

In metal matrices, homogeneity is regularly being tested by spark emission spectrometry. Unfortunately, this fast and easy method is not applicable to all matrices. In the case of wood, soil, ceramics, and others, activation analysis offers a practicable alternative. Whenever possible and recommendable, certification analysis is performed by a large number of laboratories using a great variety of analytical methods. Assuming that each method comes with a systematic deviation, chances are good to find the "true" value when a mean is formed from a great variety of them. Photon activation analysis and neutron activation analysis with their outstanding physical principle (nuclear reaction) as well as the possibility of a purely instrumental approach or of easy determination of the chemical yield are endowed with an especially valuable status.

EXPERIMENTAL SETUP

Radiation sources are a 30-MeV linear accelerator (linac) at BAM and a nuclear reactor at Hahn-Meitner Institute. Their corresponding fluxes amount to $10^{14} \text{ cm}^{-2} \cdot \text{s}^{-1}$ each for gammas and thermal neutrons. In the special case of Si_3N_4 analysis, we had the opportunity to have access to NIST's reactor. Measurements are performed by gamma spectrometry. For this purpose, NaI detectors as well as coaxial, planar, and well-type germanium detectors, together with the appropriate electronics, are used. Photon activation of light elements delivers pure β^+ emitters. Because of the uniform character of their gamma spectra (annihilation peak only), they cannot be discriminated from each other by peak evaluation. Decay curve evaluation may offer some help, but normally, radiochemical separation steps have to be inserted prior to the measurement of ^{11}C , ^{13}N , ^{15}O , and ^{18}F .

RESULTS

Results of the homogeneity testing of soil BRM 5 will be reported as well as the results of the certification campaign of Si_3N_4 for Al, Ca, Co, Fe, Mg, Na, W, N, and C concentrations and additionally for the *a/b* phase ratio.

4. New Modes of Certifying NIST Standard Reference Materials, and the Role of Neutron Activation Analysis, Robert R. Greenberg (NIST)

Standard reference materials (SRMs) are certified reference materials (CRMs) issued under the National Institute of Standards and Technology (NIST) trademark that are well characterized using state-of-the-art measurement methods and/or technologies for chemical composition and/or physical properties. Traditionally, SRMs have been the primary tools that NIST provides to the user community for achieving chemical measurement quality assurance and traceability to national standards. There are two aspects of certification—one legal, the other scientific. Legally, the certification process indicates that an NIST SRM carries the full weight and legal authority of both the U.S. Department of Commerce and NIST in that these are official materials authorized by appropriate federal laws and regulations. NIST SRMs are incorporated into many regulatory requirements as measuring tools for assuring quality and for achieving traceability to the U.S. national measurement system developed and maintained by NIST.

The scientific aspects of certification are also of importance to the analyst. The goal of any SRM certification is to report the "true value" of a given property(ies) under investigation and the level of confidence in the true value. Therefore, NIST measurement results are accompanied by quantitative statements of uncertainty. To ensure that such statements are consistent with each other and with current international practice, the NIST policy for evaluating and expressing the uncertainty adopts in substance the approach recommended by the International Committee for Weights and Measures (CIPM).

Historically, NIST has used three basic modes for certification:

1. measurement by method(s) of high precision and for which sources of bias have been rigorously investigated; the applicability of the method(s) have been demonstrated and documented across a range of diverse matrices
2. measurement by two or more independent and reliable methods whose estimated uncertainties are small, relative to the accuracy required for certification or SRM purposes and use
3. measurement via a network of qualified laboratories.

Until recently, NIST has provided two types of values on certificates: certified and noncertified values (those previously given for information only were noncertified values).

In response to increased customer needs for documentation and clearly defined terms associated with assigned values of reference materials and the value-assignment process, we provide definitions and descriptions of the terms used for assigned values of NIST SRMs, NIST traceable reference materials, and reference materials intended chemical measurements. The terms and modes as described are applicable for reference materials for chemical measurements issued by NIST as of October 1, 1998. We have also split the noncertified values into two different types: reference and information values. The basic principles remain unchanged; however, NIST's defined modes provide a clearer link between the nature of the value-assignment process and the definition of the assigned value (e.g., certified value, reference value, information value). The strength of the measurement link is directly related to the mode(s) used in the value-assignment process.

There are a total of eight defined modes: three basic modes for value assignment that lead to certified values and five value-assignment modes that provide reference values and/or information values. An NIST Certified Value represents data reported on an SRM certificate for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been fully investigated or accounted for by NIST. An NIST Reference Value is a best estimate of the true value provided on an NIST certificate, certificate of analysis, and/or report of investigation where all known or suspected sources of bias have not been fully investigated by NIST. An NIST Information Value is considered to be a value that will be of interest and use to the SRM/reference material user, but insufficient information is available to assess the uncertainty associated with the value.

For the last 35 yr, NAA in its various forms has provided major contributions to the certification of NIST SRMs.

5. INAA Keeping Pace with Analytical Quality in the Certification of Reference Materials, Elisabete A. De Nadai Fernandes (CENA-Brazil), Vera Maria L. Ponçano A. Silva (IPTE-Brazil), Mitiko Saiki (IPEN-Brazil), Peter Bode (Delft UT-Netherlands), Robert R. Greenberg, Donald Becker (NIST)

The National Metrology Plan (PNM) in Brazil was conceived in 1998 as the result of a strategic effort between national and international experts and organizations. Its aim was to define the necessary actions to ensure that the competence for measurement will be available to the Brazilian society by the year 2002, thus inducing competitiveness and economic and social development of the country. In the same year, a multi-institutional project was approved with the objective of contributing to the organization of the activities involved in the production and distribution of certified reference materials and based on a critical analysis of market demand. This project, with proposed implementation in 1999, will also identify centers of national compe-

tence, existing or potential, that can act as reference laboratories. These centers are of fundamental importance for the establishment of metrology in chemistry in Brazil.

The Instituto de Pesquisas Tecnológicas do Estado de São Paulo (IPT) is the only entity in Brazil officially developing and producing certified reference materials. Celebrating the 100th anniversary of its foundation, IPT maintains the tradition of developing activities connected with normalization and industrial quality, especially in the field of preparation and certification of reference material with an international level of confidentiality (ISO/REMCO). Such activities started in 1975 in technical cooperation with the National Institute of Standards and Technology (NIST) and with the financial support of the São Paulo state government, under the responsibility of the Center for Reference Materials. Since then, >100 different types of reference material (steels, cast irons, bronzes, ores, minerals, oils, etc., in the form of chips, disks, powders, or liquids) have been produced and certified with the main objective of providing consumers (chemistry, petrochemistry, siderurgy, and metallurgy industries) with materials with assured quality measurements in compliance with ISO and international trade requirements. The credibility of IPT's certified reference materials can be derived from their wide acceptance in the importing countries (United States, United Kingdom, Germany, France, South Africa).

The certification of IPT reference materials has been carried out mostly by interlaboratory programs, with the participation of six to ten laboratories, that have provided information about the chemical or physicochemical properties of such material. The certificates include all the necessary statistical data, such as means, standard deviations, confidence intervals, and also the summary of the analytical methods employed, conforming to ISO Guide 31.

In 1978, a phosphatic rock concentrate was among the first ore reference materials produced by IPT, including manganese ores, iron ores, limestones, clays, feldspars, glass sands, and fluorospar. Some are already out-of-stock, but the majority are still commercially available. Those with exhausted stocks, but still in demand, have been replaced by new entries. This is the case of the phosphatic rock (IPT 18) for which the new entry of reference material, the IPT 18A, is already out of stock. Such material was offered in a powdered form (<0.075 mm) and certified for the constituents P_2O_5 , CaO, SiO_2 , F, soluble Fe_2O_3 , soluble Al_2O_3 , MgO, Na_2O , K_2O , and SrO, using classical analytical methods (gravimetry, volumetry, and coulometry). Neutron activation analysis has not been used for the certification procedure at IPT.

Phosphatic rock can be used per se or as raw material to produce phosphoric acid for phosphatic fertilizers. The knowledge of composition of phosphatic rock is of utmost importance for the fertilizer industry to certify its products to be appropriate for the recommended use in agriculture. Phosphate rocks are natural deposits of phosphorus- and calcium-containing minerals. Therefore, trace element concentrations may vary, depending on the geological origin of the deposits. The fertilizer industry has to determine not only the trace elements of agricultural interest but also elements such as Cu, Cd, Ni, Zn, Co, Pb, and Mn, which are considered to be of potential environmental concern. The trace element characterization of this kind of reference material (IPT 18 and IPT 18A) is therefore needed to support the quality control at the laboratories of the fertilizer industry, agricultural laboratories, and laboratories involved in environmental control. It was conceived that INAA would be useful for this because it is an independent and nondestructive multielement technique.

In the first intercomparison study, four INAA laboratories were contacted for participation: Radiochemistry Division, IPEN/CNEN, São Paulo, Brazil; Radioisotopes Laboratory, CENA/USP, Piracicaba, Brazil; IRI, Delft University of Technology, The Netherlands; Analytical Chemistry Division, NIST, Gaithersburg, Maryland. To harmonize the analytical approach envisaging the statistical treatment data, each laboratory was requested to perform six replicates from a single sample and to determine as many elements as possible, including those conventionally de-

termined via wet analysis, following routine analytical procedure. The results for 30 elements, 10 REEs (La, Ce, Nd, Sm, Eu, Gd, Tb, Dy, Yb, Lu), Al, Ba, Ca, Cl, Co, Cs, Fe, Hf, K, Mg, Mn, Na, Sc, Sb, Sr, Ta, Th, U, and Zn, are currently under statistical evaluation for their appropriateness in the final characterization and certification of this material, which is expected to be incorporated as the third entry of the IPT phosphatic rock concentrate by the end of 1999.

6. Preparing and Characterizing Standards for Hydrogen in a Titanium Alloy, Richard M. Lindstrom, Rick L. Paul, H. Heather Chen-Mayer (NIST)

The presence of excess hydrogen in a structural titanium alloy reduces its mechanical strength. If the hydrogen concentration exceeds ~100 mg/kg, titanium hydride precipitates as a separate phase, preferentially at grain boundaries. As a result, controlling the hydrogen concentration is crucial. Standard methods for analysis (e.g., American Society for Testing and Materials E1447) are destructive, using high temperature in inert gas or in vacuum to extract the hydrogen. These methods are rapid but assume that all the hydrogen present is extracted, and they also require materials with known composition for calibration. In a related area, quantitative nondestructive assay by neutron radiography or tomography also requires artifact standards with known hydrogen content. Methods have been set in place at the National Institute of Standards and Technology to produce standard reference materials (SRMs) and other standards to satisfy these needs.

The reaction $Ti + H_2 = TiH_2$ is reversible. From the free energy of formation (105 kJ/mol), one may calculate that the equilibrium pressure of H_2 is below 10^{-8} Pa ($<10^{-13}$ atm) at room temperature, and 5 MPa (50 atm) at 800°C. The reaction is rapid above 500°C. Specimens with known hydrogen content are prepared by degassing a weighed quantity of titanium alloy in vacuum at high temperature and reacting it with a known volume of hydrogen gas in a closed vessel. The composition is stable at room temperature.

The accuracy of the concentration thus achieved is limited by the pressure and volume measurements in the reaction system (accuracy >0.5%) and by any residual hydrogen left after bake-out. For additional certainty, the hydrogen concentration measured volumetrically is confirmed by several methods of lower accuracy or sensitivity. For high concentrations (above ~100 mg/kg), weighing the sample before and after treatment gives easily measurable changes in good agreement with the volume dosing. Prompt-gamma activation analysis with cold neutrons¹ (CPGAA) is specific for hydrogen, but limited counting statistics make measurements below 100 mg/kg imprecise. More sensitivity, but more matrix dependence, is obtained from neutron incoherent scattering² (NIS). This method can be used to measure as little as a few tens of mg/kg, which is useful to confirm the efficiency of the initial bakeout.

The process was validated with a small-scale dosing system constructed of copper tubing and quartz. A series of 10-g batches of 1-mm Ti alloy sheet (6% Al, 4% V) was prepared by the procedure outlined earlier. The metal was cleaned with solvents, weighed, and degassed at up to 900°C with continuous turbopumping. After reweighing and reevacuating, hydrogen was admitted to the system, and the temperature rose to 500 to 600°C, where reaction was rapid. Equilibration was promoted by holding the samples at 300 to 400°C overnight, then cooling to room temperature; the gas was quantitatively absorbed. Analysis showed good agreement between the volumetric measurements and independent CPGAA (Table I) and NIS determinations. Several specimens of SRM 654b, in the form of a 3.5-cm-diam, 1.9-mm-thick, 82-g billet, were loaded with hydrogen up to 800 mg/kg as calibrants for neutron-tomography measurements using this