Outgassing of volatile compounds:

A comparison of measurement methods

Outgassing – Causes and consequences

'Outgassing' refers to the release of volatile, mostly organic substances (VOCs) from materials, such as phthalates, siloxanes or amines, which are often used as additives and plasticisers. Outgassing particularly affects plastics and adhesives, sealing materials or coatings. The outgassing substances can be chemically/physically bound as well as just trapped in the material. The release, usually due to thermal, chemical or physical stress can take the form of gas, particles or vapours. [1, 2, 3]

There are various outgassing mechanisms. During desorption, molecules that are physically bound to the surface are released. Another mechanism is the chemical decomposition and release of small molecules, for example from a polymer chain. Volatile materials can also reach the surface by diffusion from the inside of the matrix, determined by the diffusion coefficient. [4, 3]

Various factors influence outgassing. Higher temperatures accelerate reactions and diffusion, while a reduction in pressure promotes outgassing due to a higher pressure gradient. The choice of material and surface properties also have an influence. Porous and large surfaces can adsorb volatile molecules better. [5, 3]

Outgassing can impair the functionality of technical systems. Released substances can deposit on surfaces or cause surface damage. This can lead to malfunctions in the functionality of cameras or sensors, for example. The loss of additives can weaken material properties and favour premature ageing. Outgassing can also cause indoor air pollution or pressure increases in cleanrooms and vacuum atmospheres, thus negatively impacting product quality and productivity. In addition to the technical risks, outgassing also poses a health and environmental hazard. [1, 3]

Outgassing is critical in many areas: in space travel, the vacuum of space causes accelerated outgassing, which leads to damage to highly sensitive instruments. In semiconductor manufacturing technology, VOCs can deposit on surfaces. As at the production of semiconductors the size range of individual molecules is involved, the deposits lead to misprocessing and thus to the smallest surface defects, which disrupts functionality and reproducibility. In medical technology, outgassing substances must not be allowed to enter the body. In the automotive and construction industries, too, outgassing substances must be prevented from contaminating interiors and causing health risks. [1, 2, 6]

The use and development of low-emission materials is therefore crucial for the longevity and functionality of sensitive instruments as well as for safety. This requires precise measurements in accordance with established standards and guidelines. [4] There are various standards and methods that have their origins in specific industries, but are now often used across the board. We present the most important methods in the following comparison.

Comparison of important methods for outgassing assessment

The most common methods include VDA 278, derived from the automotive industry, ASTM E595, developed from the European Space Standards and ASTM D972 for lubricants. Another common method is residual gas analysis, which is not based on any standards.

VDA 278 [7]

VDA 278 is a standard developed by the German Association of the Automotive Industry for determining the proportion of condensable and non-condensable volatile substances from non-metallic materials. It is a standard test method for safeguarding the air quality in vehicle interiors.

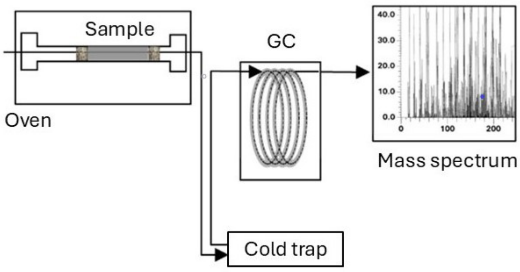

Figure 1: Device structure VDA 278. [7]

In accordance with VDA 278, a sample is heated in a desorption tube for a defined period of time. The volatile substances are carried by a carrier gas stream into a cold trap and collected. The cold trap is then heated up, the substances evaporate and are led to a gas chromatographic separation coupled to a mass spectrometer (GC-MS). To determine the VOC value, the tube is heated to 90°C for 30 minutes and again to 120°C for 60 minutes to determine the proportion of condensable substances (fog value, derived from *fogging*). Volatile condensable and non-condensable substances (if detectable) are quantified as individual substances.

ASTM E595 [8, 9]

ASTM E595 is a standard of the ASTM Committee on *Space Simulation and Applications of Space Technology*. It describes the measuring apparatus and the procedure for determining mass loss and analysing condensable and non-condensable volatile substances. Similar specifications can also be found from the E*uropean Cooperation for Space Standardisation (ECSS)* under ECSS-Q-ST-70-02C.

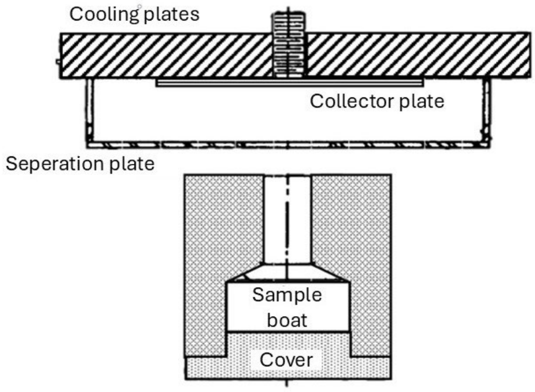

Figure 2: Device structure ASTM E595. [9]

The measuring device consists of several measuring chambers, each comprising a heated sample chamber and a collector chamber with a cooling and collector plate. The collector chambers are separated from each other by separation plates.

In accordance with ASTM E595, a sample is heated to 125 °C for 24 hours in a vacuum to release volatile substances. These are transferred to the collector chamber, where the condensable substances condense on the collector plate. This allows the proportion of *condensable volatile collective material (CVCM)* to be calculated. The *total mass loss (TML)* is also determined.

The *water vapour regained (WVR)* can then be determined by storing the previously measured sample for 24 h at 50 % humidity. In comparison according to ECSS-Q-ST-70-02C, the mass loss without the absorbed amount of water (*recovery mass loss, RML*) is determined by exposing the sample to a higher humidity of 65 %. Furthermore, the European Space Standards specify maximum values for materials with space applications.

RGA [10, 11]

Finally, it is also possible to determine the outgassing of a material by means of a residual gas analysis (RGA). There is no standard or guideline for this.

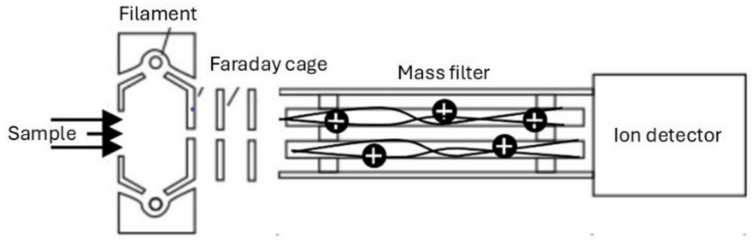

Figure 3: Device structure RGA. [10]

In this measurement method, the outgassing of a material is determined by ionising the released substances. A hot filament coil emits electrons, which knock electrons out of the material and form positive ions. These ions are separated by a mass filter according to their charge-to-mass ratio and channelled to the ion detector. A deep vacuum ensures an unhindered gas flow. The ion detector determines the ions and their fragmentation patterns, allowing the neutral substances to be identified. If the substance composition is known, calibration coefficients can be used to determine the relative composition. The detection limit is 3 ng/cm³.

ASTM D972 [12]

ASTM D972 defines the mass loss due to evaporation of lubricating oils and greases, and thus enables them to be evaluated for specific applications.

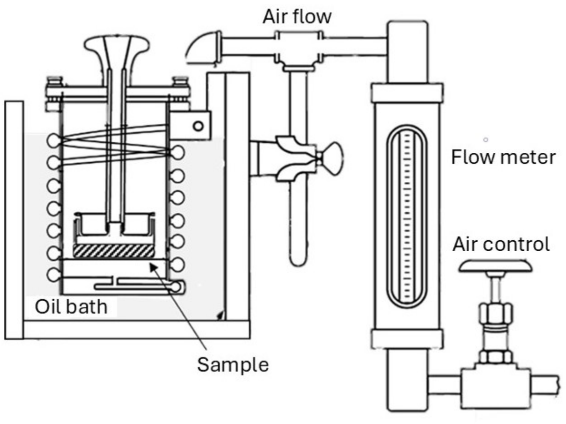

Figure 4: Device structure ASTM D972. [12]

For the measurement according to ASTM D972, a lubricant sample is exposed to a temperature of 100 - 150 °C for 22 hours. The substances outgassing from the sample are removed by a defined air flow. After the sample has cooled down, the mass difference is measured in order to determine the total proportion of volatile components. Further analysis of the vaporised substances is not planned as part of this measurement.

Comparison of outgassing detection methods [9, 7, 12, 8, 10, 11]

	VDA 273		ASTM D972	ASTM E595	RGA
	VOC	Fog			
Vacuum	x	x	X	$7 \cdot 10^{-5}$ mbar	Ultra-high vacuum
Temperature	90 °C	120 °C	100 °C – 150 °C	125 °C	x
Time	30 min	60 min	22 h	24 h	10 h (Vacom)
Measurement principle	Vaporisation due to increased temperature		Vaporisation through hot air flow	Vaporisation due to reduced pressure and high temperature	Vaporisation through ionisation
Determination	GC-MS		Gravimetric	Gravimetric	MS
Sample quantity	30 ± 5 mg		20 g	200 mg	x
Total mass loss	x		**Evaporation loss [%]:** $EL = \frac{m(S_I) - m(S_F)}{m(S_I)} \cdot 100$	**Total mass of outgassing material [%]:** $TML = \frac{m(S_I) - m(S_F)}{m(S_I)} \cdot 100$	x
Volatile, non-condensable substances	**VOC-Value (90°C) [µg/g]:** $VOC = R_{f,T} \cdot \frac{A(\text{Substance peak})}{1000 \cdot m_I}$		x	x	Hydrogen, fluorine components, hydrocarbons and carbon oxides
Volatile, condensable substances	**Fog-Value (120°C) [µg/g]:** $Fog = R_{f,\,HD} \cdot \frac{A(\text{Substance peak})}{1000 \cdot m_I}$		x	**Condensable portion of outgassing material [%]:** $CVCM = \frac{m(CP_F) - m(CP_I)}{m(S_I)} \cdot 100$	x
Further parameters	**Response factor from calibration [µg]:** $R_f = \frac{m\,(\text{Reference})}{A(\text{Substance peak})} \cdot 1 \cdot 10^6$		x	**Mass of water absorbed [%]:** $WVR = \frac{m(S_{F'}) - m(S_F)}{m(S_I)} \cdot 100$	H_2O

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