QUALITY ASSURANCE OF ANALYTICAL RESULTS IN ENVIRONMENTAL SAMPLES BY MEANS OF PARTICIPATION IN INTERCOMPARISON ROUND

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ABSTRACT

In developing countries, limited resources in the laboratories hinder quality assurance. One way to overcome this problem is to participate in international interlaboratory comparison rounds in order to asses the reliability and accuracy of the results, given by a particular laboratory.

Considering that nuclear analytical techniques play an important role in the determination of minor and trace elements in biological and environmental samples, we report the performance of our neutron activation analysis and x ray fluorescence laboratories and how these laboratories have improved the quality of their results by participating in international analytical programmes for environmental samples such as: sediments, air filters, soil, water, algae, and herbs.

The results of our participation in intercomparison round for quality assurance organized by AQCS-IAEA, and other institutes are presented, out of 103 reported results 91 were satisfactory.

1. INTRODUCTION

As a result of industrialization for improving human life quality, global environmental conditions have changed rapidly and the international concern on environmental pollution is very high. Therefore, accuracy and reliability in determination of toxic as well as nutrient elements in environmental samples including air, soil, and water are very important to understand the pollution problems. Instrumental neutron activation analysis (INAA) and the recently developed x ray fluorescence (EDRXF) have become two of the most powerful techniques for the non-destructive, simultaneous multielemental analysis of trace elements of environmental and biological samples.

In the last ten years our laboratories have participated in intercomparison rounds, for collaborative studies in candidate reference material, in proficiency tests, to trace systematic errors in the routine, to assure the reproducibility of our results, and; to demonstrate our analytical capacities, accuracy and bias.

Considering the ISO 17025[1] annual requirement for quality assurance, our laboratory participated in the IAEA activities under the AQCS programmes and others as shown in Table 1.

Table 1. Participation in Interlaboratory Comparison.

Date	Organizer	Kind of comparison	Sample
September, 1996	IAEA-AQCS[2]	Intercomparison run	IAEA-392 algae
February, 1998	IAEA- XRF Seibersdorf Laboratory[3]	Proficiency Test	IAEA SL-1 sediment
May, 2000	IAEA- Section of Nutritional and Health[4]	Quality Control Study NAT 7	Air Filter P and V
July, 2000	IAEA-ARCAL XXVI RLA/4/013[5]	Proficiency Test	IAEA SL-1
January, 2001	Institute of Nuclear Chemistry and Technology Warsawa-Poland[6]	Collaborative study on the determination of trace elements in two candidate reference material	Tea leaves, Mixed Polish herbs
April, 2002	IAEA-ARCAL RLA/80/31[7]	Exercise of intercomparison laboratory	Water 110402 A Water 100402 A
May, 2002	IAEA- Swedish International Food Administration[8]	Interlaboratory Test	Simulated diet D Carrot purée

As a result of many intercomparison rounds, enough useful information, to asses laboratory performance, are available.

2. FACILITIES AND METHODS

Facilities and equipments for k_0 based neutron activation analysis

The RP-10 IPEN Nuclear reactor's is a pool type reactor with a thermal power of 10 MW generated by a core containing MTR TYPE fuel element 20 % U-235 enriched (U_3O_8). Five control rods (fork type) made of Cadmium, silver and Indium are utilised to operate the reactor. Graphite and Beryllium reflector elements surround the core. Samples are irradiated in a well thermalized position about 15 cm. out the core, (Neutron flux 1.0 * 10^{14} n * cm^{-2} * s^{-1})

Analytical procedure

Samples were carried out by the k_0 neutron activation analysis method. Standard solutions containing 10000 μg Na were prepared, 250 μL or 50 μL of this solution were put into a polyethylene vials depending on irradiation time. Samples (about 100mg) also were prepared and put into polyethylene vials; sample and standard were encapsulated and irradiated, with a nominal thermal flux in the range 1.6 to 3 * 10^{13} n cm^{-2} s^{-1} and cadmium to epi-cadmium flux ratio about 66 and 33. Gamma spectrometry measurements were carried out with a CANBERRA GC1518 intrinsic Germanium detector with 1.8 keV of resolution and relative efficiency of 15 %, coupled to a CANBERRA 2025 amplifier connected to a CANBERRA S 100 multichannel card. Spectra mathematical processing was carried out using the DBGamma V 5.0 programme. F, α and saturation factor were calculated using macros developed in Excel. The concentration was done using a software developed at our laboratory.

Facilities and equipment of X Ray Fluorescence Energy dispersive

The System of Energy Dispersive of X Ray Fluorescence (EDXRF) has a spectrometer with ^{109}Cd source, an ORTEC Si-Li detector with a resolution of 190 eV at 5.9 keV, a multichannel PC card PCA-II Nucleus used for spectra analysis.

Analytical procedure

The sample was dried at 80 °C during 20 hr. About 1 g of dry sample was taken mixed with 0.1 g of pure cellulose, homogenised and pelletised, the pellets 25 mm of diameter were measured at the x ray fluorescence system using ^{109}Cd as a source during 56000 s, because of the low activity of the radioactive source (0.07055 mCi). The spectra evaluation was made using AXIL software and the element concentration calculated by elemental sensitivity method.

3. RESULTS AND DISCUSION

The results were reported according to the requirements of the organisers in nearly all of the events we reported for each of the six replicate required including their respective standard deviation. The results were evaluated considering the recommendations given by the Guide ISO/IEC 43 Proficiency Testing by Interlaboratory Comparison[9], and following the standard IAEA procedure for an interlaboratory comparison[6]. The results corresponding to our laboratories are shown in Fig. 1 to 11 and the discussion is centred on the unsatisfactory results. In order to asses the analytical process, six kinds of certificate reference material: SRM 1648, IAEA 336, BCR-CRM-320, NIST 1573 a, simulated diet A and NIST 679 were chosen as common environmental samples, the results for the reference material used in each event are shown in Tables 2 and 3.

Table 2 Analytical results (in mg/kg) for environmental reference material

Element	Lichen IAEA 336		Urban Particulate SRM 1648		River Sediment BCR-CRM-320	
	This work n = 6	Certified Values R. Values 95 %	This work n = 6	Certified Values	This work n = 6	Certified Values
Al	714	(680)	3.32 ± 0.07 *	3.27 ± 0.16 *	79.1 ± 3.7	76.7 ± 3.4
As	0.64 ± 0.05	0.63 ± 0.08	117 ± 6	115 ± 10		
Br	12.08 ± 0.8	12.9 ± 1.7	---	---		
Co	------	-----	17 ± 1	18		
Cr	0.98 ± 0.16	(1.06)	423 ± 11	403 ± 12	160 ± 3	138 ± 7
Cu	4.6 ± 0.7	3.6 ± 0.5	----	-----		
Fe	438 ± 45	430 ± 50	4.00 ± 0.15 *	3.91 ± 0.10 *		
K	1872 ± 183	1840 ± 200	1.04 ± 0.07 *	1.05 ± 0.01 *		
Mn	63.9 ± 4.2	63 ± 7	766 ± 0.18	(860)		
Na	317 ± 21	320 ± 40	------	--------		
Sb	-----	-----	48 ± 2	(45)		
Sc	----	------	6.6 ± 0.2	(7)		
Ti	----	----	0.40 ± 0.03 %	(0.4)		
V	1.47 ± 0.10	(1.47)	129 ± 4	140 ± 3		
Zn	32.7 ± 3.4	30.4 ± 3.4	0.48 ± 0.02 %	0.476 ± 0.014 %	157 ± 16	142 ± 3

( ) Reference value * results in %

Table N° 3 Analytical results (in mg/kg) for environmental reference materials

Element	Tomato leaves NIST 1573 a		Simulated diet A		Brick clay NIST 679	
	This work n = 6	Certified Values	This work n = 3	Certified Values	This work n = 5	Certified Values
Al	513 ± 82	(598)	---------	----------	10.81 ± 0.25	11.01 ± 0.34 *
As	-----	-----	--------	--------	9.4 ± 0.2	----------
Ca	4.8 ± 0.1 *	5.5 *	---------	----------	----------	----------
Cl	6694 ± 168	(6600)	---------	----------	----------	----------
Co	--------	--------	< 0.05	0.021 ± 0.01	26.2 ± 0.5	(26)
Cr	---------	--------	--------	----------	125 ± 31	109.7 ± 4.9
Cu	--------	--------	< 3	2.60 ± 0.15	----------	---------
Fe	--------	--------	86.25 ± 2.75	81.2 ± 4.8	9.48 ± 0.13 *	9.05 ± 0.21 *
K	2.60 ± 0.09	(246)	11943 ± 227	11222 ± 372	2.46 ± 0.03 *	2.13 ± 0.03*
La	2.39 ± 0.2	(2.3)	----------	---------	---------	---------
Mg	10.6 ± 0.02 *	(1.2)	----------	---------	0.85 ± 0.13 *	0.755± 0.009*
Mn	237 ± 4	(246)	5.53 ± 0.01	5.69 ± 0.47	1715 ± 29	(1730)
Na	128 ± 7	(136)	1731 ± 38	1613 ± 48	1356 ± 20	1304 ± 38
Rb	--------	--------	9.45 ± 0.84	8.85 ± 0.07	209 ± 11	(190)
Sb	--------	-------	--------	---------	1.1 ± 0.1	----------
Sc	0.09 ± 0.02	(0.1)	--------	---------	23.4 ± 0.4	----------
Ti	--------	---------	---------	----------	0.566 ± 736 *	0.577 ± 0.033*
V	0.93 ± 0.14	(0.835)	--------	---------	163.2 ± 8.6	---------
Zn	---------	-------	---------	---------	157 ± 16	(150)

( ) Reference value * results in %

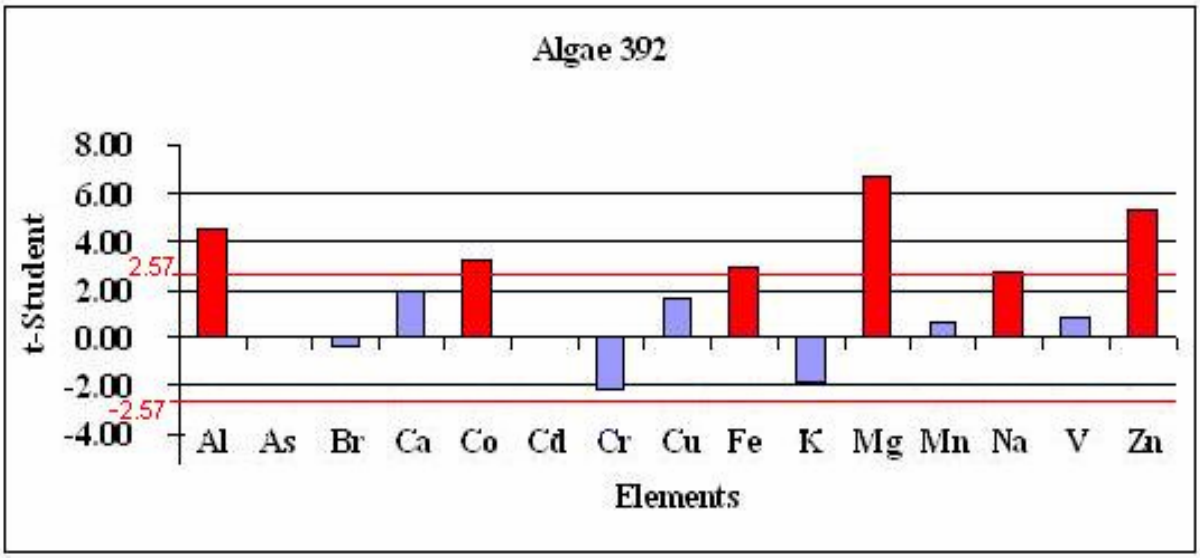

Figure 1. Evaluation by t-student of Algae 392 sample.

In order to compare our results with the intercomparison accepted mean, we calculated the t-student for Algae 392 sample, absolute values of t-student higher than 2.57 are considered an unsatisfactory. For 15 elements analysed, 6 had questionable results, which are shown as dark bars in Fig 1. The concentration of Al, Mg, Na and Zn were high due the influence of sample vial; this is a polyethylene material which contains: 29 μg of Al, 2.4 μg of Mg, 2.8 μg of Na and 58 μg of Zn and they were not discounted from the calculus; the methodology was changed afterwards in order to avoid this error The high value reported for Co to a radioactive contamination of the detector which was used at that time. The Fe value is the result of very poor statistic counting for that level of concentration.

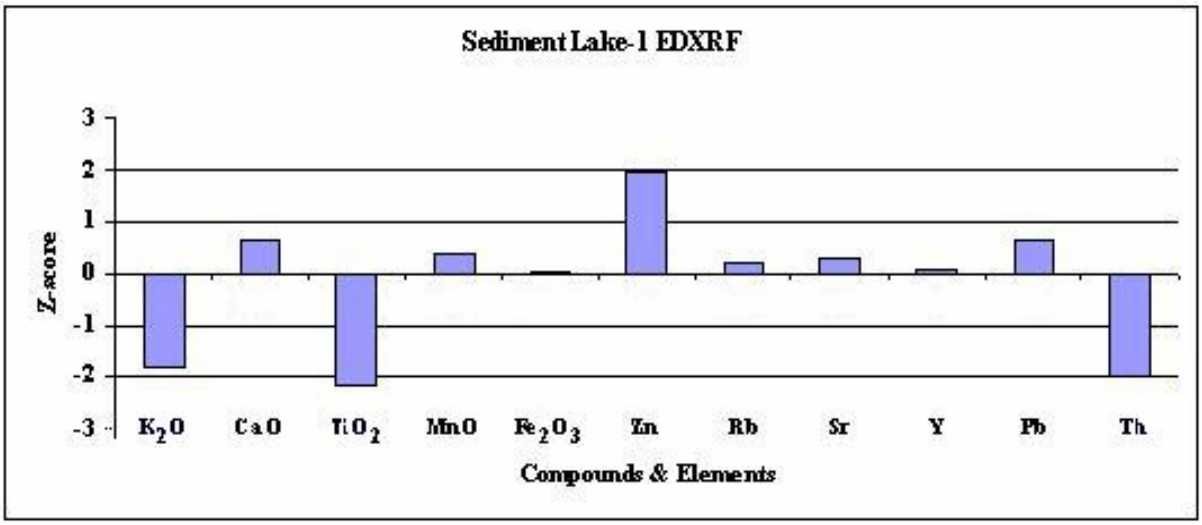

Figure 2. Evaluation by Z-score of IAEA SL-1 sediment by XRFDE.

Figure 2 shows the results of evaluation by Z-score for the proficiency test in trace elements in IAEA SL-1, sediment lake sample, there were not unsatisfactory Z-score so all determinations passed the test.

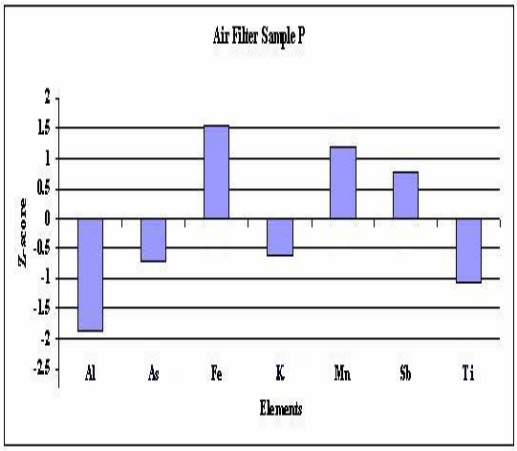

Figure 3. Evaluation by Z-score of air filter sample P.

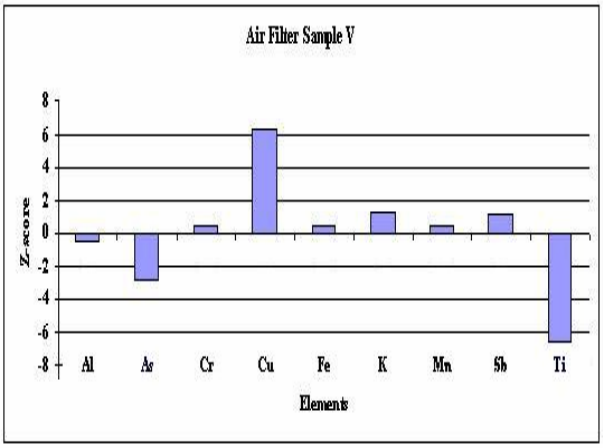

Figure 4. Evaluation by Z-score of air filter sample V.

Figure 3 shows the results of the NAT 7 quality control study, for the air filter sample P, we can observe that all results were satisfactory. In the case of the air filter sample V (Fig. 4) as the concentration of the elements were too low, we irradiated during 1800 s instead of our standard of 60 s in our routine procedures, this produced a high Cu concentration and low Ti concentration due to spectral interference of ^{56}Mn Compton edge, and an inadequate evaluation of ^{66}Cu at 1039 keV and ^{51}Ti at 320 keV.

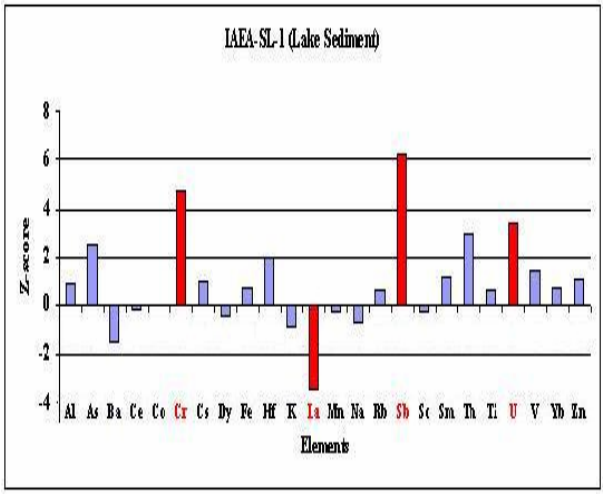

Figure 5. Evaluation by Z-score of IAEA SL-1 sample INNA-k_0

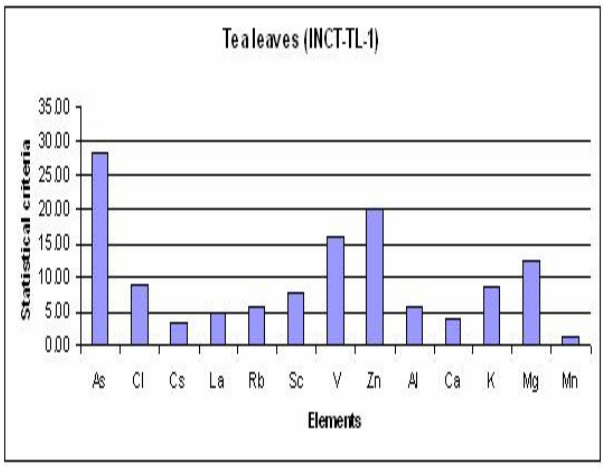

Figure 6. Evaluation by Statistical Criteria of Tea Leaves (INCT-TL-1)

In relation to the proficiency test in Lake Sediment sample IAEA-SL-1, 24 elements were reported, 4 of them were unsatisfactory (see Fig 5). Sb concentration was rather high because the contribution of ^{56}As at 562.8 keV in ^{122}Sb at 563.8 keV was not corrected. The Cr, U and La elements with low energy presented problems with the calculated efficiency curve then, they needed a new calibration in efficiency curve.

Figure 6 shows the evaluation of tea leaves (INCT-TL-1) sample, the results calculated according to statistical criteria[6], out of 13 results, 3 of them were unsatisfactory. The As and Mg were reported under limit of quantification, and the Zn was slightly high because the vials had zinc and we did not discounted.

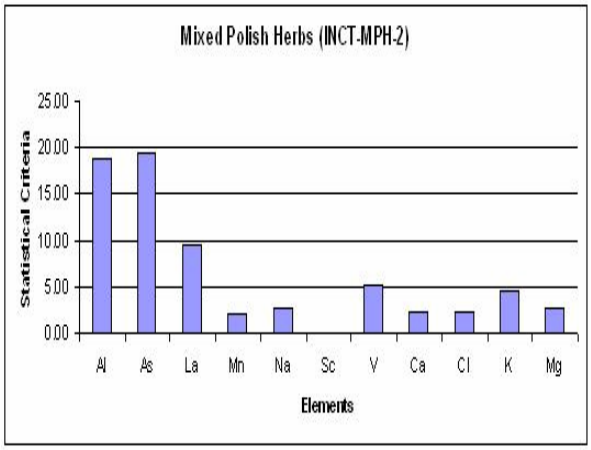

Figure 7. Evaluation by Statistical Criteria of Mixed Polish herbs.

The evaluation of the results according to statistical criteria of the mixed polish herbs (INCT-MPH-2) is illustrated in Figure7, all of 11 elements reported were satisfactory

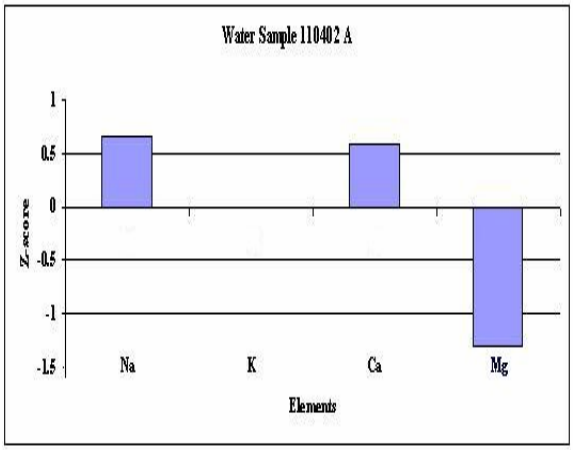

Figure 8. Evaluation by Z-score of Water 110402 Sample.

In relation of water sample (Figure 8) It shows, 3 out of 4 elements were satisfactory. The K value reported was also satisfactory because we reported K = <10 mg/L and the accepted value was 6.1 mg/L

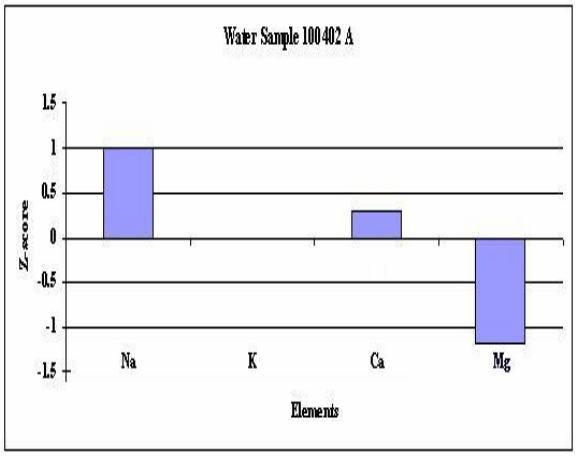

Figure 9. Evaluation by Z-score of Water 100402 sample.

Figure 9 shows the proficiency test for water samples, we did not have unsatisfactory results, inclusive K was satisfactory, because we reported result was K = <10 mg/L, and the accepted value was 0.63 mg/L

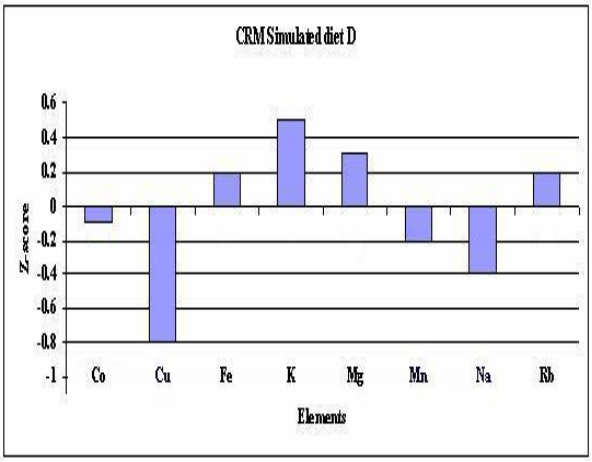

Figure 10. Evaluation by Z-score of Simulated diet D Sample.

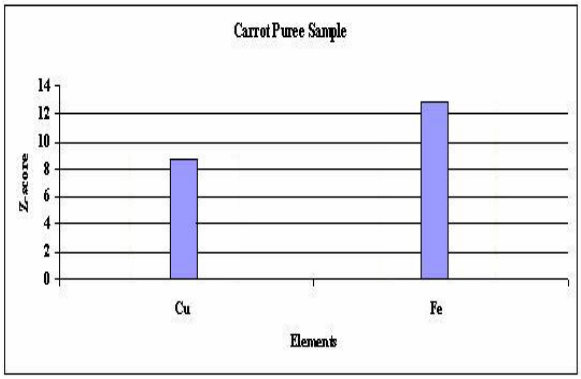

Figure 11. Evaluation by Z-Core of Carrot purée sample.

The proficiency test in food samples (Fig.10), CRM Simulated diet D sample illustrated we did not have unsatisfactory results and the carrot purée sample our reported results (Fig 11) were under limit of detection: Cu <2 mg/kg and Fe < 20 mg/kg, The accepted results were Cu = 0.515 mg/kg, and Fe = 2.386 mg/kg

Table 4. Shows the evolution of our performance along the time in which out of 108 reported results, 93 were satisfactory and, 15 unsatisfactory.

Z-score	1996 Sept.	1998 Feb.	2000 May	2000 July	2001 Jan.	2002 April	2002 May
Z < 3	9	11	14	20		8	10
Z > 3	6	0	2	4		0	0
Statistical Criteria IAEA <20% < 10%					21		
Statistical Criteria IAEA >20% > 10%					3		

4. CONCLUSIONS

In the last two proficiency test carried out in 2002, our result passed the test, showing that our quality control was improved, as we take into account all of our error sources.

The participation in this events allowed us to study the trackability, to know the budget of errors, improving them, to take the corrective actions and over all to be convinced that without a quality system under of the requirements of the ISO 17025 would have been more difficult to reach tangible conclusions about quality control.

5. ACKNOWLEDGEMENTS

The authors want to give our acknowledgements to the IAEA for giving us the opportunity of improving our results by its different programmes, activities and projects through experts, assessors and auditors.

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