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THE USE OF GC-MS TO SUPPORT STABILITY ASSESSMENT OF DENSITY REFERENCE LIQUIDS

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Abstract – Density measurements are frequently associated to specific requirements in order to evaluate the quality of a process or to determine mass and/or volume of the material. Certified reference liquids can be used to assure metrological traceability of density measurements to the International System of Units (SI) with uncertainty lower than 0.005 %. This paper presents the new approach of the Italian Istituto Nazionale di Ricerca Metrologica (INRIM) to set density standards.

The procedure involved accurate density determinations of some liquid samples, to be used as references, on which in addition analysis by means of gas-chromatography coupled with mass spectrometry (GC-MS) was performed to support homogeneity and short-term stability. In this exercise GC-MS analyses on two chlorinated liquids (namely tetrachloroethylene and trichloroethylene) were carried out before and after density measurements. The results obtained with the two different techniques were encouraging. Samples that had undergone to variations in density value showed also different gas-chromatographic profiles. In the same time, samples that had not undergone to density variations kept similar gas-chromatographic profiles. The results support the approach of combining independent methods in order to set physico-chemical properties of reference materials (RM), univocally.

Keywords: density, reference liquids, mass spectrometry

1. INTRODUCTION

The demands to accelerate the practical realization of the Mutual Recognition Arrangement (MRA) and to clarify metrological traceability of measurement results have become more and more urgent in the field of measurement standards. In particular, there is an increasing need for measuring the density in a way traceable to the International System of Units (SI).

Density measurements are frequently associated to specific requirements in petroleum, alcohol, brewing and food industry during manufacturing process and for quality control. Different methods and various instruments are used for solids, liquids and gases and the choice of the most adequate one is usually determined on the basis of measurement conditions, required precision, physical status and available amount of the sample to be measured [1]. Water is a density standard material that has been used as reference liquid since ancient time to calculate both density and volume of other materials. Similarly to water, mercury has been used as a standard but for high density. Recently, silicon objects and several certified reference liquids are distributed by National Metrology Institutes (NMIs) or are traceable to them, to be used for assuring metrological traceability of density measurement results with an uncertainty lower than 0.005% [2].

The suitability of a liquid to become a reference material (RM) for density measurements requires some investigations in terms of homogeneity, short and long-term stability in the density values according to [3, 4].

Most RMs are prepared as batches of items (e.g. bottles, vials, or test pieces). The final step in the preparation of many RMs is the subdivision into usable items.

A material is usually homogeneous and stable with respect to a given characteristic if the difference between the values of the tested characteristic from one part (item) to another is negligible when compared to the uncertainty budget due to its characterisation.

Pure compounds are usually expected to be homogeneous and short-term stable, moreover the certificated values are not expected to deviate from the "true" value by more than the stated measurement uncertainty. Anyway differences due to impurities, interferences or irregularities which may be due to undetected problems during the preparation, could affect the certificated values of the items of the same batch (within-bottle homogeneity).

The establishment of a proper testing procedure is a complex task and it should be carried out with great care to account for all relevant contributions which affect the certificated property values of the tested RM.

In addition to density measurements, information deriving from an independent analytical technique is useful to better assess the properties of the candidate reference liquids. In the classical study individual samples, prepared at the same time (i.e. as a batch), under identical conditions, are tested at different stages in agreement to [4] (Fig. 1).

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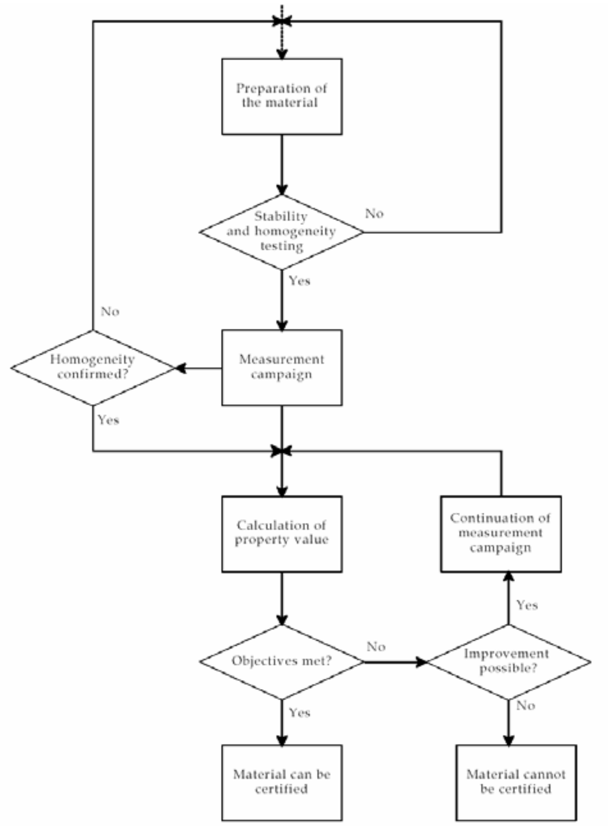

Fig. 1. Outline of the experimental procedure for the certification of an RM according to [4].

A new procedure which involves accurate density determinations of liquid samples, in addition to analysis by means of gas-chromatography coupled with mass spectrometry (GC-MS), was initially introduced by the Italian Istituto Nazionale di Ricerca Metrologica (INRIM) in order to get more information concerning the chemical and physical characteristics of liquid samples of the same batch which were supplied by the Austrian institute BEV as pilot laboratory of the EURAMET project 1019.

This paper presents this new approach devoted to check the homogeneity and the short-term stability of RMs as well as to set density reference standards.

Two particular applications have been taken into account as examples hereinafter: i) checking the homogeneity "between-bottles" of tetrachloroethylene samples supplied by BEV in the EURAMET 1019 and ii) assessing the short-term stability of trichloroethylene studied at INRIM as possible reference standard of density.

2. MATERIALS AND METHOD

2.1. Materials

2.1.1 Tetrachloroethylene

In agreement with the Technical Protocol of EURAMET project 1019, BEV prepared and supplied four different liquid samples to participants that were supposed to determine their density value.

Fig. 2. Preparation of the samples before the density determinations and the gas-chromatography analysis.

INRIM received among the four liquids, two bottles, 1 L each, of tetrachloroethylene (purity > 95 %) identified with the numbers 29 and 30, respectively.

2.1.2 Trichloroethylene

A suitable amount of trichloroethylene (purity > 95 %) was purchased from a commercial source. The whole amount was initially stored and mixed into a large stainless steel tank, to preserve the composition of the sample from losses due to adsorption and volatilization, contamination by external substances and reaction between constituents of the sample and the container.

Just before performing the density determinations and the gas-chromatography analysis of the designed liquid, several amber glass bottles were filled with approximately 1 L of sample each and then capped with Teflon-lined screw-caps. In the same time some vials with capacity of 10 mL were filled and sealed with a Teflon cap too and stored as witness. Each individual bottle was provided with an identification number (Fig. 2).

2.2. Density measurements

Density measurements of the liquid to be tested were made by hydrostatic weighing at different temperatures. The Zerodur® volume-density standard (solid density standard) SLV1 (57 mm diameter and 253 g mass) was used for this purpose.

The hydrostatic method is based on the classical Archimedes' principle which states that the up thrust on a body dip into in a fluid is equal to the weight of the fluid displaced by the body. The buoyancy of the SLV1 is measured with a balance by comparison against mass standards.

All components of the INRIM hydrostatic weighing facility were cleaned with ethanol, dried and aligned underneath the balance.

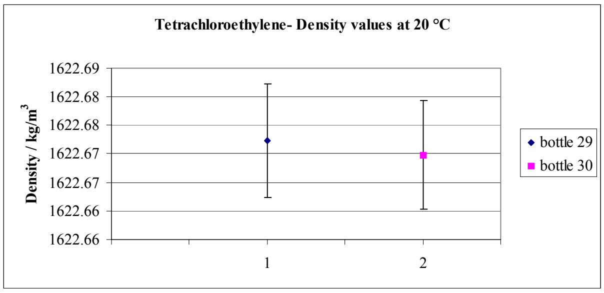

Fig. 3. Density values at 20°C of tetrachloroethylene contained in bottles 29 and 30. The bars show the uncertainty at 2 σ confidence level.

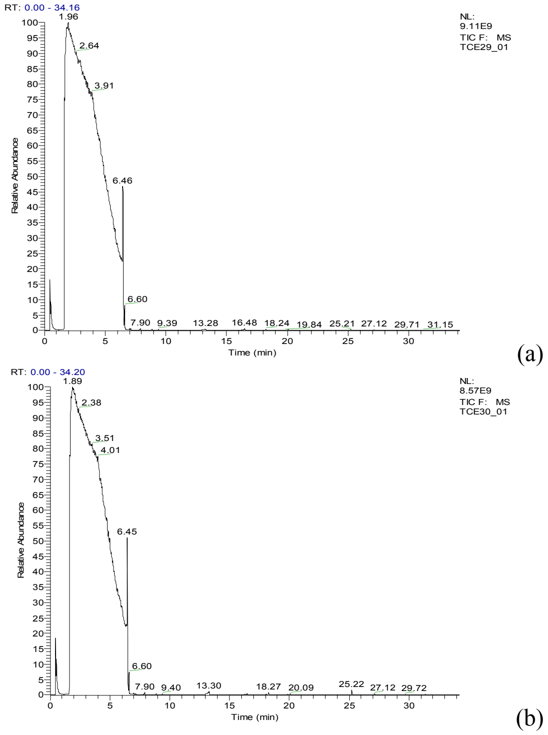

Figure 4. Gas-chromatograms of the two samples of tetrachloroethylene, a) bottle 29, b) bottle 30.

The liquid to be tested was transferred gently through a pipe from its bottle to the sealed glass vessel containing the density standard SLV1. The gentle transfer of the liquid from the bottle or from the vessel was caused by an external force due to a pressure difference. In the same time, after the transfer of the liquid, some vials were filled with it to be tested by GC-MS.

The liquid samples were kept at the target temperature for about 12 hours (usually overnight), then the density of the liquid samples was measured at several temperatures.

2.3. GC-MS analysis

GC-MS analyses were carried out by means of a gas-chromatograph coupled with a single quadrupole mass spectrometer Focus DSQ II (Thermofisher Scientific), equipped with an electron impact (EI) source. The column used for the gas-chromatographic separation was a Thermo TR-5msSQM (length 15 m, internal diameter 0.25 mm, film thickness 0.25 µm). The mass spectra were acquired in scan mode in order to identify the different compounds present in the liquid samples. Different samples

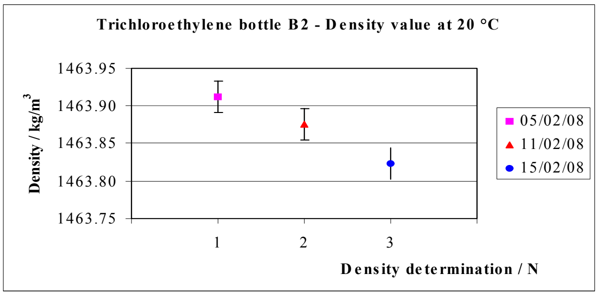

Fig. 5. Repeated density values at 20°C of trichloroethylene contained in the bottle B2. The bars show the uncertainty at 2 σ confidence level.

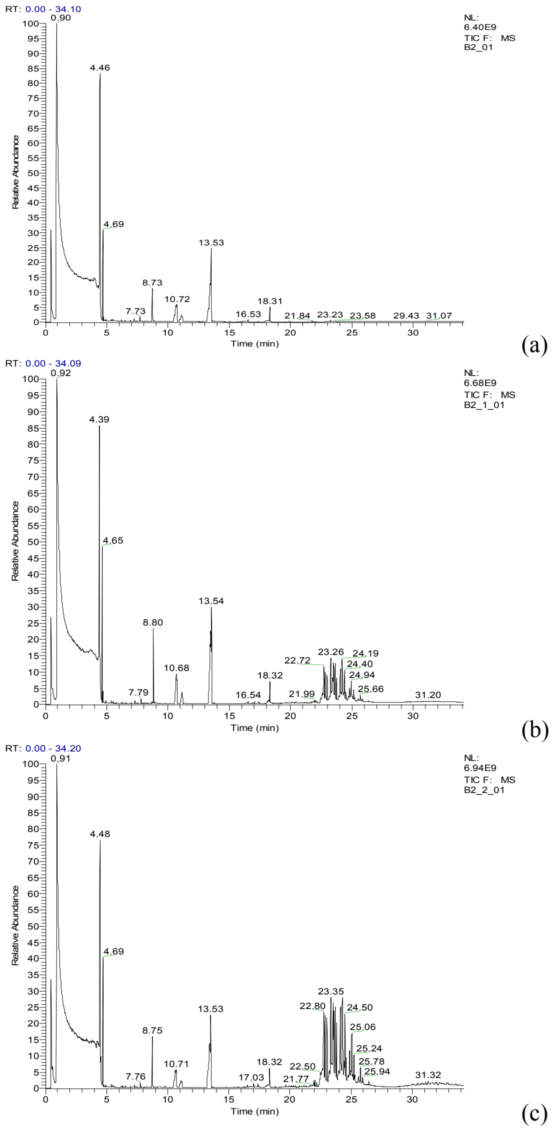

Fig. 6. Gas-chromatograms of the trichloroethylene samples subjected to different temperature cycle.

of the same liquid were analysed using the same operative conditions to compare the chromatograms.

3. RESULTS AND DISCUSSION

3.1. Tetrachloroethylene

A between-bottle homogeneity study aims to determine the between-units variation, where the units are represented by the bottles. Typical experimental set-up for a between-bottles homogeneity takes into account several samples or sub samples of the same batch to obtain an unbiased estimate of the heterogeneity of the material.

The density value at 20 °C of the two tetrachloroethylene samples contained in the bottles 29 and 30 respectively was initially determined. Eleven weighing sequences were carried out at 20 °C. The average of the differences of temperature recorded by two thermometers close to the sphere were within 0.001 K.

The density values determined for both bottles are in agreement within the declared uncertainties at 2 σ confidence level (Fig. 3).

Before the liquid was moved into the vessel for the density measurements, a sample from each bottle was analysed by GC-MS. The gas-chromatograms are shown in Fig. 4a and 4b respectively for the bottles 29 and 30.

Both gas-chromatograms show the same profile and do not highlight differences in the composition of the two samples, thus confirming the density results.

3.2. Trichloroethylene

The stability study aims mainly to determine the uncertainty contribution (to the property value) due to i) storage (long-term stability) and ii) transport (short-term stability). The long-term stability concerns the remaining instability of the RM under optimal storage conditions for an established time. Short-term stability is therefore only relevant as uncertainty component when the transport of a RM (e.g. from the producer to the user) affects the stability of the material more than storage conditions do. It is therefore important to determine these conditions accordingly and to study the stability of the material. The short-term stability study is typically carried out at different temperatures, to investigate the effect of different temperatures on the properties of the material.

Samples of trichloroethylene contained in the bottle identified as B2 underwent density determination twice according to the following temperature cycle: 20 °C, 15 °C, 30 °C and 20 °C again. Ten weighing sequences were performed at each temperature. The average of the differences of temperature recorded by the two thermometers close to the sphere was within 0.001 mK in the whole temperature range.

The results for density measurements at 20 °C are reported in Fig. 5.

A sample of trichloroethylene before density determination was analysed by GC-MS (Fig. 6a). At the end of the measurements series to determine the density at 20 °C, a small amount of liquid was withdrawn by a pipette and the samples were analysed via GC-MS at the end of each temperature cycle. The results are reported in Fig. 6b and 6c respectively.

Comparing the gas-chromatograms of Fig. 6, it can be seen that groups of peaks having retention times in the range between 22 and 26 minutes show higher intensity after the first temperature cycle (Fig. 6b), intensity which further increases after the second temperature cycle (Fig. 6c). The interpretation of the mass spectra reveals that these peaks correspond to alkyl phenyl esters of carbonic acid. Considering the mechanical set-up of the density facility, a possible cause of pollution might derive from the substitution of the previous Teflon® o-ring with a new Viton® o-ring, which occurred just before these density measurements, that could have released some impurities. Also the density values at 20 °C (Fig. 5) seem to be reduced of about 25 ppm at the end of each temperature cycle. It has to be underlined that the two methods of investigation show a changing in the characteristics of the tested sample. Moreover the density and GC-MS results confirm the instability of trichloroethylene due to the temperature.

4. CONCLUSIONS

The choice of GC-MS as a complementary technique to density measurement for checking the liquid stability is due to the intrinsic features of the technique itself. Indeed, due to its high selectivity and sensitivity, it can give the typical results required in trace analysis; in addition, the use of mass spectrometry provides the opportunity to identify the compounds present in a sample by comparing the mass spectra obtained in the analysis of the sample in scan mode with the ones collected in international libraries.

The results obtained with the two different techniques were encouraging. Samples that had undergone to variations in density value showed also different gas-chromatographic profiles. In the same time, samples that had not undergone to density variations kept similar gas-chromatographic profiles.

Additional work on other liquid samples is foreseen in order to prove a correlation between the already observed behaviours.

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