BUREAU INTERNATIONAL DES POIDS ET MESURES

COMITÉ CONSULTATIF POUR LA QUANTITÉ DE MATIÈRE

Rapport de la 2e session
Report of the 2nd Meeting

1996

Organisation intergouvernementale de la Convention du Mètre

COMITÉ CONSULTATIF
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SESSION DE 1996

MEETING IN 1996

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LISTE DES SIGLES UTILISÉS DANS LE PRÉSENT VOLUME
LIST OF ACRONYMS USED IN THE PRESENT VOLUME

1. Sigles des laboratoires, commissions et conférences
Acronyms for laboratories, committees and conferences

*BCMN/CBNM	Bureau central de mesures nucléaires/Central Bureau for Nuclear Measurements, IMMR-CCE, Geel (Belgique), *voir* IMMR/IRMM
BCR	Bureau communautaire de référence de la Communauté économique européenne/Community Bureau of Reference of the Commission of the European Communities
BIPM	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)
*CBNM	*voir* IMMR/IRMM
CCQM	Comité consultatif pour la quantité de matière
CGPM	Conférence générale des poids et mesures
CIPM	Comité international des poids et mesures
EUROMET	European Collaboration in Measurement Standards
IMMR/IRMM	(ex BCMN/CBNM) Institut des matériaux et mesures de référence/Institute for Reference Materials and Measurements, Geel (Belgique)
IRMM	*voir* IMMR
ISO	Organisation internationale de normalisation/International Organization for Standardization
IUPAC	*voir* UICPA
KRISS	(ex KSRI) Korea Research Institute of Standards and Science, Taejon (Rép. de Corée)
*KSRI	Korea Standards Research Institute, Taejon (Rép. de Corée), *voir* KRISS
LGC	Laboratory of the Government Chemist, Teddington (Royaume-Uni)
LNE	Laboratoire national d'essais, Paris (France), *voir* BNM
*NBS	National Bureau of Standards, Gaithersburg (É.-U. d'Amérique), *voir* NIST

* Les laboratoires ou organisations marqués d'un astérisque soit n'existent plus soit figurent sous un autre nom.

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

NIM	Institut national de métrologie/National Institute of Metrology, Beijing (Rép. pop. de Chine)
NIMC	National Institute of Material and Chemical Research, Tsukuba (Japon)
NIST	(ex NBS) National Institute of Standards and Technology, Gaithersburg (É.-U. d'Amérique)
NMi	(ex VSL) Nederlands Meetinstituut, Delft (Pays-Bas)
NPL	National Physical Laboratory, Teddington (Royaume-Uni)
NRC	Conseil national de recherches du Canada/National Research Council of Canada, Ottawa (Canada)
NRCCRM	National Research Centre for Certified Reference Materials, Beijing (Rép. pop. de Chine)
NRLM	National Research Laboratory of Metrology, Tsukuba (Japon)
PTB	Physikalisch-Technische Bundesanstalt, Braunschweig et Berlin (Allemagne)
SP	(ex Statens Provningsanstalt) Sveriges Provnings- och Forskningsinstitut/Swedish National Testing and Research Institute, Borås (Suède)
UICPA/IUPAC	Union internationale de chimie pure et appliquée/International Union of Pure and Applied Chemistry
VNIIM	Institut de métrologie D.I. Mendéléev/D.I. Mendeleyev Institute for Metrology, Saint-Pétersbourg (Féd. de Russie)
*VSL	Van Swinden Laboratorium, Delft (Pays-Bas), *voir* NMi
VTT	Technical Research Centre of Finland, Espoo (Finlande)

2. Sigles des termes scientifiques
Acronyms for scientific terms

CRM	*voir* MRC
DSC	Analyse calorimétrique à compensation de puissance/Differential Scanning Calorimetry
ICP-MS	Spectrométrie de masse d'un plasma induit par une source micro-onde/Inductively Coupled Plasma Mass Spectrometry
IDMS	Spectrométrie de masse avec dilution isotopique/Isotope Dilution Mass Spectrometry
MRC/CRM	Matériaux de référence certifiés/Certified Reference Materials
SI	Système international d'unités/International System of Units
TIMS	Spectrométrie de masse avec thermo-ionisation/Thermal Ionization Mass Spectrometry

COMITÉ CONSULTATIF POUR LA QUANTITÉ DE MATIÈRE

MEETING IN 1996

Note on the use of the English text

To make its reports and those of its various Comités Consultatifs more widely accessible, the Comité International des Poids et Mesures has decided to publish an English version of these 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.

Note sur l'utilisation du texte anglais

Afin de faciliter l'accès à ses rapports et à ceux des divers Comités consultatifs, le Comité international des poids et mesures a décidé de publier une version en anglais de ces rapports. Le lecteur doit cependant noter que le rapport officiel est toujours celui qui est rédigé en français. C'est le texte français qui fait autorité si une référence est nécessaire ou s'il y a doute sur l'interprétation.

THE BIPM

AND THE CONVENTION DU MÈTRE

The Bureau International des Poids et Mesures (BIPM) was set up by the Convention du Mètre 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 Convention du Mètre*.

The task of the BIPM is to ensure world-wide unification of physical measurements; its function is to:

— establish the fundamental standards and scales for measurement of the principal physical quantities and maintaining the international prototypes;
— carry out comparisons of national and international standards;
— ensure the co-ordination of corresponding measuring techniques;
— carry out and co-ordinate measurements of the fundamental physical constants relevant to these activities.

The BIPM operates under the exclusive supervision of the Comité International des Poids et Mesures (CIPM) which itself comes under the authority of the Conférence Générale des Poids et Mesures (CGPM).

Delegates from all the Member States of the Convention du Mètre attend the Conférence Générale which, at present, meets every four years. At each meeting the Conférence Générale receives the Report of the Comité International on the work accomplished, its function being to:

— discuss and instigate 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;
— adopt the important decisions concerning the organization and development of the BIPM.

The Comité International 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 Convention du Mètre. The principal task of the CIPM is to ensure world-wide 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 (1937) and ionizing radiation (1960), to time scales (1988) and to amount of substance (1993). 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 a new building for a library and offices was opened.

Some forty physicists or technicians work in the BIPM laboratories. They mainly conduct metrological research, international comparisons of realizations of units and

* As of 31 December 1996, forty-eight States were members of this Convention: Argentina (Rep. of), Australia, Austria, Belgium, Brazil, Bulgaria, Cameroon, Canada, Chile, China (People's Rep. of), Czech Republic, Denmark, Dominican Republic, Egypt, Finland, France, Germany, Hungary, India, Indonesia, Iran, Ireland, Israel, Italy, Japan, Korea (Dem. People's Rep. of), Korea (Rep. of), Mexico, Netherlands, New Zealand, Norway, Pakistan, Poland, Portugal, Romania, Russian Federation, Singapore, Slovak Republic, South Africa, Spain, Sweden, Switzerland, Thailand, Turkey, United Kingdom, U.S.A., Uruguay, Venezuela.

verifications of standards. An annual report, published in the Procès-Verbaux des séances du Comité International des Poids et Mesures gives the 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 Comités Consultatifs, whose function is to provide it with information on matters that it refers to them for study and advice. These Comités Consultatifs, which may form temporary or permanent working groups to study special topics, are responsible for co-ordinating the international work carried out in their respective fields and for proposing recommendations to the CIPM concerning units.

The Comités Consultatifs have common regulations (*BIPM Proc.-Verb. Com. Int. Poids et Mesures*, 1963, **31**, 97). They meet at irregular intervals. The chairman of each Comité Consultatif is designated by the CIPM and is normally a member of the CIPM. The members of the Comités Consultatifs are metrology laboratories and specialized institutes, agreed by the CIPM, which send delegates of their choice. In addition, individual members are appointed by the CIPM, and there is also a representative of the BIPM. At present, there are nine such committees:

1. The Comité Consultatif d'Électricité (CCE), set up in 1927;
2. The Comité Consultatif de Photométrie et Radiométrie (CCPR), new name given in 1971 to the Comité Consultatif de Photométrie (CCP) set up in 1933 (between 1930 and 1933 the preceding committee (CCE) dealt with matters concerning photometry);
3. The Comité Consultatif de Thermométrie (CCT), set up in 1937;
4. The Comité Consultatif pour la Définition du Mètre (CCDM), set up in 1952;
5. The Comité Consultatif pour la Définition de la Seconde (CCDS), set up in 1956;
6. The Comité Consultatif pour les Étalons de Mesure des Rayonnements Ionisants (CCEMRI), set up in 1958 (in 1969 this committee established four sections: Section I (Measurement of 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 Comité Consultatif des Unités (CCU), set up in 1964 (this committee replaced the "Commission for the System of Units" set up by the CIPM in 1954);
8. The Comité Consultatif pour la Masse et les grandeurs apparentées (CCM), set up in 1980;
9. The Comité Consultatif pour la Quantité de Matière (CCQM), set up in 1993.

The proceedings of the Conférence Générale, the Comité International and the Comités Consultatifs are published by the BIPM in the following series:

— *Comptes rendus des séances de la Conférence Générale des Poids et Mesures;*
— *Procès-Verbaux des séances du Comité International des Poids et Mesures;*
— *Sessions des Comités Consultatifs.*

The Bureau International also publishes monographs on special metrological subjects and, under the title "*Le Système International d'Unités (SI)*", a booklet, periodically up-dated, 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.

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 Convention du Mètre.

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POUR LA QUANTITÉ DE MATIÈRE

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SWEDISH NATIONAL TESTING AND RESEARCH INSTITUTE [SP], Borås.

The Director of the Bureau International des Poids et Mesures [BIPM], Sèvres.

AGENDA
for the 2nd Meeting

1. Opening of the meeting and welcome by the President.
2. Traceability to the mole.
3. Reports of working groups established at the first meeting of the CCQM:
   - 3.1 Isotope dilution mass spectrometry;
   - 3.2 Coulometry;
   - 3.3 Gravimetry;
   - 3.4 Titrimetry;
   - 3.5 Determination of freezing point depression;
   - 3.6 Proposal for international comparison on the measurement of organic substances.
4. CIPM interlaboratory study II on gas analysis: interim report.
5. International comparison of lead in water: progress report.
6. Proposal for international comparison in gas analysis.
7. Strategy document for the period 1996-2000: discussion of draft.
8. BIPM activities.
9. Other business.
10. Date of the next meeting.

REPORT

OF THE

COMITÉ CONSULTATIF POUR LA QUANTITÉ DE MATIÈRE

(2nd Meeting — 1996)

TO THE

COMITÉ INTERNATIONAL DES POIDS ET MESURES

by J. McLAREN, Rapporteur

The Comité Consultatif pour la Quantité de Matière (CCQM) held its second meeting at the Bureau International des Poids et Mesures (BIPM), at Sèvres. Four sessions took place, on 14 and 15 February 1996.

Present:

R. KAARLS, Member of the CIPM, President of the CCQM.

Delegates from member laboratories and organizations:

Bureau National de Métrologie: Laboratoire National d'Essais [BNM-LNE], Paris (A. MARSCHAL).

D. I. Mendeleyev Institute for Metrology [VNIIM], St. Petersburg (L. KONOPELKO, I. NEKHLUDOV).

Institute for Reference Materials and Measurements [IRMM], Geel (P. DE BIÈVRE, P. TAYLOR).

International Union of Pure and Applied Chemistry [IUPAC] (F. INGMAN).

Korea Research Institute of Standards and Science [KRISS], Taejon (HUN Young So).

Laboratory of the Government Chemist [LGC], Teddington (B. KING).

National Institute of Material and Chemical Research [NIMC], Tsukuba (M. KURAHASHI).

National Institute of Standards and Technology [NIST], Gaithersburg (H. G. SEMERJIAN, R. L. WATTERS Jr).

National Physical Laboratory [NPL], Teddington (M. J. T. MILTON).

National Research Centre for Certified Reference Materials [NRCCRM], Beijing (PAN Xiu-Rong, ZHAO Min).

National Research Council of Canada [NRC], Ottawa (J. W. McLAREN).

National Research Laboratory of Metrology [NRLM], Tsukuba (C. TAKAHASHI).

Nederlands Meetinstituut [NMi], Delft (A. ALINK, E. DE LEER).

Physikalisch-Technische Bundesanstalt [PTB], Braunschweig (G. DUBE).

Swedish National Testing and Research Institute [SP], Borås (M. MÅNSSON).

The Director of the Bureau International des Poids et Mesures [BIPM] (T. J. QUINN).

Also present:

P. GIACOMO (Director Emeritus of the BIPM); R. S. DAVIS, D. LE COZ (BIPM).

Absent:

National Institute of Metrology [NIM], Beijing.

1. Opening of the meeting and welcome by the President

The President opens the meeting and welcomes the participants. A revision to the original agenda to include two new items: "Traceability to the Mole" and "Proposed BIPM Activities in Metrology in Chemistry" is proposed. The President notes that a total of six documents relating to the first topic (CCQM/96-5, 6, 14, 15, 17, 18) has been received. He then invites the Director of the BIPM to make a few introductory remarks.

Dr Quinn reminds participants of the purpose of the CCQM, as outlined in the terms of reference included in Section 1.2 of the report of the first meeting. For the benefit of those not present at the first meeting, he briefly reviews the decisions taken at that meeting, in particular the establishment of working groups to develop working documents for proposed primary methods of chemical analysis.

Dr McLaren is appointed Rapporteur, to be assisted by Dr Davis.

The revised agenda is adopted.

2. Traceability to the mole

A presentation is made by Dr Milton to complement the written proposal (CCQM/96-17) submitted by the NPL concerning the establishment of

traceable standards and reference materials. The proposal concerns the definition of a primary standard of amount of pure substance, which would be the outcome of the use of a primary method of measurement (as defined by the first CCQM in 1995). Dr Milton emphasises that amount of substance is an *extensive* quantity and that the primary standard of amount of pure substance would be labelled with the value of its *extensive* amount of substance in moles. It is not intended that it would be disseminated in the same way as a reference material: in some cases it might only exist transiently or within the operation of an experimental method. Prof. De Bièvre cautions against any tendency to suggest that physical artefacts are necessary to establish traceability of amount-of-substance measurements to the Système International d'Unités (SI). Further discussion of this proposal is deferred until the final session of the meeting, at which time Dr Quinn recommends that the final sentence of Section 9.1.5 of document CCQM/96-17 be modified to read: "Such a standard will not necessarily be disseminated as a physical artefact." It is agreed that any further suggestions for modification will be sent by 30 April 1996 to Dr Milton who will prepare a revised document by 30 May 1996. It is recommended by Prof. De Bièvre that the revised document be reviewed by the IUPAC Analytical Chemistry Division and the International Atomic Weights Commission.

Prof. De Bièvre makes a presentation, based on three written submissions (CCQM/96-5, 6 and 9) on traceability of the result of an amount-of-substance measurement to the mole, illustrating how this can be achieved through isotope dilution mass spectrometry.

After some discussion, it becomes clear that there is a strong body of opinion that the concepts of "traceability to the mole" and "realization of the mole" should be abandoned, and that instead we should encourage the use of the term "traceability to the SI". It is decided to form an *ad hoc* working group on the terminology of traceability comprising Prof. De Bièvre, Dr de Leer, Dr Dube, Dr Milton, Dr Watters and the Director of the BIPM. This working group meets in separate session on several occasions during the course of the meeting, and prepares a document "Traceability to the SI in measurements in chemistry" for consideration by the CCQM during the final session. The following text is provisionally approved by the CCQM, with the direction that the final version in the minutes will include the definition of a primary method of measurement[1].

[1] A primary method of measurement is a method having the highest metrological qualities, whose operation can be completely described and understood, for which a complete uncertainty statement can be written down in terms of SI units, *and whose results are, therefore, accepted without reference to a standard of the quantity being measured.*

Traceability to the SI of measurements of amount of substance in chemistry

The definition of traceability in the *International vocabulary of basic and general terms in metrology* reads as follows:

Traceability: *property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties.*

Traceability can, therefore, be understood as the demonstration of quantified links, with their uncertainties, between the results of a measurement and national or international measurement standards.

Traceability is not an end in itself. The purpose of establishing traceability is to ensure that measurements at the end of a traceability chain can be stated with quantified uncertainties in SI units so that they are accurate, comparable with measurements made by other methods and in other domains, and stable in the long term (*see* Resolutions 1, 2 and 7 of the 20th CGPM (1995)).

Strictly, traceability to the SI in measurements of amount of substance — or of any other quantity — requires that the measurements be made using a primary method of measurement, which is correctly applied and stated with an evaluated uncertainty.

There may be other, indirect, ways of establishing traceability to the SI, beyond those covered by primary methods of measurement, and these are under study by the CCQM.

These other indirect ways may include, among others:

— combinations of methods that are not established as primary but have combined uncertainties where the evaluation requires the incorporation of the links to national or international measurement standards of each SI unit involved;

— comparison with reference materials of the same or similar substance, or with a mixture of substances, which are themselves linked to the SI through a chain of other comparisons, culminating in a measurement using a primary method; the uncertainty components due to the matrix effects must be evaluated;

— comparison with other standards which realize or represent an accurate chemical composition (e.g. standard gas mixture generator, standard UV spectrometer for ozone determination) which themselves are linked to the SI.

Note that atomic masses, molar masses, and various fundamental constants, such as the Faraday and the Avogadro constants, provide essential links to the SI for pure materials and well defined systems. Their uncertainties have already been evaluated.

3. Reports of working groups established at the first meeting of the CCQM

3.1 Isotope dilution mass spectrometry

Prof. De Bièvre, task leader for the working group on isotope dilution mass spectrometry (IDMS), introduces two descriptions of the principles of IDMS distributed to the CCQM (as CCQM/96-9) before the meeting. One of these is a previously published paper (*Anal. Proc.*, 1993, **30**, 328-333), while the other is an unpublished draft document. He asks the CCQM to indicate which is the preferred document for further development into the final version; it is indicated that the draft is preferred.

Dr King asks whether the description of IDMS provided in the draft document is sufficiently general to include organic ID analysis. After some discussion, it is agreed that the working group will produce three documents: a general document on the principles of IDMS, a detailed protocol for inorganic IDMS, and a detailed protocol for organic IDMS. It is also agreed that the terminology of the principles and protocols documents will be harmonized.

Referring to the detailed protocol for inorganic IDMS by inductively coupled plasma mass spectrometry (ICP-MS) prepared by Dr Watters and colleagues at the NIST (CCQM/96-12), Dr So asks whether a separate protocol for thermal ionization mass spectrometry (TIMS) will also be prepared. Dr Watters agrees to do this.

Dr Marschal introduces a brief note (CCQM/96-8), submitted to the CCQM by the BNM-LNE, in which matrix matching is demonstrated to be a successful route to high accuracy ICP-MS determination of zinc in BCR milk powder CRM 063R.

The discussion is concluded with agreement that further comments and suggestions for the document on the principles of IDMS will be sent, by 7 April 1996, to Prof. De Bièvre who will prepare a final draft by 1 September 1996.

3.2 Coulometry

Prof. Pan, task leader for the working group on coulometry, makes a presentation based on the previously circulated document (CCQM/96-4).

The document is favourably received by the CCQM; it is noted that coulometry is particularly applicable to the characterization of high purity substances.

Dr Marschal asks whether it is possible to identify one of the two coulometric techniques described in the document (constant-current and controlled-potential coulometry) as superior for metrological purposes; the response is that the superior technique depends on the details of the measurement.

It is agreed that any further comments will be sent, by 7 April 1996, to Prof. Pan who will prepare a final draft by 1 September 1996.

3.3 Gravimetry

Dr Watters, task leader for the working group on gravimetric analysis, makes a presentation based on the previously circulated document (CCQM/96-13) and gives an example in which classical gravimetry is combined with instrumental methods of analysis to improve the accuracy of sulphate determination.

It is agreed that any further comments will be sent, by 7 April 1996, to Dr Watters who will prepare a final draft by 1 September 1996.

A presentation is then made by Mr Alink, task leader for the working group on static and dynamic gas mixtures, based on the previously circulated document (CCQM/96-20). In subsequent discussion, it is noted that this topic has no direct connection with classical gravimetry, so that it is perhaps inappropriate to have both under the heading “Gravimetry”. Dr Kaarls asks whether there is duplication of the work of ISO/TC 158 (Analysis of gases).

It is agreed that further comments will be sent to Mr Alink before 1 June 1996, after receipt of further information from the ISO committee, and that Mr Alink will prepare a final draft by 1 November 1996.

3.4 Titrimetry

On behalf of Dr Worswick, task leader for the working group on titrimetry, Dr King makes a presentation based on the previously circulated document on titrimetry (CCQM/96-1). It is concluded that titrimetry can satisfy the requirements for a primary method, although it depends upon gravimetry which surpasses it for accuracy in particular applications. A system of standardization, starting with gravimetry of high-purity silver, is proposed as a possible basis for further experimental work. An international comparison on the determination of ethanol in water is proposed.

Dr Watters notes that titrimetry is used routinely at the NIST for certification of calibration standard solutions, and that the primary source

of uncertainty arises from differences between the apparent end point of the titration and the equivalence point.

Dr Marschal reports work done by titrimetry, gravimetry and colorimetry at the BNM-LNE to check the accuracy of commercial standard solutions. A draft report of this activity (without the formal numbering) is distributed to participants for information. Dr Marschal then expresses the opinion that a system of standardization based on silver is not feasible for many determinations, e.g., the determination of copper, as it would involve too many steps. There is general agreement with this opinion.

Dr Marschal suggests considering the possibility of establishing a set of primary substances for titrimetry, which could be used in one or two steps to calibrate the most frequently used calibration solutions. The specific task of the BIPM could be:

— to establish and validate this list;

— to promote the verification of consistency between batches of such primary substances issued by metrology laboratories.

It is agreed that any further comments will be sent, by 7 April 1996, to Dr King who will prepare a final draft by 1 September 1996.

3.5 Determination of freezing-point depression

A presentation based on the previously circulated document on the determination of freezing-point depression (CCQM/96-3) is made by Mrs Zhao, who notes that some typographical errors in this draft have yet to be corrected. She notes that some materials already available at the NRCCRM (γ-BHC and benzene) could be used for an international comparison.

It is agreed that this method is especially useful for determination of the purity of organic compounds, but that a fundamental condition is that the impurities must be soluble in the bulk phase. Dr Watters notes that, since the procedure is a standard additions method, linearity over a suitable range of concentration must be demonstrated by conducting experiments with more than one spike. Prof. Pan replies that the method is comparative and not based on standard additions. When measuring the purity of a substance, two melting curves are made, one with the original sample and the other with the original sample plus a small amount of impurity (a reagent). The impurity content of the original sample can be calculated by comparison of the two melting curves. More impurity may be added but the purpose is not to determine a calibration curve, so linearity is not an issue.

It is agreed that any further comments will be sent, by 7 April 1996, to Mrs Zhao who will prepare a final draft by 1 September 1996.

A presentation is then made by Dr Månsson on an equilibrium method of purity determination by differential scanning calorimetry (DSC), as described in document CCQM/96-19. This method has the advantages that

it may be applied to samples as small as 10 mg, and be implemented on a commercially available instrument. As in the method described by Mrs Zhao, impurities must be soluble in the bulk phase. In discussion, Dr King notes that this method is used at the LGC for determination of the purity of pesticide compounds.

It is agreed that any further comments will be sent, by 7 April 1996, to Dr Månsson who will prepare a final draft by 1 September 1996.

3.6 Proposal for an international comparison on the measurement of organic susbtances

Dr King introduces the proposed protocol for a CCQM exercise on the measurement of organic substances by IDMS. He notes that the document circulated at the meeting (CCQM/96-2, revised) differs from the previously distributed version of the protocol in that it is now recommended that the first round involve the measurement of only naphthalene, rather than both naphthalene and pp′-DDE, and that the lower concentration has been raised to 0,5 μg/g. Dr King reports a considerable difference of opinion among potential participants as to the degree of detail required in the protocol, and advises that the LGC has decided to take a “middle road” in developing the protocol. He also indicates willingness on the part of the LGC to accept results by methods other than IDMS. When asked by the President to suggest a time scale for the exercise, Dr King suggests that three to six months should be allowed for the preparation of the samples and that participants should be allowed a minimum of three months for completion of the analyses.

In general the protocol is favourably received. Prof. De Bièvre applauds the choice of a simple substance at relatively high concentration for the first round. Much of the ensuing discussion, however, revolves around reservations by several members of the CCQM about the use of a deuterium-labelled isotopic spike as opposed to a ^{13}C-enriched spike. In the end it is recommended that, if for reasons of cost or lack of availability it is not feasible to obtain ^{13}C-enriched naphthalene for the comparison, pp′-DDE (for which ^{13}C-enriched material is available at reasonable cost) should be chosen as the analyte.

The following laboratories indicate their intention to participate in the comparison: IRMM, KRISS, LGC, NIMC, NIST, NMi, NRC, NRCCRM and PTB. It is agreed that any further suggestions or comments should be sent to Dr King by 7 April 1996.

4. CIPM interlaboratory study II on gas analysis: interim report

Mr Alink makes a presentation on the results of the second CCQM exercise on analysis of binary gas mixtures (CO, CO_2, NO and SO_2 in N_2).

He reports some practical difficulties in the transport of cylinders to and from participating laboratories and shows additional data for NO, received after distribution of the interim report (CCQM/96-11). He notes that results for SO_2 have not yet been received. With the exception of an occasional outlier, results received to date suggest international comparability to within limits of ± 1 %. Mr Alink notes that, in some cases, reported uncertainties appear to be overly pessimistic, given the agreement among laboratories.

Prof. De Bièvre cautions against the CCQM undertaking an "$n+1^{th}$" international comparison, similar to comparisons carried out by other bodies. He also questions the rejection of outlying results on the basis of *a posteriori* statistical evaluation of results; the emphasis in these metrological comparisons should be the study of *a priori* concepts. Dr Quinn, and several others, support this opinion. Dr Watters recommends that a more detailed analysis of uncertainty be carried out in order to arrive at a "target uncertainty" for the exercise.

Mrs Zhao recommends that, in future exercises, the initial pressure be indicated on each cylinder; she also asks the co-ordinators to consider means by which participants would be able to keep the cylinders for a suitable period after submission of results, so as to be able to repeat analyses in the event of a discrepancy.

It is agreed that the deadline for submission of remaining results for this exercise will be 1 July 1996, and that Mr Alink will prepare a final report, including a detailed uncertainty analysis, by 1 November 1996.

5. International comparison of lead in water: progress report

The detailed protocol for the CCQM study on the determination of lead in aqueous acid solution by isotope dilution ICP-MS (CCQM/96-12) is presented by Dr Watters. He notes that some guidance on the components of uncertainty remains to be added as an appendix. The document is very favourably received. It is agreed that any further comments or suggestions will be sent, by the end of February 1996, to Dr Watters who will then be able to arrange for distribution of the kits in March. Participants are asked to submit results to Dr Watters by 1 October 1996.

6. Proposal for international comparison in gas analysis

Mr Alink presents the results of a survey of potential participants in future CCQM interlaboratory studies in the domain of gas analysis (CCQM/96-21). This raises several questions, including whether or not the CCQM should involve itself in small studies of interest to relatively few participants.

Dr Watters questions the value of additional exercises on simple binary mixtures, and suggests that it would be better to challenge the robustness of

the methods in use for these simple mixtures with more difficult samples. Dr Milton supports this view, proposing that the CCQM attempt to make the link with real measurement requirements using for example benzene, BTX and ethanol. Dr de Leer suggests that emphasis should be placed on attempts to bring methods used in this type of analysis up to the level of primary methods.

It is agreed that Mr Alink will prepare a proposal for next year's activities by 1 November 1996.

Dr Semerjian expresses his concern about the potential proliferation of international comparisons, not only for gas analysis, but for other types of analysis as well. Dr Quinn shares this concern, pointing out that the need for demonstrable equivalence between national laboratories has been increased by the requirements of various accreditation programmes and bilateral agreements. He suggests that each Consultative Committee of the CIPM draw up a limited list of key international comparisons on the basis of which principal laboratories could demonstrate equivalence. Dr Semerjian agrees, and urges the CCQM to begin immediately to establish a framework for developing such a list.

7. Strategy document for the period 1996-2000: discussion of draft

The President introduces the draft CCQM strategy document for the period 1996-2000 (CCQM/96-10). The document comprises two main sections: a list of assumptions underlying the work of the CCQM, and a list of work to be carried out. After a rather unfocussed discussion, Dr Quinn reminds the committee of the list of activities agreed at the first meeting, and suggests that a review of progress on these activities should form the basis for the strategy document. The President agrees to develop a revised version of the strategy document by 1 November 1996.

In view of the concerns raised by Dr Semerjian and Dr Quinn about the proliferation of international comparisons, it is agreed to set up a CCQM working group on the equivalence of national measurement standards, its task being to develop a proposal defining the minimum number of activities required to establish equivalence of broadly applicable national measurement standards. Representatives from the following organizations agree to participate in this working group: BIPM, BNM-LNE, KRISS, LGC, NIST, NMi, NPL and VNIIM. Dr Semerjian agrees to be the task leader.

8. BIPM activities

The President advises the CCQM of the need to make preliminary recommendations to the CIPM regarding the development of experimental facilities for metrology in chemistry at the BIPM. Prof. De Bièvre strongly

recommends that the BIPM have an active programme in order to bolster its scientific credentials regarding measurements in chemistry. There is general agreement that this would be desirable, but that any facilities developed at the BIPM should be devoted entirely to work at the highest metrological level, and should be designed to complement rather than duplicate facilities available in the member laboratories of the CCQM. Dr Watters expresses the opinion that activities in coulometry, gravimetry and titrimetry might offer opportunities for synergy with current BIPM activities.

9. Other business

For information, Dr Milton presents a report on a proposed EUROMET programme of comparisons of primary methods for measuring amount of substance in gas mixtures (CCQM/96-16).

Prof. De Bièvre notes that a document on IDMS which he has submitted (CCQM/96-7) has not been discussed; he suggests that it be placed on the agenda for the next meeting.

10. Date of next meeting

It is agreed that the next meeting of the CCQM will take place on 20-21 February 1997.

The President thanks the participants for their participation and contributions, and the BIPM staff for their co-operation. He closes the meeting.

February 1996
revised June 1996

APPENDIX Q 1

Working documents
submitted to the CCQM at its 2nd meeting

(*see* the list of documents on page Q 13)

ANNEXE Q 1

Documents de travail présentés à la 2e session du CCQM

Ces documents de travail peuvent être obtenus dans leur langue originale sur demande adressée au BIPM.

Document CCQM/

96-1 Report of the CCQM working group on titrimetric analysis, by R. Worswick, 14 p.

96-2 LGC (Royaume-Uni). — CCQM International Comparison on the Determination of Organic Compounds, by K.S. Webb and R.D. Worswick, 10 p.

96-3 NRCCRM (Rép. pop. de Chine). — CCQM working document on determination of freezing point depression (Draft), 9 p.

96-4 NRCCRM (Rép. pop. de Chine). — CCQM Working Document on Coulometry (Draft), 10 p.

96-5 IMMR (Belgique). — Traceability of Measurements to SI: How Does it Lead to Traceability of Quantitative Chemical Measurements ?, by P. De Bièvre, In *Accreditation and Quality Assurance in Analytical Chemistry*, H. Günzler ed., Springer-Verlag, 1996, 159-193.

96-6 IMMR (Belgique), NMi (Pays-Bas), NIST (É.-U. d'Amérique). — Measurement Principles for Traceability in Chemical Analysis, by P. De Bièvre, R. Kaarls, H. S. Peiser, S. D. Rasberry and W. P. Reed, 18 p.

96-7 IMMR (Belgique). — Comparison of Ionization Techniques for their Potential to Carry out "Metrological" Measurements of Isotope Amount Ratios, by P. De Bièvre, H. J. Dietze, K. G. Heumann and G. Ramendik, 5 p.

96-8 BNM-LNE (France). — Short note to BIPM-CCQM: High-accuracy ICP-MS: "Calibration by identical", an alternative to IDMS ?, by A. Marschal and G. Labarraque, 2 p.

96-9 IMMR (Belgique). — Isotope Dilution Mass Spectrometry (IDMS), by P. De Bièvre, 21 p.

Document CCQM/

96-10 NMi (Pays-Bas), BIPM. — Strategy for the Period 1996-2000, by R. Kaarls and T. J. Quinn, 3 p.

96-11 NMi (Pays-Bas). — CCQM-Interlaboratory Study II on Primary Gas Mixtures – Interim report, by A. Alink, 20 p.

96-12 NIST (É.-U. d'Amérique). — Isotope Dilution Mass Spectrometry using ICP-MS Protocol for CIPM, by E. S. Beary, J. D. Fassett, K. R. Eberhardt and R. L. Watters Jr, 30 p.

96-13 NIST (É.-U. d'Amérique). — Gravimetry as a Primary Method of Measurement, by C. M. Beck II and R. L. Watters Jr., 17 p.

96-14 VNIIM (Féd. de Russie). — Comments on the CCQM definition of primary methods of measurement, by Yu. I. Alexandrov, 15 p.

96-15 UICPA. — Memo to 2nd meeting of the CCQM: Comments on symbols and notation, by I. M. Mills, 5 p.

96-16 NPL (Royaume-Uni). — Proposed Programme of Inter-Comparisons of Primary Methods for Measuring Amount, by P. G. Quincey, P. T. Woods and M. J. T. Milton (in collaboration with IRMM, Belgium ; BNM-LNE, France ; NMi, Netherlands ; PTB, Germany and VTT, Finland), 2 p.

96-17 NPL (Royaume-Uni). — The Mole – Establishing Traceable Standards and Reference Materials, by M. J. T. Milton, P. T. Woods and P. G. Quincey, 8 p.

96-18 IMMR (Belgique). — CITAC Action – Criteria for Traceability of Amount of Substance (Chemical) Measurements to the Appropriate Unit, the Mole, in the International System of Units, by P. De Bièvre, 4 p.

96-19 SP (Suède). — Purity Determination by Thermal Analysis – Equilibrium Method, by M. Månsson, 9 p.

96-20 Report of the CCQM working group on gravimetry – static and dynamic gas mixtures (NMi, BNM-LNE, NPL, PTB, VNIIM), 6 p.

96-21 NMi (Pays-Bas). — Survey for additional studies on gas mixtures (Note on progress 1996-02-09), by A. Alink, 3 p.

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