in larger deficiency in the agroindustrial by-products analyzed. In many cases the detection limit values were given for these two elements because their concentrations were very low. Other elements presented adequate concentrations as compared to the required values for domestic animals. In some samples the concentrations of Cr, Fe and Se exceeded by a little bit the maximum tolerable concentration.

The results for the elements As, Cd, Hg and Sb, often considered toxic, are presented in Table 3. All the samples presented Cd concentrations below their detection limits, which are reported in this work. The detection limits value was calculated according to KEITH et al.[7]

Conclusions

Instrumental neutron activation analysis was successfully applied to the determination of thirteen essential elements and four toxic elements in agroindustrial by products, allowing us to evaluate mineral contents in domestical animal feeding with sufficient accuracy.

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