

NUCLEAR ANALYTICAL METHODS AS INTERFACE OF ENVIRONMENTAL AND TRACEABILITY EVALUATIONS

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Abstract

Nuclear Analytical Methods (NAM) could provide the basic tools for certifying environmental natural-matrix and for verifying environmental and radioanalytical test samples for the traceability evaluation. The effects of environmental pollution on soil-plant-water system are under observation of worldwide scientists reunited in different national and international scientific organizations and analytical laboratories. An example of the use of radioanalytical methods to probe key questions about the environmental media evaluation in view of the element patterns of the main pollutants was been tested and further described.

Keywords: *Nuclear Analytical Methods, traceability, elements, environment assessment*

Introduction

Natural-matrix of environmental samples provides the basis for the assessment of the cleanliness of the natural ecosystems, the air quality and consequently the human health environmental conditions.

In the present project, some environmental pollution indicators, such as some known biomonitors, soil and others, all from a natural ecosystem greatly affected by natural and anthropogenic causes, should to be characterized by several spectrometric methods of activation analysis at the microtron MT-25 and XRF analysis. The space and time integrated sampling of surface area over transects should to reveal pollution sources, the physical and biological status of the region.

NAM traceability

The main objectives of the NAM include measurements on the composition and nature of matter in space and time, in order to gain quantitative and qualitative information on their uncertainties, validation and traceability to known standards.

Traceability is defined as the property of a result of a value measurement whereby it can be compared with an appropriate standard, through an unbroken chain of comparisons, all having stated uncertainties. Usually such a testing method is applied considering generally international or national accepted standards. The test samples from nature should be similar to those routinely tested by participating laboratory in the comparison exercise.

Generally applied, there are two ways to establish traceability of the element levels in the biological material:

1. To use an absolute method as activation analysis by direct measurements;
2. To use an etalon e.g. to relate the found values to the level in a certified reference material of similar composition and element concentration; the etalon should to be measured together with the unknown sample.

Biological matrices can vary substantially from each other. Most, however, contain various amounts of interfering elements, making them potentially problematic to analyze.

Samples with too different concentration levels of the analyte pose another type of problem. For example, if the element concentration is too high to be analyzed by the direct measurement, the sample suffers a radiochemical pretreatment. If this preparation is too larger, the matrix can be changed to a level where it no longer will have the same influence on the analyte, thus becoming an entirely different analysis.

Any NAM procedure consists of sampling and sample preparation, measurement of the test sample, evaluation of the measurement (data reduction), and reporting measurement results in terms of an estimate of the measurand amount and its uncertainty. The detectable analyte depends on the selectivity of the analytical procedure (Figure 1). In a sequence presentation, it is a step by step procedure of *information quantification-localization interpretation*.

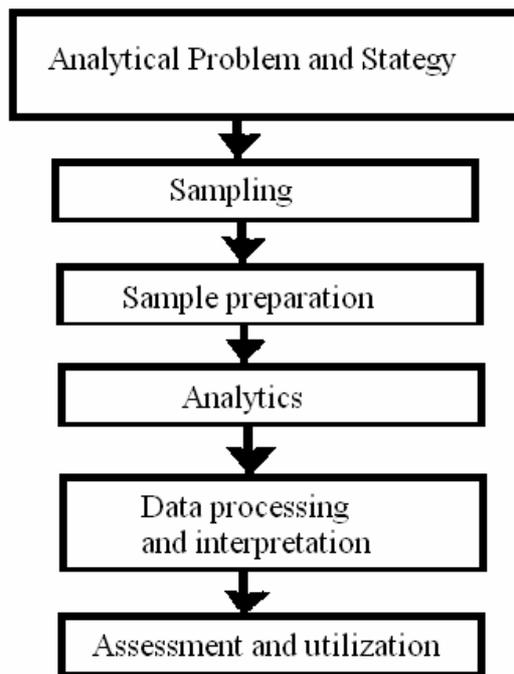


Figure 1. Procedure of analytical method

Reference materials

Reference Materials (SRM OR CRM) are materials of whose chemical composition is sufficiently homogeneous and well established to be used for calibration and/or assessment of analytical method and also for etalonate the measured values to material. In many analytical determinations, the reliability of measurements is based on the reference materials. The certification of references materials should include the primary methods (i.e. methods of a highest metrological quality) to make property values traceable to SI-unit (Figure 2).

CRMs have the form of pellets, globules, shot, wires and bars, intended to be used as amount of substance standard. They can be constituted from pure elements, blends or synthetic mixtures, or even spiked or unspiked real-life standards. The pure elements can be used as:

- the amount of substance standard, if all impurities are known as determined in stated uncertainty limits;
- the chemical composition standards, if the high quality content of the all metallic traces are at ultra trace level certified.

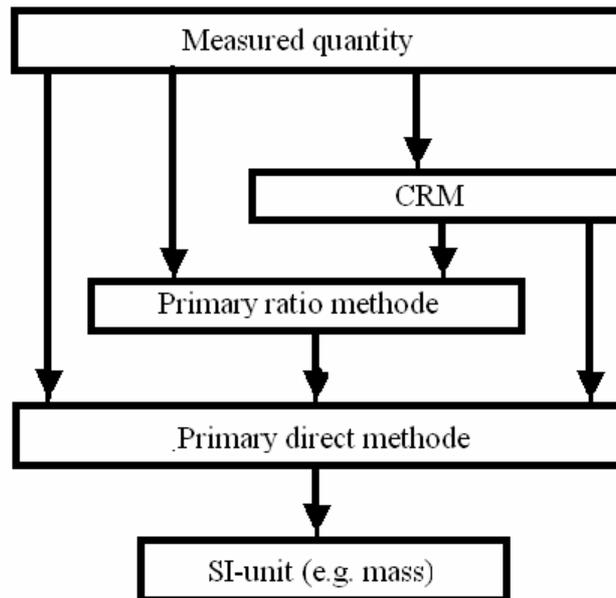


Figure 2. Traceability of a measurement result

In the routine analytical evaluation of biological materials, a matrix-matched reference material of a similar composition as the measurand better to be used as a control sample.

Measurement assurance

The measurement assurance approach is generally understood as the measurement quality control for the high-level calibration analytical procedures (NIST, NBS). For the most applications, measurements with insufficient accuracy can result in erroneous consequences. Then it has to be established a monitoring of the state of routine statistical quality control of the experiments in order to assure a quantified measurement uncertainty. Without a valid uncertainty statement and evidence that that the measurement process remains in an assured state of statistical control, no one can determine whether a given measurement is adequate for the intended scope. Since the uncertainty of a calibration process may change with time, the traceability of the measurement is foreseen in measurement assurance. In general, the sources of standard uncertainty in NAM procedure should be grouped according to the step by step analysis into four categories: i) preparation of the sample and comparator; ii) irradiation; iii) γ -ray spectrometry measurement; iv) radiochemical separation, if performed.

Application: Traceability of trace elements in some biological materials

In environmental studies, traceability is the proof of trueness of a peculiarity observed in the element concentration data overall set.

Continuous efforts are done for the improvement of analytical measurement of environmental pollutant concentrations, including trace heavy metals. Vegetation is often of primary interest monitoring method in polluted areas to stabilize soil with respect to wind and water erosion and to minimize downward translocation of contaminants. Field and analytical evaluations are needed to quantify the effects of vegetation on the leaching of metals.

Several research monitoring projects of the main author (see list of references) is currently underway and their main features is the assessment and improving of the environmental quality in the studied territory.

Impact of mobility of pollutants on vegetation was monitored by the two types of biomonitors used to indicate the level of regional pollution, namely mosses and agricrops. They were sampled according to transect of 55 km from the frontier RO-HU up to Western Carpathians, accounting for 880 km² network. The *Pleurozium schreberi* mosses were chosen for this monitoring study as they are widely spread in the investigated area. As crop monitoring results, the concentration values of maize constituents were used in presentation.

AA and XRF analytical measurements were performed to determinate concentrations of heavy metals in vegetation samples. The CRMS wheat RJI, moss DK-1 and chernozem CII-3 were used for precision, quality assurance and control (QA/QC) for element measurements. The precision of analytical procedures was expressed as StDev which ranged from 5-10 %. The recovery rates of measured elements ranged as 68-92 %.

The concentrations of the most significant elements for the survey done are shown in Table 1 as overall mean values charactering the low altitude (plain) area.

The values along transect are expressed as biological concentration factor (BCF) and translocation factor (TF). BCF is done by the ratio between element concentration in plant root and that in own soil:

$$BCF = \frac{C_{element_{root}}}{C_{element_{soil}}} \quad (1)$$

TF is the ratio between element concentration in plant shoot to that in plant root:

$$TF = \frac{C_{element_{shoot}}}{C_{element_{root}}} \quad (2)$$

Table 1. Mean values in mosses and crops (mg/kg)

Metal	Mosses		Crop root		Crop shoots		Soil	
	Mean	StDev (%)	Mean	StDev (%)	Mean	StDev (%)	Mean	StDev (%)
As	0.58	21	0.26	15	0.22	8	1.7	12
Cd	0.35	15	0.23	21	0.15	11	1.4	3
Cr	8.5	13	16.2	10	14	23	35.7	16
Cu	48.2	25	38.6	15	26	15	38.5	5
Ni	10.7	27	15.7	19	12	12	32	13
Pb	44.9	17	21.8	14	18.2	25	28.5	18
Sb	0.21	9	0.16	23	0.13	12	0.31	9
V	11.4	20	17	11	10.3	13	85.3	12
Zn	38.8	16	58	24	54	9	64	10

Accumulation of selected metals varied greatly among plants species due to differences in the mechanism of element uptake. The crop species monitored was efficient to absorb and translocate more than one metal from roots to shoots. The results indicated that none of the plants were recognized as hyperaccumulator because they accumulated heavy metals less than 1000 mg/kg.

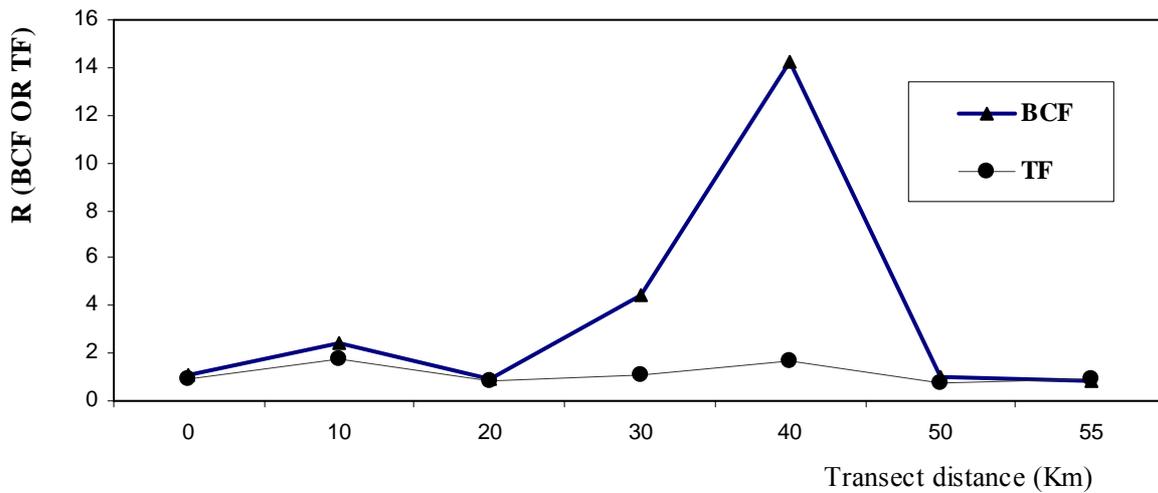


Figure 1. BCF and TF for lead concentration in crops

Note: A part of the experimental material (measured spectra) is still under processing. When the work will be ready, several aspects as demonstration of traceability for environmental radionuclide measurements, and the basis for measurement comparison over time comparing with data from literature are foreseen. There is expected more information on the metal accumulation and mechanisms of plant growing on contaminated soil to survive.

References

- [1] Cameron JM (1977). Measurement assurance, NBS Report:77-1240
- [2] Croarkin C (1983). Measurement assurance programs Part II: Development and implementation. NBS Special Publication: 676-II
- [3] Currie, LA (1995). J Pure & Appl Chem 67:1699
- [4] Ehrlich CD, Rasberry SD (1998). J Res NIST 103:93
- [5] EURACHEM (1995). Quantifying uncertainty in analytical measurement. 1st Ed.
- [6] ISO/IEC Guide 43-1 (1997). Internat. Org. for Standardization, Genève, Switzerland
- [7] Liu H, Probst A, Liao B (2005). STOTEN 339:153
- [8] MO 147 (1998). Romanian Law of Metrology
- [9] C. Oprea, S. Filip, A. Baluta, P. Pater, M. Fener, G. Istvan, A. Teusdea, M. Costea (2005). Environment & Progress 3:273
- [10] Oprea C, Maslov OD, Gustova MV, Belov AG, Szalanski PJ, Oprea IA, (2009). Vacuum 83 1:S162
- [11] Oprea CD, Mihul A, (2003). Romanian Rep in Phys 55 32:91
- [12] Oprea C, Gustova MV, Oprea IA, Maslov OD, Belov AG, Ciofu R, (2011). Proceedings of ISINN-18, 322
- [13] Oprea C, Maslov OD, Gustova, MV, Belov AG, Oprea IA, Ciofu R, Mihul A (2010). Proceedings of ISINN-17, 91
- [14] Parkany M (ed) (1993). Quality assurance for Analytical Laboratories, Royal Society of Chemistry, London, UK
- [15] Thompson M and Wood R (1995). J Pure & Appl Chem 67:49
- [16] Zschunke A (2000). Accred Qual Assur 5:441
- [17] Zschunke A (ed) (2000). Reference materials in analytical chemistry. Springer, Berlin Heidelberg New York
- [18] Yoon J, Cao X, Zhou Q, Ma LQ (2006). STOTEN 368:456