

AIR DENSITY MEASUREMENT FOR MASS CALIBRATION

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Abstract: The measurement of air density is crucial for any high accuracy mass calibration and is of particular importance when comparing weights of dissimilar materials such as stainless steel and platinum iridium. The current limit of accuracy to which air density can be determined is the major source of uncertainty in the dissemination of the mass scale for the majority of National Measurement Institutes.

Until fairly recently the main method for the determination of air density was by calculation from measurements of temperature, pressure and humidity using the equation recommended by the CIPM (Comité International des Poids et Mesures). Recently a number of laboratories, including the National Physical Laboratory in the UK, have developed artefact sets for the direct measurement of air density gravimetrically. This paper describes the development of the NPL artefacts and compares their results with those from the CIPM equation.

NPL have also been investigating alternative methods for the determination of air density including the use of an air refractometer, a vibrating U-tube densitometer and an Aerostat "floating" element device. The development, use and relative merits of these three methods will be described as will their current levels of performance and potential future accuracies. Discrepancies between the calculated value for air density from the CIPM equation and direct measurement by artefacts and the other methods described will also be discussed.

Keywords: CIPM Air Density Equation, Air Density Artefacts, Refractometer

1 INTRODUCTION

The measurement of air density is necessary in the field of mass measurement to allow buoyancy corrections to be made when comparing weights of different volume in air. It is particularly important when comparing weights of different materials or when making mass measurements to the highest accuracy. For the calibration of kilogram weights air buoyancy corrections range from a few milligrams when comparing similar materials such as stainless steel, to nearly 100 milligrams when comparing stainless steel and platinum-iridium and over 450 milligrams when comparing platinum iridium and silicon. For the present definition of the kilogram the effect of air buoyancy is the most significant uncertainty contribution in its dissemination and will be a significant factor in the work investigating alternative definitions.

2 AIR DENSITY DETERMINATION BY MEASUREMENT OF PARAMETERS

The standard method for determining air density involves the measurement of temperature, pressure and humidity. From these measurements, and taking into account carbon dioxide concentration for the best accuracy, the density of the air can be calculated. The empirical formula for the calculation of air density recommended by the *Comité International des Poids et Mesures* (CIPM) was derived by Giacomo [1] and modified by Davis [2]. Table 1 shows typical and best achievable uncertainties for the calculation of air density from the above parameters using the CIPM formula.

When comparing primary kilogram standards, made of platinum-iridium alloy, with secondary kilogram standards, made of stainless steel, there is a difference in volume of approximately 80 cm^3 . This gives a buoyancy effect of nearly 100 mg in air of standard density (1.2 kg/m^3). Table 1 shows the best uncertainty achievable for the measurement of air density from parameters is $1.33 \text{ in } 10^4$ which gives an uncertainty of 13 micrograms when comparing kilograms of platinum-iridium and stainless steel. This is, by a factor of about 4, the largest contribution to the uncertainty of mass of NPL's best stainless steel kilograms. These uncertainties and those given subsequently in the table are quoted at $k=1$. Even given the ability to make more accurate measurements on the parameters, the accuracy with which the air

density can be determined will always be limited by the 100 ppm uncertainty associated with the empirical equation.

Table 1. Routine and best measurement capabilities by measurement of parameters

	Routine Measurement		Best Capability	
	Uncertainty	ppm	Uncertainty	ppm
Temperature (°C)	0.1	360	0.01	36
Pressure (mbar)	0.5	500	0.05	50
Humidity (% RH/°C dew pt.)	5%	350	0.25°C	58
CO ₂ content (ppm)	-	-	50	21
CIPM Equation		100		100
Total (x 10⁻³ kg/m³)	0.86	720	0.16	133

3 AIR DENSITY DETERMINATION BY WEIGHING OF ARTEFACTS

Recently a number of national standards institutions and commercial weight manufacturers have developed artefacts for the direct measurement of air density. In general these consist of a pair of artefacts of different volumes designed for use on a commercial mass comparator, the measured weight difference of the artefacts being proportional to the density of the air at the time of weighing. Knowing the mass and volume difference between the artefact pair allows the density of the air to be calculated.

3.1 NPL artefacts for the direct measurement of air density

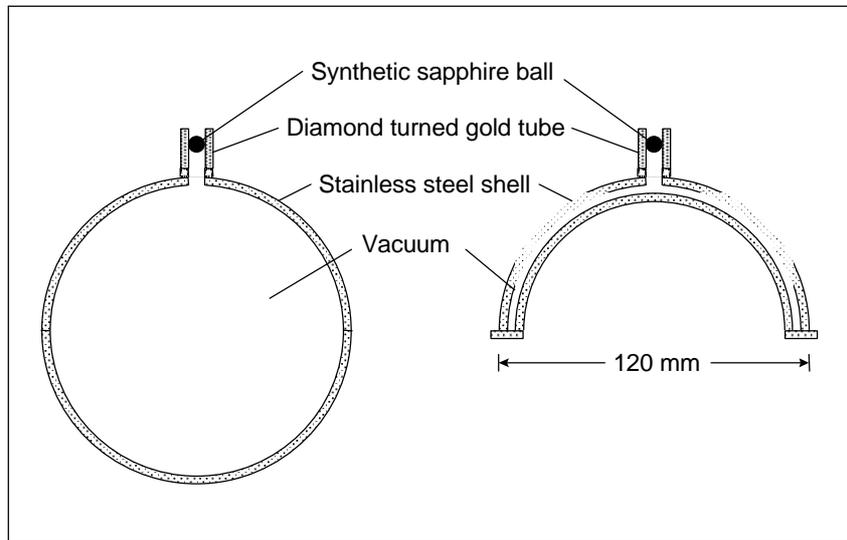


Figure 1. Schematic of NPL air density artefacts

The basic form of the NPL designed artefacts is shown in Figure 1. The artefacts are based on stainless steel hemispherical shells and when assembled have a mass of approximately 1 kilogram and a volume difference of approximately 770 cm³. This volume difference gives a differential buoyancy effect of nearly 1 gram in air of standard density. Thus the artefacts need only be compared to an accuracy of 10 micrograms to achieve an air density reading to an accuracy of 1 in 10⁵. The artefacts are assembled from essentially similar components and so are well matched in mass and in both internal and external surface areas. The mass of the artefacts was determined in the un-sealed condition by comparison with stainless steel kilogram standards with the need for only very small buoyancy corrections.

The artefacts were evacuated and sealed by means of a sapphire ball pressed into a diamond turned gold tube. This arrangement was chosen to provide a good seal while preserving the mass of the artefacts and to give well defined internal and external volumes. The mass change on the evacuation of the artefacts, due to outgassing of their internal surfaces, can be assumed to be the same for both artefacts because of the matching of the internal surface area and condition. The assembled artefacts are shown in Figure 2.

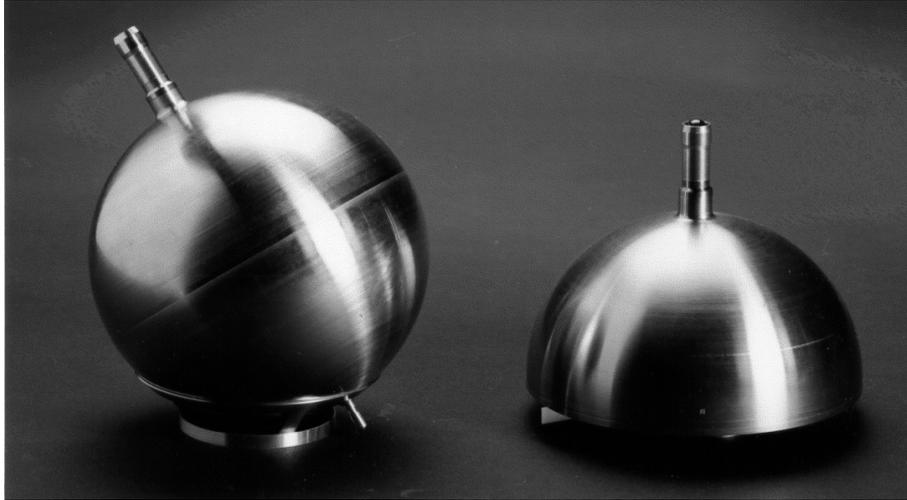


Figure 2. Assembled NPL air density artefacts

After evacuation and sealing the volumes of the artefacts were measured by hydrostatic weighing. Two pairs of artefacts were manufactured to allow the artefacts of similar volumes (spheres and hemispheres) to be compared with each other in air with only a small buoyancy correction. Such comparisons were made following hydrostatic weighing to monitor artefact stability and to check the integrity of the seals.

3.2 Commercial artefacts for the direct measurement of air density

The form of the commercial artefacts is shown in Figure 3. As with the NPL artefacts their volumes were determined by hydrostatic weighing. The assembled artefacts were weighed in vacuum to determine their true mass values.

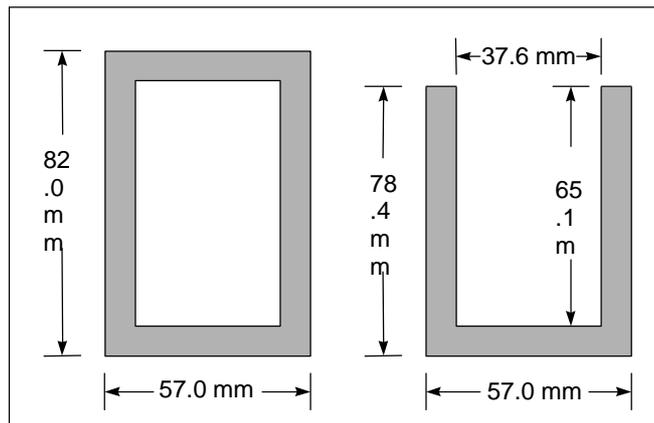


Figure 3. Schematic of commercial air density artefacts

3.3 Calibration of NPL and commercial air density artefacts

The performance of NPL and commercial artefacts was assessed against the standard method for calculating air density using the CIPM equation.

Table 2 shows the uncertainties associated with the mass and volume measurements for the two sets of artefacts and the overall contribution of these values to the uncertainty in air density measured using each artefact pair.

Table 2. Uncertainty contributions from artefact calibration

	Commercial Artefacts		NPL Artefacts	
	Measurement Uncertainty	Contribution to air dens. uncertainty (ppm)	Measurement Uncertainty	Contribution to air dens. uncertainty (ppm)
Mass of larger artefact (μg)	39	406	110	120
Mass of smaller artefact (μg)	15	156	104	114
Vol. of larger artefact ($\times 10^{-3} \text{ cm}^3$)	1.7	21	9.5	12
Vol. of smaller artefact ($\times 10^{-3} \text{ cm}^3$)	1.6	20	2.1	3
Total unc. on air dens. ($\times 10^{-3} \text{ kg/m}^3$)	0.52	436	0.20	166

It can be seen that the major source in the uncertainty of the measured air density comes from the uncertainty in the mass of the artefacts. The uncertainty of mass for both sets of artefacts comes predominantly from their instability. In weighing the un-sealed NPL artefacts uncertainties of less than 20 micrograms were achieved, but the instability of the artefacts afterwards means that an overall uncertainty of about 100 micrograms must be assigned. Similarly, weighing the commercial artefacts in vacuum gives an uncertainty of less than 15 micrograms but some instability in the values of these artefacts has also been noted increasing the uncertainty on their mass values to 40 micrograms in the worst case.

The uncertainty contributions in Table 2 show that while it may theoretically be possible to achieve an uncertainty of 1.7×10^{-4} on air density with the NPL artefacts, the commercial artefacts are limited to an uncertainty of 4.4×10^{-4} due to instability in their relative mass values and their smaller buoyancy effect (100 mg) compared with the NPL artefacts (1 gram).

4 AIR DENSITY DETERMINATION BY REFRACTOMETRY

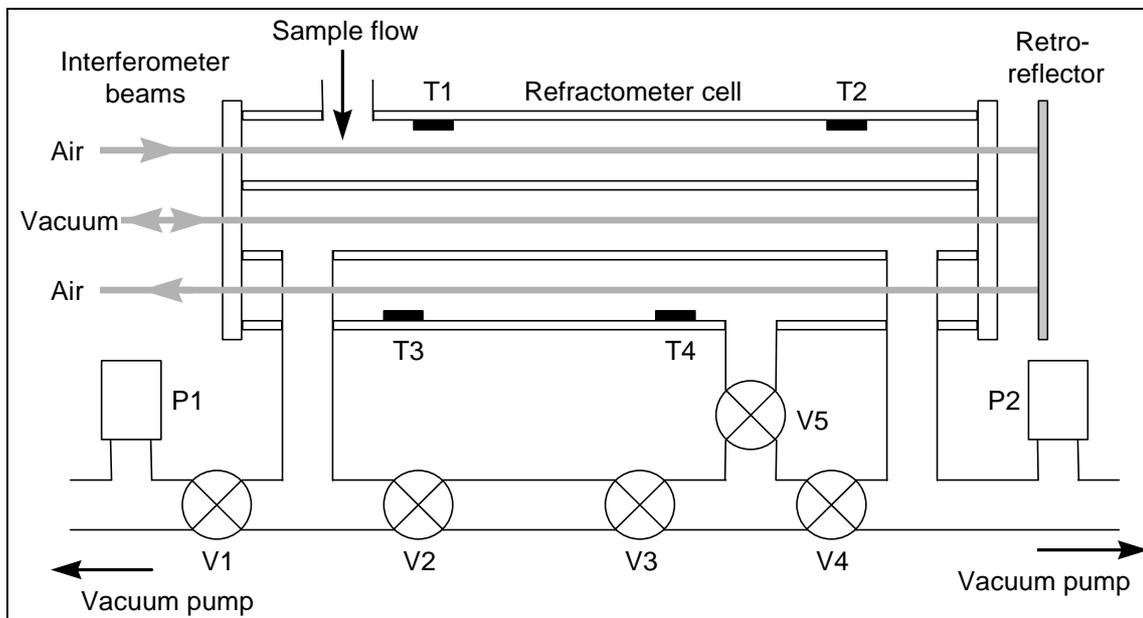


Figure 3. Schematic of NPL refractometer

Another indirect method for the determination of the density of air is by refractometry. The refractive index of air is measured using a refractometer which compares the wavelength of light in a vacuum with that in a sample of the air to be measured using interferometry. By this means, and using the equation derived by Edlén [3], the refractive index of the air can be derived. Figure 3 shows the basic configuration

of the NPL refractometer [4] indicating the position of Penning gauges (P) temperature sensors (T) and pneumatic valves (V).

Having measured the refractive index of the air its absolute density can be calculated from equation (1).

$$r_{air} = \frac{2}{3} \cdot \frac{\sum M_i}{\sum A_i} \cdot (n - 1) \quad (1)$$

where M_i and A_i represent respectively the molecular weight ratios and refractivities of the component gases of the air and n is its refractive index. For the purpose of this comparison the refractometer has been used to measure only changes in the density of the air as this overcomes problems regarding determination of the ratios of the constituent gases in the ambient air.

5 COMPARISON OF AIR DENSITY DETERMINATION METHODS

The commercial and NPL artefacts, together with the NPL refractometer, have been compared with a standard parametric air density measuring kit. Mass measurements were made using a Mettler AT10005 ten kilogram mass comparator. The parametric air density kit consisted of two 100 Ω platinum resistance thermometers (PRTs) feeding a Tinsley temperature bridge, a Druck DPI 140 barometer and a Michell series 3000 dew point meter. The uncertainties on these instruments were 0.01°C, 0.05 mbar and 0.25 °C respectively. These combined with the uncertainty in the CIPM equation gave an overall uncertainty in the calculated air density of 133 ppm or $1.6 \times 10^{-4} \text{ kg/m}^3$.

Figure 4 shows typical deviations in the air density measured by the artefact and refractometry methods when compared with the CIPM equation. The graph shows that both the artefact pairs give an air density value lower (by 0.006 kg/m^3 on average) than that calculated using the equation. The standard deviations of the air densities measured by the artefacts is of the order of 0.001 kg/m^3 and, given the different methods by which they were initially calibrated, the difference in the measured values is significant.

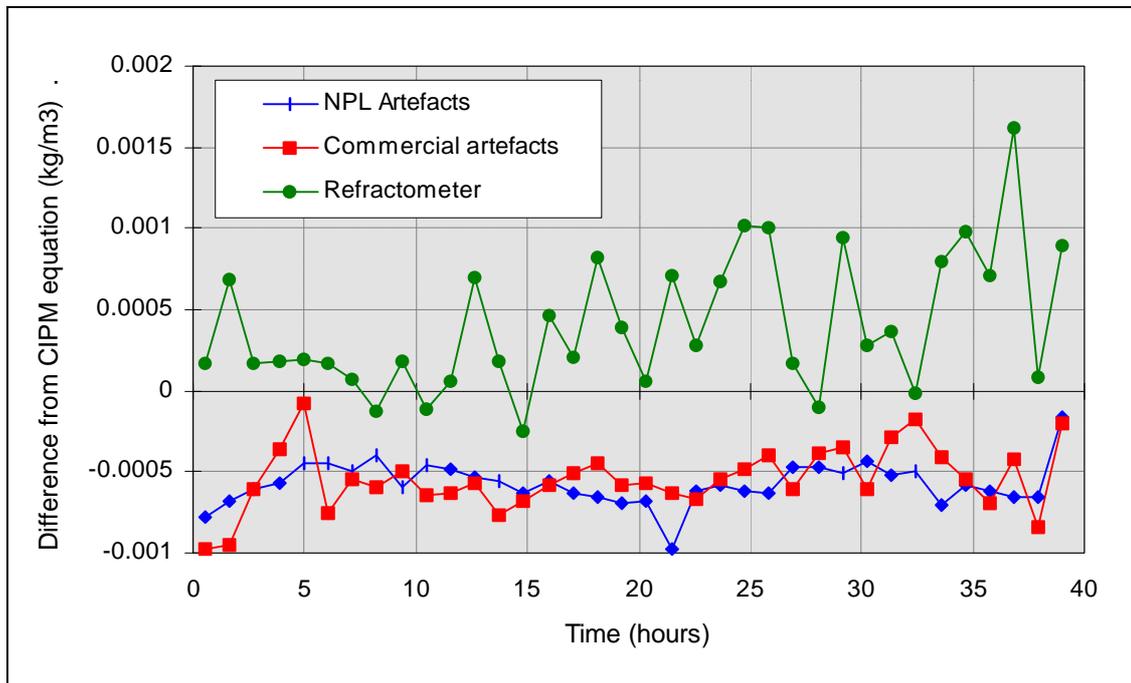


Figure 4. Comparison of artefacts and refractometer with CIPM equation

The refractometer was calibrated by comparison with the result from the CIPM equation before the test and the results shown have been calculated based on this comparison. Agreement between the refractometer and the equation is reasonable at the start of the test but at the end the results have drifted up and the spread is also greater. This indicates that perhaps 40 hours is too long to run the device without re-calibration. The overall standard deviation of the refractometer results was 0.006 kg/m^3 over the 40 hour period.

6 CONCLUSIONS

While it is possible for a pair of artefacts to give a measurement of air density which is both independent of the CIPM equation and of a similar accuracy, the ultimate uncertainty of the method is limited by the mass stability of the artefacts. To obtain a better uncertainty than is achievable via the equation the artefacts should have a large volume difference (at least 200 cm³), good surface finish and well matched external surface areas. Thought should also be given to the shape of the artefacts to avoid the effect of thermal instability inside the weighing chamber of the balance on which they are used.

A major drawback with the use of artefacts is that they occupy two stations on a weighing carousel which could otherwise be used for mass standards. They also have a much longer measurement interval than temperature, pressure and humidity sensors, and, by necessity, cannot be used to measure air density at the exact time the other weights on the carousel are being measured. This makes this method particularly sensitive to errors caused by short term fluctuations in air density.

The refractometer gives another, largely independent, approach to air density measurement. However, it is limited in that it can generally only measure changes in air density and cannot be used to measure absolute values unless the composition of the ambient air can also be determined. The refractometer must be regularly checked against the CIPM equation. It also requires compensation for temperature (and for humidity variations of above 2% RH) and should ideally be used drawing air from around a balance in a sealed enclosure.

7 ALTERNATIVE METHODS FOR THE DETERMINATION OF AIR DENSITY

Given the discrepancy between the air density measured by the artefacts and calculated from the CIPM equation, NPL has been investigating alternative methods for the measurement of air density. These methods should be both independent of the CIPM equation and also offer better potential accuracy than can be achieved by this method. Also, given the expense of assembling a parametric air density measurement facility to the highest accuracy and the inefficiency of the artefact approach, methods which potentially offer cheaper and easier to use alternatives should be considered.

NPL hope to be able to evaluate a method for measuring air density using a resonance sensor. This approach has been used effectively in both the measurement of liquid density and atmospheric pressure. By modifying such a sensor and calibrating it with suitably pure gas samples it is hoped to provide an independent assessment of the accuracy of the artefact and parametric approaches to air density measurement.

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