

For the Love of Chemistry

Penned by Connie Hayes, CEO

This month we are honoring our founder, Dr. Theodore Rains, with a reprint of an interview he gave *Analytical Consumer* in 1990, the year High-Purity Standards was founded.



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Much has changed since 1984 when Dr. Rains began production of the popular NIST 3100 series at NBS/NIST. There now exist numerous ISO 17034:2016 accredited Certified Reference Material manufacturers. This community of manufacturers has had several decades to experience and address the needs and challenges uncovered by the systematic use of NIST traceable standards. Yet, much remains the same, including the practices that he established at High-Purity Standards (HPS), which are well embedded in our manufacturing Standard Operation Procedures.

The cornerstone of our CRMs, especially our ICP standards, is the traceability to the NIST SRM 3100 series. For that, HPS follows the NIST Policy on Metrological Traceability¹. Using those manufacturing processes established by Dr. Rains, such as the use of pure materials, clean acid for manufacture, and stressing the importance of dissolving each material in enough of the correct acid, the uncertainties remain low and the concentration is ensured by analysis against the NIST SRMs.

As you read the article from 1990, I am certain you will see the origin of much of what we do in the manufacture of our ICP standards.

Ted Rains on Inorganics

Sourced from Analytical Consumer, October 1990

Analytical Consumer talked to Dr. Theodore Rains, for 25 years the expert on inorganic standards at the National Institute of Standards and Technology (formerly the National Bureau of Standards). Ted, who just retired from NIST, graduated from Eastern Kentucky University in 1950, and went to Oak Ridge in 1951, where we specialized in flame emission spectroscopy, completing his PhD at the University of Tennessee at the same time.

In 1965, Ted joined the staff of the Division of Analytical Chemistry at NBS. His instrumental work focused on flame atomic absorption. While at NIST, he saw a growing need for high purity standard solutions. In 1984, he began producing and certifying spectrometric standard solutions, in cooperation with the Office of Standard Reference Materials (OSRM). These solutions are certified to an accuracy of +/- 0.3%. As a result, he developed analytical methods with a precision of 0.1-0.2% (relative).

In his years at NIST/NBS, Ted found only one sample he couldn't dissolve (fused Th_2O_3), and had only one valid complaint about an SRM spectrometric standard solution - he used "8N" HCl to dissolve the tellurium; because the final acid concentration was only about 1.5 N, the Te precipitated. Since then, he checks the normality of his acids.

He has been consulting with "2-3 dozen" companies on sample preparation and analysis problems, and he has taught courses at University of Maryland, Georgetown University, and with the ACS. Ted retired from NIST in June, and he has gone on to found his own company, High-Purity Standards (P.O. Box 30188, Charleston, SC 29417, 803-556-3411), where he manufactured inorganic standards, as well as continuing to consult and teach.

This year's FACSS meeting in Cleveland honors Ted with the Theodore Rains Symposium.

Your standards are possibly the most important part of your chemical analysis. If they are wrong, everything is wrong. At one time, nearly every analytical chemistry lab made their own inorganic standards; they were too important to trust to someone else. Now the demand for premixed standards has exploded, particularly for environmental analysis, and labs find themselves too busy to make and check their own standards.

How good are purchased standards? Making a stable, accurate standard takes a skilled analytical chemist a lot of time and effort. Are all the manufacturers of standards putting in the required effort? And if they aren't, what should a buyer do to protect the lab's analytical integrity?

Making an accurate standard

NIST aims for accuracy in standards; they certify concentrations that are method independent, so that they can be used equally well for ICP, AA, colorimetry, etc. Each standard is checked by several methods to verify its concentration to +/- 0.3%. The prepared spectrometric standard solutions at NIST standard are stable for at least a year with proper treatment. Though the standards are expensive, you don't need a lot, since their purpose is for verifying the actual standards you use from day to day, whether you make them or buy them.

A top-quality standard starts with the best available raw materials - greater than 99.99% purity for all elements except Be, which is no better than 99.5%. NIST doesn't rely on assays by their suppliers; they check every lot by DC arc. If too many impurities are found, they dissolve the material and analyze again by the best method for the contaminants. They also check stoichiometry if they are using salts; the ratio of metal to anion is not always exactly what the chemical formula promises.

Ted weighs everything twice, checking himself for consistency to within 1 part in 10,000. He ignites oxides before weighing to a constant weight. Metals are pickled and air dried in a class 100 clean area before weighing. He points out that rare earth oxides pick up O₂ and CO₂ from the air and need more than drying; he points out that you can put a rare earth oxide on a balance and watch the weight increase.

NIST prepares their own high-purity acids by sub-boiling distillation. "High purity" acids purchased from suppliers, Ted has found, are often no better, and are sometimes worse, than reagent grade acids. They quickly pick up impurities from their glass bottles. Since temperature and pressure variations during distillation affect normality of the final acid, he always checks each batch by titration. After distillation, acids are checked for 70 elements in DC arc; the limit for impurities is less than 2 ppm total.

The next step is preparation of the final standard in 2 liter calibrated volumetric flasks. Ted does not make up stock solutions and dilute for large-scale manufacture; dilution adds another increment to the uncertainty in the concentration. He first dissolves the raw material in fresh acid in a Teflon beaker, then transfers it to the volumetric flask. Standards accurate to +/- 0.3% demand extreme accuracy in each step.

He stresses the importance of dissolving each material in enough of the right acid. The key to stable solutions, according to Ted, is having plenty of acid. Tin, for example, may hydrolyze and precipitate unless you maintain the analyte in 60% acid. The type of acid is equally important; anions must be compatible with the element dissolved. Silver will precipitate if chloride is present. Gold, on the other hand, must have chloride present.

After preparation and bottling in acid-washed and clean-air dried high-density polyethylene bottles, Ted selects 2-3 bottles at random for a final check by AA or flame emission for gross errors in pipetting and dilution.

Quality in Standards

The NIST takes extreme care to make their standards accurate. They are, after all, the standards against which all other standards are judged. Manufacturers rarely take all the precautions against errors Ted described. How accurate are the standards on the market? NIST (then NBS) tried an experiment to see (details to be published in *Analytical Chemistry*).

At the time, 34 companies were selling inorganic standards, mostly for AA and ICP analysis. All were claiming that their standards were "traceable" to NBS standards. NIST ordered 1,000 ppm single element standards of six "easy" elements, placing the order anonymously through a college.

Each standard was certified for a concentration of 1,000 +/- 10 ppm. Ted analyzed each one, and found a concentration range of 925-1607 ppm for the major elements. He found contaminants, as well; Si (from glass) was present in all, and one standard contained nearly 1% potassium. Because no manufacturer was better than the others, Ted assumes that the quality found is probably typical of the standards business. No manufacturer names will ever be released, of course.

Although each certificate claimed that the standard was “traceable” to NBS standards, Ted noted that not one of the six manufacturers had purchased an NBS standard within the past year.

The conclusion? Don’t trust the certificate that comes with your purchased standards, either for concentration or “traceability”. Do your own QC before using standards (see suggestions later in the article).

Traceability Defined

Nearly every manufacturer of inorganic standards claims that the concentration is “traceable” to a NIST standard. It has become a buzzword that manufacturers misuse and customers do not understand. According to NIST, traceability is the “ability to trace - an unbroken, identifiable, and demonstrable pathway” to a NIST standard. It’s not enough to simply claim traceability; all measurements, from the NIST to the final standard, must be documented. If a standard is traceable, it has been analyzed against a NIST standard after all dilutions and dissolutions are complete. In fact, it’s not a bad idea to ask for the complete documentation of traceability from a manufacturer, if it matters to you. If their response seems silly (like some in the examples below), find another supplier.

Some examples of questionable claims of “traceability” from suppliers:

- The weights they used to weigh out raw materials had been bought from, and certified by, NBS - in 1935.
- AN NBS SRM 1643A Trace Element in Water standard was used to certify concentrations of a 1,000 ppm standard, many orders of magnitude greater in concentration than the check standard.
- A stock solution was analyzed against NIST standards and diluted - without checks on the dilution procedures. The supplier also assumed that a single test of the stock solution “proved” that their raw materials were good, so they didn’t reanalyze future stock solutions unless they changed suppliers.
- Products weren’t checked against a NIST standard because they used the same quality assurance procedures for QC and “didn’t need to test” against an outside standard. Yet they claimed traceability.
- One supplier claimed analysis of a standard by “gravimetric” analysis, consisting of evaporating dryness and weighing the residue. This gives you total solids, not concentration!

Doing Your Own QC

If manufacturers aren’t going to QC their standards before shipment, you must do it yourself before using them. Decide in advance how good your numbers must be - usually within the precision of your measurement method - and check the standards to that level of accuracy.

Buy 10,000 ppm standards of the elements you need from NIST; they are expensive, you won’t use much, and they are stable for at least a year when stored carefully sealed. Treat the NIST standards like precious resources; never pipette from the bottle, and recap tightly after each use. Also, buy high-purity acids from NIST to match each standard, for dilution.

Dilute NIST standards to the nominal concentration of the standards you want to check; the 1,000 ppm standard should also be stable for a year, if diluted properly and stored in high-density polyethylene bottles. If your purchased standards are 1,000 ppm, this is the solution to use for checking. If you must dilute further, you can store 50-100 ppm standards, but store lower levels for no more than a couple of days. Check stock solutions of your calibration standards against the NIST standard when you prepare them, and again every 6 months or so.

To check a purchased or prepared standard with a NIST standard, calibrate your instrument with either the purchased or NIST standards. Alternately analyze the purchased standard and the NIST, 8-10 analyses each. Take the average of each set of measurements; the two averages should agree within the precision of the instrument. If they don’t, complain to the standards manufacturer.

Do periodic QC checks of your calibration standards to make sure your calibration and restandardization standards are still good. Ted noted that “EPA kits” of standards sometimes contain incompatible elements. Even though the manufacturers claim one year lifetime, they may not actually be stable that long (Multi element standards made according to EPA specifications - in the CLP statement of work or SW 846 - are stable combinations). If you use multi element “restandardization” or “update” standards, check them often; the elements may not be compatible, and they may be less stable than single element standards.

Sources of Error in Standards

In addition to instability due to precipitation, transpiration of water through the walls of plastic bottles is a major source of error with time. Water evaporates through the plastic walls of low density polyethylene bottles. If you half fill such a bottle with water, cap it tightly, and leave it on the shelf, it will gradually collapse, as water vapor escapes the bottle. This happens in full standards bottles as well; as water evaporates, the concentration of the standard will increase about 0.5-1% in a year. The rate of increase is much less in high density polyethylene: about 0.1-0.2% per year in tightly capped bottles with heat shrink plastic over the caps. Opened bottles will lose water at a much faster rate.

Dipping pipettes into a stock solution is one of the more common ways to contaminate a solution. Ted always pours his stock solution into a graduated cylinder, pipettes from the cylinder, and discards the excess. The small amount of wasted standard is insurance against measurement errors from contaminated standards.

Diluting a standard with plain water is a certain way to precipitate some elements. Ted once received a complaint that “there wasn’t any tin” in a 10,000 ppm Sn standard; when he analyzed the standard at NBS, it was 10,000 ppm. The customer had made a 1,000:1 dilution with deionized water, reducing the 60% acid matrix to 0.06%. The tiny precipitate created by the 10 ppm solution was invisible, and the customer didn’t realize that all the tin was on the walls of the volumetric flask. Always dilute with the same acid used to prepare the standard in the first place.

Standards for graphite furnace atomic absorption must be prepared with minimum acid to prevent damage to the instrument. Because of potential instability, these standards should be prepared fresh every day.

Glassware used for dilution must be calibrated by weighing the amount of deionized water they contain to the mark. Ted recommends never using less than a 5 mL pipette and never diluting to more than 100 mL for best accuracy. Even “Class A” glassware has to be checked for accuracy; Ted always calibrates his class A volumetric flasks. He has found that about 10% of class A flasks are outside the +/- 0.02% tolerance on volume. He once found a 4liter flask with an actual volume of 4.044 liters.

Using plastic-tipped “micropipettes” is another source of serious error. Those pipetting by air pressure are neither reproducible nor accurate. Positive displacement models are quite reproducible, and are suitable for accurate dilutions after calibration.

Cleaning laboratory glass or plastic by leaching in acid eliminates another source of contamination. If you use plastic pipette tips (calibrated of course), rinse them well in 20% HNO₃, followed by a distilled water rinse. Then pre-rinse any pipette or tip with some of the solution you will be pipetting, as well. Avoid the yellow plastic tips if you plan to analyze cadmium; the color is cadmium yellow.

