

Present Status of the Different Approaches to the Re-Definition of the Kilogram

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ABSTRACT

The unit of mass, the kilogram, remains the only base unit in the International System of Units which is still defined in terms of a physical artefact. The scope of the work reported here is to describe and review the progress of the three main approaches concerned with providing a re-definition of the kilogram. Following on, areas of research in which NPL's Mass and Density Standards group can make a significant contribution to the possible future re-definition of the unit of mass are recommended.

The three approaches are the *Avogadro project*, the *Watt balance* and the *Ion counting method*. The aim of both the Avogadro and Ion counting approaches is to relate the kilogram to an atomic mass: the Avogadro project through measurements made on artefacts manufactured from silicon single crystals; the Ion counting method through the accumulation of gold atoms. The Watt balance approach relates the kilogram to electrical units by equating mechanical and electrical power.

The main recommendation of this report is that NPL should participate in the Avogadro project through the measurement of the mass of silicon artefacts. This will require the characterisation of the surface properties of these artefacts and its effect on the mass stability in both ambient and vacuum environments. Furthermore, the techniques developed to weigh these artefacts in vacuum could be used in support of the Watt balance project.

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Approved on behalf of the Managing Director, NPL,
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1 INTRODUCTION

The unit of mass, the kilogram, remains the only base unit in the International System of Units (SI) which is still defined in terms of a physical artefact. By definition:

the kilogram (kg) is equal to the mass of the international prototype of the kilogram

The international prototype of the kilogram is made of an alloy of platinum (90%) and iridium (10%) and is kept at the International Bureau of Weights and Measures in Sèvres, France. It is disseminated by the calibration of national prototype kilograms, which are official copies of the international prototype of the kilogram. The main problems associated with this definition are well understood and can be summarised as:

- The international prototype can be damaged or even destroyed.
- Its mass is not well defined (it accumulates surface contaminants and is difficult to clean reproducibly).
- The international prototype ages in an ill-determined manner (its mass may have changed, by perhaps as much as 50 μg in the last 100 years).
- The national prototype kilograms have to be returned to BIPM every five years to have their mass values re-determined. This is time-consuming and carries a risk of damage whilst being transported.

This document reports on the present status of the various approaches concerned with providing a possible new definition of the kilogram.

2 OVERVIEW

2.1 CRITERIA FOR A NEW DEFINITION

As long ago as 1870, when James Clerk Maxwell [1] defined the well known requirement that physical units should not be founded on macroscopic quantities but on the properties of the “imperishable and unalterable molecules”, metrologists were called upon to consider the

possibilities of redefining the kilogram. Any new definition will have to satisfy certain basic requirements:

- i) It must be based on one or more fundamental physical constants, allowing the kilogram to be realised by many National Measurement Institutions (NMIs). This has three important benefits:
 - Ensures the future stability of the kilogram.
 - Allows international intercomparisons between realisations at the NMIs thereby giving a greater confidence in the reproducibility of the kilogram.
 - Provides scope for future improvement in the uncertainty with which the kilogram can be realised, by means of improved measurement of the relevant fundamental physical constants.
- ii) It must be consistent with the current definition. Before being accepted as such, a period of monitoring against the international prototype of the kilogram will have to take place. Practically, this will imply that a future definition must be capable of being realised to an uncertainty of 1 part in 10^8 .
- iii) It must be independently verified by at least two laboratories.

Other important considerations may be: practicality and cost to maintain; the path taken from the fundamental physical constants to the realisation; and the possible benefit to derived SI units dependent on mass.

2.2 DIFFERENT APPROACHES

Three possible approaches have been identified for further study, which I have designated the *Avogadro project*, the *Watt balance* and the *Ion counting method*. There are currently other approaches being pursued [2] but the Avogadro and Watt balance projects are the most advanced in terms of the progress made and the level of commitment by the various NMIs involved.

Visits have been made to three laboratories, identified as world-leaders in the scope of their research, to discuss the progress to date. They are:

Physikalisch-Technische Bundesanstalt¹, Germany; Avogadro and Ion counting projects
 Istituto di Metrologia “G. Colonnetti”², Italy; Avogadro project
 National Physical Laboratory, United Kingdom; Watt balance

The remainder of this report describes the backgrounds to these approaches, the progress made to date and the techniques and apparatus currently used. Section 3 discusses the Avogadro project, Section 4, the Watt balance and Section 5, the Ion counting method.

3 AVOGADRO PROJECT

3.1 BACKGROUND

One of the options is to relate the kilogram to an atomic mass. The kilogram would then be defined as the mass of a fixed number of atoms of a definite species. For this definition to be viable:

The mass of the individual atom expressed in the present-day unit of mass would have to be known with sufficient accuracy for the new mass scale to agree with the former one, and

It should be possible to state the number of atoms in a macroscopic volume of a substance.

These requirements amount to an accurate determination of the Avogadro constant N_A and of the relative nuclide masses

Physikalisch-Technische Bundesanstalt, D-38116 Braunschweig, Germany

² Istituto di Metrologia “G. Colonnetti”, CNR, I-10135, Torino, Italy

The relationship

$$1 \text{ kg} = 10^3 N_A u \quad \dots\dots\dots(1)$$

would serve as the defining equation.

where N_A is the Avogadro constant and is defined as *number of atoms in 0.012 kg of the carbon isotope ^{12}C , and thus the number of entities in a mole of substance*
 $u = m(^{12}\text{C})/12$ is the atomic unit of mass, to which the relative nuclide masses are referred, and $m(^{12}\text{C})$ the mass of one ^{12}C atom in kilograms

3.2 EXPERIMENTAL REALISATION

To realise this approach, a perfect single crystal is assumed (see section 3.3). For a single crystal artefact, whose molar mass M and volume V_0 of the unit cell (with n atoms) are known, the mass m of the crystal can be derived from a determination of its volume V if N_A is known:

$$m = (M/N_A) (V.n/V_0) \quad \dots\dots(2)$$

ie m = mass of a single atom multiplied by the number of atoms present

Re-arranging the above equation we get:

$$N_A = (M/\rho) / (V_0/n) \quad \dots\dots\dots(3)$$

ie N_A = molar volume V_m divided by atomic volume V_a

where ρ is the density of the artefact and is calculated from its mass m and volume V

This approach, therefore, is reduced to the problem of measuring N_A with a relative uncertainty of $1 \cdot 10^{-8}$.

3.3 SILICON SINGLE CRYSTAL

3.3. Silicon

To determine N_A with a very high accuracy, a practically perfect single crystal is required. Silicon single crystals have been chosen as they are commercially available (see section 3.11) in almost perfect structure and purity. Table 1 lists some of the physical properties of silicon.

Table 1 Properties of Silicon	
Atomic weight	28.085
Atomic number	14
Molar volume	12.059 cm ³ mol ⁻¹
Isotopes	²⁸ Si, ²⁹ Si, ³⁰ Si
Crystal structure	face-centred cubic
Electron structure	3s ² 3p ² (valency = 4) covalent bonding
Lattice spacing	$a_0 = 0.543\ 102\ \text{nm}$ $d_{220} = 0.192\ 015\ \text{nm}$
Atoms per unit cell	8

The crystal structure of silicon is face-centred cubic (fcc) with cell edge length a_0 and 8 atoms per fcc unit cell. To determine the unit cell volume V_0 , and hence the atomic volume V_a , the spacing of the (220) lattice planes d_{220} is measured. From simple co-ordinate geometry, the unit cell length a_0 is equal to $\sqrt{8}\ d_{220}$ and the atomic volume is calculated as:

$$V_a = \frac{a_0^3}{8} = \sqrt{8}\ d_{220}^3 \dots\dots\dots(4)$$

and equation (3) can be written:

$$N_A = (M/\rho) / \sqrt{8} d_{220}^3 \dots\dots\dots(5)$$

This equation suggests a direct approach to re-determining N_A , known as the *X-ray Crystal Density Method* because the lattice spacing is measured using x-ray interferometry (see section 3.10). From equation 3 it can be seen that N_A relates quantities on the macroscopic scale and the atomic scale; N_A is nothing but the ratio of the molar volume V_m (see section 3.5.2) and the atomic volume V_a , and the following quantities must be measured:

- i) Volume V_a occupied by a single silicon atom, derived from the knowledge of the structure and lattice spacing d_{220} of an almost perfect, highly pure silicon single crystal. These measurements therefore include precise determinations of the content of impurity atoms and self-point defects in the crystal structure (see section 3.12).
- ii) Macroscopic density ρ (see section 3.6) of the same crystal, determined from the measurement of an artefact's volume (see section 3.8) using optical interferometry techniques and its mass (see section 3.7) by conventional weighing methods.
- iii) Molar mass $M(\text{Si})$ determined from the measurement of the isotopic composition (see section 3.5) of the silicon crystal. Silicon has three stable isotopes ^{28}Si , ^{29}Si and ^{30}Si .

The values of $M(\text{Si})$, ρ and d_{220} are applicable only to the artefact on which they are determined and the assumption of uniformity is implicit; even if all values refer to the same crystal, they will be measured at different locations within the crystal. Therefore, only artefacts grown from a single crystal are suitable. Other important assumptions of the x-ray crystal density (XRCD) method are:

- All unit cells are cubic and contain 8 atoms; departures from 8 and cubic shapes are related to the presence of defects and impurities and must be corrected for their presence (see section 3.12).
- Molar mass $M(\text{Si})$ of silicon isotopes alone; vacancies and impurity atoms are not considered in $M(\text{Si})$ measurements but self-interstitials are.

$M(\text{Si})$ and ρ combine to give the molar volume V_m which is independent of isotopic composition.

3.3.2 Spheres

The silicon artefacts for the Avogadro project are manufactured as near-perfect spheres (see section 3.13). This represents the most convenient shape when determining volume, and a sphere is less likely to be damaged as it has no corners or edges. A silicon sphere with a mass of approximately 1 kg and density of $2\,300\text{ kg m}^{-3}$ will have a diameter of around 90 mm.

3.4 AVOGADRO CONSTANT

3.4.1 Measurement History

The concept of using x-ray techniques to measure N_A has been in evidence since the mid 1920's. However, the driving force for renewed interest came in 1965 with the design of the first x-ray interferometer by Bonse and Hart [3] and in the early 1970's with the development of the scanning x-ray interferometer (see section 3.10.3). This heralded the start of the XRCD approach to determining N_A .

National Bureau of Standards

It was at the National Bureau of Standards³ (NBS), now NIST in the USA, that this new approach was pioneered, aiming to achieve an uncertainty of less than part per million (ppm) in the measurement of N_A . The potential of scanning x-ray interferometers to give a sub-ppm value for the unit cell volume led to a re-examination of the remaining terms in equation (5) and led NBS to specify that the campaign for the re-determining of N_A should include:

A density scale based on solid artefacts. Previously, water had been used as a density standard but its uncertainty would be limited to approximately 6 ppm.

Absolute isotopic abundance measurements performed on the specific specimens used in

³ Now known as the National Institute of Standards and Technology (NIST), Gaithersburg, MD 20899, USA

the density determinations. Up till then, the assignment of molar masses to individual samples had been based on geochemical abundance averages

An initial attempt at a total characterisation of the silicon single crystals.

This programme of work led to the publication in 1974 [4] of a new value of N_A , determined completely independently at NBS, with an uncertainty of 1.2 ppm, with contributions from the density of 0.5 ppm and the molar mass 0.7 ppm.

Physikalisch-Technische Bundesanstalt

Following on from NBS's work, PTB in Germany embarked on a programme to improve the lattice spacing measurements through development of a series of scanning x-ray interferometers (see section 3.10.5). PTB is currently developing facilities to determine the molar mass of silicon single crystals, which will enable PTB to perform a completely independent measurement of N_A .

Institute for Reference Materials and Measurement

Since the mid 1980's the Institute for Reference Materials and Measurement⁴ (IRMM) in Belgium has embarked on a programme to determine the absolute isotopic abundances, required to determine the molar mass, through the use of mass spectroscopy. Since the initial work performed by NBS, the IRMM has been the only laboratory measuring the molar mass.

Istituto di Metrologia "G. Colonnetti"

IMGC in Italy has developed a scanning x-ray interferometer and has facilities to determine the density of silicon crystals, first by reference to solid volume standards and then through interferometric and mechanical contact measurements.

National Research Laboratory of Metrology

The National Research Laboratory of Metrology⁵ (NRLM) in Japan has firmly established a programme of work to determine the density of silicon crystals and has now completed development of a scanning x-ray interferometer.

⁴ Institute for Reference Materials and Measurement, European Commission, Joint Research Centre, B-2440 Geel, Belgium

⁵ National Research Laboratory of Metrology, Tsukuba, Ibaraki 305, Japan

Council for Scientific and Industrial Research

Since 1987 the Council for Scientific and Industrial Research⁶ (CSIRO) in Australia has developed the technology to manufacture spherical silicon artefacts to the exacting standards of the Avogadro project. CSIRO is soon to finish development of an optical interferometer which will enable them to determine the volume of these artefacts.

3.4.2 Progress

XRCD Method

The main requirement in providing a new definition of the kilogram by this method, is that N_A must be determined with a relative uncertainty of $1 \cdot 10^{-8}$ or better. The first reported value in the new era of the XRCD method was by NBS in 1974 [4], with a measurement uncertainty of $1.2 \cdot 10^{-6}$. The task, therefore, was to improve the measurement of N_A by two orders of magnitude - a huge undertaking! In practice, this requires the same order of improvement for the three main measured parameters given in equation 5: molar mass, density and lattice spacing.

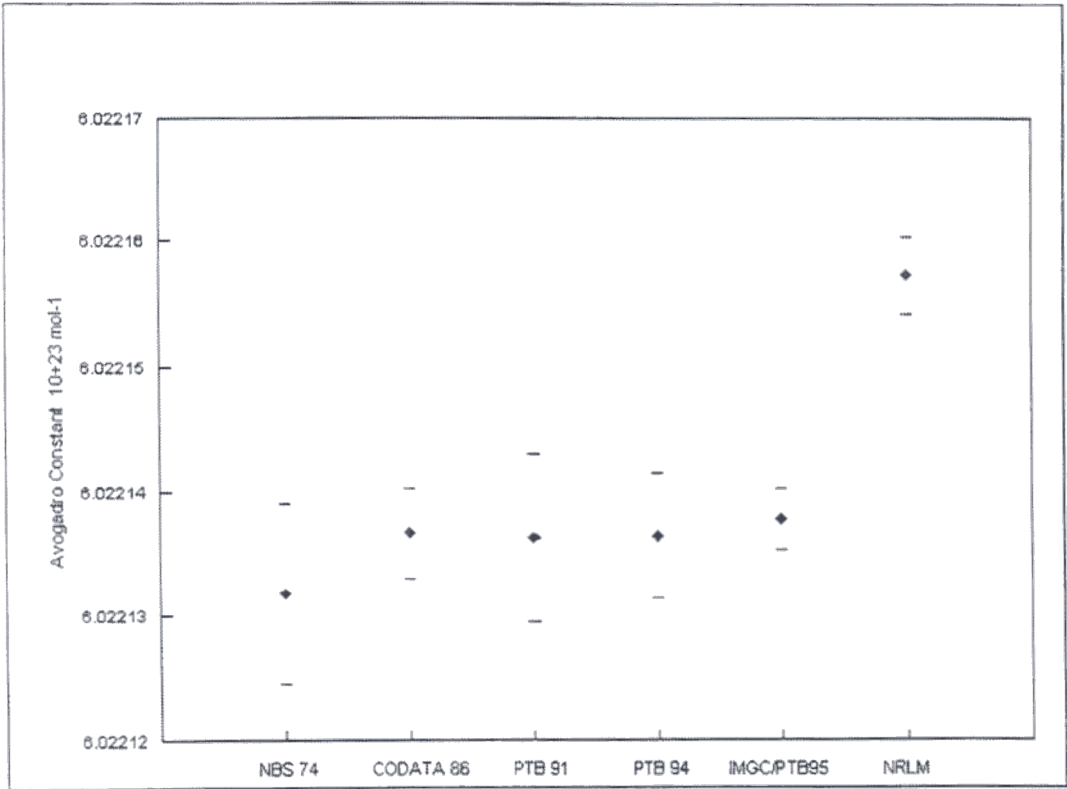
Since 1974, values have been reported by PTB [5] [6], in conjunction with IRMM who provide the molar mass measurements. The latest reported uncertainty, also being the lowest, was that determined by collaboration between IMGC and PTB in 1995 [7] of $4.2 \cdot 10^{-7}$. However, an up-to-date value would have an uncertainty approaching $1 \cdot 10^{-7}$ as the measurement of the molar mass (which provides the largest contribution to the uncertainty in N_A) can now be determined with an uncertainty of around $1 \cdot 10^{-7}$ (see section 3.5.3). This capability represents the current state of the Avogadro project.

Table 2 reports the results of measurements of the Avogadro constant since 1974, along with the latest reported value from CODATA Task Group on Fundamental Constants. This information is also shown in Graph 1. The column headed 'Crystal' has been included to identify the silicon single crystal on which the measurements were performed. This information has been included in other tables within this report.

⁶ CSIRO Division of Telecommunications and Industrial Physics, National Measurement Laboratory, Lindfield, NSW 2070, Australia

Table 2					
Values of the Avogadro Constant Determined by the XRCD Method					
Source	Date	Crystal	$N_A \cdot 10^{23} \text{ mol}^{-1}$	$10^{-6} U_{\text{rel}}$	$10^{-6} D^*$
NBS	1974	D1,D2,D3	6.022 131 8(73)	1.21	- 0.81
CODATA	1986	-	6.022 136 7(36)	0.59	-
PTB	1991	WASO 17	6.022 136 3(68)	1.13	- 0.07
PTB	1994	WASO 17	6.022 136 5(51)	0.85	- 0.03
IMGC / PTB	1995	WG,MO,W3,WP,CZ	6.022 137 9(25)	0.42	+0.02
NRLM	-	-	6.022 157 3(31)**	0.51	- 3.40
* Relative difference to CODATA 86					
** To be published					

Graph - Measurement History of Avogadro Constant



CODATA

The CODATA Task Group on Fundamental Constants was established in 1969 to provide a set of accurate values for the basic constants and conversion factors. New values of the fundamental constants are calculated from both 'indirect' and 'direct' methods and then adjusted on a least-squares basis; an indirect value for N_A is calculated from the relationships between the fundamental constants, a direct value from the XRCD method. The result is calculated using an appropriate weighting factor based on the respective uncertainties of the two methods, the XRCD method having the lower uncertainty. The indirect method of calculating N_A is based on the formula:

$$N_A = \frac{1}{2} R_H F \left(\frac{2e}{h} \right) \dots\dots\dots(6)$$

where R_H is the quantised Hall resistance
 F is the Faraday constant
 e is the elementary charge
 h is the Plank constant

The latest of these adjustments was carried out in 1986 [8] in which the molar volume obtained by NBS and the lattice parameter obtained by PTB were used as input quantities.

NRLM

The final value included in Table 2 has been determined by NRLM but has yet to be published. As can be seen, this is in very poor agreement with those calculated by NBS, PTB and IMGC, differing by some 3 ppm. This value has been calculated from density and lattice spacing measurements made by NRLM and the molar mass determined by the IRMM.

In an attempt to explain this discrepancy, a sample of a crystal belonging to PTB (supplied by Wacker-Chemitronic⁷) was sent to NRLM for measurement of its density and lattice spacing. The NRLM's measurements were in good agreement with those made by PTB. Thus, experimental error has been ruled out.

⁷ Wacker-Chemitronic GmbH, D-84479 Burghausen, Germany

The source of the discrepancy is now believed to lie in the presence of voids (possibly filled with hydrogen) formed during the manufacturing process. The presence of voids would cause a discrepancy in the density and, hence, molar volume of silicon. One of the main assumptions of the Avogadro approach is that the molar volume is the same for all silicon single crystals. A major obstacle in determining the source of the problem is that Shin-Etsu (see section 3.11), the manufacturer of silicon single crystals supplying the NRLM, will not disclose the techniques employed when growing the silicon.

Measurements at PTB made using infra-red spectroscopy (see section 3.12.3) to detect the presence of voids have so far failed to do so. However, infra-red spectroscopy may not be sufficiently sensitive to be able to detect these voids. The search for this discrepancy is now a major concern within the participating laboratories. A new technique, being pioneered at Harvard University, Massachusetts, may provide the solution to the problem. It should be possible to diffuse copper through a sample of silicon so that it fills any voids present. Mass spectrometry could then be used to detect and quantify the amount of copper retained in the crystal.

3.5 MOLAR MASS

3.5. Background

Since 1974 all measurements of the molar mass have been made at the IRMM using their heavily modified mass spectrometer (see section 3.5.3). However, PTB has now started developing a new technique based around prompt (η, γ) spectroscopy (see section 3.5.4). Both methods exploit the fact that molar masses of silicon's three stable isotopes $M(^i\text{Si})$ (where $i = 28, 29$ and 30) are known with much smaller relative uncertainties of around $2.5 \cdot 10^{-8}$ [9]. Measurement of the molar mass of naturally occurring silicon thus relies on determining the ratio of the isotopic abundances within the sample.

NOTE: To calculate the molar mass of the isotopes one does not need to have knowledge of N_A . By definition, the molar mass of the isotope ^{12}C is equal to 12 g exactly. Therefore, one needs only to determine the relative atomic masses of the isotopes with respect to ^{12}C , which can be done with the uncertainty stated.

The molar mass of naturally occurring silicon has now been determined with a relative uncertainty of $1.3 \cdot 10^{-7}$ [10] by the IRMM.

3.5.2 Molar Volume

Both the molar mass and density of silicon single crystals can vary significantly (by up to several parts in 10^5) between high-purity crystals grown by the same technique (see section 3.11). One of the basic assumptions of the XRCD method is that their quotient, the molar volume V_m , is the same for all crystals. Hence, it is this parameter which is usually reported when comparing the efforts of the laboratories to determine the molar mass. Table 3 reports some of the values of molar volume determined to date. This information is also shown in Graph 2. Table 4 reports values of the molar mass.

Table 3 Molar Volume Measurements on Silicon Single Crystals					
Source	Date	Crystal	Molar Volume $\text{cm}^3 \text{mol}^{-1}$	$10^{-6}U_{\text{rel}}$	$10^{-6}D^*$
NBS	1974	D1,D2,D3	12.059 042 7(90)	0.75	17.97
NBS	1987	D1,D2,D3	12.058 808(11)	0.94	- 1.49
IMGC	1988	Si2-FZ	12.058 843(29)	2.40	1.33
IMGC	1988	Si1-CZ	12.058 842(29)	2.40	1.33
PTB	1991	WASO (17.2,7.3,17.5)	12.058 822(13)	1.08	- 0.33
PTB	1994	WASO 17	12.058 823(9)	0.75	- 0.25
IMGC / PTB	1994	W3,WP, CZ	12.058 826(5)	0.42	-
NRLM	-	-	12.058 864(3)**	0.25	3.15
* Relative difference with respect to IMGC / PTB 1994					
** To be published					

The IMGC result determined in 1988 [11] provided convincing evidence that the molar volume is the same for all crystals. Si1-CZ and Si2-FZ are two crystals grown by two different techniques, namely the Czochralski and float-zone methods (see section 3.11.1) and have molar masses and densities which differ by approximately $1 \cdot 10^{-6}$ but their molar volumes were found to agree to better than $1 \cdot 10^{-7}$.

Within experimental uncertainty, values of molar volume published by PTB and IMGC have also established this assumption. This was the case until a preliminary value reported by the NRLM. However, this value is believed to be in error due to the presence of voids (see section 3.4.2) within the crystals grown by Shin-Etsu.

Graph 2 - Molar Volume Measurements given in Table 3

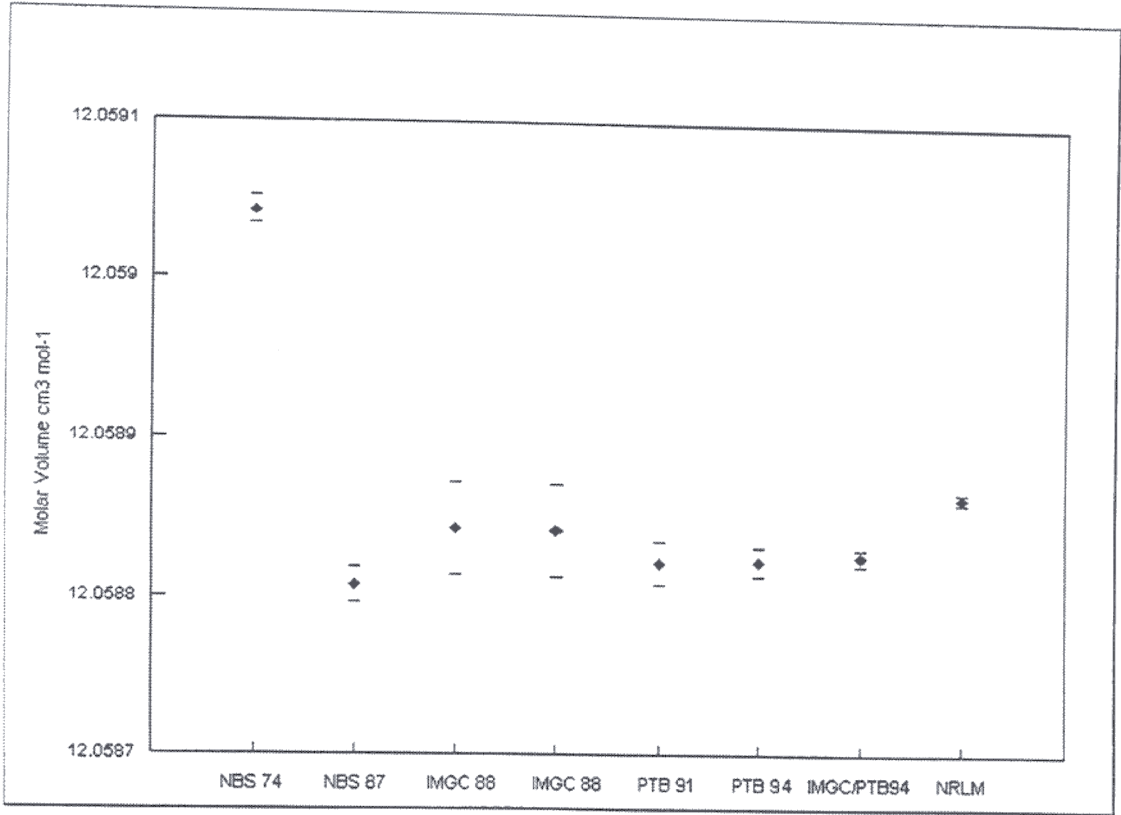


Table 4 Molar Mass Measurements on Silicon Single Crystals				
Source	Date	Crystal	Molar Mass g mol ⁻¹	10 ⁻⁷ U _{rel}
NBS	1974	SRM 990	28.085 532(21)	7.5
IRMM / IMGC	1988	Si2-FZ	28.085 476(65)	23.0
IRMM / IMGC	1988	Si1-CZ	28.085 441(65)	23.0
IRMM / PTB	1991	WASO 17.2	28.085 382(23)	8.2
IRMM / PTB	1994	WASO 17.2	28.085 383 1(89)	3.2
IRMM / IMGC	1993	WP	28.085 421 2(84)	3.0
IRMM / NRLM	1995	JAP	28.085 583 3(55)	2.0
IRMM / PTB	1996	WASO 17.2	28.085 384 2(35)	1.3

3.5.3 IRMM Mass Spectrometer

Background

The IRMM started work on its first mass spectrometer in 1980 and has been involved with collaborative research projects with PTB, IMGC and NRLM to obtain improved values of the molar mass of naturally occurring silicon; their first result was published in 1988 with a reported relative uncertainty of $2.3 \cdot 10^{-6}$, their latest value, published in 1996, has been improved to $1.3 \cdot 10^{-7}$ [10].

Principle

The molar masses of silicon's three stable isotopes are known with a much smaller relative uncertainty of approximately $2.5 \cdot 10^{-8}$. Thus the problem is reduced to determining the 'absolute' value of the abundancies of these isotopes. The molar mass $M(\text{Si})$ of silicon can then be expressed as:

$$M(\text{Si}) = \sum f_i M(^i\text{Si}) \quad .(7)$$

where f_i is the fractional abundance of isotope i
 $M(^iSi)$ is the molar mass of the isotope i

This equation can be expressed in terms of the abundance ratios R_{ij} measured relative to the abundance of one isotope j :

$$M(Si) = \frac{\sum f_i M(^iSi)}{\sum f_i} = \frac{\sum [f_i M(^iSi)]/f_j}{(\sum f_i)/f_j} = \frac{\sum R_{ij} M(^iSi)}{\sum R_{.j}} \dots\dots\dots(8)$$

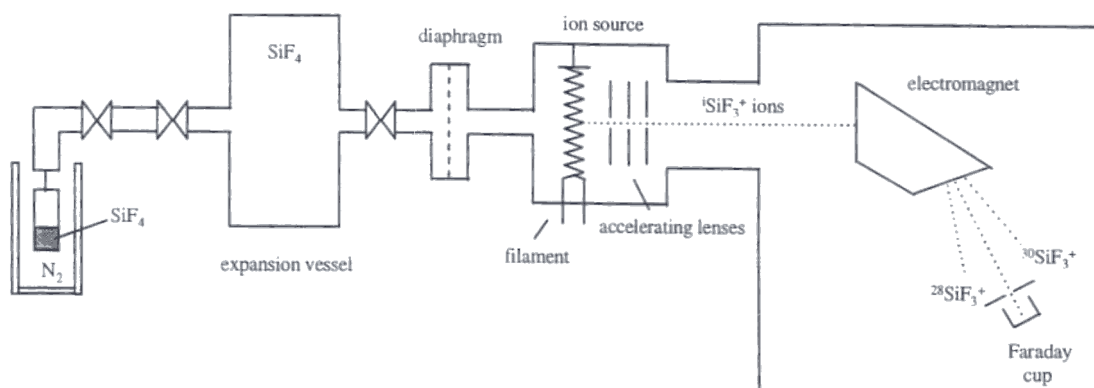
since $\sum f_i = 1$

To determine the abundance ratios, IRMM has developed a mass spectrometer [12] of unrivalled capability in gas isotope abundance measurements. The measurement method requires the conversion of silicon from a single crystal into gaseous silicon tetrafluoride SiF₄ [13], as the most precise measurements can be achieved on gases. In addition, synthetic silicon isotope mixtures (ie synthetic ratios of abundances approximating natural isotopic composition of silicon) are prepared. These mixtures are prepared using gravimetric weighing techniques from enriched isotope material. In this manner, mixtures of known isotopic composition can be used to calibrate the mass spectrometer.

Apparatus

Figure 1 is a schematic diagram of the IRMM Mass Spectrometer. The apparatus basically consists of an ion source, an electromagnet and detection system (Faraday cup). At the heart of the mass spectrometer is a heavily modified commercial mass spectrometer manufactured by Finnigan-MAT in Bremen, Germany.

Figure 1 - IRMM Mass Spectrometer (based on a diagram given in [12])



The inlet system comprises a vessel containing the SiF_4 which has been cooled to liquid nitrogen temperatures. SiF_4 gas is boiled-off into the expansion vessel before being allowed to pass through a diaphragm to the ion source, where its constituent molecules are ionised (ie $^{28}\text{SiF}_3^+$, $^{29}\text{SiF}_3^+$ and $^{30}\text{SiF}_3^+$). The ion beams are then accelerated towards the electromagnet, which then scans the ion beams over a single Faraday cup. Ion currents are measured for the ions $^{28}\text{SiF}_3^+$, $^{29}\text{SiF}_3^+$ and $^{30}\text{SiF}_3^+$ and are paired to obtain ion current ratios I_i / I_j . These ratios are proportional to R_{ij} of the corresponding fractional isotope abundance f_i / f_j . Scaling the conversion of ion current ratios into isotope abundance ratios R_{ij} (determining the proportionality factors) is accomplished by means of the synthetic isotope mixtures.

Progress

The abundance ratios can now be determined with a relative uncertainty of $3 \cdot 10^{-5}$ which leads to an uncertainty of around $1 \cdot 10^{-7}$ in the calculated molar mass. To achieve this present level of uncertainty the following sources of error have to be corrected for:

Gas adsorption

Adsorption of molecules by the walls of the expansion vessel will effect the isotopic composition of the SiF_4 gas. Its effects are most significant at the initial stages of a measurement, when the adsorption sites on the walls are free and adsorption faster.

Mass discrimination

Gas flows from the expansion vessel to the ion source through a molecular leak (diaphragm) which consists of a gold-foil (of approximate thickness $50\text{ }\mu\text{m}$) with 15 holes (each with an approximate diameter of $15\text{ }\mu\text{m}$). Gas effusion through the foil is assumed to be have characteristics of pure molecular flow as the pressure in the expansion vessel is around 1 Pa, which means that the mean-free path of molecules is around 0.01 m. Simple kinetic gas theory predicts that the flow-rate of the molecules under these conditions is inversely proportional to the square root of the molecular masses of the different species. As molecules containing lighter isotope effuse through the molecular leak at a higher rate, the gas in the expansion vessel becomes progressively enriched with heavier isotope. Thus, the desired 'initial' isotope ratio of the gas sample is obtained by the extrapolation to the time when the valve is first opened between the expansion vessel and the diaphragm.

Ionisation Probabilities

The ionisation probabilities can be regarded as the same for all isotopes of one element to much better than $1 \cdot 10^{-5}$ and hence a correction is not necessary.

Residual Effects

After corrections have been made for adsorption and mass discrimination effects there is still is a small systematic error observed when measuring the abundance ratios of the synthetic mixtures. This systematic error is quantified and applied as a correction to the measured abundance ratios.

Outlook

The preparation of synthetic mixtures is reaching the limits of present technology and a large investment will be required to advance this work further, a necessary step if the molar mass uncertainty is to be reduced below $1 \cdot 10^{-7}$. The IRMM are presently trying to procure the necessary funding for this next stage of development research.

3.5.4 PTB Prompt (η,γ) Spectrometry

Background

The measurement of the molar mass of silicon with a relative uncertainty better than $1 \cdot 10^{-7}$ represents the greatest technical problem within the Avogadro project at present. The IRMM has advanced mass spectrometry to this current level of uncertainty. However, PTB believes that to reduce the uncertainty to even lower levels will be extremely difficult using mass spectrometry and has therefore embarked on their own programme of work, using a new approach of prompt (η,γ) spectrometry [14]

Principle

The basis of this approach involves the capture of thermal neutrons (with an energy $E_n \leq 25 \text{ meV}$) by nuclei within the sample under investigation. After capturing a neutron, the nucleus is in an excited state and will lose energy to achieve its ground state. It does this through the emission of γ-rays and there can be many stages to the decay process. However, in this application, only γ-rays resulting from the direct transition of the nucleus to its ground state are considered. Analysis of the γ-rays is according to their energy and intensity; energies are used to identify all the nuclides present, whilst the intensity (ie number of counted γ-rays at a given energy) gives the relative abundances of the isotopes. The following equation is used to determine the isotopic abundances of natural silicon:

$$N(t, E_\gamma) = \frac{m N_A}{M} \sigma({}^A_ZX, E_n) \cdot I({}^A_ZX, E_\gamma) \cdot \eta(E_\gamma) \cdot \Omega \cdot \Phi_0(t) \quad t \dots\dots\dots(9)$$

where

- $N(t, E_\gamma)$ Number of detected events of a distinct γ-energy E_γ as a function of time t
- m Mass of a distinct isotope in the neutron beam
- N_A Avogadro constant
- M Molar mass of an isotope
- $\sigma({}^A_ZX, E_n)$ Capture cross section of the isotope A_ZX for the (η,γ) reaction at thermal neutron energy E_n
- $I({}^A_ZX, E_\gamma)$ Relative transmission probability of the isotope A_ZX with the γ-energy E_γ
- $\eta(E_\gamma)$ Relative efficiency of the high purity Germanium detector for the γ-energy E_γ

Ω	Solid angle
$\phi_0(t)$	Time dependence of the neutron flux
t	Life time

Apparatus

To perform on-line prompt (η, γ) analyses, one must have access to a nuclear reactor equipped with a neutron guide tube of known curvature for the selection of thermal neutrons. Until recently, these conditions were available at PTB but their reactor has now been closed down. Instead, PTB have booked a site to set-up their experiment at the Institut Max von Laue Paul Langevin (ILL) reactor at Grenoble, France at a cost of £25k per year. This facility provides the greatest neutron flux of any reactor in the world, being 5 000 times greater than that at PTB and around 1 000 greater than that of nuclear power stations. This has resulted in many more γ -rays being detected in each peak (typically 10^{15}) of the spectrum.

At Grenoble, the neutron guide tube has a length of 110 m, a radius of curvature of 28 km and an internal surface finish comparable to that of best optical components. A pure chromatic beam of thermal neutrons (with a wavelength λ of approximately 1.8 Å) emerges from its end where the silicon sample is placed. PTB has five, highly-pure Germanium detectors to provide detection of the γ -rays. The cost of a single detector is around £150k.

Progress

Since the project was started two years ago the following results have been achieved:

- i) Identification of all the isotopes (silicon and impurities) present in silicon samples of different isotopic enrichments.
- ii) Measurement of the atomic mass differences of the silicon isotopes. This has been achieved with a relative standard uncertainty of a few parts in 10^{10} (PTB believe ultimately a few parts in 10^{13} will be achievable).

The final step will be to determine the isotopic abundances of silicon. However, to achieve an uncertainty of $1 \cdot 10^{-7}$ in the molar mass, will require the thermal neutron capture cross-section, for each isotope, to be known with a relative uncertainty of $1 \cdot 10^{-5}$, an order of magnitude better

than presently known. PTB aims to determine these cross-sections by direct comparison against highly enriched Uranium-235 and Plutonium-239.

3.6 DENSITY

3.6. Background

The density of silicon artefacts can be measured either directly by mass and volume measurements or by comparison with a reference standard. In the direct approach the volume is determined through a combination of interferometric and mechanical contact measurements (see section 3.8.2).

The comparison with a standard is usually done by hydrostatic weighing, in which the artefact is immersed in a liquid of density ρ_{liq} and the buoyancy effect of the liquid on the artefact, proportional to its volume V , is measured from the apparent loss of mass according to the relation

$$\rho_{liq} V = m - m_a \quad \dots(10)$$

where m is the mass of the artefact
 m_a is the mass equilibrating the artefact immersed in the liquid

If the reference is the liquid, the volume is computed directly from equation 10; if the reference is a solid standard (as in most cases) the volume is obtained by comparing buoyancy forces.

3.6.2 Progress

Table 5 reports the progress of density determinations of silicon artefacts. The NRLM has now measured the density with a relative uncertainty of $1 \cdot 10^{-7}$ [15] which represents a combination of mass and volume measurements. In this case, the volume was determined by interferometric methods. This direct approach has the potential to achieve the lowest uncertainties, as the volume standards used when performing hydrostatic weighings, have their volumes determined by the

same interferometric apparatus.

Section 3.7 gives details of the mass measurement of silicon artefacts, whilst Section 3.8 gives details of the volume measurements.

Table 5 Density Measurements on Silicon Artefacts					
Source	Date	Crystal	Density g cm ⁻³	10 ⁻⁷ U _{rel}	Technique
NBS	1974	D3	2.329 000 3(22)	10.4	hydrostatic
IMGC	1988	Si2-FZ	2.329 035 6(14)	6.0	interferometric
IMGC	1988	Si1-CZ	2.329 033 1(18)	7.7	hydrostatic
PTB	1991	WASO 17.3,17.5	2.329 031 9(18)	7.7	hydrostatic
IMGC	1993	WP	2.329 033 81(38)	1.6	interferometric
IMGC	1995	Si3	2.329 083 50(36)	1.5	interferometric
NRLM	1995	S4	2.329 040 40(24)	1.0	interferometric
NRLM	1995	S5	2.329 040 60(25)	1.0	interferometric

3.7 MASS

3.7.1 Background

The most accurate method of determining the density of a silicon artefact is by direct measurement of its mass and volume. Ultimately, the mass will have to be determined with a relative uncertainty of $1 \cdot 10^{-8}$ and, as the artefacts have a nominal mass of 1 kg, this would mean with an uncertainty not exceeding 10 µg. The mass value of a silicon artefact can be determined by comparison with stainless steel standards on a balance used as a comparator.

PTB, IMGC and NRLM have all developed balances capable of determining the mass of silicon artefacts. Commercially available 1 kg balances cannot accommodate the silicon artefacts due to

their relatively large volume compared to that of stainless steel weights of the same nominal mass, which the balances are designed to accommodate.

Weighing Environment

To date, all mass measurements have been performed in air at atmospheric pressure. The NRLM balance (see section 3.7.4) has the capability of being evacuated but has not been used in this mode. The main disadvantage of this approach is the large buoyancy correction that has to be applied due to the volume difference between the stainless steel standards and the silicon artefacts. The measurement of the air density will be the limiting factor on the uncertainty achieved.

Both PTB and NRLM determine the air density by monitoring the mass difference between two stainless steel artefacts that have the same nominal mass and surface area but different volumes. IMGC are reliant on measuring the ambient conditions at the time of the weighing and using the formula [16] recommended by the Bureau International des Poids et Mesures (BIPM) to calculate the air density. Although the use of air density artefacts is potentially the best method (the uncertainty of the BIPM equation is 1 part in 10^4) the volume difference of the artefacts must be as large as possible and their mass sufficiently stable.

The present artefacts do not meet either of these requirements. In a recent intercomparison between PTB, NRLM and IMGC [17], in which the mass values of four silicon artefacts were determined by each laboratory, the uncertainties reported by PTB and NRLM ranged from 90 μg to 110 μg but the agreement between the mass values was as poor as 200 μg . The source of the discrepancy was not understood and the adsorption or de-sorption of contaminants was put forward as a possible contributing factor. A further possibility is the instability of the oxide layer which forms on the artefacts (see section 3.9) after their manufacture. This layer may be porous and affect the mass stability of the artefacts as the ambient conditions change or foreign matter is accumulated.

Weighing the spheres in a vacuum would negate the necessity for a buoyancy correction but it is not understood what effect, if any, subsequent cycling of the artefacts in and out of an evacuated environment would have on them.

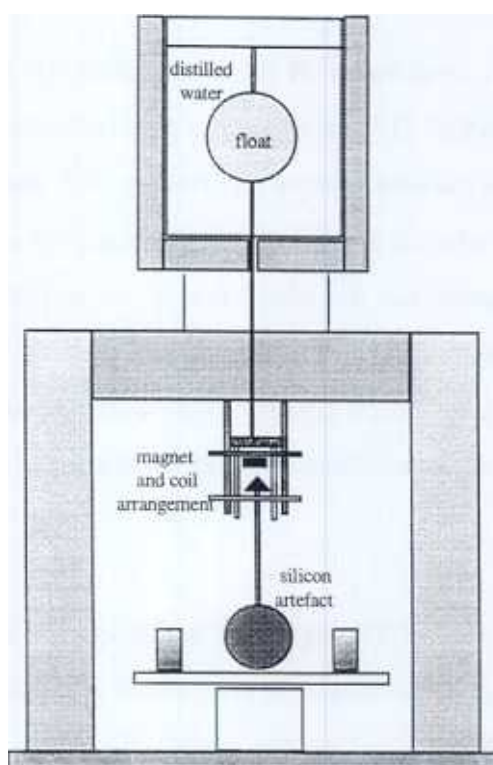
3.7.2 Mass Measurement at PTB

Balance

Figure 2 is a schematic diagram of the 1 kg mass comparator [18] developed by PTB to determine the mass of silicon artefacts. A hollow float is suspended in distilled water and gives a buoyancy effect of 1 kg. The weighing pan is connected to the flotation mechanism via a magnet and coil, whilst an optical sensor maintains the vertical alignment of the pan by providing feedback to the coil. The geometry of the magnet and coil has been arranged so that the horizontal position of the weighing pan is always maintained.

The apparatus cannot be evacuated due to the floatation chamber. Instead, the weighings are performed in a hermetically sealed environment. The weight-exchanger features six positions allowing the comparison of a silicon artefact with a mass standard whilst the air density is determined using the two artefacts. This balance was first developed in 1985 and since then has undergone several modifications.

Figure 2 - PTB 1 kg Mass Comparator



Performance

A symmetrical weighing scheme minimises the inherent instability of the float arrangement and a standard deviation as low as 2 µg can be obtained. Uncertainties in the mass value of a silicon artefact have been calculated as 120 µg, if the air density is calculated using the BIPM formula, and 90 µg, if the air density artefacts are used. However, PTB's target uncertainty is 15 µg.

A significant problem is the stability of the air density artefacts. Their 'true' mass difference has to be quantified prior to using the artefacts to determine the air density and has to be determined by weighing the artefacts in vacuum, since in air, any measured mass difference would be due to the air buoyancy. Repeated weighing in vacuum, whilst exposing the artefacts to air in between, led to a relatively poor agreement in the 'true' mass difference giving rise to an uncertainty of around 10 µg. PTB had hoped for around 3 µg which would enable the air density to be measured with a relative uncertainty of $3 \cdot 10^{-5}$ and would lead to an uncertainty of 15 µg when determining the mass of a silicon artefact.

It would seem unlikely that this level of performance could be achieved with the present artefacts, which have a volume difference of only 80 cm³. This is constrained by the use of a commercial balance (a Mettler HK1000MC which has been placed within a chamber which can be evacuated) to determine the true mass difference of the artefacts.

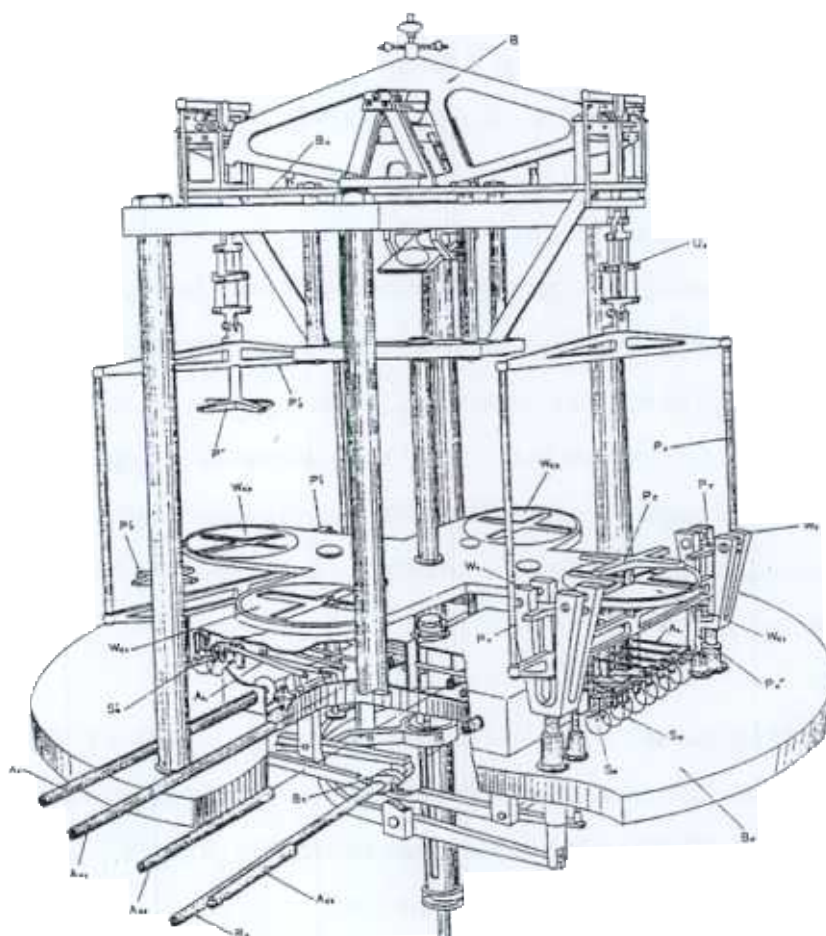
3.7.3 Mass Measurement at IMG

The 1 kg balance used to determine the mass of silicon artefacts is that used on their 1 kg hydrostatic weighing apparatus and is described in section 3.8.5.

3.7.4 Mass Measurement at NRLM

Figure 3 is a schematic diagram of the NRLM-2 primary balance [19]. It was developed in 1984, primarily for the comparison of platinum-iridium and stainless steel artefacts, and incorporates a 'built in' pair of air density artefacts. It is housed in an hermetically sealed chamber which is capable of being evacuated to 0.7 Pa. It is equipped with large weighing pans making it ideally suited to the measurement of the silicon artefacts.

Figure 3 - NRLM kg Mass Comparator (taken from [19])



3.8 VOLUME MEASUREMENT

3.8.1 Background

A silicon sphere with a nominal mass of 1 kg will have an approximate diameter of 9 cm and corresponding volume of 380 cm³. To determine N_A with a relative uncertainty of $1 \cdot 10^8$ will require the volume to be determined with the same uncertainty. The two methods which have been used to determine the volume are interferometric / roundness and hydrostatic weighing.

3.8.2 Interferometric and Roundness Measurements

Measurement of a sphere's volume is determined either through a combination of interferometric and mechanical contact roundness measurements or through interferometric measurements only. In either case, optical interferometry is used to determine diameter by placing a sphere within an etalon. To achieve an uncertainty of $1 \cdot 10^{-8}$ in the volume, the diameter will have to be determined with a relative uncertainty of $3 \cdot 10^{-9}$ (i.e. 0.3 nm). Furthermore, the measured diameter must be corrected for the phase-shift of reflected light from the oxides that exist on a sphere's surface. The thickness of these oxide layers is determined by ellipsometry (see section 3.9). The lowest uncertainty achieved in the volume measurement using interferometric methods is $8.9 \cdot 10^{-8}$ [15] by the NRLM.

3.8.3 Hydrostatic weighings

Measurement of a sphere's volume is determined by comparison with one or more reference volumes in a suitable liquid. The reference volumes are themselves near-perfect spheres usually manufactured from either Zerodur or silicon. This method does not have the potential accuracy of the interferometry / roundness measurements as a reference sphere's volume has itself to be determined by that method. The lowest uncertainty of volume achieved by hydrostatic weighing methods is $6.7 \cdot 10^{-7}$ [17] at PTB.

3.8.4 IMGC Interferometric Apparatus

Background

A sphere's volume is determined through a combination of interferometric and mechanical contact roundness measurements. Geometrical considerations [20] have shown that the error in the volume of a near perfect sphere having a diameter equal to the mean of diameters over all directions, is less than 1 part in 10^{10} . To determine the mean diameter a laser interferometer is used to measure a reference diameter and then roundness profiles are made over 18 meridians passing through this diameter. This process is repeated for another diameter orthogonal to the first. For each meridian, the least squares circle is determined and its diameter calculated from the measured reference diameter and the deviation of the least squares circle from this diameter. The mean diameter over all the meridian planes is taken as representing the equivalent sphere diameter.

A simple calculation of the volume of the sphere then follows.

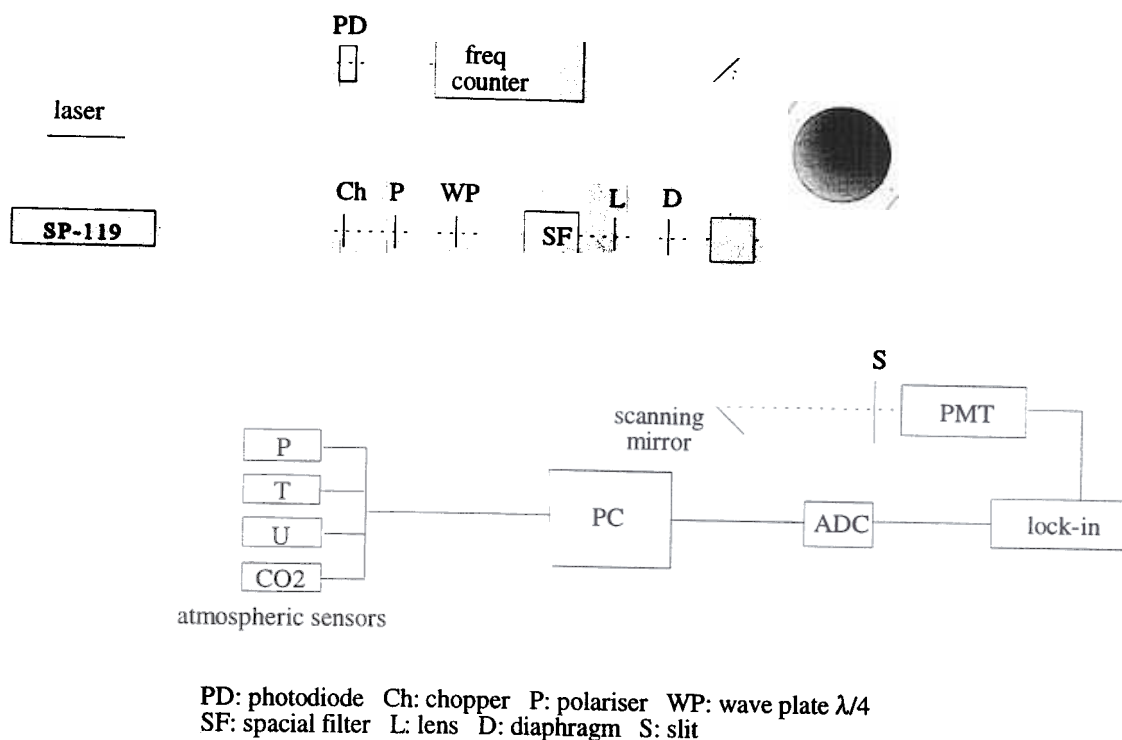
Interferometer

IMGC developed its first interferometer for the measurement of diameter in 1981 and was used to determine the volume of near perfect spheres manufactured from Zerodur. These spheres were used as volume reference standards on their hydrostatic apparatus (see section 3.8.5).

The present day interferometer [21], shown in Figure 4, is based on a Saunders type geometry where a sphere is placed between two parallel etalon plates of accurately known separation. A diameter is obtained by measuring the two sphere-etalon gaps and subtracting their sum from the length of the etalon. The interferometer is capable of measuring the diameter with an uncertainty of ± 3 nm, which requires the fractional order of interference to be measured to around 1/100 th of a fringe. Combining these results with those of mechanical roundness measurements the IMGC is able to determine the volume of a sphere with a relative uncertainty approaching $1 \cdot 10^{-7}$, which represents an improvement of an order of magnitude compared with the measurement capability at IMGC 10 years ago.

Whilst the interferometer is not in an enclosure, the laboratory is 18 m below ground level and has chilled water circulating in its walls, giving very low temperature gradients of around 10 mK across the room. This is an important contributing factor to achieving the present-day uncertainties. Vibration is minimised by mounting the interferometer on a pneumatic table placed directly onto the concrete floor.

Figure 4 - IMGC Interferometer (based on a diagram given in [21])



The main features of the interferometer are:

A single-mode laser of wavelength λ is used, requiring preliminary measurement of the diameter to within $\pm \lambda/4$ by independent means.

The same optical configuration is used to measure both the etalon length and the gaps with a sphere in the etalon. This is achieved through use of a point-source, as opposed to an extended collimated one, typical for a Saunders type interferometer. A benefit from this approach is that the etalon length can be determined at exactly the same point as the gaps are measured and in the same measurement cycle. To determine the etalon's length, a sphere is raised by means of a simple mechanism and the light beam travels through a hole in the lifting mechanism.

Calculation of the fringe fraction is by angular scanning and photoelectric detection of the fringes. A mirror is used to scan the resultant fringe pattern (Newton's rings) across a slit mounted in front of a photomultiplier tube. The distribution intensity of the fringe pattern is recorded and spatially digitised for analysis. The fringe fraction at the centre of the

pattern is determined by comparing its intensity with that of the observed minima and maxima. Scanning the fringe pattern avoids having to physically move the etalon when determining the fringe fraction. A mechanical chopper serves to give the measured intensity a datum-base corresponding to exterior/background illumination.

Note: As there exists a 180° phaseshift between the two combined reflected beams, a maximum will be observed when the separation between the beams is a half number of wavelengths and a minimum when the separation is a whole number of wavelengths.

Planned Improvements

Despite the laboratory's impressive temperature control, stability of a sphere's temperature is the largest contributing factor in the overall uncertainty. Planned future improvements to the apparatus will be to mount the interferometer either in a temperature enclosure (similar to the interferometer being developed at PTB) or in a vacuum enclosure (as at NRLM). Unwanted temperature fluctuations due to the presence of the operator will be removed by automating the system. This will also lead to a reduction in the time to complete a measurement cycle. With these improvements IMGC hopes to limit temperature gradients to 1 mK and achieve a relative uncertainty of around $3 \sim 5 \cdot 10^{-8}$ in the volume measurement.

Mechanical Contact Measurements

A Talyrond 30 mechanical contact gauge [22] is used to measure the profile of an artefact. Custom built control software allows the machine to sample many more points than in its original format. The Talyrond is mounted on a hydraulically damped optical table and with these modifications is capable of measuring displacements with an uncertainty of $\pm 1\text{--}2$ nm.

An advantage of combining interferometric and mechanical contact measurements over that adopted by NRLM, who determine the volume directly by averaging over 70 diameters measured interferometrically, is that many more points on the spheres surface are sampled (in total 6 480 for each set of 18 meridians)

For each measured meridian, the compensation of spindle error is made using a multi-stepping technique. A sphere is rotated through 10 equi-spaced steps and at each step, the profile is measured and averaged over 4 consecutive runs. The displacement of the Talyrond is calibrated

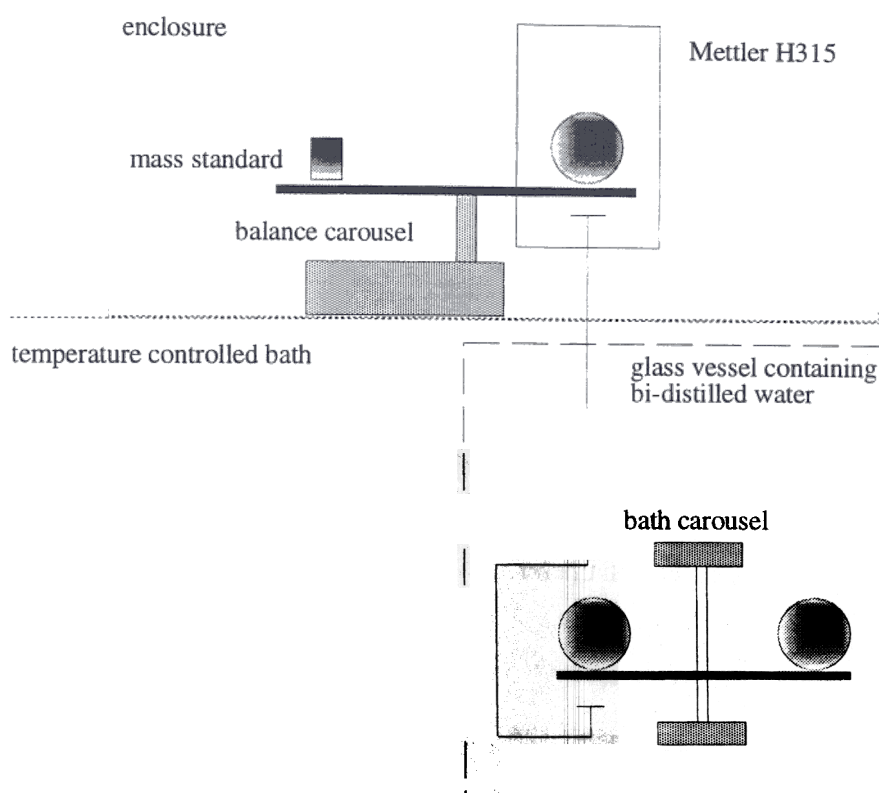
using a piezo-capacitive translator (QueensGate DPT) which in turn is calibrated using an interferometer to an accuracy of ± 1 nm.

3.8.5 IMGC Hydrostatic Weighing Apparatus

1 kg Apparatus

The 1 kg hydrostatic weighing apparatus [23], used for determining both the mass and volume of the silicon spheres, is shown in Figure 5. It consists of a Mettler H315 balance, mounted in a temperature enclosure, suspended over a temperature controlled water bath. It has been fully automated and is operated from a PC.

Figure 5 - IMGC 1 kg Hydrostatic Weighing Apparatus



The balance has been extensively modified with a beam restoring servo system and optical sensing circuit incorporating a four-quadrant split photo-diode. Resolution of this balance is now around $1 \mu\text{g}$ and is capable of achieving a standard deviation of $10 \mu\text{g}$ for a weighing scheme in air. The

weight-exchanger mechanism consists of two devices, one for weighings in air and one for the weighings in water. Both devices can hold up to six objects.

Measurement of the mass is achieved by direct comparison against stainless steel standards. The air density is calculated from measurement of the ambient conditions at the time of weighing. Temperature stability within the enclosure is relatively poor, with gradients of around 100 mK.

The volume is determined by weighing the sphere against a reference volume standard whilst immersed in pure water. Temperature stability of the water is good, with typical gradients of around 2 mK. IMGC have a total of six reference spheres, three manufactured from Zerodur and three from silicon. The best measurement capability of the apparatus is around $7 \cdot 10^{-7}$.

100 g Apparatus

IMGC has a 100 g hydrostatic weighing apparatus [24] which is identical in operation to their 1 kg apparatus. It has recently been used for a study into the effect of silicon oxide and sub-surface damage layers on the density of silicon [25].

3.8.6 PTB Interferometer

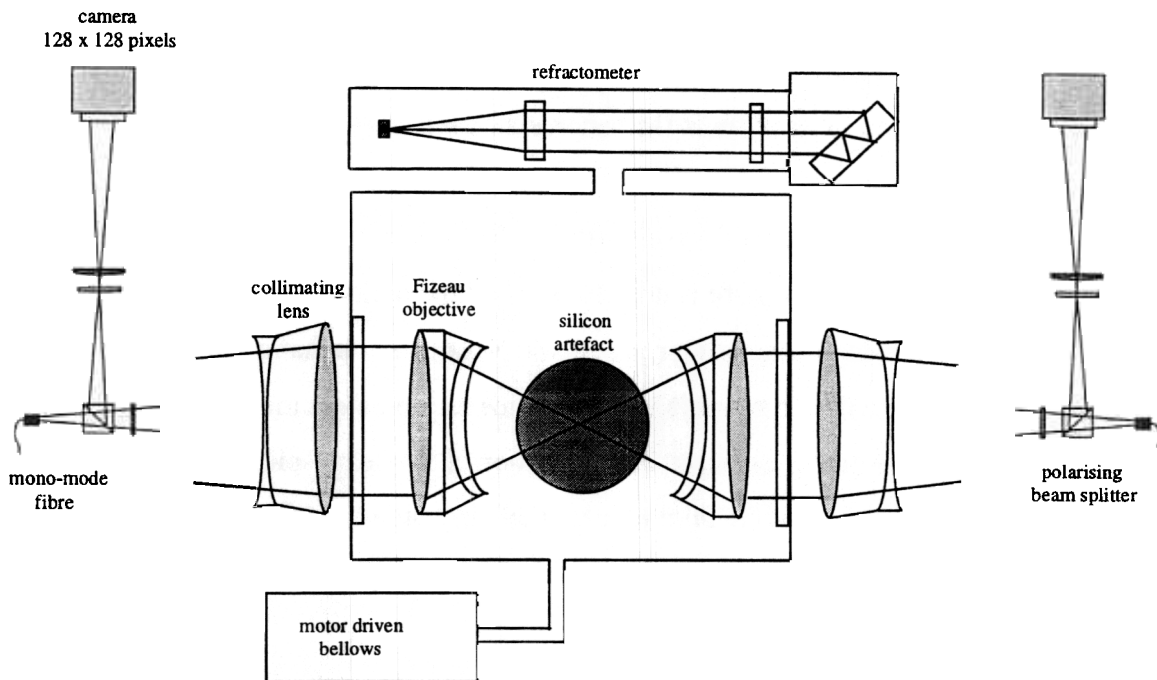
Background

PTB is currently in the final stages of development of a novel interferometer which will be used to determine the diameter of silicon spheres. This apparatus represents a departure from the interferometers at IMGC and NRLM, which are based on a Saunders type geometry and use plane wavefronts to determine the sphere diameter.

Interferometer

Figure 6 shows the PTB interferometer [26]. The etalon consists of two spherical reference surfaces with the sphere to be measured placed centrally between these surfaces. As a result, the form of the measuring wave is adapted to the surface being measured. This means that not only the one diameter on the optical axis can be evaluated, but many are obtained (around 16 400), corresponding to the aperture angle of the optical system (60°) and the number of discrete photodiodes in the electronic camera matrix. A benefit of being able to measure a large number of diameters is that mechanical contact measurements do not need to be made.

Figure 6 - PTB Interferometer (based on a diagram given in [26])



Operation

When determining diameters two configurations are measured. The first is of the empty etalon, which has a spacing of around 150 mm. Measurements can be made from either side, with the other beam interrupted. In the second configuration, the sphere is placed inside the etalon, and the gaps are measured.

The reference surfaces are adjusted to give less than one optical order of interference between themselves and the sphere. Consequently, no fringes are observed and one must have a means of determining the order of interference. PTB has developed a phase-stepping algorithm, whereby the 90° phase steps required are obtained by changing the optical path length (OPL). To achieve this, the refractive index of the air in the interferometer can be varied by changing the air pressure in the chamber. Pressure is controlled by means of a refractometer and computer controlled motor-driven bellows. For a measurement, the pressure is changed in four equal steps. The magnitude of each step depends on the separation of the reflecting surfaces and is around 8.5 mbar when measuring the gaps.

A sphere can be rotated around two axes, using motors with angle encoders, in a controlled

manner. In total, thirteen positions are required to cover the whole surface. Accurate positioning of the sphere within the etalon is achieved using kinematic mounts. To measure the empty etalon, the sphere is lifted, and the optical beam passes through a hole in the lifting device. Design of kinematic mounts/lifting mechanism is critical and must ensure that the forces due to the weight of the sphere on the etalon remain unchanged between these two positions and that no deformation of the etalon takes place at the nanometre level.

An Iodine stabilised He-Ne laser (of wavelength $\lambda = 633 \text{ nm}$) is mounted on a separate optical bench and a mono-mode optical fibre is used to transmit the light to the etalon. The beam then passes through a polarising beam-splitter, a $\lambda/4$ wave-plate, a collimating lens and the Fizeau objective. The combined reflected beam follows the same return path until deflected by the beam splitter where it is imaged onto the camera. A combination of the beam splitter and a wedge angle of 6° on the end of the mono-mode fibre ensures that very little light is reflected back into the laser. Cost of the two Fizeau objectives is around £15k.

The temperature within the chamber is stabilised to within a few mK. Temperature controlled water is ducted around the chamber's walls and internal copper fins act as heat sinks. A PRT is used as a reference thermometer, with differences measured by thermocouples placed around the chamber. Thermocouples are not a significant heat source.

Development Stages

The interferometer has been designed with the aim of achieving an uncertainty of $\pm 0.3 \text{ nm}$ in the diameter measurement. For a silicon sphere, with a diameter of 90 mm, this will lead to a relative uncertainty in the volume of $1 \cdot 10^{-8}$. To date, evaluation of the interferometer has been carried out using a non-transparent sphere made of adsorbing filter glass. Development stages have been:

- i) Sphere and reference surfaces adjusted so that less than one fringe appears in the field of view.
- ii) Variation of the refractive index of air required to change the OPL by one integer interference order was measured. Basically determined by observing when the intensity difference between the two interference patterns disappears.

- iii) Next, data of a sequence of five interference patterns, each differing by a phase-step of $\lambda/4$ were obtained. After evaluation of the first group of images 1..4 and then the second group 2..5, the value of the actual phase step width can be derived from the phase difference of the two groups. When this difference, for each pixel, is plotted against the phase obtained for the first group, a characteristic curve is observed if there is a deviation from the exact phase step width. The observed standard deviation is a measure of the accuracy of the interference evaluation and was measured as 0.1 nm.
- iv) Reproducibility has been evaluated. For a typical adjustment of the interferometer, the distribution of the evaluated phase (ie fringe fraction for each pixel) varies only within half an interference order. This corresponds to the variation of distances between the surface of the sphere and the spherical reference surfaces. The difference between two corrected phase distributions measured for slightly different adjustments was evaluated and found to be less than 2 nm. This result was disappointing and is an order of magnitude greater than the required uncertainty.
- v) Finally, in order to determine the diameter from the topography of the sphere and reference surface, the sphericity of the reference surfaces will have to be evaluated. This will be achieved using a multi-stepping technique similar to that employed for mechanical contact roundness measurements.

Modifications

PTB believe the reason for the relatively poor reproducibility is due to the effect that changing the air pressure has on the Fizeau objectives. Each objective consists of five lenses with air gaps in between. When the pressure is changed, the pressure between the lenses does not change at the same rate and causes distortion. PTB asked Zeiss, the manufacturer of the objectives, to drill small holes in the lenses but this proved insufficient to overcome the problem. A further contributing factor may have been the change from differential micrometer screws (used for lens adjustment) to piezo screws, which can be operated remotely and do not require the removal of the chamber lid for each adjustment. Unfortunately, the piezo screws do not hold the lenses as rigidly as former ones and the stability against pressure changes is not as good.

As a result, PTB have abandoned the pressure scanning method as a means to change the OPL.

Instead, a laser diode will be used to scan the wavelength. A frequency range of 4 ~ 6 GHz is required to change the OPL by one optical order for the gaps.

3.8.7 PTB Hydrostatic Weighing Apparatus

Background

To date, volume measurements at PTB have been performed with their 1 kg hydrostatic weighing apparatus [27]. The volume of a silicon sphere is determined by comparing it with the mean volume of two reference standards, whilst immersed within a liquid. A relative uncertainty of 1.5×10^{-6} can be obtained and originates mainly from the uncertainties in the volume standards. PTB also have an apparatus employing a flotation method to compare the densities of silicon artefacts. Density differences have been measured with a relative uncertainty of $1 \cdot 10^{-7}$.

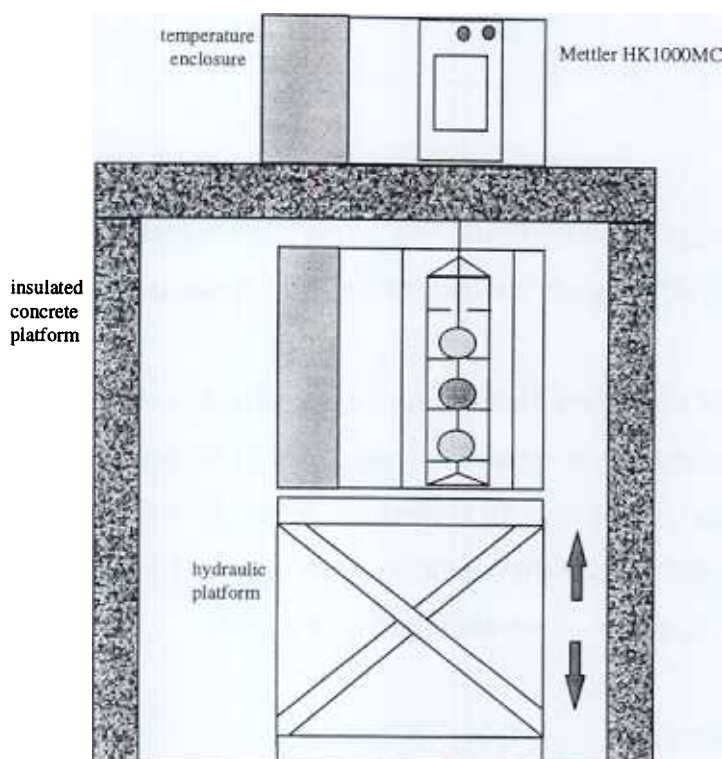
1 kg Hydrostatic Weighing Apparatus

Figure 7 shows the basic layout of the apparatus. It consists of a Mettler HK1000MC balance mounted over a Tamson TMV 70 temperature controlled bath. The silicon sphere and standards are immersed within the inner vessel supported on a cradle with three weighing positions. With the aid of motor-driven manipulators the artefacts can be alternately lowered on to a suspension frame which is directly connected to the balance.

PTB's reference volumes are near-perfect spheres which have been manufactured from Zerodur. Their volumes have been determined by comparison with artefacts which, in turn, have had their volumes determined by interferometric methods. The relative uncertainty in their volume is 10^{-6} .

The buoyant liquid used is an organic oil ($C_{15}H_{32}$), chosen for its low surface tension, high solubility for air (which prevents the formation of bubbles on the immersed bodies) and low thermal expansion. However, the density of the oil is only 0.75 g cm^{-3} . A higher density fluoro-carbon oil (FC40) has been used but its compressibility was too high, resulting in a relatively large density gradient. Temperature gradients within the inner vessel are typically 0.2 mK.

Figure 7 - PTB 1 kg Hydrostatic Weighing Apparatus



Flotation Apparatus

The PTB flotation apparatus [28] is used to compare the densities of small samples of silicon with a relative uncertainty of $1 \cdot 10^{-7}$. It has been used to check the homogeneity of silicon ingots from which spheres for the Avogadro project have been manufactured.

The flotation method involves observing the equilibrium of the gravitational force and the buoyant force acting on a wholly immersed solid, which then neither rises or sinks in a liquid, since the density of the liquid becomes equal to that of the solid.

Description

The apparatus consists of a hermetically sealed glass vessel which is filled with the flotation liquid; a mixture of 1,2,3-tribromopropane (of approximate density 2.41 g cm^{-3}) and 1,2-dibromoethane (2.18 g cm^{-3}). The ratio of the liquids is adjusted until the silicon sample is in

equilibrium with the mixture. This vessel is connected to a second 'header' vessel, the height of which can be varied. In this manner, the density of the liquid can be varied for each sample until equilibrium is achieved. The relative density between the samples is then given by:

$$\frac{\Delta\rho}{\rho_{Si}} = C (P_2 - P_1) \dots\dots\dots(11)$$

where P_x is the pressure for equilibrium of the two samples
 C is the difference in compressibility of the liquid and silicon

The samples are placed within two Teflon cages which prevent them moving vertically by more than ± 5 mm. Each sample can be arrested independently whilst the other is allowed to float. A sample's movement (± 0.001 mm in 10 seconds) is detected with a cathetometer. Pressure is controlled by changing the height of the header vessel to within ± 1 mm over a range of 500 mm. The temperature of the liquid is controlled to within ± 0.1 mK.

3.8.8 NRLM Interferometer

Background

NRLM have developed a scanning optical interferometer [15] to determine the diameter of a sphere in vacuum. To determine the mean diameter, 70 individual diameter measurements are made for a sphere. The mean diameter is then calculated by fitting the measured diameters to a series of spherical harmonics [29]. A relative uncertainty in the volume measurement of $8.9 \cdot 10^{-8}$ has been reported [15].

Interferometer

The configuration of the interferometer is similar to that at IMGC; based on an etalon used in a Saunders type geometry. A sphere is mounted on an independent platform within the etalon. The etalon itself is mounted on a translation stage of a monolithic flexure hinge mechanism so that the etalon can be scanned against the sphere. A frequency-stabilised He-Ne laser is used as the source.

Operation

Modulated fringes are observed when the etalon is scanned along the beam axis. The fractional

order of interference for the sum of the two gaps between the sphere and the etalon determined by measuring the interference fringes at the centre of the fringes detected using photodetector.

The laser beam is chopped by an electro-optic modulator and signals from the photodetector are amplified by lock-in amplifiers. The etalon is scanned by a piezoelectric transducer and its displacement detected by a linear voltage differential transducer (LVDT). The fractional order is determined by computing the phase-difference between the outputs from the lock-in amplifiers. The diameter is then calculated by subtracting the sum of the gaps from the length of the etalon.

The etalon has been placed within a chamber which is evacuated and equipped with a water jacket. Temperature-controlled water is circulated through the jacket to keep the temperature of the etalon within the chamber less than 1 mK. The chamber is evacuated to a pressure less than 10^{-4} Pa, so that the effect of the refractive index of air on the vacuum wavelength is less than 1 part in 10^6 . The frequency of the laser is monitored using an iodine-stabilised He-Ne laser. By measuring the beat frequency between the two lasers, the vacuum wavelength of the laser is calibrated.

ELLIPSOMETRY

3 Background

Light reflected from pure silicon is known to undergo a phase shift of 80° . This is not the case, however, for light reflected from the oxides that form the surface of the silicon artefacts after manufacturing; the phase-shift being less than 80° . This leads to an apparent displacement of the surface when its diameter is measured interferometrically. The magnitude of this effect is up to 90% of the thickness of these layers. Measurement of the thickness of these layers using NRLM [1] would indicate that the thickness of these layers is around 100 nm. This is not the case, however, as the thickness of these layers depends on the crystal orientation. A correction of this magnitude is a very significant error, only 1 nm on the diameter would result in a 1% error in the volume measurement. One possible means by which the thickness of these layers may be measured is by using ellipsometry. NRLM has already set up such facilities and PT is currently working on the project.

3.9.2 Principle

Ellipsometry exploits the change in the polarised state of an electromagnetic wave that occurs when it is reflected from a surface, which is related to the dielectric function of the surface. If a sample is isotropic and homogeneous, for a given wavelength λ of light, the change in the polarisation is dependent only on the thickness of the layer, the angle of incidence of the light and the dielectric function ϵ . In the case for silicon, the layer that forms is made up of several different oxides and the dielectric function determined by ellipsometry is an average over the region penetrated by the incident light. This is known as the effective dielectric function $\langle\epsilon\rangle$.

In the most common experimental configuration, linear polarised light is incident on the surface and the elliptical polarisation status of the reflected light is analysed. The measured quantity is given by:

$$\rho = \tan\psi e^{i\Delta} = \frac{r_p}{r_s} \quad (12)$$

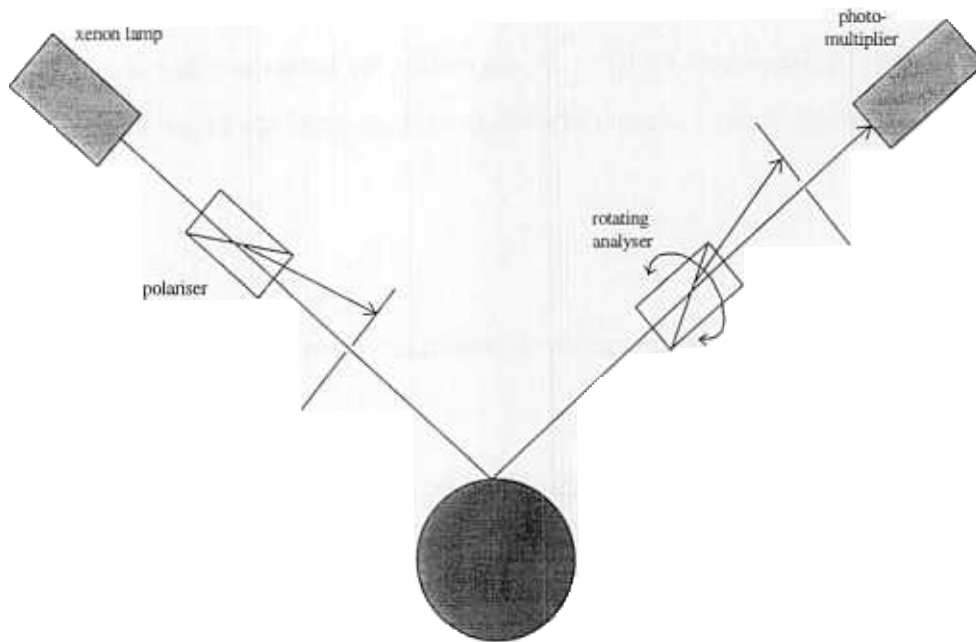
where ψ and Δ are the relative amplitude and the relative phase change between the components of the electric-field vector parallel (p) and perpendicular (s) to the plane of the incident wave

r_p and r_s are the complex reflection coefficients for the p and s directions

From measurement of $\tan\psi$ and $\cos\Delta$ the dielectric constant and the thickness of the layer can be determined. This technique relies on the substrate, in this case silicon, being optically well characterised (dielectric constant and absorption coefficient, k).

There are several different types of ellipsometer. Both the NRLM and PTB use a photometric one with a rotating analyser. Figure 8 shows the configuration of a typical rotating analyser ellipsometer. The polariser and analyser are made from a (uniaxial) birefringent material (i.e. quartz or calcite). A slit is placed after the polariser so that only one of the emerging plane polarised beams is incident on the silicon sample. Elliptically polarised light is reflected from the surface.

Figure 8 - A Typical Rotating Analyser Ellipsometer



The polarisation status of the reflected beam is determined by rotating the analyser at a constant frequency. The shape of the ellipse is transferred into a sinusoidally varying intensity by the rotation of the analyser. The signal at the detector is maximum (minimum) when the transmission axis of the analyser is parallel (perpendicular) to the major axis of the ellipse. In this manner, the amplitude of the parallel and perpendicular electric-field vectors are determined. Orientation of the major axis with respect to that of the plane polarised wave incident on the sample will give the phase change of these vectors.

3.10 LATTICE SPACING

3.10.1 Background

The most accurate measurements of the (220) lattice spacing of silicon d_{220} have been made using scanning x-ray interferometers and have a relative uncertainty of 3×10^{-8} . However, as a cubed term is involved when converting from the lattice spacing measurement to the unit cell volume

(equation 4) this leads to a relative uncertainty of approximately 1×10^{-7} in the volume and so further improvements have yet to be made. Three laboratories have developed scanning x-ray interferometers, namely IMGC, PTB and NRLM.

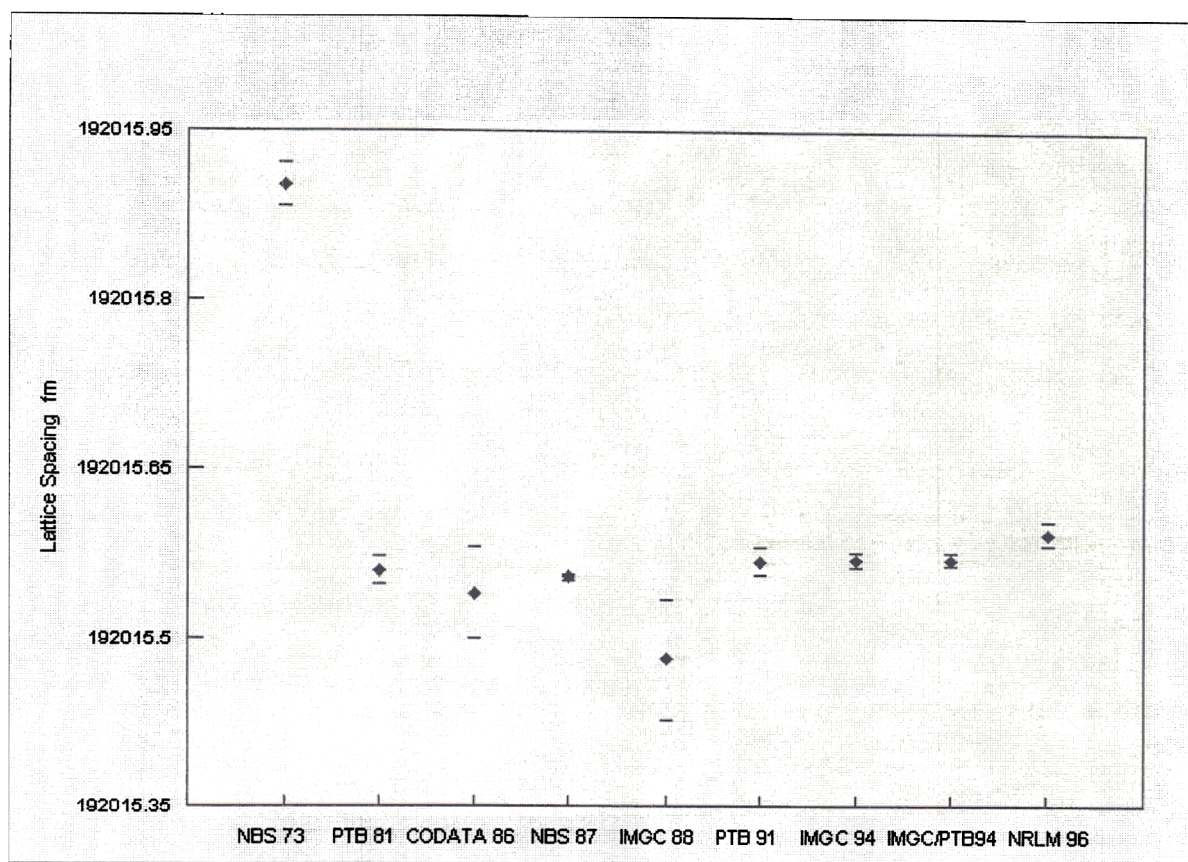
Furthermore, lattice comparators (3.10.7), which enable the lattice spacing of a reference crystal to be used to determine that of another crystal, have been developed by PTB and NIST.

3.10.2 Progress

Table 6 reports the most significant measurements of the lattice spacing d_{220} made to date. This information is also shown in Graph 3.

Table 6 Lattice Spacing d_{220} of Silicon				
Source	Date	Crystal	Lattice Spacing fm	$10^{-8} U_{\text{rel}}$
NBS ^{ab}	1973	D3	192 015.902(19)	9.9
PTB ^{ab}	1981	WASO-4.2A	192 015.560(12)	6.2
CODATA ^b	1986	-	192 015.540(40)	20.8
NBS ^{ab}	1987	D3	192 015.554(02)	4.7
IMGC ^b	1988	-	192 015.480(54)	28.1
PTB ^c	1991	WASO-17.1	192 015.568(12)	6.2
IMGC ^c	1994	MO	192 015.569(06)	3.1
IMGC / PTB ^c	1994	W3, WP, WG MO, WASO-4.2A	192 015.570(05)	3.1
NRLM ^c	1996	n-type silicon, FZ	192 015.593(10)	5.2
(a) not corrected for C and O contents				
(b) $t_{68} = 22.5 \text{ }^{\circ}\text{C}$, vacuum				
(c) $t_{90} = 22.5 \text{ }^{\circ}\text{C}$, vacuum				

Graph 3 - Lattice Spacing values given in Table 6



NBS obtained the first measurement of the lattice spacing made with a scanning x-ray interferometer in 1973 [4] with a reported relative uncertainty of $9.9 \cdot 10^{-7}$. Eight years latter, PTB reported a more accurate value with an relative uncertainty of $6.2 \cdot 10^{-7}$ [30] but this differed from the earlier NBS value by $1.8 \cdot 10^{-6}$, a discrepancy larger than the measurement uncertainty reported by NBS. This PTB value was included in the last adjustment of the fundamental physical constants (see section 3.4.2) and the result was published in CODATA 86. Further investigation led NBS to discover an error in their measurement which accounted for the discrepancy with PTB's value and led to a new value published in 1987. IMGC published their first value in 1988 [31] and was in good agreement with that of PTB.

In 1991, PTB related d_{220} lattice spacing measurements to the content of crystal impurities [5] and laid the basis for the extrapolation of a unique value. From this point onwards lattice spacing measurements could be reported on a consistent basis and in 1994 IMGC reported the lowest relative uncertainty achieved to date of $3.1 \cdot 10^{-8}$ [32]. This value was in excellent agreement with

orted by PTB 99 but differed from that published by NRLM by 0.001° [1]. However, further correction to the NRLM value has yet to be made because the measurements performed in the PTB were on a different sample. The homogeneity of the sample has been investigated by measuring the channel spacing with an X-ray interferometer. The PTB and IMGC ingo have been thoroughly characterised.

Finally in 1999, all the lattice spacing based measurements made both IMGC and PTB and used the 1999 determination of N_A [1]. This represents the presence of the lattice spacing. However, both IMGC and PTB already developed the general scanning X-ray interferometers which should open the way for the final push towards the target uncertainty required for the Avogadro project.

X-ray Interferometry

Principle

The principle of the combined X-ray and optical interferometer. The X-ray interferometer is made from a silicon single crystal and machined such as to form three parallel lamellae approximately 800 nm thick which are perpendicular to the 220 lattice plane. The interferometer is then cut into three pieces which are aligned with respect to each other with sub-atomic accuracy (the same accuracy as a single crystal). Furthermore, the three lamellae must be equally spaced from the central lamella.

An X-ray beam incident on the first crystal splitter is split into two coherent beams which are diffracted through the lamella. These beams are diffracted by the second crystal mirror and recombine at the third analyser to form an interference pattern. The period of the interference pattern is equal to the lattice spacing of the 220 planes and can be observed directly. This is the principle of X-ray optical interferometry where the fringe spacing is related to the length of the incident radiation. Interaction of this combined X-ray and optical interferometer with a crystal lattice produces a Moiré fringe pattern the variations of which are measured by the X-ray beams. Translation of the analyser crystal in a direction perpendicular to the lattice planes will produce periodic variations in the intensity of the beams, the period being equal to the lattice spacing.

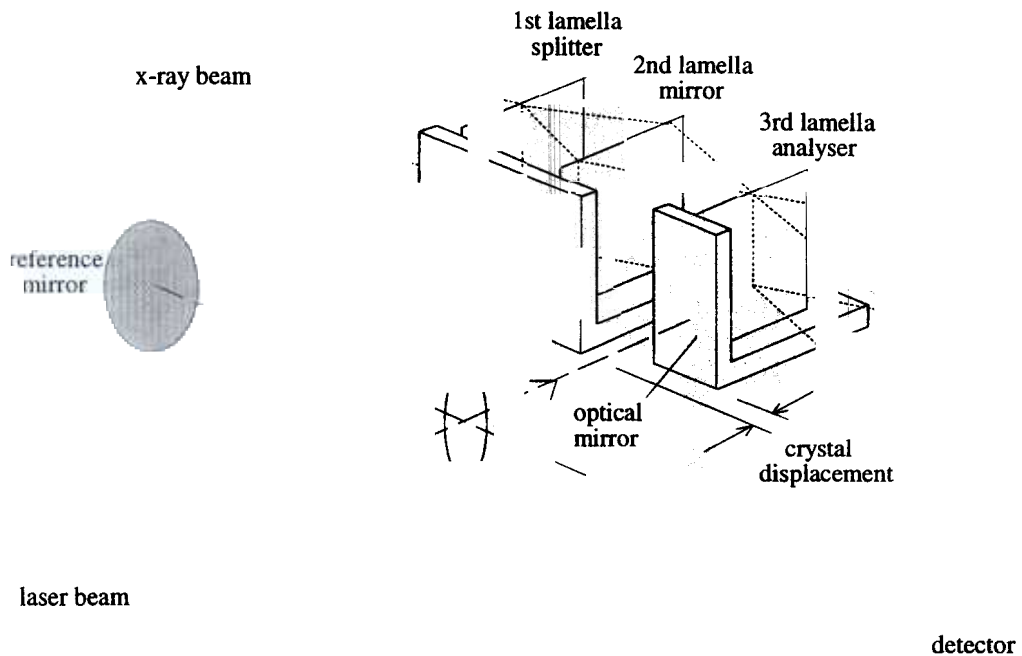
In order to determine the lattice spacing, it is necessary to measure the distance the analyser crystal moves with respect to the mirror and beamsplitter. This is achieved using an optical interferometer. The side of the two components of the x-ray interferometer are polished to form optical mirrors. As the analyser moves, the displacement is measured by counting the number of x-ray fringes and optical fringes through which it moves. The lattice spacing is then obtained by dividing the number of optical fringes by the number of x-ray fringes and multiplying the optical fringe spacing (usually $\lambda/2$). The lattice spacing is calculated as:

$$d_{220} = (m/n) \lambda/2 \dots\dots\dots(13)$$

where m is number of optical fringes
 n is the number of x-ray fringes
 λ is the wavelength of the laser

The larger the displacement, the more accurate the measurement of the lattice spacing. IMGC can now move the analyser 1 mm whilst still maintaining the alignment of the two pieces of silicon. This is ten times greater than PTB and NRLM have achieved with their apparatus.

Figure 9 - Combined X-ray and Optical Interferometer (based on a diagram given in [48])



Design Considerations

Account must be taken of the additional degrees of freedom (pitch and yaw) of the analyser crystal and of the adverse effect of environmental disturbances on the alignment of the two components. Consequently, successful operation requires very stringent thermal, vibrational and geometric tolerances. The thermal requirements are met by placing the interferometer in a vacuum system and removing any heat sources from within. The maintenance of lattice alignment represents a much more formidable task and the main points can be summarised as:

Method and equipment for the adjustment of the analyser crystal so as to re-establish lattice coherence.

Correction for Abbe errors and rotation of the analyser during translation. These must not exceed a few nanoradians.

Transverse movement of the analyser must be limited to a few nanometres.

Reach a compromise between the opposing needs of maximum displacement and high stiffness (to reduce vibration).

All scanning interferometers employ elastic guides to carry the separate analyser crystal. A guide

is constructed from flexure-hinges and a piezo-electric drive to provide movement of a bar on which a crystal is mounted. Accurate design and machining of the flexure-hinges are essential for a tilt-free movement, but the driving force will elastically deform the moveable bar and eventually limits displacement. Reduction of tilt may be obtained by either passive or active compensation. In the first-case, additional torques are applied by magnets, as used at PTB, in proportion to the displacement. In the second, employed by IMGC and NRLM, a two-axis rotation stage rests on the moveable bar and an optical servo-control system detects tilts and applies corrections necessary to counter them.

3.10.4 IMGC X-ray Interferometer

The principle of measurement is as described in section 3.10.3. The main novelty is the development of an optical measurement technique and servo control system which corrects for unwanted movements of the analyser during translation. The value of the lattice spacing published in 1994 [32] was obtained by operating over a 80 μm scan. Since, IMGC has constructed a new guide [34] which has increased the scan range to 2 mm. This should ensure the continuing improvement in the measurement of the lattice spacing of silicon.

3.10.5 PTB X-ray Interferometer

Background

PTB have been actively measuring the lattice spacing of silicon for over 20 years and, at present, have an x-ray scanning interferometer [5] and an x-ray comparator (see section 3.10.7). An essential process for both devices is the preparation of the silicon and the manufacture of the lamella.

Crystal Preparation and Manufacture of Lamella

PTB buy their silicon ingots direct from Wacker, the largest of several silicon manufacturers in Europe. The ingots supplied to PTB are grown using the float-zone technique (see section 3.11.1). Their diameter is approximately 4 inches and axis of the rod is approximately [100]. The silicon has very low carbon and oxygen concentrations and is grown in a nitrogen atmosphere to prevent swirl defects.

The first step in the preparation is to determine the orientation of the ingot with respect to the [100] axis to within $\pm 0.5^\circ$. A slice is cut from the ingot and its orientation is measured by taking a Laue picture. This is a standard technique where the crystal under examination is illuminated with characteristic white x-ray radiation from an x-ray tube (ie broad continuous frequency range emitted by a standard x-ray tube). A film is placed in front of the sample and a series of diffraction spots is obtained. From measurement of the spots' position on the film and comparison with standard maps, the crystal's orientation can be determined.

The silicon must be examined for defects such as dislocations and inclusions. This is done using high resolution x-ray diffraction topography [35]. The crystal is aligned to reflect x-rays from a set of Bragg planes and the diffracted beam is recorded on a film. In the case of a perfect crystal, the image of the diffracted beam is uniform. Crystal imperfections are revealed as variations in the spatial intensity of the diffracted beam.

The x-ray interferometer is then machined using diamond cutting tools and the final step is the etching of the surface to remove surface damage which occurs during machining. The crystal is glued to a support and left in a bath of sulphuric acid (H_2SO_4) for several days before being rinsed with water. Material is then etched with hydrofluoric acid (HF) followed by nitric acid (HNO_3).

Interferometer

The main significant difference between PTB's interferometer and that of IMGC, is that the IMGC interferometer has the capability to continually monitor and adjust the orientation of the analyser crystal to maintain the lattice geometry whilst it is being scanned. This has ultimately led to the IMGC uncertainties being lower than that of PTB. However, PTB is in the process of developing a new scanning 'angle' interferometer with an improved optical interferometer capable of resolving to 0.1 pm when detecting 'zero crossings' of fringes, providing the same resolution as IMGC. A novel feature of the new x-ray interferometer will be that the second 'mirror' lamella will be split in two. This will facilitate the correction for unwanted movements of the lamella during translation and extend the translation range of the analyser crystal to 1 mm.

3.10.6 NRLM X-ray Interferometer

Background

NRLM has recently published its first measurements of the lattice spacing. These have been manufactured from a silicon ingot provided by the Shin-Etsu company (see section 3.11.2).

Interferometer

The NRLM interferometer is very similar in principle to that used at IMGC. Again, optical circuits measure the rotation of the analyser crystal and provide feedback to reduce this motion. Translation of 100 μm has been achieved for the analyser crystal [36].

3.10.7 Lattice Comparator

The difficulties of direct measurements by scanning interferometers and the need to transfer the calibration embodied by the interferometer crystal to other silicon crystals have led PTB, along with NIST, to develop lattice comparators. Both comparators are based on the same principle and, as the technical requirements are considerably relaxed, allow the comparison of an unknown crystal with that of a reference to a relative uncertainty of around $1 \cdot 10^{-8}$ [37].

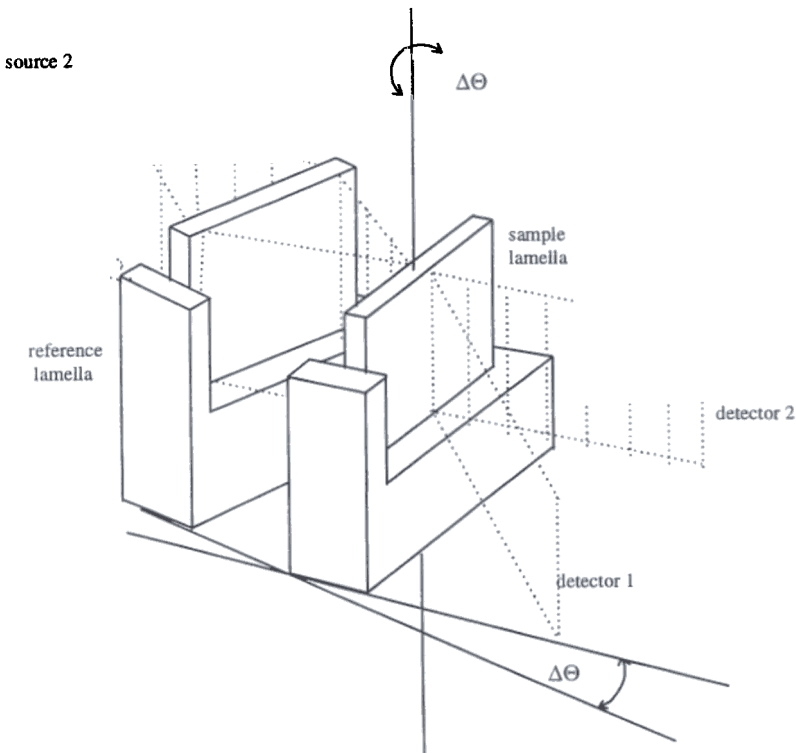
The operating principle of a double-source double-crystal comparator is shown in Figure 10. The reference crystal is of high quality and its lattice parameter is known. It is mounted, together with the sample on the axes of a double-crystal diffractometer. The two x-ray sources with identical targets are aligned so that the $K\alpha_1$ radiation lines are diffracted from the reference crystal. The crystal to be examined is placed at the point of intersection of the two diffracted beams and aligned parallel to the reference crystal. If the two crystals have the same lattice parameter, both the diffracted beams from the reference crystal will be diffracted by the sample and both detectors will measure a maximum in intensity. If however, the lattice parameters are different, it will be necessary to rotate the sample about the point of intersection of the two incident beams in order to obtain the peak in intensity of both diffracted beams. The angular separation between the two peaks is an indication of the difference in lattice parameter between the two samples.

In the case of different lattice spacings, the difference in the lattice spacing is given by:

$$\frac{\Delta d}{d} = \frac{1}{2}(\Delta\Theta + C)\cot\Theta \quad .(14)$$

where Δd is the difference in lattice spacing
 d is the lattice spacing of the reference crystal
 $\Delta\Theta$ is the difference in angle between the two positions of maximum intensity
 Θ is the Bragg angle of reference crystal
 C is a correction for angle shift, required if alignment is defective.

Figure 10 - Double-Source Double-Crystal Comparator (based on a diagram given in [48])



3.11 CRYSTAL GROWTH

3.11.1 Background

Silicon crystals are the key material in electronics today as this technology is based almost exclusively on silicon single crystal. Modern electronic devices require the silicon crystals to be of very high purity and crystalline perfection. Because of the beneficial effect of oxygen during the high-temperature device processing, most electronic devices are made from the oxygen-rich crucible-pulled Czochralski silicon. In experiments to determine the Avogadro constant, only the purer float-zone grown silicon can be used.

About 12 000 tonnes of silicon single crystals are produced in a year and some 90% is used for the manufacture of electronic devices. Of this, 85% is grown from the Czochralski (CZ) techniques, the remainder from the float-zone (FZ) technique [38]. Electronic devices require very pure, perfect crystals and are particularly sensitive to electrically active elements (eg B, Al, P, As, Sb) and fast-diffusing metallic impurities, in particular Cu, Ni and Fe. They are less sensitive to carbon and oxygen, the main impurities in FZ and CZ silicon. As a result, the production process for semiconductor silicon is optimised to remove the electrically active and fast-diffusing metallic impurities. Typically concentrations are reduced to below 0.001 parts in 10^9 , whereas carbon fractions of up to 200 parts in 10^9 are tolerable. However, oxygen is a special case. The FZ crystals contain only about 0.02 parts in 10^9 oxygen.

In contrast to the electronics industry, the Avogadro projects require crystals which have lower contents of carbon and oxygen, because these elements appreciably alter the lattice spacing and density of a silicon crystal. FZ crystals with a lower than average carbon and oxygen content are obtained by appropriate selection from current production. For the Avogadro project to date it has been a case of trying to select the best ingots from the current production. But this is not always successful.

3.11.2 Manufacturers

Wacker-Chemitronic

Wacker-Chemitronic, Europe's largest producer of silicon single crystal, has had a close working

relationship with PTB over a number of years and supplies much of the silicon used by PTB and IMGC. Recently, Wacker-Chemitronic has produced for the Avogadro project an ingot that is supposedly extremely pure. PTB, IMGC and NRLM are all to have spheres manufactured by CSIRO from this ingot. However, early measurements of its impurity concentrations at PTB would indicate that its purity is not as good as hoped for.

Shin-Etsu

Shin-Etsu supply the silicon used by NRLM. However, the techniques employed in its growth are not known as Shin-Etsu do not publish details for fear of international competition.

3.12 IMPURITY MEASUREMENT

3.12.1 Background

Knowledge of the concentration of impurities is essential to correct the lattice spacing measurements. Silicon can be grown in large crystals with very good crystalline perfection and a contamination by impurities of around 10 parts per billion. The bonding between silicon and the light impurity atoms is mainly covalent and the bond lengths can be different from that of a silicon-silicon bond (approximately 0.235 nm). This difference produces a local lattice distortion which modifies the average lattice spacing. Thus it is necessary to know both the concentration of residual impurities in the crystals used and the average distortion they induce.

There are three mechanisms by which impurities can exist within the lattice structure of silicon:

- Impurity atoms occurring on regular lattice sites by substituting silicon atoms
- Impurity atoms on interstitial lattice sites increasing the number of atoms per unit cell
- Silicon vacancies and silicon self-interstitials. Swirl defects are formed when an agglomerations of vacancies or self-interstitials form

The main residual impurities of silicon crystals grown by the float-zone method are carbon, oxygen and nitrogen, which is usually added to the growth atmosphere of float-zone silicon to add mechanical strength and prevent the formation of swirl defects. Carbon is substitutional, oxygen

and nitrogen are interstitial. All are electrically inactive as they keep their normal valence and their influence on lattice spacing is only that of averaging the local distortion they produce. Table 7 gives the typical concentrations of these impurities found in nitrogen doped FZ grown silicon.

Table 7 Typical Impurity Concentrations in Nitrogen Doped FZ Grown Silicon		
Impurity	Type	N° atoms cm ⁻³
Carbon	Substitutional	< 10 ¹⁶
Oxygen	Interstitial	< 10 ¹⁶
Nitrogen	Interstitial	5 . 10 ¹⁴
Silicon	Vacancies	5 . 10 ¹⁴
Silicon	Interstitial	5 . 10 ¹⁴

An impurity content of 1 . 10¹⁶ atoms cm⁻³ will change the Avogadro constant by 1 . 10⁻⁷.

3.12.2 Infra-Red Spectroscopy

Infra-red spectroscopy can be used to measure the content of carbon, oxygen and nitrogen atoms within silicon [39]. Pure silicon is infra-red inactive, as there are no electric dipoles associated with the covalent bonds between the silicon atoms. However, this is not the case for the bonds formed between the impurity atoms and silicon. At specific infra-red frequencies, these bonds can be made to vibrate and will result in the absorption of the incident radiation giving rise to a distinct spectrum. Analysis of this spectrum will give the concentration of the various impurity atoms. The use of infra-red spectroscopy to analyse silicon is fairly common-place in the relevant industries.

3.12.3 Spectroscopy at PTB

Infra-red Spectroscopy

PTB have three apparatus covering the following ranges:

- i) 4 ~ 600 wavelength numbers, evacuated
- ii) 150 ~ 5 000 wavelength numbers, purged with dry air
- iii) 4 000 ~ 10 000 wavelength numbers, purged with dry air

PTB utilise a 'background substitution' method to detect peaks due to the presence of impurities. The basis of the technique is the 'subtraction' of a spectrum obtained for 'pure' silicon from that determined on the sample being investigated. The remaining peaks are due to the impurity atoms. A 'pure' spectrum of silicon is obtained by preparing various samples with significantly reduced content of carbon, oxygen and nitrogen atoms (ie reduced content of carbon can be obtained at the expense of introducing other impurities when growing silicon). This process is repeated for oxygen and nitrogen impurities and a spectrum built-up for 'pure' silicon.

Raman Spectroscopy

Raman spectroscopy is being developed as a method to determine the composition of the oxide surface layer. This may provide an important model that can be utilised by ellipsometry to provide a more accurate measurement of the thickness of these layers.

Raman spectroscopy can be used to identify molecules by examining the frequencies present in light scattered by molecules. A monochromatic incident beam consists of a stream of photons of the same energy. When the beam passes through a Raman active sample, photons may collide with the molecules, give up some of their energy, and emerge (in a different direction) with a lower energy and frequency. These scattered photons give rise to *Stokes radiation*. Other photons may collect energy from the molecules and emerge as higher frequency *anti-Stokes radiation*.

3.13 SPHERE MANUFACTURE

3.13.1 Background

Silicon single crystal spheres with as near-perfect a geometry as possible are required for the Avogadro project. In principle, regular solid shapes such as cylinders or cubes would be suitable artefacts for the precise measurements of dimensions and volume. However, such objects are unsuitable as they have sharp edges and corners, which are difficult to produce and can be easily

damaged. The ideal shape for an artefact is a sphere, provided it has negligible error in sphericity. Because it has no sharp edges or corners its volume may be determined by one parameter, its mean diameter.

The closer a sphere is to being perfect, the smaller the errors when determining its volume by interferometric methods. Surface properties are also very important. Any sub-surface damage to the crystalline structure will cause a deviation from the density of crystal and will need to be quantified and a correction made. At present, CSIRO is the only laboratory world-wide with the necessary knowledge and expertise to manufacture spheres with the demanding specification required for the Avogadro project.

3.13.2 CSIRO

Background

CSIRO now manufacture spheres of silicon single crystal [40] for all laboratories making volume measurements within the Avogadro project. The first sphere was manufactured at CSIRO in 1987 for IMGC. Since then, improvements have been made to the fabrication process, mainly as a result of upgrading their capabilities of measuring roundness. Spheres can now be manufactured with the following tolerances:

Peak-to-valley error of sphericity < 60 nm

Mean deviation of the error surface relative to a least-square sphere of around 15 nm

Micro roughness < 0.2 nm rms

Improvements

A major limitation in 1987 was the inability to measure and characterise the sphericity with sufficient accuracy to be able to make meaningful improvements during the fabrication processes of grinding and polishing. Only two-dimensional measurements of roundness could be made for characterising the shape of a sphere. Since then, a major part of the development has been to extend and modify the standard roundness measurements, made using a Talyrond 73 machine, to account for instrument errors and to develop analytical procedures to generate high precision and three-dimensional data. These measurement procedures complemented CSIRO's existing fabrication expertise.

Due to the relatively large diameter of the silicon spheres, surface micro roughness analysis is restricted and CSIRO was originally only able to examine the surface using a stereo microscope. This did not allow the fine structure to be examined or the surface roughness to be quantified. The acquisition of a WYKO TOPO 3D non-contact surface profiler has changed this, allowing quantitative information on defects and roughness on a sphere's surface.

3.13.3 Fabrication

Stages



The grinding and polishing of the spheres is performed essentially to traditional precision optical grinding and polishing procedures. Three stages are used in the fabrication process:

- The shaping of a rough sphere from a cylindrical ingot using diamond tools
Rough grinding with coarse abrasives such as silicon carbide
- Fine grinding with aluminium oxide loose abrasives down to 1 μm
Polishing using an optical polishing pitch and a suitable slurry oxide

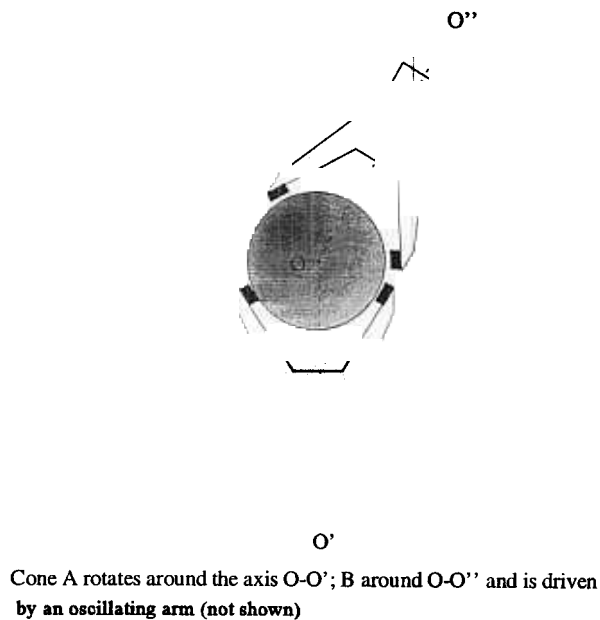
Rough Grinding



Prior to this process, CSIRO use a universal glass-grinding machine and diamond cutters to shape a rough sphere. This is followed by manual rough grinding with loose abrasives in a conical grinding tool of mild steel which rotates on a spindle. The basic conical tools (shown in Figure 11) are used for all grinding and polishing operations of a sphere. Due to a sphere's continually diminishing diameter during grinding, the basic concept of the tool used is its ability to constantly adjust to the ever diminishing diameter, allowing it to grind its way in to the straight internal face of the cone.

The whole process of grinding is a manual one, requiring great skill and expertise from the craftsman. Control must be exercised when rotating the sphere randomly by hand, while relying on a bias this must create, to remove more material from the high regions on a sphere's surface.

Figure 11 - Conical Grinding Tools (based on a diagram given in [40])



From the very beginning of producing a sphere, a high level of symmetry in the shape must be established and maintained. After pre-shaping the sphere with the universal glass-grinder, the sphere goes through a number of manual rough grinding stages using silicon carbide and aluminium oxide loose abrasives (starting with 120 grit silicon carbide and finishing with 40 μm grit aluminium oxide) an operation which takes several days in total. At this stage, the sphere will have a peak-to-valley error of sphericity of around 2 μm .

Fine Grinding

The process of fine grinding becomes progressively more critical with the use of successively finer abrasives; once fine grinding is completed with 1 μm grit, surface smoothness and roundness may only be further improved with polishing. An error here will mean that the sphere has to be scrapped as to remove the necessary material would require the grinding to go back several stages and the sphere would become out of tolerance on its mass and diameter requirements.

CSIRO use Microgrit aluminium oxide abrasive powders for their fine grinding. Six grades of successively finer powders are used from 25 μm to 1 μm . A brass tool is used for grades 25 μm to 15 μm followed by a Pyrex tool to minimise the likelihood of scratches occurring on contact between the sphere's surface and the tool. The sphere's roundness is monitored throughout the

fine grinding process by making measurements with the Talyrond. On completion with the 1 μm grit a full sphericity measurement is made, the major objective being to establish that a sphere has good symmetry and is not in any great way elongated, an important pre-requisite before final polishing.

Polishing

It takes approximately 10 hours to completely polish the sphere free from all residual grinding marks. As the base for the polishing, the same conical tools are used and optical polishing pitch is the only suitable polisher matrix which guarantees the surface quality and roundness of the sphere. A host of polishing conditions such as polisher size, pitch flow, charging of the pitch surface with polishing agent, slurry distribution, pressure, speed and the polisher surface conditions contribute to an imbalance of the friction experienced by the two cones in contact with the sphere!

After final polishing, the quality of the sphericity and surface roughness is such that the cubic nature of the crystal structure can be observed on the overall geometry of the sphere, with highs appearing at the corners and lows in the centre of a cube. The cubic shape of the sphere is intrinsic to the silicon crystal and may ultimately be the limitation in advancing to produce the next-generation spheres of superior roundness.

4 NPL WATT BALANCE

4.1 BACKGROUND

The NPL moving-coil watt balance was developed to provide a means of linking the electrical and mechanical watt. From this measurement, the ampere and volt could be expressed in terms of the SI units of mass (kilogram), length (metre) and time (second). Furthermore, the volt generated by this apparatus could be compared with that generated by the Josephson effect [41] to obtain an improved value of the Josephson constant K_J .

Two electrical units need to be obtained in terms of the base SI units of mass, length and time in order to ensure that consistent SI units can be derived for remaining electrical measurements. The unit of resistance, the ohm Ω , can be realised from a calculable capacitor [42] in terms of the metre and the defined values of the velocity of light and magnetic permeability of free space with an uncertainty of around 1 part in 10^7 . The other electrical unit to be so determined has been the ampere, by using some form of current balance [43] but its uncertainty of a few parts in 10^6 was far larger than now required. Furthermore, working standards of voltage and resistance could be realised through the Josephson and quantum Hall effects which have the potential to be much more accurate. However, in using the Josephson and quantum Hall effects [41], one has to assign values to two constants, the Josephson constant K_J and the von Klitzing constant R_K respectively, to gain the volt V and the ohm Ω . The only means of doing so were through the current balance and calculable capacitor. This led to large discrepancies in the value assigned to the Josephson constant K_J by the various national standards laboratories.

The development of the first watt balance [44] allowed the Josephson volt to be determined with an uncertainty of around 1 part in 10^7 within the SI system of units. Since then, a second generation watt balance has been developed at NPL with the aim of reducing this uncertainty toward a few parts in 10^9 . Once achieved, this balance could be used to realise the kilogram with the same uncertainty. The main difference from the first apparatus, is that the balance is now within a chamber which can be evacuated.

4.2 PRINCIPLE

The concept of the NPL moving-coil balance can be explained thus. Consider a straight, conducting wire of length l carrying a current I in a uniform applied magnetic flux density B perpendicular to l . The force on the conductor is given by:

$$F = B I l = m g \quad \dots(15)$$

where m is the mass of an artefact used to balance the force and g is the local acceleration due to gravity.

If the same conductor, without the current, is moved with a velocity v in a direction perpendicular to B and l , a voltage V is induced across its ends:

$$V = B l v \quad \dots(16)$$

Eliminating the product Bl from these two equations one gets:

$$V I = m g v \quad \dots\dots\dots(17)$$

The left side of equation .7 is recognised as the electrical watt, whilst the right, the mechanical watt. Furthermore, if the current produces a voltage V across a resistor whose value R is known is SI units then one can write the following equations:

$$V = (m g v R)^{1/2} \quad \dots(18)$$

$$I = (\frac{m g v}{R})^{1/2} \quad \dots\dots\dots(19)$$

$$m = \frac{V^2}{R g v} \quad \dots\dots\dots(20)$$

Equations 18 and 19 allow the volt and ampere to be realised in terms of SI units of mass, length, time and resistance. In 1990, the Comité Consultatif d'Électricité (CCE) approved the moving-coil balance as a primary means of realising the SI unit of the ampere and, by comparison against a Josephson array, a new value was assigned to the Josephson constant J_K allowing the Josephson volt to be determined with an uncertainty of around 1 part in 10^7 . Furthermore, through equation 20, the stability of the kilogram could be monitored in terms of the Josephson effect used to measure V and the quantum Hall effect used to measure R . If the uncertainty in the volt generated by the apparatus could be improved to 1 part in 10^8 , the moving-coil balance could be used to realise the kilogram with an equivalent uncertainty.

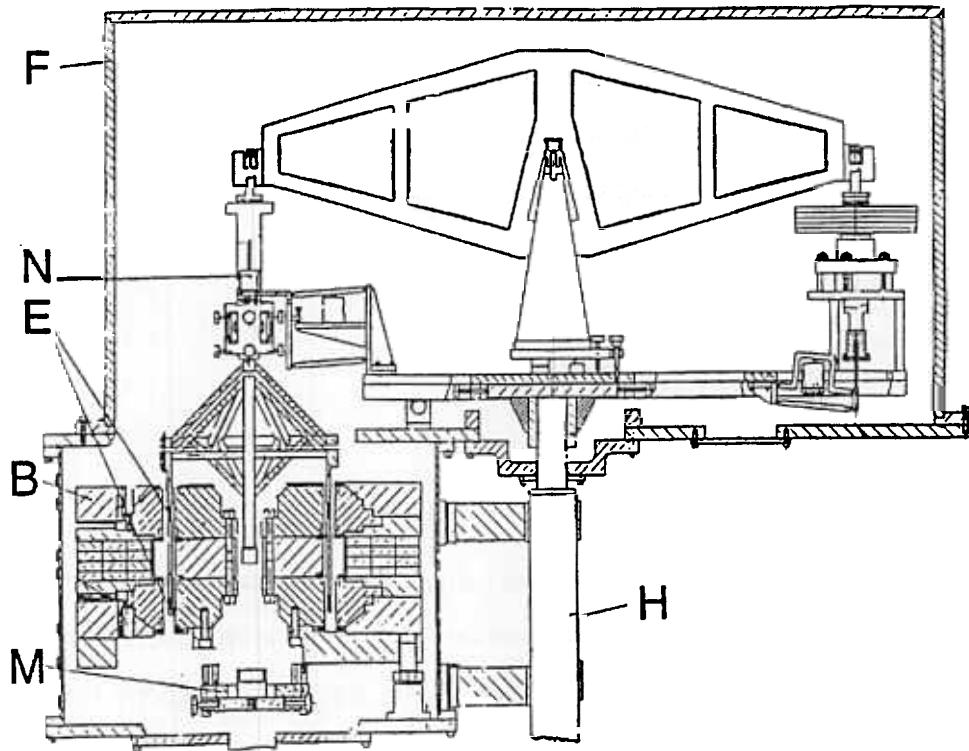
4.3 MOVING-COIL BALANCE

Figure 12 is a cross-section through the second generation NPL moving-coil balance, with the coils E and 1 kg mass standard N suspended from the left side of the beam and a tare mass from the right side. The two-horizontal circular coils are in the radial magnetic flux of a large permanent magnet B whilst the mechanism which lowers the 1 kg mass standard for weighing is arranged above this.

A coil and magnet on the right side of the beam applies corrective forces for maintaining a near-constant velocity when the coil is moved. A vertical laser beam passes upward through a beam-splitter M to a cube-corner fixed in the centre of the coils. The beam-splitter reflects a second beam horizontally to a cube-corner fixed to the magnet. This constitutes a Michelson interferometer which measures the coil position and velocity. In principle, instantaneous values for the velocity v and the induced voltage V are required for the exact moment the coil passes through the weighing position, but in practice the magnetic flux and coil can be shaped so that V/v is almost constant and the average over a finite distance is adequate.

The whole apparatus is enclosed in a vacuum chamber F which is mounted on springs and oil-filled dampers to minimize floor transmitted vibration. The temperature of the apparatus, and in particular of the magnet, is controlled by means of re-circulating the air within a cabin which surrounds the apparatus. The temperature of the magnet now drifts at a rate up to 0.1 mK per hour, which produces a flux change of up to $4 \cdot 10^{-8}$ per hour.

Figure 12 - NPL Watt Balance (taken from [49])



The force F caused by a current I flowing in the coil is opposed by that of a mass m subjected to the local acceleration due to gravity g . The value of the current is adjusted until equilibrium is achieved. In a separate experiment, the coil is moved with a linear velocity v to induce a voltage V . The equality of mechanical and electrical power implied by the definition of the Ampere then allows equation 17 to be stated. In this manner, neither the dimensions of the coil nor the density and distribution of the magnetic flux need to be measured. These parameters had to be determined for the original current balances and provided the limiting factor to their achievable uncertainties.

4.4 PLANNED IMPROVEMENTS

Josephson Array

The construction of a Josephson array within the laboratory housing the moving-coil balance has just been completed. This will allow the stability of voltage generated during the dynamic stage

of the measurement process to be monitored to around 1 part in 10^9 . The main benefit of having an array in the lab is the time response of the measurement, allowing for improved control over the movement of the coil.

Vibration

Any lateral vibration of the coil will cause a lack of correlation between the velocity measurement made with the interferometer and the voltage induced in the coil. Whilst the apparatus is mounted on springs and oil-filled, ambient acoustic vibrations can cause the springs to vibrate. Plans to reduce this form of vibration are to either place the springs within the vacuum chamber or build a 'solid' chamber around the apparatus.

Transfer of gravitational acceleration

The value of the local acceleration due to gravity g is measured in the laboratory using a commercial AXIS absolute gravimeter. This measurement is performed during a static weighing cycle. Local gradients in g around the room can be determined by moving the gravimeter to different locations. A correction is then applied for the displacement between the gravimeter and the position of the mass standard on the balance. However, a further correction to allow for the local distortion of g due the bulk of the permanent magnet has yet to be made.

Mass stability

Because of the mass standard's close proximity to the permanent magnet, it is subjected to a strong magnetic flux and therefore is manufactured from a material with a very low magnetic permeability. Mass standards used with the NPL moving-coil balance are manufactured from oxygen-free, high-purity copper and are plated with gold to protect them from corrosion.

Ultimately, the mass of these standards will have to be determined with an uncertainty of $10\ \mu\text{g}$ or better but, at present, their uncertainty is of the order of $50\ \mu\text{g}$. This will require an improvement in the uncertainties arising from the calibration chain of mass standards maintained in air to the value of the copper artefacts in vacuum. This will require a better understanding of the techniques employed during weighings made in vacuum and quantifying the effect on the stability of artefacts cycled between atmospheric and vacuum pressures.

4.5 OTHER WATT BALANCES

4.5.1 NIST moving-coil balance

The moving-coil balance developed at NIST [45] does not, at present, have the measurement capability of the balance at NPL. The principle reason is that originally the NIST balance used a water-cooled solenoid to generate its magnetic field but its magnitude (2 mT) was such that it only induced a voltage of about 20 mV and a force equal to a mass of 100 g. The water-cooled solenoid has now been replaced with a superconducting solenoid which is now capable of producing the required magnetic field strength but the apparatus has still to be used in vacuum.

4.5.2 Swiss Federal Office of Metrology

The Swiss Federal Office of Metrology⁸ are in the process of developing a moving-coil balance, based around a commercial 1 kg balance (Mettler HK1000MC). Due to the mass of the coil arrangement the balance will be limited in use to a mass standards of 100 g. Development of this apparatus should be finished within a couple of years.

⁸ Swiss Federal Office of Metrology, Lindenweg 50, CH-3084 WABERN, Switzerland

5 ION COUNTING

5.1 BACKGROUND

PTB has embarked on an experiment to directly measurement the atomic mass of a nuclide m_a . In common with the Avogadro project, the kilogram could then be re-defined in terms of a fixed number of these atoms. A mono-nuclidic ion flux would be collected and accumulated to an amount that can be weighed with sufficient accuracy. Simultaneously, the ion current would be measured and integrated as a means of counting the number of atoms collected. In this manner, the accumulated mass could be related to the atomic mass. From knowledge of the relative atomic masses [9] the atomic mass unit u may also be determined. The proposed method could lead to a re-definition of the kilogram if a relative uncertainty in the measurement of the m_a of $1 \cdot 10^{-8}$ is achieved.

Main steps of the experiment are:

- i) Generate an intense ion beam in vacuum
- ii) Accumulate the ions inside an appropriate collector and weigh them
- iii) Measure and integrate the ion current during the accumulation time

The mass m of the accumulated atoms (neutralised ions) could then be calculated as:

$$m = \frac{m_a}{e} \int_0^{t_m} I(t) dt \quad \dots\dots\dots(21)$$

where t_m is the accumulation time
 e is the elementary charge
 $I(t)$ is the ion current

If the ion current $I(t)$ is measured by the voltage drop U over a resistance R , and if U and R are measured using the Josephson and quantum Hall effects respectively, the atomic mass m_a can be measured in terms of the kilogram, and is a function only of the accumulated mass m , the microwave frequency $f(t)$, irradiated onto the Josephson junction, and the accumulation time t_m .

Assuming that a quantised Hall resistance, through which flows a current $I(t)$, is given by $R_H=h/n_1.e^2$ and the corresponding voltage is given by the Josephson voltage $U(t)=n_2.h.f(t)/2e$, the current $I(t)$ of equation 21 can be replaced and re-arranged to give:

$$\frac{1}{m_a} = \frac{1}{2} n_1 n_2 \frac{1}{m} \int_0^{t_m} f(t) dt \dots\dots\dots(22)$$

where n_1, n_2 are integer numbers of the quantum steps

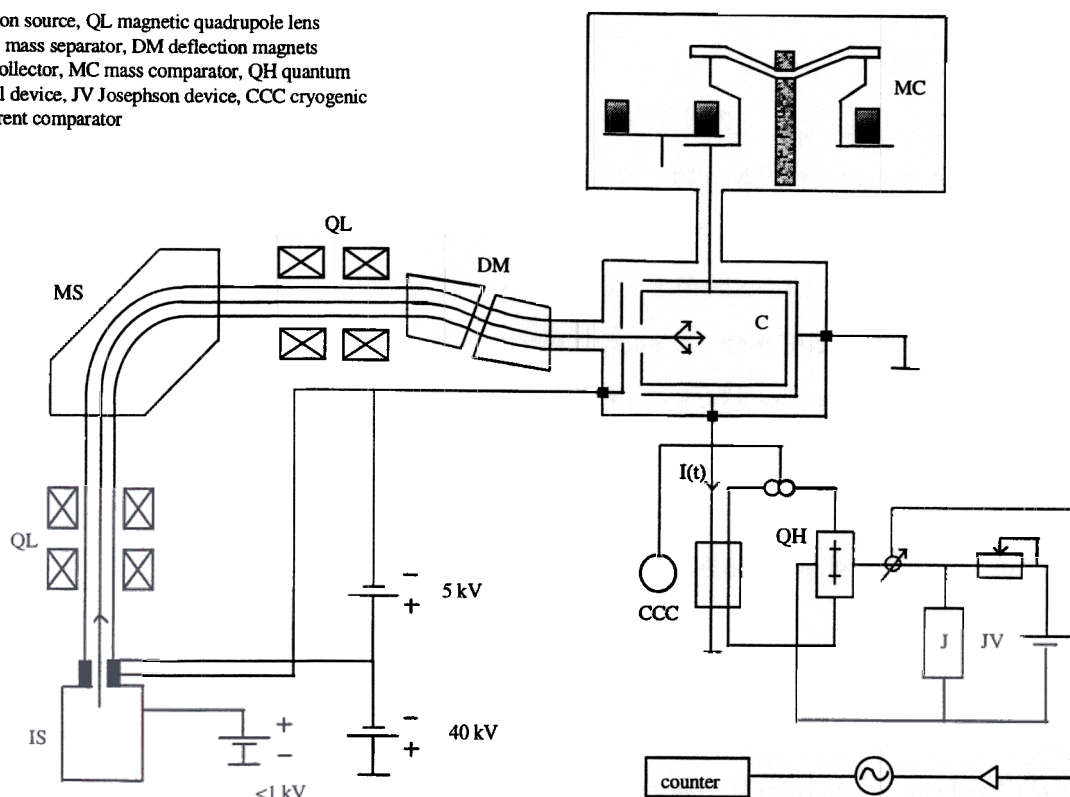
5.2 APPARATUS

Figure 13 shows the concept of the apparatus [46]. To date, the vacuum chambers and pumps, ion source (plasma discharge), magnetic quadrupole lenses, mass separator and deflection magnets have been assembled. An ultra-high vacuum is essential to avoid contamination of the accumulated ions through adsorption (see section 5.3.5).

PTB’s plans are to initially measure and integrate the current using secondary standards of resistance, voltage and time. The construction of a balance, whose design has been based on the flexure-strip balance at BIPM, is underway in the PTB workshops. The cost of the apparatus assembled to date is around £700k.

Figure 13 - Concept of Ion Accumulation Experiment (based on a diagram given in [46])

IS ion source, QL magnetic quadrupole lens
 MS mass separator, DM deflection magnets
 C collector, MC mass comparator, QH quantum
 Hall device, JV Josephson device, CCC cryogenic
 current comparator



5.3 PROGRESS

5.3.1 Gold (^{197}Au)

Gold will be used as it has a relatively large atomic mass, a natural isotopic abundance of 100% and is chemically inert with a low vapour pressure. It is hoped to achieve an ion current of around 10 mA which would enable 10 g of gold atoms to be accumulated in 6 days. This will provide a sufficient amount to weigh with an uncertainty of $\pm 1 \mu\text{g}$,

5.3.2 Ion Source

The ion source is an argon plasma source having a gold sputter electrode. The experiment will require an ion current of around 10 mA and a filament life-time of 6 days. However, there is no commercial source capable of achieving this specification. The present source has a life-time of

40 hours and can only achieve a current of μA . PTB will have either to develop or modify an existing source. A possibility may be one based on a hollow cathode.

5.3.3 Sputtering

At present, the greatest problem to overcome is the effect of sputtering. The binding energy of gold atoms is only a few keV. In order to produce a high ion current, a large voltage must be applied to the ion source and therefore a high energy beam (approximately 10 keV) emerges. For ions arriving at the collector with this energy, their sputter-rate will be greater than 1 (ie for every arriving ion, more than one will be removed from the surface). Even at 1 keV, the sputter-rate is around 1 %. Decelerating the beam to the point where less than 1 in 10^8 accumulated atoms are sputtered from the surface is not possible. The solution, therefore, is to both decelerate the beam and design a suitable shaped collector to retain the sputtered atoms.

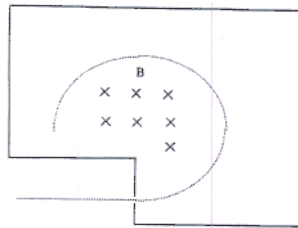
As a result of slowing the ions, they now have a greater divergence (inherent due to temperature of beam and electrostatic repulsion) and an electrostatic lens for focusing the beam onto the collector has been developed. However, the performance of this lens is not as good as hoped for and a more efficient device, probably based on a magnetic lens, must be developed.

5.3.4 Collector

The design of the collector will be crucial as no more than 1 in 10^8 of the accumulated atoms can be allowed to escape. Initially, a simple collector will be used in the form of a cylinder with a small aperture and corrugated base, to reduce the chance of a sputtered gold atoms escaping through the aperture:



Ultimately, a more complicated arrangement will be required, possibly with a magnetic field passing through the collector so that the path of the ion beam is circular:



So far, mathematical modelling (using Trim.Sp and Marlowe software packages) has been carried out to predict sputter rates and optimum design of the collector. PTB will start the development of a collector shortly and has planned the following experimental stages:

Use a quartz crystal balance (QCB) as a target to determine the sputter-rate.

Use a QCB to weigh material sputtered in different directions from a target.

Introduce a time-of-flight (TOF) mass spectrometer to determine the mass spectrum of sputtered material, to identify contaminants picked up from residual gas in vacuum system and from ion source.

This work, together with the delivery and installation of the balance, will constitute the programme for the next two years.

5.3.5 Contamination

Contamination of the accumulated gold atoms must be reduced below the level of 1 part in 10^8 . Foreign material originating from the ion source, such as argon and tungsten, should be deflected from the collector by the mass separator. However, due to the extreme temperature of the ion source, material can be removed from the surrounding walls and therefore PTB has specified that the chamber is to be constructed from stainless steel which is molybdenum free; two combined molybdenum atoms will have a similar atomic mass to gold and would not be deflected from the collector by the mass separator.

Collisions with the remaining gas molecules in the vacuum system may create new foreign particles travelling along the beam trajectory. Therefore, ultra-high vacuum conditions and another magnetic deflection area, just in front of the collector, is to be implemented.

6 CONCLUSIONS AND RECOMMENDATIONS

6.1 GENERAL

The Avogadro and Watt balance projects are the two major international approaches to the re-definition of the kilogram. They are also the most advanced in terms of progress made. The Ion counting project at PTB was started much more recently, and as such, is further behind. There are still many technical problems to be overcome prior to the apparatus being completed.

The progress made by the Avogadro and Watt balance projects is at a similar stage; both can realise their respective approaches with an uncertainty of around 1 part in 10^7 . If one approach was said to have an edge, it would be the NPL Watt balance as it is centred around one apparatus. The Avogadro project is spread throughout four national standards laboratories and the IRMM, in Belgium.

The aim of both projects, however, is not just an improved definition of the kilogram, and whichever ultimately succeeds in this respect, the other will still have an important role to play. Both projects will provide an important input in future adjustments by CODATA to the fundamental physical constants. The Avogadro project also has the following spin-offs:

- Support to the silicon manufacturing industry. Through characterisation of silicon in terms of its impurity contents and, in particular vacancies, it will aid the continuing miniaturisation of semiconductor technology based on silicon.
- New techniques in nanotechnology. Length transducers, such as the Combined Optical and X-ray Interferometer (COXI) [47] at NPL, have been developed solely from the technology of the lattice spacing measurements with scanning x-ray interferometers. Also, the emerging technology of angle measurements.
- Amount of substance measurements. Through the development of the Avogadro mass spectrometer, the IRMM now has the technology of providing a primary means for the realisation of amount of substance measurements within the SI system of units, with unprecedented accuracy.

The NPL Watt balance has the following spin-offs:

- Realisation of the ampere and volt in the SI system of units.
- Improvement in the measurement of the Josephson constant K_J towards 1 part in 10^8 .
- Electronics and analysis techniques developed for the moving-coil balance, particularly in the areas of low-noise computer-controlled measurements and power supply technology, are being used in many research areas within NPL and, in one instance, development by a commercial company.

6.2 AVOGADRO PROJECT

The three main parameters which need to be determined are the molar mass, density and lattice spacing. What follows is a summary of the possibility for NPL involvement in each area.

6.2.1 Molar Mass

Mass Spectrometer

The mass spectrometer developed at the IRMM is a highly specialised apparatus. The expertise gained by the IRMM in manufacturing the synthetic isotope mixtures and the modification of the mass spectrometer has been developed over almost 20 years. The apparatus alone has cost around £1 million to develop. For these reasons, it is not an area in which NPL could participate within the scope of the NMS Mass Programme.

Prompt (η, γ) spectroscopy

The successful development of the prompt (η, γ) spectroscopy at PTB may very well prove vital for the Avogadro project in terms of the race to provide a re-definition of the kilogram. Again, the expertise needed and size of the required budget would rule out NPL involvement.

6.2.2 Density

The density of a silicon artefact is determined from a combination of mass and volume measurements.

Mass

The measurement of the mass of a silicon artefact has been largely overlooked by the participants within the Avogadro project and thought to be relatively straightforward. However, with the other measurement disciplines now trying to push below the 1 part in 10^7 level, measurement of mass is becoming much more significant.

To achieve or better this level of uncertainty, techniques will have to be developed to characterise silicon artefacts in terms of surface adsorption, of both contaminants and water vapour. This will require a much better understanding of the surface oxides that form on the surface. Measurements in air will also require the development of air density artefacts to determine the large buoyancy corrections required.

If the artefacts are to be weighed in vacuum, then the de-sorption of contaminants will have to be studied. In addition, one must consider what effect the cycling of artefacts in and out of vacuum may have on their long-term stability. Furthermore, new analytical techniques developed from performing measurements in vacuum would be of direct benefit to the NPL Watt balance project.

At NPL we have the necessary expertise and apparatus to perform this research and, in doing so, could provide a valuable contribution to the Avogadro project: in the Mass and Density Standards group we have a 1 kg balance which can be used at atmospheric and vacuum pressures; within the Centre for Materials Measurement and Technology (CMMT) are apparatus capable of performing surface analyses. The ellipsometry measurements, needed to determine the thickness of surface oxide layers, could be bought-in from Southampton University.

Volume

If the Avogadro project were to succeed in providing a new definition of the kilogram, the demand for silicon artefacts would be great, with potentially hundreds manufactured worldwide. Having a facility to determine the volume of these artefacts would then take on a new significance. From a silicon ingot, several artefacts would be manufactured and the characterisation of each ingot, in terms of the molar mass and impurity content, is likely to be made by one of a few laboratories with the necessary expertise. However, to determine the mass of an artefact (equation 2) one also has to measure its volume. This measurement capability would probably be

limited to the larger NMIs.

Development of an interferometer at NPL would be unlikely to be of much benefit to the Avogadro project over the next few crucial years. IMGCC, PTB and NRLM have all developed interferometers. CSIRO is in the process of doing so. For NPL to compete with the present technology is likely to take several years. However, in the circumstance of the Avogadro project succeeding, it would be very beneficial for NPL to have this capability both in terms of international recognition and the potential business of hundreds of artefacts worldwide. Initially, provision of such a facility will involve no significant new research, but requires the construction of a design proven by one of the laboratories named above.

6.2.3 Lattice Spacing

This is perhaps the most advanced area within the Avogadro project in terms of progress made. The lattice spacing can now be determined with a relative uncertainty of a few parts in 10^8 and the next generation of scanning x-ray interferometers is under development. As with the molar mass, the expertise and budget required to develop the x-ray technology would preclude NPL from getting involved. Experience gained at NPL through the COXI apparatus is not directly relevant to developing scanning x-ray interferometers; the COXI apparatus is reliant on knowing the lattice spacing of its silicon crystal and cannot be used in reverse.

6.3 WATT BALANCE

The mass of the gold-plated copper artefacts, used in the Watt balance project at NPL, will need to be determined with an uncertainty of 1 part in 10^8 or better. The weighings will have to be performed in vacuum and, in common with the measurement of silicon artefacts, will require the characterisation of the artefacts with regard to surface adsorption and cycling in and out of vacuum. An alternative might be to provide artefacts made from a different material, but having a very low magnetic permeability, which have been thoroughly characterised. Artefacts manufactured from silicon would meet this requirement. Analytical techniques developed through research on silicon artefacts could be used to good effect in providing support for the Watt balance project.

6.4 ION COUNTING

PTB are interested in the possibility of collaboration with NPL on their Ion counting project; in particular, the development of a new ion source and magnetic lens to help focus the ion beam. However, with many technical problems still to be overcome before the development of the apparatus can be completed, this approach would appear to be significantly behind that of the Avogadro and Watt balance projects.

6.5 RECOMMENDATIONS

The Avogadro project is a very important international project, involving strong collaboration among the NMIs involved. If NPL does not take this opportunity to participate, and the project were to succeed in providing a re-definition of the kilogram, we would be at a considerable disadvantage.

By developing the expertise to determine the mass and surface contamination effects of silicon artefacts NPL could make a significant contribution to the Avogadro project as a whole. It would also provide vital experience if the use of silicon artefacts was to become common-place. For these reasons, a programme of research to achieve these aims should take priority. The techniques learned from this research could also be used in support of the NPL Watt balance project.

A facility to determine the volume of silicon artefacts would provide NPL with an important measurement discipline. However, the development of an interferometer should take second priority until the likely impact of silicon artefacts within mass metrology becomes clearer.

ACKNOWLEDGEMENTS

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