Volatile Compounds from Leather – Measurements and Characteristics

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Leather as interior material is a symbol of a high quality standard. One of this is low emission of volatile organic compounds (VOC). In automotiv industry the control of VOC-Emission from interiors began 20 years ago. In the meantime there are a lot of different emission test methods. The most important methods are VDA 270, VDA 275, VDA 277 and VDA 278. Further methods are based on these methods. Furthermore there are many emission chamber tests (e.g. VDA 276).

Each method is suitable to analyze characteristic substance groups. The VDA 275 analyzes formaldehyde and another aldehydes (e.g. Acetaldehyde) and ketones. The VDA 277 (static Headspace) analyzes the classic volatile organic compounds (C4 – C12). The result is a sum value in µgC/g. Calibration substance is Acetone. The VDA 278 (dynamic Headspace) analyzes the heavy volatile compunds. This method has two parts: the first run (VOC-Value) is 30 min at 90°C and a second run is 60min at 120°C (Fog-Value). Calibration substances are Toluol (VOC-Value) and Hexadecane-C16 (Fog-Value). One receives results in µg/g including a list of emitted substances. Fogging and smell tests are special tests with sum values or notes (see Table 1).

Table 1: Typical emission test results from leather

VDA 277	60 – 120 µg C/g
VDA 278 – VOC	200 – 800 µg/g
VDA 278 – Fog	400 – >4000 µg/g
VDA 275	n. n. – 20 mg/kg
Fogging – gravimetric	3 – 5 mg
Smell (VDA 270 – C3)	note 3-4 bis 4-5

Finished Leather content water (7-15%). This has a great importance on the analysis. The water disturbs the GC-analysis in VDA 277 and VDA 278. Bevor performing VDA 277 drying of leather (24h Calcium chloride) is necessary. The high water content of leather requires for VDA 278 a reduction of sample weight from 30 mg for plastic materials to 10 mg for leather.

Finished leather consists of collagen, tanning agents, fat liquors, colours and finish systems. Many years of intensiv working on emission analytics at th FILK-Institute shows that collagen, colours and tannig agents emit no significant quantities of volatile compounds. Only tanning agents containing formaldehyde (for example condensation products of formaldehyde with phenol) can lead to problems with the formaldehyde emission.

The fat liquors consist of high molecular compounds: modified natural oils and fats or synthetic products such polymer dispersions, modified fat alcohols and acids. This compounds lead to high fogging values. Modern fat liquors in the automotive industry have very high molecular weights with better fogging characteristics.

Modern finish systems for furniture and automotive leather are based on water. For good processing this systems contents substances such Glycol ethers, Triethylamine or NMP (N-Methylpyrolidone). Table 2 shows the characteristic volatile compounds from finished

leather. Table 3 shows which finished leather component determines the emission test results from the different methods.

Table 2: Volatile Compounds from Finished Leather

Finish Systems	N–Methylpyrrolidone (NMP), Triethylamine, Glycol ether (z.B. 1-Methoxy-2-propanol, Butylglycol, Butyldiglycol, Dipropylenglycolmethylether, Dipropylenglycoldimethylether, 2-(2-Ethoxyethoxy)ethanol, 1-Methoxy-2-propylacetate (MPA),
Acid Regulators	Formic acid, Acetic acid
Stabilisators, Fungizides	Chlor-m-cresol (CMK), o-Phenylphenol (OPP), 2-(Thiocyanomethylthio)-benzothiazol (TCMTB), 2-Octyl-2H-isothiazol-3-on (OIT(Z)), Butylated Hydroxytoluene (BHT), dimeric BHT
Fat liqours	linear and branched Alkanes (C12-C26), Alkylbenzens (C9-C11), linear and branched fat alkoholes (C12-C20), fat acids and fat acid esters, Chloralkanes, saturated and unsaturated Aldehydes (C1-C12, e.g. Formaldehyde, Hexanal, Nonanal), Alkylfuranes, Chlorparaffines, Adipic acid esters
Specials	Siloxanes (Trimethylsilanol), aromatic compounds in fat liqours

Table 3: Determination of Emission Test Results through Finished Leather Components

Component	**VDA 277** ***Static Headspace***	**VDA 278** ***Dynamic HeadspaceThermodesorption***	**VDA 275** ***Formaldehyde***	**Fogging**	**VDA 270 Smell**
Collagen	-	-	-	-	-
Tanning Agents	+	+	+++	++	+++
Fat Liquors	+++	++++	-	++++	+++
Colours	-	-	-	-	-
Finish System	+++	++	+	++	+

- no influence, + - very weak influence, ++ - weak influence, +++ - strong influence, ++++ - very strong influence

The different emission test methods analyze different substance groups. Figure 1 shows a comparison of chromatogramms from VDA 278, VDA 277 and an emission chamber test. The VDA 278 analyze primarily the high volatile compounds from the fat liqour and stabilisator systems. This compounds are parts of this systems (e.g. dimeric BHT, Adipic acid esters, see table 2) or degrated products from the fats and oils (e.g. fat acids and esters). The VDA 277 analyze the volatile compounds from the finish system and low moleculare degretad compounds of fat liquors (e.g. Aldehydes and Alkylfuranes). Aldehydes and alkylfuranes are oxidation products of unsaturated compounds in the fat liqours such oleic acid derivates.

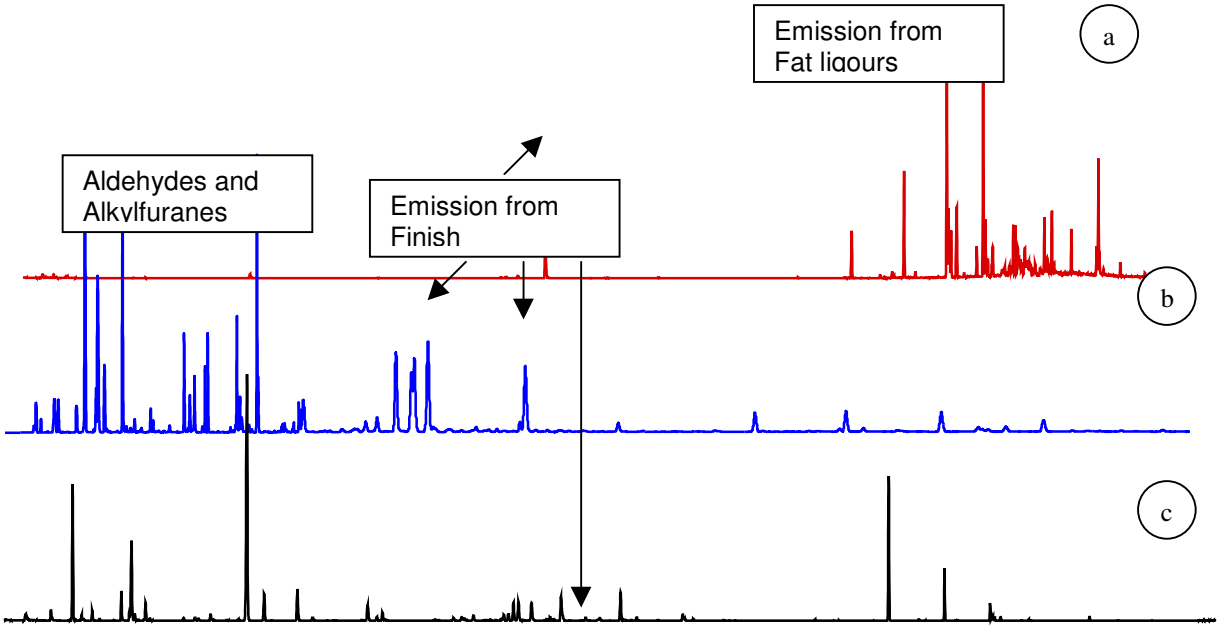

Figure 1: Comparison Chromatograms VDA 278 (a) – VDA 277 (b) – Emission Chamber (c) from a finished leather

Leather is an inhomogenous and porous material and a good adsorbent. Leather adsorbs compounds by the gaseous phase and by direct material contact during the storage with another materials. If the adsorbates bonding (e.g. Formaldehyde, Nonylphenols) to collagen matrix from leather then the desorption becomes decreased. In this case one can analyzes the adsorbates by emission tests for a long time (many months). Normal organic solvents desorb in short time (some days) but small contents can be analyzed still longer time.