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PRODUCTION AND CERTIFICATION OF REFERENCE MATERIALS: EXAMPLES OF I.N.Ri.M. ACTIVITIES

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Abstract: Some I.N.Ri.M activities dealing with the preparation of reference standards and the certification of reference materials in the chemical field are presented. Their main characteristics, as well as the description of the used procedures and some indications on the uncertainty evaluation of all the significant sources are given.

Keywords: reference materials, metrology, gas mixtures, electrolytic conductivity, trace metal determination

1. INTRODUCTION

Analyses in the environmental as well as in food and nutritional areas imply the determination of various analytes, sometimes at very low concentration, in different and complex matrices. Accurate and reliable, hence traceable, measurement results are needed. Certified reference materials (CRMs) can be used at this purpose.

The National Institute of Metrological Research (I.N.Ri.M.) has among its duties the development, the maintenance and the dissemination of primary standards for establishing a correct traceability chain at national level. At the same time, it must act as connection between national and international metrology. For this reason, above all in the fields of chemistry and of environment, I.N.Ri.M. has been developing research activities on reference materials, dealing both with the preparation of primary reference materials and the reference material certification.

2. PURPOSE

In this work, some I.N.Ri.M. activities dealing with CRMs are presented. In particular, it focuses on the preparation of Certified Reference Solutions (CRSs) for electrolytic conductivity, Primary Reference Gas Mixtures (PRMs), and on I.N.Ri.M. contribution in the certification of various reference materials by determining trace metals by means of Instrumental Neutron Activation Analysis (INAA).

2.1. Certified Reference Solutions for electrolytic conductivity

CRSs for electrolytic conductivity prepared at I.N.Ri.M. are composed of ultra pure water and potassium chloride salt in different concentrations. At international level the employment of KCl has been chosen for its specific properties; it does not absorb humidity and is chemically inert. It is inexpensive, commercially available with high purity and in solution it dissolves completely and steadily in K^+ and Cl^- ions.

The electrolytic conductivity is a macro-descriptor parameter which allows to provide quickly and at low cost information on ion concentration in the solutions. If very low conductivity values (less than 1 μS/cm) are considered, this parameter enables to check the purity of water. Therefore it is a very useful and exploited parameter in pharmaceutical, environmental and microelectronic sectors. The CRS permits to the operator to calibrate the conductivity meters in *situ*, into the company, with a suitable periodicity chosen by the operator himself. Typically, the CRS is provided in 500 ml Pyrex bottles, with an hermetically closed cap with a seal, and equipped with label and analysis certificate.

The CRS production process consists of several steps carried out following the guidelines reported on the specific documents for the reference material producers [1,2]. After a particular washing process of the glassware the preparation of the solution is undertaken dissolving different amounts of KCl in ultra pure water depending on the aimed conductivity values, and afterward it is distributed in the bottles. The electrolytic conductivity value is determined employing the primary measurement system developed at I.N.Ri.M [3], that was tested in turn by the participation in three International Measurement Comparisons [4-6]. As an alternative the conductivity value is obtained using the secondary measurement system calibrated by comparison with the primary so that the traceability to the units of the International System (SI) is maintained. An homogeneity study [7] of solution among the bottles is carried out with a high resolution conductivity meter (WTW InoLab TetraCon 325) which allows to execute a fast and reliable measurement. The measurement is carried out taking a solution sample from each bottle belonging to the same solution batch, and determining the conductivity value with the conductivity meter. The variability of the conductivity value obtained among the bottles is then accepted only if it is lower than the conductivity meter resolution. In this case the homogeneity contribution results negligible in the uncertainty budget. Since the solution can be polluted during the time due to the air contact (contamination by CO_2 and by NH_3), or because of a desorption from the bottle glass, a solution stability study is carried out in order to establish how acceptable is the value drift within a specific uncertainty. Also in this case the WTW conductivity meter is used. The measurements are carried out taking different samples from the same bottles in time. The variance obtained by the measurements with the conductivity meter is one of the uncertainty contributions assigned to the solution conductivity value. According to the requirements given by the Guide to the Expression of Uncertainty in Measurement [8], the evaluation of all the uncertainty contributions is undertaken, considering the homogeneity and stability contributions as well as the ones connected to the primary or secondary measurement system and to the temperature. Finally, the analysis certificate associated to the CRS is delivered according to the requirements of reference documents [9].

2.2. Primary Reference Gas Mixtures

I.N.Ri.M. has a research activity on the preparation of PRMs by the gravimetric method [10].

The gravimetric method [11] is a primary method which consists in the introduction in two or more steps of determined amounts of gases (parent gases, which can be either pure gases or gas mixtures of known composition) in an evacuated cylinder. The mass of gas introduced in each step is measured. The mass fraction and then the molar fraction of each component is calculated from weighing data. Small uncertainty, direct relation to SI units, realization of a virtually infinite number of mixtures and the easiness of cylinder transportation, allowing their use in field, are the advantages of this method.

A facility for evacuating and filling cylinders and a device for high precision weighing were realized at I.N.Ri.M. Also in this case, the preparation steps of PRMs are carried out following the guidelines reported on the specific documents for the reference material producers [1,2]. Mixtures are prepared in aluminium alloy cylinders having a volume of 5 L. Before the filling steps, they are previously evacuated and treated to eliminate impurities. The weighing of cylinders is a critical step, since the determination of a small mass of gas introduced in a cylinder, which has a large mass and a large volume, requires attention to achieve good accuracy. For this purpose, the device for high accuracy weighing was planned to automatize the exchange of two cylinders, the one in which the gas mixture is prepared and the reference one. The mass comparison of the two cylinders reduces the correction due to the buoyancy effect. Calibrated mass standards are used to keep the mass difference between the two cylinders within 1 g, to optimise the mass comparator performance [11,12]. After the preparation, mixtures are homogenized by mechanical rolling and then analytically checked by means of Non Dispersive Infra Red (NDIR) spectroscopy in order to verify the whole preparation process. Mixtures stability is investigated by replicating the analytical measurements at regular intervals. The mixtures preparation process was validated by the participation in two International Measurement Comparisons [10] with very good results.

2.3. Certification of Reference Materials

INRIM activities in the inorganic chemistry field are focused on analysis of trace elements in environmental, biological, forensic and high purity materials samples [13,14]. In these activities development and validation of specific analytical methods are included. INAA and Graphite Furnace – Atomic Absorption Spectroscopy (GF-AAS) are employed as analytical techniques.

The certification activity of RM is carried out by participating in various international comparisons proposed in the CIPM and EURAMET frameworks.

In trace elements determination, INAA has been used as main analytical technique. It is based upon the conversion, of stable atomic nuclei in radioactive ones by irradiation with neutrons. The subsequent detection of the gamma radiation is performed using High Purity Germanium (HPGe) detectors. The irradiations are performed in the Triga Mark II Nuclear Reactor of the University of Pavia.

Irradiation time is selected basing on the decay life time of the element in analysis. It can vary from 30 to 500 seconds for short life elements and from 4 to 40 hours for medium and long life elements. Moreover irradiation time depends on the sample matrix and on the neutron flux. The element’s concentrations data are obtained measuring characteristic gamma-rays by isotopic specific neutron reaction. Gamma spectroscopy is carried out by high resolution detectors coupled to computerized multi-channel analysers. All the concentration results are obtained by comparator INAA (using primary standards).

3. RESULTS

3.1. CRSs for electrolytic conductivity

Currently I.N.Ri.M. develops CRSs for electrolytic conductivity in the range between 50 μS/cm and 1.3 S/m with an associated uncertainty lower than 0,7 %, at a temperature of 25 °C. Figure 1 shows an example of a stability study of a solution with conductivity value of 214,9 μS/cm at 25 °C. Four bottles have been used for verifying the stability for six months. When a bottle is run out of solution another one is opened. In the graph it is possible to note the increasing trend of conductivity value for each bottle. The swelling behaviour is due to the solution contamination with air CO_2 each time the bottle is opened. The variance of the whole set of measurements during six months is evaluated considering the maximum range within which the conductivity values are included and assigning a rectangular distribution. Depending on the conductivity range, the stability study and the associated uncertainty contribution are useful to evaluate the solution expiry date. For high conductivity solutions (more than 1400 μS/cm) the uncertainty value is assigned considering a solution stability of one year; while for low conductivity solutions the stability is guaranteed for six months. Currently, the uncertainty contribution due to the homogeneity among bottles is negligible; instead, the contribution due to stability is among the dominant ones. For each provided CRS, a bottle is kept in the laboratory in order to enable a periodical check of the conductivity value in case of customer complaint.

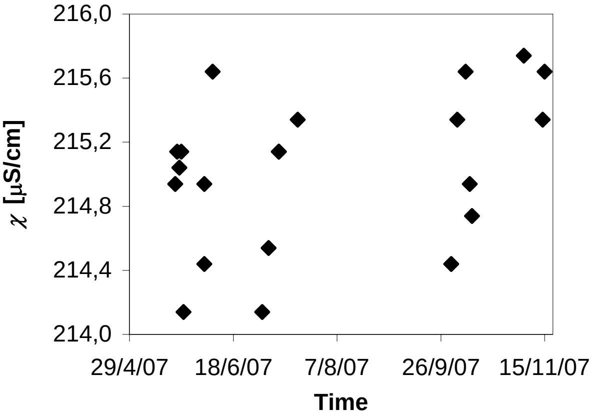

Fig. 1. Stability study for six months on a solution with electrolytic conductivity of 214,9 μS/cm at 25°C.

3.2. PRMs

At present, primary mixtures of carbon dioxide in matrices of nitrogen and of synthetic air at automotive emission level (10-14 % mol mol^{-1}) and at ambient level (200-400 μmol mol^{-1}) are prepared at I.N.Ri.M., having standard uncertainties deriving from preparation of some μmol mol^{-1}. The choice of carbon dioxide as analyte derives both from its environmental relevance as a greenhouse gas and from its role in some metrological measurements (buoyancy effect in calibration of mass standards, air refraction index in length measurements, solubility in water in electrolytic conductivity).

Uncertainty on PRMs concentration, u_{PRM}, is calculated (eq. 1) according to the uncertainty propagation law [8]:

$$u_{PRM} = \sqrt{u_{grav}^2 + u_{purity}^2 + u_{stab}^2} \qquad (1)$$

where u_{grav} derives from the gravimetric preparation and comprises also the uncertainty on molar masses of analytes, u_{purity} is the contribution due to the purity of parent gases and u_{stab} comes from the mixture stability. Each term takes into account the possible covariances between the different input quantities. At the moment, the term u_{stab} is the largest one. It is evaluated as the standard deviation of the differences among the analytical values, obtained during the NDIR verifications for the stability assessment, and the preparation weighing data. In figure 2 an example of the stability study carried out on seven different mixtures of CO_2 at ambient level in matrix of N_2 and of synthetic air is reported. After 24 months from the preparation, no significant trend can be observed. The dispersion of values leads to a relative standard uncertainty due to stability between 0,01 and 0,2 %. Similar studies carried out on mixtures at emission level lead to a relative standard uncertainty of about 0,3 %.

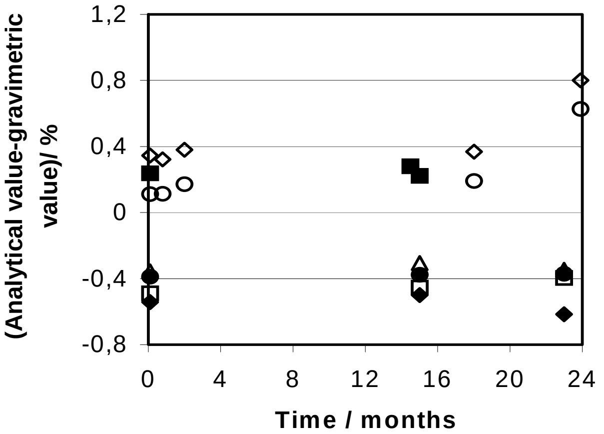

Fig. 2. Stability study for 24 months on 7 mixtures of CO_2 at ambient level.

The observed discrepancy between the two different concentration levels is due to the lower sensitivity of the NDIR analyser used for emission concentration.

3.3. Certification of Reference Materials

For the evaluation of the combined uncertainty in INAA analyses, typical chemical analysis contributes from sample mass, primary standards mass (solution concentration and dilution), moisture correction, blank etc. are considered. Moreover about 30 different parameters can be added specifically for the INAA, but only the most significant are really evaluated. They concern: irradiation parameters neutron flux exposures (i.e. irradiation position); count efficiency (i.e. solid angles with detector); counting statistics (i.e. baseline radiation from matrix); count rate effect (i.e. counting statistics and pulse pileup); potential interferences and their correction. An example of uncertainty budget for the determination of chromium and iron in an aluminium alloy is presented in table 1.

The certifying activities have allowed the attainment of reference material certification related to human health safety (nutritional and environmental related problems) as well as to technological problems (high purity materials). Of particular relevance is INRIM participation in the certification of SRM 2783 a simulated urban aerosol (PM.

sub.2.5) that has been deposited onto filter media and is certified for elemental content.

Table 1. Example of uncertainty budget for INAA analysis.

Uncertainty source	Type of evaluation	Contribution (%)	
		Cr	Fe
Counting statistics for samples	A	0,25	0,90
Counting statistics for standards	A	0,15	0,65
Blanks	A	Neglected	0.05
Isotopic abundances	B	Neglected	Neglected
Neutron fluence and irradiation geometry	B	0,5	0,5
Neutron self-shielding	B	Neglected	Neglected
Neutron scattering	B	Neglected	Neglected
Counting geometry	B	0,5	0,3
Gamma-ray self-absorption	B	0,1	0,08
Effect of half life	B	Neglected	Neglected
Pulse pileup and live time correction	B	0,1	0,1
Interfering nuclear reaction	B	Neglected	Neglected
Gamma-ray interferences	B	Neglected	Neglected
Sample mass	B	0,03	0,03
Standards mass	B	0,25	0,25
$\boldsymbol{u_c}$		**0,82**	**1,29**
***U* (*k*=2)**		**1,64**	**2,57**

The successful participation in the international comparisons permitted the declaration of the following CMCs in the BIPM database [15]: iron, chromium, manganese in aluminium alloy, arsenic, selenium in fish tissue.

In the field of applied research, the activity has been focused on atmospheric pollution related problems (indoor, urban, remote areas, bio monitors) as well as on studies related to neurodegenerative diseases (Parkinson).

4. DISCUSSION

The realization of the above CRMs is performed according to specific documents for reference material producers [1,2]. In addition the participation with success to related international comparisons underpin their value and mutual comparability with similar CRMs produced by other National Metrological Institutes. The certificated values, in terms of stability and uncertainties are comparable with the ones obtained by other NMIs and are satisfactory for the main user requirements.

It is noteworthy that the proposed I.N.Ri.M. reference materials are produced and characterised by means of primary methods, which are at the top level in terms of metrological characteristics.

A particular attention has to be paid to INAA, being a technique which is not very common as it requires the presence of a nuclear reactor for sample treatment. INAA presents some important peculiarities: high sensitivity, multielementary analyses, high accuracy and precision. If compared with other techniques commonly used for the determination of trace elements in various matrices, it presents many other advantages: it can be used for the analysis of micro-samples (fraction of milligrams); it is a non-destructive analysis, as the sample digestion is not necessary; the chemical state and the physical form of the analyte do not affect the analysis and elements such as H, C, N, O, Si, do not affect the determination of others. In addition, there are many adjustable experimental parameters for optimizing the experimental design and it is suitable for determination of total elemental content up to 10^{-9} g or less.

At present, the number of I.N.Ri.M. products is still limited, but well supported by the results obtained in international comparisons. The availability of increased human resources will enable I.N.Ri.M. to enlarge its contribution to the international community.

5. CONCLUSIONS

I.N.Ri.M. activities related to CRMs, even if relatively recent, are encouraging. In order to consider the needs of establishing a correct traceability chain to allow the metrological activities of the national bodies, accredited and field laboratories involved in various sectors related to the environment, food and nutrition, other developments are in progress. The declaration of new CMCs on the BIPM database related to CRMs production is foreseen.

Recently I.N.Ri.M. attended an International Comparison about seawater salinity measurement [16] to expand I.N.Ri.M. measurement capabilities to high conductivity values (more than 5 S/m) and to offer new CRSs of interest for the marine community. Moreover the development of a flow system with a closed-circuit which allows to avoid pure water contamination is in progress. This new measurement system will permit to expand the measurable conductivity range to values lower than 1 μS/cm, and to produce the correspondent CRSs in order to satisfy the growing needs in the pharmaceutical sector.

As for PRMs, the preparation of gravimetric mixtures of NO_X in nitrogen and in synthetic air has just started and it will be extended to other analytes, such as CO, CH_4, C_3H_8 and their combination to meet traceability needs at national level. Purity of parent gases is also under investigation and hopefully it will allow to reduce the uncertainty on the composition. Some investigations are still needed for a better evaluation of uncertainty deriving from the stability.

Furthermore, the analytical methods developed for the RM certification by INAA, will be applied to actual and future studies, in particular related to element determination in biological fluid, in air particulate matter, in brain tissues to study neurodegenerative diseases, and to other studies about health and environment.

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