

Improving Thermal Extraction Method Reproducibility through Instrument Temperature Calibration in the Sample Position

Yunyun Nie, Eike Kleine-Benne, Lars Büngener

GERSTEL GmbH & Co. KG, Eberhard-Gerstel-Platz 1, 45473 Mülheim an der Ruhr, Germany

KEYWORDS

Thermal extraction, VDA 278 method, material emission analysis, automobile interior material, thermal desorption, TDS 3, temperature, temperature calibration, flow rate.

ABSTRACT

The influence of variations in desorption temperature, desorption flow and sample preparation on VDA 278 analysis method [1] robustness and reproducibility is studied using a wide variety of samples from automobile interior materials: polypropylene (PP) granulate, polyurethane (PU) foam, leather, Duroplastic plastics and paint. It is shown that a temperature difference of just two degrees at 90°C or at 120°C can lead to an emission deviation of ± 20 percent. Also, desorption flow is shown to have significant influence on paint stripe emission values while there is little influence on samples like PP granulate.

A software feature “VDA 278 calibration” is presented, which enables temperature calibration by just a few mouse-clicks. Examples shown are adjustment of the temperature to 90°C and 120°C respectively as required in the VDA 278 method, with a deviation smaller than $\pm 1.0^\circ\text{C}$.

INTRODUCTION

Thermal desorption instruments are widely used for determination of emissions of volatile organic compound from materials. One technique is direct thermal extraction in which a material sample is placed directly in a thermal desorption tube. An inert gas is supplied under controlled conditions (temperature and flow) transferring released compounds from the material sample to a gas chromatography system. For example, VDA 278, a well-known method for determination of organic emissions from vehicle interior materials, is based on direct thermal extraction.

When performing direct thermal extraction, the desorption temperature is the most critical method parameter with even small changes resulting in large variations. Consequently, temperature precision should be tightly controlled and verified. If needed, the temperature should be adjusted to the required value. In addition, the temperature should ideally be measured exactly where the sample material is positioned in order to give a correct value. This means that the temperature should be measured inside the thermal desorption tube while this is placed in the TDS 3 instrument.

A dedicated adapter is available for direct temperature measurement inside the TDS tube and MAESTRO software features have been developed to subsequently adjust the temperature to the correct value within a range of $\pm 1.0^\circ\text{C}$. For VDA 278 method based work, the two temperatures adjusted to are 90°C and 120°C. This means that different instruments can be adjusted to

the same exact temperatures in order to ensure reliable and reproducible results from instrument to instrument and from laboratory to laboratory. The temperature sensor is traceable to a certified standard. In this work, the influence of extraction temperature and gas flow on the emission behavior of materials was investigated.

EXPERIMENTAL

All materials were analyzed according to the VDA 278 method. First, for two samples of each material VOC emissions (volatile organic compounds) were determined; after that with the second sample FOG emission was determined (condensable organic compounds “fogging effect”). In order to get an idea of the variance of determined emission rates, for some samples, several replicate runs were done.

Thermal Desorption GC/MS Instrument:

GERSTEL Thermal Desorption System TDS 3 fitted with a TDS A2 autosampler

Agilent 7890 GC and 5973 MSD

HP Ultra 2 column 50 m x 0.32 mm ID, 0.52 µm film

Thermal Extraction and GC/MS method parameters as specified in VDA 278:

VOC analysis: 30 min @ 90°C and 82 mL/min, Cryofocusing @ -150°C

FOG analysis: 60 min @ 120°C and 82 mL/min, Cryofocusing @ -150°C

In a first step, a set of samples, representing a variety of sample types, were analyzed following the VDA 278 methodology and VOC and FOG values were determined. Table 1 lists all results.

Samples were selected with the aim of covering a broad range of emission profiles, from low emitting materials like Duroplastic plastics to high emitting materials like PU foam. In addition, some sample materials analyzed, such as Duroplastic Plastics are known to emit high boiling compounds, whereas others, such as polypropylene are known to emit both high- and low boiling compounds.

In a second step, method parameters deemed likely to significantly affect analysis results were varied in order to get quantitative information about the impact. The parameters in question were the temperature of the material and the flow rate of the inert gas during thermal extraction.

RESULTS AND DISCUSSION

Influence of extraction temperature variation on VOC and FOG data. The sample temperature is a very important parameter for thermal extraction because it affects the diffusion rates of compounds in a sample as well as release or vaporization of compounds from the sample. Figure 1 and Figure 2 show the influence of the sample temperature on the VOC and FOG emission rates. All figures show a marked grey area representing the $\pm 20\%$ emission rate range around VDA 278 method temperature set points. The aim of this study regarding temperature induced deviations was to determine the temperature accuracy required in order to meet the VDA 278 method quality criteria. For VOC emissions, temperatures of 85°C, 88°C, 90°C, 92°C and 95°C were chosen. For FOG emissions, 115°C, 118°C, 120°C, 122°C and 125°C were chosen.

Table 1. VOC and FOG data for all tested materials obtained following the VDA 278 method.

Sample	VOC	FOG
Polypropylene (PP) Granulate (25 ± 2 mg, one piece)	189 ± 18 µg/g	1241 ± 30 µg/g
Polyurethane (PU) foam (15 ± 2 mg)	611 ± 30 µg/g	890 ± 45 µg/g
Leather (10 ± 2 mg)	195 ± 31 µg/g	522 ± 15 µg/g
Duroplastic plastic (20 ± 3 mg, Ø 3.5 mm, punch tool)	4,5 ± 0.3 µg/g	29 ± 2 µg/g

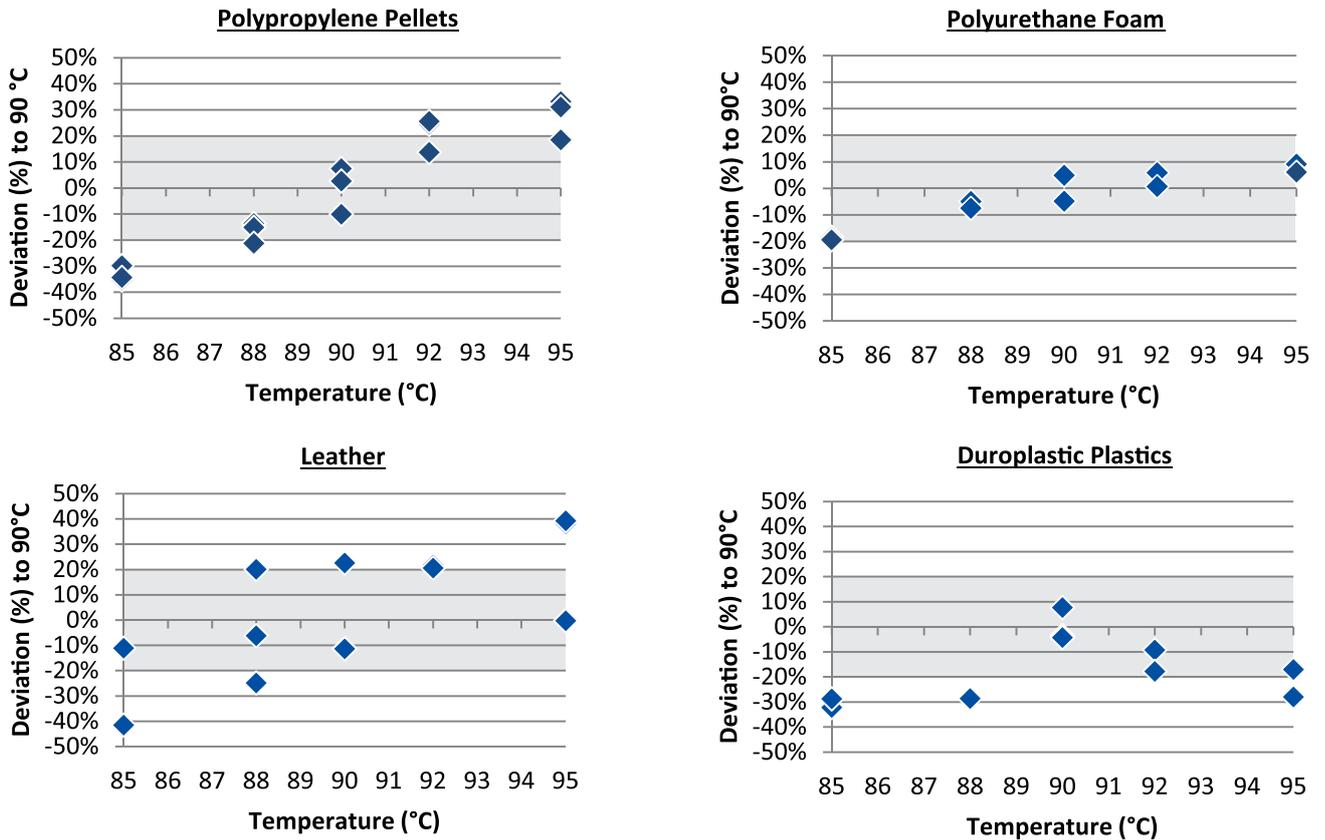


Figure 1. Temperature induced deviation (%) of VOC emission rates compared to the emission rate obtained at 90°C (marked grey area represents $\pm 20\%$ criteria, two or three runs were performed at each temperature).

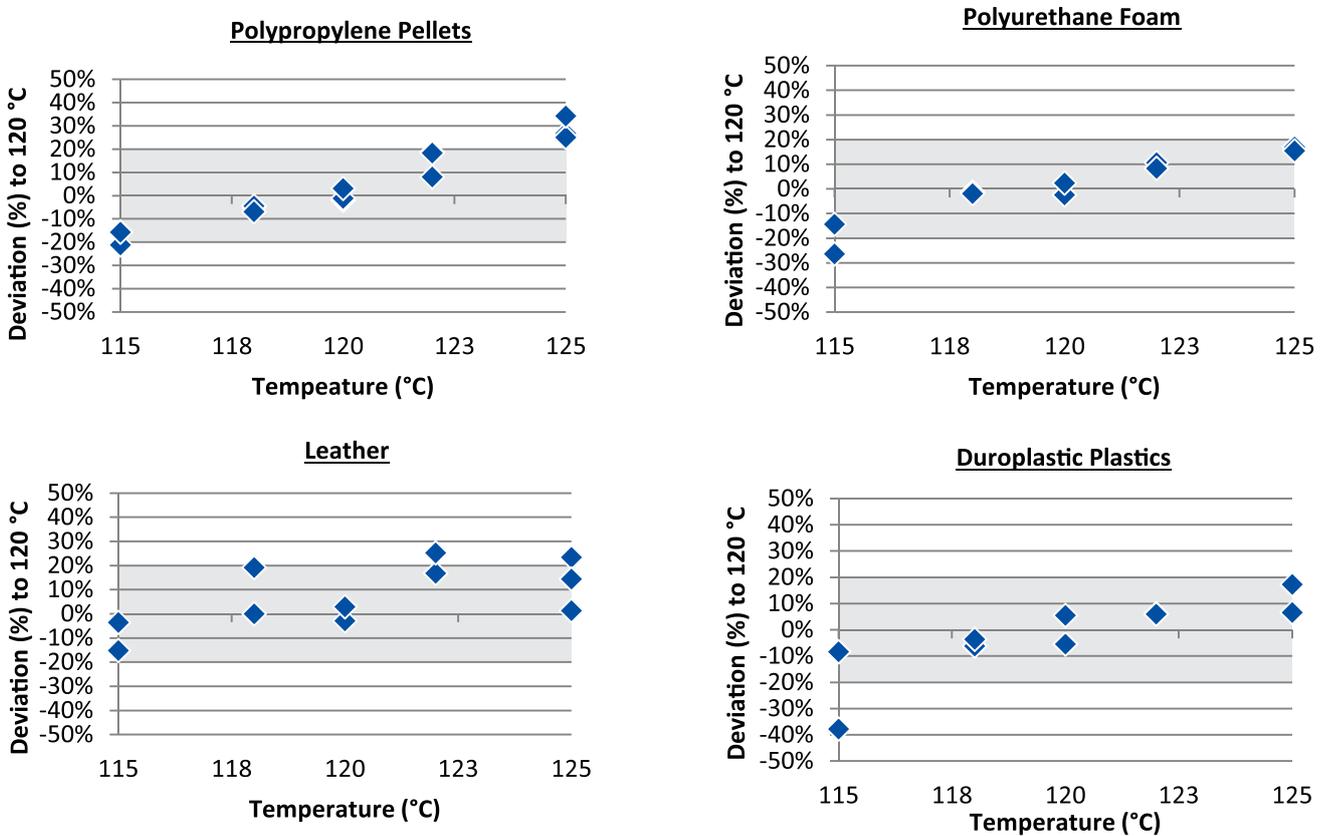


Figure 2. Temperature induced deviation (%) of FOG emission rates compared to the emission rate obtained at 120°C (marked grey area represents $\pm 20\%$ criteria, two or three runs were performed at each temperature).

For polypropylene and polyurethane the emission rate variations as a function of extraction temperature are obvious. For VOC emissions, a temperature variation larger than 2°C will lead to a variation of emission values larger than 20 %. For Fog emissions at higher temperature, a temperature variation larger than 2-5°C will lead to a variation of emission values larger than 20 %. Emission rates of leather and Duroplastic plastics show a broader spread, indicating that in addition to the temperature, other effects like sample preparation or homogeneity are important.

Influence of extraction flow variation on VOC and FOG data. Direct thermal extraction is rightly considered a dynamic headspace technique. In addition to temperature, the extraction flow through the desorption tube that holds the sample is a parameter that affects the amount of released compounds. Consequently, the influence of the extraction flow on the emission rates was studied in this work. Five flow rates were used: 60, 70, 82, 90, and 100 mL/min. The standard flow rate prescribed in VDA method 278 is 82 mL/min.

For the first set of samples, changing the flow didn't affect emission rates very much. For example in Figure 3 results for polypropylene pellets are shown. Within a broad range of flow rates from 60 mL/min to 100 mL/min, the VOC and FOG emission values are still within the $\pm 20\%$ criteria. In contrast to the solid pellets, a much thinner material was analyzed, for which emissions might deplete the analytes quicker. Figure 4 shows results obtained from paint applied on aluminum foil (30 mm x 3 mm). Here a clear dependency of emission rates on extraction flow can be seen. It seems that flow variations will lead to an underestimation of both VOC and FOG emission values. Furthermore, several of the determined emission values fell outside the $\pm 20\%$ criteria.

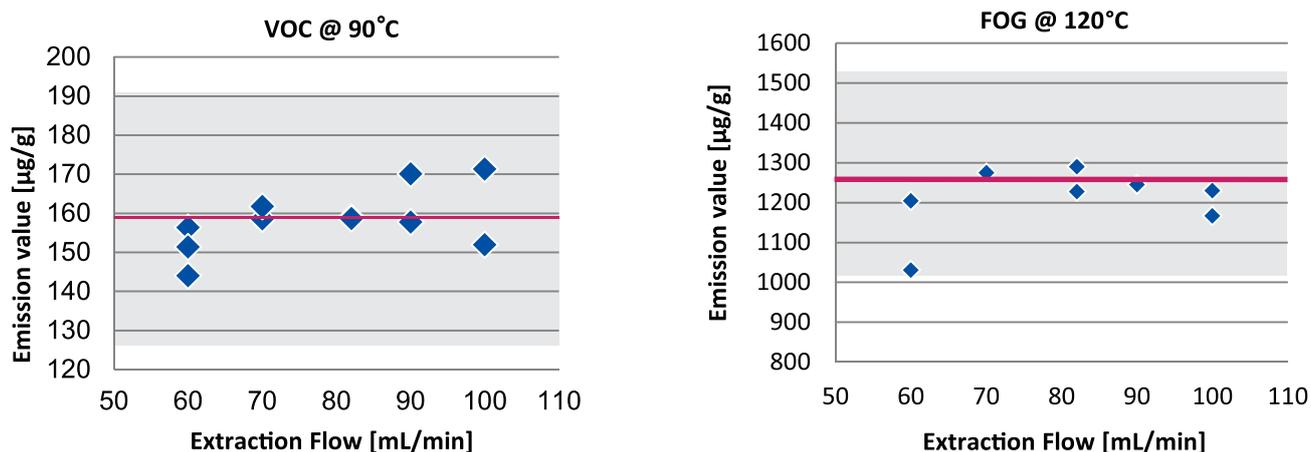


Figure 3. Influence of extraction flow on VOC and FOG emission for polypropylene pellets (marked grey area represents $\pm 20\%$ criteria, two or three runs for each flow level).

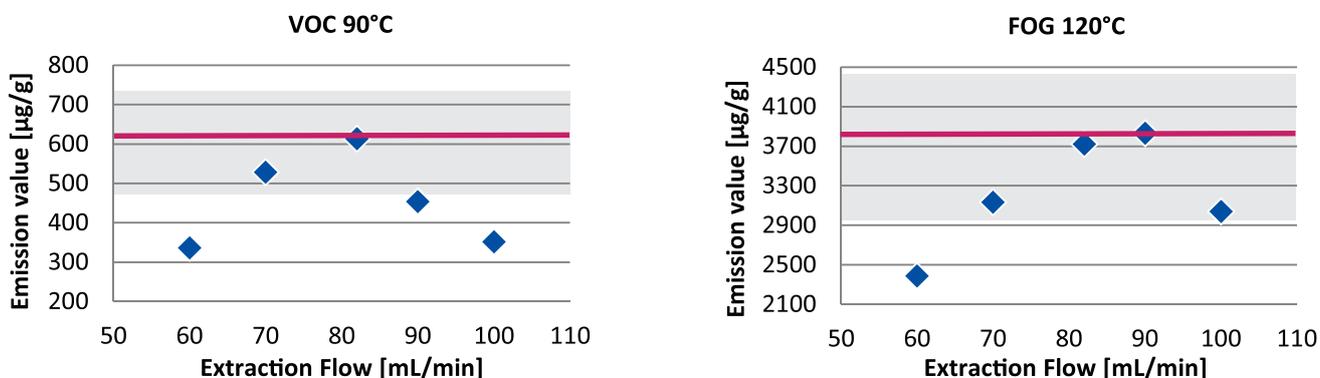


Figure 4. Influence of extraction flow on VOC and FOG emission for a paint applied on aluminum foil (marked grey area represents $\pm 20\%$ criteria).

We took a closer look at the changes of peak patterns of PP granulate and paint stripe emissions with varying flow rate: Typical peaks of the chromatograms obtained from PP granulate and paint stripe at 90°C were chosen, and normalized against the first peak area for each sample. As can be seen in Figure 5, the peak pattern changed only slightly when desorption flows were varied from 60 to 100 mL/min, even though a slight increase in peak area was seen for all compounds with increasing desorption flow. But the peak patterns of paint samples applied to aluminum foil changed dramatically, for example, for peak B and D: The higher the flow rate, the lower the emission value obtained. For peak C, the result was reversed. It is conceivable that for the paint stripe sample, the emission value depends on a gas phase transfer (external diffusion), which is strongly influenced by the linear gas velocity.

Flow rates were controlled through a highly accurate mass flow controller. Based on our results obtained from the paint stripe, a flow variation within 5 mL/min for VOC test and a flow variation within 10 mL/min for FOG test lead an emission variation of less than 20 %. At the specified flow of 82 mL/min, the mass flow controller easily meets these criteria.

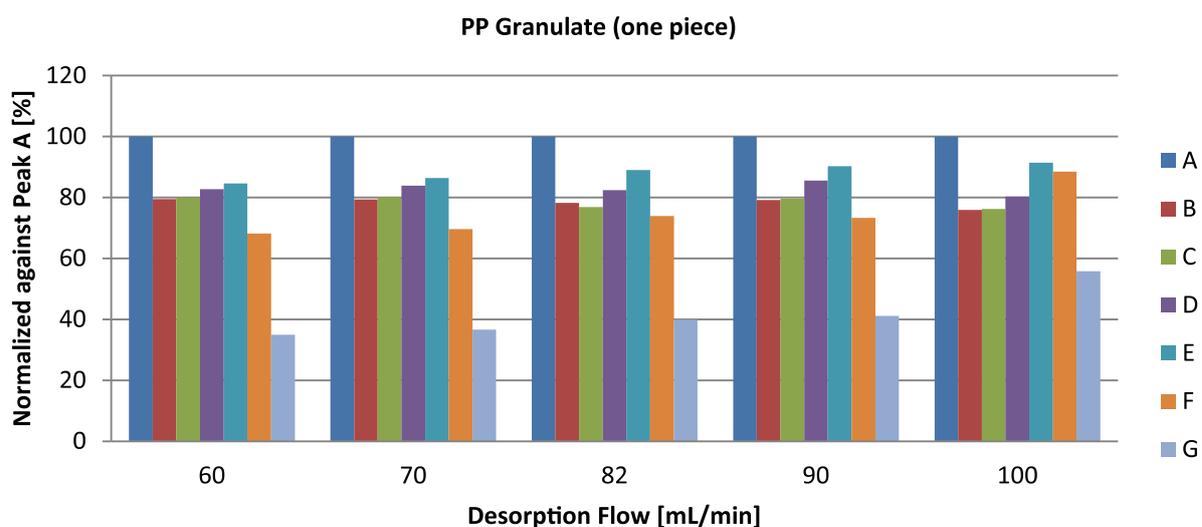


Figure 5. Normalized peak patterns of PP granulate (one piece) at different flow rates.

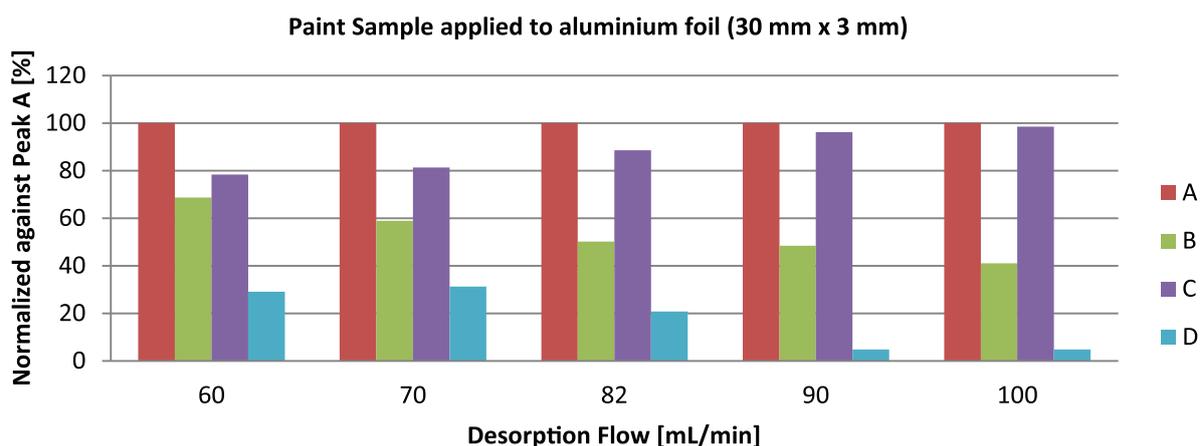


Figure 6. Normalized peak patterns of paint sample applied on aluminum foil (30 mm x 3 mm) at different flow rates.

Extraction Temperature Validation

In order to determine the temperature in the sample area of the TDS desorption tube with a high degree of accuracy, a simple yet reliable method was developed. The method is based on a thermocouple Type T, the tip of which is held in place in the middle of the TDS desorption tube's marked sample position using a specially developed adapter (Figure 9). The temperature is easily read using the accompanying measurement device (Figure 10). In this way, the actual sample temperature can be determined with a high degree of confidence.



Figure 9. Adapter for sample area true temperature measurement in the TDS 3.



Figure 10. Temperature measurement device.

Temperature Adjustment for VDA method 278 analysis.

In the event that a TDS system does not meet the required temperature accuracy for the quality criteria of VDA method 278, a new feature “VDA 278 calibration” in Maestro software is now available in order to help the analyst correct the situation. It offers the user automated temperature adjustment with a couple of mouse-clicks. The sample temperature at the 90°C and 120°C levels will be adjusted very close to the required value with a deviation smaller than $\pm 1.0^{\circ}\text{C}$. Temperatures are adjusted over the full temperature range from 30°C to 350°C and error values at 90°C and 120°C are reported.

CONCLUSION

Emission rates for VOC and FOG analytes from materials determined by VDA method 278 depend on accurate settings of extraction parameters, such as extraction temperature and gas flow. The results presented here show that the desorption flow can be changed up to as much as $\pm 5\text{-}10$ mL/min without affecting emission results more than $\pm 20\%$. This accuracy is easily achieved using modern instrumentation. However, control of the extraction temperature in the heated sample zone to within a range of not more than $\pm 2^\circ\text{C}$ is needed in order to ensure accurate results.

The GERSTEL VDA 278 Calibration Kit ensures that the user will get a TDS desorption tube temperature variation smaller than $\pm 1^\circ\text{C}$ for the set points 90°C and 120°C . The calibration is performed through temperature measurements directly in the sample position of the TDS in question on site in the customer laboratory. This ensures that reproducible results can be obtained from instrument to instrument and from laboratory to laboratory.

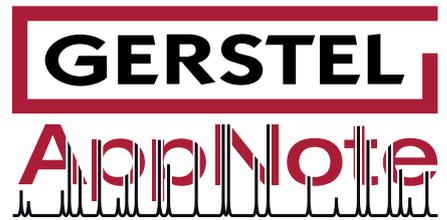
The feature “VDA 278 calibration” in Maestro software offers the user an automated temperature calibration procedure performed with just a few mouse-clicks. Using this procedure, the TDS sample temperature will be calibrated at 90°C and at 120°C with a deviation smaller than $\pm 1.0^\circ\text{C}$. The measurement tools needed, a software-dongle as well as a user manual are available in the “TDS VDA 278 Kit”. This kit provides an extension of the TDS OQ/PV procedures and is especially adapted for laboratories performing analysis following VDA method 278 allowing them to produce accurate and reliable results from sample emission tests.

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REFERENCE

- [1] Thermal Desorption Analysis of Organic Emissions for the Characterization of Non-Metallic Materials for Automobiles. VDA278. s.l. : *Verband der Automobilindustrie*, **2011**.



GERSTEL GmbH & Co. KG

Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany

+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.

701 Digital Drive, Suite J
Linthicum, MD 21090
USA

+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG

Wassergrabe 27
CH-6210 Sursee
Switzerland

+41 (41) 9 21 97 23
+41 (41) 9 21 97 25
swiss@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.

1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsu-dai Ekimae Bldg 4F
Japan

+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP

10 Science Park Road
#02-18 The Alpha
Singapore 117684

+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd

Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District

Shanghai 201206
+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

GERSTEL Brasil

Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil

+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

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