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Preparation of Thermodesorption Tube Standards: Comparison of Usual Methods Using Accuracy Profile Evaluation

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Abstract: In order to quantify organic impurities in gas produced from renewable sources, thermal desorption coupled with GC-MS or GC×GC-MS is very useful. However, the preparation of the standard tubes appears not to be trivial. For that, different strategies, based on commercial setups, have been developed. The goal of this study was to compare the classical manual deposit of a liquid standard solution with other commercial methods such as gas stream assisted deposit and vaporization followed by adsorption assisted by gas stream. A standard mixture of 48 compounds from different families was used for the comparison of the performances of the three strategies using the accuracy profile methodology. A global validation score was attributed to each strategy as well as a score according to family of compounds and boiling point range, in order to provide a detailed comparison of the techniques. On the set of studied molecules, commercial setups were found to be more efficient than the manual deposit.

Keywords: thermal desorption; quantification; accuracy profile; GC×GC-TOFMS

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1. Introduction

The direct injection of a gas sample into GC-FID or GC-MS is often not sensitive enough to analyze low concentration compounds inside gaseous matrices. Thus, a preconcentration step may be necessary and can be achieved by means of sorption tubes. Trapped compounds are then released and injected into the GC via a thermal desorption (TD) process [1,2]. Another advantage of sampling with tubes is the possibility to carry out the sampling on site and to simply send the tubes to the laboratory for further analysis [3]. Some examples of this strategy are found in the case of biogases [1,4], natural products [5], or to monitor industrial processes such as CO_2 capture [6], etc.

It has been shown recently that GC×GC is a very useful tool for the detailed characterization of the impurities in complex samples such as biogases [7]. However, for accurate quantitative analysis using TD coupled with GC or GC×GC, gaseous or liquid calibration samples [8] are required.

This paper is related to the preparation of TD-GC×GC calibration samples using a liquid standard mixture containing 48 VOC. The following three techniques were studied and compared: the first one, the simplest, is the manual deposit (MD) of the calibration solution directly on the head of the tube; the two other techniques were gas stream assisted deposit (GSAD) [1,9–11], and vaporization followed by adsorption assisted by gas stream (VGSD) [6,12–14].

The evaluation and comparison of the performances of the three calibration methods were carried out using the accuracy profile methodology, a statistical tool developed for method validation at the beginning of the 21st century [6,15–20]. This tool was applied

by Marlet and Lognay to validate a TD-GC-MS method using a GSAD setup for the analysis of monoterpenes [11]. Recently, it was also applied successfully with a multi-response combination strategy, to compare the quantitative performances of different mass spectrometers for the determination of allergens in cosmetics [21]. In this paper, another implementation of the accuracy profile methodology was described to compare the performance of the three preparation techniques of thermodesorption standard tubes for further application to the quantitative analysis of biogas and related samples.

2. Materials and Methods

2.1. Standard and Tubes

The reference air indoor standard solution (48 VOC, reference 40353-U) and Tenax TA tubes (poly(2,6-diphenylphenylene oxide)), reference 30131-U were supplied by Sigma-Aldrich (Saint-Quentin-Fallavier, France). The standard solution was composed of acetone, benzene, bromodichloromethane, 1-butanol, 2-butanone, chloroform, dibromochloromethane, decane, decanal, 1,4-dichlorobenzene, 1,2-dichloroethane, dichloromethane, 1,2-dichloropropane, 2,4-dimethylpentane, dodecane, ethanol, ethylbenzene, 2-ethyltoluene, 3-ethyltoluene, 4-ethyltoluene, heptane, hexane, hexadecane, limonene, 4-methyl-2-pentanone, nonanal, nonane, octane, pentadecane, α-pinene, β-pinene, 1-propanol, 2-propanol, styrene, tetrachloroethylene, tetradecane, 1,2,4,5-tetramethylbenzene, toluene, trichloroethylene, tridecane, 1,2,3-trimethylbenzene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, 2,2,4-trimethylpentane, undecane, o-xylene, m-xylene, and p-xylene, at 1000 µg/mL in methanol/water (19:1 *v:v*).

A 2 µL gas tight syringe supplied by Hamilton (Villebon sur Yvette, France) was used to collect and dispense the liquid samples.

2.2. Tube Preparation

To apply the accuracy profile evaluation methodology, several series, i.e., combinations of calibration and validation tubes, were required. Calibration tubes were loaded using three different protocols corresponding to the three techniques to be compared. For the three protocols, the same syringe was used for sampling. A 1 µL sample volume was taken between a 0.2 µL volume of air (sandwich injection).

1. Manual deposit (MD) (Figure 1A) was performed by directly delivering the syringe content to the sorbent at the head of the tube. The needle was in direct contact with the retaining gauze.
2. Gas stream assisted deposit (GSAD) (Figure 1B) was performed using the Calibration Solution Loading Rig (CSLR) from Markes International (Bridgend, UK). The tube was locked with a ferrule to the system and the solution was added via direct contact with the sorbent retaining gauze at the head of the tube through a septum. Helium, used as carrier gas at 50 mL/min flowrate. was applied at the same time as the introduction of the syringe. The syringe remained in place for 0.25 min and the helium was flown 3 min after the start of the deposit for a total volume of 150 mL of gas
3. Vaporization followed by adsorption assisted by gas stream (VGSD) (Figure 1C) was performed using the Adsorbent Tube Injector System from Sigma-Aldrich (Saint-Quentin-Fallavier, France). The tube was locked with a ferrule to the system and the solution was injected in the vaporization chamber heated at 140 °C (stabilized at least 1 h before experiments). Helium was used as the carrier gas at a 50 mL/min flowrate and applied at the same time as the injection. The syringe remained in place for 0.25 min and the helium was flown 3 min after injection for a total volume of 150 mL of gas.

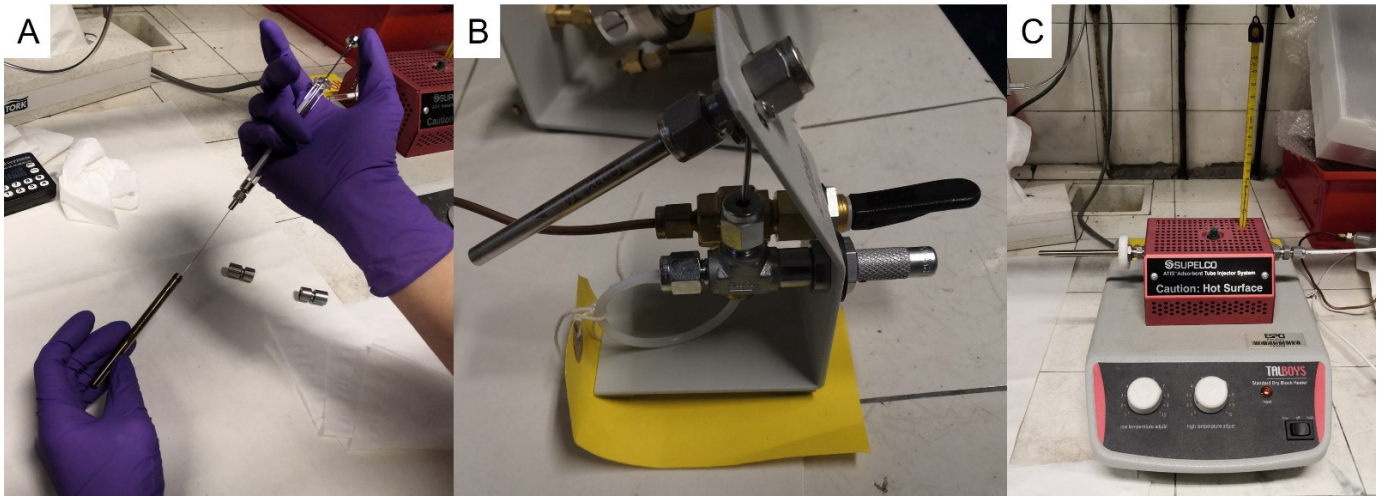

Figure 1. Illustrations for Manual deposit (MD) (**A**), Gas stream assisted deposit (GSAD) (**B**), Vaporization followed by adsorption assisted by gas stream (VGSD) (**C**).

For validation tubes, methane was used as the carrier gas instead of helium. MD validation tubes were loaded with 150 mL of methane before being deposited.

For each series, 12 calibration tubes and 9 validation tubes were loaded [22]. The four calibration levels 10, 7, 4 and 1 ng for each compound deposited on the tube were loaded with helium or without gas (MD). The three validation levels 8.5, 5.5 and 2.5 ng for each compound deposited on the tube were loaded with methane. This concentration range was chosen for two reasons, namely (i) this range was determined based on previous GCMS experiments carried out on real biogases; (ii) a short validation range is more likely to highlight and exacerbate differences between the three calibration techniques. The objective of using methane as gas for the validation tube was to mimic a matrix of renewable gases. Since 21 tubes were loaded for each series, 4 series performed for each technique and 3 loading techniques tested, 252 tubes were prepared for this study.

2.3. TD-GC×GC-MS Method

All tubes were analyzed using a system composed of a TD100-xr from Markes International (Bridgend, UK), hyphenated with a GC×GC-TOFMS Pegasus BT4D from LECO (Villepinte, France).

Tubes were desorbed at a flowrate of 50 mL/min and 270 °C for 10 min into a cold trap "General Purpose" U-T11GPC-2S (Markes International, Bridgend, UK) at −30 °C containing graphitized carbon. Then, the cold trap was desorbed towards the GC×GC at 300 °C for 5 min with a split flow of 20 mL/min, and a column inlet flow of 1.2 mL/min with helium as carrier gas.

The separation was performed using a column set composed of an apolar column in the first dimension 30 m × 0.25 mm × 0.25 µm Rxi-5ms (Restek, Lisses, France) and a medium polar column in the second dimension 1.1 m × 0.1 mm × 0.1 µm DB 1701 (Agilent, Les Ulis, France). The GC×GC was used with a temperature program starting at 40 °C, held for 2 min then heated up to 250 °C at 3 °C/min. The temperature of the secondary oven was set 5 °C higher than the primary oven, and the modulator temperature was set 5 °C higher than the secondary oven. The modulation period of the quad jet modulator was 4 s (consisting of 2 cycles with 1.5 s of hot jet and 0.5 s of cold jet).

The mass spectrometer was used with electron ionization at 70 eV, using a scan range of m/z 45–300 at a scan frequency of 200 Hz.

Data processing was handled using ChromaTOF software 5.51 from LECO (Villepinte, France). All integrations were made on the most abundant m/z for each compound. The ChromaTOF software automatically integrated peaks on the 1D chromatogram with a "target analyte finding" method (TAF), followed by a manual checking

2.4. Accuracy Profile Evaluation

An accuracy profile is a tool developed in the first decade of 21st century [16], for its use in method validation. It is a useful tool that aids the analyst in determining whether method performance is compliant with its requirements, i.e., its acceptance limit (λ). It is based on an evaluation of the trueness and intermediate precision. The acceptance limit is a threshold value, fixed by users in relation to the method objectives. The method performance is characterized by the β tolerance interval, which is the interval that contains, in terms of the average, a proportion β of the future results that will be generated by the method.

For each calibration technique, accuracy profiles were built for each compound with a homemade Excel 2019 (Microsoft, Redmond, WA, USA) spreadsheet containing macros to avoid wasting time on repetitive calculation tasks.

3. Results and Discussion

3.1. Separation of Standard Solution

The column set and the modulation period were set using the air indoor standard solution as a reference. This reference standard contains 48 compounds with a boiling point ranging from 40 to 287 °C; they belong to various chemical families of compounds (i.e., alkanes, aromatics, alcohols, ketones, aldehydes, halogenated, terpenes) and have different polarities. After method development and optimization, all compounds were separated except two pairs of isomers, m-xylene and p-xylene, and 1-ethyl-3-methylbenzene and 1-ethyl-4-methylbenzene. The 2D chromatogram of the standard mix is provided in Figure 2.

3.2. Accuracy Profiles Determination

In the present study, for each of the three calibration techniques, four series of calibration and validation sample analyses were performed with various days and operators for each series. Each series comprised four levels for calibration samples and three levels for validation samples. For each level, three tubes were used. As a consequence, one series represented 21 tubes. For each calibration technique, accuracy profiles were determined individually for the 46 compounds, since two critical pairs were not separated, namely m/p-xylene and 3/4-ethyltoluene. The acceptance limit (λ) was set at 40% considering the intrinsic variability of the TD-GC×GC-MS methods, and the tolerance limit (β) was set at 80%, which represents four future values out of five inside the tolerance interval in terms of the average. Then, the validated range, corresponding to the zone where the tolerance interval was inside the acceptance limits, was determined for each compound (all accuracy profiles are presented in Figure S4 in the Supplementary Materials). The score obtained for this profile corresponded to the percentage of the validated range by reference to the validation range (Figure 3).

In the first instance, the comparison was possible between techniques for each compound. Different situations could occur, with a validation for the entire range of concentrations or only for a part of it, as illustrated in Figure 4. The technique which presented a full validated range (score 100) for the highest number of compounds was the VGSD with 24 compounds validated out of 46. This behavior is illustrated for example by the case of mesitylene (Figure 4(A1–C1)). However, for five compounds (1-propanol, p-xylene, dodecane, tridecane and pentadecane) the validated range was larger for the GSAD technique than for the VGSD technique as evidenced by propan-1-ol in Figure 4(A3–C3). For the MD, there was only a partial validation for nine compounds as illustrated by hexadecane in Figure 4(A2–C2).

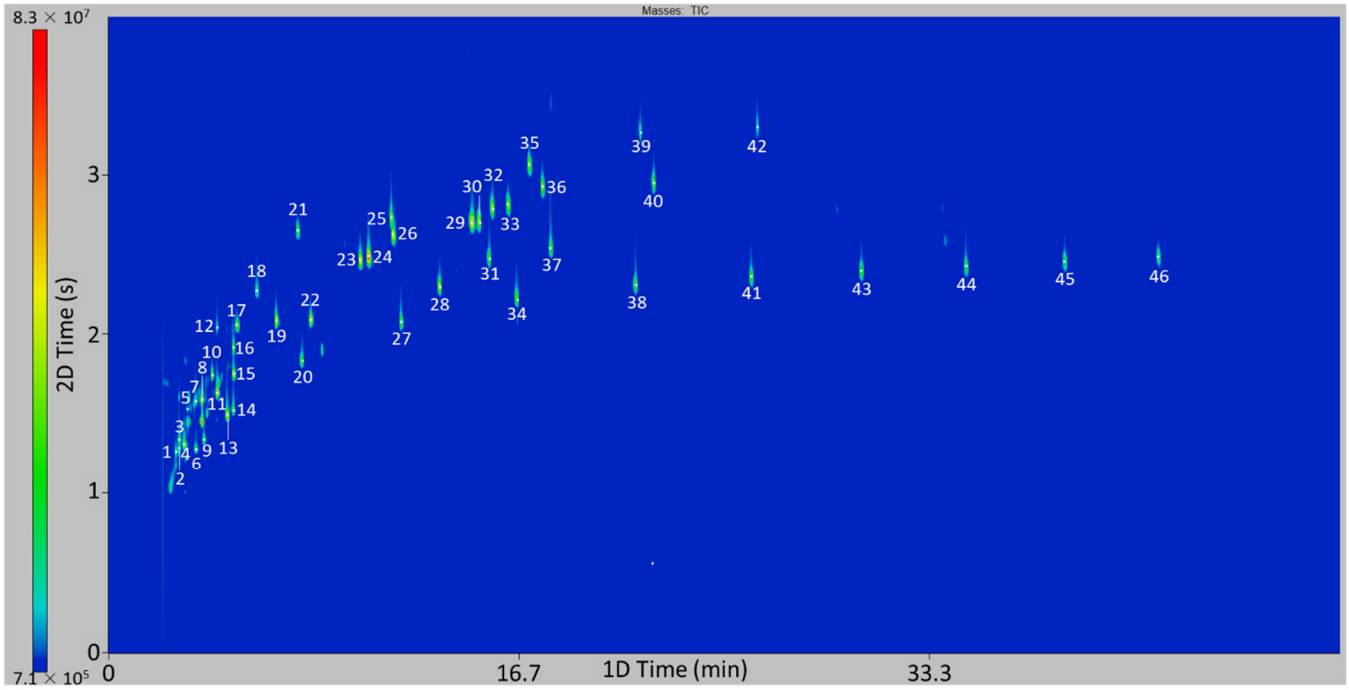

Figure 2. TD-GC×GC-MS chromatogram of 48 VOC standard: 1 ethanol; 2 acetone; 3 2-propanol; 4 methylene chloride; 5 1-propanol; 6 n-hexane; 7 2-butanone; 8 chloroform; 9 2,4-dimethylpentane; 10 1,2-dichloroethene; 11 benzene; 12 1-butanol; 13 isooctane; 14 heptane; 15 trichloroethene; 16 1,2-dichlorpropane; 17 bromodichloromethane; 18 4-methyl-2-pentanone; 19 toluene; 20 octane; 21 dibromochloromethane; 22 tetrachloroethene; 23 ethylbenzene; 24 p/m-xylene; 25 styrene; 26 o-xylene; 27 nonane; 28 α-pinene; 29 1-ethyl-3/4-methyl-benzene; 30 mesitylene; 31 β-pinene;32 1-ethyl-2-methyl-benzene; 33 1,2,4 trimethylbenzene; 34 decane; 35 1,4 dichlorobenzene; 36 1,2,3-trimethylbenzene; 37 limonene; 38 undecane; 39 nonanal; 40 1,2,4,5 tetramethylbenzene; 41 dodecane; 42 decanal; 43 tridecane; 44 tetradecane; 45 pentadecane; 46 hexadecane. Analytical conditions are described in the experimental part.

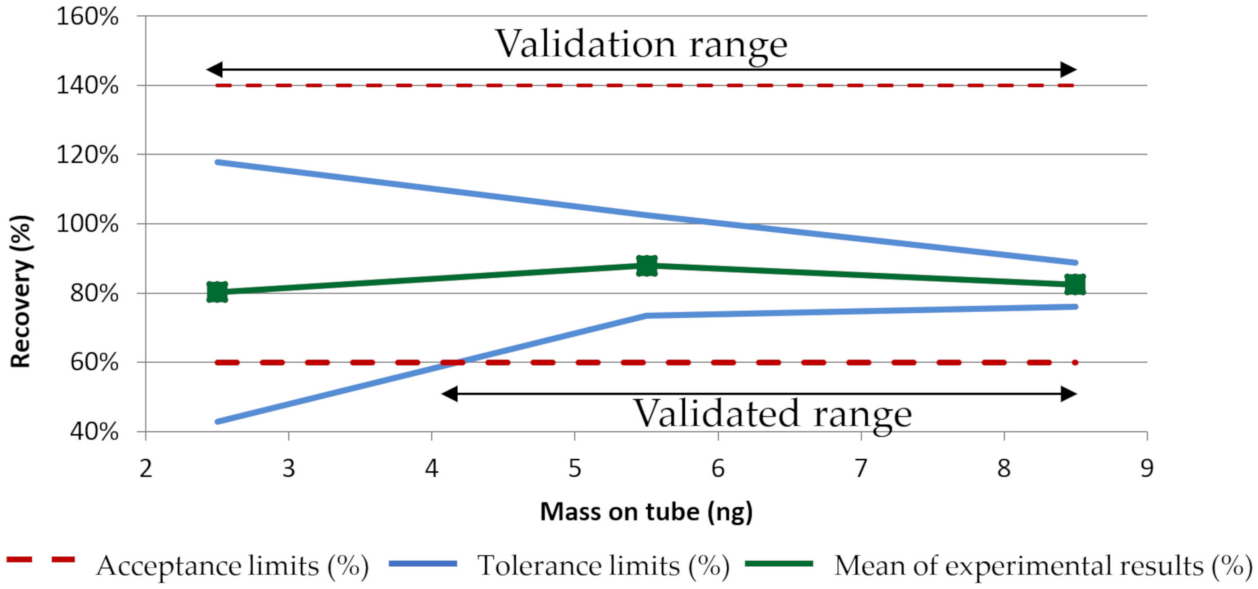

Figure 3. Accuracy profile example (mesitylene (30)), validated range 72/100.

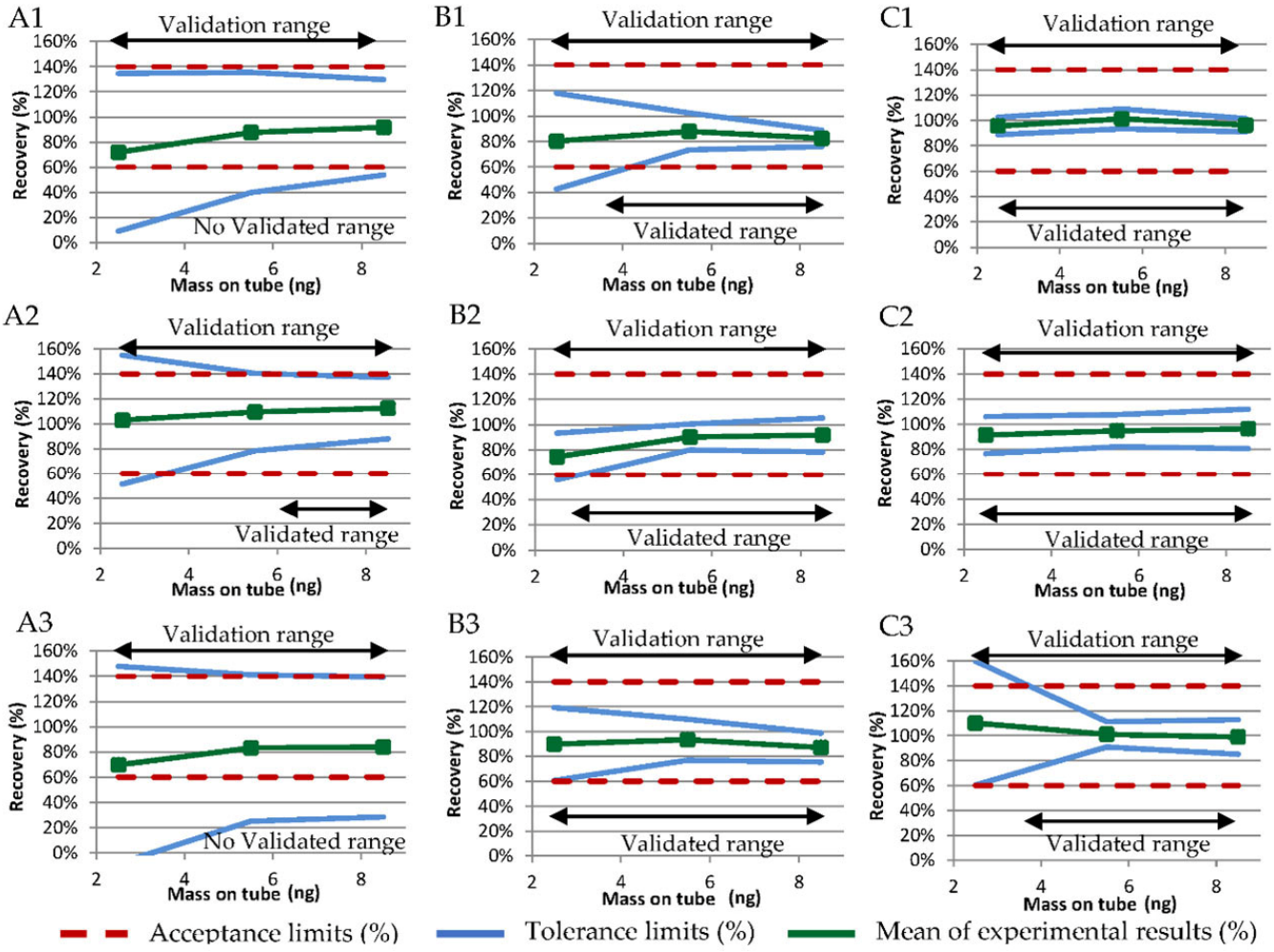

Figure 4. Examples of Accuracy Profiles with the corresponding validation score for mesitylene (30), (**A1**) MD score 0, (**B1**) GSAD score 72, (**C1**) VGSD score 100; hexadecane (46), (**A2**) MD score 45, (**B2**) GSAD score 91, (**C2**) VGSD score 100; 1-propanol (5), (**A3**) MD score 0, (**B3**) GSAD score 100, (**C3**) VGSD score 80.

It can also be noted that 26 compounds out of 46 had a fully validated range in, at least, one technique; among these compounds, seven presented a 100 score both in the VGSD and the GSAD techniques (1,2 dichloro-ethane, trichloroethane, bromodichloromethane, dibromochloromethane, tetrachloroethylene, 1-ethyl-4-methylbenzene, 1,4-dichlorobenzene). These compounds belong to the halogenated family meaning that this type of compound seemed to be well deposited when the technique involved a gas stream.

3.3. Score Calulations

After determining the validated range for each compound (percentage of validated range are presented for each compound in Table S1), the global mean scores, for all the compounds, were calculated for each technique according to the methodology proposed by Remy et al. [21] A comparison of the global scores between the different calibration techniques is presented in Figure 5.

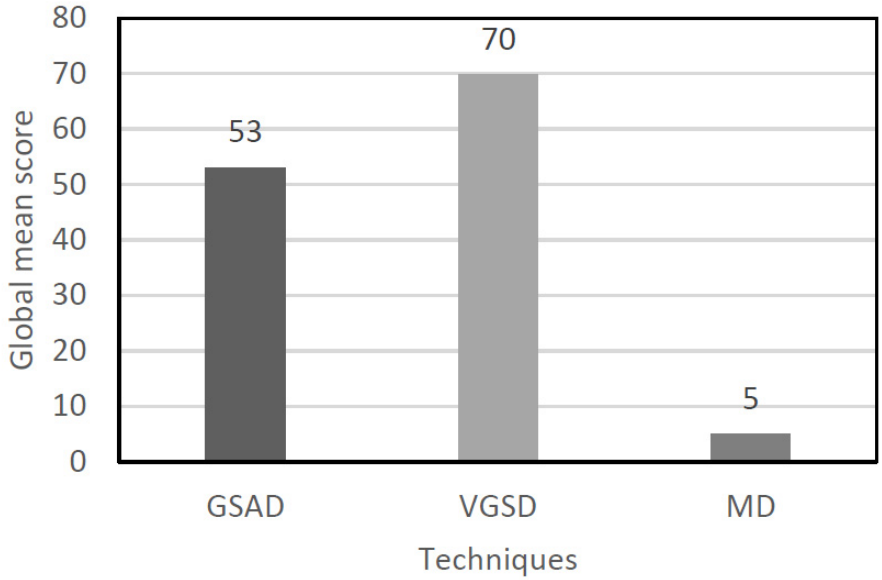

Figure 5. Global score of the three calibration techniques.

VGSD had the highest mean score of validation with 70%. The addition of a gas stream for the MD (i.e., GSAD) permitted the validation range to rise from 5 to 53%. This meant that a simple addition of gas stream can help the deposition of compounds compared to the classic MD.

Then, compounds were classified according to their range of boiling temperature (16 compounds between 0 and 100 °C, 10 between 100 and 150 °C, 15 between 150 and 200 °C, 6 between 200 and 300 °C) and mean scores were calculated for each class and each technique (Figure 6).

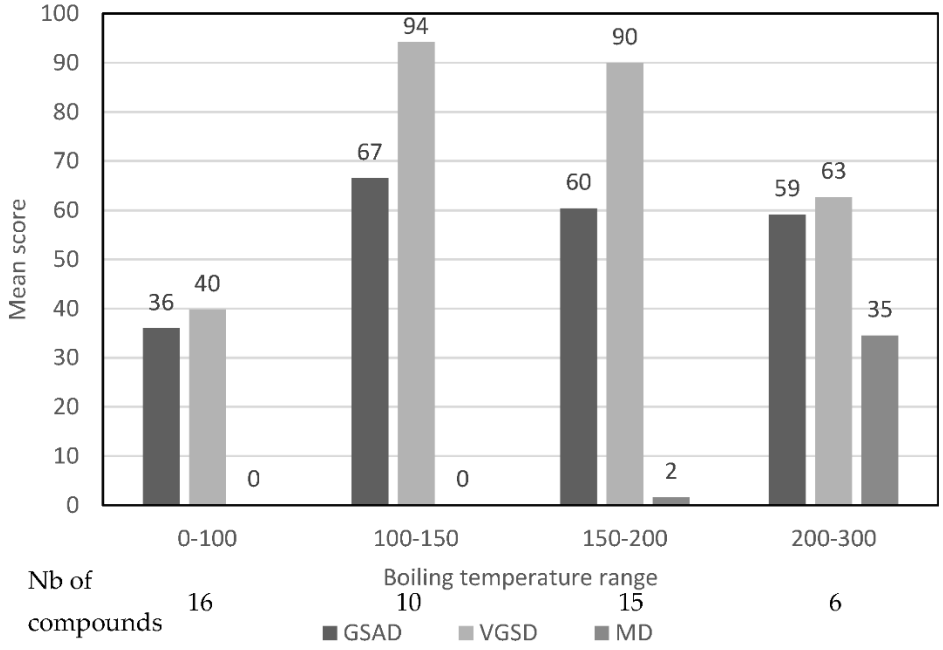

Figure 6. Score by boiling temperature range.

An observation could be made that the VGSD had higher validation results (mean validation score of 94 and 90%) with compounds possessing a boiling temperature close to the temperature of the VGSD apparatus, 140 °C. For compounds with a boiling temperature below 100 °C or higher than 200 °C the VGSD and the GSAD had similar mean validation

scores. It can also be noted that the MD had a mean validation score of 35%, its highest score, only for compounds with a boiling point of higher than 200 °C.

The results were also studied according to the chemical families (i.e., alcohol, aldehyde, alkane, aromatic, halogenated, ketone, terpene); their mean validation scores were calculated and are reported in Figure 7.

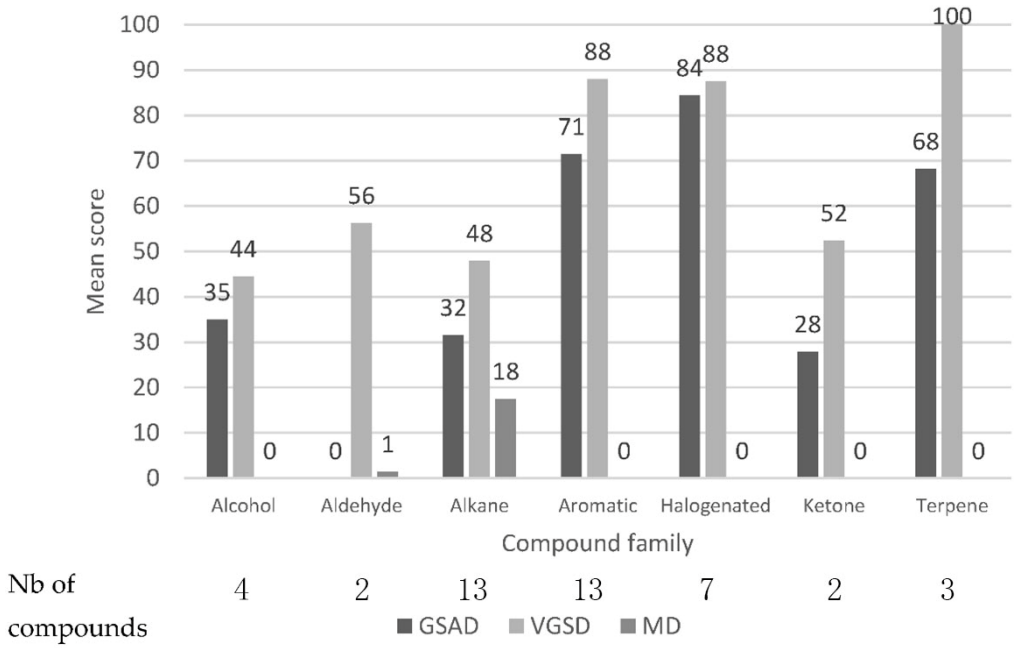

Figure 7. Score by chemical family.

In almost every family, the mean scores were slightly higher for VGSD than for GSAD, except for aldehydes where there was no validated range for GSAD. The MD only provided a validation score for the alkanes with more than 11 carbon atoms.

Despite VGSD being found to be the most efficient technique from this evaluation, it presents two main drawbacks compared to the two other techniques. (i) The vaporization chamber needs to be heated 1 h before the experiments to allow equilibration of the temperature. (ii) Owing to the three following points: the heating of the chamber, the presence of a septum, and the need for cleaning the chamber, there is a risk of pollution and carry over (examples are provided in Supplementary Material Figures S1–S3) which leads to requirement of more regular monitoring and maintenance. Moreover, comparing the duration of the three techniques, a six-point calibration curve required 10 min for MD, 20 min for GSAD, and 100 min for VGSD, including the time needed for cleaning the cell and for heating the device.

Considering both the evaluation using accuracy profiles, the ease of implementation and the duration of operations, the GSAD technique appeared as the best compromise in terms of reliability and time investment to prepare standard tubes for the calibration in TD-GC-MS.

4. Conclusions

In the investigated range of concentrations using the accuracy profile evaluation, VGSD was found to be the most efficient among the tested techniques for the preparation of standards for quantitative analysis in TD-GC×GC-TOFMS in terms of accuracy, with a global score of 70% for the mean validated range.

Gas stream assistance implemented in the GSAD significantly improved the performance of MD with global scores of, respectively, 53 and 5% for the mean validation range. From a practical point of view, GSAD appeared to be the best compromise for a lab that needs implement quantitative analysis in TD-GC-MS considering not only the performance

evaluated using an accuracy profile but also the time involved to perform the loading of tubes.

In the investigated low range of concentration, MD should be avoided if accurate quantification is required and limited only to qualitative analysis.

Some families of polar compounds such as amines and acids, were not represented in the standard mixture. Complementary tests should be performed in order to investigate the behavior of these polar compounds. Possible future developments should look towards the automatization of the GSAD, or the use of preheated GSAD without vaporization.

This study showed, once again, the possibility of using the accuracy profile methodology as a powerful tool for the comparison of quantitative performances of analytical methods.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/separations9080226/s1, Figure S1: Chromatogram of a GASD loaded tube; Figure S2: Chromatogram of a VGSD loaded tube with a slight pollution (red circles around pollution peaks); Figure S3: Chromatogram of a VGSD loaded tube with an important pollution (red circles around pollution peaks); Table S1: Validation Range of each compound with each technique; Figure S4: Accuracy profile of all compounds.

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