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Determination of Air Density with Buoyancy Artefacts

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Abstract

When comparing mass standards with large volume differences the density of air is one of the largest uncertainty components for mass. The air density can be determined by direct weighing using buoyancy artefacts or it can be calculated from the CIPM 81/91 formula. A small relative difference (about $6\cdot10^{-5}$) between these two methods exists. The aim of the present work is to verify this difference and to gain experience on vacuum weighing and on the stability of weights. Two buoyancy artefacts with different volumes were utilized. The artefacts were compared in vacuum and in air. From the weighing results air density was calculated and compared with the CIPM formula. The following value for the relative air density difference was obtained 4 x 10^{-5} (u=7 x 10^{-5}).

Key words: air density, buoyancy artefacts, vacuum weighing

1. Introduction

The mass of an object can be determined by comparing its mass with known mass standards. The comparison is usually carried out in air using a mass comparator. The weighing results are corrected for air buoyancy. Air buoyancy depends on the volume difference of the compared objects and on the air density. Volumes can be determined with sufficiently small uncertainties using e.g. the hydrostatic weighing methods.

The air density is usually calculated from the measured air parameters using an equation recommended by CIPM [1,2]. The equation requires values for air temperature, pressure, humidity (relative humidity or dew point) and CO_2 content. These parameters are relatively easy to determine even in routine measurements. The relative standard uncertainty of the formula is about $6.5\cdot10^{-5}$ [1,3]. The combined standard uncertainty of the input parameters is of the same order of magnitude or higher.

Air density can also be determined with two specially designed buoyancy artefacts. The artefacts are compared in vacuum and in air. The artefacts should have large volume difference. The air buoyancy artefacts method was developed by Kobayashi [4]. The method has been applied by many laboratories [5-9]. With the buoyancy method the air density can determined with a relative uncertainty which can be smaller than 10^{-5} [3].

Recently it has been found that the CIPM formula gives too low values for the air density [10]. This was revealed when the CIPM formula was compared with the results from the air buoyancy artefacts method. The relative difference between the artefact results and the CIPM formula is about 6.4×10^{-5} [10]. The difference was practically independent on the values of temperature, pressure or humidity. The reason for the discrepancy has been found to be the Ar content of air, which has been too low. The CIPM formula uses a value 9.17 mmol/mol whereas recent re-determination gave a value 9.332 mmol/mol [11]. This change increases the molar mass of dry air by 6.6×10^{-5} which is in good agreement with air density results.

Main reasons for the increased interest in the buoyancy method are smaller uncertainty and the ability to reveal mass changes due to vacuum – air transfer. The new definition of the kilogram will most probably be such that the kilogram will be defined in vacuum. This makes mass changes due to the vacuum – air transfer important. Such changes can be studied with buoyancy artefacts.

In the present work air density values from the CIPM formula are compared with simultaneous weighing results with buoyancy artefacts. Also the stability of the artefacts are presented.

2. Air Density Determination

2.1 The CIPM 81/91 formula

The formula for the density of air can be obtained from the equation of state of a non-ideal gas. It can be presented in the following form as recommended by CIPM 81/91 [1,2] .

$$\rho_a^{CIPM} = \frac{pM_a\left[1 - x_v\left(1 - {M_v}/{M_a}\right)\right]}{ZRT} \qquad (1)$$

In CIPM recommendation the following parameters are fixed by ; molar mass of dry air M_a , molar mass of water M_v , molar gas constant R and the forms and coefficients of the compressibility factor Z and mole fraction of water vapour x_v . The formula requires measurements of air parameters, such as humidity (here hidden in mole fraction of water vapour), temperature T, pressure p and possibly the amount of carbon dioxide in air.

2.2 Air buoyancy artefacts method

The air buoyancy artefacts method requires a comparison of two artifacts in air and in vacuum. To reduce surface effects the surface area and surface finish and the material of the artefacts should be the same. Also the masses should be similar. The volume difference should be as large as possible.

When the buoyancy artifacts are weighed in air their mass difference is

$$\Delta m_{air}=\Delta I_{air}+\rho_a\Delta V \qquad (2)$$

where ΔI_{air} is the indication difference of the mass comparator for the two artifacts and ΔV is their volume difference.

In vacuum no buoyancy correction is required and the mass difference is the indication difference.

$$\Delta m_{vac}=\Delta I_{vac} \quad . \qquad (3)$$

If the surface area difference of the artifacts is ΔS and the mass absorption coefficient is σ then the relation between the mass differences is

$$\Delta m_{air} =\Delta m_{vac} + \sigma\Delta S \;\; . \qquad (4)$$

For polished stainless steel surfaces the absorption coefficient σ is usually small (below 0.5 µg/cm^2). By combining (2)-(4) the air density is obtained from the relation:

$$\rho_a^{art}=(\Delta I_{vac}-\Delta I_{air} +\sigma\Delta S)/\Delta V \; . \qquad (5)$$

If ρ_a in (2) has been calculated using (1) then the difference in air density between the artefacts method and the CIPM formula is

$$\Delta\rho_a= \rho_a^{art} - \rho_a^{CIPM} = (\Delta m_{vac} - \Delta m_{air})/ \Delta V. \qquad (6)$$

In (6) the surface absorption has been omitted.

3. Experimental Details

3.1 Mass Comparator

The weighing was performed with a 1 kg mass comparator (Mettler HK1000MC) enclosed in a vacuum chamber. The mass comparator is the same as in [6]. The weight handler has been renewed. The pumping system consists of a turbo-molecular pump and a scroll pump. The turbo-molecular pump is fixed to the vacuum chamber. A scroll pump is connected to the turbo pump with a 10 m long flexible vacuum tube. The lowest pressure which can be reached in 3 days is about 0,01 Pa.

The temperature of air is measured with Pt100 sensors connected to a digital thermometer. The resolution of the thermometer is 1 mK. The self heating of the sensors in still air is about 5 mK and the time constant is about 50 s. The main temperature sensor is located close to the weighed mass at about half height of the weight. Another sensor is located higher on the opposite end on the weighing chamber. The temperature difference between the sensors is about 10 mK.

Air pressure is measured with a barometer which has a capacitive silicon sensor. The resolution of the barometer is 1 Pa. The sensor is approximately at the same height as the weight.

The humidity of air is measured either with a cooled mirror dew point hygrometer or a capacitive relative humidity sensor. The dew point hygrometer needs air circulation. The circulated air can be returned to the chamber. If the relative humidity sensor is used it is compared with the dew point hygrometer before closing the chamber.

The CO_2 contents is measured with an infrared absorption sensor located outside the weighing chamber. The resolution is 1 µmol/mol. The sensor is calibrated with a reference gas consisting of 377(10) µmol/mol CO_2 in artificial dry air.

3.2 Buoyancy artefacts

MIKES has buoyancy artefacts which have been manufactured in 1994. The nominal mass of the artefacts is 1 kg. The artefacts have been used in Ref [6]. Table 1 gives the main properties of two artefacts. One artefact is a hollow cylinder and the other is a bobbin shape. The volume difference is about 53.8 cm^3. We also have a third artefact, which is solid cylinder. It is used in surface sorption studies. The sorption coefficient when the weights were moved from vacuum to air was about 0.2 $\mu g/cm^2$.

4. Measurements and Results

The mass difference between the buoyancy artefacts were measured several times in air and in vacuum during the time period 3.8.2005 – 23.8.2007. Usually the measurement in vacuum took 1-2 week and the measurements in air 2-4 weeks. Fig. 1 shows the mass difference of the artefacts in air and in vacuum. The air density is obtained from (1). The indication differences in air depend on the air density. Table 2 shows the results in numerical form. Also the time periods when the measurements were made are given. Relative air density differences between the artefact method and the CIPM formula is given in Fig. 2. The results are also given in Table 2. The stability of the mass of the bobbin shape buoyancy artefact is given in Table 3.

5. Uncertainties

In tables 4 and 5 the uncertainty budgets for the CIPM formula and for the buoyancy artefacts method are given. In the CIPM formula the uncertainties are straightforward to calculate. The sensitivity coefficients can be found in Ref [1]. The uncertainty components due to temperature, pressure and humidity are of the same order of magnitude. The uncertainty of the formula have not been included.

The uncertainty of the buoyancy artefacts method depends on weighing results in vacuum and in air and on the volume difference. Also the stability of the buoyancy artefacts is an important uncertainty component. The sensitivity coefficients for the indication difference is $1/\Delta V/\rho_a$ and for the volume it is $1/\Delta V$.

6. Conclusions

The uncertainty of the buoyancy artefacts method is largely determined by the instability of the artefacts. This can be seen in Fig. 1 and in Table 3. One possible reason for the instability is contamination in vacuum. After vacuum measurements we usually fill the chamber with pure nitrogen. To have more reproducible results we have cleaned the artefacts two times during the measurements. For cleaning we have used pure alcohol in an ultrasonic bath followed by rinsing in distilled water. Cleaning is not recommended but in our case it gives more reproducible results. For some weights the mass increases about 20 µg after each vacuum exposure.

In the buoyancy artefacts method for weighing results in air we have used values which have been taken both before and after with vacuum weighing. Often It seems that the values before the vacuum are more reliable.

In this study the relative standard uncertainty of the CIPM method is $5\cdot10^{-5}$ and that of the air buoyancy method is $4.9\cdot10^{-5}$. The relative difference for air density between the two methods is $(\rho_a^{art} - \rho_a^{CIPM})/\rho_a = 4\times10^{-5}$ ($u=7\times10^{-5}$). This result is somewhat smaller than the earlier result 6.4×10^{-5} [10]. Within the uncertainties the values agree. Our uncertainty can not be significantly improved with present artefacts and mass comparator.

References

[1] P. Giacomo, Equation for the determination of the density of moist air (1981), Metrologia 18, (1982) 33-40

[2] R. S. Davis, Equation for the determination of the density of moist air (1981/91), Metrologia 29, (1992) 67-70

[3] A. Picard, H. Fang, Three methods of determining the density of moist air during mass comparisons, Metrologia 39, (2002) 31-40

[4] Y. Kobayashi, Y. Nezu, K. Uchikawa, S. Ideda, H. Yano, Prototype kilogram balance II of NRLM, Bull. NMRL 35, (1986) 143-58

[5] M. Gläser, R. Schwartz, M. Mecke, Experimental determination of air density using a 1 kg mass comparator in vacuum, Metrologia 28, (1991) 45-50

[6] K. Riski, H. Kajastie, Mass measurements with density artefacts at reduced pressure, Proc. IMEKO TC3, Warszawa September 5-8, 1995

[7] S. Davidson, Air density measurement for mass calibration, IMEKO 2000, TC3, Vienna, September 25-28, 2000

[8] A. Pickard, H. Fang, Mass comparisons using air buoyancy artefacts, Metrologia 41, (2004) 330-332

[9] J.W. Chung, M. Borys, M. Firlus, W.G. Lee, R. Schwartz, Bilateral comparison of buoyancy artefacts between PTB and KRISS, IMEKO TC3, 2005

[10] A. Pickard, H. Fang, M. Gläser, Discrepancies in air density determination between the thermodynamic formula and gravimetric method: evidence for a new value of the mole fraction of argon in air, Metrologia 41, (2004) 396-400

[11] S.Y. Park, J.S. Kim, J.B. Lee, M.B. Esler, R.S. Davis, R.I. Wielgosz, A re- determination of the argon content of air for buoyancy corrections in mass standard comparisons, Metrologia 41, (2004) 387-395

Table 1, Main characteristics of the buoyancy artefacts

	Hollow	Bobbin
Diameter	55.8 mm	56.0 mm
Height	73.2 mm	67.8 mm
Volume	178.8730(7) cm^3	125.0516(5) cm^3
Surface area	168.89(5) cm^2	169.06(5) cm^2
Volume difference	53.8214(9) cm^3	
Surface roughness, R_a	< 0.1 μm	
Magnetic susceptibility	0.003(1)	
Volume exp. coeff.	$4.8 \cdot 10^{-5}$ /K	
Density (material)	7997 kg/m^3	
Material	AISI 317LMN (Cr 18, Ni 17, Mo 4, Mn 2)	

Table 2, Results of the buoyancy artefacts measurements in vacuum and in air. The masses are in milligrams.

Dates	Δm_{vac}	Dates	Δm_{air}	Δm_{vac}-Δm_{air}	$\Delta\rho_a/\rho_a$
4-6/05	42.6553	8/05	42.6531	0.0022	0.000033
12/06	42.6569	9-10/06	42.6538	0.0030	0.000047
1-2/07	42.6622	1/07	42.6605	0.0017	0.000026
2/07	42.6811	7/07	42.6786	0.0025	0.000039
8/07	42.6785	8-9/08	42.6753	0.0032	0.000049
average					0.000039

Table 3, Stability of the bobbin shape buoyancy artefact

Date	m - 1 kg (mg)	
8.6.2005	2.953	
		vacuum
24.8.2005	2.988	
		cleaning
9.12.2005	2.922	
2.11.2006	2.991	
		2 x vacuum
		cleaning
4.7.2007	2.962	
		vacuum
21.8.2007	2.986	
		cleaning
7.9.2007	2.945	

Table 4, Uncertainty budget for air density determination using CIPM formula

	u		$u_i(\rho_a)$	
Temperature	0.005	K	2.1E-05	kg/m^3
temperature gradient	0.005	K	2.1E-05	kg/m^3
self heating	0.002	K	8.2E-06	kg/m^3
pressure	3	Pa	3.6E-05	kg/m^3
height correction	1	Pa	1.2E-05	kg/m^3
Dew point	0.1	K	3.4E-05	kg/m^3
CO_2	20	mmol/mol	9.8E-06	kg/m^3
$u_c(\rho_a^{CIPM})$			6.0E-05	kg/m^3
$u_c(\rho_a^{CIPM})/\rho_a$			5.0E-05	

Table 5, Uncertainty budget for the buoyancy artefacts method

Mass difference in vacuum	*u*		$u_i(\rho_a)/\rho_a$
additional weights	0.0008	mg	
indication difference	0.0010	mg	
balance sensitivity	0.0005	mg	
repeatability	0.0015	mg	
$u_c(\Delta I_{vac})$	0.0020	mg	
Mass difference in air			
additional weights	0.0005	mg	
indication difference	0.0010	mg	
balance	0.0005	mg	
repeatability	0.0015	mg	
absorption	0.0010	mg	
$u_c(\Delta I_{air})$	0.0022	mg	
Air density			
$u_c\ (\Delta I_{vac}-\Delta I_{air})$	0.0030	mg	4.2E-05
Volume difference	0,0009	cm^3	1.7E-05
$u_c(\rho_a^{art})/\rho_a$	4.9E-05		

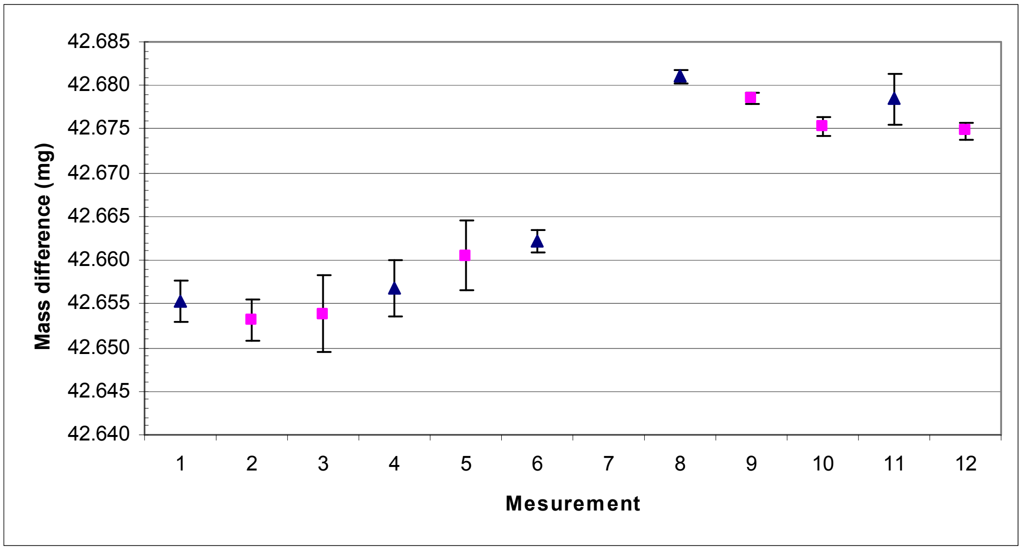

Figure 1. Mass differences of the buoyancy artefacts measured in vacuum (triangles) and in air (squares) using the CIPM formula. The error bars are standard deviation of results.

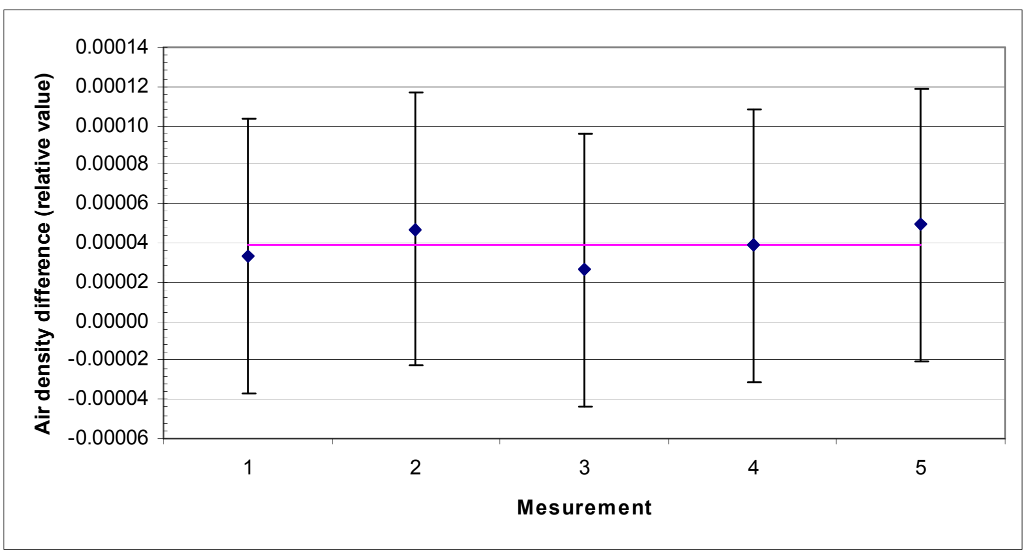

Figure 2. Relative air density difference between the artefacts method and the CIPM formula. Solid line is the average of the results. The error bars are standard uncertainties.