Bureau International des Poids et Mesures

Consultative Committee for Amount of Substance: metrology in chemistry (CCQM)

Report of the 10th meeting
(22– 23 April 2004)
to the International Committee for Weights and Measures

Comité international des poids et mesures

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Note:

Following a decision made by the International Committee for Weights and Measures at its 92nd meeting in October 2003, Reports of meetings of Consultative Committees will henceforth be published only on the BIPM website in the form presented here.

Full bilingual printed versions in French and English will no longer appear.

T.J.Quinn,
Director BIPM,
November 2003.

LIST OF MEMBERS OF THE CONSULTATIVE COMMITTEE FOR AMOUNT OF SUBSTANCE: metrology in chemistry
as of 22 April 2004

President

Dr R. Kaarls, member of the International Committee for Weights and Measures.

Executive Secretary

Dr R. Wielgosz, International Bureau of Weights and Measures [BIPM], Sèvres.

Members

Bureau National de Métrologie, Laboratoire National d'Essais [BNM-LNE], Paris.

Centro Nacional de Metrología [CENAM], Mexico.

D.I. Mendeleyev Institute for Metrology, Gosstandart of Russia [VNIIM], St Petersburg.

Danish Institute of Fundamental Metrology [DFM], Lyngby.

Institute for Reference Materials and Measurements [IRMM].

International Atomic Energy Agency [IAEA].

International Federation of Clinical Chemistry and Laboratory Medicine [IFCC].

International Organization for Standardization, Committee on Reference Materials [ISO-REMCO].

International Union of Pure and Applied Chemistry [IUPAC].

Korea Research Institute of Standards and Science [KRISS], Daejeon.

National Institute of Metrology [NIM]/National Research Centre for Certified Reference Materials [NRCCRM], Beijing.

National Institute of Standards and Technology [NIST], Gaithersburg.

National Measurement Laboratory CSIRO [NML CSIRO]*, Lindfield/National Analytical Reference Laboratory – Australian Government Analytical Laboratories [NARL-AGAL], Pymble.

National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology [NMIJ/AIST], Tsukuba.

National Physical Laboratory [NPL]/Laboratory of the Government Chemist [LGC], Teddington.

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* Now the National Measurement Institute, Australia [NMIA], also incorporating the NARL.

National Research Council of Canada [NRC], Ottawa.

NMi Van Swinden Laboratorium, Nederlands Meetinstituut [NMi VSL], Delft.

Physikalisch-Technische Bundesanstalt [PTB]/Bundesanstalt für Material-forschung und -prüfung [BAM]/Federal Institute for Materials Research and Testing, Braunschweig and Berlin.

Slovak Institute of Metrology/Slovenský Metrologický Ústav [SMU], Bratislava.

State Laboratory [SL], Dublin.

Swedish National Testing and Research Institute [SP], Borås.

Swiss Federal Office of Metrology and Accreditation [METAS], Wabern/Swiss Federal Laboratories for Materials Testing and Research [EMPA], St Gall.

The Director of the International Bureau of Weights and Measures [BIPM], Sèvres.

Observers

Central Office of Measures/Glówny Urzad Miar [GUM], Warsaw.

Centro Español de Metrología [CEM], Madrid.

CSIR - National Measurement Laboratory [CSIR-NML], Pretoria.

Istituto di Metrologia G. Colonnetti, Consiglio Nazionale delle Ricerche [IMGC-CNR], Turin.

National Metrology Institute of Turkey/Ulusal Metroloji Enstitüsü [UME], Gebze-Kocaeli.

National Office of Measures/Országos Mérésügyi Hivatal [OMH], Budapest.

National Physical Laboratory of India [NPLI], New Delhi.

Standards, Productivity and Innovation Board [SPRING], Singapore.

1 OPENING OF THE MEETING; APPOINTMENT OF THE RAPPORTEUR; APPROVAL OF THE AGENDA

The Consultative Committee for Amount of Substance: Metrology in chemistry (CCQM)* held its tenth meeting at the International Bureau of Weights and Measures (BIPM), at Sèvres on 22-23 April 2004.

The following were present: L. Besley (NML CSIRO), P. Charlet (BNM-LNE), K. Chiba (NMIJ/AIST), P. De Bièvre (ISO-REMCO), E.W.B. de Leer (NMi VSL), M. del Rocio Arvizu-Torres (CENAM), D.L. Duewer (NIST), R. Dybkaer (IFCC), H. Emons (IRMM), H. Ent (NMi VSL), A. Fajgelj (IAEA/IUPAC), B. Güttler (PTB), H.-P. Haerri (METAS), W. Hässelbarth (BAM), E. Hwang (KRISS), T. Ihara (NMIJ/AIST), H.D. Jensen (DFM), R. Kaarls (President of the CCQM), Y. Kustikov (VNIIM), Hongmei LI (NRCCRM), J.V. Lara-Manzano (CENAM), B. Magnusson (SP), M. Máriássy (SMU), A. Marschal (BNM-LNE), R. Matschat (BAM), W.E. May (NIST), J. McLaren (NRC), M.J.T. Milton (NPL), Y. Mitani (CENAM), D.W. Moon (KRISS), I. Nehls (BAM), K. Okamoto (NMIJ/AIST), H. Parkes (LGC), M. Sargent (LGC), M. Seah (NPL), H.-Y. So (KRISS), R. Sturgeon (NRC), P. Taylor (IRMM/IUPAC), J. Thijssen (University Medical Centre Utrecht), A.J. Wallard (Director of the BIPM), M.C. Walsh (SL), M. Weber (EMPA), S. Wood (LGC), Fangdi WU (NRCCRM), Yadong YU (NRCCRM).

Observers: I. Akdag (UME), A. Botha (CSIR-NML), E. Deák (OMH), M. Gallorini (IMGC-CNR), M.T. López Esteban (CEM), W. Louw (CSIR-NML).

Invited: L.A. Barrie (WMO), V. de Souza (INMETRO), M.A. Getrouw (INMETRO), D. Ivanova (NCM), G. Massif (Fundacion Chile), A. Padilla (WHO), V.M.L. Ponçano (IPT), W. Richter, L. Siekmann (Institut für Klinische Biochemie), A. Squirrell (NATA), A. Williams.

Also present: P. Giacomo, T.J. Quinn (Emeritus Directors of the BIPM); M. Esler, P. Moussay, C. Thomas, J. Viallon, R. Wielgosz (BIPM).

Excused: G. Steffen (WHO), W. Kozlowski (GUM), A. Narizano (Laboratório del Uruguay), V. Vilker (NIST).

Absent: NIM.

The President, Dr Kaarls, welcomed participants to the tenth meeting of the CCQM. He particularly welcomed representatives of the intergovernmental organizations that were working with the CCQM, and Prof. Andrew Wallard who was attending his first meeting of the CCQM in his new role as Director of the BIPM.

Prof. Wallard welcomed the CCQM to the BIPM. He said that the work on metrology in chemistry at the BIPM had been proposed for expansion at the CGPM held in 2003. Subsequently, the BIPM

* For the list of acronyms, click here.

had been able to recruit two new scientists and was planning to receive an attached scientist from one of the national metrology institutes (NMIs). He confirmed that work in this area would continue to be top of the list of priorities for expansion in the years to come.

The President said he had asked Dr Milton to act as rapporteur and was delighted that he had accepted. Dr Wielgosz would assist him.

The agenda was approved without modification.

2 REPORT OF THE NINTH MEETING

The report of the ninth meeting was approved.

3 CCQM POLICIES

The President told the meeting that he had been asked to develop a document that summarized CCQM policies. He referred to a draft (CCQM/04-17)* that he had discussed with the Joint Committee of the Regional Metrology Organizations and the BIPM (JCRB) and the CIPM.

He said that the CCQM is one of the Consultative Committees established by, and which reported to the CIPM. It operates according to the rules set out by the CIPM. The President of the CCQM is appointed by the CIPM, in general being a member of the CIPM. Membership of the CCQM is decided by the CIPM in accordance with criteria defined by the CIPM. The CCQM could establish working groups and, under certain conditions, invitees from other expert laboratories may usefully participate in its pilot studies.

The aims of the CCQM listed in CCQM/04-17 were:

- to establish global comparability through traceability to the SI;
- if traceability to the SI is not yet feasible, to other internationally agreed references (for example WHO units);
- to contribute to the establishment of a globally recognized system of national measurement standards and facilities, and

* Unless underligned, working documents are on restricted access to members of the CCQM.

- to contribute to the implementation and maintenance of the Mutual Recognition Arrangement of the CIPM (the CIPM MRA).

It was essential that the CCQM was effective in collaborating with other intergovernmental organizations, sometimes establishing joint committees as vehicles for facilitating cooperation.

Drs May and Emons observed that the priorities of the CCQM should encompass all types of certified reference materials (CRMs) as well as work on "higher order" measurements and primary methods. Dr Taylor suggested that the CCQM should have a role in supporting NMIs in their interactions with field laboratories. Dr Marschal advised that the CCQM should not over reach itself.

The President concluded that an updated version of the document on "CCQM Rules and Policy" will be issued later this year.

4 REPORTS OF WORKING GROUPS

4.1 Organic analysis

Dr May presented his report (CCQM/04-19) on progress made by the Organic Analysis Working Group (OAWG). The group had met twice during the year, once at the CENAM and once at the BIPM. They were working with the Bio-Analysis Working Group (BAWG) on the metrological characterization of DNA and protein. The OAWG was active in developing links with the regional metrology organizations (RMOs), and at least five RMO comparisons were in progress in the area.

He reported that two key comparisons had been completed, and results published in the BIPM key comparison database (KCDB):

- CCQM-K25 (PCBs in sediment), this concerned five congeners chosen to be typical of the 150 typically found in environmental samples.
- CCQM-K27.a and .b (ethanol in aqueous solution at forensic and commodity levels), the samples used for CCQM-K27.a had been spiked gravimetrically with ethanol, whilst those used for CCQM-K27.b were from commercial red wine after stabilization by irradiation. There was also a subsequent study involving three laboratories presented on the same chart as the key comparison itself. The results of the subsequent comparison were approved for publication in the KCDB.

He reported the results of the latest pilot studies conducted by the group on the analysis of the purity of atrazine (CCQM-P20.c) and chlorpyrifos (CCQM-P20.d). A workshop would be held in October 2004 to discuss the results of these pilot studies. In the future, this series of pilot studies would be continued, and the BIPM had proposed new studies on therapeutic drugs and a non-peptide hormones.

He also reported the results of pilot studies on organic solutions: PAHs in organic solution (CCQM-P31.a), PCBs in organic solution (CCQM-P31.b) and chlorinated pesticides in organic solution (CCQM-P31.c). The results of the studies had not been as good as expected, and it was necessary to undertake a key comparison in this area, since there were published CMCs which needed to be supported by comparison results. He proposed to proceed to a key comparison for PAHs in solution (CCQM-K38), chlorinated pesticides in solution (CCQM-K39) and the PCB congeners in solution (CCQM-K40).

Dr Sturgeon asked whether the differences observed in the pilot studies largely arose from the choice of calibration materials? Dr May replied that the choice of calibration material and the assessment of its purity was considered to be part of a laboratory's capability.

The results of a key comparison (CCQM-K27 subsequent) using the quantitative nuclear magnetic resonance (NMR) method and involving the BAM were reported. Poor values achieved in an earlier study had been greatly improved by the choice of a deuterated solubilizer instead of DMSO.

Dr May presented the results of a homogeneity study that had been performed on the samples to be used for CCQM-P40. The study demonstrated that sample homogeneity would limit the degree of equivalence that could be demonstrated. A further study of the effect of sample size on achievable measurement uncertainty would be carried out.

The NIST had carried out some statistical analysis that compared the performance of the NIST in studies on PAHs, PCBs and pesticides. They found that the performance of the NIST across these materials was coherent, but results from some other laboratories were not. He advocated the use of the term "coordinating laboratory" in lieu of "pilot laboratory" to avoid confusion with the term "pilot studies". He said that the OAWG would act as an advisory panel for the organic compound purity assessment programme at the BIPM.

Dr May introduced a number of new comparisons that the OAWG wished to undertake:

- CCQM-P31.b.1, PCB congeners in solution to be run in parallel to CCQM-K40;
- CCQM-P57, PCB congeners in mussel tissue extract;
- CCQM-P67, PCB congeners in mussel tissue;
- CCQM-P61, volatile organic compound (VOCs) in solution;
- CCQM-P68, anabolic steroids in urine;
- CCQM-P69, PAHs in soils/sediments.

All comparisons were approved.

6.2 Inorganic analysis

Dr Sargent presented his report (CCQM/04-18) of the Inorganic Analysis Working Group (IAWG), which had met twice since the last CCQM, once at St Gallen and once at the BIPM. There were seven key comparisons and eight pilot studies in progress. He presented a detailed report on four of these key comparisons:

- CCQM-K28 (TBT in sediment). This key comparison, coordinated by the LGC and the NRC, had been operated in parallel with a pilot study (CCQM-P43) which had also included DBT as an analyte. The calculation of the key comparison reference value (KCRV) for the TBT had been based on a median with the exclusion, on technical grounds, of one outlying result. The results from DBT showed good agreement amongst all participants.
- CCQM-K29 (anions in solution). This key comparison was coordinated by EMPA following a successful pilot study (CCQM-P32). Results for chloride agreed with the KCRV derived from gravimetric preparation. Results for phosphate also agreed, but the uncertainty had been expanded to allow for the presence of some di-phosphate in the samples.
- CCQM-K33 (minor elements in steel). This key comparison had been run in parallel with a pilot study CCQM-P56, and was coordinated by three laboratories (BAM, NIST and NMIJ), following a previous pilot study (CCQM-P25). The measurands were Cr, Ni, Mn, and Mo in low-alloy steel.
- CCQM-K35 (low sulphur in fuel) at 40 µg/g, run in parallel to a pilot study (CCQM-P26.1) that included samples at 10 µg/g. The actual level of sulphur in the blank is a major consideration at these low levels. The two levels reflect current and future regulated levels of sulphur in fuel around the world. The working group had discussed whether the uncertainty of one laboratory could be reduced by dividing by the square root of *N* to follow standard practice. He concluded that although there were significant analytical differences between the NMIs, they were able to meet the requirements to measure high and low levels of sulphur in diesel fuel. Further work at the CCQM was not required in the immediate future.

Dr Wielgosz emphasized that it was not acceptable to change an uncertainty by dividing by the square root of *N*, after the results of a comparison had been revealed. Dr Sargent agreed. Dr Milton asked whether the change to the median in place of the mean from CCQM-K28 was justified when the difference between them was very small. Dr Sargent said that the median could be more robust against outlying results when there were small numbers of data.

Dr Sargent made three proposals for new key comparisons to be carried out by the IAWG:

- CCQM-K42 (constituents of Al-alloy) to be run with a pilot study (CCQM-P34.1) Nine participants from six countries had agreed to participate in this key comparison and the pilot laboratory would be the BAM. It was proposed that five elements (Fe, Cu, Mn, Cr and Zn) would be measured. A pilot study (CCQM-P34) had shown some evidence for technique-related bias in this type of measurement.
- CCQM-K43 (methyl(Me)-mercury in salmon) to be run with a pilot study (CCQM-P39.1). This key comparison would involve measurements of Hg, MeHg, Pb, As and Se in samples of freeze-dried tuna. The levels of Hg were close to those chosen for regulation within the EU. It would follow on from a successful pilot study (CCQM-P39) in which five institutes out of 21 participants had been able to measure all five analytes. Dr Sargent observed that this pilot study had been very valuable and had been an important opportunity to involve a range of reference laboratories that were not NMIs.
- CCQM-K44 (trace elements in sewage sludge). This key comparison would include four elements (Cr, Hg, Ni and Zn) required to support a range of CMCs. The samples would also be used for a pilot study (CCQM-P70), EUROMET 784 and IMEP exercises.

Dr Marschal asked what made the work on aluminium and steel samples relevant to the CCQM when the spread of results amongst the CCQM laboratories was similar to that of industrial participants? Dr Matschat confirmed that this represented the "state of the art" for such measurements.

Dr Sargent proposed five pilot studies:

- trace analysis of high purity nickel (CCQM-P62);
- platinum group elements in an automobile catalyst (CCQM-P63);
- trace elements in soyabean powder (CCQM-P64);
- chemical composition of clay (CCQM-P65);
- metals in fertilizer (CCQM-P66).

These were all approved. He also reported that a representative from the IAEA had made a presentation on stable isotope measurements and that a pilot study might be planned in this area in the future.

He concluded that good progress had been made with the projects and that participation had been widened by the involvement of a number of new laboratories in pilot studies.

4.3 Gas analysis

Dr de Leer presented his report (CCQM/04-21) on the work of the Gas Analysis Working Group (GAWG), which had met twice since the last CCQM, once in St Petersburg and once at the BIPM. It had held workshops on the use of generalized least-squares regression methods in gas analysis and on standards for ambient air quality. He reported on progress made by the working group on a series of key comparisons and pilot studies:

- CCQM-K15 (CF_4 and SF_6 at emission levels) was being piloted by the KRISS. There were four participants in the key comparison and two in a related pilot study. All participants were comparable with the KCRV to within their estimated uncertainty.
- CCQM-K16.a and CCQM-K16.b (natural gas) had been completed and the final report had been approved for equivalence. The results of a pilot study (CCQM-P49) involving two participants had subsequently been written up into a report.
- CCQM-K22 (eight hazardous air pollutants - chlorinated VOCs). This key comparison had six participants who were all in agreement with the KCRV for all components. The results of the NRCCRM would be included in a pilot study report (CCQM-P71). The coordinating laboratory was NMIJ. The results will provide good underpinning for a range of CMCs.
- CCQM-K26.a and CCQM-K26.b (NO and SO_2 at ambient levels). This key comparison is in progress and would be the first exercise carried out by the GAWG for which the KCRV would not be based solely on the results of gravimetric preparation. The pilot laboratory (NPL) had prepared hierarchies of gravimetric standards from two different sources of NO to avoid possible difficulties with the purity of the raw material. The process for developing the KCRV had been discussed. It could be based on either the certifications of the travelling standards carried out by the pilot laboratory or on a consensus (e.g. mean) of participant's values.

- CCQM-K23 (natural gas). This key comparison will repeat CCQM-K1.e, CCQM-K1.f and CCQM-K1.g (with the addition of *i*-butane). This would enable new laboratories to underpin their capabilities.
- CCQM-K41 (H_2S in nitrogen). The NIST would act as the pilot laboratory for this key comparison and had developed a protocol.
- CCQM-P41 (greenhouse gases – carbon dioxide and methane). This pilot study had involved the distribution of standards from the pilot laboratory as well as the submission of standards to the pilot laboratory. Two participants from the WMO were internally consistent but exhibited a bias with respect to the KCRV defined by the NMIs for methane.

He also described the results of some further statistical analysis of the results of CCQM-P23 carried out by the NPL. The analysis was based on measurements made by GC-TCD at the NIST and indicated that the standard deviation of the residual deviations from the fitted calibration relationship was 0.002 % relative to the value of 50 000 µmol/mol. This result provided the first ever confirmation that uncertainties claimed for gravimetric preparation of stable gas standards were valid.

The BNM-LNE and the BAM had collaborated to develop a protocol for a comparison of dynamic mixing methods. The BIPM was carrying out a pilot study (CCQM-P28) of ambient ozone measurements. This will be finished by the end of 2004, with a workshop for participants to be organized by the BIPM in April 2005.

He also described some work done by members of the GAWG to measure the argon content of ambient air. This was required to calculate the buoyancy correction for mass artefacts of different densities. The agreed CIPM value was 9.17 mmol/mol. The KRISS had measured the argon content of air by mass spectrometry and found a value of 9.332 mmol/mol ± 6 µmol/mol. This value would explain an anomaly in the calculation of buoyancy by NMIs working in this field. The KRISS and the BIPM were preparing a paper describing the measurements performed, to be submitted to *Metrologia* for publication.

Dr de Leer described plans for future activities by the GAWG. These would include a key comparison of measurements of ammonia in nitrogen, a repeat of CCQM-K1.a and CCQM-K1.b covering carbon monoxide in nitrogen and carbon dioxide in nitrogen. A number of proposals had been made for 'high accuracy' comparison of gravimetrically produced standards, including studies of *n*-hexane in methane, NO in nitrogen and natural gas. These would be discussed in the October meeting of the GAWG. In conclusion, he said that there was an increasing requirement for key comparisons to underpin CMC claims of some "exotic" VOCs as well reactive species including butanol and formaldehyde.

4.4 Electrochemical analysis

Dr Máriássy presented his report (CCQM/04-20) on the work of the Electrochemical Analysis Working Group (EAWG), which had met twice since the last meeting of the CCQM.

He reported that CCQM-K34 (assay of KHP) was underway. Results were available from CCQM-P52 (pH of carbonate buffer), which was being held before a key comparison (CCQM-K18)

on the same system. Results from 11 participants were within 0.01 pH units for a standard buffer composition and 0.015 pH units for an "unknown" buffer. Results were also available from CCQM-P47 (electrolytic conductivity) which had involved a solution of HCl in water at 0.05 S/m and HCl in water at 0.005 S/m. The overall level of agreement had been good, but there were large differences in the estimated measurement uncertainty. The group were developing an approach to establishing the KCRV.

Future plans included key comparisons of pH close to 9.2 and 1.7, and a further key comparison of electrolytic conductivity.

The meeting of the EAWG had also included technical presentations from a number of participants including: some results of studies at the NIST and the NPL on the stabilization of Ag electrodes; the correlation between pH and the assay of compounds; and finally the calculation of conductivity in the low range from literature data. They had also discussed the difficulty of underpinning capabilities that were not close to the values of the established primary buffers. It had been agreed that this difficulty might be noted in the "comment" column of the CMCs.

He reported that the difficulty caused by an incorrect value published in the European Pharmacopoeia discussed last year had been resolved satisfactorily.

4.5 Surface analysis

Dr Seah presented his report (CCQM/04-23) on the work of the Surface Analysis Working Group (SAWG). He explained that the work of the group spanned length scales from 0.1 nm to 100 µm with a large number of different techniques capable of giving information from material properties through to full chemical structure. Consequently, he proposed that the name be changed to "surface and micro/nanoanalysis".

A full report of the pilot study of measurements of SiO_2 on Si (CCQM-P38) had been published. The results showed much better consistency than previous studies. The XPS method was developed during the study and improved by an order of magnitude. It also showed that TEM, which had been the favoured method, had significant type B uncertainties that had not previously been understood. The study had significantly improved the understanding of measurements of SiO_2 on Si at scales of less than 8 nm. It would be followed by a key comparison also coordinated by the NPL (CCQM-K32). The measurand had been carefully formulated as "amount of substance of SiO_2 in ultra-thin layers expressed in nm of SiO_2". This key comparison would produce results in time for the next meeting of the CCQM.

Dr Guettler said that TEM should not be omitted since it was capable of producing results that were traceable to the SI. Dr Seah said that the Type B uncertainties undermined its capabilities. In response to a question from Dr May, Dr Seah confirmed that the techniques do not all measure the same quantity. He said that XPS was highly linear with a well-defined zero point and could be calibrated with full traceability by either NR or GIXR.

The group had carried out a technology "foresight" exercise amongst the eight NMIs at the meeting – several of which provide CRMs. Fourteen areas for future pilot studies had been identified, of which the highest priorities were:

- Fe-Ni alloy films;
- N and C in carbide coatings;
- standard-free quantification by EPMA;
- Hf silicate, high-K dielectric surface composition; and
- multilayer thickness and phase stability in a SiGe multilayer.

He concluded by saying that standardless analysis was an important goal for work in the area, since CRMs can be very expensive. They would seek to develop proposals for pilot studies for these priority areas with early emphasis on:

- carbon contents in precipitates and surface layers;
- nitrogen contents in surface layers; and
- standard-free quantification in energy dispersive x-ray spectroscopy.

The President thanked Dr Seah and said it was pleasing that this newly-founded working group was making such good progress. A number of members of the CCQM made alternative proposals for the name of the group, but the President proposed that any possible change to the name of the group be kept under review.

4.6 Bio-analysis

Mrs Parkes presented her report (CCQM/04-22) on the work of the Bio-Analysis Working Group (BAWG) which had met twice since the last CCQM, once in Tokyo and once at the BIPM. She said that the IFCC and WHO provided essential input into the work of BAWG and was pleased that they were involved. A joint session of the BAWG had been held with the OAWG.

She reported on the results of CCQM-P44 which was concerned with the Quantitative PCR (Q-PCR) method. The purpose of the study was to quantify a DNA sequence and determine the factors contributing to the variability of Q-PCR measurements. A reference value had been determined for the comparison, but this had been difficult because of the wide variability in the submitted results. An analysis of the results by ANOVA showed wide variation in both the inter- and intra-plasmid dilution. Some subsidiary analysis using discriminant function analysis had also been carried out, but no single factor had been identified that could account for the majority of the variation. However, it had been shown that it was important to maintain a separate laboratory area for PCR analysis and to have an experienced operator. The group had also received presentations on inter-laboratory studies of Q-PCR in Canada and Japan that gave similar results. A workshop on uncertainty in biological measurements had been held to support the CCQM-P44 exercise. The group was proposing a second round (CCQM-P44.1) for the pilot study with a more prescriptive protocol and a greater emphasis on data processing.

Dr Duewer said that the results of CCQM-P44 indicated that the measurement was not well defined and that the results were not surprising for an exponential process such as PCR. Consequently, the statistical analysis should focus on the logarithm of the results. Dr Dybkaer made the comparison with pH which was handled as the logarithm of an ionic quantity.

Mrs Parkes also reported on the results of CCQM-P53 (AFLP) coordinated by the AGAL. A material had been developed for the study that would be distributed later in the year.

She also reported on proposed future pilot studies:

- CCQM-P54 (DNA "primary" quantification), this was based on an LC-IDMS method developed at the LGC. The initial aim would be to determine the base sequence and size of an oligonucleotide.
- CCQM-P55 (protein and peptide quantification by mass spectrometry). The protocol for this pilot study was being developed by the LGC, the NIST and the PTB. This study was relevant to the growing area of protein analysis. The aim would be to develop appropriate reference materials for complex peptide and protein/proteome measurements.

She described a study performed by the KRISS on phosphorous analysis in DNA using ICP-OES. This has the potential to be a primary method for DNA measurements although it has the disadvantage of using a large amount of material.

Dr May said it was important to separate the activities of the BAWG from those of collaborating laboratories, which might generate intellectual property rights. Mrs Parkes agreed. She proposed three new pilot studies.

- CCQM-P58 (fluorescent measurements in ELISA). Fluorescence is widely used in biological analysis for ELISA, flow cytometry and other types of measurement. Although there are some fluorescence standards available, there are few that are suitable for biological applications. The aim of the study would be to look at the factors influencing the uncertainty of ELISA and lead to the development of some reference plates in the 96–well format. There was wide interest in this proposal.
  In response to a question from Prof. Emons, she confirmed that the study would not attempt to study the whole ELISA process, only the fluorescence aspect of the measurement. Prof. Thijssen suggested that ELISA might not be the best example for this study. Mrs Parkes explained that there was substantial expertise on ELISA within the group so it was a good choice.
- CCQM-P59 (protein structure by circular dichroism). This study would underpin measurements of the higher-order structure of proteins. An inter-laboratory trial carried out by the NPL showed a substantial lack of comparability between measured CD spectra of proteins. The pilot study will involve the distribution of samples of protein and is planned to involve expert laboratories.
- CCQM-P60 (DNA extraction). This study would look at the extraction of DNA with a focus on the methods used for the measurement of genetically-modified material.

Mr Squirrell asked how the type of method discussed could define measurement uncertainty when there was no metrological traceability, often because the measurand was ill defined? The President said this was an interesting question that would continue to be discussed. Dr Marschal asked whether the field was sufficiently mature for the work of CCQM? Dr Quinn said that the CCQM could not avoid acting in areas because they were not sufficiently mature. When a field is in its early stages of development it is often the best time for metrologists to become involved.

All of the proposed studies were approved.

4.7 Key comparisons and CMC quality

Dr McLaren gave a report (CCQM/04-24) on the work of the Key Comparison and CMC Quality Working Group (KCWG) which had held its first meeting two days previously. He had established the group by asking for nominations from the chairs of the CCQM working groups and the RMO working groups. There were sixteen members.

The role of the KCWG was "to verify, at the global level, that the CMC review process within all the RMO's is uniformly comprehensive and adequately thorough". The meeting had covered three areas; the review of cycle V CMCs, a discussion of the review process itself and the identification of "gaps" in the coverage provided by the key comparisons.

He described the review of the cycle V CMCs which had made use of a restricted access website maintained by the BIPM. A total of 194 CMCs had been received in twelve measurement service categories from four of the RMOs. He also proposed a timescale for the submission of cycle VI CMCs. He concluded that the CMC process was working, but that there were still issues associated with the limited number of key comparison results.

Dr Besley asked whether the CCQM could establish a system whereby the reports of peer reviews were available for use in the CMC review process? The President suggested that this was a point of general interest to the JCRB. The Director said that the JCRB would debate the whole area of quality assurance of the NMIs, both accredited and peer reviewed. He said that there had been a proposal to allow requests for "on-site peer reviews" to resolve complex issues raised by specific CMCs. Dr May agreed with the view that peer review reports should be made available.

Dr Besley asked who should initiate the re-review of CMCs following the results of a new key comparison? Dr Wielgosz said that the JCRB had issued a paper on this subject (JCRB-8/10).

The President thanked the chairs of all of the working groups for their reports and their hard work during the year.

4.7.1 Review of document CCQM/01-08

Dr McLaren introduced the revised version (CCQM/04-11) of the "Criteria for the Acceptance of Certified Reference Materials in Appendix C of the CIPM MRA" originally circulated as CCQM/01-08. He explained that the text of the MRA did not explicitly refer to the role of CRMs but it did refer to ISO 17025, which did not cover all aspects of CRM production. However, some specific issues relevant to CRM production were covered by ISO Guide 34, which was not specifically referred to in the MRA. He said it was often the case that the production and certification of CRMs was not carried out by a single NMI.

The proposal to revise CCQM-01/08 had been initiated by Dr Taylor and Prof. Emons. Subsequently, the President had been involved.

Dr Marschal expressed his view that the CMC database should not duplicate the COMAR database.

Dr May said that the NIST did not believe there was a need for this document, because the CIPM MRA already laid down the necessary conditions.

Dr de Leer said that a model of measuring CRMs at a single laboratory used by the GAWG in CCQM-P23 was directly applicable to determining the comparability of some CRMs; for example Cu in solid and sediment. The new model had given good results and could be highly cost-effective. He suggested that this model should become the principle one used by the CCQM for carrying out comparisons. Prof. Emons said he agreed with the principle, but that the trend away from duplication would make such a model for comparisons difficult to use in the future.

The President thanked the CCQM for their input. He asked the small group of members that had re-drafted the document to continue to improve it in time for the next meeting of the JCRB.

4.7.2 Reporting results of RMO supplementary comparisons and pilot studies

Dr Wielgosz introduced document CCQM-03/02 that explained the procedures for RMO supplementary key comparisons. These should be approved by the RMO and then by the relevant working group of the CCQM. Some comparisons might remain in the RMOs.

4.7.3 Reports on RMO activities

The President asked the chairs of the RMO working groups covering the same technical areas as the CCQM to give reports on their work.

Prof. So, the chairman of the Quality Management Working Group of the APMP reported on its activities (CCQM/04-25). He said that the group had 27 participants from 11 countries. The CMC review process had been improved by holding meetings of the TC chairs within the APMP during the year. Four specialists had carried out the intra-regional reviews of CMCs. The APMP was developing templates for technical procedures that could be used by developing countries. They were also sharing information about quality systems, including peer review reports. An *ad hoc* committee on materials metrology had been established. The APMP was carrying out key comparisons on: gas mixtures (automotive emission mixtures and ethanol in air), organic measurements (p,p'-DDE in fish oil) and inorganic analysis (Cd in rice flour).

Dr Kustikov reported on the work of the COOMET technical committee on chemical measurements chaired by Prof. Konopelko from the VNIIM. They were active in the review of CMCs and received useful support from their two associate members – Germany and Slovakia. The committee was active in all areas, but most active in gas analysis. Financial constraints limited involvement in the working groups of the CCQM. They were involving expert laboratories in the region in the work of the CCQM working groups.

Dr Charlet reported on the work of the EUROMET/METCHEM technical committee (CCQM/04-12). He had taken over from Mrs Deák as the chair in May 2003. The annual meeting was attended by 50 participants and also included the election of convenors for four working groups. EUROMET was strongly involved with an initiative to implement a “European Research Area” in metrology, which aimed to increase cooperation between the member states. This had identified metrology in chemistry as one of its priorities. The technical committees were developing new types of

cooperation to support this including the development of models for a distributed infrastructure for metrology in chemistry.

Dr Louw presented the work of metrology within the SADC (CCQM/04-26). It had one laboratory with substantial capability in chemistry and three with developing activities. Seven CMCs had been accepted and eight were under review in Cycle V. Recently, they had participated in the Surface Analysis and Bio-Analysis Working Groups of the CCQM and submitted the first CMC in the area of surface analysis.

Dr May presented his report about metrology in chemistry in the SIM (CCQM/04-27). The range of investment in chemical metrology varied widely between members and a work programme had been developed that reflected this. Awareness seminars were being organized within the sub-regions of the SIM. All of the comparisons had a focus on training in order to improve capability – possibly to the point where NMIs could participate in future activities of the CCQM. Five proficiency assessment studies had been carried out, covering: trace elements in water, pH, automotive emission gases, cholesterol in serum and ethanol in an aqueous matrix. Further activities were planned, including repeating the studies that were expected to lead towards further involvement in the CIPM MRA in the region.

Prof. So said that APMP would welcome sharing of samples used for some of the SIM studies.

5 A ROBUST APPROACH TO THE DETERMINATION OF CCQM KEY COMPARISON REFERENCE VALUES AND UNCERTAINTIES

Dr Duewer from the NIST introduced his paper entitled "A robust approach for the determination of CCQM KCRVs and uncertainties" (CCQM/04-15 and CCQM/04-34). He said that the set of data from the key comparisons of the CCQM was unique in his experience because it was a condition of submitting data that the uncertainties should be meaningful. He made the observation that the KCRV could be considered as representing one of three things, namely:

- observed performance of participants;
- "typical" performance of participants; or
- true value of the measurand.

Consequently there was a difference between the requirements for the use of descriptive or inferential statistical approaches. He advocated the use of a mixture-model probability density function (MM-PDF). He showed an example of its application to the results of CCQM-K25 and went on to categorize different methods according to whether they were "robust" or "symmetric to outliers". The robust methods generally provide better inference than non-robust methods when the samples were not from the same population. He also introduced an inferential approach to estimating "how far the light shines" based on "Z-scores".

The President thanked Dr Duewer for his presentation and said that the working groups would discuss the matter further. Dr Hässelbarth said that the paper was timely and could be usefully developed with inputs from statistical experts from other NMIs.

6 ISO REMCO: DRAFT OF ISO GUIDE 35

Dr Wielgosz reported that he had attended a meeting of the ISO REMCO which had asked him to circulate a draft of ISO Guide 35 amongst the CCQM. This document had subsequently been accepted. A report (CCQM/04-08) on recent REMCO activities had been submitted to the CCQM.

Dr de Leer informed the CCQM about the aim of the newly created International Advisory Group on Reference Materials (IAGRM).

7 BIPM PROGRAMME OF METROLOGY IN CHEMISTRY

Dr Wielgosz introduced his report (CCQM/04-35) on work at the BIPM in the field of metrology in chemistry.

The report of the new BIPM organic programme (CCQM/04-04) to extend the CCQM-P20 series of comparisons based on a new laboratory facility at the BIPM had been accepted. This series would also play a role in supporting the work of the JCTLM. The programme would initially focus on two areas: steroid hormones and therapeutic monitored drugs. A number of direct and indirect methods would be used at the BIPM. There would be collaboration with both the LGC and the NMIJ. He said that an area for future consideration was the purity of food additives.

He reminded the CCQM about the ongoing pilot study at the BIPM on ozone analysis. He explained that participants had been visiting the BIPM over the previous six months.

There had been collaboration with Drs Bremser and Hässelbarth from the BAM on the development of generalized least-squares methods for data analysis (CCQM/04-03). The BIPM was also developing a “second generation” standard reference photometer and developing a gas-phase titration facility as an independent method to determine ozone amount fractions. This had led to a proposal for the BIPM to coordinate a pilot study of the GAWG that would compare standards of NO in nitrogen.

He explained that the Chemistry section at the BIPM had coordinated work within the GAWG to re-determine the amount fraction of argon in the atmosphere.

He acknowledged the work of his colleagues at the CCQM in the BIPM Chemistry section and those NMIs that had collaborative programmes with the BIPM. Drs May and Sargent indicated their support for the work in organic analysis.

8 UPDATE ON THE BIPM KEY COMPARISON DATABASE, KCDB

Dr Thomas said that the KCDB was operating well and its operation had been reviewed as part of the BIPM Quality System. She said that a "KCDB Newsletter" would be produced that would include information about the decisions of the JCRB.

Dr May said that all the working group chairmen were very grateful to her for her work in checking all data thoroughly before entering it into the KCDB.

9 INTERNATIONAL ATOMIC ENERGY AGENCY, IAEA

Dr Fajgelj gave a presentation about the work of the IAEA (CCQM/04-09), which was concerned with the "peaceful use of atomic energy throughout the world". He reported that they had an on-going programme on standards and quality systems. They produced reference materials, for example: natural matrix reference materials characterized for radionucleides, stable isotopes and trace metals. They also carried out comparisons and proficiency tests. The IAEA had previously assigned the value of reference materials based on inter-laboratory comparisons, but in the future would aim to provide metrological traceability to the SI.

The President thanked Dr Fajgelj for his report and welcomed the increasing emphasis on metrological traceability by the IAEA.

10 WORLD METEOROLOGICAL ORGANIZATION, WMO

The President welcomed Dr Barrie from the WMO who gave a report (CCQM/04-28) on the WMO's Global Atmosphere Watch Programme (GAW). It coordinated global measurements of the atmosphere, including greenhouse gases, reactive gases and solar ultraviolet. The programme had a specific structure, which involved a network of global and regional monitoring stations. Each measurand of interest to the WMO had a central calibration laboratory that maintained and disseminated primary standards. He welcomed the links between these laboratories and the BIPM, and the laboratories active in the CCQM Gas Analysis Working Group (GAWG).

A consistent set of terminology was being developed for use by the GAW and he welcomed input from the CCQM.

Standardization of ultraviolet measurements was carried out through a centre operated by the NIST and the NOAA together with a regional travelling standard operated by the EC-JRC (Ispra).

The IHALICE programme was the first attempt to establish a long-term record of hydrocarbon concentration in the atmosphere.

The President thanked Dr Barrie for his presentation. Dr de Leer said that he was pleased that two GAW laboratories had recently participated in a comparison organized by the GAWG.

11 WORLD HEALTH ORGANIZATION, WHO

Dr Padilla gave a presentation of the work (CCQM/04-29 and -30) of the WHO in the area of *in-vitro* diagnostics. She explained the difficulties faced by the WHO in standardizing biological products which could not be standardized by physico-chemical methods alone. The WHO disseminates reference preparations that define internationally-recognized units of biological activity. Approximately 70 % of these materials are in the *in-vitro* diagnostics area. These materials are largely freeze-dried and value-assigned through WHO collaborative studies. They are finally submitted for approval to the WHO Expert Committee on Biological Standardization (ECBS).

Each group of products has an expert working group. They have to develop standards to meet existing requirements (e.g. the replacement of the HbsAg IS), new requirements (e.g. nucleic acid amplification) and emerging requirements (e.g. prion diseases).

She said that there were substantial challenges including addressing existing, new and emerging technologies that will have an impact on public health. It would be necessary to keep pace with new standardization approaches and coordinate with other standard-setting organizations (for example the BIPM, ISO and the EC). It was also necessary to ensure that developing countries have access to

appropriate reference materials. They were planning a consultation on Global Measurement Standards and their use in the *in-vitro* biological diagnostic field.

The President thanked Dr Padilla for her presentations. In response to an example from Prof. Emons, Dr Padilla and Prof. Thijssen agreed that there was much to be learned from further collaboration between the WHO and the CCQM.

12 JOINT COMMITTEE ON TRACEABILITY IN LABORATORY MEDICINE, JCTLM

The President welcomed Prof. Thijssen to the meeting and drew participants' attention to the text of the "Declaration of cooperation between the CIPM, IFCC and ILAC for the establishment of a joint committee on traceability in laboratory medicine (JCTLM)" (CCQM/04-05).

Prof. Thijssen gave a report on the work of the JCTLM (CCQM/04-31). He re-iterated that a major reason for the establishment of the JCTLM had been the EU *In-vitro* Diagnostic (IVD) Directive, with its requirements for metrological traceability. He gave the example of how measurements of HbA1c had been made traceable to the SI following the hierarchical approach defined by ISO 17511.

The aim of the JCTLM was "to support the comparability and equivalence of measurement results in laboratory medicine, through worldwide accepted traceability". This should be done through establishing a consensus on matters of science and metrology in the context of medical applications.

Two working groups had been established. He particularly thanked Drs May and Schimmel the chairs of WG1, and their work which had led to the publication of a first list of higher order reference materials and reference measurement procedures for laboratory medicine and *in-vitro* diagnostics.

12.1 JCTLM WG1

Dr May described the background to the establishment of WG1 of the JCTLM (CCQM/04-06 and -32). It had established review teams in the eight highest priority areas for analysis. Traceability to the SI was possible for measurements in five of these. These review teams included representatives from laboratory accreditation organizations, the NMIs, professional societies and the IVD industry. Materials under consideration had been sorted into one of three lists:

- alpha list – meeting all requirements;
- beta list – provisionally acceptable;
- gamma list- does not meet requirements.

Subsequently, the alpha and beta lists had been combined to form two lists: List I, traceable to the SI and List II, international conventional reference materials. A quality manual had been prepared to document the review process.

At the time of the meeting, List I had 100 reference measurement procedures for 58 different health status markers, together with 150 reference material entries for 96 measurands. Some studies had been carried out under repeatability conditions to determine the comparability of reference materials.

Work was underway in the compilation of List II. The definition of materials in this list had been refined to specify reference materials that have been value-assigned using an internationally-agreed protocol.

He thanked Dr Wielgosz and his colleagues at the BIPM for their hard work in establishing a website to host the JCTLM compilations.

12.2 JCTLM WG2

Prof. Siekmann reported on the work of WG2 of the JCTLM, which was concerned with the identification of reference laboratories. He said that these would be identified on the basis of the level at which they operated and their scope of accreditation. The working group was establishing a database incorporating information about the methods and accreditation of each laboratory.

They were proposing to organize "ring trials" for reference laboratories. He showed examples of the results for a ring trial of measurements of cholesterol. He compared these with the results of CCQM-P6 and CCQM-K6, which studied the same analyte. He presented results for other measurands including: creatinine sodium, glucose, an enzyme (ALT), albumen, progesterone and digitoxin.

The President thanked Prof. Thijssen, Dr May and Prof. Siekmann for their work.

12.3 Cooperation with the Codex Alimentarius Commission

The President explained that the CCQM had been invited to join the Inter-Agency Meeting (IAM) and had become an observer to the Codex Alimentarius Commission.

Dr Wielgosz explained that several documents were available, including a report of a workshop on "Comparability and Traceability in Food Analysis" held at the BIPM (CCQM/04-02), a draft report of the last "Inter-Agency Meeting" in the field of methods of analysis and sampling (CCQM-04/14), and an IAM document on the harmonization of analytical terminology (CCQM/04-07).

Dr Walsh presented her paper on CCQM activities in support of the food analysis community (CCQM/04-16). She explained that the conclusions and priorities that emerged from the workshop held at the BIPM (CCQM/04-02) included the need for validated methods that provide information on uncertainty as well reference materials that have traceable values with stated uncertainties. It had concluded that it should build on the activities of the CCQM and utilize the expertise of existing

laboratory networks. Several actions had been identified. These included the identification of further requirements for reference materials.

The Codex Alimentarius had established a series of committees. In particular, the Codex Commission on Methods Analysis and Sampling (CCMAS) was devoted to general issues, including methods of analysis and sampling. Four types of methods were defined in their procedure manual: defining (or empirical), reference, alternative approved and tentative methods. In future, the methods of analysis submitted to the CCMAS, for Type II and III methods, will have to contain a set of criteria, and an analyst may use any alternative method provided it conforms to the criteria set. An expected outcome of this changed approach will be an increased requirement for CRMs to validate methods and estimate measurement uncertainty. A policy statement on the use of measurement uncertainty had been agreed by the Codex.

She presented the results of some proficiency tests (CCQM/04-33) and noted that future comparisons covering vitamins A (or E) and butyric acid, would be of use to the food analysis community. Additionally, future work might cover: PAHs, chloramphenicol, aflatoxins, nitrates and proximates.

The President thanked Dr Walsh for her presentation.

13 DESIGNATION OF OTHER INSTITUTES

The President explained that a document was in preparation discussing the “designation” of institutes. He explained that the original motivation for document CCQM/04-10 had been to lay down the criteria for the use of very expensive facilities, such as NAA. He explained that there were criteria within ISO/IEC 17025 that applied to sub-contracting, although not all of these criteria were applicable to the certification of CRMs.

14 VOCABULARY

The President explained that a new draft (CCQM/04-13 and 13a) of the VIM was available for comment and that CCQM members should provide formal comments through their NMIs.

18 FUTURE CCQM WORKSHOPS

The President suggested that a workshop on "primary methods" might be held during the next CCQM. In the future it might also be worth discussing the analysis of key comparison results.

19 CCQM RESOLUTIONS

There were none.

20 ANY OTHER BUSINESS: DATE OF NEXT MEETING

The next meeting of the CCQM will be held during the week of 11-15 April 2005.

The President thanked all members of the CCQM for their participation.

He also thanked Dr Marshal, who is retiring, for his long-lasting friendship and contributions to the development and understanding of metrology in chemistry and to the work of the CCQM.

M.J.T. Milton, Rapporteur
July 2004
revised October 2004

Table 1. A framework for CCQM key comparisons and pilot studies						
Description	**Reference No.**	**Pilot laboratory**	**Start date**	**Status (as of 12/05/2004)**	**Comments**	**Working group**
Health						
Clinical diagnostic markers						
Cholesterol in serum	CCQM-P6	NIST	1998	Completed; progression to key comparison proposed		OAWG
Cholesterol in serum	CCQM-K6	NIST	1999	Approved for equivalence		OAWG
	CCQM-K6 subsequent	NIST	2001	Approved for equivalence		OAWG
Glucose in serum	CCQM-P8	NIST	1999	Completed; progression to key comparison proposed		OAWG
Glucose in serum	CCQM-K11	NIST	2001	Approved for equivalence		OAWG
Creatinine in serum	CCQM-P9	NIST	1999	Completed; progression to key comparison proposed		OAWG
Creatinine in serum	CCQM-K12	NIST	2001	Approved for equivalence		OAWG
Electrolyte elements, steroids and hormones in serum and urine						
Trace elements (Pb, Se) in serum	CCQM-P14	NIST/LGC	1999	Abandoned (see next)		IAWG
Ca in serum	CCQM-P14	IRMM/SP	2001	Completed; progression to key comparison proposed		IAWG
Ca in serum	CCQM-K14	IRMM	2003	Approved for equivalence		IAWG
Anabolic steroids in urine	CCQM-P68	NARL	2004/2005	Planned		OAWG
Hormones in serum						
Food						
As in shellfish	CCQM-P11	NIST	2001	Completed; progression to key comparison proposed		IAWG
As in fish or shellfish	CCQM-K31	NIST	2002	Approved for equivalence		IAWG
Pb in wine	CCQM-P12	IRMM	2000	Completed		IAWG
Pb in wine	CCQM-K30	IRMM	2003	Protocol complete	Run in parallel to CCQM-P12.1	IAWG
Elements (e.g., Cu, Cd, Zn) in wine	CCQM-P12.1	IRMM	2003	Protocol complete	Run in parallel to CCQM-K30	IAWG
As, Se, Hg, Pb, methyl-Hg in tuna fish	CCQM-P39	IRMM	2003	Protocol complete		IAWG
Cd, Zn in rice	CCQM-P29	IRMM/NMIJ	2001	Completed	Run in parallel to CCQM-K24	IAWG
Cd in rice	CCQM-K24	IRMM	2001	Completed	Run in parallel to CCQM-P29	IAWG
Metals in synthetic food digest	CCQM-P13	LGC	2001	Completed		IAWG
Organic contaminants in mussel tissue	CCQM-P40	NIST	2003	Planned		OAWG

Methyl-mercury in salmon fish	CCQM-K43	IRMM	Nov. 2004	Planned	Run in parallel to CCQM-P39.1	IAWG
PCB congeners in solution	CCQM-P31.b.1	NIST	2004	Planned	Run in parallel to CCQM-K40	OAWG
PCB congeners in tissue extract	CCQM-P57	NIST	2004	Planned		OAWG
PCBs congeners in tissue	CCQM-P67	NIST	2004	Planned		OAWG
Methyl-mercury in salmon fish	CCQM-P39.1	IRMM	Nov. 2004	Planned	Run in parallel to CCQM-K43	IAWG
Trace elements in soyabean powder	CCQM-P64	NRCCRM	Sep. 2004	Planned		IAWG
Antibiotics in meat						
Growth hormones in meat						
Vitamins and minerals						
GMO's (DNA, proteins)						
Pesticide residues						
p,p´-DDE in isooctane	CCQM-P2	LGC	1997	Completed		OAWG
p,p´-DDE in corn oil	CCQM-P4	LGC	1998	Completed; progression to key comparison proposed		OAWG
p,p´-DDE in fish oil	CCQM-K5	LGC	1999	Approved for equivalence		OAWG
Gamma-HCH in fish oil	CCQM-P10	LGC	1999	Repeated (see next)		OAWG
Gamma-HCH in fish oil 74 ng/g, 240 ng/g	CCQM-P10.2	LGC	2000	Completed		OAWG
p,p'-DDT in fish oil	CCQM-P21	LGC	1999	Completed; progression to key comparison proposed		OAWG
p,p'-DDT in fish oil	CCQM-K21	LGC	2000	Approved for equivalence		OAWG
Drinking water						
Organics (EPA list)						
Trace elements						
Microbiological						
Environment						
Water						
Waste water (EPA list)						
Cd and Pb in natural water	CCQM-K2	IRMM	1998	Completed		IAWG

Atmospheric pollutants						
Greenhouse gases CO_2, CH_4 - ambient levels	CCQM-P41	NMi	2002	In progress		GAWG
SF_6, CFCs - emission levels	CCQM-K15	KRISS	2003	Report in progress Draft B	Run in parallel to CCQM-P51	GAWG
SF_6, CFCs - emission levels	CCQM-P51	KRISS	2003	Report in progress Draft B	Run in parallel to CCQM-K15	GAWG
Ozone - ambient levels	CCQM-P28	BIPM	2003	In progress		GAWG
Primary standard gas mixtures						
CO in N_2	CCQM-K1.a	NMi	1998	Approved for equivalence		GAWG
CO_2 in N_2	CCQM-K1.b	NMi	1998	Approved for equivalence		GAWG
NO in N_2	CCQM-K1.c	NMi	1998	Approved for equivalence		GAWG
SO_2 in N_2	CCQM-K1.d	NMi	1998	Approved for equivalence		GAWG
Natural gases (Types I, II, III)	CCQM-K1.e,.f,.g	NMi	1998	Approved for equivalence		GAWG
NO in N_2 (EUROMET)	EURO-QM-K1.c	NMi	2002	Approved for equivalence		GAWG
Natural gas (Type IV)	CCQM-K16.a	BAM/NMi	2001	Approved for equivalence	Run in parallel to CCQM-P49.a	GAWG
Natural gas (TypeV)	CCQM-K16.b	BAM/NMi	2001	Approved for equivalence	Run in parallel to CCQM-P49.b	GAWG
Natural gas (Type IV)	CCQM-P49.a	BAM/NMi	2001	Completed	Run in parallel to CCQM-K16.a	GAWG
Natural gas (Type V)	CCQM-P49.b	BAM/NMi	2001	Completed	Run in parallel to CCQM-K16.b	GAWG
Natural gas (Repeat) / (LPG)	CCQM-K23	NMi	2004	Planned		GAWG
CO, CO_2, propane in N_2	CCQM-K3	NMi	1998	Approved for equivalence		GAWG
CO, CO_2, propane in N_2 (EUROMET)	EURO-QM-K3	NMi	2000	Approved for equivalence		GAWG
CO, CO_2, propane in N_2 (APMP)	APMP-QM-K3	KRISS	2000	Approved for equivalence		GAWG
CO in nitrogen ($50\,000 \times 10^{-6}$, 1000×10^{-6}, 10×10^{-6}) Gravimetry	CCQM-P23	NMi	2000	Complete		GAWG
Benzene/toluene/xylene (BTX) in N_2/air	CCQM-K7	NIST	1999	Approved for equivalence		GAWG
BTX in N_2 (low conc. 10×10^{-9}–30×10^{-9})	CCQM-K10	NIST/NPL	2001	Approved for equivalence		GAWG
Dynamic mixing methods	CCQM-P24	LNE	2002	Complete		GAWG
NO_2 in air (10×10^{-6})		NIST	2003	Abandoned		GAWG
VOCs in air	CCQM-K22	NMIJ	2003	Report in progress Draft B	Run in parallel to CCQM-P71	GAWG
COS and H_2S in methane	CCQM-P?		2004			GAWG
H_2S in air/nitrogen	CCQM-P42		2003	Planned		GAWG
NH_3 or HCl in air/nitrogen	CCQM-P?		2004			GAWG
NMHC	CCQM-K?		2004			GAWG

Reactive gases-ambient levels - NO in N_2	CCQM-K26.a	NPL	2003	In progress	Run in parallel to CCQM-P50.a	GAWG
Reactive gases-ambient levels - SO_2 in air	CCQM-K26.b	NPL	2003	In progress	Run in parallel to CCQM-P50.b	GAWG
Reactive gases-ambient levels - NO in N_2	CCQM-K50.a	NPL	2003	In progress	Run in parallel to CCQM-K26.a	GAWG
Reactive gases-ambient levels - SO_2 in air	CCQM-K50.b	NPL	2003	In progress	Run in parallel to CCQM-K26.b	GAWG
H_2S in nitrogen	CCQM-K41	NIST		Planned		GAWG
VOCs in air	CCQM-P71	NMIJ	2003	Report in progress Draft B	Run in parallel to CCQM-K22	GAWG
HAP's						
Contaminants in soils/sediments/incinerator ash						
Pb/Cd in sediments	CCQM-P15	IRMM	1999	Completed; progression to key comparison proposed		IAWG
Pb/Cd in sediments	CCQM-K13	IRMM	2000	Approved for equivalence		IAWG
Pb/Cd in sediments	CCQM-K13 subsequent	NIST	2000	Approved for equivalence		IAWG
Elements in synthetic digest solutions	CCQM-P16	NMi	1999	Abandoned		IAWG
PCBs in sediments	CCQM-P17	NRC/NIST	2000	Completed; progression to key comparison proposed		OAWG
PCBs in sediments (PCBs 28,101,153,170)	CCQM-K25	NIST/NRC	2001	Approved for equivalence		OAWG
TriButylTin in sediment	CCQM-P18	LGC/NRC	2001	Completed; progression to key comparison proposed		IAWG/OAWG
TriButylTin in sediment	CCQM-K28	LGC/NRC	2003	Report in progress Draft B		IAWG
DiButylTin in sediment	CCQM-P43	LGC/NRC	2003	Report in progress Draft B		IAWG
Metals in hard rock mine wastes						
Trace metals in sewage sludge	CCQM-K44	IRMM	Dec. 2004	Planned	Run in parallel to CCQM-P70, EUROMET 784 and IMEP	IAWG
PAHs in soils/sediments	CCQM-P69	CENAM/BAM	2004/2005	Planned		OAWG
Trace metals in sewage sludge	CCQM-P70	IRMM	Dec. 2004	Planned	Run in parallel to CCQM-K44, EUROMET 784 and IMEP	IAWG
Metals in biological tissues						
Toxic metals in recycled plastics PET						

Advanced materials						
Semiconductors						
Ultratrace metals in high-purity semiconductors GaAs						
Boron in Si	CCQM-P33	PTB	2003	Planned		IAWG
SiO_2 on Si film thickness	CCQM-P38	NPL	2002	Completed; progression to key comparison proposed		SAWG
SiO_2 on Si film thickness	CCQM-K32	NPL		Planned		SAWG
Metal alloys						
Minor elements in steel	CCQM-P25	NMIJ/NIST/ BAM	2002	Report in progress; progression to key comparison proposed		IAWG
Minor elements in steel	CCQM-K33	NMIJ/NIST/ BAM	2003	Planned	Run in parallel to CCQM-P56	IAWG
Constituents in aluminium alloy	CCQM-P34	BAM	2001	Report in progress		IAWG
Constituents of an aluminium alloy	CCQM-K42	BAM	Oct. 2004	Planned	Run in parallel to CCQM-P34.1	IAWG
Constituents of an aluminium alloy	CCQM-P34.1	BAM	Oct. 2004	Planned	Run in parallel to CCQM-K42	IAWG
Trace analysis of high purity nickel	CCQM-P62	BAM	Jun. 2004	Planned		IAWG
Minor elements in steel	CCQM-P56	NMIJ/NIST/ BAM	2003	Planned	Run in parallel to CCQM-K33	IAWG
Polymers and plastics						
Leachates						
Trace metals						
Catalysts						
Pt, Rh in vehicle exhaust catalysts						
Platinum group elements in an automotive catalyst	CCQM-P63	LGC	Aug. 2004	Planned		IAWG
Commodities						
Industrial SO_2 in stack emissions	CCQM-K1.d					
Moisture in fossil fuels						
Sulfur in fuels	CCQM-P26	IRMM/NIST	2001	Completed		IAWG
Sulfur in fuels (lower levels)	CCQM-P26.1	NIST	2003	Report in progress Draft B		IAWG
Sulfur in fuels (lower levels)	CCQM-K35	NIST	2003	Report in progress Draft B		IAWG
Metals in lubricating oils						
Natural gases	CCQM-K1.e,.f, g CCQM-K16.a,.b					
Sucrose						
Cement - Ca, Si, Al, S, Ti, Na, Mg						

Ore composition						
Rare-earth elements						
Precious metals						
Source of origin/adulteration						
Determination of metals in fertilizer	CCQM-P66	NIST	Oct. 2004	Planned		IAWG
Alcohol content						
Ethanol in aqueous matrix (forensic and commodity levels)	CCQM-P35	BAM/LGC	2001	Completed; progression to key comparison proposed		OAWG
Ethanol in aqueous matrix (for. level 1×10^{-6})	CCQM-K27.a	LGC/BAM	2002	Approved for equivalence		OAWG
Ethanol in aqueous matrix (for. level 1×10^{-6})	CCQM-K27.a subsequent	NIST	2003	Approved for equivalence	Run in parallel with SIM pilot study	OAWG
Ethanol in aqueous matrix (commod. level 100×10^{-6})	CCQM-K27.b	LGC/BAM	2002	Approved for equivalence		OAWG
Forensics						
LSD in urine	CCQM-P27	LGC	2001	Completed		OAWG
Drugs of abuse in urine	CCQM-P27.1	NARL	2004	Planned		OAWG
Explosives residues						
Ethanol in air	CCQM-K4	NPL	1999	To Appendix B		GAWG
Ethanol in air (EUROMET)	EURO-QM-K4	NPL	2000	Approved for equivalence		GAWG
Ethanol in air (APMP)	APMP-QM-K4	NMIJ	2000	Approved for equivalence		GAWG
Pharmaceuticals						
Biotechnology						
Genomics, proteomics						
DNA quantification	CCQM-P44	NIST/LGC	2002	Complete: repeat study		BAWG
DNA profiling	CCQM-P53	NARL	2003	Planned		BAWG
DNA primary quantification	CCQM-P54	LGC	2004	Planned		BAWG
Peptide/protein quantification	CCQM-P55	LGC	2004	Planned		BAWG
Q-PCR (repeat)	CCQM-P44.1	NIST/LGC	2004	Planned		BAWG
Fluorescence in ELISA	CCQM-P58	NPL/NIST	2004/2005	Planned		BAWG
Protein structural measurements by CD	CCQM-P59	NPL/NIST		Planned		BAWG
DNA extraction - reference method	CCQM-P60	IRMM	2004/2005	Planned		BAWG

General analytical applications						
Purity of materials metals, salts, organics, etc.						
KCl, NaCl, $K_2Cr_2O_7$	CCQM-P7	NIST				
Hydrochloric acid	CCQM-P19	NIST	1999	Completed 2001		EAWG/IAWG
Purity of HCl	CCQM-P19.1	NIST	2002	Complete		EAWG/IAWG
Acetanilide, benzoic acid, and naphthalene	CCQM-P5	NIST	1998	Completed 1999		OAWG
TBT chloride	CCQM-P20.a	NARL	2001	Completed		OAWG/IAWG
o-xylene	CCQM-P20.b	NIST	2002	Completed		OAWG
Atrazine	CCQM-P20.c	NARL	2004	Report in progress		OAWG
Chlorpyrifos	CCQM-P20.d	NARL	2004	Report in progress		OAWG
Purity analysis of parent gases incl. H_2O	CCQM-P45	LNE	2002	Planned	EUROMET workshop	GAWG
NMR study	CCQM-P3	BAM	1998	Completed 1999		OAWG
NMR study	CCQM-P3.2	BAM	1999	Completed 2000		OAWG
Assay of potassium hydrogen phthalate (KHP)	CCQM-P36	SMU/NIST	2002	Report in progress; progression to key comparison proposed		EAWG/IAWG
Assay of potassium hydrogen phthalate (KHP)	CCQM-K34	SMU	2003	In progress		EAWG/IAWG
Calibration solutions						
Trace elements in water Pb	CCQM-P1	NIST	1997	Completed 1998		
Elemental solution standards (Al,Cu,Fe,Mg)	CCQM-P30	EMPA/LNE	1999	Completed 2000		IAWG
Elemental solution standards (Al,Cu,Fe,Mg)	CCQM-K8	EMPA/LNE	1999	Approved for equivalence		IAWG
Anions in calibration solutions	CCQM-P32	EMPA	2001	Completed; progression to key comparison proposed		IAWG
Anions in calibration solutions	CCQM-K29	EMPA	2003	Report in progress Draft B		IAWG
Organic calibration solutions (PAHs)	CCQM-P31.a	NIST	2003	Planned		OAWG
Organic calibration solutions (PCBs)	CCQM-P31.b	NIST	2003	Planned		OAWG
Organic calibration solutions (Chlorinated pesticides)	CCQM-P31.c	NIST	2003	Planned		OAWG
Preparation of inorgic calibration solutions	CCQM-P46	NIST	2003	Planned		IAWG
VOCs in organic solvents	CCQM-K37	KRISS/NIST	2003	Planned		OAWG
PAHs in solution	CCQM-K38	NIST	Nov. 2004	Planned		OAWG
Chorinated pesticides in solution	CCQM-K39	NIST	Nov. 2004	Planned		OAWG
PCB congeners in solution	CCQM-K40	NIST	2004	Planned	Run in parallel to CCQM-P31.b.1	OAWG
PCB congeners in solution	CCQM-P31.b.1	NIST	2004	Planned	Run in parallel to CCQM-K40	OAWG
Volatile organic compounds (VOCs) in solution	CCQM-P61	CENAM/NIST	2004/2005	Planned		OAWG

pH standards						
pH 7.0 (Phosphate)	CCQM-K9	PTB	1999	Approved for equivalence		EAWG
pH 7.0 (Phosphate) PTB-SMU bilateral	CCQM-K9 subsequent	PTB	2002	Approved for equivalence		EAWG
pH 4.1 (Phthalate)	CCQM-K17	PTB	2001	Approved for equivalence		EAWG
pH 10.1(Carbonate)	CCQM-K18	SMU	2003	Protocol complete	Run in parallel to CCQM-P52	EAWG
pH 10.1(Carbonate)	CCQM-P52	SMU	2003	Protocol complete	Run in parallel to CCQM-K18	EAWG
pH 9.2 (Borate)	CCQM-K19	PTB	2004	Planned		EAWG
pH 1.7 (Tetroxalate)	CCQM-K20			Planned		EAWG
Fundamental studies of pH standards	CCQM-P37	SMU	2002	Completed		EAWG
Electrolytic conductivity	CCQM-P22	DFM	2001	Completed		EAWG
Electrolytic conductivity (low level)	CCQM-P47	NMi	2003	Planned		EAWG
Electrolytic conductivity (0.5 S/m)	CCQM-K36.a			Planned		EAWG
Electrolytic conductivity (0.005 S/m)	CCQM-K36.b			Planned		EAWG
New proposals						
Uranium isotope ratio in synthetic saline matrix	CCQM-P48	IRMM	2003	Planned		EAWG
Chemical composition of clay	CCQM-P65	CENAM	Oct. 2004	Planned		IAWG

APPENDIX T 1.
Working documents submitted to the CCQM at its 10th meeting

With the exception of document CCQM/04-15, access to working documents submitted to the CCQM at its 10th meeting is restricted to CCQM members.

Document
CCQM/

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04/15 NIST (United States). — A Robust Approach for the Determination of CCQM Key Comparison Reference Values and Uncertainties, D.L. Duewer, 25 pp. (open access)

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