7 CHEMISTRY  (R.I. WIELGOSZ)

7.1 Ozone photometer comparison programme
(J. Viallon and R.I. Wielgosz; P. Moussay)

The BIPM is coordinating the ozone (ambient level) comparison (CCQM-P28). Fourteen laboratories have participated in the comparison since July 2003, each spending up to one week at the BIPM. Each laboratory’s national or transfer standard has been compared against BIPM-SRP27. A further 13 laboratories are expected to participate in the comparison and measurements are foreseen to end in December 2004.

An informal comparison of the newly acquired ozone reference standard of the IMGC with the BIPM-SRP27 reference standard has been performed. The IMGC instrument was designed and built by the KRISS. The comparison has allowed the degree of equivalence of the reference standards to be determined. Possible sources of measurement bias were investigated, and have been addressed during the characterization of BIPM-SRP33. IMGC will participate in the CCQM-P28 pilot study in October 2004.

7.1.1 Statistical treatment of comparison results

A collaboration with Dr W. Bremser from BAM on the statistical treatment of the pilot study results was initiated in January 2004. The focus of the project is the use of the generalized least-squares method to compare measurement results of two ozone photometers. Dr W. Bremser has adapted the program B_Least, developed for use with ISO 6143, to compare ozone photometer measurements. The new version of the programme allows various correlations between the measurement results to be considered, and will correctly demonstrate how the number of measurement results affects the result of a comparison.

7.1.2 SRP characterization

The construction of BIPM-SRP33 at the BIPM was completed in July 2003. The optical bench was manufactured at the BIPM. The instrument was characterized by comparison with BIPM-SRP27 and found to be comparable within its calculated measurement uncertainty. The instrument has been used to investigate possible sources of bias in SRP measurements.

The accuracy of the temperature measurement in the SRP has been evaluated. A temperature gradient is evident along the gas cells within the instrument and has been measured in all SRPs maintained at the BIPM. The corresponding relative error in the measured value of the ozone mole fraction due to the temperature gradient has been shown to be as large as 0.5 %. A temperature control unit (TCU) to equilibrate the gas cell temperature has been designed and constructed at the BIPM. The TCU has been installed on BIPM-SRP31, 32 and 33 and shown to reduce the temperature gradient within the gas cells to less than 0.1 °C, reducing the bias in measured ozone mole fraction values to negligible levels.

The pressure difference in the gas cells of SRPs (within cell and between cell variations) has been verified. The maximum difference in pressure measured was consistent with the uncertainty budget currently in use.

The effect of optical design on the optical path length and, consequently, on the measured ozone mole fraction within SRPs has been investigated. The SRP design has been modified to allow the manual variation of the light beam alignment. In the current SRP design, the optical windows are perpendicular to the optical axis. Modified optical window holders have been designed and constructed with the windows a few degrees away from perpendicular. The redesigned optical system has confirmed the presence of multiple reflections within the gas cells, resulting in relative differences of 0.5 % in the ozone mole fraction measurements. Further characterization of the optical path length is limited by the poor collimation of the beam from the Hg lamp. A feasibility study on the incorporation of a laser based light source into the SRP has been completed.

7.2 Primary NO₂ gas standard facility
(M. Esler and R.I. Wielgosz; P. Moussay)

A primary gas standard facility for the dynamic preparation of nitrogen dioxide gas standards is being developed. The facility is based upon a magnetic suspension balance system, which was replaced by the manufacturer in April 2003. The new system has been tested, and analysis of the Allan variance of time series measurements has confirmed that it now meets the required stability specifications. Full
software control of the facility is now underway with the development of a dedicated program for communications, data acquisition and automation. The development of the facility will continue during the following period. The completed facility will ultimately act as a primary reference for NO$_2$ mass fraction measurements for gas-phase titration.

7.3 Gas phase titration facility (M. Esler and R.I. Wielgosz)

A gas-phase titration (GPT) facility as a second, potentially, primary method for ozone concentration measurements has been constructed. The system employs the mass-flow-controlled dynamic dilution of high-concentration nitrogen monoxide gas standards. Changes in NO concentration are monitored with a chemiluminescence analyzer and compared with the loss of ozone determined from UV absorption. The system has been fully automated. The first version of this facility relied on calibrated mass flow controllers (MFC) for values of gas flow. An examination of the uncertainty budget for the measurement results revealed that the MFCs are a dominant contributor to the overall uncertainty of the measurement result. Four molblocs have been purchased and are being integrated into the system to allow real time measurement of gas flow at considerably reduced uncertainty. Validation of the facility is currently underway. It is planned that the redesigned facility will participate in CCQM-P28 (ozone, ambient level).

7.4 NO gas standard comparison facility (M. Esler and R.I. Wielgosz)

A facility for the comparison of NO gas standards with nominal amount fractions of 50 µmol/mol has been established for the comparison of NO gas standards to be used for gas-phase titration. The behavior of two NO analyzers based on independent detection principles, UV absorption and chemiluminescence, has been analyzed. The uncertainty in the measurement results was reduced by optimizing the experiment design to minimize the Allan variance on time series measurements of NO amount fraction. Calibration curves were analyzed with generalized least-squares (GLS) regression, allowing the uncertainty in both axes to be taken into account. It has been demonstrated for the first time that using this measurement procedure, that NO gas standards can be analyzed with a measurement uncertainty arising from their analysis which is of the same order of magnitude as the uncertainty in their value determined from their gravimetric preparation. A suite of 13 gravimetric primary reference NO/N$_2$ gas mixtures has been purchased, from two different NMIs, together with a set of commercial secondary NO/N$_2$ mixtures for use in the GPT system. A procedure for the labeling of the secondary standards relative to the primary standards is being evaluated. The completed facility will be used to ensure that the measurements of the amount fraction of NO in the GPT system are traceable to primary gravimetric gas standards. In addition, the BIPM has recently proposed a CCQM pilot study which would begin in 2005 on the comparison of NO gravimetric mixtures, using the NO facility. Twelve NMIs have expressed interest in participating in such a comparison. A protocol for the proposed study is in preparation.

7.5 Composition of air (M. Esler and R.I. Wielgosz)

The KRISS have undertaken a determination of the mole fraction of argon in air in order to resolve the discrepancy in methods for the determination of air density. The importance of these measurements to mass metrology was presented to the CCQM Working Group on Gas Analysis by the BIPM. The KRISS value of 9.331 mmol/mol has been reported with a combined standard uncertainty of only 3 µmol/mol. The use of this value removes the discrepancy between methods for the determination of air density. Two papers reporting the details of the argon amount measurement and its consequences for mass metrology have been prepared by the KRISS and the BIPM Chemistry and Mass sections, and were submitted in June 2004 for publication in Metrologia.

7.6 Organic analysis programme (R.I. Wielgosz)

A detailed BIPM work programme in the field of organic pure substances was presented to the CCQM Working Group on Organic Analysis in September 2003 and the CCQM in April 2004. The long-term aim of the programme is to enable the BIPM to engage in and support the CCQM international programme of purity assessment comparisons and contribute to the development of robust approaches and methodologies for the determination of purity. This will require the extension of the CCQM-P20 series of comparisons for purity determination, the establishment of BIPM laboratory facilities to support these activities, the establishment of international liaisons to support and promote the programme. The programme will thereby ensure that the international comparisons of the CCQM...
provide agreed and documented methodologies for purity determination. The programme will not require the BIPM to produce reference materials.

In the initial five year period, the BIPM will establish its programme of purity assessment of select organic pure substances, and link this to the CCQM series of organic substance purity comparisons. In considering pure organic substances for study, the BIPM has prioritized the requirements in laboratory medicine for pure clinically relevant analytes, which would be required for the establishment of reference measurement systems. The initial period of the programme will therefore focus on the purity assessment of clinically relevant steroids and therapeutic monitored drugs. The BIPM has established collaborative projects with the LGC and the NMIJ/AIST to coordinate comparisons on these substances. This will enable the programme to be linked to the programme of comparisons of the CCQM and relevant to the activities of the JCTLM.

The BIPM organic substance purity laboratory is currently being established, and two scientists have been recruited and will join the staff in the autumn of 2004.

7.7 Publications, lectures, travel: Chemistry section

7.7.1 External publication


7.7.2 Travel (conferences, lectures and presentations, visits)

M. Esler to:
- University of Nottingham (United Kingdom), 24-29 August 2003, to attend and present poster at the 2nd International Conference on Advanced Vibrational Spectroscopy;
- BNM-LNE, Paris (France), 8-9 September 2003, to attend the EUROMET Workshop on Gas Purity;
- University of Wollongong (Australia), 12 February 2004, to give a seminar on the BIPM chemistry programme;
- NARL/AGAL (Australia), 13 February 2004, to give a seminar on the BIPM chemistry programme;


J. Viallon and P. Moussay to UBA, Langen (Germany), 22-25 March 2004, to install SRP19 in their laboratory and reproduce the comparison with BIPM-SRP31 performed in BIPM.

R.I. Wielgosz to:
- WHO, Geneva (Switzerland), 26-27 July 2003, to participate in a WHO informal consultation on the preparation, characterization and establishment of WHO international standards and other biological reference materials;
- NIST, Gaithersburg (United States), 4-5 September 2003, to participate in the JCTLM Working Group 1 meeting on reference materials and reference measurement procedures;
- CENAM, Querétaro (Mexico), 11-12 September 2003, to participate in the CCQM Organic Analysis Meeting and present the BIPM Organic Analysis Programme;
- VNIIM, St Petersburg (Russian Fed.), 1-3 October 2003, CCQM Gas Analysis Meeting and present thus use of GLS for ozone reference standard comparisons, and progress with CCQM-P28;
- WHO, Geneva (Switzerland), 6-7 October 2003, to participate in a WHO working group on international reference preparations for testing diagnostic kits used for the detection of HBsAg and anti-HCV antibodies;
• NIST, Gaithersburg (United States), 8-9 January 2004, to draft the JCTLM Working Group 1 quality manual as part of the “Quality and Implementation Group”;
• Sofia (Bulgaria), 10-13 February 2004, to attend the EUROMET Metchem plenary and Gas Analysis Working Group meeting and present the BIPM organic and gas analysis programmes and JCTLM activities;
• IAEA (Vienna), 17 February 2004, for a meeting of the IUPAC Analytical Chemistry Division and IUPAC Working Party for Harmonization of Quality Assurance and present a lecture of “Key Comparison, the MRA and CMCs: An International Measurement Infrastructure”;
• WHO, Geneva (Switzerland), 26-27 February 2004, for the WSC High-level Workshop on International Standards for Medical Technologies;
• Budapest (Hungary), 5 March 2004, to represent the BIPM at the International Agency Meeting (for organizations working in the field of analysis and sampling of food);
• Chicago (United States), 8-11 March 2004, to present the International Mutual Recognition Arrangement at PITTCON 2004;
• London (United Kingdom), 5-6 April 2004, for a meeting on organic pure substance reference materials at the LGC (Teddington), and a meeting at the Food Standards Agency on reference values for proficiency testing scheme materials;
• WHO, Geneva (Switzerland), 7-8 June 2004, to participate in a WHO Consultation on Global Measurement Standards and their use in the in vitro Biological Diagnostic Field;
• IRMM, Geel (Belgium), 28 June 2004, to present “Towards an international measurement infrastructure for Chemical Metrology” at a meeting on Establishing Metrology Infrastructure in South Eastern European Countries;
• ICC, Geneva (Switzerland), 30 June 2004, to represent the BIPM at the 27th session of the Codex Alimentarius Commission.

7.8 Activities related to external organizations
R.I. Wielgosz is the BIPM representative to the World Meteorological Organization (WMO) and the World Health Organization (WHO). He represents the BIPM and CCQM at ISO REMCO. He is a member of the editorial board of Accreditation and Quality Assurance.

7.9 Activities related to the work of Consultative Committees
R.I. Wielgosz is the Executive Secretary of the CCQM, and a member of its working groups on gas and organic analysis. A workshop on “Comparability and Traceability in Food Analysis”, was organized at the BIPM, and a summary of the workshop was published in Accreditation and Quality Assurance (2004, 9, 521-522). M. Esler and J. Viallon are members of the CCQM Working Group on Gas Analysis.

7.10 Activities related to the JCTLM
R.I. Wielgosz is Secretary of the Joint Committee for Traceability in Laboratory Medicine, JCTLM, and a member of its review team on “Quality Systems and Implementation”. The first meeting of the Executive Committee was held at the BIPM, following the signing of a declaration of co-operation between the CIPM, IFCC and ILAC, formally establishing the joint committee and inviting organizations with technical competence in the field to participate in its activities.
A JCTLM list of higher order reference materials and measurement procedures has been published on the BIPM website. This first list refers to well-defined chemical entities or internationally recognized reference method-defined measurands. The reference materials and measurement procedures included in this category are those that provide values that are traceable to SI units, e.g., electrolytes, enzymes, drugs, metabolites and substrates, non-peptide hormones and some proteins.
7.11 Visitors to the Chemistry section

- Mrs P.M. Gomez and Mr D.G. Madruga (ISCIII), 8-12 September 2003.
- Mrs M. Jansee van Rensburg (CSIR-NML), 11 September 2003.
- Mrs S. Goldthorp (Environment Canada), 20-24 October 2003.
- Dr D.W. Zickert and Mr D. Schwalser (METAS), 17-21 November 2003.
- Mrs S. Havrlantova (CMI), 20 November 2003.
- Dr J.C. Woo (KRISS), 1-5 December 2003.
- Dr M.P. Sassi and Mr E. Malgeri (IMGC-CNR), 26-30 January 2004.
- Mrs T. Macé and Mr C. Sutour (BNM-LNE), 2-6 February 2004.
- Mr D.V. Rumyanstev (VNIIM), 16-20 February 2004.
- Mr J. Walden (FMI), 1-5 March 2004.
- Mrs M. Froelich and Mr A. Wolf (UBA Austria), 29 March – 2 April 2004.
- Mrs S. Langer and Mr B. Magnusson (SP), 3-7 May 2004.
- Mr B. Sweeney (NPL), 25-28 May 2004.
- Mrs B. Frigy, Mrs I.G. Váraljai and Mr D. Laszlo (IEM-DEP), 7-11 June 2004.
- Mr V. Stummer (UBA Germany), 21-25 June 2004.
- Dr C. Murthy (CMS-NML/ITRI), 29 June 2004.

7.12 Guest worker

- Dr J. Norris (NIST), 16 June – 1 August 2003.