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Liquid density determination by using a solid density standard

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Workshop on Hydrometer Calibration
21 -23 November, 2006

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Density

Density is a quantity derived from mass and volume (kg/m^3)

$$\rho = \frac{m}{V} = \frac{mass}{volume}$$

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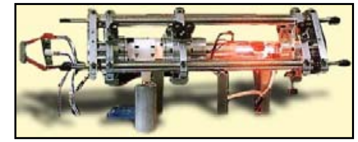
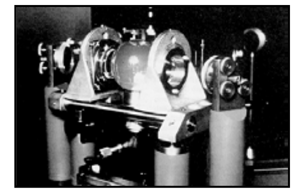


Mass Standard

Length Standard



Primary Standard
Solid Density Standard

Secondary Standard
Solid Density Standard

Water

Liquid Density Standards

Solids

Air density

Density meters, Hydrometers, solids and liquids

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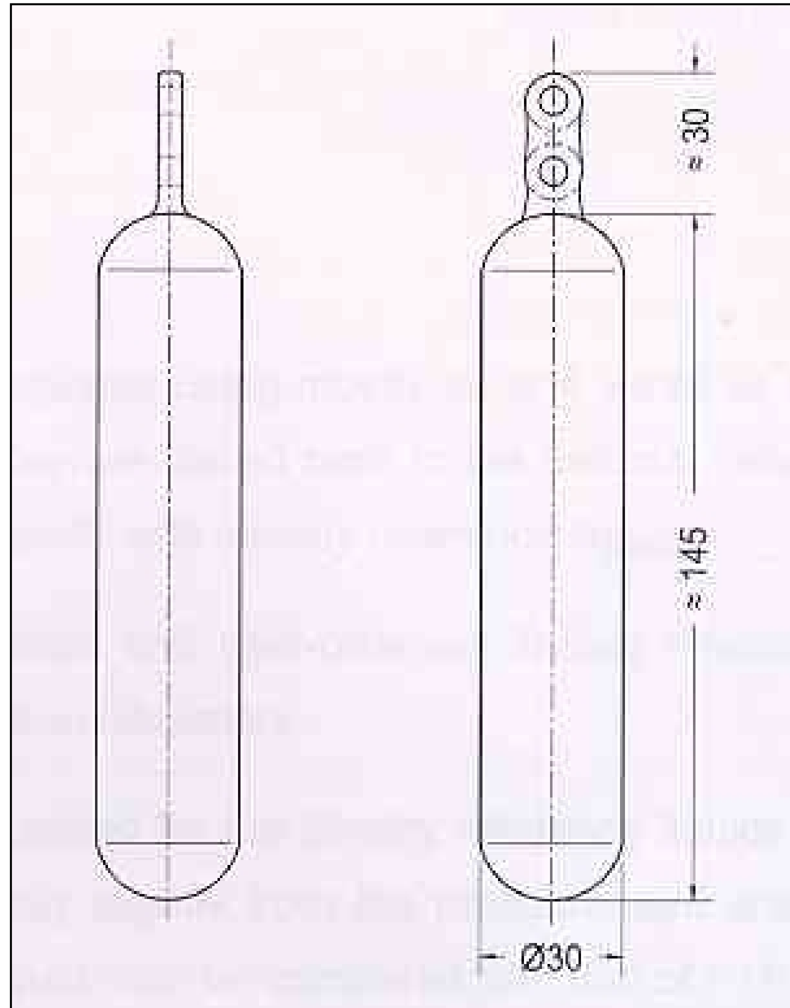

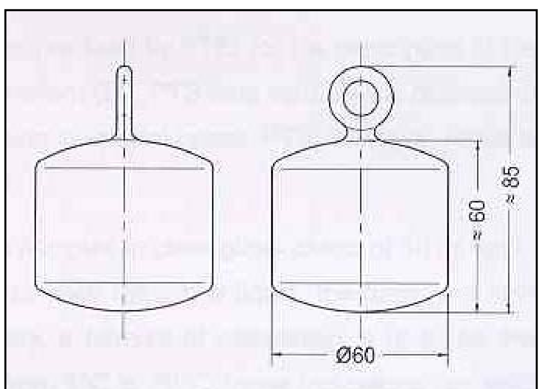

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Materials used for solid density standards

Material	Density	Cubic thermal expansion coefficient
Silicon single crystal	≈ 2,3 g cm^{-3}	6 x 10^{-6} K^{-1}
Fused silica	≈ 2,2 g cm^{-3}	1,5 x 10^{-6} K^{-1}
Zerodur	≈ 2,5 g cm^{-3}	0 x 10^{-6} K^{-1}
BK8 (Optical glass)	≈ 2,6 g cm^{-3}	26,7 x 10^{-6} K^{-1}
Others…		

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Liquids used as density standards

Liquid	Density at 20ºC
Isooctane	≈0,690 g/cm^3
n-nonane	≈ 0,720 g/cm^3
Ultra pure water	≈ 0,998 g/cm^3
2,4 dichlorotoluene	≈ 1,250 g/cm^3
Tetrachloroethene	≈ 1,650 g/cm^3
Others…	

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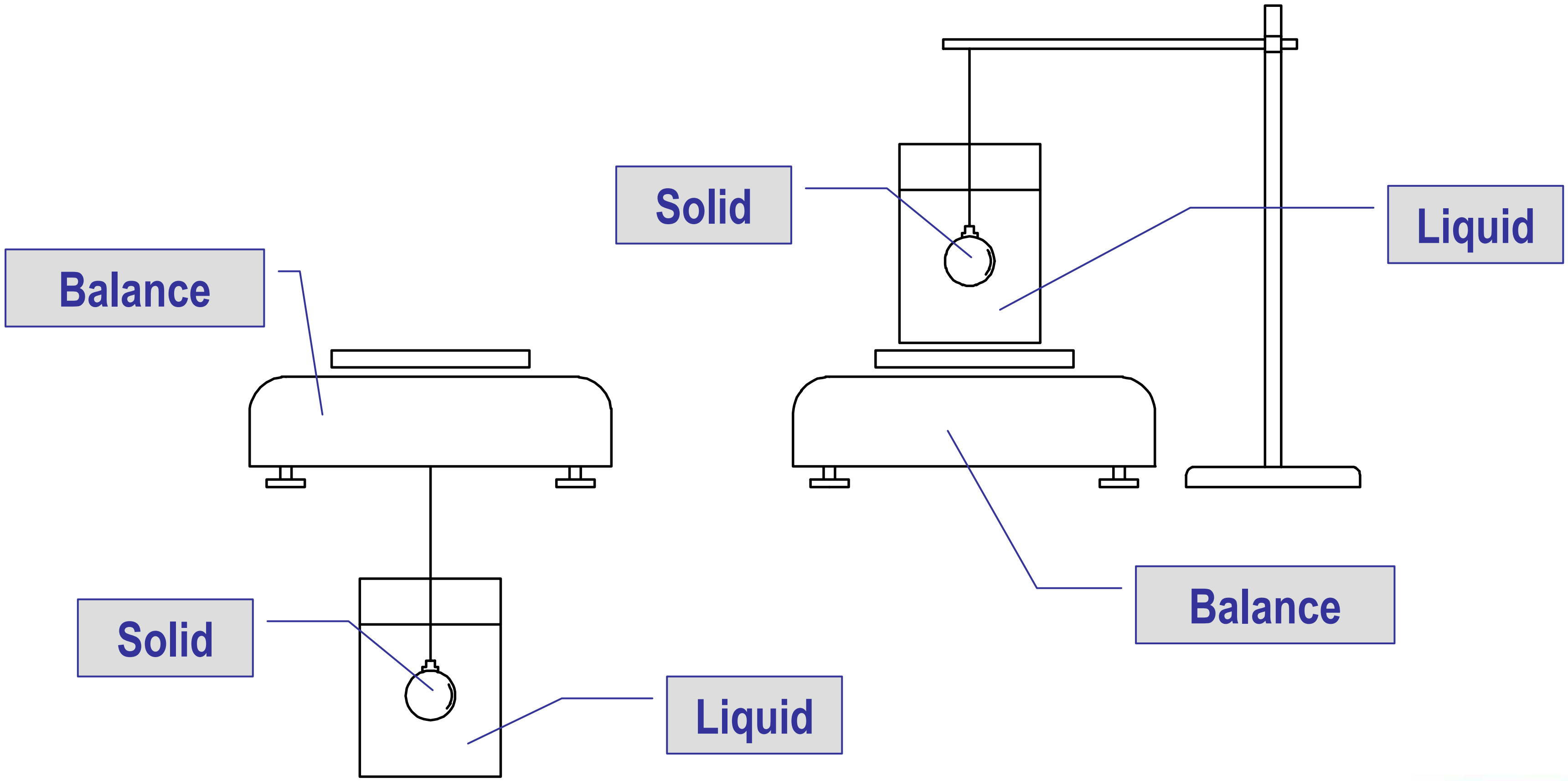
Hydrostatic weighing



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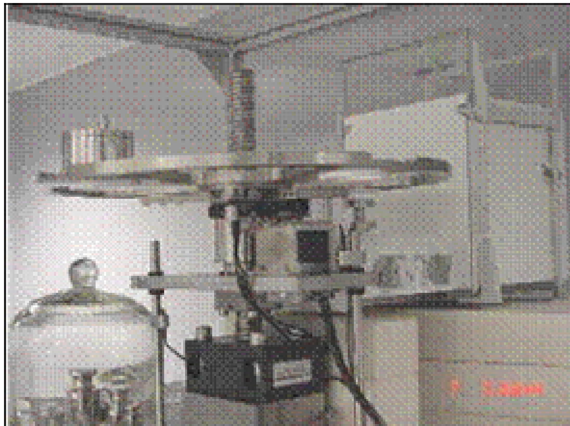

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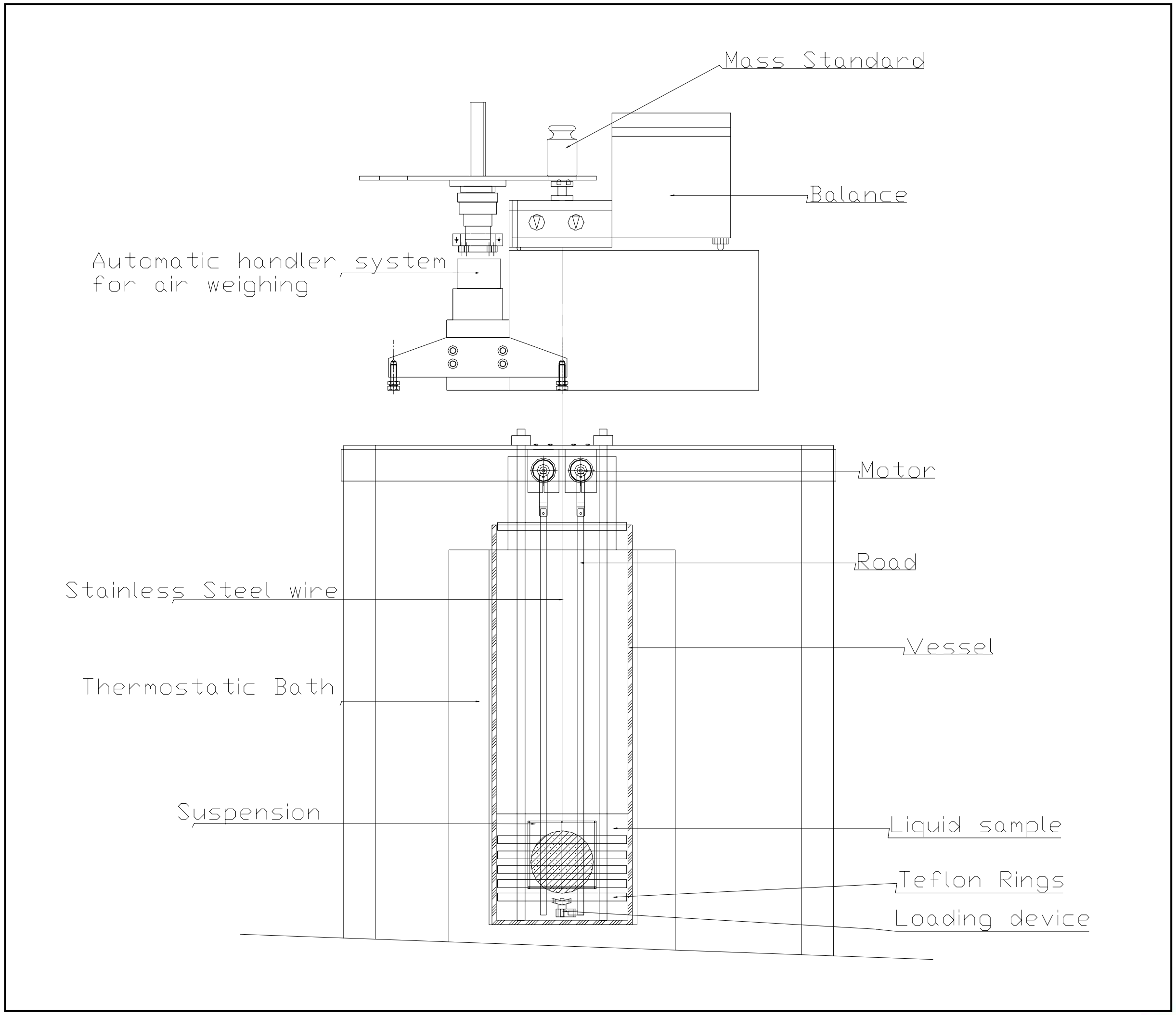

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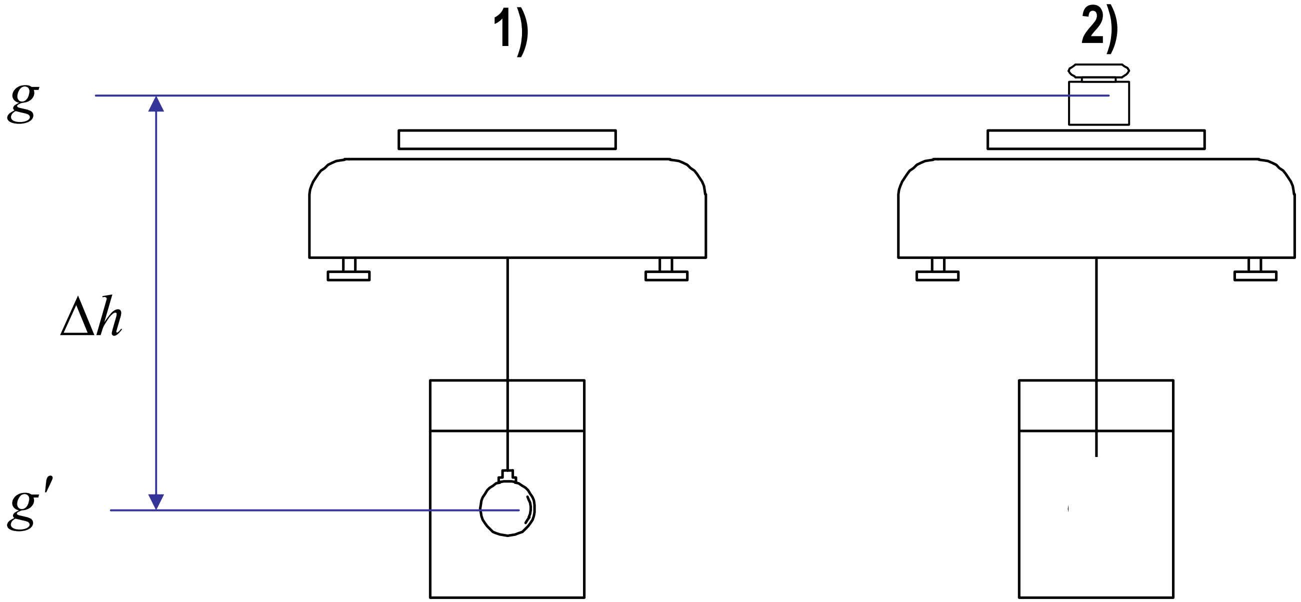
Hydrostatic weighing system

Hydrostatic weighing for liquid density measurement



1) $$I_{ds}k\theta = g'\cdot\left[m_{ds} - \rho_L V_{ds}\cdot\left[1+\alpha_{ds}\left(t_{liq}-t_{ref}\right)\right]\cdot\left[1-\beta_{ds}\left(p_{liq}-p_{ref}\right)\right] + \left(\frac{\pi\gamma_{liq}d}{g'}\right)\right]$$

2) $$I_{ms}k\theta = g\cdot\left[m_{ms} - \rho_{air} V_{ms}\left[1+\alpha_{ms}\left(t_{air}-t_{ref}\right)\right]\cdot\left[1-\beta_{ms}\left(p-p_{ref}\right)\right] + \left(\frac{\pi\gamma_{liq}d_0}{g'}\right)\right]$$

$$g' = g\cdot\left[1-\left(\frac{\partial g}{\partial h}\right)\cdot\left(h_{ms}-h_{ds}\right)\right] \qquad 1 \approx \left[1-\beta_{ms}\left(p-p_{ref}\right)\right]$$

Evaluation of the liquid density

Solving the weighing equations for the liquid density and applying the temperature correction the pressure correction in order to evaluate the liquid density at reference conditions

$$\rho_{L(T,P)} = \left\{ \left[\frac{m_{ds} - m_{ms} + \rho_{air} V_{ms} \left[1 + \alpha_{ms} \left(t_{air} - t_{ref}\right)\right] - \Delta m S b^{-1} - Gc - Mc}{V_{ds} \cdot \left[1 + \alpha_{ds} \left(t_{liq} - t_{ref}\right)\right] \cdot \left[1 - \beta_{ds} \left(p_{liq} - p_{ref}\right)\right]} \right] + \alpha_{liq} \left(t_{liq} - t_{ref}\right) \right\} \cdot \left[1 - \beta_{liq} \left(p_{liq} - p_{ref}\right)\right]$$

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Where,

ρ_L	**Liquid density at the measured temperature and pressure [kg m^{-3}]**
m_{ds}	**Mass of the density standard [kg]**
V_{ds}	**Volume of the density standard at 20ºC and 101325 Pa [m^3]**
α_{ds}	**Thermal expansion coefficient of the zerodur [K^{-1}]**
β_{ds}	**Isothermal compressibility coefficient of the density standard [Pa^{-1}]**
β_{ms}	**Isothermal compressibility coefficient of the mass standard [Pa^{-1}]**
m_{ms}	**Mass of the mass standards (weights of stainless steel) [kg]**
V_{ms}	**Volume of the mass standards at 20ºC [m^3]**
α_{ms}	**Thermal expansion coefficient of the stainless steel [K^{-1}]**
α_{liq}	**Thermal expansion coefficient of the test liquid [kg m^{-3} K^{-1}]**
β_{liq}	**Isothermal compressibility coefficient of the test liquid [Pa^{-1}]**

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ρ_{air}	Air density [kg m³]
t_{air}	Air temperature [ºC]
t_{liq}	Liquid temperature [ºC]
t_{ref}	Temperature of reference, 20ºC
p	Atmospheric pressure [Pa]
p_{liq}	Pressure in the liquid [Pa]
p_{ref}	Pressure of reference, 101 325 Pa
Δm	Mass difference between sphere and the mass standards in divisions of the scale [d]
Sb^{-1}	Inverse of the sensitivity of the balance [kg d⁻¹]
Gc	Gravity correction due to the height difference of gravity centers between the mass standard and the density standard [kg]
Mc	Meniscus correction due to the elongation of the stainless steel wire when the sphere is placed in the suspension [kg]

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Mass difference

$$\Delta m = \left(I_{ds} - I_{ms}\right)\left(1 - \frac{\rho_{air}}{\rho_{ms}}\right)$$

I_{ds} **Reading of the density standard placed in the suspension (in the liquid) [d]**

I_{ms} **Reading of the mass standard placed in balance pan (in the air) [d]**

ρ_{ms} **Density of the mass standards (≈ 8 000 kg m^{-3})**

Inverse of the sensitivity

$$Sb^{-1} = \frac{m_{sw}}{I_{ms} - I_{ms+sw}}$$

m_{sw} **Mass of the sensitivity weight [kg]**

I_{ms+sw} **Reading of the mass standard and the sensitivity weight placed in balance pan (in the air) [d]**

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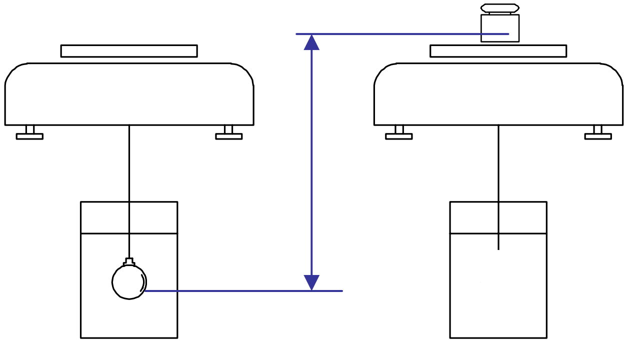
Gravity correction

$$Gc = \left(\frac{m_{ms}}{g}\right) \cdot \left(\frac{\partial g}{\partial h}\right) \cdot \left(h_{ms} - h_{ds}\right)$$



g **local gravity acceleration [m s^{-2}]**

$\frac{\partial g}{\partial h}$ **local gravity gradient [s^{-2}]**

h_{ms} **height of the gravity center of the mass standard [m]**

h_{ds} **height of the gravity center of the density standard [m]**

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Meniscus correction

$$M_C = \frac{\pi\gamma_{liq}}{g} \cdot \left[d_0 - d\right]$$

γ_{liq}	**Surface tension coefficient of the test liquid [N m^{-1}]**
d	**Diameter of the wire with the density standard placed in the suspension [m]**
d_0	**Diameter of the wire without the density standard placed in the suspension [m]**

Evaluation of the liquid density uncertainty

Applied the GUM method to the mathematical model,

$$\rho_{L(T,P)} = \left\{ \left[\frac{m_{ds} - m_{ms} + \rho_{air} V_{ms} \left[1 + \alpha_{ms}\left(t_{air} - t_{ref}\right)\right] - \Delta m S b^{-1} - Gc - Mc}{V_{ds} \cdot \left[1 + \alpha_{ds}\left(t_{liq} - t_{ref}\right)\right] \cdot \left[1 - \beta_{ds}\left(p_{liq} - p_{ref}\right)\right]} \right] + \alpha_{liq}\left(t_{liq} - t_{ref}\right) \right\} \cdot \left[1 - \beta_{liq}\left(p_{liq} - p_{ref}\right)\right]$$

The standard uncertainty of the liquid density

$$u\left(\rho_{L(T,P)}\right) = \sqrt{\sum_{i=1}^{N} \left[c_i u\left(x_i\right)\right]^2} = \sqrt{\sum_{i=1}^{N} \left(\frac{\partial \rho_{L(T,P)}}{\partial x_i} \right)^2 u\left(x_i\right)^2}$$

The effective degree of freedom of the liquid density uncertainty evaluation

$$\nu_{eff}\left(\rho_{liq\ (T,P)}\right) = \frac{u\left(\rho_{liq\ (T,P)}\right)^4}{\sum_{i=1}^{N} \frac{u_i^{\ 4}\left(\rho_{liq\ (T,P)}\right)}{\nu_i}}$$

The expanded uncertainty evaluated using the effective degrees of freedom

$$U\left(\rho_{liq(T,P)}\right) = k \cdot u\left(\rho_{liq(T,P)}\right)$$

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Numerical example

Solid density standard		
material	zerodur	g
mass	1001.334	g
unc.	0.000125	g
volume	394.85082	cm^3
unc.	0.0004	cm^3
alfa	0.00E+00	/°C
hight of g.c.	0.0455	m
beta	1.10E-11	/Pa
pressure of reference	101325	Pa
temperature of reference	20	°C
gravity	9.78084615	m/s^2
δg/δh =	-0.000003086	m/s^2
Test liquid	Pentadecane	
surface tension γ	0.027	N/m
alfa of liquid	0.00070	g/(cm^3 K)
unc.	0.00005	g/(cm^3 K)
beta of liquid	8.50E-10	/Pa
unc.	5.00E-11	/Pa
temperature of reference	20.000	°C
pressure of reference	101325	Pa

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Mass standards		
Nominal value	697.965	g
Mass correction	0.0008626	g
Mass	697.965863	g
unc.	0.00006425	g
Volume	87.3079	cm^3
unc.	0.068	cm^3
alfa of mass standard	4.80E-05	/°C
high of gravity center	0.0148	m
air temperature	21.62	°C
unc.	0.085	°C
atmospheric pressure	80896.4	Pa
unc.	4.3	Pa
relative humidity	49.769	%
unc.	3.001	°C
air density	0.0009505	g/cm^3
unc.	4.73E-07	g/cm^3
liquid temperature	20.007	°C
unc.	0.008	°C
mass diference	-9.97E-03	g
standard deviation	0.00031	g
number of cycles	6	
Dh weight vs sphere	-1.3938	m
Dh liquid level - sphere	0.1	m
unc.	0.005	m
liquid density	0.769	g/cm^3
pressure over the sphere	81642.32	Pa
unc.	100	Pa
meniscus correction	4.59907E-07	g
gravity correction	0.00030694	g
temperature correction	-4.8916E-06	g/cm^3
pressure correction	1.000016730	

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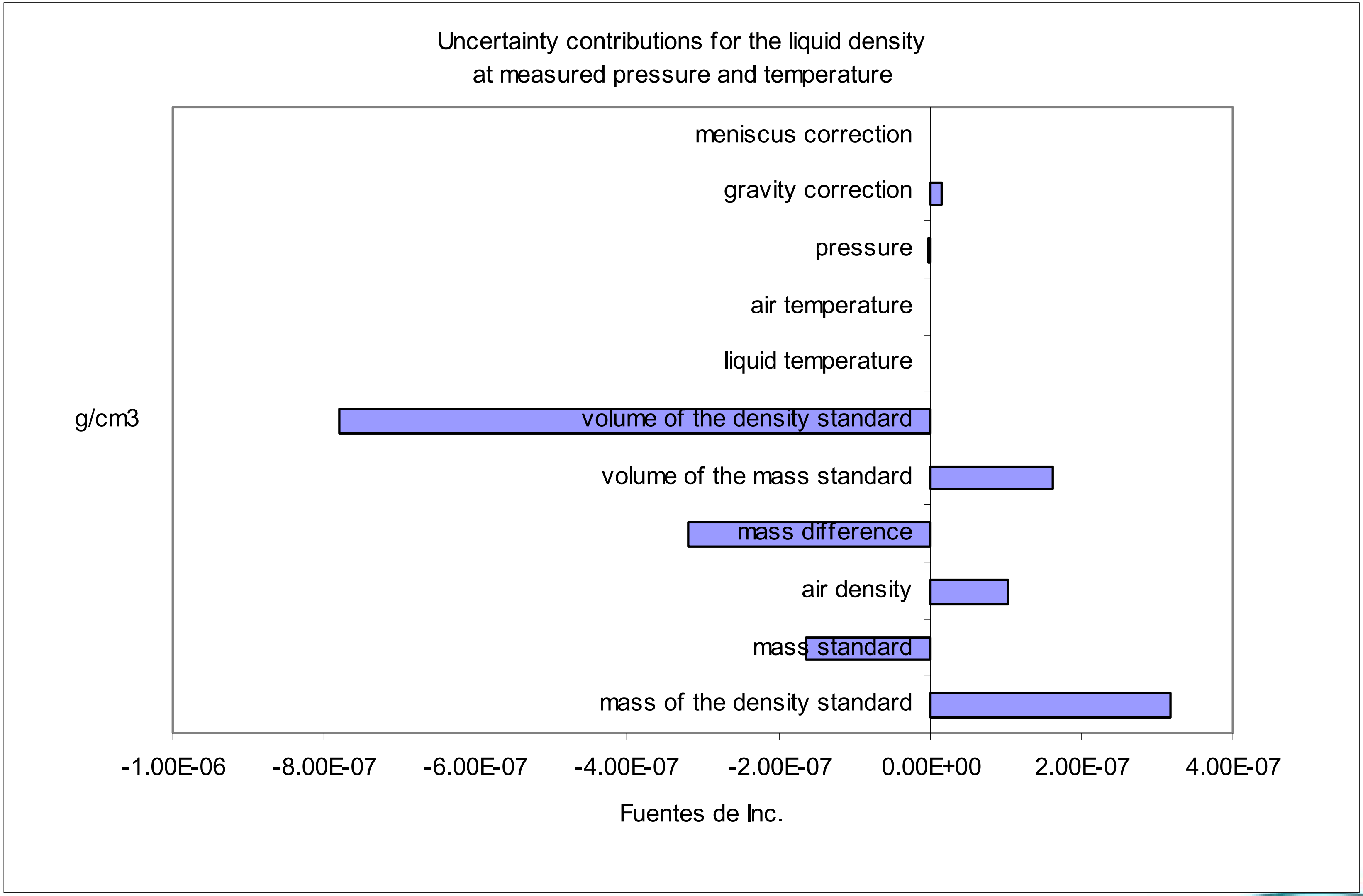
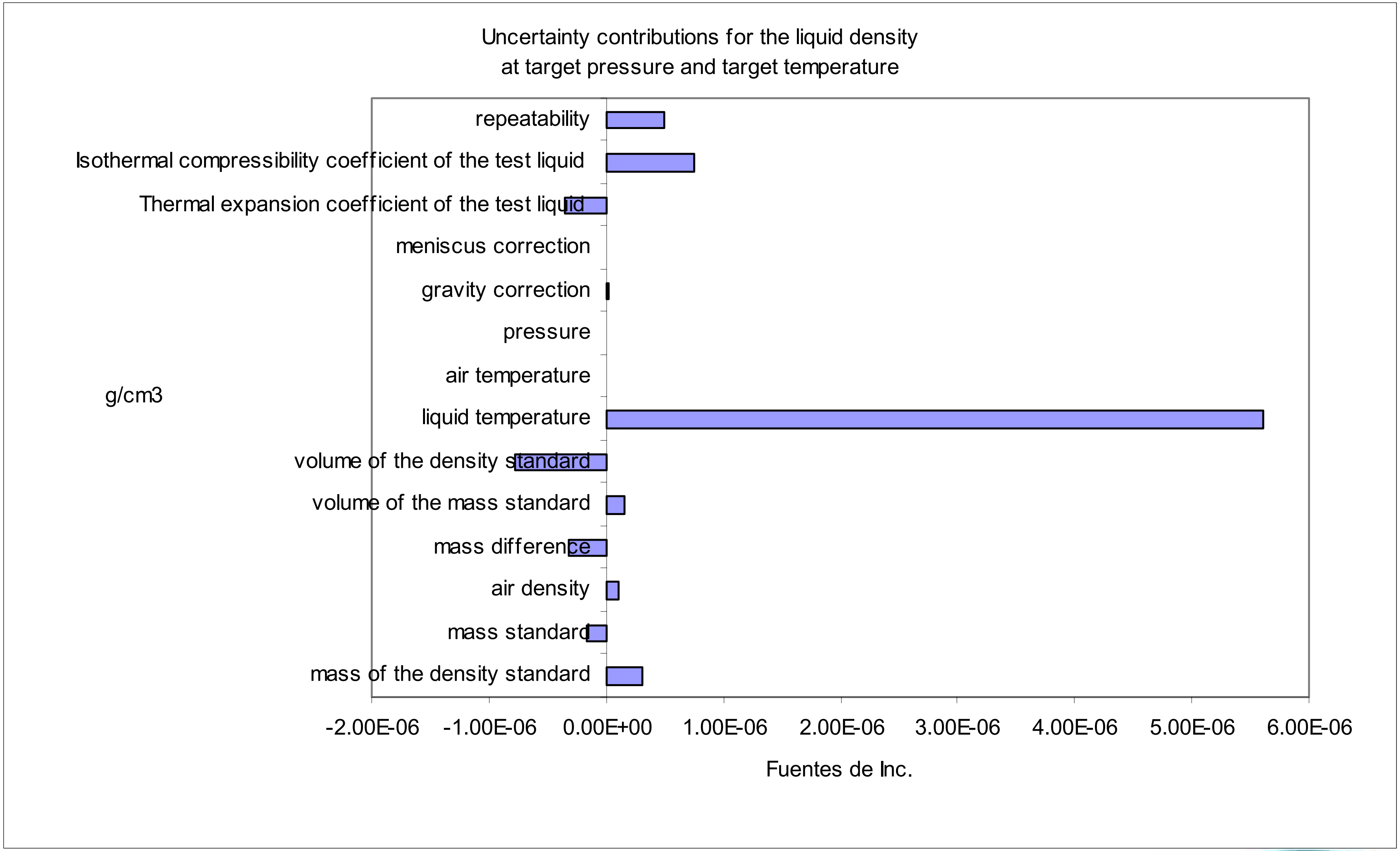
liquid density (t,p)	0.7685453	g/cm^3
unc. (k=1)	9.3E-07	g/cm^3
degrees of freedom	130.24	
relative uncertainty (k=1)	1.2E-06	
liquid density (T,P)	0.7685630	g/cm^3
unc. (k=1)	5.8E-06	g/cm^3
degrees of freedom	111.05	
relative uncertainty (k=1)	7.5E-06	


Uncertainty contributions for the liquid density
at measured pressure and temperature
meniscus correction
gravity correction
pressure
air temperature
liquid temperature
volume of the density standard
volume of the mass standard
mass difference
air density
mass standard
mass of the density standard
g/cm3
-1.00E-06
-8.00E-07
-6.00E-07
-4.00E-07
-2.00E-07
0.00E+00
2.00E-07
4.00E-07
Fuentes de Inc.


Uncertainty contributions for the liquid density
at target pressure and target temperature
repeatability
Isothermal compressibility coefficient of the test liquid
Thermal expansion coefficient of the test liquid
meniscus correction
gravity correction
pressure
air temperature
liquid temperature
volume of the density standard
volume of the mass standard
mass difference
air density
mass standard
mass of the density standard
g/cm3
-2.00E-06
-1.00E-06
0.00E+00
1.00E-06
2.00E-06
3.00E-06
4.00E-06
5.00E-06
6.00E-06
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