2009 International Nuclear Atlantic Conference - INAC 2009
Rio de Janeiro,RJ, Brazil, September27 to October 2, 2009
ASSOCIAÇÃO BRASILEIRA DE ENERGIA NUCLEAR - ABEN
ISBN: **978-85-99141-03-8**

PERFORMANCE OF IPEN-CNEN/SP NEUTRON ACTIVATION ANALYSIS LABORATORY FOR MICROELEMENT DETERMINATIONS IN PROFICIENCY TESTING

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ABSTRACT

The performance of Neutron Activation Laboratory, IPEN – CNEN/SP, was evaluated for the Ca, Fe, K, Mn, Na and Zn determinations in animal feed samples for ruminants through a proficiency test (PT) program. This PT program is organized by Embrapa Cattle Southeast to evaluate laboratories that analyze animal feed samples. Considering the fractions of satisfactory z-scores (%) of evaluated analytes to determine the laboratories performance, the general performance indicator obtained by IPEN – CNEN/SP ranged from 90 to 95% of the satisfactory results during the period of participation in the evaluation, four years.

1. INTRODUCTION

Proficiency testing (PT) is an important tool to evaluate the performance of analytical laboratories for quality assurance and to demonstrate the competence of laboratory staff to the accreditation bodies. One of the main purposes of PT is the identification of problems related to the analytical procedures and then if necessary, taking corrective or preventive actions. In addition, the participation in proficiency programs is a requirement of ISO/IEC 17025 (2001) Standard for accreditation and/or qualification of an analytical test by national or international regulatory agencies [1]. Proficiency testing involves regular circulation of test samples to be analyzed by laboratories participating in the program, and subsequent assessment of the resulting data by the organizing body.

Instrumental Neutron Activation Analysis (INAA) is a multielemental method relatively free from the matrix effect and therefore it has metrological quality [2]. The Neutron Activation Laboratory of Nuclear and Energy Research Institute (LAN – IPEN – CNEN/SP) has been actively participating in proficiency testing and inter-laboratory programs involving different types of matrices such as biological, geological and environmental [3].

This study presents the performance of the LAN – IPEN – CNEN/SP for the Ca, Fe, K, Mn, Na, and Zn determinations in animal feeds samples for ruminants over the last four years.

This program was organized by Embrapa Cattle Southeast. Currently, a total of 52 laboratories of different public and private sectors participate of the inter-laboratory comparison study, and they are proceeded from universities, governmental research centers, laboratories of Embrapa, and private companies, representing all the Brazilian regions [4]. The results of the analysis of forage, feedstuff and mineral supplement samples (two aliquots of each matrix) were used to monitor the laboratory performance in months of May, July, August and October from 2005 to 2008.

2. STAGES OF PROFICENCY TESTING: PROTOCOL AND PREPARATION OF MATERIALS

The organizational structure of this proficiency testing used operational procedures based on Brazilian Association of Technical Standards (ABNT NBR ISO/IEC 17025:2005 [5] and International Harmonized Protocol for proficiency testing in analytical laboratories [6]. Thus, for any kind of sample, the organization has done the following: the coordinator organized the preparation of material to make it homogeneous, and also its validation. The samples were distributed to participating laboratories according to a schedule. For each participant a set of 24 samples was sent divided into 4 batches. Each batch consisted of 6 samples: forage, feedstuff, mineral supplement and three reference samples (forage, feedstuff, mineral supplement). The schedule of transmission of results was always in the middle of May for batch-1, mid-July for batch-2, end of August for batch-3 and mid-October for batch-4. The results were sent via internet to the PT program coordinator in order to carry out statistical treatments to evaluate the performance of the laboratories.

Statistical evaluation was performed using the *z score* (Equation 1), recommended by the standards ABNT ISO/IEC GUIA 43-1 [5] and the International Harmonized Protocol for proficiency testing in analytical laboratories [6].

$$\mathbf{z = (x_i - X)/ s} \quad . \tag{1}$$

Where, "x_i" is the result informed by the participating laboratory, "X" is the median and "s" is robust standard deviation, both were calculated according to the literature [5, 6].

To evaluate the performance of the laboratory the following criteria were considered: - the result is satisfactory when $|z| \leq 2$, the result is questionable if $2 < |z| < 3$ and the result is unsatisfactory when $|z| \geq 3$. To calculate the indicator of performance of the laboratory (Equation 2) were considered the number of satisfactory results, the "questionable" results received weight one (1) and the unsatisfactory results, weight two (2).

$$\mathbf{ID\ (\%) = 100 - [N \times 100/ NE] - MP} \quad . \tag{2}$$

Where "ID" is the performance indicator, "N" is the number of questionable and unsatisfactory results, "NE" is the total number of results for all elements that were sent, and "MP" is the weighted average.

3. EXPERIMENTAL

3.1. Sample and Standards Preparation for the Analysis

Aliquots of about 200 mg of forage or feedstuff and about 40 mg of mineral supplement samples were weighed in a properly cleaned polyethylene vial using a Shimadzu AEM-5200 analytical balance. Standards of elements (Ca, Fe, K, Mn, Na, and Zn) were prepared by dilution of Spex certified standard solutions by an appropriate factor. The diluted standard solutions were pippeted onto Whatman filter papers, using Eppendorf variable volume pipettes. After drying, the elemental standards were placed in polyethylene vials in the same geometry of the samples. Simultaneously the moisture content in forage and in feedstuff samples was determined in order to present the results on dry weight.

3.2. Irradiation and counting

Two types of irradiation were carried out at the IEA-R1 nuclear research reactor. In first, samples and Mn standard were irradiated together in a polyethylene container for 20 seconds. After approximately 90 minutes the ^{56}Mn radionuclide was measured in the sample and in the Mn standard afterwards. In the second irradiation, the samples and standards (Ca, Fe, K, Na and Zn) were irradiated together in an aluminum container for 4 hours. The ^{47}Ca, ^{42}K, and ^{24}Na were measurement after a 3-day decay period, while ^{59}Fe and ^{65}Zn were measured after a 10-day period. The thermal neutron flux utilized ranged from 4 x 10^{12} to 1 x 10^{13} n cm^{-2} s^{-1}.

The equipment used to measure the gamma-radiation was Canberra hyperpure Ge detector (Model GX2020) coupled to an Integrated Signal Processor (Model 1510) and MCA System 100, both from Canberra. The detector used had a resolution (FWHM) of 0.9 keV for 122 KeV gamma-ray of ^{57}Co and 1.9 keV for 1332 keV gamma-ray of ^{60}Co.

4. RESULTS AND DISCUSSION

The performance indicator (ID) data obtained by the LAN – IPEN – CNEN/SP for the period 2005-2008, for determination of Ca, Fe, K, Mn, Na, and Zn contents in forage, feedstuffs and mineral supplement samples are shown in Tables 1, 2 and 3, respectively.

Table 1. Performance indicators (ID), in %, of the LAN-IPEN for Ca, Fe, K, Mn, Na and Zn contents in forages

	ID %				
Year	Round 1	Round 2	Round 3	Round 4	Mean
2005	85.7	85.7	100	71.4	85.7
2006	100	100	85	100	96.3
2007	NP	100	100	85.0	95.0
2008	85.0	85.0	100	100	92.5

NP- not participated

Table 2. Performance indicators (ID), in %, of the LAN-IPEN for Ca, Fe, K, Mn, Na and Zn contents in feedstuffs

	ID %				
Year	Round 1	Round 2	Round 3	Round 4	Mean
2005	100	100	100	100	100
2006	100	100	100	100	100
2007	NP	85.0	100	100	95.0
2008	100	100	85.0	85.0	92.5

NP- not participated

Table 3. Performance indicators (ID), in %, of the LAN-IPEN for Ca, Fe, Mn, Na and Zn contents in mineral supplements

	ID %				
Year	Round 1	Round 2	Round 3	Round 4	Mean
2005	85.7	100	100	60	86.3
2006	100	85.0	100	100	96.3
2007	NP	100	100	100	100
2008	100	100	59.0	100	89.8

NP- not participated

The annual performance of the laboratory was evaluated by calculating the arithmetic mean of the all ID data obtained in the year. This annual parameter was coded in this study as IDA. Figure 1 shows the annual performance indicator (IDA) in % of the LAN-IPEN. In general, the performance of LAN – IPEN – CNEN/SP, for the determinations of Ca, Fe, K, Mn, Na, and Zn in matrices as used in this study, was satisfactory (IDA > 90%). The number of results that were considered unsatisfactory was 3.

The main sources of errors in analytical results may be originated from the: quality of standards, irradiation geometry of standards and samples and interference of the method. A possible problem of interference that might occurs is the gamma ray spectral interference of Sc in the determination of Zn, mainly for mineral supplement samples in which the concentration of Sc is high. The peak of 1120 keV of ^{46}Sc interferes in the peak of 1115 keV of ^{65}Zn.

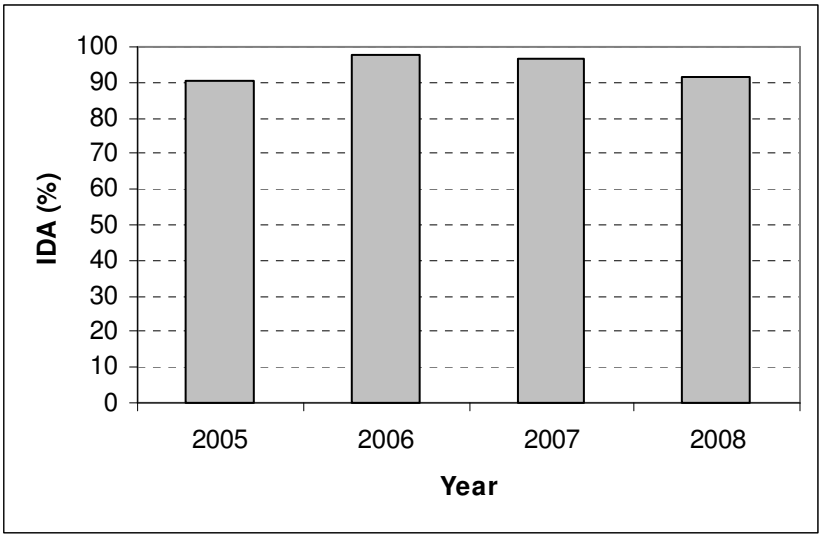

Figure 1. Annual performance indicator, IDA (%), of the LAN-IPEN.

5. CONCLUSIONS

This study demonstrated the good performance of the LAN – IPEN – CNEN/SP to determine Ca, Fe, K, Mn, Na and Zn in materials used in animal nutrition that contain large concentration ranges of these elements. The participation in the proficiency testing has been an important contribution to the continuous improvement of LAN – IPEN – CNEN/SP quality system.

ACKNOWLEDGMENTS

The authors wish to thank CNEN, EMBRAPA, CNPq and FAPESP from Brazil for financial support.

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