International Standards

- Overview of International Benchmarking of CSTL Analytical Measurement Capabilities [Willie May, Reenie Parris and Analytical Chemistry Division Staff]

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CSTL Program: International Standards

Sub-Task Title and CSTL Database Designation:

Technical Highlight Title: International Benchmarking of CSTL Analytical Measurement Capabilities

Authors: Willie E. May, Reenie M. Parris and Analytical Division Staff

Abstract: International agreements and decisions concerning trade and our social well-being are increasingly calling upon mutual recognition of measurements and tests between nations. The absence of such mutual recognition is considered to be a technical barrier to trade and environmental and health-related decision-making. In recent years, mutual recognition agreements have been established related to testing and calibration services and in respect of the bodies accrediting such activities. All of these rest upon the assumption of equivalence of national measurement standards and reliability of the link between national measurement standards and the relevant testing services in each country. ACD is extensively involved in efforts to establish intercomparability of chemical measurements with National Measurement Institutes both globally and regionally in the Americas. ACD staff participate and provide leadership in the International Committee of Weights and Measures-Consultative Committee on the Quantity of Material (CCQM) and the Chemical Metrology Working Group of the Interamerican System for Metrology (SIM) working groups, in comparison studies, and in the critical review of chemistry Calibration and Measurement Capability (CMC) claims of NMIs submitted for publication in the BIPM Key Comparison Database for Appendix C of the CIPM MRA. NIST claims comprise about 1000 of approximately 3000 NMI CMC claims for chemistry that will be included in the BIPM Database by the beginning of 2003. Since beginning in the late 1990's, 53 CCQM comparison studies have been completed or are underway; NIST has participated in 46 of these—serving as the pilot or copilot laboratory for 18 studies. Published Key Comparison results can be viewed at: http://www.bipm.fr/enus/8_Key_Comparisons/database.html, http://icdb.nist.gov/).

Purpose: International agreements and decisions concerning trade and our social well-being are increasingly calling upon mutual recognition of measurements and tests between nations. The absence of such mutual recognition is considered to be a technical barrier to trade and environmental and health-related decision-making. In recent years, mutual recognition agreements have been established related to testing and calibration services and in respect of the bodies accrediting such activities. All of these rest upon the assumption of equivalence of national measurement standards and reliability of the link between national measurement standards and the relevant testing services in each country. In October 1999, the Directors of National Metrology Institutes (NMI) for the thirty-eight member states of the Meter Convention signed the mutual recognition arrangement (CIPM MRA) on national measurement standards and calibration and measurement certificates issued by national metrology institutes. This MRA provides a framework for assessing the degree of equivalence between the measurement capabilities and standards issued by NMIs or NMI-designated labs throughout the world. It requires: 1) demonstration of a system for assuring quality of each NMI's measurement

services, 2) evidence of successful participation in formal, relevant international comparisons, and 3) declaring and document calibration and measurement capabilities (CMCs).

In support of US chemical measurement infrastructure, NIST successful participation in relevant comparisons is used to:

- Compare NIST Definitive and Reference Methods for Chemical Analysis with other methods used to establish national measurement standards around the world
- Assist in the verification of NIST primary standards
  - primary gas mixture suites
  - elemental standard solutions
  - primary spectrometer
- Assess and document NIST (US) chemical calibration and measurement capabilities (CMCs) with those of other countries around the world
  - CIPM MRA

Major Accomplishments: ACD is extensively involved in efforts to establish intercomparability of chemical measurements with National Measurement Institutes both globally and regionally in the Americas. NIST has taken a leadership role in the International Committee of Weights and Measures-Consultative Committee on the Quantity of Material (CCQM) and the Chemical Metrology Working Group of the Interamerican System for Metrology (SIM) in order to assure the effective, fair and metrologically sound implementation of this MRA. CCQM working groups are responsible for selecting and overseeing the operation of key comparisons that address chemical measurement-related issues. ACD staff participate and provide leadership in working groups, in comparison studies), and in the critical review of chemistry Calibration and Measurement Capability (CMC) claims of NMIs submitted for publication in the BIPM Key Comparison Database for Appendix C of the CIPM MRA. NIST claims comprise about 1000 of approximately 3000 NMI CMC claims for chemistry that will be included in the BIPM Database by the beginning of 2003.

During FY01-02, ACD participated in 25 CCQM comparison studies; serving as the pilot or copilot laboratory in 13 of these. Since beginning in the late 1990's, 53 CCQM comparison

NIST Activities in FY 01-02 within the Framework for CCQM Key Comparisons and Pilot Studies

Health	**9 KCs completed or underway; NIST leads 7**
Food	**7 KCs underway; NIST leads 1**
Food & Env.	**Pesticide Residues, 7 completed or underway**
Environment	**Water, 1 underway**
	Atmospheric Pollutants, 3 underway, NIST leads 2
	Point Source Emissions, 1 underway
	Primary Gas Standards, 16 underway, CSTL leads 3
	Contaminants in soils/sediment, 6 underway, NIST leads 2
Advanced Materials	**Semiconductors, 1 underway**
	Metal Alloys, 2 underway, NIST leads 1
Commodities	**1 underway, NIST lead**
Forensics	**4 underway**
Pharmaceuticals	**None planned**
Biotechnology	**Five areas identified**
General Analytical	**Calibration Solutions, 4 underway, NIST leads 1**
	pH Standards, 4 underway

studies have been completed or are underway; NIST has participated in 46 of these—serving as the pilot or copilot laboratory for 18 studies. Published Key Comparison results can be viewed at: http://www.bipm.fr/enus/8_Key_Comparisons/database.html, http://icdb.nist.gov/).

The field of chemical metrology is so diverse, broad and multidimensional (measurands, concentrations, matrices, etc.) that an immense number of key comparison studies can be envisioned as needed to cover this field. As illustrations of strategies being used to expand leverage of these studies, recent CCQM comparisons in the organic analytical area include:

- the continuation of a series of studies to evaluate NMIs' purity assessment of organic materials for use as primary standards
- in the healthcare area, a series of studies (piloted by NIST ACD) to provide a measure of the capabilities of NMIs for measuring well-defined organic analytes of clinical interest in serum. NIST piloted initial studies and subsequent key comparisons for the determinations of serum cholesterol, glucose and creatinine.
    - Cholesterol is lipophylic and present in serum primarily as fatty acid esters.
    - Glucose is highly water-soluble and also associates strongly with proteins.
    - Creatinine is very polar, present at much lower levels than cholesterol, and its determination requires considerable care to assure separation from creatine, without interconversion between creatinine and creatine.

- In the environmental area, an ensemble of comparisons to provide the framework for assessing the capabilities of participating laboratories to measure chlorinated pesticides in lipid samples in the range of 70 ng/g to 6000 ng/g was completed; studies to assess measurement of chlorinated hydrocarbons in sediment are in progress; and, studies for Organic Calibration Solutions (PCBs, PAHs, Pesticides) and Organic Contaminants in Tissue are being developed.
- A pilot and subsequent key comparison of Ethanol in Aqueous Matrix comprised materials suitable for the forensic community (ethanol in water at two levels) and a stabilized wine material for the commodity sector.

The NIST results for these comparisons were in good agreement with the key comparison reference values or other indicators of the "best" values for these studies. Examples of NIST performance in these organic comparisons are shown in the figures below. (See separate FY02 ACD Technical Activity Reports for figures of comparisons illustrating results of inorganic, pH, conductivity and gas mixture studies.)

In five pilot and key comparisons in the inorganic area in which NIST participated this year: CCQM-P11 Arsenic in Shellfish, CCQM-K24 Cadmium in Rice, CCQM-P29 Zinc in Rice, CCQM-P13 Synthetic Food Digest, and CCQM-P25 Minor Elements in Steel, it is noteworthy that in these intercomparisons we have applied the four of the main inorganic analytical techniques of the Division: Optical Spectrometry, Mass Spectrometry, Instrumental Neutron Activation Analysis, and X-ray Fluorescence Spectrometry. The NIST results for these comparisons were in good agreement with the key comparison reference values or other indicators of the "best" values for these studies.

In FY 2002, NIST participated in 4 pilot studies connected with international benchmarking of classical (assay) techniques, pH metrology, and anion solutions. The results of each study

indicated that the NIST measurements are at the state of the art for the respective measurement. Results for the pH and assay studies also revealed sources of systematic bias that are difficult to detect using results obtained at a single NMI.

Over the past year, NIST participated in CCQM-P23 Preparation of Gravimetric Gas Standards Pilot Study and CCQM-K16 Natural Gas Key Comparison. As the year ends we are also participating in CCQM-P41 Greenhouse Gases Pilot Study, and working with NMIJ (Japan) on the prototype for the CCQM-K22 VOCs Key Comparison. The results of each study indicated that the NIST measurements are at the state of the art for the respective measurement.

The Systema Interamericano de Metrologia (SIM) is the metrological regional organization (RMO) that includes the United States. RMOs have the responsibility for carrying out supplementary comparisons and other actions within their regions to support mutual confidence in the validity of calibration and measurement certificates through the Joint Committee of the RMOs and the BIPM (JCRB). They are also responsible for review of calibration and measurement capabilities (CMCs) of their member NMIs. In order to most effectively address the unique needs of the 34 countries within SIM whose capabilities in chemical metrology span a very broad range, the SIM program initially has focused on training and capability assessment rather than participation in MRA- driven Key and Supplemental Comparisons. During the past year, six intercomparison exercises were completed to assess the proficiency of SIM NMI's and/or their designated collaborators for addressing chemical measurement problems within their regions and the Americas. ACD staff participate and provide leadership in SIM working groups, have piloted and participated in all eleven SIM performance assessment (comparison) studies, have conducted workshops and laboratory training, and have led the critical review of SIM Calibration and Measurement Capability (CMC) claims. SIM has approximately 1140 CMC entries scheduled for inclusion in the BIPM database by the start of FY03.

In addition to these global and regional activities, we are also establishing a limited number of strategic bilateral collaborations and intercomparisons with NMIs around the world. For example, our collaboration with the Netherlands Measurement Institute (NMi) for determining the equivalence of primary gas standards has resulted in a formal "Declaration of Equivalence" that is recognized by the U.S. EPA and European environmental regulatory bodies as documenting the equivalence between seven NIST and NMi primary gas mixture suites. A bilateral comparison of optical transmittance at five visible wavelengths and for transmittance levels between 1.0 and 10^{-3} is currently underway between NIST and the National Physical Laboratory (NPL) of the UK. This is the first international comparison for the second-generation CSTL reference spectrophotometer and is a precursor to an anticipated Memorandum of Cooperation and Declaration of Equivalence between NIST/CSTL and NPL with respect to optical transmittance. Equivalence between the NIST and NPL transmittance scales is expected to ease the regulatory traceability burden for end users, especially multinational pharmaceutical companies. Our formal agreement with NRC-Canada (via the NAFTA Treaty) for cooperation in marine environmental studies has fostered collaborations in the certification of a several certified reference materials important for trade and environmental decision-making between the U.S. and Canada. We have a Cooperative Arrangement with NIMC (Japan) for collaborative efforts in the area of pure volatile organic compound standards. These highly pure reference compounds will serve as primary references for many of our gas mixture SRMs and our quantitative reference

database (SRD-79). Several additional strategic bilateral arrangements with other National Metrology Institutes /Standards laboratories are being discussed.

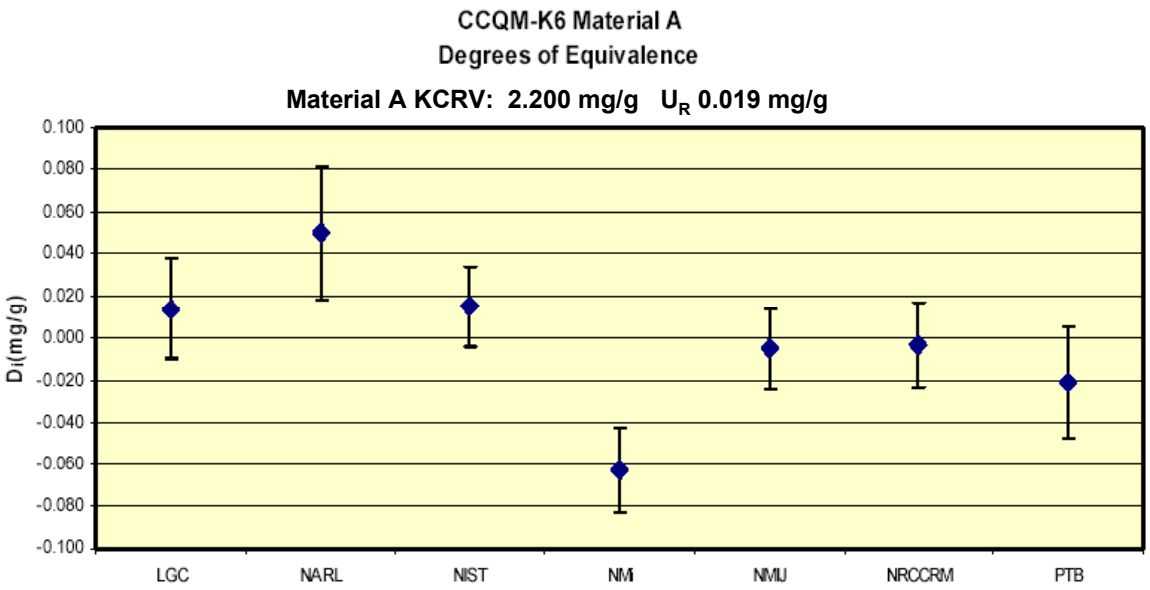
ACD continues to work with CITAC (Cooperation in International Traceability in Analytical Chemistry) to establish practical, yet metrologically sound, vertical traceability links between the NMIs and chemical testing labs in the various countries and regions around the world.

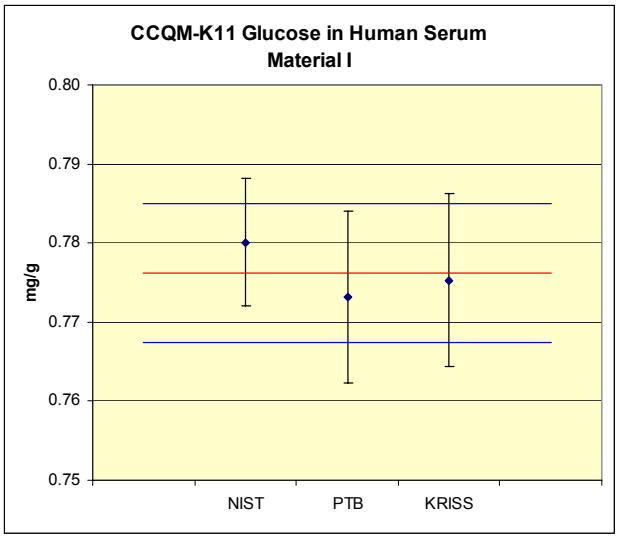
Impact: To serve US interests, it is important that NIST demonstrates and documents the equivalence of its chemical measurements with those of other NMIs. This is essential for NIST (for benchmarking and establishing veracity of NIST standards), for NIST partners (e.g., other NMIs), and for NIST customers (industry, regulatory agencies, end users of NIST services).

Future Plans: In ACD, we continue to assess needs of the US measurement community and strategically prioritize our international benchmarking activities to support these needs.
ACD has increased its participation and leadership in relevant international organizations and in activities to promote acceptance and confidence in US measurements. For chemical measurements, the number of comparisons is increasing and the application areas widening. Of 36 CCQM comparisons now in the planning stages, ACD has agreed to pilot at least 9 of these.

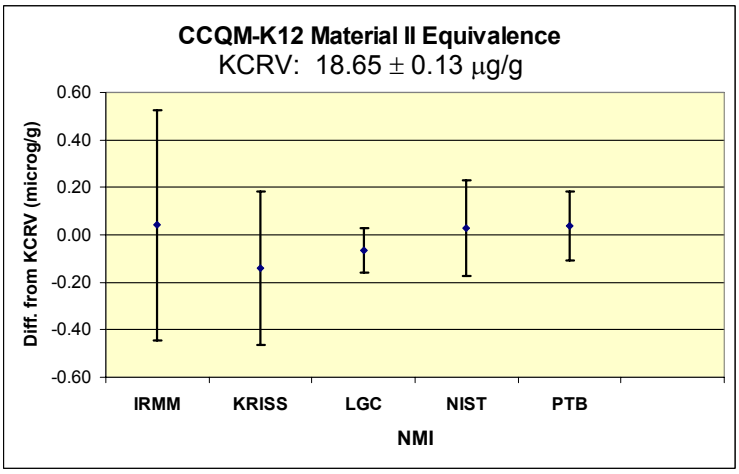
In further support of recognition and acceptance of claims for chemical measurements made within the Analytical Chemistry Division, ACD is planning for a second international peer review of our chemical measurement and standards programs by a group of international chemical metrology experts (the first was conducted in October of 1999) and a review of ACD's System for Assuring Quality and its implementation.

CCQM-K6 Cholesterol in Human Serum

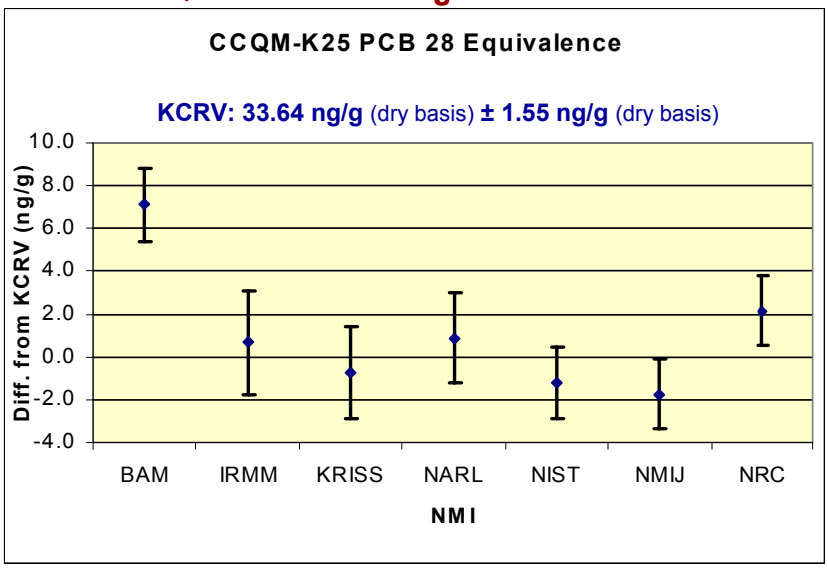




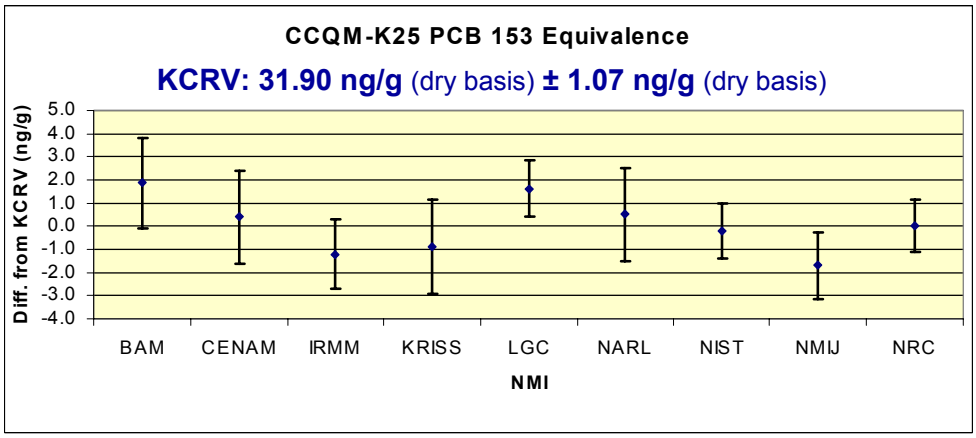
Creatine in Human Serum



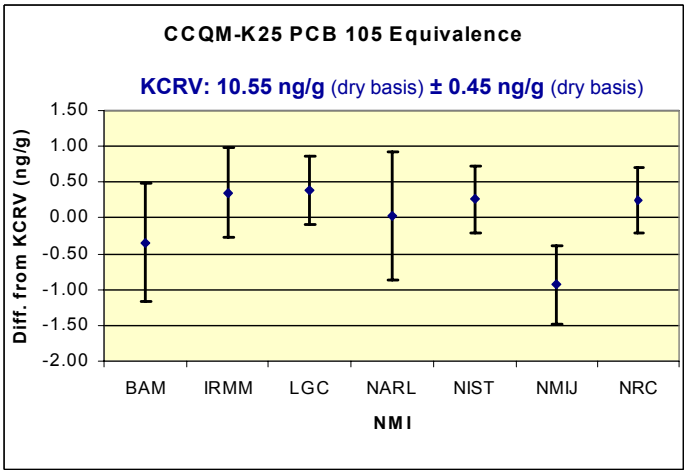
CCQM-K25: PCB Congeners in Sediment



CCQM-K25: PCB Congeners in Sediment

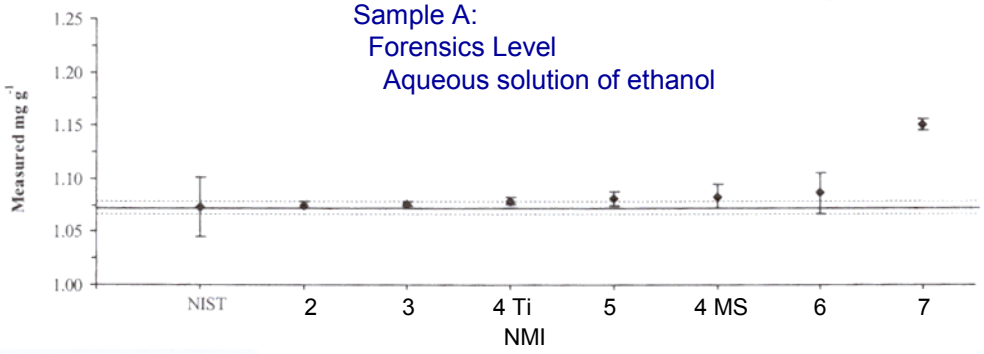


CCQM-K25: PCB Congeners in Sediment

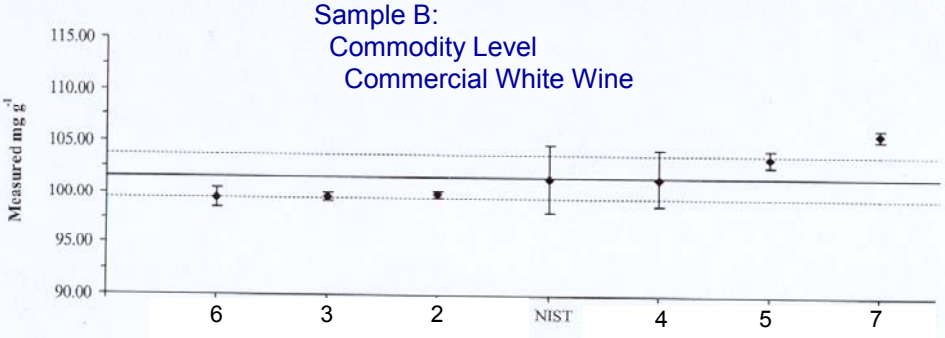


CCQM-P35: Ethanol in Aqueous Matrix

Sample A:
Forensics Level
Aqueous solution of ethanol



Sample B:
Commodity Level
Commercial White Wine



CSTL Program: International Standards

Sub-Task Title and CSTL Database Designation:

Technical Highlight Title: International Benchmarking of CSTL Inorganic Analytical Measurement Capabilities

Authors: Robert Greenberg, John Fassett, Karen Murphy, Rolf Zeisler, Elizabeth Mackey, Lee Yu, Laura Wood, John Sieber, Anthony Marlow

Abstract: ACD successfully participated in five pilot and key comparisons of the inorganic working group of the CCQM this year: CCQM-P11 Arsenic in Shellfish, CCQM-K24 Cadmium in Rice, CCQM-P29 Zinc in Rice, CCQM-P13 Synthetic Food Digest, and CCQM-P25 Minor Elements in Steel. The NIST results for these comparisons were in good agreement with the key comparison reference values or other indicators of the "best" values for these studies. It is noteworthy that in these intercomparisons we have applied the four of the main inorganic analytical techniques of the Division: Optical Spectrometry, Mass Spectrometry, Instrumental Neutron Activation Analysis, and X-ray Fluorescence Spectrometry.

Purpose: Key comparisons are an important method of demonstrating the claimed measurement capabilities of national metrology institutes (NMIs), as well as establishing the equivalence of measurements made by different NMIs. To serve US interests, it is important that NIST successfully participates in relevant measurement comparisons under the CIPM Mutual Recognition Arrangement.

Major Accomplishments: Analytical Chemistry Division (ACD) successfully participated this year in four pilot and one key comparisons of the inorganic working group of the CCQM: CCQM-P11 Arsenic in Shellfish, CCQM-K24 Cadmium in Rice, CCQM-P29 Zinc in Rice, CCQM-P13 Synthetic Food Digest, and CCQM-P25 Minor Elements in Steel. NIST led the pilot study on Arsenic in Shellfish, which was based on an oyster tissue similar to SRM 1566b. Arsenic is a toxic element and, thus, its determination in oyster tissue, a food matrix, is of general concern. Results were received from eleven laboratories from nine countries (Figure 1). The NIST results of (0.1287 ± 0.0015) µmol/g were in excellent agreement with the mean of (0.1279 ± 0.0016) µmol/g determined from all participants except one, which apparently had problems with their analysis. After the results became available, the CCQM decided to continue on to a key comparison for Arsenic in Shellfish (CCQM-K31).

The rice comparison was split into both a key and pilot comparison. Thus, for those participants who felt comfortable with their Cd measurement capabilities, they could register for the key comparison CCQM-K24. The same material was used for a pilot comparison CCQM-P29 Zn and Cd in rice. We chose to participate in the key comparison; the NIST ID-ICP-MS and INAA determinations were combined and reported. This result was in excellent agreement with the 10 other laboratories [NIST: (14.36 ± 0.23) nmol/g; CCQM: (14.40 ± 0.09) nmol/g (Figure 2)]. For the pilot comparison, the two NIST Zn results (ID-ICP-MS and INAA) were reported separately. Likewise, the Zn results were in excellent agreement [NIST ID-ICP-MS: (0.3554 ± 0.0067) µmol/g; NIST INAA: (0.3559 ± 0.0095) µmol/g; CCQM: (0.3527 ± 0.0024) µmol/g]. The major

source of uncertainty for all NIST measurements in both K24 and P29 was in achieving a dry-mass basis weight. It was recognized that the CCQM-P29 Zn data was of "key comparison" quality as well. Rather than continue on to a key comparison, it was decided to accept that "the light of K24 shines at least as far as Zn." Cadmium in rice represents a toxic element in food; zinc is a nutritional element.

The Pilot Study CCQM-P13 Metals in Artificial Food Digest was proposed by LGC to benchmark measurement of nutritional, essential and toxic elements in foods. They proposed to avoid the difficulty in assigning a consensus key comparison reference value by spiking a synthetic matrix solution with gravimetrically known amounts of the target analytes: Ca (nutritional), Cu (essential) and Cd (toxic). Thus, issues associated with both dissolution and homogeneity were avoided. We decided to determine only the elements Ca and Cu; we felt that our capabilities for Cd had been demonstrated adequately in previous studies. We have been applying ICP-OES methodology with standards addition calibration in our recent certification measurements of food. (This year we made certification measurements for SRM 2387 Peanut Butter, SRM 2385 Spinach, and Milk Powder.) Thus, we felt it was most appropriate that this method be used in the Pilot Study. The results for Ca and Cu were +1.3 % and –0.8 % relative to the reference values, respectively. The average deviation from the reference values were –0.5 % and +3.5 % respectively. The observation was made that the laboratories using IDMS had larger deviations, -2.1 % and +3.8 %, illustrating again that it is not the technique that endows accuracy but the skill of the laboratories that apply the technique.

The metal and metal alloy industries are huge and the economic impact of chemical measurements is very large. The range of commercial metal and alloy materials is also very large and, thus, it has been a challenge to identify the appropriate measurement activity for CCQM in this area. The first study evolved from proposals by NMIJ (Japan), BAM (Germany), and NIST. Designated CCQM-P25, it is for minor elements (Cr, Mo, Ni, and Mn) in a low-alloy steel. These elements control specific steel properties. ACD determined all elements in the steel using its recently developed matrix independent XRF borate fusion method, and three elements (Cr, Mn and Mo) were determined by INAA. We also coordinated the submission of results from 4 U.S. industry laboratories. The end-of-year deadline for this study meant that comparative results have not yet been formally revealed. However, results were shown graphically at the Fall 2002 CCQM Inorganic Working Group meeting, and the NIST results were consistent with those submitted by other NMIs.

Impact: We have successfully demonstrated the accuracy of four of our main inorganic analytical techniques of the Division: Optical Spectrometry, Mass Spectrometry, Instrumental Neutron Activation Analysis, and X-ray Fluorescence Spectrometry, as well as our comparability with other NMIs. In addition, we have applied these methods to a number of quite different matrices thus providing an indication of how far the light shines.

Future Plans: We will continue to participate in CCQM comparison as appropriate to demonstrate and document our measurement capabilities in support of support US national interests.

Figure 1. Final results for CCQM-P11

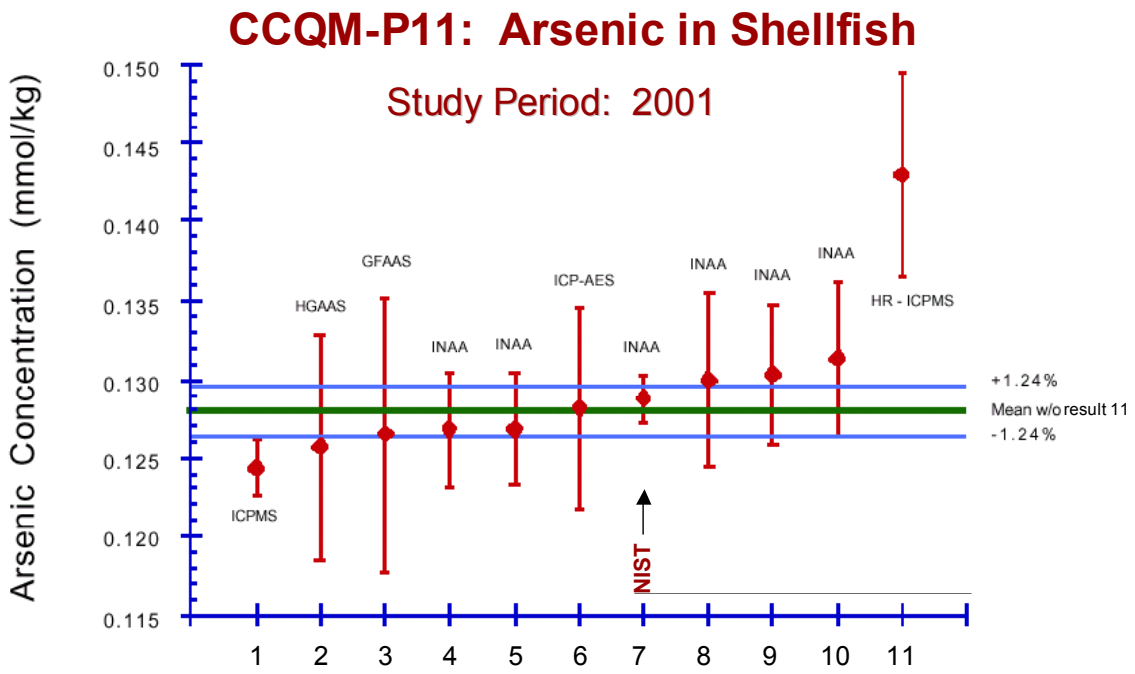
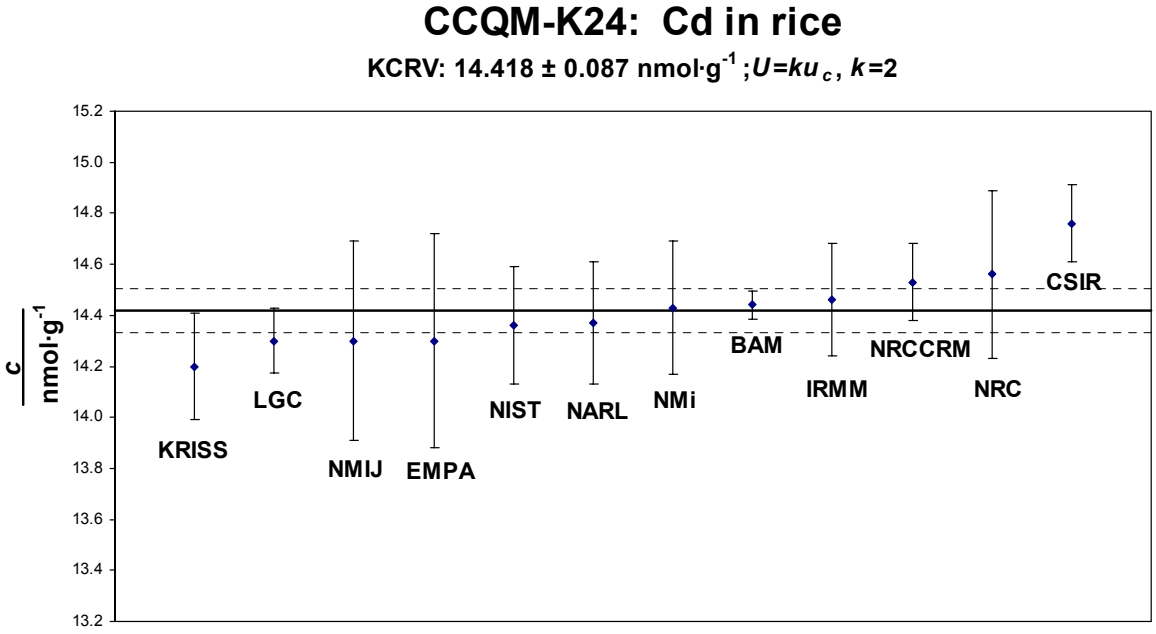


Figure 2. Reported results for CCQM-K24



CSTL Program: International Standards

Sub-Task Title and CSTL Database Designation:

Technical Highlight Title: International Benchmarking of CSTL Classical and Electroanalytical Measurement Capabilities

Authors: Kenneth Pratt

Abstract: In FY 2002, NIST participated in 4 pilot studies connected with international benchmarking of classical (assay) techniques, pH metrology, and anion solutions. Each study was performed under the auspices of the Comité Consultatif pour le Quantité de Matière (CCQM) and was designed to assess the factors that govern the agreement attained among the participants [national metrology institutes (NMIs)] for the given measurand. The results of each study indicated that the NIST measurements are at the state of the art for the respective measurement. Results for the pH and assay studies also revealed sources of systematic bias that are difficult to detect using results obtained at a single NMI.

Purpose: Each pilot study evaluated the degree of agreement obtained for the given measurand for each NMI. The pilot study in most cases served as a preliminary trial to a future key comparison (KC), the quantitative results of which will fix the international acceptance of measurements by each NMI (including NIST). Also, the pilot studies investigated systematic, uncontrolled sources of bias that limit the agreement obtained between NMIs. This second justification utilizes the information obtained from different NMIs performing a given primary measurement using their own realization to obtain information not attainable by a single NMI performing its primary measurement alone.

The pH pilot study (CCQM-P37) was performed in an effort to elucidate systematic effects that contributed to unexpectedly large deviations of certain NMIs (not including NIST) in the previous pH KC, CCQM-K17.

The HCl assay pilot study (CCQM-P19.1) was undertaken to minimize the effects of packaging and shipping which were observed in the HCl solution distributed to the participants in CCQM-P19, the previous study. CCQM-P19.1 also had a wider range of NMIs participating and therefore included a better evaluation of H^+ and Cl^- assay methods. NIST was the coordinating laboratory.

Major Accomplishments: CCQM-P36 [potassium acid phthalate (KHP) assay] provided information on the importance of CO_2 interference in assay of this widely-used acidimetric standard and exposed a ca. +0.04% bias at NIST that had arisen since the latest KHP SRM certification. CCQM-P19.1 (HCl assay) vindicated the use of improved packaging to eliminate the influence of packaging on participants' results and provided the first statistically useful comparison of H^+ and Cl^- assays. CCQM-P37 (fundamental pH study) revealed obscure factors connected with primary pH (Harned) cell design and usage that should result in improved uncertainties for future NIST pH SRMs. The CCQM-P32 results (PO_4^{3-} and Cl^- anion solutions) supported the NIST claims for measurement capability for the respective measurements.

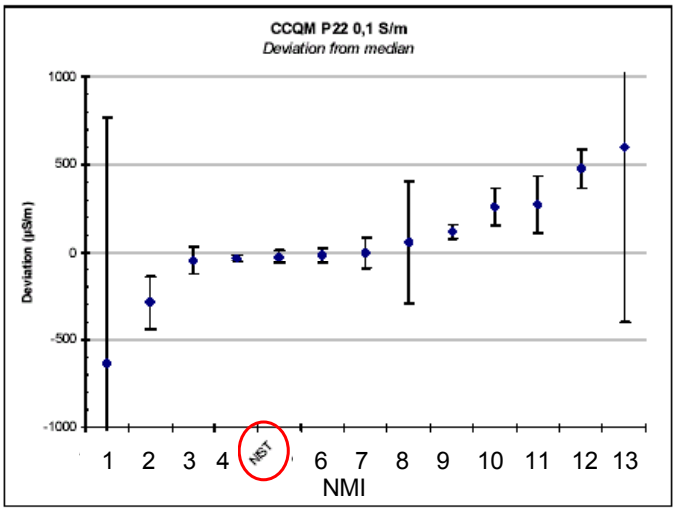
Future Plans: The results of the pilot studies in KHP assay and anion solutions provided the first estimate under CCQM auspices of the international agreement that is attainable for the respective measurands. These pilot studies are likely to result in corresponding future KCs that underpin the claims of measurement capability for the participating NMIs (including NIST).

The results of the HCl assay and fundamental pH studies provided essential information regarding primary pH measurements and systematic sources of uncertainty that impact all primary pH measurements. These results directly impact details of the methodology used by the NMIs participating in already planned future pH KCs.

CCQM-P22: Conductivity

(primary and secondary measurements)

Study Period: 2001

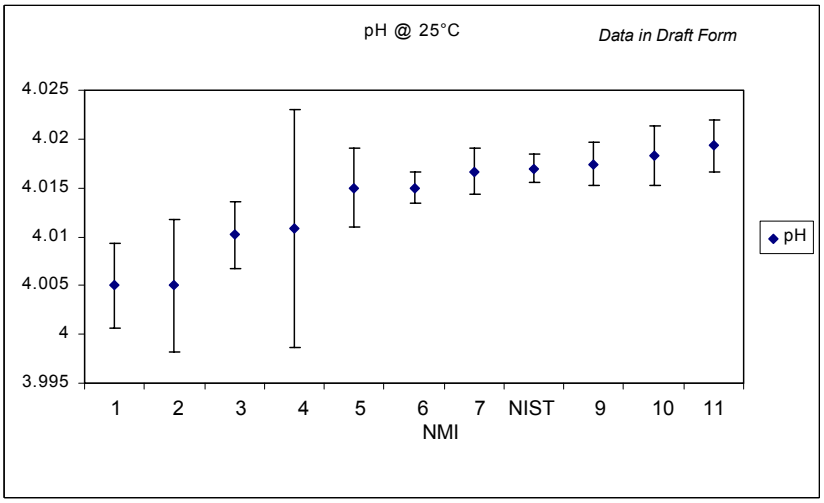


Nominal 0.1 S/m (1000 µS/cm)

CCQM-K17: pH of Phthalate Buffer Solutions

pH nominal value: 6.9 at 25 °C Dates of Study: 2001

[15 °C, 25 °C, 37 °C]



CSTL Program: International Standards

Sub-Task Title and CSTL Database Designation:

Technical Highlight Title: International Benchmarking of CSTL Capabilities in Gas Metrology

Authors: Franklin Guenther

Abstract: Over the past year, NIST participated in CCQM-P23 Preparation of Gravimetric Gas Standards Pilot Study and CCQM-K16 Natural Gas Key Comparison. As the year ends we are also participating in CCQM-P41 Greenhouse Gases Pilot Study, and working with NMIJ (Japan) on the prototype for the CCQM-K22 VOCs Key Comparison. Each study is performed under the auspices of the Comité Consultatif pour le Quantité de Matière (CCQM) and was designed to assess the comparability attained among the participants [national metrology institutes (NMIs)] for the given measurand. The results of each study indicated that the NIST measurements are at the state of the art for the respective measurement. Results for CCQM-P23 revealed a bias among the NMIs which was traced back to the isotopic abundance of C13 in the pure carbon monoxide used to prepare the gas standards. Once this difference was factored into the results, all the NMIs were in good agreement.

Purpose: Each study evaluated the degree of agreement obtained for the given measurand for each NMI. The pilot studies in most cases serve as a preliminary trial to a future key comparison (KC), the quantitative results of which will fix the international acceptance of measurements by each NMI (including NIST). Also, the pilot studies investigated systematic, uncontrolled sources of bias that limit the agreement obtained between NMIs. This second justification utilizes the information obtained from different NMIs performing a given primary measurement using their own realization to obtain information not attainable by a single NMI performing its primary measurement alone

Major Accomplishments: The CCQM-P23 Preparation of Gravimetric Gas Standard Pilot Study was intended to study the source of uncertainty in the preparation of primary gas standards. Carbon Monoxide was chosen because it was thought that this measurand was not difficult to handle and analyze. Thus it should be relatively straight forward to determine small uncertainty sources. The results showed major biases between the NMIs, especially NIST and KRISS (Korea). After much work at NIST and several other NMIs, the source of the bias was traced to differences in the C13 abundance of the pure carbon monoxide (CO). It turns out that gas suppliers strip out the C13 CO from the pure gas to sell to producers of isotopically pure organic compounds. The result is that primary standards produced with the depleted C13 CO will show a bias on certain non-dispersive infrared analyzers (NDIR). The bias is not seen in gas chromatographic methods. This result has major implications in the automotive industry, where measurements are needed to within 1 % of the true value to meet regulations.

The CCQM-K16 Natural Gas Key Comparison was intended to measure the comparability of Natural Gas measurements at the participating NMIs. Unlike past comparisons, this natural gas included the heavy hydrocarbons. Due to shipping problems, NIST was able to analyze only one of the two cylinders sent to participants. NIST's results show excellent agreement with the

majority of the NMIs. A similar Pilot Study was organized by NIST for the SIM countries. This study indicated that there remains much work to be done in SIM to bring the comparability among SIM NMIs in line with the CCQM.

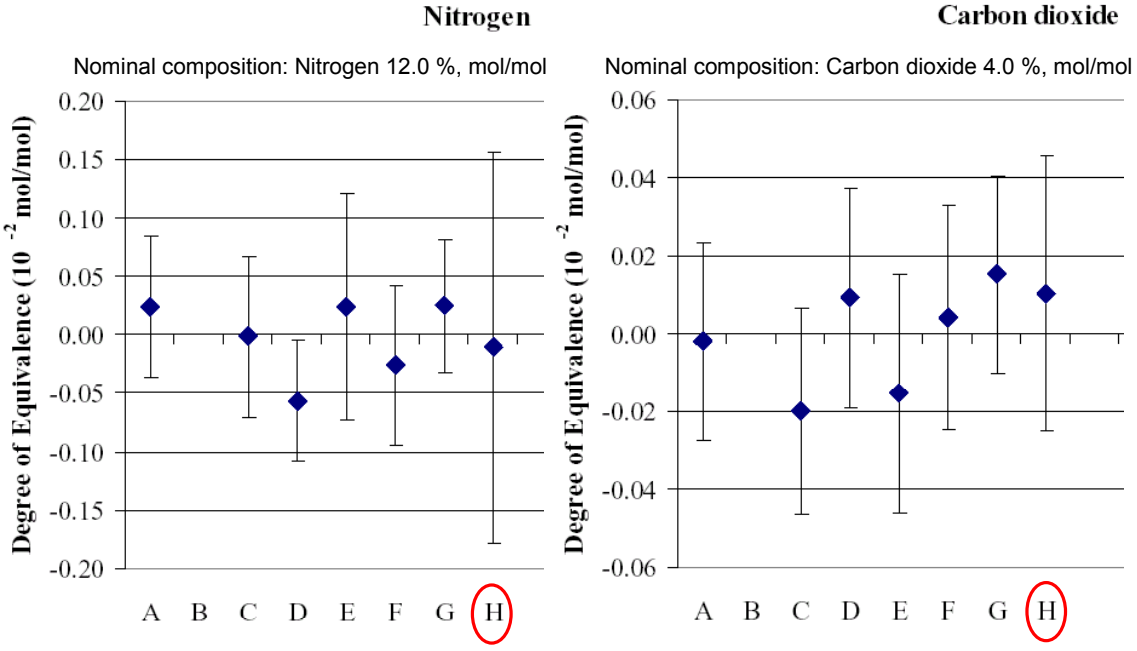
Future Plans: Presently the CCQM-P41 Greenhouse Gases Pilot Study is proceeding, and will be completed by early 2003. This study will demonstrate the comparability of the NMIs for methane and carbon dioxide. This will set the stage for future comparisons in global warming gases, and hopefully enable efforts to mitigate and control emission of these gases internationally. The CCQM is working closely with the World Meteorological Organization to link the measurement of these gases in the atmosphere to the SI.

NIST is working with NMIJ in Japan on the proposed CCQM-K22 Volatile Organic Compounds (VOC) in Air. During the past year NIST has analyzed a prototype VOC standard for NMIJ. In the coming year, NIST will host two guest scientists from NMIJ. The scientists will be working here on VOC primary gas standards. Also in the spring George Rhoderick will be visiting NMIJ to view their capabilities in VOC gas standard preparation.

CCQM-K16a: Gas mixture - Natural Gas Type IV (low calorific mixture)

Period of Study: 2001 12 measurands

NIST is Lab "H"



CSTL Program: International Standards

Sub-Task Title and CSTL Database Designation:

Technical Highlight Title: Collaboration with BIPM to Develop an Advanced Primary Ozone Photometer

Authors: Pamela Chu, James Norris, Franklin Guenther

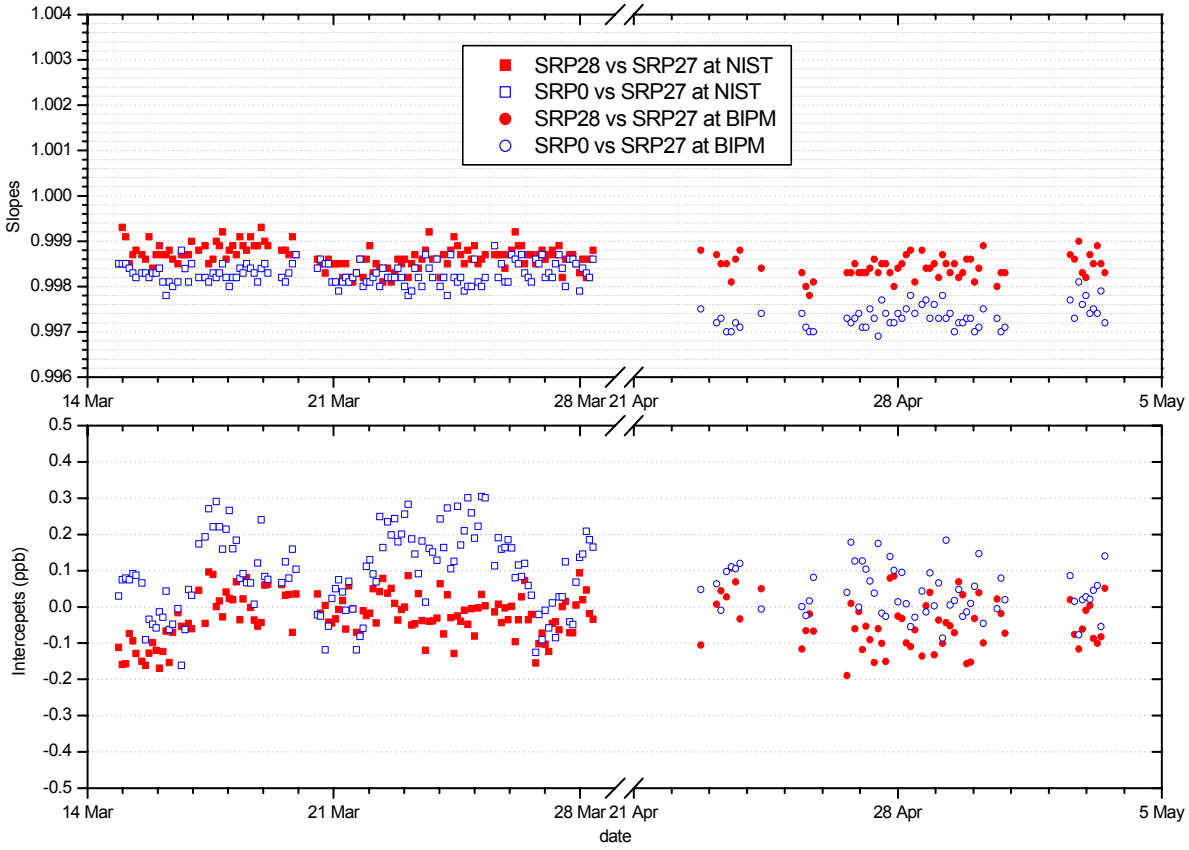
Abstract: The concentration of ozone in the atmosphere remains a significant issue from both scientific and political perspectives. Ozone, at tropospheric levels, is a health concern and contributes to global climate change as a greenhouse gas, while stratospheric ozone protects earth from harmful UV radiation. Since 1983, NIST has provided Standard Reference Photometers (SRPs) based on UV photometry to ten US Environmental Protection Agency (EPA) facilities to provide an infrastructure for the calibration and traceability of ozone measurements within the US. More recently, the international interest in ozone measurements has prompted fifteen foreign laboratories to acquire SRPs. While the SRP has nobly served monitoring communities for many years, the current research effort is focused on coupling state-of-the-art measurement technologies with national primary gas standards to provide an advanced primary ozone standard, which will improve SI-traceability and comparability of global ozone measurements.

Purpose: To support the growing national and international need of improved ambient ozone measurements, NIST is partnering with BIPM to develop advanced primary ozone reference standards and to share the dissemination of secondary or transfer standards. The basic project plan includes 1) Transfer the current ozone "national reference photometer" technology to BIPM. 2) Performance assessment of the current technology with respect to current and future ozone measurement requirements. 3) Develop a primary reference standard with capabilities of SI-traceability verification.

Major Accomplishments: During FY 2002, two new SRPs were built, extensively compared to the principal NIST reference photometer (SRP 2), and transferred to BIPM. A 0.5 % calibration bias between SRP 2 and the SRPs transferred to BIPM has been noted and an on going effort is dedicated towards identifying and eliminating this bias. To assess the current comparability of global ozone measurements, a pilot ozone key comparison will be initiated fall of 2002. An advanced photometer demands instrumentation with high sensitivity, accuracy, precision, and rapid time response for measuring chemical species at atmospheric levels (nmol/mol and lower). A number of in-situ techniques are being considered, including time-gated laser-induced fluorescence detection, laser absorption spectroscopy, and cavity ring-down spectroscopy for detection of relevant chemical species and possible contaminants in the carrier gas. Collaborations with researchers developing state-of-the-art instrumentation to measure NO_2, NO, and O_3 at trace levels have been established.

Impact: The advanced primary ozone photometer will provide an internationally validated ozone standard that can be used to anchor all ozone measurements through a defined traceability structure.

Future Plans: Two additional SRPs will be built for BIPM with participation of BIPM staff to accelerate the transfer of the current technology. Evaluation of potential instrumentation for the advanced primary reference standard will be initiated during FY 2003.



Comparison of NIST-constructed Standard Reference Photometers for Ozone measurements: SRP 0 at NIST and SRPs 27 and 28 now located at BIPM