Bureau International des Poids et Mesures

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

8th Meeting (April 2002)

Note on the use of the English text

To make its work more widely accessible the International Committee for Weights and Measures publishes an English version of its reports.

Readers should note that the official record is always that of the French text. This must be used when an authoritative reference is required or when there is doubt about the interpretation of the text.

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THE BIPM AND THE METRE CONVENTION

The International Bureau of Weights and Measures (BIPM) was set up by the Metre Convention signed in Paris on 20 May 1875 by seventeen States during the final session of the diplomatic Conference of the Metre. This Convention was amended in 1921.

The BIPM has its headquarters near Paris, in the grounds (43 520 m^2) of the Pavillon de Breteuil (Parc de Saint-Cloud) placed at its disposal by the French Government; its upkeep is financed jointly by the Member States of the Metre Convention.

The task of the BIPM is to ensure worldwide unification of physical measurements; its function is thus to:

- establish fundamental standards and scales for the measurement of the principal physical quantities and maintain the international prototypes;
- carry out comparisons of national and international standards;
- ensure the coordination of corresponding measurement techniques;
- carry out and coordinate measurements of the fundamental physical constants relevant to these activities.

The BIPM operates under the exclusive supervision of the International Committee for Weights and Measures (CIPM) which itself comes under the authority of the General Conference of Weights and Measures (CGPM) and reports to it on the work accomplished by the BIPM.

Delegates from all Member States of the Metre Convention attend the General Conference which, at present, meets every four years. The function of these meetings is to:

- discuss and initiate the arrangements required to ensure the propagation and improvement of the International System of Units (SI), which is the modern form of the metric system;
- confirm the results of new fundamental metrological determinations and various scientific resolutions of international scope;
- take all major decisions concerning the finance, organization and development of the BIPM.

The CIPM has eighteen members each from a different State: at present, it meets every year. The officers of this committee present an annual report on the administrative and financial position of the BIPM to the Governments of the Member States of the Metre Convention. The principal task of the CIPM

is to ensure worldwide uniformity in units of measurement. It does this by direct action or by submitting proposals to the CGPM.

The activities of the BIPM, which in the beginning were limited to measurements of length and mass, and to metrological studies in relation to these quantities, have been extended to standards of measurement of electricity (1927), photometry and radiometry (1937), ionizing radiation (1960), time scales (1988) and to chemistry (2000). To this end the original laboratories, built in 1876 -1878, were enlarged in 1929; new buildings were constructed in 1963-1964 for the ionizing radiation laboratories, in 1984 for the laser work, and in 1988 for a library and offices. In 2001 a new building for the workshop, offices and meeting rooms was opened.

Some forty-five physicists and technicians work in the BIPM laboratories. They mainly conduct metrological research, international comparisons of realizations of units and calibrations of standards. An annual report, the *Director's Report on the Activity and Management of the International Bureau of Weights and Measures*, gives details of the work in progress.

Following the extension of the work entrusted to the BIPM in 1927, the CIPM has set up bodies, known as Consultative Committees, whose function is to provide it with information on matters that it refers to them for study and advice. These Consultative Committees, which may form temporary or permanent working groups to study special topics, are responsible for coordinating the international work carried out in their respective fields and for proposing recommendations to the CIPM concerning units.

The Consultative Committees have common regulations (*BIPM Proc.-Verb. Com. Int. Poids et Mesures*, 1963, **31**, 97). They meet at irregular intervals. The president of each Consultative Committee is designated by the CIPM and is normally a member of the CIPM. The members of the Consultative Committees are metrology laboratories and specialized institutes, agreed by the CIPM, which send delegates of their choice. In addition, there are individual members appointed by the CIPM, and a representative of the BIPM (Criteria for membership of Consultative Committees, *BIPM Proc.-Verb. Com. Int. Poids et Mesures*, 1996, **64**, 124). At present, there are ten such committees:

1 the Consultative Committee for Electricity and Magnetism (CCEM), new name given in 1997 to the Consultative Committee for Electricity (CCE) set up in 1927;

2 the Consultative Committee for Photometry and Radiometry (CCPR), new name given in 1971 to the Consultative Committee for Photometry (CCP) set up in 1933 (between 1930 and 1933 the CCE dealt with matters concerning photometry);

3 the Consultative Committee for Thermometry (CCT), set up in 1937;

4 the Consultative Committee for Length (CCL), new name given in 1997 to the Consultative Committee for the Definition of the Metre (CCDM), set up in 1952;

5 the Consultative Committee for Time and Frequency (CCTF), new name given in 1997 to the Consultative Committee for the Definition of the Second (CCDS) set up in 1956;

6 the Consultative Committee for Ionizing Radiation (CCRI), new name given in 1997 to the Consultative Committee for Standards of Ionizing Radiation (CCEMRI) set up in 1958 (in 1969 this committee established four sections: Section I (X- and γ-rays, electrons), Section II (Measurement of radionuclides), Section III (Neutron measurements), Section IV (α-energy standards); in 1975 this last section was dissolved and Section II was made responsible for its field of activity);

7 the Consultative Committee for Units (CCU), set up in 1964 (this committee replaced the "Commission for the System of Units" set up by the CIPM in 1954);

8 the Consultative Committee for Mass and Related Quantities (CCM), set up in 1980;

9 the Consultative Committee for Amount of Substance: metrology in chemistry (CCQM), set up in 1993;

10 the Consultative Committee for Acoustics, Ultrasound and Vibration (CCAUV), set up in 1998.

The proceedings of the General Conference, the CIPM and the Consultative Committees are published by the BIPM in the following series:

- *Reports of the meetings of the General Conference on Weights and Measures;*
- *Reports of the meetings of the International Committee for Weights and Measures;*
- *Reports of the meetings of Consultative Committees.*

The BIPM also publishes monographs on special metrological subjects and, under the title *The International System of Units (SI)*, a brochure, periodically updated, in which are collected all the decisions and recommendations concerning units.

The collection of the *Travaux et Mémoires du Bureau International des Poids et Mesures* (22 volumes published between 1881 and 1966) and the *Recueil de Travaux du Bureau International des Poids et Mesures* (11 volumes published between 1966 and 1988) ceased by a decision of the CIPM.

The scientific work of the BIPM is published in the open scientific literature and an annual list of publications appears in the *Director's Report on the Activity and Management of the International Bureau of Weights and Measures*.

Since 1965 *Metrologia*, an international journal published under the auspices of the CIPM, has printed articles dealing with scientific metrology, improvements in methods of measurement, work on standards and units, as well as reports concerning the activities, decisions and recommendations of the various bodies created under the Metre Convention.

LIST OF MEMBERS OF THE CONSULTATIVE COMMITTEE FOR AMOUNT OF SUBSTANCE: metrology in chemistry

as of 18 April 2002

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.

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.

National Research Council of Canada [NRC], Ottawa.

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

Office Fédéral de Métrologie et d'Accréditation [METAS], Wabern/Swiss Federal Laboratories for Materials Testing and Research [EMPA], St Gall.

Physikalisch-Technische Bundesanstalt [PTB]/Bundesanstalt für Material-forschung und -prüfung [BAM], Braunschweig and Berlin.

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

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

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.

Centro Nacional de Metrología [CENAM], Mexico.

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.

Consultative Committee for Amount of Substance: metrology in chemistry

Report of the 8th Meeting

(18–19 April 2002)

Agenda

1 Opening of the meeting; agenda; appointment of a rapporteur.

2 Report of the seventh meeting.

3 Reports of working groups:

- 3.1 Surface analysis;
- 3.2 Organic analysis;
- 3.3 Inorganic analysis;
- 3.4 Gas analysis;
- 3.5 Electrochemical analysis;
- 3.6 Bioanalysis;
- 3.7 Key comparisons.

4 Update of the BIPM key comparison database:

- 4.1 Update of CMC claims for chemistry;
- 4.2 Criteria for the acceptance of CRMs in CMC claims;
- 4.3 How far does the light shine?;
- 4.4 Linking RMO key comparisons and subsequent bilateral comparisons to CCQM key comparisons;
- 4.5 Publication of the reports;
- 4.6 Publicity for the KCDB.

5 Participation of NMIs and other institutes in pilot studies and key comparisons.

6 Importance of peer reviews and appropriate accreditation.

7 Covering the costs incurred in subsequent bilateral comparisons.

8 Criteria for the designation of laboratories having responsibility for chemistry CMC claims.

9 Traceability in laboratory medicine.

10 The BIPM programme of metrology in chemistry:

- 10.1 The CIPM/WMO Memorandum of Understanding;
- 10.2 Recent activities in the Chemistry section;
- 10.3 Future developments.

11 Results of the workshop on traceability.

12 Other business; date of next meeting.

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

The Consultative Committee for Amount of Substance: metrology in chemistry (CCQM) held its eighth meeting at the International Bureau of Weights and Measures (BIPM), at Sèvres, on 18-19 April 2002.

The following were present: L. Besley (NML CSIRO), T. Catterick (LGC), P. Charlet (BNM-LNE), P. De Bièvre (IRMM/ISO-REMCO), E.W.B. de Leer (NMi VSL), R. Dybkaer (IFCC), H. Ent (NMi VSL), A. Fajgelj (IAEA), G.L. Gilliland (NIST), B. Güttler (PTB), H.-P. Haerri (METAS), S. Hart (NARL-AGAL), W. Hässelbarth (BAM), R. Kaarls (President of the CCQM), M. Kurahashi (NMIJ/AIST), Y. Kustikov (VNIIM), Yunqiao Li (NIM), L. Mackay (NARL-AGAL), B. Magnusson (SP), A. Marschal (BNM-LNE), W.E. May (NIST), J. McLaren (NRC), B. Milman (VNIIM), M.J.T. Milton (NPL), K. Okamoto (NMIJ/AIST), H. Parkes (LGC), J.C. Petersen (DFM), T.J. Quinn (Director of the BIPM), W. Richter (PTB), M. Sargent (LGC), M. Seah (NPL), H.G. Semerjian (NIST), Hun-Young So (KRISS), R. Sturgeon (NRC), P. Taylor (IRMM/IUPAC), Jianping Wang (NRCCRM), M. Weber (EMPA), P. Woods (NPL), Fangdi Wu (NRCCRM), Yadong Yu (NRCCRM), A. Zschunke (BAM).

Observers: I. Akdag (UME), M. del Rocio Arvizu-Torres (CENAM), E. Castro Galván (CENAM), E. Deák (OMH), W. Kozlowski (GUM), K. Lal (NPLI), Sihai Li (SPRING Singapore), M.T. López Esteban (CEM), W. Louw (CSIR-NML), M. Máriássy (SMU), Y. Mitani (CENAM), M. Sega (IMGC-CNR).

Invited: V.M.L. Ponçano (IPT), A. Squirrell (CITAC), M.C. Walsh (SL).

Also present: P. Giacomo (Director Emeritus of the BIPM); A.J. Wallard (Deputy Director of the BIPM); M. Esler, J. Viallon, C. Thomas, R. Wielgosz (BIPM).

Excused: M. Grasserbauer (IRMM).

Absent: NIM.

Dr Quinn welcomed the CCQM to the BIPM. He said that this was the first meeting held at the BIPM for which all the meeting papers had been made available electronically.

The agenda was approved without modification.

The President thanked Dr Milton for preparing the report of the seventh meeting. He proposed Dr Milton as rapporteur for the meeting, to be assisted by Dr Wielgosz. This proposition was accepted

2 REPORT OF THE SEVENTH MEETING

The report of the seventh meeting was approved.

3 REPORTS OF WORKING GROUPS

3.1 Surface analysis

Dr Seah presented his report on the work of the Working Group on Surface Analysis (CCQM/02-10). A pilot study (CCQM-P38) had been approved at the seventh meeting of the CCQM. It involved thirty-four groups in twenty-seven laboratories from thirteen countries. It would make use of eleven different techniques some of which were highly precise (such as ellipsometry) and some of which produced results that were traceable to the International System of Units (SI) (such as electron microscopy). Traceability is achieved for many of the methods by reference to the lattice spacing of silicon measured by transmission electron microscopy (TEM). The other methods can achieve traceability by comparison with TEM. The organization of this pilot study under the auspices of the CCQM was a unique opportunity to coordinate such an activity internationally.

Preparing suitable samples for the pilot study that are free from contamination is a significant problem. The NPL has established cleaning methods that leave only 0.13 nm of carbonaceous matter on the surface. The samples will be shipped in fluoroware containers and will include shapes that have been chosen to meet the requirements of different sample chambers. The NPL has mapped the uniformity of the samples by ellipsometry and

chosen regions that are uniform to within 1 %. The ellipsometry measurements have been validated by x-ray photoelectron spectroscopy (XPS), and found to be comparable to within 0.13 nm (corresponding to approximately one third of an atomic layer).

The accuracy of the study is expected to be at least a factor of twenty better than the present "state of the art", as represented by two recent publications in the literature. The pilot study should provide the data to improve the traceability of the methods involved. Some participants have already requested that they retain their samples in order to provide traceability for their measurements in the future. It is proposed to organize a key comparison after the completion of the study.

The proposed work of the group is of relevance to a wide range of industry and particularly to the emerging applications of nanotechnology. An inventory of equipment at national metrology institutes (NMIs) used for micro and nano-surface analysis has been prepared.

Draft terms of reference for the Working Group on Surface Analysis have been prepared as follows:

- to develop pilot studies and carry out key comparisons of national measurement standards for surface and micro/nano-analysis;
- to assist in identifying and establishing inter-laboratory work to improve the traceability of surface and micro/nano-analysis;
- to establish and update a work plan to be adopted by the CCQM;
- to discuss and review the scope of the working group and to liaise with other working groups related to nanotechnology.

Achieving traceability for surface analysis measurements is often beyond the scope of individual NMIs and coordinated activity is required. Proposals for future work items are included in the document CCQM/02-10. These include measurements of the dopant distribution in silicon, light elements in metals, the composition of hard coatings, and surface layers on polymers.

Dr Semerjian welcomed the report and highlighted the importance of the group emphasizing absolute measurements that require traceability. Dr Besley said that the NML CSIRO was participating in order to underpin their capability to measure the oxide layer on the silicon artefacts used in the Avogadro project.

The President welcomed the proposal for a key comparison, but stressed that in principle only NMIs or other designated institutes would be able to participate. He wished the group success with their pilot study and suggested

that they bring their proposal for a key comparison to the next meeting of the CCQM.

3.2 Organic analysis

Dr May presented his report of the work of the Working Group on Organic Analysis which had met twice since the last CCQM.

The results of two key comparisons (CCQM-K5 and -K6) had been published in the BIPM key comparison database.

The results of CCQM-K21 (pp'-DDT in fish oil) were presented as a draft B report. The key comparison reference value (KCRV) was based on the mean of the results with the uncertainty given by the standard error of the mean. The CCQM agreed that after circulation and approval of the final report by working group chairmen, the comparison results would be entered into the BIPM key comparison database. Key comparison CCQM-K21 was the last of an ensemble of comparisons which have provided the framework for assessing the capabilities of participating laboratories to measure chlorinated pesticides in lipid samples in the range from 70 ng/g to 6000 ng/g. The working group has no further plans to organize key comparisons for chlorinated pesticides in lipid matrices.

Three comparisons of measurements of diagnostic markers were presented in draft A form: CCQM-K11, -K12 and a subsequent comparison based on CCQM-K6. These key comparisons with their preceding pilot studies may provide a basis for the evaluation of measurement capabilities of participating NMIs for other well-defined organic analytes in serum.

Three laboratories had participated in CCQM-K11 (glucose in serum) and had achieved a good level of comparability in a sample typical of a natural level, but a poorer level of comparability for a fortified sample. It was proposed that the latter results be published in the report of the comparison, but not be entered into the database or used as the basis for establishing degrees of equivalence.

The results of CCQM-K12 (creatinine in serum) were presented. It had been preceded by a pilot study (CCQM-P8) and had been based on samples used for the IMEP-17 comparison. (The KRISS had offered to have its results for material 1 withdrawn since they had been disclosed by IMEP-17. The working group agreed that this was not necessary.)

A proposal is being developed for linking to the main comparison the results of the comparison held subsequently to CCQM-K6, which had involved the NARL, the NIST and the VNIIM.

The provisional results of CCQM-K25 (PCBs in sediment) were presented. Five PCB congeners within the sample had been measured using IDGC/MS. All nine participants had been able to report results for four of the congeners, but two participants had not been able to report results for PCB 28. The working group recommended that where laboratories had reported values in the knowledge that their results were biased by co-eluents, these values should not be entered into the statements of equivalence in the database, although the results would be in the final report of the key comparison. There will be some further discussion within the working group to ensure that the uncertainties have been estimated on a comparable basis.

The results of the following pilot studies were presented:

- CCQM-P18 (tributyltin in sediment).
- CCQM-P20.a (tributyltin chloride) based on samples provided by the LGC.
- CCQM-P20.b (o-xylene) will be organized by the NIST. This study will also include participants from the Working Group on Gas Analysis.
- CCQM-P20.c (with either atrazine, diuron or tetracycline) using samples from the NARL which will be the pilot laboratory.
- CCQM-P27 (LSD in human urine), in which three laboratories had participated. It is now proposed to hold a comparison of a wider number of forensic drugs in urine (CCQM-P27.1).
- CCQM-P35 (ethanol in an aqueous matrix). It is now proposed to carry out a key comparison using two concentrations of ethanol in water (CCQM-K27.a) and one of ethanol in stabilized wine (CCQM-K27.b).

A proposal was made to undertake a pilot study of organic contaminants in fish or muscle tissue. It was agreed that the NIST would act as the pilot laboratory for the study on organic contaminants in tissue (CCQM-P40). Analyses that had been discussed, but which would not be proposed for pilot studies, included: petroleum-derived soil contamination; growth hormones in meat; moisture in oil; and food toxins.

The Working Group on Organic Analysis had also discussed the possible role of the BIPM in this area.

The President thanked Dr May for his report.

3.3 Inorganic analysis

Dr Sargent presented a report of the work of the Working Group on Inorganic Analysis which had met twice since the last CCQM.

The results and final report of CCQM-K8 (elemental solution standards) have been published on the BIPM key comparison database. Key comparison CCQM-K13 (lead and cadmium in sediment) was complete, and it was agreed that its publication in the BIPM key comparison database (KCDB) would proceed after circulation and approval of the report by CCQM chairs. One key comparison, CCQM-K24 (cadmium in rice) was in progress. It was agreed that one participant (EMPA) in CCQM-P29 (cadmium and zinc in rice) could submit their results for cadmium as part of CCQM-K24.

He presented the results of five pilot studies, all of which would be followed by key comparisons:

- CCQM-P11 (arsenic in fish) with the NIST as pilot laboratory (to be followed by CCQM-K31). Satisfactory agreement had been achieved amongst ten participants. The results of an eleventh participant deviated significantly from the reference value, but a problem had been identified and corrected.
- CCQM-P12 (lead in wine) led by the IRMM (to be followed by CCQM-K30). Satisfactory agreement was achieved between fifteen participants.
- CCQM-P14 (calcium in serum) led by the IRMM (to be followed by CCQM-K14). Agreement had been achieved amongst the nine participants within their estimated uncertainties.
- CCQM-P18 (tributyltin in sediment) led by the NRC and the LGC (to be followed by CCQM-K28). Very satisfactory agreement had been achieved between the participants.
- CCQM-P32 (chloride and phosphate in solution) led by the EMPA (to be followed by CCQM-K29). The results from the eleven participants agreed to within better than 0.5 %.

A further six pilot studies were in progress at the time of the meeting, and a further four are at the preparation stage. Proposals were made for several new pilot studies:

- CCQM-P26.1, sulphur in fuel (as a follow-up to CCQM-P26).
- CCQM-P12.1, elements (including copper) in wine (based on a sample also used for the key comparison of Pb in wine), led by the IRMM.
- CCQM-P43, dibutyltin in sediment.

- A proposal was received from the NIST to follow up CCQM-K8 with an exercise (CCQM-P46) that would require all participants to prepare and certify calibration solutions and submit them to the pilot laboratory. The study will involve some of the elements used in CCQM-K8 together with some elements that are more challenging to analyse.
- A proposal was made by the IRMM to measure the uranium isotope amount ratio in synthetic salty matrix samples. This study (CCQM-P48) might involve a lot of non-NMI participants. The proposal would be of value to the IAEA and reflected the trend towards such measurements being carried out at concentration levels found in the environment.
- A proposal was submitted by the IRMM to measure elements including mercury in tuna fish (CCQM-P39); this would extend the scope of CCQM-P11 to further elements and organic-metallic species.

It was proving difficult for the Working Group on Inorganic Analysis to identify laboratories that could act as pilot laboratories in all areas for which there were calibration and measurement capability (CMC) claims.

The President thanked Dr Sargent for his report.

3.4 Gas analysis

Dr de Leer presented his report on the work of the Working Group on Gas Analysis which had met twice since the last CCQM.

The final and approved report of CCQM-K7 (benzene, toluene and xylene (BTX) in air) was presented. As discussed previously, it had been necessary to carry out an additional bilateral comparison with one participant since the first standard had been lost in transit. The KCRV was based on the gravimetric value of the standards used for the comparison. There had been a difficulty in calculating the degree of equivalence for one laboratory that had submitted its results with an uncertainty expanded with a factor of three (rather than two which is most commonly used).

The final report of CCQM-K10 (benzene, toluene and o-xylene in air) was presented and approved. This key comparison involved the same participants as CCQM-K7 and was based on a sample at a concentration level ten times lower.

The final report of EUROMET.QM-K4 was presented. The results were very satisfactory, indicating degrees of equivalence comparable with the results of CCQM-K4. After some discussion, it was agreed that the estimated uncertainty submitted by the CSIR-NML could be corrected to eliminate a

mistake in its calculation. Three laboratories that had also participated in CCQM-K4 took part in the comparison. It was agreed that as the reference values for both comparisons were based on the gravimetric value of the standards the EUROMET degrees of equivalence did not require any correction. The results of two laboratories (BNM-LNE and NPL) were used to confirm that the reference value was reasonable in both cases. The third laboratory (VNIIM) had significantly improved its performance between the two comparisons. The report was approved for entry into the BIPM key comparison database.

Additionally, the technical work of APMP.QM-K3 had been completed, but a final report was not available at the meeting. In the course of this comparison, the KRISS and the NMIJ had observed that the fraction of ethanol in air decreased when the gas was expanded into an empty cylinder. Further studies by the NMi and the NPL had quantified this effect and found it to be less than 0.1 % (relative to the value), which was considered insignificant.

The results of CCQM-K16 (ten component natural gas) were presented. It comprised eight participants and had used standards at two concentrations prepared independently by the BAM and the NMi. The report of the comparison was in the draft A stage at the time of the meeting and a draft B report was in preparation.

The Working Group on Gas Analysis has also carried out a study into aspects of the methodology used by NMIs to prepare gas standards (CCQM-P23). It was intended to investigate whether the gravimetric values used for primary gas standards are as reliable as is indicated by their claimed uncertainty. The study required each participant to submit a standard of CO in nitrogen to the pilot laboratory (NMi) for analysis. The sensitivity of the NDIR analyser employed by the pilot laboratory to the isotopic composition of the carbon monoxide used in the standards revealed that in certain cases commercially available carbon monoxide can be isotopically depleted. This was confirmed by further studies performed by the KRISS and the NIST. It is also possible that there may have been an effect on the results of comparisons CCQM-K1.a and -K3, both of which involved the analysis of CO.

A protocol is being prepared for a pilot study of greenhouse gases (CO_2 and methane in air) formerly agreed as CCQM-K14 and subsequently renumbered CCQM-P41. Various issues raised by the working group, including the possible influence of argon in the mixture, had suggested that it would be prudent to carry out a pilot study prior to a key comparison of these analytes.

An analysis of the CMCs agreed for gas analysis has indicated at least nine groupings of gas mixtures for which there have been no key comparisons at the CCQM. The Working Group on Gas Analysis proposes to carry out the following comparisons:

- emission level concentrations of H_2S (CCQM-P42), NH_3 and HCl;
- odorant species (such as OCS and H_2S in methane);
- purity analysis of gases (CCQM-P45);
- purity analysis of organic species (including CCQM-P20.b (o-xylene)) with the Working Group on Organic Analysis.

In addition, two comparisons that were initially proposed at a regional level will be undertaken at the CCQM level. The KRISS will organize a comparison of CFCs and SF_6 at emission levels in (CCQM-K15) and the NPL will lead a comparison of NO and SO_2 at ambient levels (CCQM-K26.a and -K26.b respectively).

The President thanked Dr de Leer for his report, and remarked that he was particularly pleased that a representative of the World Meteorological Organization (WMO) had attended the meeting and had given an excellent presentation of the activities of the WMO in this field.

3.5 Electrochemical analysis

The President thanked Dr Richter for his work in acting as chairman of the Working Group on Electrochemical Analysis. Following the retirement of Dr Richter from the PTB, the President asked Dr Máriássy from the SMU to take over as chairman of the working group. Dr Máriássy presented a report on the work of the group, which had met twice since the last CCQM and had also held joint meetings with the Working Group on Inorganic Analysis.

A subsequent bilateral comparison had been carried out between the PTB and the SMU in order to link the new SMU result to the results of CCQM-K9. Dr Semerjian asked how the link between the bilateral and key comparisons had been made. Dr Máriássy explained that the PTB had acted as a “linking” laboratory between the two comparisons. The subsequent bilateral comparison had been necessary because of a calculation error discovered by the SMU. The CCQM approved the addition of the bilateral comparison result to the BIPM key comparison database. Dr Quinn explained that it might not have been necessary to carry out a subsequent bilateral comparison if the CCQM had been asked whether it was acceptable to correct the mistakes made by the SMU. Dr May said that it was important that the same

approach to this type of issue should be taken by each of the working groups. The Working Group on Key Comparisons should be involved in ensuring a uniform approach.

The results of CCQM-K17 (phthalate buffer) were presented to the meeting as a draft A report. The KCRV had been calculated using a weighted mean of the submitted results.

A pilot study (CCQM-P22), organized by the DFM, of primary and secondary conductivity measurements was being carried out. Solutions had been used at two conductivities, one of them near the value specified by the OIML. Agreement between the participants was better at the higher level (0.28 S/m) than at the lower level (0.1 S/m). The pilot laboratory had distributed duplicate samples to some participants who had then returned them in order to assess the extent of any changes during transit. A further pilot study (CCQM-P47) on low-level conductivity standards was proposed. The study (CCQM-P19.1) on the purity of hydrochloric acid solutions was still in progress.

A pilot study (CCQM-P37) was in progress that was investigating whether there were any unidentified sources of uncertainty in the operation of the Harned cell as a primary method. Further key comparisons of carbonate (CCQM-K18), borate (CCQM-K19) and tetroxalate (CCQM-K20) buffers are planned.

The President thanked Dr Máriássy for his report.

3.6 Bioanalysis

Dr Gilliland and Mrs Parkes presented reports (CCQM/02-06 and -07) on the work of the Working Group on Bioanalysis which had met twice since the last CCQM. It had been decided that the working group should adopt the name “bioanalysis” in order to maintain consistency with the other working groups.

The most recent meeting was attended by representatives from eighteen NMIs. A proposal had been developed by the LGC and the NIST (CCQM-P44 described in CCQM/02-08) for a pilot study on DNA quantification. It would involve providing samples for plasmid DNA testing by Q-PCR. The method measures the ratio of a genetically modified inserted gene to a “housekeeping” gene. It is used for the detection of pathogens in food as well as cryptosporidia in water. It is also employed for gene expression studies and measurements of viral load. The gene inserted will not resemble any known gene in order to avoid possible contamination. It will

involve amplification of the sequence by PCR to a level where the product can be weighed directly. It was expected that a protocol would be available by September 2002. The reference material could be used in a series of studies that would progressively contribute towards the determination of contributions to the uncertainty budget.

The group planned to establish liaison with other organizations including the World Health Organization (WHO), the Codex Alimentaris and the IFCC. Additional ideas had been developed by members of the working group. Dr Resch-Genger from the BAM had developed a proposal for a pilot study in the area of fluorescence, which is an important part of many biological methods, but has not been studied in a metrologically rigorous way. It will involve liaison with experts in radiometry at the NMIs and the CCPR. Dr Bailey from the NPL had developed a proposal for a pilot study in the area of rapid protein measurements using circular dichroism and UV-visible spectroscopy. Sub-working groups would be established to follow up both of these proposals for pilot studies.

The working group had also started to discuss the scope for the use of SI units in bioanalysis. Some examples had been identified where this appeared to be appropriate.

It was proposed to hold a "think-shop" at the IRMM in November 2002. The objective would be to discuss a rational approach to the development of a measurement infrastructure for bioanalysis. Three themes would be discussed: genes, proteins and cells.

The President thanked Dr Gilliland and Mrs Parkes for their report.

3.7 Key comparisons

Dr Semerjian presented a summary (CCQM/02-23) on the status of all of the CCQM key comparisons and pilot studies.

4 UPDATE OF THE BIPM KEY COMPARISON DATABASE

Dr Thomas gave a demonstration of the use of the KCDB maintained by the BIPM. A large number of CMCs were included from the field of amount of

substance. She also showed how a subsequent bilateral comparison might be presented alongside the key comparison on which it is based.

4.1 Update on CMC claims for chemistry

Dr May presented a report (CCQM/02-05) from the two meetings held to carry out an inter-regional review of the CMC claims. These meetings had involved representatives of the APMP, COOMET, EUROMET, SADCMET, SIM and the BIPM. Agreement of the CMCs had been in three rounds. In the first round, 821 CMCs covering gases were approved and subsequently published in the database in May 2001. In the second round, 1432 CMCs covering other categories were approved and published in March 2002. A final round including 750 CMCs covering metal alloys, advanced materials and fuels was under way at the time of the CCQM meeting. It had been decided that CMCs covering molecular spectroscopy would be reviewed by the CCPR and reformatted for entry into the chemistry section of the database. The new CIPM viscosity *ad hoc* group would review viscosity CMCs.

In the future, CMCs for chemistry will only be reviewed at an inter-regional review meeting once each year. It was planned that the chair of the inter-regional review would rotate amongst the regional metrology organizations (RMOs). It was also proposed that the CCQM working groups play a part in the review of CMCs in order to provide more comprehensive technical and scientific evaluation.

Several members of the CCQM expressed their views that RMOs should take the lead in reviewing the CMCs and that the system should not have too much redundancy, particularly as the same people are involved in many of the groups.

Representatives of each of the RMOs gave their views. Dr Mackay said that she had organized a review within the APMP of all CMCs received from other regions. It had been particularly difficult to deal with the wide variation in the accredited scope of different NMIs. Dr Kustikov said that COOMET had found the inter-regional review to be a very useful exercise. Mrs Deák said that the EUROMET had only reviewed a sample of 10 % of CMCs received from other regions, which was in contrast to the APMP approach. Dr Mitani said that the SIM had found the inter-regional review to have been a useful exercise in building confidence. Dr Louw from SADCMET said that since only South Africa had CMCs in their region, they had asked the APMP to assist in the review and he was grateful to them.

In summarizing the discussion, the President said that the CCQM working groups should be involved but must avoid becoming burdened by this activity to the exclusion of their principal activities. He asked all involved in the process to develop some written guidance as to how the process should be conducted. The RMOs should continue to take the prime responsibility for ensuring that the process operates efficiently. There should also be a process for re-reviewing CMC claims. He asked whether there should be a stronger link between the inter-regional review committee and the CCQM Working Group on Key Comparisons.

Dr Quinn reminded the CCQM that when the Mutual Recognition Arrangement (MRA) was approved, it was envisaged that the Appendix B and Appendix C processes could be quite separate. It was now proving useful to establish links between them.

4.2 Criteria for the acceptance of CRMs in CMC claims

Dr Taylor introduced a paper (CCQM/02-13) written jointly by himself and collaborators at the BAM, IRMM and the LGC. He described the role of ISO-REMCO in establishing international guidance for CRM producers such as ISO Guides 34 and 35. However, neither of these documents made any reference to the CIPM MRA. He proposed that an *ad hoc* group be formed to establish closer links with ISO-REMCO and to develop the criteria used by the CCQM for the inclusion of CRMs in Appendix C.

The President said that the guidelines for the acceptance of CRMs into Appendix C of the MRA had been formulated in document CCQM/01-08, but it would be useful for the CCQM to liase more formally with ISO-REMCO. Dr Fajgelj pointed out that at least seven attendees at the CCQM participate in ISO-REMCO, so there should be no difficulty with establishing such a liaison. A number of attendees brought the meeting's attention to the history of ISO-REMCO and to the fact that its scope is not limited exclusively to either chemistry or CRMs.

Dr McLaren suggested that, if there is a lack of confidence in CRM production at the NMIs, then the requirements of ISO Guide 34 might be added to those of ISO Guide 25 referred to in the MRA (paragraph 7.3). This view was supported widely.

It was concluded that the CCQM should strengthen its links with ISO-REMCO and that ISO Guides 34 and 35 should be added to ISO Guide 25 as being part of the requirements for entries in the Appendix C database. Additionally, the role of peer review should be recognized as a means of

increasing confidence in NMIs' CMC claims relating to CRM production and certification.

4.3 How far does the light shine?

The President encouraged the working groups to consider and report on which calibration and measurement capability claims or range of such claims would be underpinned by the results of each key comparison.

4.4 Linking RMO key comparisons and subsequent bilateral comparisons to CCQM key comparisons

The President said that many of the issues that had arisen had now been resolved. He expected this to become less of a contentious issue as further examples were produced.

4.5 Publication of the reports

Dr Wielgosz drew the attention of the CCQM to a recent editorial published in *Metrologia* (CCQM/02-12) regarding the new *Technical Supplement* to *Metrologia*. This will enable the final reports of key comparisons to be cited through a reference to the *Metrologia Technical Supplement*. The electronic version of the *Technical Supplement* would include a short abstract and a hypertext link to the text of the document stored in the KCDB. The BIPM planned to provide a similar facility for accessing the reports from pilot studies. It would still be possible to submit reports of comparisons that contain original scientific research for publication in the peer-reviewed section of *Metrologia*.

4.6 Publicity for the KCDB

Dr Wielgosz drew the attention of the CCQM to some activities that the BIPM had undertaken to publicize the availability of the KCDB. These included requested publications in the *Eurachem Newsletter* and the *VAM Bulletin*, as well as demonstrations of the KCDB to participants at the PITTCON conference in New Orleans on a stand maintained by the NIST. In the field of gas analysis, the BIPM presented a poster entitled "International comparability of gas standards" at the ISO/TC 158 Second Gas Analysis Symposium held in Maastricht. This was well received by delegates and representatives of the speciality gas industry.

The President confirmed that the CIPM was concerned that the KCDB should be promoted to as many user communities as was possible. The Director offered to make a template for promotional posters (CCQM/02-25, -26, -27 and -28) available through the BIPM website so that members could have the opportunity to prepare translations for their own use.

5 PARTICIPATION OF NMIS AND OTHER INSTITUTES IN PILOT STUDIES AND KEY COMPARISONS

The President said that participation in key comparisons was only available to NMIs, designated NMIs or other designated laboratories. The qualifications for participating in pilot studies were less restrictive.

6 IMPORTANCE OF PEER REVIEWS AND APPROPRIATE ACCREDITATION

The President commented that these issues were being addressed by NMIs, and no further discussion was required at this time.

7 COVERING THE COSTS INCURRED IN SUBSEQUENT BILATERAL COMPARISONS

The President explained that the Joint Committee of the Regional Metrology Organizations and the BIPM (JCRB) was concerned about the costs incurred by a pilot laboratory when a subsequent bilateral comparison is requested. Drs Mackay and Besley pleaded for developing countries to be treated fairly

if costs were imposed. It was agreed that it should be possible to charge for such work, but that such costs should not be applied unfairly.

8 CRITERIA FOR THE DESIGNATION OF LABORATORIES HAVING RESPONSIBILITY FOR CHEMISTRY CMC CLAIMS

The President reminded the CCQM that governments or NMIs having the official authority to do so were free to designate appropriate laboratories to take the role of an NMI in specified areas. However, there have been complaints from companies in some countries when private firms were designated as NMIs. Although such designations were not within the authority of the CCQM, attendees should be informed that difficulties had occurred on some occasions with such arrangements.

9 TRACEABILITY IN LABORATORY MEDICINE

The Director of the BIPM told the meeting that the BIPM had worked together with some of the NMIs, the WHO and the IFCC to form a Joint Committee for Traceability in Laboratory Medicine. The committee had been established in response to the need to establish a network of reference laboratories in laboratory medicine. A symposium would be held in June 2002 at the BIPM bringing together representatives of industry, regulation and the NMIs to discuss traceability in the field of laboratory medicine.

10 BIPM PROGRAMME OF METROLOGY IN CHEMISTRY

10.1 The CIPM/WMO Memorandum of Understanding

Dr Quinn told the CCQM of the Memorandum of Understanding with the WMO (CCQM/02-03), and he hoped to establish a similar agreement with the WHO.

10.2 Recent activities in the Chemistry section

Dr Wielgosz introduced Drs Viallon and Esler who had both joined the BIPM during the previous year. He reported that the BIPM planned to carry out comparisons of nationally maintained ozone reference standards. The project is in collaboration with the NIST, and the construction of two ozone standard reference photometers (SRP 27 and 28) was completed at the NIST in January 2002. The comparability of these instruments with those operated at the NIST was evaluated and found to be consistent with the uncertainty evaluation of the measurement results. At present there are CMC claims from seven NMIs for ozone at ambient levels shown on the BIPM key comparison database, but there are no key comparisons available to evaluate the degree of equivalence between them. The BIPM will act as the pilot laboratory for CCQM-P28, which will be a prelude to an ongoing key comparison for this measurand. The final comparison programme will enable comparisons of nationally maintained ozone reference standards to be performed at the rate required.

A research programme has been initiated at the BIPM to compare the results of ozone concentration measurements based on UV photometry with those determined by gas-phase titration. It is expected that further work to investigate the possible sources of systematic error in ozone reference standards based on UV photometry will lead to improvements in the design of the SRP.

10.3 Future developments

Dr Quinn said that he intended to ask the CIPM for an increased budget for the chemistry programme at the BIPM. At the time of the meeting there were three people in the Chemistry section and it was planned to increase the number to four. In addition, he hoped to recruit three more people to work in

organic analysis and three others to work in bioanalysis, either as BIPM staff or on secondment from NMIs.

Dr Okamoto said that it would be an enormous undertaking to initiate significant work in organic purity analysis. The Director replied that it would be possible for the BIPM to employ some highly qualified scientists and to carry out some useful research in certain niche areas.

Dr Semerjian said that he did not share the view that it was essential to employ research staff in order to support the CCQM. He was concerned that there had not been sufficient consultation with the CCQM. Dr Quinn said that the CIPM was constrained by the timetable required to submit budget proposals to the quadrennial CGPM. It was therefore necessary for the BIPM to make proposals in broad terms for its programmes in order to move into some areas that are developing very rapidly.

Dr Dybkaer said that the establishment of such a programme at the BIPM sent a signal to the world about priorities for research. Dr Hart said that she was in favour of establishing a budget, but it was important to identify the needs that the BIPM was seeking to respond to, rather than just identify the technologies with which it wanted to work.

Dr Quinn said that it was clear that a more detailed proposal was required to gain wider support. He undertook to develop an outline proposal with the organic analysis and bioanalysis working groups in order to do this, and then to circulate these to the CCQM.

The President said that it was essential that the BIPM could speak with authority on matters of metrology in chemistry in all fields of application.

11 RESULTS OF THE WORKSHOP ON TRACEABILITY

It was agreed that the workshop (CCQM/02-24) had been a success and that it would be useful to arrange another in the future on a similar theme.

12 ANY OTHER BUSINESS; DATE OF NEXT MEETING

The President thanked the Director and his staff for their tremendous efforts in organizing all of the CCQM meetings held during the week.

The next meeting of the CCQM will be in the week of 7 to 11 April 2003.

M.J.T. Milton, Rapporteur

revised December 2002

APPENDIX Q 1.
Working documents submitted to the CCQM at its 8th meeting

(see the list of documents on page 39)

LIST OF ACRONYMS USED IN THE PRESENT VOLUME

1 Acronyms for laboratories, committees and conferences

AGAL	Australian Government Analytical Laboratories
APMP	Asia/Pacific Metrology Programme
BAM	Bundesanstalt für Materialforschung und -prüfung, Berlin (Germany)
BIPM	International Bureau of Weights and Measures/Bureau International des Poids et Mesures
BNM	Bureau National de Métrologie, Paris (France)
BNM-LNE	Bureau National de Métrologie, Laboratoire National d'Essais, Paris (France)
CCPR	Consultative Committee for Photometry and Radiometry/Comité Consultatif de Photométrie et Radiométrie
CCQM	Consultative Committee for Amount of Substance: metrology in chemistry/Comité Consultatif pour la Quantité de Matière: métrologie en chimie
CEM	Centro Español de Metrología, Madrid (Spain)
CENAM	Centro Nacional de Metrología, Mexico (Mexico)
CIPM	International Committee for Weights and Measures/ Comité International des Poids et Mesures
CITAC	Cooperation on International Traceability in Analytical Chemistry
COOMET	Cooperation in Metrology among the Central European Countries
CSIR-NML	Council for Scientific and Industrial Research, National Metrology Laboratory, Pretoria (South Africa)
CSIRO*	see NML CSIRO
DFM	Danish Institute of Fundamental Metrology, Lyngby (Denmark)
EMPA	Swiss Federal Laboratories for Materials Testing and Research, St Gall (Switzerland)
EUROMET	European Collaboration in Measurement Standards

* Organizations marked with an asterisk either no longer exist or operate under a different acronym.

GUM	Glówny Urzad Miar/ Central Office of Measures, Warsaw (Poland)
IAEA	International Atomic Energy Agency
IFCC	International Federation of Clinical Chemistry and Laboratory Medicine
IMEP	International Measurement Evaluation Programme
IMGC-CNR	Istituto di Metrologia G. Colonnetti, Consiglio Nazionale delle Ricerche, Turin (Italy)
IPT	Instituto de Pesquisas Tecnológicas, São Paulo (Brazil)
IRMM	Institute for Reference Materials and Measurements, European Commission
ISO	International Organization for Standardization
ISO-REMCO	International Organization for Standardization, Committee on Reference Materials
IUPAC	International Union of Pure and Applied Chemistry
JCRB	Joint Committee of the Regional Metrology Organizations and the BIPM
KRISS	Korea Research Institute of Standards and Science, Daejeon (Rep. of Korea)
LGC	Laboratory of the Government Chemist, Teddington (United Kingdom)
LNE*	Laboratoire National d'Essais, Paris (France), see BNM
METAS	(formerly the OFMET) Swiss Federal Office of Metrology and Accreditation/Office Fédéral de Métrologie et d'Accréditation, Wabern (Switzerland)
MRA	Mutual Recognition Arrangement
NARL	National Analytical Reference Laboratory, Canberra and Pymble (Australia)
NIM	National Institute of Metrology, Beijing (China)
NIMC*	National Institute of Material and Chemical Research, Tsukuba (Japan), see NMIJ/AIST
NIST	National Institute of Standards and Technology, Gaithersburg (United States)
NMi VSL	NMi Van Swinden Laboratorium, Nederlands Meetinstituut, Delft (The Netherlands)
NMI	National Metrology Institute
NMIJ/AIST	National Metrology Institute of Japan, National Institute of Advanced Industrial Science and Technology, Tsukuba (Japan)

NML CSIRO	National Measurement Laboratory, CSIRO, Lindfield (Australia)
NPL	National Physical Laboratory, Teddington (United Kingdom)
NPLI	National Physical Laboratory of India, New Delhi (India)
NRC	National Research Council of Canada, Ottawa (Canada)
NRCCRM	National Research Centre for Certified Reference Materials, Beijing (China)
NRLM*	National Research Laboratory of Metrology, Tsukuba (Japan), see NMIJ
OFMET*	Office Fédéral de Métrologie, Wabern (Switzerland), ses METAS
OIML	Organisation Internationale de Métrologie Légale
OMH	Országos Mérésügyi Hivatal/National Office of Measures, Budapest (Hungary)
PITTCON	Pittsburgh Conference
PSB*	Singapore Productivity and Standards Board (Singapore), see SPRING
PTB	Physikalisch-Technische Bundesanstalt, Braunschweig and Berlin (Germany)
RMO	Regional Metrology Organization
SADCMET	SADC Cooperation in Measurement Traceability
SIM	Sistema Interamericano de Metrología
SL	State Laboratory, Dublin (Ireland)
SMU	Slovenský Metrologický Ústav/Slovak Institute of Metrology, Bratislava (Slovakia)
SP	Sveriges Provnings- och Forskningsinstitut/Swedish National Testing and Research Institute, Borås (Sweden)
SPRING	(formerly the PSB) Standards, Productivity and Innovation Board, Singapore (Singapore)
UME	Ulusal Metroloji Enstitüsü/National Metrology Institute, Marmara Research Centre, Gebze-Kocaeli (Turkey)
VNIIM	D.I. Mendeleyev Institute for Metrology, Gosstandart of Russia, St Petersburg (Russian Fed.)
VSL*	Van Swinden Laboratorium, Delft (The Netherlands), see NMi
WHO	World Health Organization
WMO	World Meteorological Organization

2 Acronyms for scientific terms

BTX	Benzene, Toluene, Xylene
CFC	Chlorofluorocarbon
CMC	Calibration and Measurement Capabilities
CRM	Certified Reference Materials
DNA	Deoxyribonucleic Acid
IDGC/MS	Isotope Dilution Gas Chromatography/Mass Spectrometry
KCDB	BIPM Key Comparison Database
KCRV	Key Comparison Reference Value
NDIR	Non-dispersive Infrared
PCB	Polychlorinated Biphenyl
PCR	Polymerase Chain Reaction
SI	International System of Units
SRP	Standard Reference Photometer
TEM	Transmission Electron Microscopy
XPS	X-ray Photoelectron Spectroscopy