J.RADIOANAL.NUCL.CHEM.,LETTERS 164 (4) 265-274 (1992)

NEUTRON ACTIVATION ANALYSIS OF THE DISTRIBUTION OF INORGANIC ELEMENTS AMONG FIVE VARIETIES OF BRAZILIAN CORN

M.J.A. Armelin, V.A. Maihara, M.B.A. Vasconcellos, D.I.T. Fávaro, V.F. Nascimento*

Radiochemistry Division,
Instituto de Pesquisas Energéticas e Nucleares,
Comissão Nacional de Energia Nuclear,
Caixa Postal 11049 - Pinheiros,
CEP 05499 - São Paulo - SP, Brasil

*Centro de Energia Nuclear na Agricultura,
Caixa Postal 96, CEP 13400 - Piracicaba - SP, Brasil

Received 21 January 1992
Accepted 29 January 1992

Instrumental neutron activation analysis (INAA) was applied to determine the elements Br, Ca, Cl, Cu, Fe, I, K, Mg, Mn, Na, Rb, S, V, Zn in five varieties of Brazilian corn, resulting from the studies carried out in order to increase their protein contents. The accuracy of the method was evaluated by means of reference material analysis. In general, the precision of the method was lower than 15%, except for Cu, I and S. Sensitivity and detection limit were also determined. Besides, tryptophan contents were determined. It was observed that the tryptophan content in improved corn samples was twice as large as in the normal samples. However, the same ratio was not observed in the inorganic element contents.

Elsevier Sequoia S. A., Lausanne
Akadémiai Kiadó, Budapest

INTRODUCTION

In the last years, researchers involved in the genetic improvement of corn, similarly to those from Wheat and Corn Improvement International Center, located in Mexico, have developed studies in order to increase the nutritive value of the protein contained in this foodstuff. Corn production with larger contents of lysine and tryptophan, two essential amino acids for the human diet and for animals such as swines and birds, was in this way attained.

In the present work, it is proposed to estimate the concentration of some important inorganic nutritient elements in five varieties of corn obtained as a result of these studies, as well as to verify whether a correlation between the contents of tryptophan and mineral elements exists or not.

Inorganic elements concentrations were measured by instrumental thermal neutron activation analysis. This method allows to obtain information about concentrations of a large number of elements simultaneously and it has been applied to the analyses of biological materials by several researchers[1-5] during the last years.

In this work the accuracy of the method was evaluated by means of reference material analyses.

At least four determinations were obtained for each element in each sample and, in this way, the precision of the method was estimated. Sensitivity and detection limit were also determined for all analyzed elements.

EXPERIMENTAL

Sample collection and preparation

Four of the corn samples used in this study were provided by the Genetic Department of Luiz de Queiroz Agronomy School (ESALQ), Piracicaba-SP, and another one by the Brazilian Company for Agropecuary Research (EMBRAPA). This last corn sample was planted in two different places and the product obtained was analyzed.

An aliquot of about 60 g of each kind of corn was picked up from the total amount of the sample, by quartering process. These aliquots were rinsed several times with distilled, de-ionized water to remove external impurities, and then dried at 50 ^{o}C for 72 h. After cooling to room temperature, samples were ground until all the powder passed through a 40 mesh sieve.

Aliquots weighing about 200 mg were sealed in clean polyethylene bags for irradiation.

Preparation of standards

Stock solutions of elements were prepared by dissolution of the elements, or their salts, spec-pure, in suitable reagents. Aliquots (20-100 µl) taken from such solutions were pipetted on analytical filter paper (Whatman No 42) for irradiation. After drying, filter papers were transferred to clean polyethylene bags.

Four sets of standards containing the following elements were prepared: 1.) Ca, Cu, I, Mg, S, V; 2.) K, Mn, Na, Cl; 3.) Rb, Zn; 4.) Br, Fe.

Irradiation and counting

Two types of irradiation were carried out. In one case, the sample and standard sets 1 and 2 were irradiated together in nylon tubes, for a period of 5 min; after a cooling period of 2.5 min, the following radionuclides were measured: ^{49}Ca, ^{38}Cl, ^{66}Cu, ^{128}I, ^{27}Mg, ^{37}S, while the radionuclides ^{42}K, ^{56}Mn, ^{24}Na were measured after 90 min. In the other case, the sample and standard sets 3 and 4 were irradiated together in aluminium tubes, for a period of 8 h. The counting was carried out after 3 d to detect ^{82}Br, and after 10 d to detect ^{59}Fe, ^{86}Rb, ^{65}Zn. The thermal neutron flux was approximately $3x10^{12}$ $n.cm^{-2}$ $.s^{-1}$.

Countings were carried out using a high resolution solid state ORTEC POP TOP Ge detector, with a resolution of 2.1 keV for the 1332 keV peak of ^{60}Co. The detector was coupled to a 4096-channel analyzer. Data reduction was carried out using minicomputers and one or both of the following softwares for spectral analysis: Program FALA[6] in BASIC language, and Program GELIGAM in ORACL language from Ortec.

RESULTS AND DISCUSSION

In order to check the validity of the method, the following reference materials, Rice Flour/NIES-CRM-10A and Citrus Leaves/NBS-1572, were analyzed. Results obtained in this work and values presented in the certificate of analysis[7,8] are shown in Table 1. Vanadium value remained uncertified in those reference materials.

Concentration of inorganic elements and tryptophan in corn samples are presented in Table 2. In general,

TABLE 1

Results obtained for Reference Materials Rice Flour (NIES-CRM-10A)[7] and Citrus Leaves (NBS-SRM-1572)[8]

Element	Concentration unit	No. of determinations	Mean ± SD This work	Published value
Br*	$\mu g\ kg^{-1}$	7	344 ± 28	300
Ca*	$mg\ kg^{-1}$	5	91 ± 15	93 ± 3
Cl*	$mg\ kg^{-1}$	4	312 ± 46	260
Cu*	$mg\ kg^{-1}$	5	4.6 ± 1.2	3.5 ± 0.3
Fe*	$mg\ kg^{-1}$	6	12.0 ± 1.3	12.7 ± 0.7
I**	$\mu g\ g^{-1}$	6	2.2 ± 0.5	1.84 ± 0.03
K*	$g\ kg^{-1}$	7	2.5 ± 0.2	2.8 ± 0.08
Mg*	$g\ kg^{-1}$	6	1.2 ± 0.2	1.34 ± 0.08
Mn*	$mg\ kg^{-1}$	5	32.9 ± 2.1	34.7 ± 1.8
Na*	$mg\ kg^{-1}$	6	10.7 ± 0.9	10.2 ± 0.3
Rb*	$mg\ kg^{-1}$	4	4.2 ± 0.2	4.5 ± 0.3
S**	$g\ kg^{-1}$	4	4.8 ± 1.3	4.07 ± 0.09
Zn*	$mg\ kg^{-1}$	6	25.6 ± 1.2	25.2 ± 0.8

*Rice Flour/NIES-CRM-10A[7].
**Citrus Leaves/NBS-SRM-1572[8].

the precision of the method was lower than 15%, except for Cu, I and S.

The alternative for getting a better precision for Cu and I results could be to decrease the Compton background, by means of radiochemical separations of the element to be determined. Since the element S does not present favorable nuclear characteristics for its activation with thermal neutrons, its sensitivity is low (Table 3).

A possible occurrence of systematic error might happen in the analysis of Mg since ^{27}Mg can also be pro-

TABLE 2

Results of analysis of inorganic elements in different varieties of corn by neutron activation analysis

Variety		ESALQ: VD-2 (Opaque)		ESALQ: VF-1 (normal)		ESALQ: VF-1: 2 (Opaque)	
Element Energy used, keV	Concentr. unit	No of determin.	Concentr. (mean±SD)	No of determin.	Concentr. (mean±SD)	No of determin.	Concentr. (mean±SD)
Br(776)	mg kg^{-1}	4	(4.2±0.3)	4	(6.5±0.8)	4	(0.45±0.06)
Ca(3083)	mg kg^{-1}	6	(76±12)	5	(67±11)	5	(46±9)
Cl(1642)	mg kg^{-1}	6	(657±87)	4	(929±185)	5	(474±71)
Cu(1039)	mg kg^{-1}	4	(26±5)	4	(12±3)	4	(15±3)
Fe(1099)	mg kg^{-1}	4	(28±2)	6	(25±4)	6	(20±3)
I (442)	µg kg^{-1}	4	(335±68)	4	(134±38)	4	(481±114)
K (1525)	g kg^{-1}	7	(4.4±0.2)	8	(3.7±0.2)	6	(4.1±0.2)
Mg(1014)	g kg^{-1}	7	(1.10±0.07)	8	(1.20±0.1)	6	(1.17±0.05)
Mn(846)	mg kg^{-1}	7	(6.7±0.9)	7	(5.3±0.3)	5	(7.8±0.4)
Na(1368)	mg kg^{-1}	7	(6.9±1.2)	6	(4.4±0.9)	5	(4.7±0.8)
Rb(1076)	mg kg^{-1}	6	(9.8±0.5)	6	(5.9±0.4)	6	(7.7±0.2)
S (3102)	g kg^{-1}	6	(1.7±0.3)	7	(1.5±0.3)	5	(2.5±0.5)
V (1434)	µg kg^{-1}	4	(28±6)	5	(31±5)	4	(32±4)
Zn(1115)	mg kg^{-1}	6	(24±2)	6	(19±1)	6	(23±1)
Tryptophan**	%	3	(0.108±0.007)	3	(0.065±0.001)	3	(0.110±0.004)

Variety		ESALQ: VD-2 (normal)		EMBRAPA: BR-451 (White)		EMBRAPA: BR-451 (White)	
Element Energy used, keV	Concentr. unit	No of determin.	Concentr. (mean±SD)	No of determin.	Concentr. (mean±SD)	No of determin.	Concentr. (mean±SD)
Br(776)	mg kg^{-1}	4	(15.2±2.9)	4	(0.93±0.05)	4	(0.95±0.06)
Ca(3083)	mg kg^{-1}	5	(51±3)	4	(68±13)	6	(83±6)
Cl(1642)	mg kg^{-1}	6	(761±77)	4	(2674±295)	5	(716±119)
Cu(1039)	mg kg^{-1}	4	(13±3)	4	(8 ± 1)	4	(17±4)
Fe(1099)	mg kg^{-1}	6	(22±3)	6	(14 ± 1)	4	(21±4)
I (442)	µg kg^{-1}	4	(482±69)	4	(179±25)	4	(210±53)
K (1525)	g kg^{-1}	7	(3.3±0.2)	7	(4.5±0.4)	7	(3.9±0.2)
Mg(1014)	g kg^{-1}	6	(1.03±0.04)	5	(1.39±0.07)	6	(1.30±0.10)
Mn(846)	mg kg^{-1}	6	(6.6±0.7)	6	(8.5±0.7)	6	(5.6±0.4)
Na(1368)	mg kg^{-1}	6	(3.8±0.5)	8	(2.7±0.4)	6	(2.7±0.5)
Rb(1076)	mg kg^{-1}	6	(6.5±1.1)	4	(6.6±1.0)	5	(7.8±0.2)
S (3102)	g kg^{-1}	5	(2.0±0.3)	5	(2.2±0.5)	4	(2.0±0.4)
V (1434)	µg kg^{-1}	6	(23±4)	6	(24±4)	4	(16±3)
Zn(1115)	mg kg^{-1}	6	(17±1)	4	(23±3)	4	(29±1)
Tryptophan**	%	3	(0.066±0.001)	3	(0.110±0.004)	3	(0.123±0.006)

*All results are reported on a dry weight basis.
**Tryptophan content determined in Laboratory of Proteins[9] Genetics Department - ESALQ.

TABLE 3

Sensitivities and detection limits for the elements analyzed

Element	Sensitivity, counts s^{-1} mg^{-1}	Detection limits, mg kg^{-1}
Br	2483	0.02
Ca	22	2.5
Cl	74	2.5
Cu	1331	0.35
Fe	15	2.0
I	13000	0.04
K	12	6.1
Mg	60	6.1
Mn	51000	0.002
Na	412	0.18
Rb	276	0.9
S	0.4	122
V	138000	0.005
Zn	272	0.15

duced from the reaction $^{27}Al(n,p)^{27}Mg$. In this work, standards of Mg and Al were irradiated under a thermal and epithermal neutron flux to check such interference, which was verified to be negligible.

Sensitivities and limits of detection within experimental conditions are shown in Table 3. Limits of detection were calculated according to Kaiser's[9] criterion.

The calculated limits of detection were practically the same for all varieties of corn, once the matrices are similar. Therefore, values shown in Table 3 are the averages of the limit obtained for each element in each sample.

CONCLUSION

In a general way, the micronutrient contents in the plants are consequences of the elemental contents of the soil and the environment where they are grown, although there is some selectivity in absorption by different plants[10]. Then, the differences found in the inorganic element contents for the five varieties of corn, analyzed in the present work, can be due to the characteristics of the variety and the place where corn was grown.

The effect of soil composition can be observed in the variety EMBRAPA-451 that was cultivated in two different places. In this case, significant differences were found between the contents of Ca, Cl, Cu, Fe, K, Mn, Rb, V and Zn.

It was observed that the tryptophan content in the improved samples was twice as much as the content of the normal samples. However, the same ratio was not observed in mineral element contents.

*

Authors are grateful to Prof. G.A. Torsello for his helpful analysis. The experimental work was partly supported by the IAEA and CNPQ.

REFERENCES

1. D.K. Teherani, J. Radioanal. Nucl. Chem., Lett., 117 (1987) 133.

2. I.L. Sziklai, M. Ördögh, E. Molnar, E. Szabo, J. Radioanal. Nucl. Chem., Articles, 122 (1988) 233.

3. R.M. Parr, J. Radioanal. Nucl. Chem., Articles, 110 (1987) 491.

4. V.A. Maihara, M.B.A. Vasconcellos, J. Radioanal. Nucl. Chem., 122 (1988) 161.

5. N. Lavi, Z.B. Alfassi, Analyst, 115 (1990) 817.

6. F.W. Lima, L.T. Atalla, J. Radioanal. Chem., 20 (1974) 769.

7. Nat. Inst. Environ. Studies (Japan), Certificate of Analysis, CRM-10A, 1989.

8. Nat. Bur. Stand. (U.S.), Certificate of Analysis, SRM-1572, 1982.

9. H. Kaiser, Anal. Chem., 42 (1970) 26A.

10. E. Epstein, Mineral Nutrition of Plants: Principles and Perspectives, John Wiley & Sons Inc., 1972.

11. E. Villegas, E. Ortega, R. Bauer, Metodos quimicos usados en el CIMMYT para determinar la calidad de la proteina de los cereales. Centro Internacional de Mejoramiento de Maiz e Trigo. El Baton, Mexico, 1982.