AN OVERVIEW OF PROFICIENCY TESTING IN APPLICATIONS OF IONIZING RADIATION: CURRENT STATUS, SUCCESSES, SHORTCOMINGS AND FUTURE REQUIREMENTS. EXAMPLES FROM PRACTICE IN ROMANIA – 2006

Emanuela Cincu¹, Michael Woods²

¹IFIN-HH, 'Horia Hulubei' National Institute for Nuclear Physics & Engineering, Bucharest - Magurele, P.O. Box MG-6, Atomistilor Street no. 407, 077125, ROMANIA,
²Ionising Radiation Metrology Consultants Ltd, Teddington, Middlesex TW11 9PQ, UK
¹cincue@ifin.nipne.ro, ²mike.woods@blueyonder.co.uk

Abstract

Practitioners in the field of applications of Ionizing Radiation noted the unique prospects offered by this Conference and took this opportunity to bring together a wide and representative group from their own discipline of practitioners, providers of PT schemes and ILCs, reference materials and internationally measurement standards. They have explored existing practices and availability of suitable PT schemes, reference materials and standards. They have identified those areas where improvements are required, obstacles to improvements and produced recommendations that will benefit, primarily, their own discipline. These findings and recommendations are being brought to the attention of the wider community in order to share experiences and to assist in the harmonized development of proficiency testing for all practitioners.

An illustration of the above considerations stemming from the results obtained from three ILC exercises organized in 2005-2006 by the ‘ACTIVA-N’ Laboratory (IFIN-HH) in the field of peaceful applications of nuclear techniques is presented. The fields of applications envisaged: control of environmental and animal food radioactivity (a scheme of 5 labs. in Romania) and elemental analysis of stainless steel materials by two schemes: a national scheme of 3 Romanian labs which are employing nuclear, physical and chemical analytical techniques), and a European scheme composed of 5 nuclear laboratories. In all cases the U-score and Z-score criteria were applied for evaluating each laboratory performance.

Key words
Ionizing Radiation, Neutron Activation Analysis, Proficiency Testing, Inter-Laboratory Comparisons, Future Requirements, Harmonization
1 INTRODUCTION

Participation in Proficiency Testing (PT) exercises and Inter-Laboratory Comparisons (ILC) is an essential part of the measures taken by any competent organisation that conducts calibration or testing. Best practice demands that such organisations maintain quality systems that are accredited, by statutorily-recognised third party accreditation organisations, to comply with the requirements of ISO 17025 [1]. This international standard, in its Section 5.9, requires accredited organisation to “assure the quality of test and calibration results” and most accrediting organisations normally regard PTs and ILCs as being one of the most important means of achieving this. Ideally, these exercises will have target values which are directly traceable to relevant international (SI) standards. These standards are normally reproducible to a very high degree of precision.

Most scientific disciplines have developed their own schemes and protocols for such exercises and the field of applications of ionising radiation has been one of the leading disciplines in this respect. However, unlike most disciplines, ionising radiation standards are time-dependent (because of the radioactive decay process) and need to be re-established on a regular basis, the highest-level standards have a very limited activity range (less than two decades) for which direct, absolute standardisation methods are valid and, for many applications, relevant PT samples are a combination of several radionuclides of differing half-lives in a variety of chemical and physical forms, none of which match identically the routine samples that are encountered in testing. An obvious consequence of this is that the corresponding uncertainties on activity values in PT samples are relatively high (several percent) and it is virtually impossible to design PT samples which meet the needs of all, or even a large percentage of, users.

The practitioners in the field of applications of ionising radiation took this opportunity to discuss and address the particular requirements for PT and ILC exercises for their own discipline in order to highlight their particular concerns and requirements, to identify where improvements are required, the obstacles to improvements, and to produce recommendations. All of these are brought to the attention of the wider community, so that experiences can be shared with other disciplines and to assist in the harmonized development of proficiency testing for all practitioners in whatever discipline. Illustration of the PT/ILC exercises mentioned above and organized by the ‘ACTIVA-N’ Laboratory in 2006 in Romania and in the European area is given below.

2 FRAMEWORK FOR THE IFIN-HH PT/ILC - EXERCISES IN ROMANIA

The nuclear ‘ACTIVA-N’ Laboratory from IFIN-HH developed in the period 2004 - 2006 the national project no. 609, entitled “Multiple intercomparison schemes in the field of material and environment characterization by nuclear analytical techniques, extended at the European level”, within the frame of the national Program ‘INFRAS’ of the Romanian Ministry of Education & Research, which aims to implement and develop the Quality Management System in the practice of all the analytical Laboratories, whether they are involved in research or in control routine activities. The project envisaged: (1) to identify (a) if the experience of our institute might be helpful to the younger laboratories or other ones from Romania which developed,
during the last years, routine procedures for activity control in environmental samples and animal food by the nuclear $\gamma$-ray spectrometry technique according to the EC Directives; (b) to point out if the Neutron Activation Analysis technique (NAA) performance is comparable with that of other physical and chemical analytical techniques, which are currently employed in the control of the Stainless Steel charges produced in some Romanian metallurgical plants; and (2) to compare the performance of two nuclear NAA Romanian Laboratories in the elemental analysis of a special High Alloy Stainless Steel (SS 1) sample produced by the Swedish Institute for Metal Research (SIMR-KIMAB) with that obtained by similar NAA Labs. from other European countries, in order to identify (if they exist) possible discrepancies stemming from the different irradiation and standardization conditions. Another aim was to compare the performance of the whole NAA group to that of Laboratories employing atomic spectroscopy techniques, which are accepted by the European Commission for material certification; those results were obtained by the Swedish Institute SIMR - KIMAB within the frame of the International PT exercise they had launched in 2005 for analysis of the SS 1 sample.

In 2005, the ‘ACTIVA-N’ Laboratory initiated the first European mini-network of 5 NAA Labs comprising 2 from Romania (ACTIVA-N from IFIN-HH, and INR - Mioveni), and 3 others from Belgium, Hungary and Poland, having the above objectives, after we took part in the SIMR-KIMAB international PT exercise. As a consequence, it was possible to discuss all results with the NAA Labs and SIMR-KIMAB representatives, in Bucharest, at the 1st International Workshop “IWRAD-2005” (June 3-5, 2005), including comparison with the results obtained by atomic techniques. Full details will be published in October 2007 [2]. Only a summary of the results is presented here.

The NAA Network exercises continue at a high performance level with a new ILC in 2007 with results presented in the 2nd International Workshop on "Application of Ionizing Radiation & Nuclear Analytical Techniques in Industry, Medicine and Environment at High Performance" (Nuclear PT-2007), in Bucharest, October (6)7-9. All the mentioned PT/ILC exercises were initiated and developed within the frame of the INFRAS project no. 609 of the Romanian Ministry of Education & Research.

3 EXPERIMENTAL CONDITIONS AND PROCEDURES

3.1 PT/ILC Exercise by Gamma-ray Spectrometry

5 laboratories from Bucharest and other towns took part in the exercise. Three are involved in routine activity control of animal food and of some environmental and other radioactive materials by using the Gamma-ray Spectrometry technique. The material used was IAEA Soil 375, a certified material prepared by the IAEA Seibersdorf Laboratories for quality control of nuclear laboratories results. We distributed to participants 5 similar samples each comprising 100 g (the reference quantity) radioactive soil (maximum available amount of material), carefully put in identical Plexiglas boxes ($\phi$: 72 mm, h: 25 mm), and coded Lab.1 G-Spec ...Lab.5 G-Spec; the amount of soil in each box was weighed with high precision ($2 \times 10^{-3}$ %). Some laboratories used NaI(Tl) detectors, others used HPGe detectors. Preparation of standards, measurement protocols and results evaluation were those currently used by each laboratory. A common reference date (1 June 2006) was used.
3.2 PT/ILC Exercise on SS elemental composition (national scheme)

The 3 participants were 2 Romanian physical-chemical laboratories (Labs. PhC1 and PhC 2) in institutions producing SS materials and ‘ACTIVA-N’ Laboratory (IFIN-HH) which used the nuclear INAA analytical technique (no radiochemical processing). The sample was a high alloy certified material, type EURONORM-CRM No. 298-1 DUPLEX Stainless Steel (code SS CRM - D), from the Swedish KIMAB Institute for Metal Research. The original bottle was re-dispensed to provide samples for the two national partners (an amount of 10 g) and the ACTIVA-N (70 mg for 2 samples). Analysts in the physical-chemical labs applied their usual standardized chemical methods for different elements. They also used the Atomic Absorption Spectrometry technique for some elements, according to their own expertise and protocols.

The INAA procedure at ACTIVA-N comprised simultaneous irradiation in the nuclear reactor TRIGA at INR-Pitesti of samples and standards in a common small package. The stack contained 3 samples from the unknown SS-D material, and 2 standards of SS EURONORM-CRM No. 231-2 Stainless Steel (code SS-Z) from the BAM Institute. The sample mass varied between 30 and 35 mg. After irradiation, the gamma-ray spectrometry of the samples and standards identified the elements in the original material indirectly by identifying the gamma-rays emitted by the radionuclides generated by neutron reactions with the atomic nuclei of each element in the sample. 12-run sample and 16-run standard measurements assured sufficient precision to evaluate the radionuclide activities and, from there, the element concentrations.

3.3 PT/ILC Exercise on SS elemental composition (European scheme)

5 NAA laboratories participated: ACTIVA-N, Romania: Institute of Nuclear Research (INR) Pitesti, Romania: SCK-CEN Nuclear Centre, Belgium; Budapest Technical University, Hungary; Institute for Nuclear Chemistry &Technology, Warsaw, Poland. The samples comprised a special high alloy Stainless Steel material (code SS - 1) from KIMAB and each partner received of approx. 5.5 g from the original bottle. Each lab applied the INAA procedure according to its own protocols, irradiation conditions, gamma-spectrometry analyses and standardization procedures. However, the irradiation by thermal neutrons (fluence rate of $10^{12-13}$ n·cm$^{-2}$·s$^{-1}$) and the gamma–ray spectrometric analysis were performed in similar conditions. It is known that the NAA technique, if based on analysis of delayed gamma-rays, as happened in our case, is limited with regard to light elements (C...Al), but it is well applicable with high accuracy to the analysis of metallic elements. The list of elements identified by the 5 NAA labs by neutron activation comprised: $^{23}$V, $^{24}$Cr, $^{25}$Mn, $^{26}$Fe, $^{27}$Co, $^{28}$Ni, $^{29}$Cu, $^{33}$As, $^{42}$Mo, $^{51}$Sb, $^{74}$W. In the case of Romanian laboratories, Ni was better studied by using the fast neutron activation (Ni $\rightarrow$ $^{58}$Co).

4 RESULTS AND DISCUSSIONS

4.1 PT/ILC Exercise by Gamma-ray Spectrometry

Table 1 presents the synthesis of the experimental results obtained by participant laboratories in the analysis of the Soil-375 material, values of the IAEA certified reference activities of the two radionuclides $^{137}$Cs and $^{40}$K in the sample, corrected to
a reference date of June 1\textsuperscript{st} 2006. Evaluation of results was based on $u_{\text{score}}$ criteria and specific values/limits are included for easier interpretation of the results. The results were reasonably good. However, generally, they show a systematic deviation from the reference values. Discussions with participants revealed that the discrepancy factor may stem from the difference in the radioactive geometry of standards and samples, which is known to be significant when the sample–detector distance is very reduced. However, as other factors may also influence the results (the standard activity, bias of the electronic apparatus, measurement geometry, calculation procedure, etc.), it is necessary to check each step together with an experienced specialist, or/and to take part in training courses applied to that topic.

4.2 PT/ILC Exercise on SS-D elemental composition (national scheme)

Table 2 presents the comparative synthesis of the experimental results obtained by the 3 participant laboratories, the reference concentration values for the elements in the SS-D material, and the $u_{\text{score}}$ values for each laboratory. The results of our partners from industry present interesting results: a lot of elements got an excellent, or very good, or a good $u_{\text{score}}$, indicating that the methods for elemental analysis are appropriate and correctly employed. However, there are some other elements whose $u_{\text{score}}$ is out of range. In those situations, it would be helpful first to control every step of analysis, in order to identify the discrepancy source, and (if no error was revealed) it is worth investigating the operating conditions of the equipments, the calibration procedures and – finally – the adequacy of the analytical methods applied to those elements.

4.3 PT/ILC Exercise on SS-1 elemental composition (European scheme)

The results obtained in the ILC exercise were studied using the z-score parameter, although the number of laboratories was not high. The expression of the z-score parameter, according to the reference Standards [4,5] and documents [6], is the following:

\[
    z = \frac{X_{\text{Lab}} - X_{\text{Ref. assigned}}}{s}
\]

where $X_{\text{Lab}}$ is the element concentration value provided by each INAA Laboratory; $X_{\text{Ref. assigned}}$ is the value assigned as the Reference; and $s$ is the ‘fitness-for-purpose’ standard deviation [5, 6], which was established in this work as $s_{n-1}$, as this is the relevant parameter with regard to the spread of the experimental results.
<table>
<thead>
<tr>
<th>Nr. nrt</th>
<th>Radio nuclide</th>
<th>C&lt;sub&gt;ref&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;ref&lt;/sub&gt; (Bq/g)</th>
<th>C&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;score&lt;/sub&gt;</th>
<th>C&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;score&lt;/sub&gt;</th>
<th>C&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;score&lt;/sub&gt;</th>
<th>C&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;exp&lt;/sub&gt; (Bq/g)</th>
<th>U&lt;sub&gt;score&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>40K</td>
<td>0.424</td>
<td>0.008</td>
<td>0.567</td>
<td>0.051</td>
<td>1.62</td>
<td>0.363</td>
<td>0.009</td>
<td>5.2</td>
<td>4.87</td>
<td>0.16</td>
<td>6.26</td>
<td>5.032</td>
<td>0.283</td>
<td>4.25</td>
</tr>
<tr>
<td>2</td>
<td>137Cs</td>
<td>3.796</td>
<td>0.058</td>
<td>3.24</td>
<td>0.05</td>
<td>5.8</td>
<td>4.993</td>
<td>0.56</td>
<td>2.12</td>
<td>4.67</td>
<td>0.21</td>
<td>4.88</td>
<td>4.902</td>
<td>0.22</td>
<td>4.12</td>
</tr>
</tbody>
</table>

1. Updated values from the IAEA Certificate / 1991 for Soil 375

- Interpretation: using the evaluation criterion \( E_n^* \) and \( u_{score}^** \) whose definition is: \( u_{score} = E_n = \frac{|X_{analist} - X_{ref}|}{\sqrt{(u_{analist})^2 + (u_{ref})^2}} \)

- \( E_n \leq 1 \) - accepted values
- \( E_n > 1 \) - unaccepted values

- For the case of \( E_n \geq 1 \), the results are better interpreted using \( u_{score}^** \) (used by IAEA and NPL Laboratories):

  - If: \( u < 1.64 \), values do not differ significantly; - "Class: 0, excellent"
  - \( 1.64 < u < 1.96 \), values probably do not differ significantly, more data are required to confirm; - "Class: 1, very good"
  - \( 1.96 < u < 2.58 \), cannot say whether there is a significant difference without further data; - "Class: 2, good"
  - \( 2.58 < u < 3.29 \), values probably differ significantly but more data are required to confirm this; - "Class: 3, accepted"
  - \( u > 3.29 \), the values differ significantly; - "Class: 4, not accepted"

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Table 2 - Results of the PT/ILC exercise on the High Alloy Stainless Steel material (code SS-D)

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Elem</th>
<th>C_{ref} (w/w) (%)</th>
<th>C_{lab 1} (w/w) (%)</th>
<th>C_{lab 2} (w/w) (%)</th>
<th>U_{E{ph-abs}}</th>
<th>U_{score}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>2</td>
<td>Mn</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>3</td>
<td>Cr</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>4</td>
<td>Co</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>5</td>
<td>Cu</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>6</td>
<td>W</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>7</td>
<td>As</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>8</td>
<td>Mo</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
<tr>
<td>9</td>
<td>Ni</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
<td>0.00006</td>
</tr>
</tbody>
</table>
The consistency of the experimental results [2] obtained at five laboratories in four different countries was remarkable as the z-score values of 7 elements (V, Cr, Mn, Fe, Ni, As, W) were \( \leq 1.3 \), and for Co, Cu, Mo, Sb were < 1.55, lower than the warning limit of results (\( z = 2 \)). Agreement between the INAA results was also remarkable for Co, Mo, and Sb. The fact that each laboratory had implemented a Quality Management System in its activity and that four have already got accreditation of competence according to the EN ISO /IEC Standard 17025, may account for the final good results.

5 CONCLUSIONS

The common conclusion which may be drawn from all the 3 mentioned experiences is that each of them was very useful [3], both for participants and for the organizer. It is particularly important to learn in time if the measurement procedure must be improved or corrected for some errors, before some future wrong results are claimed by someone and/or become dangerous, with regard to radioactive contamination, or other effects; it is also important to be confident that your laboratory results are correct.

It is also highly important and useful to have proof as to which analytical method provides the most reliable results, for which elements, and to know which method(s) should be improved/corrected.

With regard to the effect of the third ILC exercise, the primary conclusion is that for common works at the European level, participation in European/international exercises should be compulsory to ensure confidence in both ones own and common works, as well as for giving confidence to any beneficiary who require analysis/investigation of any samples, or for other further research purposes.

In the case of the European scheme, the NAA results proved the usefulness of the NAA method in material certification, especially in case of low concentration levels where the overall combined measurement uncertainty assured by NAA is < 10\%; by comparison, the corresponding uncertainty that could be assured by the atomic spectroscopy techniques was found in the course of the international PT exercise organized by the Swedish Institute SIMR-KIMAB to be approx 100\%.

Finally, one may appreciate that the importance and effects of the PT/ILC schemes our Laboratory organized on the national & European level fully confirmed its advantages in getting/assuring improved performance in the Laboratory’s results, just as detailed in the relevant reference Standards.

REFERENCES


