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REVIEW PAPER

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# Certified reference materials in analytical chemistry – A century of NIST contribution

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**Abstract** Over the course of its first 100 years, the National Institute of Standards and Technology (NIST) has made numerous contributions to advancing the science and practice of analytical chemistry. Contributions to fundamental constants and reference data, such as determination of the Faraday, Avagadro's number, and atomic masses, began at almost the beginning of the new institution when it was formed in 1901. Instrumentation development, improvement, and reproducible methods for its use have also been an important part of the NIST effort. This paper will describe what may be the organization's most important and certainly its most unique contribution; namely, certified reference materials. Ultimately these certified reference materials would become known at NIST as standard reference materials (SRMs). It is a contribution that now has been mirrored around the world with reference materials being certified in at least 25 countries and routinely applied in more than twice that number. The result has been more accurate analyses of materials that impact our safety, health, and well-being.

## Background

As we celebrate the first century of NIST, we must note that the contributions of an organization can only originate within the minds and then hard work of the people of that organization. This is important to remember because in an article as short as this one, it is quite impossible to give fair recognition to the thousands who have produced the contributions. Let us agree then to remember those people whenever NIST or "the Bureau" are mentioned. The term Bureau is appropriate to cover the first 87% of the century. In 1901, the agency originated as the National Bureau of Standards (NBS), but soon had its name abridged to simply Bureau of Standards, in 1903. "National" was restored to the name in 1934, to differentiate it from the many state-level bureaus of standards which had been established. There was no further change until 1988, when the current name National Institute of Standards and Technology was received.

The mission of the new agency was defined in its "organic act" legislated by the United States Congress. While that very brief act makes no specific mention of reference materials, several of its key provisions would provide for their inclusion. The entire charge to the new agency was found in six provisions:

- Custody of the standards
- Comparison of the standards used in scientific investigations, engineering, manufacturing, commerce, and educational institutions with the standards adopted by or recognized by the Government
- Construction, when necessary, of standards, their multiples and subdivisions
- Testing and calibration of standard measuring apparatus
- Solution of problems which arise in connection with standards
- Determination of physical constants and the properties of materials, when such data are of great importance and are not to be obtained of sufficient accuracy elsewhere.

In 1901, the "standards" were largely seen as benchmarks for physical measurement such as mass, length, volume, and electrical quantities. It was the last of the six provisions that gave impetus to the growth of materials science and technology efforts that would expand to be the largest share of the Bureau's work from 1910 to the present. Even this emphasis did not give immediate rise to the concept of issuing certified reference materials.

At the time, chemists throughout the world were expected to develop and maintain their own lots of materials that could be used as benchmarks for calibrating or testing analyses. This practice could help with questions of laboratory internal consistency but shed little light on analytical disagreements among several laboratories. Methods were practically limited to those based immediately on first principles where standards could be physical. This still left open questions of completeness of separation, stoichiometry, purity of reagents, and other issues. Evaluating the accuracy of newly emerging instrumental methods would produce even greater need for certified reference materials to serve, first as accuracy benchmarks, and then as calibrators for quality assurance into the future.

## An urgent need

Many of the greatest technical challenges of the early twentieth century were related to materials and their performance. Construction of skyscrapers and suspension bridges would require new and stronger alloys of steel, and better quality control for Portland cement used in concrete. Tungsten alloy performance would become critical to vacuum tubes for lighting and electronics. Copper alloys would figure heavily in wiring for communications and in valves and fittings with nearly endless configurations.

Perhaps the material concerns were nowhere more critical than in the automotive fields. Practical automobiles and aircraft were on the threshold – they needed an array of new materials ranging from nodular cast irons to high strength aluminum alloys to specialized rubber to carefully tempered glass. New and vastly larger ships were on the drawing boards – they needed new alloys of corrosion resistant steel, monel, bronze, and many other improved materials. Railroad trains had already increased the speed of overland transport by an order of magnitude, but not without the cost of many lives due to material failures. Preventing future loss of lives was an urgent need that pressed the Bureau into the new venture of certifying reference materials.

In 1905, the American Foundrymen's Association approached the Bureau to see if it would assume leadership of a new work the Association had recently begun. The Association was trying to solve the problem of rail car derailments due to the fracturing of cast iron wheels. Appropriate alloys had been found and Association research showed that they would cure the problem. However, the chemical laboratories at the various foundries that supplied materials to the railroads could not analyze the materials with sufficiently consistent accuracy to provide ongoing quality assurance. The problem as the foundrymen defined it was to have a source of accurately analyzed materials having compositions at and bracketing the compositions of alloys known to be acceptable. Those "standardizing" materials could then be used by the foundries to maintain their analyses in control.

The Bureau accepted the challenge and set to work – but not alone. In fact, this very first reference material project set a precedent for cooperative efforts that would continue to this day. Included in that precedent is the idea that projects will be started only on demonstrated need and demand of the technical community. Furthermore, priority will be assigned to those projects where cooperation of the requesters is assured. This has helped the Bureau select worthy projects over the years. The cooperation has included provision or preparation of materials and contribution of data to the certification campaign. In the case of the first ever project, cooperation by the American Foundrymen's Association extended to all three of these aspects.

When the first project was completed in 1906, four materials were placed on sale together with their certified analyses to serve as the needed benchmarks. They consisted of bottles of cast iron chips which were labeled "Standardizing Iron A," through "Standardizing Iron D." Their worth was quickly realized in improved cast iron rail car wheels and an improved safety record for the railroads.

When the initial lots of materials were exhausted, they were replaced with new lots of nearly equal composition. Of course the new lots were slightly different, thus new certification campaigns were required to provide new certificates of analysis. Also different was the labeling system. By the time the second lots were prepared, the cast irons were part of a larger program of reference materials, which by about 1910, had become known as "Standard Samples." "Standardizing Iron B" became "Standard Sample No. 4 – Iron B." Standard sample numbers one and two had been assigned to other materials, so they were not available to the cast irons. Two of the original formulations of cast iron have been renewed at every exhaustion, until today. For Cast Iron C, there have now been more than 14 lots prepared over the past 95 years.

## Success inspires imitation

The success of the cast iron reference materials led to expansion of the concept into new material types. Certification work on several other alloys, iron ores, and copper slags began the same year as the cast irons were issued. All these activities caught the interest of the steel producers. A member of the Bureau's Visiting Committee, Albert Ladd Colby, was a leading authority on metallurgy and he urged the Bureau to extend its success with cast iron into the field of steel. Perhaps because it was smaller then, the Bureau was quite agile in starting new projects and new cooperative ventures. It was able to start the new effort together with the Association of American Steel Manufacturers, in 1907. A series of 17 steel standard samples emerged and started NBS-NIST on a path of support to the United States steel industry that has spanned nine decades.

By 1911, the catalog of reference materials had grown to 25 entries, all in support of chemical analysis. More importantly, the interest of the Nation's chemists was growing too, with observation of the utility of the "Standard Samples" wherever they were available. Clearly more types of materials would be needed and they were on the way with the cooperation of the American Chemical Society, and later the Portland Cement Association, the Copper Development Association, and numerous other groups.

The early work on Standard Samples at the Bureau had a profound impact on the later work of the agency. The United States Congress had initially seen the agency as being primarily dedicated to construction and maintenance of the physical standards of measurement. However, the great success of the Standard Samples work weighed heavily in steering most of the growth of the new agency into the direction of solving practical material problems, in some cases using cutting edge instrumentation and methods. Later amendments to the agency's organic act recognized the Bureau's contributions to materials characterization and development, and by 1950 provided specific authority to certify and distribute reference materials as the leading United States authority.

## Launching domestic industries

Research at the Bureau occasionally gave initiative for the production of a new SRM, and very often provided the tools needed to certify materials with a reduced uncertainty. There are also cases where the production of an SRM inspired the start of an industry new to the United States. A striking example of that occurred during the first World War. Before that war, the Bureau was distributing standard samples of sugar for three important applications: calibrating saccharimeters; measuring the heat content of fuels; and, for use in differentiating bacteria in medical laboratory tests. Germany was the source of the pure sugars which NBS characterized, certified, and sold. When the war broke out and the materials were no longer available, NBS had to produce its own pure sucrose and dextrose. The German patents and production literature were written so obliquely to protect proprietary rights from other producers that reconstruction of the production processes required almost completely original research. The results were well worth the effort because the output was not only the standard samples, but also the technology for producing low-cost dextrose that launched a new domestic industry for American sugar producers and corn farmers.

The connection with instrument manufacturers is perhaps less direct; but, nevertheless just as real. The ideas developed at the Bureau to solve all manner of analytical problems were frequently blended with the work of instrument makers to either create new instruments or impact the progress in developments of existing ones. Perhaps the tradition started with recruitment, from 1901 to 1904, of the first 24 professional staff members, six of whom were from the Johns Hopkins University. Johns Hopkins was at the time a leader in spectroscopic technology. Included in the group of six were William Noyes, Henry Stokes, and Edward Hyde. It was Noyes who first produced atomic mass data at the Bureau, reporting the weights for several elements, including hydrogen at 1.00783, in 1907. In 1905, William Coblentz joined the staff and would serve the Bureau for the next 40 years. By 1914, William Meggars had also joined the staff, and a wide variety of spectroscopic techniques were being developed which would later find their way into commercial production. Just as many of the early instrumental techniques for chemical analysis would find their basis in spectroscopy, so would the need for reference materials grow. This resulted from most spectrochemical techniques requiring reference materials as calibrants.

## Continuing efforts

Between the two World Wars, SRM activities grew slowly, but steadily. Industrial needs for materials for chemical analysis were the major, almost exclusive, impetus. Starting in World War II the needs for SRMs began to grow and change.

As a primary national laboratory for materials research, NBS contributed to the Manhattan Project through uranium studies. Among other accomplishments, NBS scientists carried out pioneering work in the separation of uranium isotopes and developed SRMs for determining the isotopic composition of materials containing uranium and plutonium. These materials continue to serve the country today for the accurate assay of enriched and depleted reactor fuels.

After the war, breakthroughs in the fields of electronics, polymer research and the spread of spectrometric instruments brought new demands for reference materials. By the 1950s special hydrocarbon blends were available for calorimetry and SRMs were being certified for such properties as pH, melting point, and radioactivity. New high temperature and super strength metal alloys were needed to meet the demands of innovations in jet aircraft and rockets. The 1950s and 1960s saw an acceleration of efforts to certify reference materials with 582 types available in the catalog in 1969. It was during this period that the Bureau began to transfer some of its efforts in reference materials to other institutions. More about this will be discussed in the section of this paper “Closing the Cycle.” During the 1960s, NBS realized that SRMs were becoming increasingly important to industry and that industrial demand would continue to grow. The Bureau also recognized the potential contribution SRMs would have in solving measurement problems in emerging areas of national need such as clinical and environmental chemistry.

Consequently, in 1964 the Office of Standard Reference Materials was established and given the responsibility for directing all SRM activities. Previously the individual technical divisions had managed separate components of the SRM program with coordination through the Analytical Chemistry Division. With the establishment of a new office, a number of new thrusts were developed. New program areas were identified and initiated, including the start of what was to become a major effort in developing SRMs for clinical chemistry.

Through the 1970s the program had its most productive decade in terms of the development of both numbers and types of SRMs. Over 600 new SRMs were certified during that period and about 250 were discontinued. By 1979, 1,060 types appeared in the catalog. Typical of the research activity into new SRM types in this period was a whole array of environmental natural matrix materials certified for inorganic constituents. Leading the list, and arguably the most important materials of their era, were SRM 1571 – Orchard Leaves, SRM 1645 – River Sediment, and SRM 1648 – Urban Particulate Material. John Taylor directed the certification of these materials. The river sediment was prepared from material dredged from the Indiana Harbor Canal, near Gary, Indiana. The material was heavily loaded with toxic metals and served as the initial benchmark for environmental studies in the field. It is also important from an analytical perspective in that these were the first environmental matrix materials to receive extensive application of the new isotope dilution mass spectrometry method, which was also used to good effect in the certification of SRM 909 – Human Serum.

During the 1980s the many advances in inorganic environmental reference materials were extended by the addition of certifications for organic analytes of environmental health concern. Some of these included PCBs in human serum, in oil, and in sediments. Also available were a variety of forms of dioxin, polynuclear aromatic hydrocarbons, halocarbons, chlorinated pesticides, and other priority pollutants.

To some extent food materials began coming into the inventory, in the 1970s and 1980s, with the introduction of such materials as wheat flour, rice flour, and freeze-dried bovine liver, oyster tissue, and spinach leaves. The efforts toward better coverage of food types really have seen the most progress in the 1990s, with work being dedicated to certifying mixed diet food materials, infant formula, and several materials for vitamin content. Efforts along these lines are sure to continue into NIST’s next century.

## Closing the cycle

As many types of reference materials matured and NIST interests turned to other technologies, efforts have been made to find institutions willing to receive transfer of the materials and responsibilities. This has been essential to permit reallocation of scarce resources to new efforts.

During the 1950s and 60s some of the first of these transfers began to take place. The extensive hydrocarbon blend project was transferred to the American Petroleum Institute. Color and fading reference materials were transferred to the American Association of Textile Chemists and Colorists, while viscosity materials went to Carnegie-Mellon University. During the 1980s, in part for security reasons, the reference materials for uranium and plutonium were transferred to the New Brunswick Laboratory of the United States Department of Energy’s Argonne National Laboratory. At the beginning of the 1990s, NIST was closing out its work on rubber compounding, so about a dozen types of rubber compounding SRMs were transferred to ASTM. These are a few of many examples of “passing the baton” on materials that NIST can no longer support.

Not all the transfer efforts have involved actual transfer of the materials. The metal materials which have figured so heavily in the early development of the reference material program, have remained at NIST, while much of the certification effort on renewal lots is undertaken by laboratories organized in cooperation with ASTM. It is highly likely that the trend will be for NIST to continue to seek partners in industry, universities, or other government agencies to provide homes for materials being closed out at NIST.

## Collaboration around the world

Especially over the past 50 years, the Bureau has nurtured strong ties for international cooperation. More recently, about 25 years ago, ISO accepted as a Council Committee a group to work on reference materials. The committee was first referred to as REMPA and very quickly had a change in name to REMCO. Strong impetus for its founding and early success was supplied by

NBS staff members such as Bill Andrus, Paul Cali, and George Uriano. REMCO has become the focus for defining the terminology and practices of reference material certification and use.

NIST has participated in many bilateral and multilateral cooperations. Some of these have had as a goal certification of a specific SRM or groups of SRMs, while others have been oriented toward helping other countries get started in the field. As an example of the latter, NIST hosted approximately 200 hundred chemists from China over the first 15 years following renormalization of relations between the 2 countries. Analysis of SRMs was part of the effort for many of the chemists. Some of them, on return to China, have established a very vital program in production of reference materials. On a smaller scale cooperative projects have been shared with Mexico following the implementation of the North American Free Trade Agreement and agreements for cooperation in metrology. Additional efforts have been carried out with Egypt, Poland, and several other countries.

Some of the most effective collaborations are those aimed at gathering data to characterize proposed new reference materials. In recent years these have included many countries contributing to the development of the infant formula and mixed diet SRMs, and a large suite of food SRMs from Canada. Other efforts have included contributions from most of the world's industrialized countries. An earlier example occurred in the late 1970s. NBS partnered with 70 individuals from 22 organizations in the United States copper industry and the ASTM to develop a series of unalloyed copper SRMs. Robert Michaelis, Jerry Hust, and Lynus Barnes directed the effort which received not only a large measure of United States industrial support, but also the contribution of data from Canada, South Africa, South America, and the European Union.

## Conclusion

The aim of this brief paper has been to highlight a few of the many contributions that NBS-NIST has made to the world through the certification and distribution of reference materials. The selection of examples only begins to probe the surface and cannot do real justice. Many chemists will, however, relate to the great feeling of success that follows analyzing an SRM from NIST and obtaining the certified values! Just as valuable can be the relief of discovering early a disagreement and thereby preventing the propagation of an error.

Reference materials have been one of the most widely realized of all the Bureau's contributions, with several million units having been circulated in the first century. Few are the chemists around the world who have not heard of the possibilities that SRMs offer for validating a method or calibrating an instrument. By sharing the ideas and technologies of reference material development, the Bureau has been a good neighbor in the world community.

Reference materials have represented some of the finest efforts produced by NIST. By successfully solving material related problems and bring attention to those successes, the work on reference materials has had a major effect on the development of the early Bureau's selection of work program and ultimately its character as an organization. It has been an exciting century for the field of reference materials in aid of analytical chemistry. Perhaps it will be seen in another 100 years as a worthy introduction to the even greater things that are yet to come.

## References

Two excellent books serve to convey the times surrounding and developments at NIST over its first 70 years. A third volume in the series is currently in preparation. The two books that have been especially useful in writing this paper are:

1. Cochrane R C (1966) In: Newman J R (ed) Measures for progress – A history of the National Bureau of Standards, and editorial consultant, U.S. Department of Commerce Library of Congress Catalog Card Number 65–62472.
2. Passaglia E, Beal K (1999) A unique institution – The National Bureau of Standards 1950–1969, U.S. Department of Commerce available from the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402–9325