

EURAMET Project 858: Hydrostatic weighing – exchange of experiences

Project outline

A bilateral comparison has been carried out between the national measurement institutes INRIM, Italy and IPQ, Portugal, in the framework of EURAMET project 858 “Hydrostatic weighing – exchange of experiences”.

The main purpose of the project was to harmonize the measurement of density by two laboratories at the highest accuracy level.

INRIM and IPQ use a similar new hydrostatic density measuring apparatus for the density determination of liquids [1], so that for the purpose of this project the two laboratory exchanged information each other concerning own procedures and the uncertainty determinations, moreover they designed a comparison on the measurements of density related to two different liquids which have to be measured at the temperatures of 20 °C, 15 °C, 30 °C and again 20 °C at the atmospheric pressure.

For the comparison, Nonane (C₉H₂₀) at 99,7 % and Trichloroethylene (C₂HCl₃) at 95,00 % have been prepared or purchased by the INRIM.

Each of the two liquids was mixed in a large container and then four glass bottles of 1 litre volume each one were filled with each sample to be tested. The individual bottle was provided with an identification number and the safety data sheet (Figure 1).

INRIM sent to IPQ by courier two bottles of each sample, keeping for itself the remaining ones.

1. Hydrostatic weighing facility at INRIM

The complete weighing facility used for this key comparison is shown in Figure 2. The liquid sample and a Zerodur sphere (SLV1) used as the reference volume-density standard (solid density standard)



Figure 1. The individual bottle was provided with the identification number and filled with the sample to be tested. The large container is on the table together the bottles.

are contained in a sealed glass vessel (Figure 3). During the weighing, the sphere rests on a suspension connected to the balance by a stainless steel wire (without any special preparation).

The sphere is raised from its suspension by means of a support connected to a driving motor. In order to maintain constant the liquid sample level a similar volume is moved into liquid. The apparatus is completely immersed in a thermostatic unit, the temperature of the liquid is measured during the weighing by two Pt100 thermometers which are near enough to the sinker and connected to an AC bridge.

During the measurements, the balance reading of the sphere on the suspension and the balance reading of the empty suspension are alternately determined.

The apparatus operates automatically through home-electronic controls and software designed for running the weighing and acquiring the data from the balance (Figure 4).

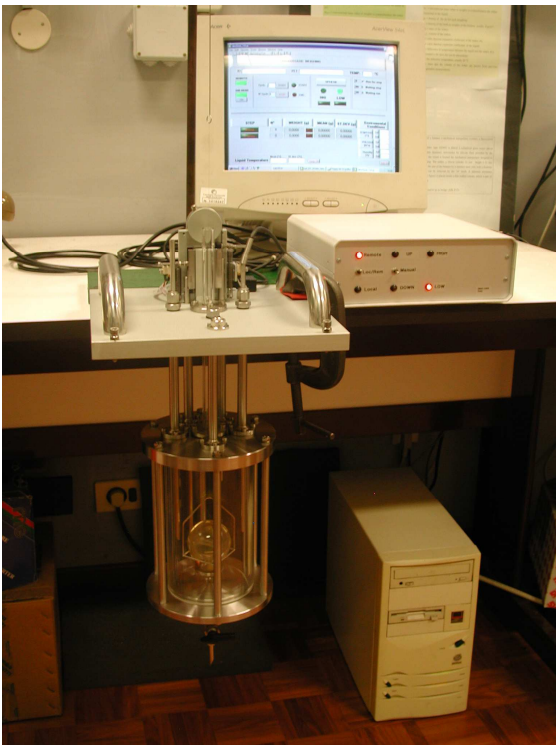


Figure 2. Facility for hydrostatic liquid density measurement

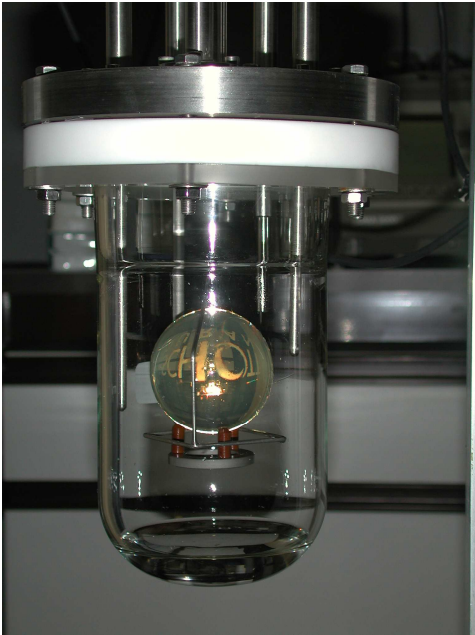


Figure 3. View of the measuring vessel, with the Zerodur density standard SLV1 inside the suspension cage.

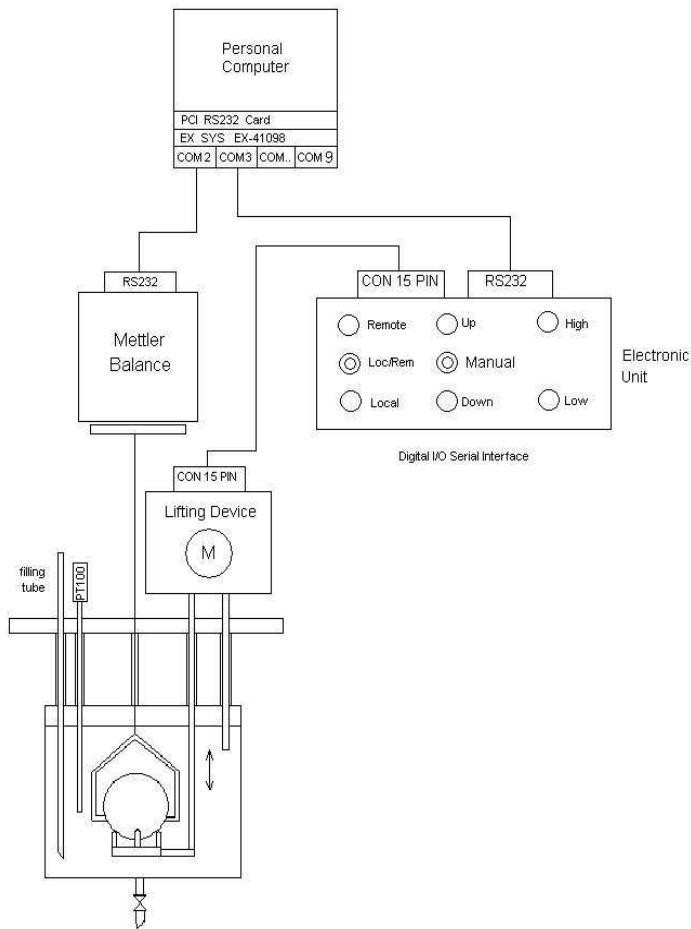


Figure 4. The sketch of the apparatus and the control system

2. Equipment

- Laboratory balance (Mettler, type AT405 g with a resolution of 0.1/0.01 mg), equipped to weigh a suspended load below the balance,
- Density reference material of known mass and volume (SLV1, Zerodur sphere: volume of 100 cm³)
- Suspension wires (stainless steel wire dia. of 0.1 mm and 0.2 mm) and holders for the different weight sizes,
- Mechanism to load and unload the density reference material holder in liquid (Hydrostatic weighing apparatus),
- Standard weights of known density,
- Environmental equipments (a portable pressure gage and a thermo-hygrometer)
- Thermometers with a resolution of 10 mK,
- Thermostat with a stability of 10 mK,
- A vision system, used to adjust the elongation of the wire when the sphere is placed in the suspension,
- A lift unit with a carriage holding the thermostat

3. Preparation of measurements

All components of the hydrostatic weighing apparatus were cleaned with ethanol, dried and assembled. The apparatus was put into the thermostatic basin of double-walled glass vessel filled with 30 litres of water whose temperature is controlled by an external thermostatic bath and aligned underneath the balance (Figure 5). Then the vessel was connected to the bottle containing the liquid to be tested through a pipe. The gentle transfer of the liquid from the bottle or from the vessel was caused by an external forces, like imposed pressure differences.

Before the measurements the liquid samples were kept on the target temperature about 12 hours (usually all night).

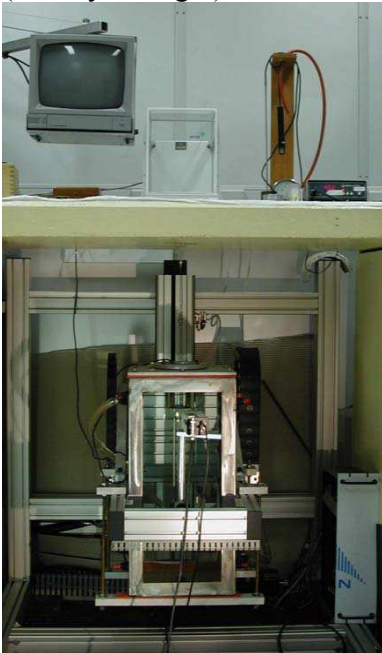


Figure 5. Facility for density of liquids

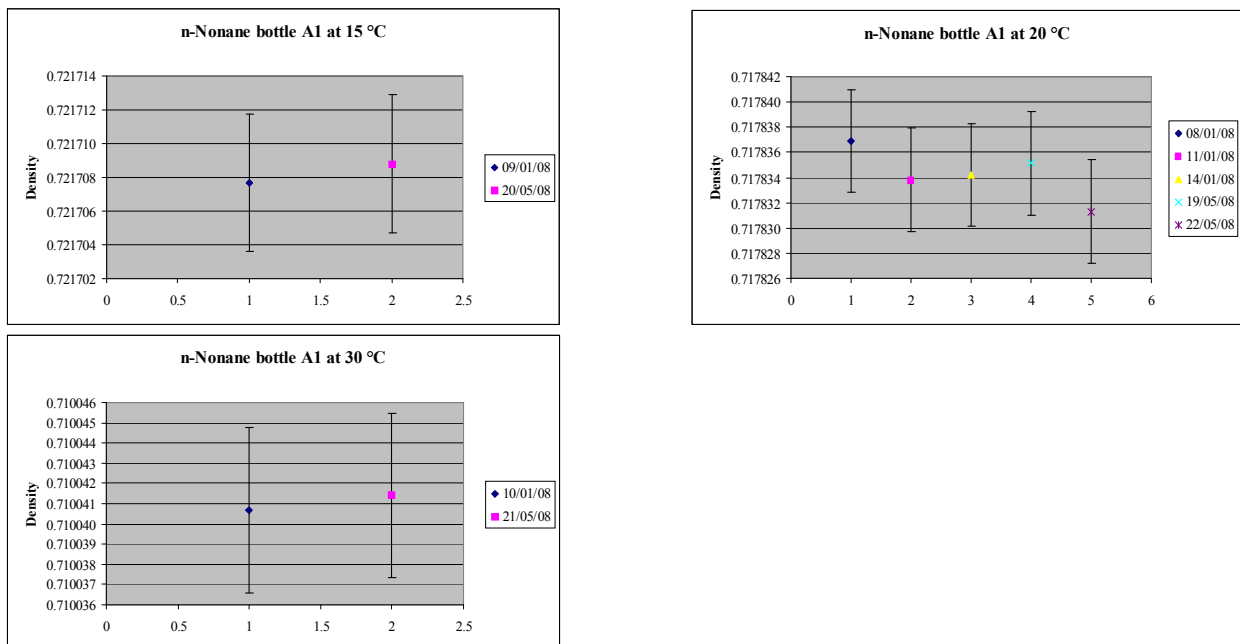


Figure 5. Comparison of the density values at 15 °C, 20 °C and 30 °C of the n-Nonane contained in the bottle A1. The bar shows the uncertainty at 1 σ level of confidence for such measurements.

3.1 Evaluation of meniscus contribution due to elongation of the wire

The different surface tension of liquids and the elongation of wire, when the suspension is empty and when the sphere is placed on it, cause a different contribution of meniscus weight in the buoyancy. Although a new method based on the correction of the elongation was introduced to INRIM for this project in order to evaluate it, such contribution didn't reveal a significant fact.

4. Sequence of the measurement procedure

Usually the procedure is performed in set of five of the following sequence:

- Weigh standard weight set related to the empty suspension,
- Weigh solid density standard (SLV1 sphere) in liquid; some additional weights could be placed on the pan in order to check the linearity of the balance scale,
- Compensate the elongation of wire in agree with 3.1 and weighing the density reference solid. (This point could be repeated for several dip level),
- Weigh standard weight set related to the empty suspension
- Record the average of measuring liquid temperatures and environmental conditions (air pressure, air temperature, air humidity).

The set took approximately one hour and half:

4.1 n-Nonane

The liquid sample contained in the bottle A1 was initially used for determining the density in agreement with the temperature cycle at 20 °C, 15 °C, 30 °C and in the end at 20 °C.

Ten density determinations were performed at each temperature. The average of the differences of temperature recorded by the two thermometers close to the sphere were within 0,004 mK in the all temperature range.

Data	Ref. Temperature °C	Density (ρ_L) g/cm ³	Uncertainty g/cm ³
08/01/08	20	0,717837	0,000004
09/01/08	15	0,721708	0,000004
10/01/08	30	0,710041	0,000004
11/01/08	20	0,717834	0,000004
14/01/08	20	0,717834	0,000004
19/05/08	20	0,717835	0,000004
20/05/08	15	0,721709	0,000004
21/05/08	30	0,710041	0,000004
22/05/08	20	0,717831	0,000004

Table 1. Density values and uncertainties, at 1 σ level of confidence, of the n-Nonane contained in the Bottle A1 in the period January – May.

In order to check the stability of the same sample, four month after the density determination were repeated within the same temperature range. Five density determinations were performed at each temperature.

Table 1 shows all density determinations with their claimed uncertainty at 1 σ level of confidence. In Figure 5 the density determination at each measured temperature are compared each other.

4.2 Trichloroethylene

The liquid sample contained in the bottle B1 was initially used for determining the density in agreement with the temperature cycle: 20 °C, 15 °C, 30 °C, and in the end at 20 °C.

A new density measurement was carried out immediately after the first one was finished, because some water was identify inside the sample.

Ten density determinations were performed at each temperature. The average of the differences of temperature recorded by the two thermometers close to the sphere were within 0,001 mK in the all temperature range.

Table 2 shows density determinations with their claimed uncertainty at 1 σ level of confidence. In Figure 6 the density determination at each measured temperature are compared each other.

Data	Ref. Temperature °C	Density (ρ_L) g/cm ³	Uncertainty g/cm ³
22/01/08	20	1,463882	0,000006
23/01/08	15	1,472232	0,000006
24/01/08	30	1,446910	0,000006
28/01/08	20	1,463754	0,000006
29/01/08	15	1,472203	0,000006
30/01/08	30	1,446806	0,000006
31/01/08	20	1,463766	0,000006

Table 2. Density values and uncertainties at 1 σ level of confidence of the Trichloroethylene contained in the Bottle B1.

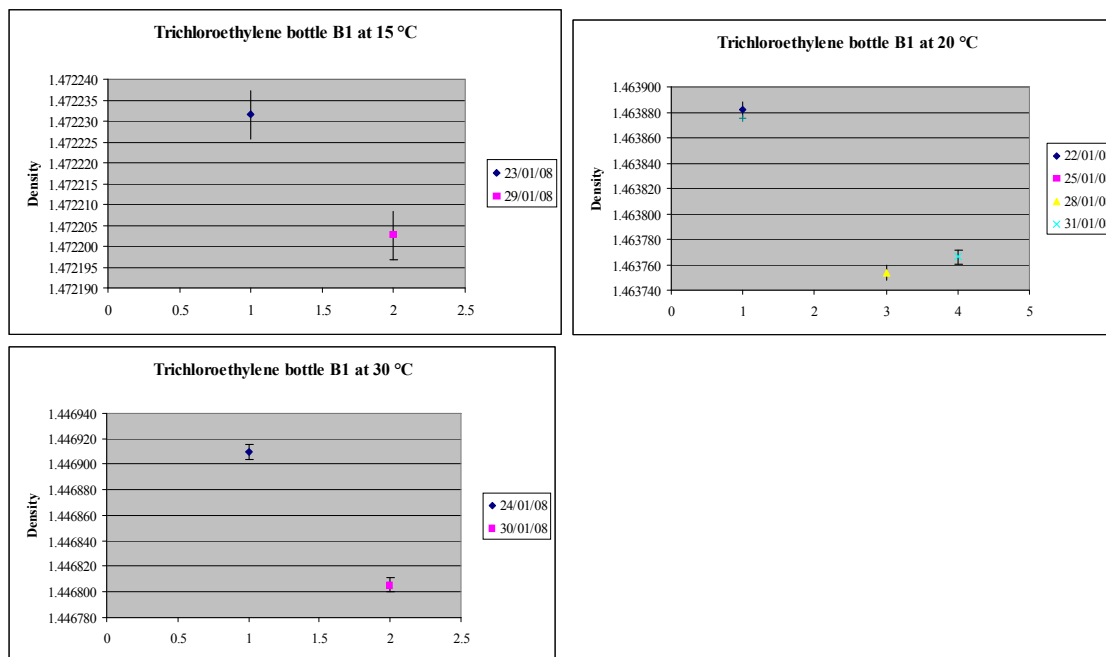


Figure 6. Comparison of the density values at 15 °C, 20 °C and 30 °C of the Trichloroethylene contained in the bottle B1. The bar shows the uncertainty at 1 σ level of confidence for such measurements.

At the end of the measurement cycle the liquid sample was removed and it was replaced with the Trichloroethylene contained in the bottle B2, after the cell had been cleaned.

Ten density determinations were performed at each temperature 20 °C, 15 °C, 30 °C, and in the end at 20 °C and then repeated again later.

The average of the differences of temperature recorded by the two thermometers close to the sphere were within 0,002 mK in the all temperature range.

Table 3 shows density determinations with their claimed uncertainty at 1 σ level of confidence. In Figure 7 the density determination at each measured temperature are compared each other.

Data	Ref. Temperature °C	Density (ρ_l) g/cm ³	Uncertainty g/cm ³
05/02/08	20	1,463912	0,000011
06/02/08	15	1,472278	0,000004
07/02/08	30	1,447018	0,000004
11/02/08	20	1,463875	0,000004
12/02/08	30	1,446988	0,000004
13/02/08	15	1,472234	0,000004
14/02/08	30	1,446941	0,000004
15/02/08	20	1,463824	0,000004

Table 3. Density values and uncertainties at 1 σ level of confidence of the Trichloroethylene contained in the Bottle B2.

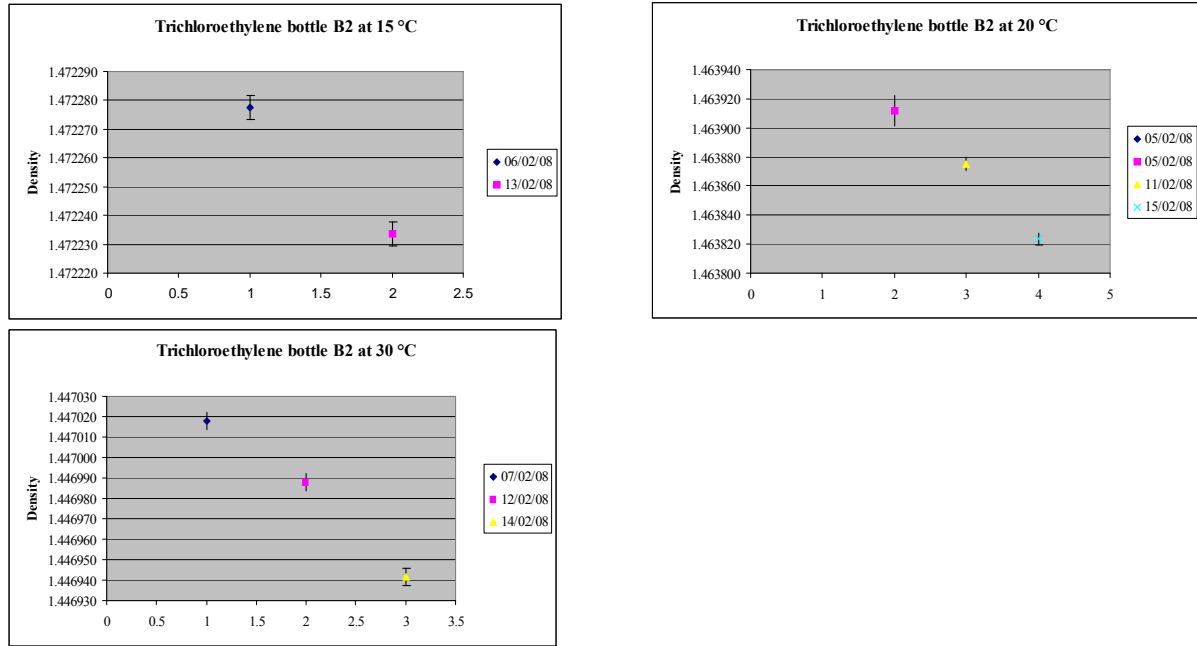


Figure 7. Comparison of the density values at 15 °C, 20 °C and 30 °C of the Trichloroethylene contained in the bottle B2. The bar shows the uncertainty at 1 σ level of confidence for such measurements.

5. Evaluation of the density

The hydrostatic method is based on the classical Archimedes' principle which states that the up thrust on a body immersed in a fluid is equal to the weight of the fluid displaced by the body.

The liquid density was measured using the SLV1 (57 mm diameter) by hydrostatic weighing, where the buoyancy of the solid density standard is measured in a balance (Mettler, type AT405) by comparison against weights (mass standards).

The formula used to calculate the liquid density ρ_L at the temperature t is the following,

$$\rho_L(t) \cong \frac{\left(M_0 - (m_L + \Delta m) \left(1 - \frac{\rho_a}{\rho_c} \right) \right)}{V_o (1 + \beta(20 - t))} \left(\frac{1}{1 + k} \right) \quad (1)$$

The liquid density at the target temperature t_R and pressure:

$$\rho_{liquid(t_R, p_o)} = \rho_{liquid(t, p)} [1 + \kappa_{liquid} (p_o - p_{sin ker})] + \alpha_{liquid} (t - t_R) \quad (2)$$

where

m_L = mass of the weights;

Δm = mass difference (read in the balance);

ρ_a = density of the air for each weighing;

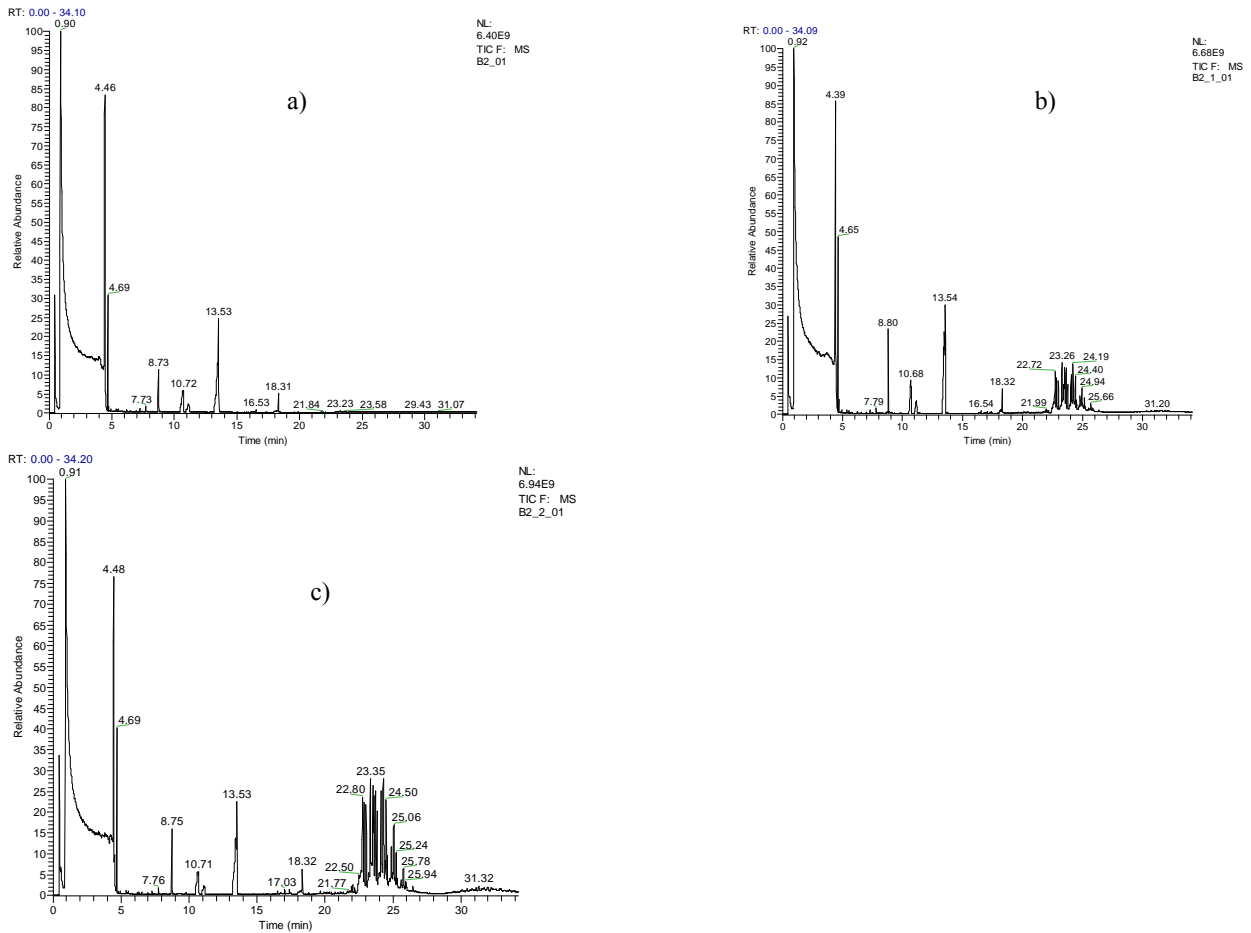


Figure 8. Gas-chromatograms of the liquid samples of Trichloroethylene contained in bottles B2. The a) is the starting condition, b) after the first cycle and c) at the end of the density measurements.

ρ_c = Conventional value of the density of the weight used to calibrate the balance, usually 8 g/cm^3 ;

M_0 = mass of the sinker at the reference temperature;

V_0 = volume of the sinker at the reference temperature;

β = cubic thermal expansion coefficient of the sinker;

$k = \frac{\partial g}{\partial h} \frac{\Delta h}{g}$ correction factor for the gravity acceleration g between the two weighing position h : at the

level of the balance chamber and at the level of the sinker. In our case this value can usually be neglected;

κ_{liquid} = compressibility of the liquid,

α_{liquid} = thermal expansion coefficient of the liquid.

6. Uncertainty of the density measurement

The uncertainty of the density measurement u_{ρ_L} is a function of the input variables; according to [4] the combined standard uncertainty is calculated by the square root of the combined variance for uncorrelated input quantities

$$u_{\rho_L} = \sqrt{\begin{aligned} & (c_1 u_{M_0})^2 + (c_2 u_{V_0})^2 + (c_3 u_{m_L})^2 + (c_4 u_{\rho_a})^2 + (c_5 u_{\rho_c})^2 + (c_6 u_{\beta})^2 + (c_7 u_{\alpha})^2 \\ & + (c_8 u_t)^2 + (c_9 u_{\delta\theta})^2 + \sum_{i=10}^n (c_i u_i)^2 \end{aligned}} \quad (3)$$

where u_{M_0} , u_{V_0} , ..., $u_{\delta\theta}$ are the standard uncertainties of the input estimates, including Type A and Type B contributions, and the *sensitivity coefficients* c_j ($j=1$ to 9), are the partial derivatives of ρ_L respect to the input variables introduced from equations (1) and (2).

The terms are $\sum_{i=10}^n (c_i u_i)^2$ some uncertainty's contributions, which can be usually neglected .

Among these contributions there are:

- the correction factor for the gravity acceleration g between the two weighing position h : at the level of the balance chambre and at the level of the sinker;
- the compressibility coefficient of the sinker,
- the compressibility coefficient of the tested liquid.

The mean values of the standard uncertainty of each term coming from equation 1, concerning our exercise are:

- standard uncertainty of the mass of the sinker $u_{M_0} = 0,000035$ g (the mass of the sinker, $M_0 = 253,750693$ g, is derived from previous measurement);
- standard uncertainty of the volume of the sinker $u_{V_0} = 0,000057$ cm³ (the volume of the sinker, $V_0 = 100,28594$ cm³, is derived from previous measurement);
- standard uncertainty of hydrostatic weighings u_{m_L} . Its estimation is based on the contributions associated with the average of the ten comparisons between the sinker and the standard, the standard uncertainty of the standards and the standard uncertainty of the balance reading $0,00008$ g;
- standard uncertainty of the density of the air $u_{\rho_a} = 0,000003$ g×cm⁻³;
- standard uncertainty of the temperature measurement u_t , it is due both to the uncertainty of the temperature measuring apparatus ($0,01$ °C) and to uniformity and stability of the liquid temperature;
- standard uncertainty of the thermal expansion coefficient of sinker u_{β} . The coefficient of thermal expansion of the sinker is given as $\beta = 0$ °C⁻¹ with an standard uncertainty $u_{\beta} = 0,15 \times 10^{-6}$ °C⁻¹;
- standard uncertainty of the thermal expansion coefficient of the liquids $u_{\alpha} = 0,05$ kg/(m³K). The coefficient of thermal expansion of the n-Nonane is $0,7$ kg/(m³K) and of trichloroethylene $1,7$ kg/(m³K);
- standard uncertainty of the difference in temperatures between the tested liquid and the sinker $u_{\delta\theta}$. The tested liquid and the sinker are expected to be at the same temperature, but the temperature difference could lie with equal probability in the estimated interval $-0,005$ °C to $+0,005$ °C. The standard uncertainty $u_{\delta\theta} = 0,003$ °C.

7. A swift comment

The n-Nonane shows a good reproducibility of the density measurements, also after the temperature changing. The measurements performed in the subsequent period are still in agreement within the uncertainty at 1σ with the previous ones. The downswings registered can be due to repeatability of the measuring method, ageing of the sample, evaporation of the light components or the chemical reactivity of the liquid tested with materials with which it can be come into contact.

The Trichloroethylene instead shows a bad reproducibility of the density values.

Taking into account the first value of density at 20 °C of the sample in bottle B1 (thought to be the only measurement before the sample has been polluted by water) such value is between the values of sample in B2.

A changing in the components of the Trichloroethylene has been recorded by gas-chromatography coupled with mass spectrometry (GC-MS). This technique, due to its high selectivity and sensibility, is able to give the typical results required in a trace analysis; in addition, the use of mass spectrometry gives the opportunity to identify the compounds by comparing mass spectra of the analytes contained in the sample with the ones collected in international libraries.

The Figure 8 shows the chromatogram of the tested sample of the bottle B2 before the cell was filled a), after the first group of measurements b) and finally at the end of the second group of measurements. Differences in the figure are shown with some peaks having retention time of about 25 minutes for which their height values increase between the first and the second cycle.

The main reasons could be due to the particular behaviour of the trichloroethylene in contact with three different plastic materials i.e a plastic pipe in Rilsan when the liquid was transferred from the bottle, the little support in the cage made up of Vespel, and finally the sealing O-ring in Viton.

The samples containing in the bottles A3 and A4 was measures in IPQ, witch values are not perfectly in agreement. Concerning the samples from bottles B3 and B4, the measurements allow to identify poor density stability for Trichloroethylene.

References

- [1] Lorefice, S., Malengo, A., Hydrostatic weighing apparatus for liquid density, IMGC-CNR Technical Report 137, November 2005.
- [2] ISO, Guide to expression of uncertainty in measurement, International Standard Organization, January 1993.