

INTENDED USE OF THE IAEA REFERENCE MATERIALS

PART I: EXAMPLES ON REFERENCE MATERIALS FOR THE DETERMINATION OF RADIONUCLIDES OR TRACE ELEMENTS

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1 INTRODUCTION

For over forty years the International Atomic Energy Agency (IAEA), through its Analytical Quality Control Services (AQCS), has prepared and distributed reference materials (RMs) to the analytical laboratories in its Member States to assist them in maintaining/improving the quality of their analytical measurements and to help them achieve internationally acceptable levels of quality assurance¹. These RMs include matrices of environmental and biological origin, characterised for primordial and anthropogenic radionuclides, stable isotopes, organic contaminants and inorganic elements. The AQCS catalogue² containing a complete list of these RMs is published biannually by the IAEA. Over ninety RMs were listed in the 1998/99 catalogue which placed the IAEA among the major producers of environmental and biological matrix RMs in the world.

Preparation, characterisation and distribution of IAEA RMs is carried out by different Sections and Units of the IAEA Laboratories located in Austria and Monaco. RMs of terrestrial origin, characterised for inorganic elements and radionuclides, are mainly prepared by the Chemistry Unit (CU) located in Seibersdorf, Austria. RMs characterised for stable isotopes, H-3 and C-14 are prepared by the Isotope Hydrology Unit located in Vienna. RMs of marine origin, characterised for radionuclides, inorganic elements and organic contaminants, are prepared by Marine Environment Laboratory located in Monaco. The selection and characterisation of RMs is performed in close co-operation with other Sections in the IAEA including: Nutrition and Health Related Environmental Studies, Industrial Applications and Chemistry, Safeguards Analytical Laboratory and the Agriculture and Biotechnology Laboratory. For this paper only the RMs of terrestrial origin, characterised for radionuclides or inorganic elements, prepared mainly by the CU are discussed.

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1.1 Common Characteristics of the IAEA-CU Reference Materials

1.1.1 Preparation and characterisation of materials. All RMs produced thus far by the CU were prepared for and characterised as a result of IAEA intercomparison exercises. These environmental and biological RMs were collected from different places around the world. They were, with a few exceptions, processed and characterised for their physical (e.g. particle size distribution) and chemical properties (e.g. matrix composition) at the IAEA Laboratories Seibersdorf, to ensure the bulk material was of suitable homogeneity for bottling. A more detailed description of these procedures can be found elsewhere.³⁻⁵ After bottling, the within and between bottle homogeneity tests were performed and, when satisfactory, an information sheet was prepared. The samples were then distributed to all laboratories which had expressed an interest in participating in the intercomparison exercise. The laboratories were supplied with the intercomparison sample(s) together (in some cases) with a quality control sample, the information sheet(s), the reporting forms and a diskette for reporting the results. The information sheet provided basic data about the chemical composition of the matrix, the minimum sample mass to be taken for analysis, the procedure for moisture determination, the number of samples to be analysed (6 recommended) and a list of elements or radionuclides to be determined. The participants were free to use whichever analytical technique and procedure they thought appropriate to analyse the elements or radionuclides requested. Recently (1997), in order to improve its assessment of the quality of reported results, the IAEA prepared a questionnaire in which it requested detailed information on the technique(s) used, the quality assurance and quality control procedures applied, and on the performance of the participating laboratories. It supplied this questionnaire in hard copy and on diskette together with the samples and other related documents.

1.1.2 Evaluation of intercomparison results. Intercomparison results reported to the IAEA are checked by IAEA staff and hard copies of data input files are sent back to the participants for confirmation and correction where necessary. All results for each analyte are then statistically evaluated according to the protocol outlined in Figure 1 in order to determine the distribution of the reported values. After the statistical identification and rejection of “outliers”, the mean value (mean of laboratory means), the standard deviation and the limits of the 95 % confidence interval are calculated. Thus far two statistical methods have been used to identify outliers. The first method is based on a non-parametric distribution of the data and elimination of outliers by the application of tests based on Tschebycheff’s inequality⁶. The second method identifies and rejects outliers by the serial application of four statistical tests: Dixon, Grubbs, the coefficient of skewness and the coefficient of kurtosis. Results are rejected if they fail at least one of the tests. The complete procedure is repeated until no other outliers are found⁷. Recently the IAEA has employed additional criteria including “expert judgement” to evaluate results. These additional criteria are discussed below.

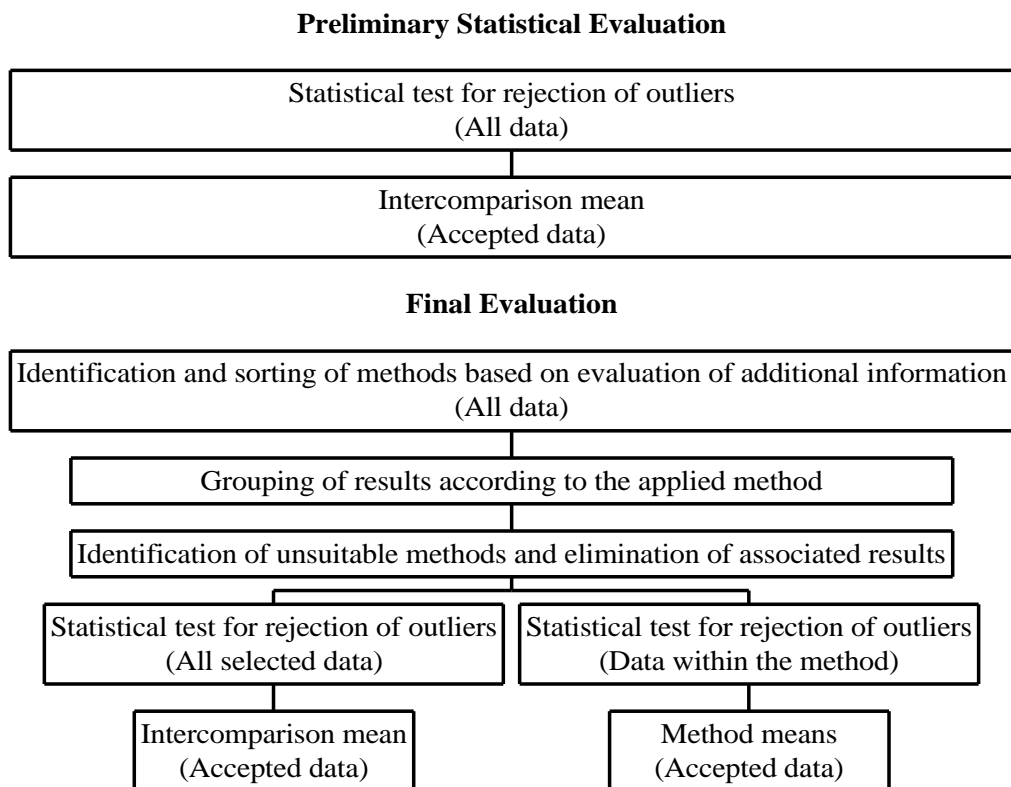


Figure 1 Evaluation procedure of the results from the IAEA-326/327 intercomparison study including “expert judgement”.

*1.1.3 Assignment of recommended and information values.** Regardless of the evaluation procedure, assignment of the final value as a recommended, information or listed value has depended on whether the value met certain criteria. These criteria included: a) a minimum number of laboratory means accepted for calculation of the overall mean, b) a maximum value for the relative uncertainty in the concentration or activity concentration range, c) a maximum value for the fraction of laboratory means rejected as outliers. These criteria have been summarised in Table 1 for the IAEA-326/327 intercomparison study.

There is also a set of criteria for assigning the information values, which are applied when the criteria summarised in Table 1 are only partially met. If neither of these criteria are fulfilled then the value is not assigned at all. The application of “expert judgement” to reject results not statistically detected as outliers by the methods mentioned in 1.1.2, was based on the quality of the data reported and the details of the analytical methods provided in the questionnaire by participants. The remaining data after the expert judgement were then statistically evaluated. Results below the limit of detection (if it was reported) were not considered in the statistical evaluation.

* Terms like certification, certified value, certified reference material, certificate, etc. have not been used in this paper as the majority of IAEA RMs do not strictly fulfil all the criteria to be classified as certified.

Table 1. *Criteria to be Fulfilled for Assignment of Recommended Values in the IAEA-326/327 Intercomparison Study*

<i>Parameter</i>	<i>Criterion</i>			
	<i>For trace elements</i>		<i>For radionuclides</i>	
Overall mean based on	≥ 10 laboratory means and ≥ 2 different analytical methods		≥ 10 laboratory means and ≥ 2 different analytical methods	
Percentage of outlying laboratory means	< 20 %		≥ 20 laboratory means when only 1 analytical method used < 30 %	
Relative standard deviation for a given mass fraction or activity concentration range	mg/kg	RSD	Bq/kg	RSD
	> 500	< ± 5 %	> 100	< ± 20 %
	100 - 500	< ± 10 %	1 - 100	< ± 30 %
	10 - 100	< ± 20 %	< 1	< ± 40 %
	0.1 - 10	< ± 30 %		
	< 0.1	< ± 40 %		

1.1.4 Information provided to the participants in the intercomparison study. For every intercomparison, each laboratory was assigned a unique code known only to itself and the IAEA. All results submitted were reported using the laboratory code to ensure anonymity. The statistical evaluation was also included in the report where outlying laboratory mean values were identified as shown in Table 2.

Table 2. *Example of a summary of results compiled for Sr-90 in the IAEA-326 intercomparison study*

For a complete data set

Radionuclide determined	Sr-90
Number of reported laboratory means	64
Number of reported independent determinations	194
Number of accepted laboratory means	51
Number of independent determinations	163
Range of all laboratory means	0.1 - 146.7 Bq/kg
Range of accepted laboratory means	4.3 - 13.8 Bq/kg
% of outlying laboratory means	20 %
Overall mean of accepted laboratory means	10.12 Bq/kg
Standard deviation of the overall mean	± 2.1
Relative standard deviation of the overall mean	± 20.8 %
Limits 95 % confidence interval	9.5 - 10.71 Bq/kg

For individual laboratory

Laboratory code	NN
Method code	B2 (Beta counting - liquid scintillation)
Number of determinations	5
Laboratory mean	19.5 Bq/Kg* (* identified as outlyer)
Standard deviation	± 2.8
Relative standard deviation	± 14.1 %
Limit of detection	not reported

The output file of the statistical evaluation could be presented graphically, grouped according to analysis methods or according to any other appropriate parameter.

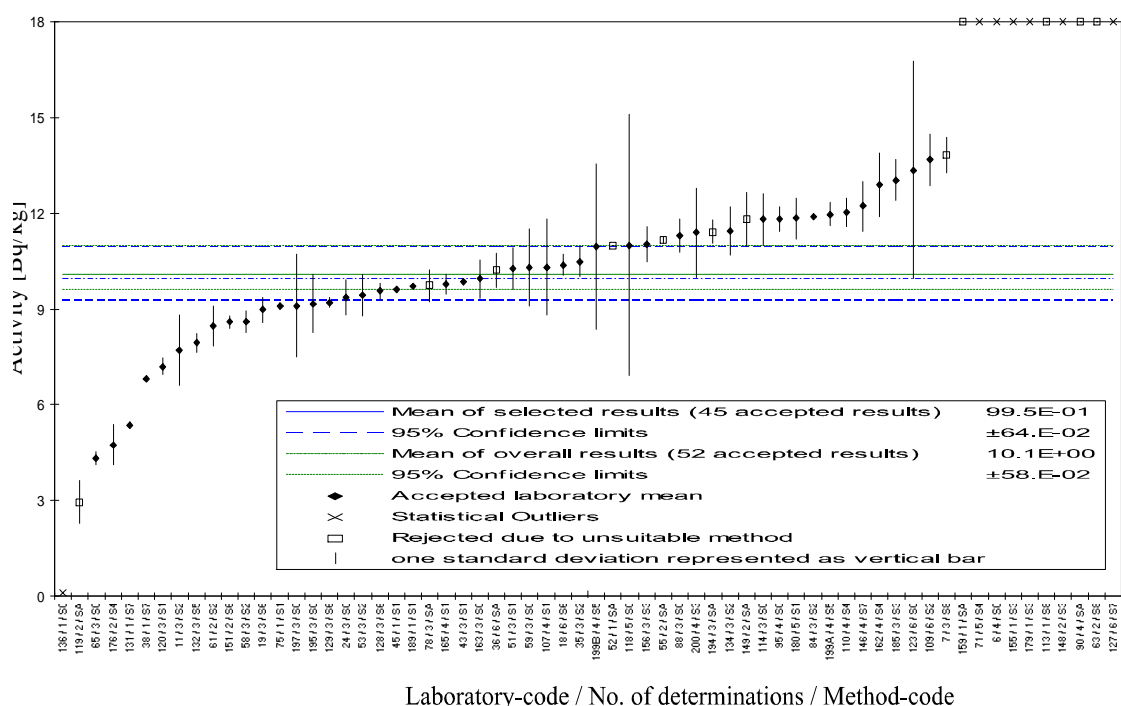


Figure 2. Graphical representation of ⁹⁰Sr results in the IAEA-326 intercomparison study which included both expert judgement statistical evaluation.

The reference sheet has included data for all analytes where the criteria for assigning recommended or information values were fulfilled. This sheet listed: recommended and the information values, the limits of the 95 % confidence interval and the number of laboratory means accepted for each analyte. Additional information provided about the RM included: designation (aim or intended use of the RM), description of the RM, information about its homogeneity, instructions for moisture determination and summary information on how the assigned values were established with a reference to the relevant intercomparison report. In certain cases, special information concerning the sample was also identified in the reference sheet, e.g. the possible presence of “hot particles” in

materials collected at the areas affected by the radioactive fallout (post Chernobyl samples, samples collected in the vicinity of nuclear testing sites, etc.)

2. INTENDED USE OF REFERENCE MATERIALS

2.1 Information Provided by the IAEA on the intended use of its RMs

Before selecting any RM(s) to evaluate a chemical procedure, the user must have first defined which parameters are to be tested. To select the most appropriate or “fit to purpose” RM, the user should consult the IAEA RM reference sheet and the related report on the intercomparison study.

Information on the appropriate use of the IAEA RM is provided in the IAEA reference sheet headed “Designation”. For example, the following statement appeared in the reference sheet for RM IAEA-373, Radionuclides in Grass: “This material is intended as a reference material for the measurements of radionuclides in environmental grass samples. It can also be used for the assessment and control of the laboratory’s analytical work, and for validation of analytical methods used in a laboratory, i.e., in general quality assurance within a laboratory and for training purposes.”^{8,9} This information provided by the IAEA is of a general nature. However, there exist many international standards and guides where the appropriate use of reference materials has been described. In general, for IAEA RMs prepared more than ten years ago the information on the intended use was not included in the relevant reference sheet, e.g. IAEA Soil-6, IAEA/V-10 Hay Powder, etc.

2.2 International Guidelines Regarding Intended Use of RMs and Applicability to the IAEA RMs

The following sections summarise international guidelines on RMs and the present status of IAEA RMs with respect to meeting each guideline. For each section it is assumed that a RM was selected, which mimics the sample as close as possible with respect to chemical composition and concentration levels of the elements/radionuclides of interest.

*2.2.1 Reference materials and assigned property values*¹⁰. The “property values” assigned to the IAEA RMs discussed in this paper are the mass fraction of trace/minor elements or the activity concentration in the case of radionuclides. Once the “property values” have been assigned, an inherent attribute of a RM is that its property value must remain stable over a defined period of time (expiration date defined). This must be supported by stability tests and ensured by maintaining it under proper storage conditions. The IAEA RMs have been selected and characterised for those analytes which are stable in storage under ambient conditions encountered in routine laboratory conditions. To confirm the stability of the IAEA RMs, stability tests must be carried out at regular intervals (at least once per year). The stability of IAEA RMs has been demonstrated many times (see section 2.2.7) and therefore the IAEA RMs fulfil the criterion to ensure stability of the RM “property values”.

*2.2.2 Establishing traceability of a measurement result*¹⁰. Traceability as it is used in this report is defined according to the International Vocabulary of Basic and General Terms in Metrology (VIM): “Traceability is the property of the result of a measurement or the value of a standard whereby it can be related to a stated reference, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.”¹¹ For IAEA RMs of terrestrial origin characterised for radionuclides or inorganic elements, the assigned values are expressed either as an activity concentration (Bq/kg, etc.) or element concentration (in some cases as a mass fraction) respectively. The kilogram and becquerel are International System of Units (SI) or units derived from the SI and

according to the definition above, the property values of an RM must be traceable to them. However, this criterion is not fulfilled when the assignment of the RM property value is based on the results of an intercomparison. Although single results or a group of results might be traceable to SI, the statistical evaluation applied to calculate the mean value destroys the traceability chain. At the IAEA Consultants' Meeting on "Traceability of IAEA-AQCS Reference Materials to SI-Units"¹², it was clearly pointed out that the assigned property values of current IAEA RMs could be considered as traceable to the respective laboratory intercomparison only and not to any other further point of reference.

The traceability issue with respect to natural matrix RMs has to be viewed in a wider perspective than within the IAEA. Most of the internationally available matrix RMs characterised for trace elements or radionuclides originate as a result of intercomparison studies and therefore fail the traceability criterion. A report, published recently by Papadakis et al., describes the establishment of a SI-traceable copper concentration in the Antarctic Sediment candidate RM by using isotope dilution combined with inductively coupled plasma mass spectrometry.¹³ This is an example where a primary method of measurement was applied. However, when these results are combined with other results derived from comparative methods of measurement (i.e. not primary) obtained in the certification campaign, the traceability of the assigned value becomes dubious (questionable?).

Although the ISO Guide 33 considers the establishment of traceability by the use of RMs; in the case of chemical RMs, only pure substances, their solutions, alloys, and gas mixtures would currently fulfil the requirements for traceability (see also 2.2.4), while the natural matrix RMs do not. It is important not to confuse the terms "traceability" and "accuracy" of the assigned property value. Even when the assigned value of an intercomparison study, is considered a "the best estimate of the property or true value", this does not by itself assure that the result is traceable. Considerable work still remains to be done in this field, including the production of traceable matrix RMs, guidance on their use and definition of their role in the analytical process once they become available. From the discussion above it must be concluded that the current IAEA RMs can not be used to establish traceability of a measurement result.

2.2.3 Determining the uncertainty of the measurement results.^{10, 14} The uncertainty of a measurement result is defined in VIM as a: "Parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand."¹¹ (In case of the IAEA RMs measurand is a mass fraction of trace elements or activity concentration of radionuclides respectively.) Here the term "uncertainty" refers to the expanded combined uncertainty, which takes into account all sources of uncertainty associated with the relevant chemical measurement process. As noted in section 1.1.1, reporting of the uncertainty of measurement results is routinely requested from the participants in IAEA intercomparison exercises. However, in the majority of cases uncertainties are not reported and the few that are would only account for some of the sources of uncertainty e.g. uncertainty due to the counting statistics in γ -spectrometric measurements. It must be pointed out that the statistical evaluation employed by the IAEA does not take into account the measurement uncertainty reported by the participants. All calculations are performed using only the accepted laboratories' mean values.

As is the case with traceability, the uncertainty in the assigned values obtained through an intercomparison study is still an open question. J. Pauwels et al. have proposed a pragmatic method for the determination of the uncertainty of property values derived from an interlaboratory comparison.¹⁵ Even such a pragmatic method requires the establishment of a full uncertainty budget for each laboratory result. Quantification of uncertainty in chemical measurements is a developing issue. With the issuance of the EURACHEM Guide on Quantifying Uncertainty in Analytical Measurements¹⁴, the basic principles and examples were provided to the analytical chemistry community, but time is needed for those principles to be fully appreciated and implemented in all laboratories. For this reason, characterisation through a small number of selected laboratories fulfilling

the highest quality criteria and employing primary methods for measurements is the preferable approach for future certification of the IAEA RMs.

Although the use of RMs for uncertainty quantification is discussed in both ISO Guide 33¹⁰ and the EURACHEM Guide¹⁴, neither provides guidance on how this should be done. A possible option is to use a RM for quantification of a specific source of uncertainty, e.g. sample digestion, recovery, etc. In this case a sufficient number of independent experiments under the same experimental conditions has to be performed. The standard deviation of the results may be ascribed as a standard uncertainty (however the distribution of data must be considered) and then included in the calculation of the combined uncertainty. It must be pointed out that for this purpose to apply the RM must be homogeneous with respect to the element/radionuclide measured. From the results of independent measurements the laboratory can establish its own mean value for a specific investigation and calculate its standard deviation for obtaining standard uncertainty. Examples of such an evaluation can be: quantification of spectral interferences in γ -spectrometry, quantification of background and matrix effects in neutron activation analysis, etc. When the homogeneity of the material satisfies the requirements of the user, the IAEA RMs can be used for evaluation of uncertainty sources - quantification of standard uncertainties.

*2.2.4 Calibration of an apparatus.*¹⁰ Quality control/assurance procedures require all measuring instruments, glassware, balances, etc., to be calibrated against traceable standards at regular intervals.^{16, 17} Especially important is the calibration of instruments (different spectrometers, etc.) that provide a result directly linked to measurands such as amount of substance, concentration, activity, activity concentration, etc. These results are normally obtained from a calibration curve or by relative measurements. In such cases, the calibration is usually performed using a calibration standard prepared from a pure chemical substance, radioactive isotope or a mixture - multielement calibration standard. These calibration standards are often available as certified reference materials.* They are characterised by primary methods of measurements, i.e., gravimetry, titrimetry, coulometry, etc. and are directly traceable to the mole (SI unit for the amount of substance). As discussed in 2.2.2, in the case of natural matrix RMs characterised by an intercomparison study, traceability to SI units is not established. For this reason most of the currently available natural matrix RMs, including those produced by the IAEA can not be used for the instrument calibration. (Special cases, like laser ablation techniques, where no other possibility for calibration than a use of matrix RM exists, require additional consideration.)

*2.2.5 Assessment of a measurement method.*¹⁰ One of the basic principles of quality assurance in analytical chemistry is that only validated methods can be used for routine analyses. Even in cases when the methods are available from the literature and peer-verified methods (intercomparison organised with various laboratories) they must be validated in the particular laboratory that is going to apply them. Methods developed in-house should undergo a complete method validation, which includes: accuracy (trueness + precision), sensitivity, selectivity, linearity, limit of detection, possible interferences, recovery and ruggedness. The use of a RM containing the analyte at a known concentration is one of the most appropriate tests to validate the method and the performance of the analyst.¹⁸ For assessment/validation of accuracy, precision and possible interferences, the composition of RM should approximate that of the actual samples and should contain the analyte at about the same concentration. For validation of sensitivity, selectivity, linearity, recovery and ruggedness, tests should be carried out at different concentration levels of the analyte. When a limit of detection is assessed, then a RM which does not contain the analyte of interest, but is similar to the actual sample in respect to matrix, would be needed. For method validation normally more than one

*Terminology in respect to calibration standards, certified reference materials, primary standards, secondary standards, etc. is not fully supported by quality requirements and classification of these materials. Further systematisation is required at the international level.

RM or a selected RM spiked with the analyte of interest at different concentrations levels is used. When selecting RMs for method validation purposes, one finds that the availability of natural matrix RMs is limited. For example, natural matrix RMs certified for radionuclides are available only from a few producers and the majority of these RMs were prepared by the IAEA. This is illustrated in Table 1 for RMs with an assigned property value for ^{90}Sr .¹⁹

Table 1 Available Environmental and Biological Reference Materials for Determination of ^{90}Sr .

Name	Code	Status	Concentration (Bq/kg)
Mediterranean Tuna Fish	IAEA-352	N	0.2
Sea Plant	IAEA-307	N	0.72
Pacific Ocean Water	IAEA-298	C	1.32
Milk Powder	IAEA-A-14	C	1.5
Marine Sediment	IAEA-368	N	1.8
Milk Powder	IAEA-321	C	3.3
Cockle Flesh	IAEA-134	N	4.8
Columbia River Sediment	NIST-SRM 4350B	N	5.3
Radionuclides in Whey Powder	IAEA-154	C	6.9
Rocky Flats Soil	NIST-SRM 4353	C	7.63
Milk Powder	IAEA-152	C	7.7
Clover	IAEA-156	C	14.8
River Sediment	GBW 08304	C	19.7
Peruvian Soil	NIST-SRM 4355	N	22
Soil	IAEA-SOIL-6	C	30.34
Animal Bone	IAEA-A-12	C	54.8
Marine Sediment	IAEA-135	N	64.5
Marine Sediment	IAEA-367	C	102
Soil	IAEA-375	C	108
Freshwater Lake Sediment	NIST-SRM 4354	C	1090
Grass	IAEA-373	C	1320

Note: N = non-certified value C = certified (NIST, GBW)
recommended value (IAEA)

When selecting an IAEA RM for method validation or performance assessment of the analyst, the user has to be aware that the results obtained by analysing these RMs can only be compared with the statistically derived mean of the accepted results of the participating laboratories. For comparing a laboratory mean value with the overall mean value of the intercomparison study (reference or information value) the mathematical formulae from ISO Guide 33 for assessment of trueness (the closeness of agreement between the average value obtained from a series of test results and an accepted reference value) can be followed:

$$-a_2 - 2\sigma_D \leq \bar{x} - \mu \leq a_1 + 2\sigma_D \quad (1)$$

where:

\bar{x} is the RM user's mean value

m is the recommended or information value (mean of laboratory means)

$a_{1,2}$ additional level of uncertainty defined by the user to meet the economic or technical limitations or stipulation

s_D is the standard deviation associated with the RM user's measurement process. It is combined from the within-laboratory fluctuation (s_w given as standard deviation s_w - RM user's results) and the between-laboratories fluctuation (s_{Lm} is a standard deviation of statistically accepted intercomparison means - information available from intercomparison report), as follows:

$$\sigma_D^2 = \sigma_{Lm}^2 + \frac{s_w^2}{n} \quad (2)$$

where:

n is the number of RM user's independent determinations

The information on between-laboratories standard deviation (s_{Lm}) is given in the related IAEA report on the intercomparison study, while the reference sheet will normally provide the reference value, the limits of the 95 % confidence interval and number of accepted laboratory means. It would be wrong to expect that only the user's results that fall between the limits of the 95 % confidence interval are satisfactory in comparison with the recommended value. The 95 % confidence interval is a statistically derived value and depends on the number of accepted laboratory means (p) in an intercomparison study. In some of the latest IAEA intercomparison studies the number of accepted means was larger than 50 and for this reason the confidence interval became unreasonably small. The value for the confidence interval should not be considered independently from other parameters (p , s_{Lm}), refer to Figure 2 for an illustration. As already pointed out, the user of the RM should consult the intercomparison report before using the IAEA RMs and drawing any conclusion as to the accuracy of his own results.

When the precision of the method is assessed by application of a RM, the user should compare the standard deviation of his results (s_w , within-laboratory standard deviation) with the required value of the within-laboratory standard deviation (s_{wo}). The required within-laboratory standard deviation (s_{wo}) may be set out by the user himself as a target value or defined by the customer of the analytical results as a specific requirement for the acceptance of these analytical results. The ratio between s_w and s_{wo} has to be calculated:

$$\chi_c^2 = \left(\frac{s_w}{s_{wo}} \right)^2 \quad (3)$$

and χ_c^2 compared with the tabulated value of χ_{Table}^2 , where $\chi_{Table}^2 = \frac{\chi_{(n-1);0.95}^2}{n-1}$.

The method assessed will be regarded as precise as required when $\chi_c^2 \leq \chi_{Table}^2$.

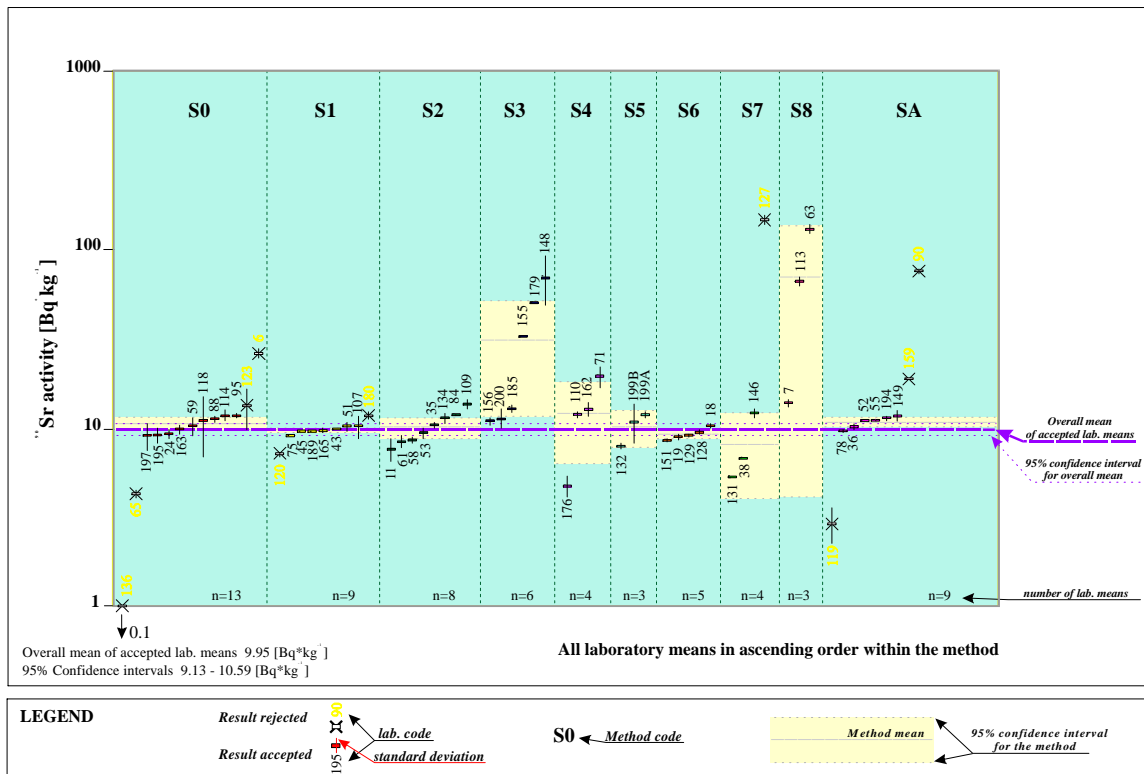


Figure 3 IAEA-326 intercomparison results grouped according to the methods applied.

2.2.6 *Use of reference materials for recovery studies.*²⁰ In principle, when no better possibility exists (use of radioactive tracers, isotope dilution techniques, etc.), recoveries could be estimated by the analysis of RMs. The recovery is the ratio of the concentration of analyte found to that stated to be present. Results obtained on test materials of the same matrix could, in principle, be corrected for recovery on the basis of the recovery found for the RM. However, the RM user has to be aware of several problems which potentially beset this use, namely: a) the validity of any such recovery estimate depends on the premise that the analytical method is otherwise unbiased; b) the range of appropriate matrix RMs available is limited; and c) there may be a matrix mismatch between the test material and the most appropriate RM available.

In the last instance the recovery value obtained from the RM would not be strictly applicable to the test material. The shortfall applies especially in sectors such as foodstuffs analysis where RMs have to be finely powdered and dried to ensure homogeneity and stability. Such treatment is likely to affect the recovery in comparison with that pertaining to fresh foods of the same kind. In case of trace element or radionuclide determinations in environmental and biological samples, i.e., soil, vegetation, human tissue, etc. the preparation of samples will be very similar to the preparation of RMs and also a digestion procedure will often be applied in the analytical process. In such a case a RM is a proper tool to assess the recovery or chemical yield. The IAEA RMs can be used for this purpose.

2.2.7 *Use of reference materials for quality control purposes.* Quality control practice requires use of quality control materials, duplicate and blank analysis and continuous observation of the analytical performance of the measurement system, including the operator. This is normally supported by the use of statistical analysis and control charts. It is not always possible to prepare a suitable quality control material in the laboratory and quite often the RMs are used for this purpose. In Figure 4 a control chart is presented showing the performance of a laboratory in ²³⁹+²⁴⁰Pu analysis using RM IAEA Soil-6 as a quality control material. This laboratory also took part in the intercomparison study and was included in the statistical evaluation of data, having its mean value very close to the

recommended value for $^{239} + ^{240}\text{Pu}$. Some trends evident from the control chart in decreasing values, especially from 1993 to 1994, have been thoroughly studied. The reason was found to be a change in concentration of the calibration standard solution due to evaporation. After a new solution was prepared, the results were again closer to the assigned mean value. As it is evident from the control chart, the majority of results are within the limits of the 95 % confidence interval over a period of seven years.

2.2.8 *Other applications.* The IAEA RMs have been successfully used for assessment of the performance of the IAEA network laboratories, e.g. the network of Analytical Laboratories Measuring Environmental Radioactivity (ALMERA). Although the mean value of such a specific laboratory intercomparison with a limited number of selected laboratories might be slightly different from the mean value of the original world-wide intercomparison, a consensus value can be established and the relative performance between the laboratories assessed accordingly. Such an intercomparison provides a sound basis for establishing the comparability of the results obtained in different laboratories analysing the same type of samples. However, there is a limitation for such type of application as the RMs are normally available to the users in limited quantities.

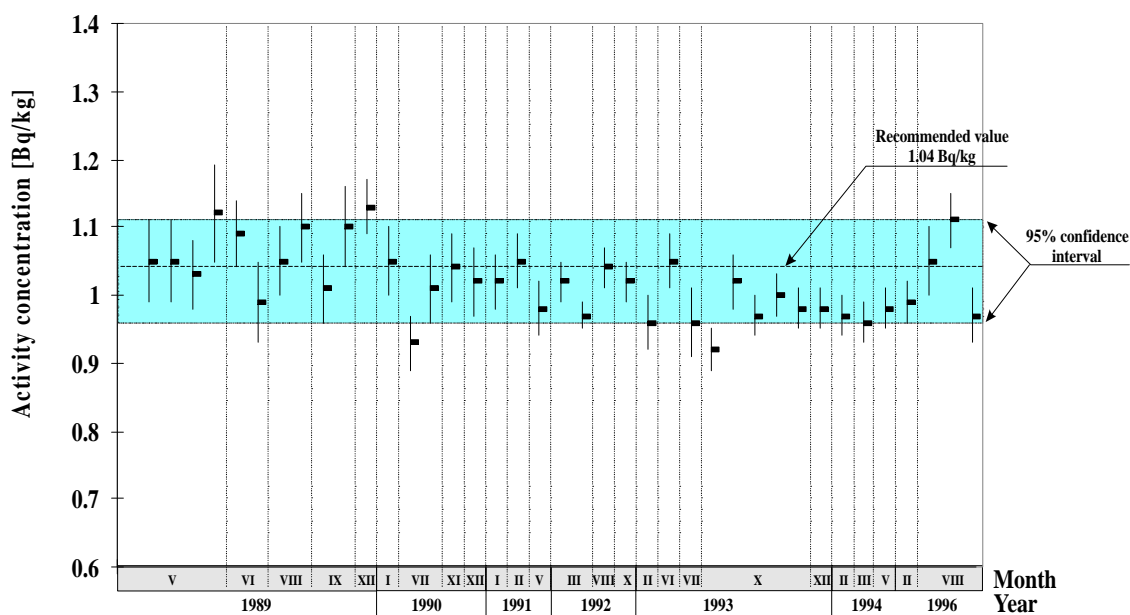


Figure 4 $^{239+240}\text{Pu}$ activity concentration measured in the IAEA-Soil-6 RM over the period 1989 - 1996.

3 FUTURE PLANS

Aware of the limitations of its RMs as outlined in this paper, the IAEA is following the latest metrological developments and requirements in the area of analytical chemistry. The IAEA efforts in the organisation of world-wide intercomparison studies continues to be regarded by its Member States as a valuable contribution to the laboratories. The IAEA intends to continue to provide this assistance, however, in a modified manner consistent with the new requirements associated with the use of RMs.

The interest in the IAEA RMs is high and around 1000 units are sold per year as shown in Figure 5. For this reason the IAEA plans to upgrade some of its RMs so that traceability either to the basic SI unit the mole (amount of substance) or derived unit Bq (activity) can be clearly established.

Materials have already been selected for upgrade based on availability and user demand. Table 3 lists the RMs under consideration for upgrading involving the determination of radionuclides.

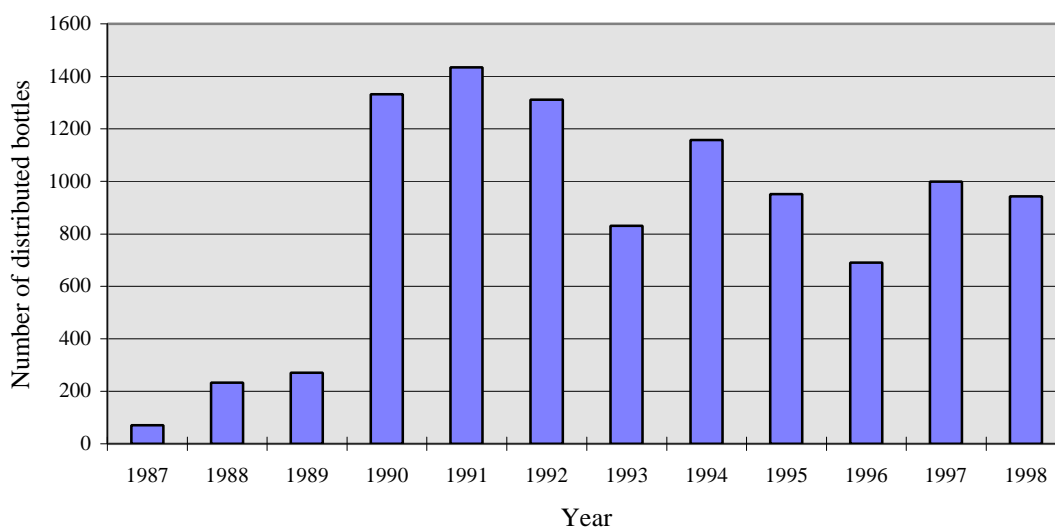


Figure 5 Number of the IAEA RMs units sold per year. Figure for 1998 includes sales up to November (Figure 5 does not include RMs produced and distributed by the Hydrology Unit neither units which were given free of charge in support of the IAEA programmes.)

For the determination of trace elements in biological or environmental samples, a similar approach is planned. A selection of a limited number of expert laboratories, performing the analysis according to prescribed protocols and with a quantified measurement uncertainty, should produce results for the certification of the IAEA RMs. Two sets of materials are already under investigation: the IAEA-390, a set of three algae materials, and a set of two membrane filters artificially loaded with urban dust collected in Vienna and in Prague.

Table 3 IAEA Intercomparison Materials Selected for Upgrade.

Code	Type	Analytes of Interest
IAEA-152	Milk Powder	K-40, Sr-90, Cs-137
IAEA-312	Soil	Ra, Th and U
IAEA-314	Stream Sediment	Ra, Th and U
Soil-6	Soil	Sr-90, Cs-137, Ra-226 and Pu-239
SL-2	Lake Sediment	K-40, Sr-90, Cs-137, Pb-210, Ra-226, Ra-228, Th-228, Th-234, U-238 and Pu-239/240
IAEA-375	Soil	K-40, Sr-90, Ru-106, Sb-125, I-129, Cs-134, Cs-137, Th-232 Ra-226, Th-228, U-234, Pu-238, U-238, Pu239/240 and Am-241

4 CONCLUSION

With ever increasing and stricter requirements being placed on the quality of analytical results by customers and regulators, the need for appropriate RMs is continuously growing. Metrological concepts pertaining to analytical chemistry require traceability of analytical measurements to be established and measurement uncertainty to be reported together with the test results. However, there is still a discrepancy between the current requirements and the tools available to fulfil these requirements. Natural matrix RMs that already fulfil the criteria for traceability to the SI units are very rare because the producers of RMs are facing the same problem as the analytical community: a) lack of primary methods of measurement, b) procedures for uncertainty quantification in analytical measurements are still not fully established or completely harmonised, c) most of the international standards related to traceability and measurement uncertainty are based on the “nature” of physical measurements, which can not directly be transferred to chemical measurements. In addition, in the absence of primary methods of measurements, it is necessary to apply more than one analytical technique for the characterisation of RMs. The internationally accepted guidance for reporting the uncertainty of such combined results is still under development. Also needed is a better defined hierarchy of RMs according to the fulfilled metrological requirements and the definition of the role of the RMs in the measurement process. RMs of different quality will always be available and a proper terminology should be developed to distinguish between them. What is the role of SI traceable RM once when available? There is no doubt that such materials would transfer the property value which will be linked to the most proper point of reference (basic SI unit(s)) and comparability of the results will be possible. But, would such a material then be used for calibration, correction of results, etc., or for quality assurance purposes as it is now? Would a traceable RM be used to link the test results on similar type of sample to the SI units? Even when these questions will be clearly answered, the RMs producers will still have the same objective: assuring that the values assigned to the RMs are the best estimates of the true value. However, there should be clear evidence how this was achieved and what is the meaning of the assigned property values and their uncertainties.

As described in this paper, the IAEA intends to follow recent developments in quality requirements for RMs. As traceable natural matrix RMs are not expected to be available in the near future, many of the RMs that are still in stock will continue to be used. It remains the responsibility of the RM user to obtain the necessary information on the quality of the assigned property values for the RM, its intended use and to use these RMs properly.

References

1. R.M. Parr, A. Fajgelj, R. Dekner, H. Vera Ruiz, F.P. Carvalho, P.P. Povinec, *Fresenius J Anal Chem*, 1998, **360**, 287.
2. International Atomic Energy Agency, ‘IAEA AQCS Catalogue for Reference Materials and Intercomparison Exercises 1998/1999’, Vienna, Austria, 1998.
3. V. Strachnov, V. Valkovic, J. LaRosa, R. Dekner, R. Zeisler, *Fresenius J Anal Chem*, 1993, **345**, 169.
4. R. Zeisler, R. Dekner, V. Strachnov, H. Vera Ruiz, *Fresenius J Anal Chem*, 1995, **352**, 14.
5. A. Fajgelj, R.M. Parr, R. Dekner, P.R. Danesi, V. Valkovic, H. Vera Ruiz, The IAEA Analytical Quality Control Services (AQCS) Programme on Intercomparison Runs and Reference Materials, Proceedings of an International Symposium on Harmonisation of Health Related Environmental Measurements Using Nuclear and Isotopic Techniques, Hyderabad, India, 4-7 November 1996, International Atomic Energy Agency, Vienna, 1997, p. 175.
6. L. Pszonicki, *Anal. Chim. Acta*, 1985, **176**, 213.

7. R. Dybczynski, *Anal. Chim. Acta*, 1980, **117**, 53.
8. V. Strachnov, J. LaRosa, R. Dekner, A. Fajgelj, R. Zeisler, Report on the Intercomparison Run IAEA-373: Determination of Radionuclides in Grass Sample IAEA-373, IAEA/AL/073, International Atomic Energy Agency, Vienna, 1996.
9. Reference Sheet IAEA-373, Radionuclides in Grass, International Atomic Energy Agency, Vienna, Austria, 1994.
10. ISO Guide 33, 'Uses of Certified Reference Materials', Revision of ISO Guide 33: 1989, International Organisation for Standardisation, Geneva, Switzerland, 1998, to be published.
11. 'International Vocabulary of Basic and General Terms in Metrology', International Organisation for Standardisation, Geneva, Switzerland, 1993.
12. Report on the Consultants' Meeting on Traceability of IAEA-AQCS Reference Materials to SI-Units, IAEA/AL/105, International Atomic Energy Agency, Vienna, Austria, 1996.
13. I. Papadakis, P. D. P. Taylor, P. De Bièvre, *J. Anal. At. Spectrom.*, 1997, **12**, 791.
14. 'Quantifying Uncertainty in Analytical Measurements', EURACHEM, First edition, 1995,
15. J. Pauwels, A. Lamberty, H. Schimmel, *Accred Qual Assur*, 1998, **3**, 180.
16. F. E. Prichard, N. T. Crosby, J. A. Day, W. A. Hardcastle, D. G. Holcombe, R.D. Treble, 'Quality in Analytical Chemistry Laboratory', Editor E.J. Newman, John Wiley & Sons Ltd. Chichester, England, 1995.
17. ISO/IEC Guide 25 : 1990 (E), 'General Requirements for the Competence of Calibration and Testing Laboratories', International Organisation for Standardisation, Geneva, Switzerland, 1990.
18. European Commission, BCR information, 'Metrology in Chemistry and Biology: A Practical Approach', Report EUR 18405 EN, Luxembourg, 1998.
19. 'Survey of Reference Materials', Volume 1, Biological and environmental reference materials for trace elements, nuclides and microcontaminants, IAEA-TECDOC-854, International Atomic Energy Agency, Vienna, 1995.
20. M. Thompson, S. L. R. Ellison, A. Fajgelj, P. Willetts, R. Wood, 'Harmonised Guidelines for the Use of Recovery Information in Analytical Measurement', IUPAC Technical Report, 1998, to be published in Pure and Applied Chemistry.