

# Development of a TDS-GC-FID method for the determination of methanol and ethanol in air

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**Abstract** A method for the determination of very volatile organic compounds (VVOC) in air was developed and successfully tested for methanol and ethanol. Carbotrap 300® (a multi-bed tube using Carbopack C®, Carbopack B® and Carbosive SIII®) was selected as sorption material for thermal desorption and tested for its suitability for emission test chamber measurements. The adsorption behaviour and the chromatographic results are influenced negatively by spiking aqueous solutions on the adsorption medium for calibration purposes. The latter effect can be reduced by blowing dry air across the adsorbent to remove the adsorbed water. Detection and quantification limits were determined for a GC-FID system and compared to GC-MS. The applicability of the method was tested with a methanol eliminating silane modified polymeric adhesive (SMP-adhesive for parquet) in an emission test chamber.

## Entwicklung einer TDS-GC-FID-Methode zur Bestimmung von Methanol und Ethanol in Luft

**Zusammenfassung** Eine Methode zur Bestimmung von sehr leicht flüchtigen Verbindungen in Luft wurde für Methanol und Ethanol entwickelt und erfolgreich getestet. Dafür wurde Carbotrap 300® (Multibettrohr aus Carbopack C®, Carbopack B® und Carbosive SIII®) als Sorptionsmedium für die Thermodesorption ausgewählt und dessen Eignung für Emissionskammermessungen untersucht. Das Adsorptionsverhalten und die chromatographischen Ergebnisse werden negativ durch die Aufgabe von wässrigen Kalibrierlösungen auf das Adsorptionsmedium beeinflusst. Durch das Überleiten von trockener Luft kann dieser Effekt verringert werden, da so das adsorbierte Wasser entfernt wird. Die Nachweis- und Bestimmungsgrenzen wurden für ein eingesetztes GC-FID-System ermittelt und mit einem GC-MS verglichen. Mit einem methanolabsplattendem silanmodifizierten Polymerklebstoff (SMP-Parquetkleber), der in eine Emissionskammer eingebracht wurde, konnte die Tauglichkeit der Methode überprüft werden.

## 1 Introduction

With increasing environmental and health awareness, the demands on building materials also increase. They should be made from low-emission components so as to minimize

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their possible adverse impact on people and the environment. As a consequence, the “Committee for health-related evaluation of building products“ (Ausschuss zur gesundheitlichen Bewertung von Bauprodukten – AgBB) has developed an evaluation system for testing the emission behaviour of construction products. In this system, the chamber air concentrations of volatile and semi-volatile organic compounds (VOCs and SVOCs) are determined after 3 and 28 days with the standard thermal desorption method using Tenax adsorption tubes [1]. Very volatile organic compounds (VVOC) with boiling points in the range of < 0 to 100 °C are not determined quantitatively, because Tenax is not appropriate for VVOCs. The VVOC class includes substances such as methanol (MeOH), ethanol (EtOH), acetone, 2-chloropropane and pentane. The two primary alcohols methanol and ethanol were chosen as VVOC examples for the method development. Some of the properties of methanol and ethanol are shown in Table 1.

Methanol and ethanol are high production volume chemicals. They are, for example, used as starting materials for the synthesis of other basic chemicals and also as solvents for resins, paints and oils [3].

A parquet adhesive based on silane-modified polymers, a so-called SMP adhesive, was selected for the practical testing of the method. According to the manufacturer, these adhesives are water- and solvent-free and consist of only one component. While absorbing water, the polymer chains, such as polypropylene glycol with methoxy-silane groups in a telechelic (terminal) configuration, condense into a three-dimensional network and cleave off methanol [4].

## 2 Problem

The established measuring methods for the determination of VOC and SVOC emissions based on thermal desorption of Tenax sorbent tubes [5] are not suitable for VVOCs. The German Research Foundation [6] has published two methods for quantifying methanol in workplace air. These are based on the adsorption of methanol on water (method 1), or on the adsorption on silica gel and extraction in water (method 2), followed by separation with gas chromatography (GC) and detection using a flame ionization detector (FID). Both methods have the disadvantage that they require high sample volumes of 10 l (method 1) and up to 20 l (method 2). In addition, the determination limit of 4.0 mg/m<sup>3</sup> for method 1 is very high. For method 2 it is significantly lower at

Table 1. Selected materials properties of methanol and ethanol [2] ( $\log K_{ow}$ : logarithmic octanol-water-distribution coefficient).

	Molar mass in g/mol	Melting point in °C	Boiling point in °C	Density in g/cm <sup>3</sup>	Vapour pressure 20 °C in mbar	$\log K_{ow}$
Methanol	32.04	-98	65	0.79	129	-0.74
Ethanol	46.07	-114	78	0.79	58	-0.3

Table 2. Properties of various single sorbents [9].

	Carbosieve SIII®	Carboxen 1000®	Carboxen 1003®	Carboxen 569®
Bulk density in g/cm <sup>3</sup>	0.66	0.47	0.49	0.61
Granular size in mesh	60 to 80	60 to 80	40 to 60	20 to 45
Pore diameter in Å	4 to 11	10 to 12	5 to 8	5 to 8
Macro porosity in cm/g	0	0.25	0.28	0.1
Meso porosity in cm/g	0.04	0.16	0.26	0.14
Micro porosity in cm/g	0.35	0.44	0.38	0.2
Surface area in m <sup>2</sup> /g	975	1 200	1 000	485

0.065 mg/m<sup>3</sup>, but requires a much longer sampling time of about 8 h. These two methods are therefore only suitable for emission analysis under these conditions.

The goal is to develop an active sampling method with relatively small sample volumes of 1 to 5 l and significantly lower limits of quantification. The application of thermal desorption is most promising, since no solvents are needed and therefore no dilution takes place [7]. Different adsorbents were tested on their ability to sorb methanol and ethanol [8]. As potentially suitable sorbents, Carbosieve SIII®, Carboxen 1000®, Carboxen 1003® and Carboxen 569® were chosen. The 3-bed combination tube Carbotrap 300® is a combination of Carboxen C®, Carboxen B® and Carbosieve SIII®. The suitability of the selected sorbent was tested in emission test chambers. As the method according to DIN ISO 16000-6 specifies sampling of humid air ((50 ± 5) % relative humidity), the influence of air humidity was also examined.

### 3 Materials and methods

For the preparation of standard solutions, the following chemicals were used: methanol (98.8%) from J. T. Baker (for organic residue analysis) and ethanol (99.8%) from AppliChem. The solvent was water, purified with Easy Pure II® system from Werner. The resistivity of the purified water was 17.9 MΩcm.

For identification and quantification of the substances in the emission test chamber air, a TDS-GC-FID system was used and its performance compared to a TDS-GC-MS system (see Section 5.2). The FID measurement system used was a gas chromatograph, type 6890, Agilent, with a Zebron WAX® Plus (polyethylene glycol) column (30 m × 0.32 mm × 0.5 µm). Helium was used as the carrier gas. The coupled thermal desorption unit was a TDSA with the cold injection system CIS 4, Gerstel, which was cooled to -100 °C with liquid nitrogen. A type 6890 gas chromatograph from Agilent with a Restek Rxi 5 separation column (60 m × 0.25 mm × 0.25 µm) was used as the second analysis system. This was coupled with an Agilent 5973 N mass selective detector and a thermal desorption system (TDSA 2 with cold injection system) from Gerstel. The following temperature programme was used for both thermal desorption units: 40 °C, at 12 °C/min to 200 °C for 0.40 min. The temperature programme of the cold injection system goes through the following steps: -100 °C for 0.70 min, at 12 °C/min to 200 °C for 5 min. After a non-split injection onto the corresponding separation column, the following column temperature programme was run: 40 °C, at 20 °C/min to 220 °C for 5 min.

In scan mode, mass-to-charge ratios of 25 to 200 were considered. In the selected ion monitoring (SIM) mode, the three

most intense masses 29, 31 and 32 were selected for methanol, and for ethanol the masses 29, 31, 45 and 46.

#### 3.1 Sorbent comparison

To compare the sorbents, three tubes with Carbosieve SIII®, Carboxen 1000®, Carboxen 1003®, Carboxen 569® and four tubes with Carbotrap 300® were spiked with 1 µl of a standard ( $c \approx 700$  ng/µl). The water used as solvent was removed with 1 l of dry synthetic air and the tubes were then analysed with the TDS-GC-FID. The Carbotrap 300® tubes were commercial products. The other tubes were prepared by filling empty tubes (Gerstel) manually with 300 mg Carbosieve SIII®, Carboxen 1000®, Carboxen 1003® and Carboxen 569®. The main characteristics of the different tubes are summarized in Table 2. All sorbents are marked as hydrophobic by the manufacturer.

#### 3.2 Characteristics of the methods

Three different concentrations (20, 200 and 2,000 ng/µl) were injected into the Carbotrap 300® tubes and then analyzed with the TDS-GC-FID and TDS-GC-MS systems, using the same TDS programme. The limits of detection and quantification for the FID system were determined according to DIN 52645 [10] with calibration points in the lower mass range from 1 to 5 ng, whereas they were estimated for the MS system using the three point calibration.

The effect of water on adsorption capacity was examined in quadruplicate. For this, the tubes were rinsed with 1 l of dry air or 1 l of humid air ((50 ± 5) %) after manual standard injection of 200 ng of methanol and ethanol in water.

#### 3.3 Recovery experiments in the 1 m<sup>3</sup> emission test chamber

To examine the applicability of the measuring method in emission test chambers, recovery experiments were performed. For this purpose two variants were tested. The variant 1 represents the sampling method according to DIN EN ISO 16000-9 (without removing water). In variant 2, 1 l of dry air was passed over the tubes after sampling, removing the water bound to the sorbents. For both variants 1 µl of a standard aqueous solution ( $c \approx 80$  µg/µl) was injected into the emission test chamber and then a 1 l sample was taken. Assuming that methanol and ethanol evaporate completely into the gas phase, the concentration in the emission test chamber should be 80 µg/m<sup>3</sup>. A temperature of (25 ± 1) °C and a relative humidity of (50 ± 5) % were selected as chamber parameters according to DIN EN ISO 16000-9. The air change rate was 0.4/h. The associated calibration functions for methanol and ethanol, for which the Carbotrap 300® tubes were also treated according to variants 1 and 2, are shown in Figures 1 and 2.

### 3.4 Emissions from an SMP adhesive

The emissions from the SMP adhesive were measured in two experiments. In the first experiment, approximately 120 g were applied on each of three glass plates sized 54 cm × 25 cm, with an individual area of 0.1196 m<sup>2</sup> (minus 1 cm for the edges) and a total area of 0.3588 m<sup>2</sup> (three plates). Taking into account the exchange of air, the area-specific air flow rate is  $q = 1.67 \text{ m}^3/\text{m}^2\text{h}$ . Using a doctor blade, the material was spread on the glass plates, keeping a 1 cm distance from the edges. Then the glass plates were placed in a 1 m<sup>3</sup> chamber of type VCE 1000 classic, Vötsch Industrietechnik. A temperature of  $(23 \pm 1) \text{ }^\circ\text{C}$  and a relative humidity of  $(50 \pm 5) \%$  were selected as chamber parameters according to DIN EN ISO 16000-9. The air change rate was 0.6/h. The emission test chamber air was sampled three times a day over the next nine days.

The second experiment was a variation in the size of the glass plate. For this purpose, a glass plate sized 27 cm × 22 cm with a total area of 0.05 m<sup>2</sup> (with a 1 cm margin) and about 50 g of glue was used. Taking into account the exchange of air, the area-specific air flow rate was  $q = 12 \text{ m}^3/\text{m}^2\text{h}$ . The emission test chamber air was sampled three times daily for seven days. The summary of experimental parameters is shown in Table 3.

## 4 Results

### 4.1 Sorbent comparison

Figure 3 shows the adsorbed amounts of methanol and ethanol (relative values) for the different sorbents. The standard deviations of the triplicate or quadruplicate determinations are shown as error bars. The comparison of the sorbents shows that all tubes used exhibit a significantly higher affinity to ethanol than to methanol. The highest adsorption capacity with respect to the target substance methanol was exhibited by Carbotrap 300® and Carboxen 1000®. Taking into account the corresponding standard deviations, there is no significant difference between these two sorbents. Carboxen 569® however, has the lowest absorption capacity with respect to methanol and ethanol. Furthermore, the adsorption capacity of the sorbents with respect to ethanol should also be noted. In that regard Carbotrap 300® adsorbs more ethanol than Carboxen 1000® – therefore the combined sorbents of Carbotrap 300® became the material of choice.

Table 3. Experimental parameters.

Experiment	Glass plate		Adhesive			Emission chamber		
	Number of glass plates	Size	Mass per plate in g	Area per plate in m <sup>2</sup>	Total area in m <sup>2</sup>	Air change rate in 1/h	Loading in m <sup>2</sup> /m <sup>3</sup>	Area specific air change rate in m <sup>3</sup> /m <sup>2</sup> h
1	3	54 cm × 25 cm	120	0.12	0.36	0.6	0.36	1.67
2	1	27 cm × 22 cm	50	0.05	0.05	0.6	0.05	12

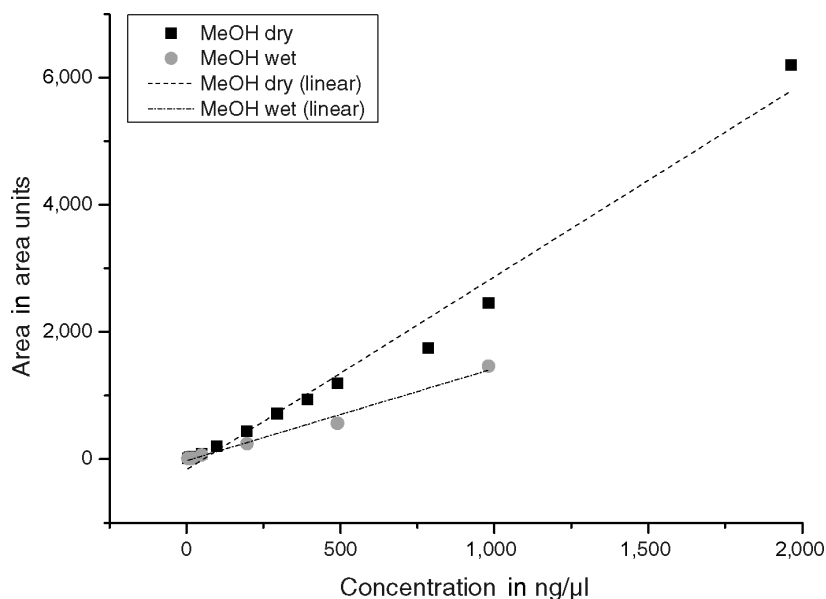


Figure 1. Calibrations of methanol according to variant 1 (wet) and 2 (dry).

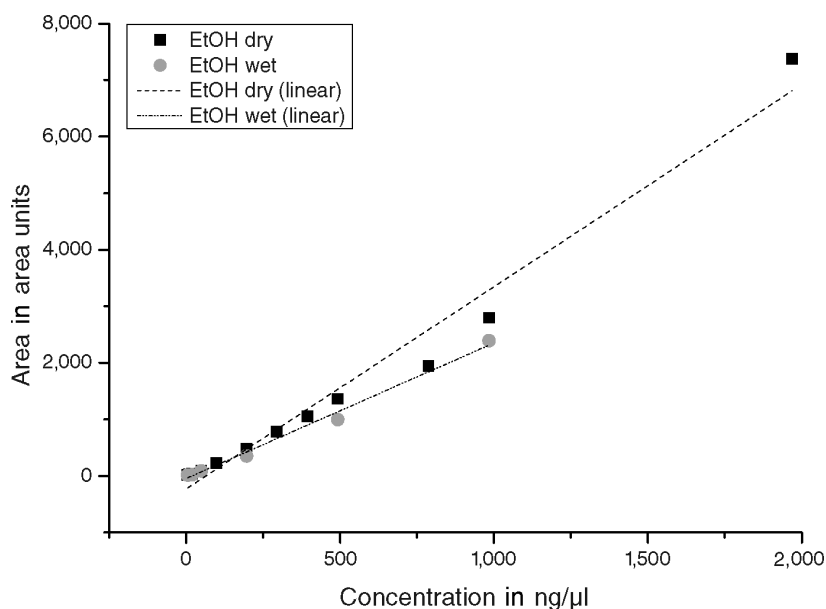


Figure 2. Calibrations of ethanol according to variant 1 (wet) and 2 (dry).

### 4.2 Characteristic values of the methods

Comparison of the scan and SIM measurements on the MS system shows that, as expected, the SIM method is more sensitive than the scan method, even if only slightly (Figure 4). Based on the three concentrations (20, 200 and 2,000 ng/μl) the limits of detection and quantification in the SIM were estimated taking the smallest mass of 20 ng as LOD (Table 4). The corresponding values for a measurement uncertainty of

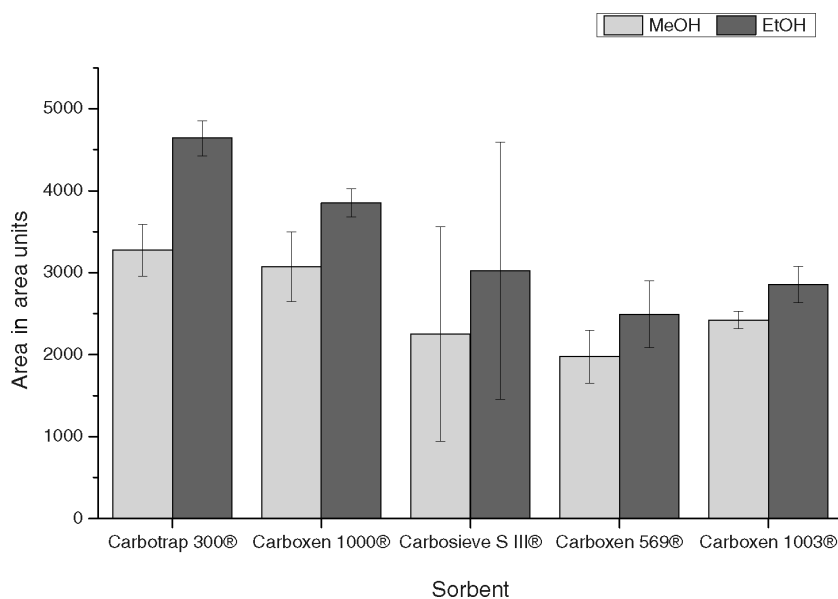


Figure 3. Sorbent comparison.

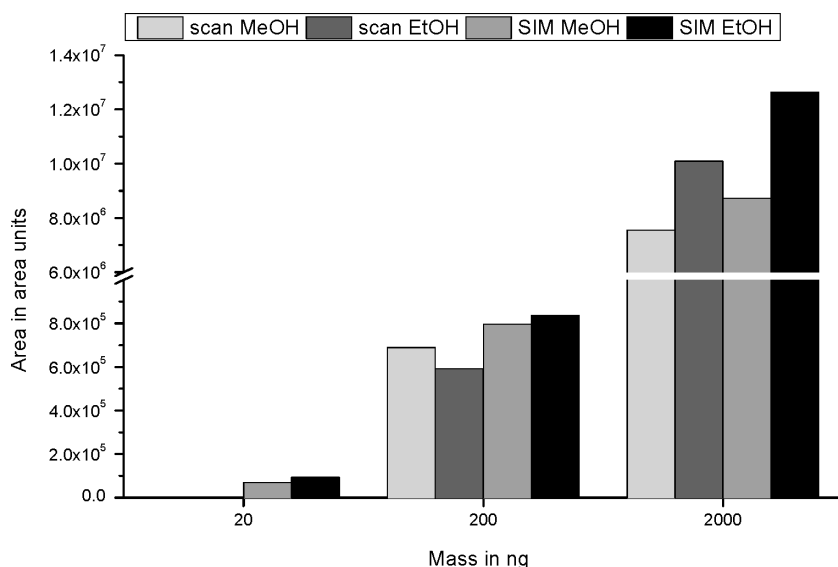


Figure 4. Comparison of scan and SIM for methanol and ethanol.

33.3% and level of error of 5% for the two substances methanol and ethanol on the FID system are summarized in Table 5. For both methanol and ethanol, the limits of detection and quantification obtained were much lower than the safety

Table 4. Estimated limits of detection (LOD) and limits of quantification (LOQ) for the MS system.

Compound	LOD in µg/m <sup>3</sup>	LOQ in µg/m <sup>3</sup>
MeOH	20	60
EtOH	20	60

Table 5. Limits of detection (LOD) and limits of quantification (LOQ) for the FID system.

Compound		LOD in µg/m <sup>3</sup>	LOQ in µg/m <sup>3</sup>
MeOH	1 l dry air	2	8
EtOH		2	9
MeOH	1 l wet air	3	15
EtOH		3	15

limits required by the German Research Foundation (MAK values). Comparison of detection and quantification limits of the FID with those of the MS (in SIM mode) shows that the FID system is much more sensitive (see Tables 4 and 5). The comparison also shows that the column used in the standard VOC analysis composed of 5% phenyl- and 95% methylpolysiloxane features much poorer chromatographic separation.

The impact of humidity on sensitivity is shown in Figure 5. For methanol and ethanol, a marked reduction of the peak areas is evident after blowing through 1 l of humid air compared to 1 l of dry air. However, for methanol the effect is greater by a factor of 3 and for ethanol by a factor of 2. The absolute standard deviation is similar for both variants, and therefore dependent on the measuring system.

#### 4.3 Recovery experiments in the 1 m<sup>3</sup> emission test chamber

The results for variants 1 and 2 are shown in Figure 6. Both variants provide good recovery rates for methanol and ethanol. In both experiment set-ups, the recovery rates for methanol are higher than the corresponding recovery rates for ethanol – 110% for variant 1 and 115% for variant 2 for methanol, and 92% for variant 1 and 102% for variant 2 for ethanol. In general, recovery rates for variant 2 are higher than those of variant 1. In addition, standard deviation of the results of variant 2 for methanol is not as high as in variant 1.

The fact that higher recovery rates can be achieved for variant 2 is surprising because a total of 2 l (1 l of humid air and 1 l of dry air) were passed over the tube in this variant. It was expected that the additional volume of air would cause small losses of methanol and ethanol. However, additional results from experiments carried out in parallel [11] confirmed the expectation – leaving the significantly improved chromatographic separation as the main cause.

By flushing the tubes with an additional litre of dry air, the water which had been adsorbed could be removed. This results in much narrower signal peaks (higher resolution) for methanol. This experiment also confirms the assumptions in Section 4.2. Because of the gaseous injection of the methanol, much less water sorbs on the sorbents. The interference from water is therefore less pronounced. Therefore, the gaseous injection (e.g. by a gas-collecting tube) is preferable over liquid injection [11]. One option for gas phase calibration is provided by a gas mixing system as developed by Richter et al. [12].

#### 4.4 SMP adhesive

The two test runs differed in the corresponding load *q* of the emission test chamber (Table 3). The comparison of the experimental results was made on the area-specific emission rates *SER<sub>A</sub>*. The methanol emissions measured in the first run were well above the calibration range in the first five days. In order to better investigate the emission behaviour in

the initial phase, another test run with a lower load followed, during which methanol quantification could be performed after only one day. The time-based progression of the area-specific emission rates is shown in **Figure 7**. Because the calibration range was exceeded, there is no data available for the higher loading (large plate) at the start of the measurement. A significant decrease of methanol emissions is apparent over the test period. The decrease features a drop which is typical for highly volatile compounds which have no sink effects. This also makes plain a major problem of VVOC analysis with respect to emissions. Due to the high vapour pressure, a rapid transition to the gas phase takes place, accompanied by high initial  $SER_A$ s which rapidly decreases in this case. To capture this pronounced dynamic, the analysis must be performed over a short period of time. This can be accomplished with the method developed.

## 5 Conclusion

The experiments show that methanol and ethanol can be quantified by thermal desorption using sorbents already available on the market. The sensitivity of a flame ionization detector is much higher than that of a single quadrupole instrument. However, the influence of humidity is problematic. Despite the hydrophobic properties of the sorbents, water bonded and impaired the chromatographic separation – which was alleviated by subsequently passing dry air through the sorbent. At  $15 \mu\text{g}/\text{m}^3$  the estimated limit of quantification for methanol is much lower than using previously developed methods, despite poorer chromatographic separation. In addition, the thermal desorption method requires much smaller sample volumes and a reduced workload. The investigations of the SMP adhesive in a  $1 \text{ m}^3$  emission test chamber gave first results of methanol emissions from these adhesives. Emission rates between 250 and  $1,200 \mu\text{g}/\text{m}^2\text{h}$  for methanol were determined after seven days.

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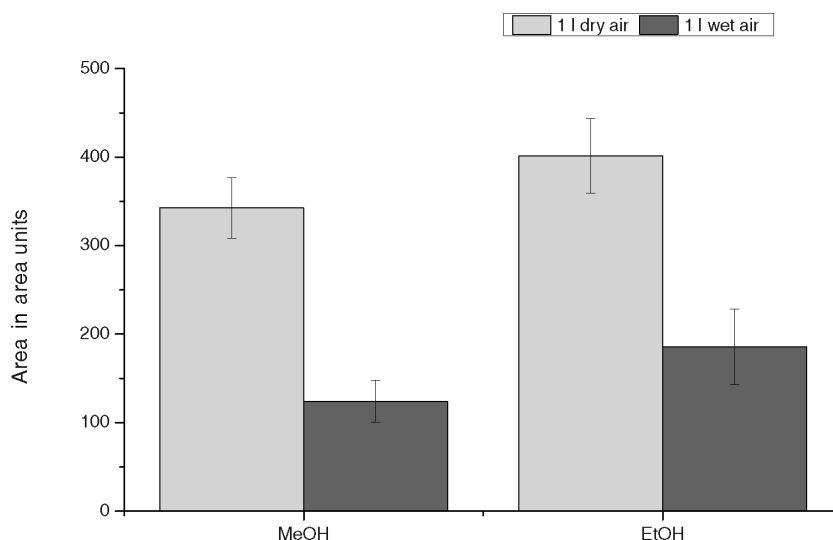


Figure 5. Comparison of blowing off by dry and wet air.

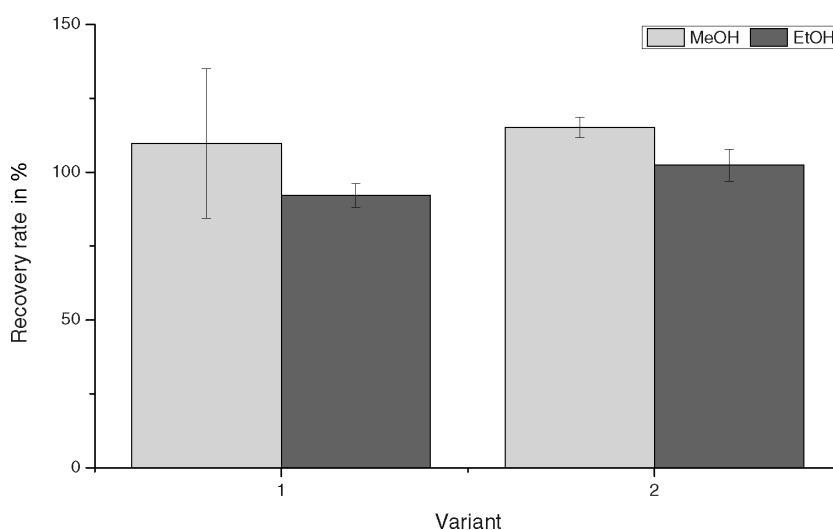


Figure 6. Recovery rates in the  $1 \text{ m}^3$  chamber.

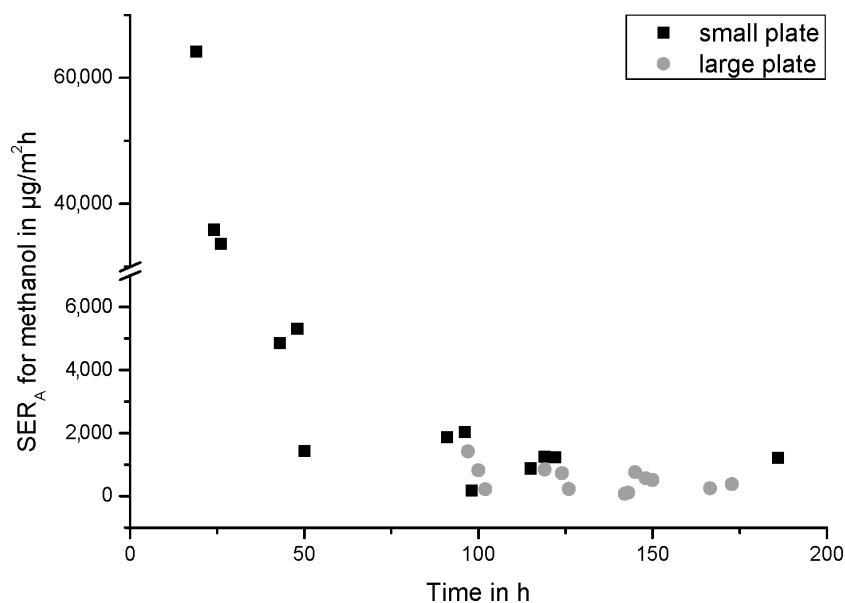


Figure 7.  $SER_A$  of methanol for the SMP adhesive as a function of time.

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