Pure & Appl. Chem., Vol. 49, pp. 1483 - 1484. Pergamon Press, 1977. Printed in Great Britain.

THE ROLE OF REFERENCE MATERIALS IN ANALYTICAL CHEMISTRY

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Abstract - Meaningful measurements in analytical chemistry are achievable when both reference materials and reference methods have been standardized. Reference materials serve as one essential foundation of analytical chemistry, especially with instrumental techniques in the exploration, mining, and metallurgical industries. Analysts in these fields continually are making measurement comparisons. For any given measurement system, meaningful comparisons are possible only when referred to the common base of reference materials. The philosophy underlying the use of reference materials in making compatible and meaningful measurements will be developed.

The planning, preparation, and characterization of reference materials are exacting tasks that must be thoroughly investigated if these materials are to successfully perform their role toward standardization and meaningful measurements. Details of the investigative procedures will be given.

In view of the many hundreds of thousands of industrial processes requiring analytical control, it is no wonder that the demand for reference materials far exceeds the world's capability to produce them. This ever widening gap has been of utmost concern to the NBS Office of Standard Reference Materials, and has led to a program to produce the essential "benchmark" reference materials to serve as the anchor points for calibration in many measurement systems. Specific examples will be presented dealing with the preparation of "benchmark" reference materials for the mineral and metal industries. Included will be studies for homogeneity testing and analytical characterization, both of which employ statistical design and evaluation.

INTRODUCTION

Analytical chemistry continues to play an increasingly important role in nearly all facets of materials development and utilization. Literally, many millions of measurements reporting on the properties of materials are made on a daily basis. Analytical systems abound with sophisticated instrumentation to provide rapid and precise measurements. Most of these, however, are dependent on comparisons with or calibration by "knowns", commonly called reference materials. The accuracy of these measurements is directly related to how well the reference materials have been characterized and the similarity of the reference materials to the "unknowns" with which the analyst must deal.

DEFINITION AND PURPOSES OF REFERENCE MATERIALS

In the context of this paper the term "reference material" is defined as one whose properties of interest have been numerically assessed and certified by a recognized laboratory or technical group. In the U.S.A. the National Bureau of Standards (NBS) has the statutory responsibility for the production, measurement, and certification of reference materials. These for many years have been called Standard Reference Materials (SRM's), and the acronym will be used in this paper.

The rationale for using SRM's in measurement systems has been well documented (Ref. 1,2,3,4). In principle and in actuality, SRM's serve as the vehicles for transmission of measurement science and technology from the standardizing laboratory, through the measurement infrastructure, and ultimately to the user laboratories.

CONCEPTS FOR MEASUREMENT COMPATIBILITY

Meaningful measurements necessarily involve the concept of measurement compatibility through accuracy. The philosophical basis for absolute measurement experiments is described by Dorsey and Eisenhart (Ref. 5). Measurements that can be rigorously related to the "true value" will, by definition, be deemed accurate measurements and all laboratories having this relationship are adjudged compatible. An accurate measurement system produces numerical values of properties of materials that are free from systematic error, are precise, and are specific.

Meaningful measurements in analytical chemistry are achievable when both reference materials and reference methods have been standardized, and when the measurement infrastructure has been rendered compatible within agreed upon limits. SRM's thus serve as an essential foundation of analytical chemistry, especially with instrumental techniques for measurements in the exploration, mining, and processing of materials.

PREPARATION OF REFERENCE MATERIALS

The planning, preparation, and characterization of SRM's are exacting tasks that must be thoroughly investigated to ensure the attainment of measurement compatibility. The purposes and requirements of the SRM's must be clearly understood prior to preparation. Since each measurement of a property involves both material variability and method imprecision, it is imperative that SRM's be rigorously characterized with respect to homogeneity. Although homogeneity requirements differ appreciably with various types of materials and with the various properties to be certified, all have the same common basis in that the materials must be sufficiently uniform to completely satisfy the end use. Two points should be emphasized. First, a statistical plan for sampling should be established. When the production process for a SRM is orderly and known, discrete selection of relatively few test samples for measurement will often provide valid statistical evaluation for the variability of the material lot. When the production process is not known, a relatively large number of random test samples must be measured, greatly increasing the complexity of the evaluation. Second, methods of test usually should be applied that are rapid and are of high precision. Although measurement accuracy usually is not necessary in homogeneity testing, the application of an accurate method of analysis may concurrently provide the basis for a certified value and its uncertainty which is attributable to material variability and to method imprecision. Statistical connotations of varying degrees of inaccuracy with varying degrees of imprecision are discussed by Eisenhart (Ref. 6). Certified values and their meaning, along with uncertainties, are discussed by Ku (Ref. 7).

Analytical Characterization

Three modes are used at NBS to measure the SRM properties for certification. In order of preference they are: (1) a reference method of demonstrated accuracy; (2) two or more independent, reliable methods; and, (3) interlaboratory participation with various methods run in parallel with a previous, similar issue of a SRM. For complex SRM's with many properties to be certified, a combination of two, or even all three, modes of measurement may be used (Ref. 8).

Examples

Based on well-documented industrial needs, the NBS, several years ago, embarked on a comprehensive program for the preparation of SRM's for the copper industry. Plans were formulated for the SRM's required for analytical control from the initial ore stage, through beneficiation and refining, to the final product stage. Although the industry-wide SRM program has not been completed, all the candidate materials have been acquired with most still undergoing characterization. The SRM's currently available include four of interest in the ore and beneficiation stages: SRM 330, Copper Ore, Mill Heads, SRM 331, Copper Ore, Mill Tails, SRM 332, Copper Concentrate, and SRM 333, Molybdenum Concentrate; and three of interest in the refining and final product stages: SRM's 394, 395, and 396, Unalloyed Copper (chip form). Specific considerations and details of the planning, preparation and characterization of these SRM's will be described.

Other examples will be selected from SRM's in progress which include iron ores, bauxites, coals, white cast irons, and aduminum- and copper-base alloys.

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