CLEANROOM SUITABLE MATERIALS

The Fraunhofer IPA Industrial alliance „CSM“

Outgassing measurements - VDI 2083-17

Cleanroom® Suitable Materials

Tokyo, December 6th, 2011

Dipl.- Biol. (t.o.) Markus Keller

Fraunhofer Institute for Manufacturing Engineering and Automation IPA

Dept. Ultraclean Technology and Micromanufacturing

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Outline of the presentation

- Motivation; initial situation
- Limits and practical example
- Material outgassing method description: guideline VDI 2083-17 (draft)
  - Sample preparation and storage
  - VOC emission measurements
  - Surface-related material specific emission rate SER_m
  - Material classification in AMC_m(or)-classes
  - Calculation model for real production scenarios
- CSM-alliance and TESTED DEVICE: databases for cleanroom certified materials and equipment

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Motivation, initial situation

What means Airborne molecular contamination (AMC):

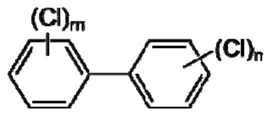
- Definition according to ISO 14644-8 (»classification of airborne molecular contamination«):

  »***presence in the atmosphere of a cleanroom*** *or controlled environment of molecular (chemical, non-particulate)* ***substances in the gaseous or vapour state*** *that may have a deleterious effect on the product, process or equipment in the cleanroom or controlled environment*«

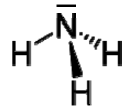
Examples for AMC:

- Acids (ac)
- Bases (ba)
- Biotoxin (bt)
- Condensable contaminants (cd)
- Corrosive contaminants (cr)
- **<u>Organic contaminants, VOC (or)</u>**
- Dopants (dp)

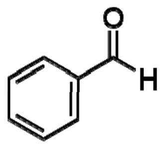
Hydrogen chloride (ac)



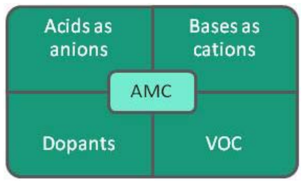
Polychlorinated biphenyles (bt)



Ammonia (ba)



Benzaldehyde (or)



(Gail, 2002)

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Motivation, initial situation

- For specific processes, an AMC-controlled environment is necessary → cleanroom technology: ISO 14644- and VDI 2083-series

ISO-AMC-Classification according to ISO 14644-8:

- Present AMC-Concentrations in a (clean)room can be determined by specific measurement techniques
- ISO-AMC-Classification based on the measured concentration [g/m³]
- Example: ISO-AMC (or) = -5,5

ISO-AMC Class	Concentration in g/m³
0	10^{0}
-1	10^{-1}
-2	10^{-2}
-3	10^{-3}
-4	10^{-4}
-5	10^{-5}
-6	10^{-6}
-7	10^{-7}
-8	10^{-8}
-9	10^{-9}
-10	10^{-10}
-11	10^{-11}
-12	10^{-12}

ISO-AMC-classes acc. to ISO 14644-8

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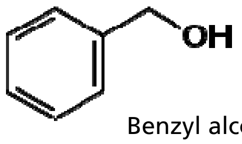
Motivation, initial situation

What means VOC?

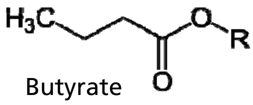
- **VOC:** Volatile Organic Compounds – Examples :

Why can some VOCs be critical for specific processes?

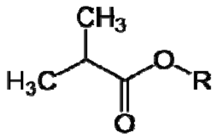
- Toxic (dioxin, PCBs,..)
- Harmful for processes (Semiconductor: Fogging on lenses,…electronic: contact failure,…)
- Harmful for products (Semiconductor: wrong doping by accident,…Life-Science: migration into the product,…)



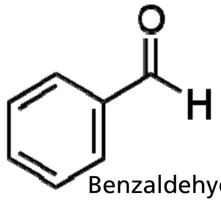
Benzyl alcohole



Butyrate



Iso-butyrate

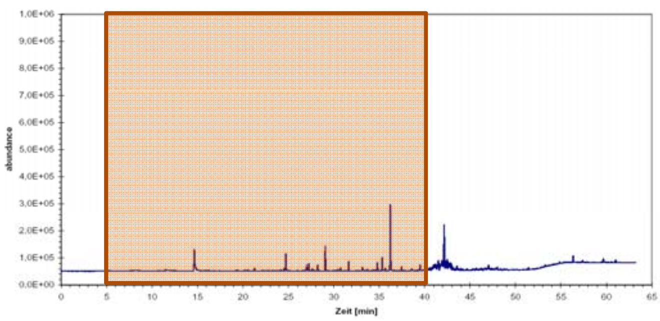


Benzaldehyde

Motivation, initial situation

What means TVOC?

- **TVOC** (definition acc. to ISO 16000-6): Sum of all volatile organic (CH-) compounds in the retention range between 6 (n-hexane) and 16 (n-hexadecane) C-atoms
- Using Gaschromatographic conditions according to VDA 278:
  - n-hexane: RT = 5,95 min
  - n-hexadecane: RT = 40.00 min



Motivation, initial situation

- Problem: There is no general method for the **classification of cleanroom materials regarding their outgassing properties.**
- Motivation: VDI 2083-17 (draft): Compatibility with required ISO-AMC-cleanliness classes (according to ISO 14644-8)

VEREIN DEUTSCHER INGENIEURE	Reinraumtechnik „Reinraumtechnik – Reinraum- und Reinheitstauglichkeit von Werkstoffen“	VDI 2083 Blatt 17

Cleanroom technology – Compatibility with required cleanliness class and surface cleanliness

Ingenieure, Düsseldorf 2008

Inhalt Seite

Limits

- IRTS Roadmap 2009-2024

Year of Production	2009	2010	2011	2012	2013	2014	2015	2016	2017	2018	2019	2020	2021	2022	2023	2024
Flash 1/2 pitch [nm]	38	32	28	25	23	20	18	15,9	14,2	12,6	11,3	10,0	8,9	8,0	7,1	6,3
AMC in Gas Phase [pptV]																
Lithography clean room																
Condensable Organics (w/GCMS retention times >benzene, calibrated to hexadecane)	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000	26000
Organics containing ex. S, P, Si)	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
Gate/furnace area Wafer																
Dopants	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10

- Reference: Hexadecan; MW = 226 g/mol
- TVOC = 26000 ppt: equals ISO-AMC class -3,6 (or)
- Critical contaminants = 100 ppt: equals ISO-AMC class -6,0 (or)
- Remark: It is assumed, that the cleanroom air supply is VOC-filtered
- TVOC payload influences the interval for active charcoal filter regeneration

Source: IRTS Roadmap 2010

Limits

- IRTS Roadmap 2003-2009

Year of Production	*2003*	*2004*	*2005*	*2006*	*2007*	*2008*	*2009*
Airborne Molecular Contaminants in gas phase (pptM) [C] [H] [R]							
Lithography—bases (as amine, amide, and NH_3)	750	750	750	<750	<750	<750	<750
Gate—metals (as Cu, $E=2\times10^{-5}$) [I]	0.15	0.1	0.1	0.07	<0.07	<0.07	<0.07
Gate—organics (as molecular weight to 250, $E=1\times10^{-3}$) [D]	80	70	60	60	50	50	50
Organics (molecular weight to C_7H_{16}) normalized to hexadecane ($C_{16}H_{34}$) equivalent	5000	4500	4000	3500	3000	3000	<2500
Salicidation contact—acids (as Cl–, $E=1\times10^{-5}$)	10	10	10	<10	<10	<10	<10
Salicidation contact—bases (as NH_3, $E=1\times10^{-6}$)	12	10	8	4	<4	<4	<4
Dopants [E]	<10	<10	<10	<10	<10	<10	<10

- VOC filtration efficacy of >90 % explains the higher values starting 2010, see IRTS Roadmap 2010-2024

Source: IRTS Roadmap 2003

Example: Waferprocessing und TDH

- Time dependend haze (TDH) as contamination onto silicone wafers. TDH is mainly caused by cleanroom atmosphere.
- Example: Wafer stored for 4 months in atmosphere enriched with acetone: Increase of LLS (localized light scatters) by the factor of 15000!

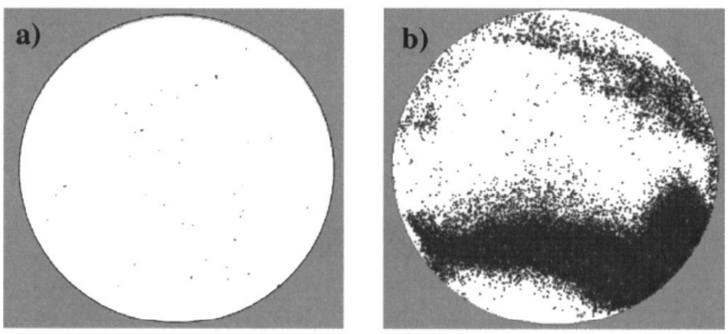


Figure 3. (a) Laser light scattering image of a SC-1-cleaned wafer. (b) Laser light scattering image of the same wafer after four months of storage in a gas atmosphere containing acetone at room temperature. The increase in LLS counts in the range from 0.12 to 0.24 µm is about 15.000.

N. Münter, W. Storm, T. Müller, B. O. Kolbesen "Analysis of Time-Dependent Haze on Silicon Surfaces" Journal of The Electrochemical Society, **150**(3) G192-G197 (2003)

Example: Waferprocessing und TDH

- Formation of TDH:

- Smaller agglomerates can reorganize to larger particles
- REM-EDX shows presence of elements S, N and O

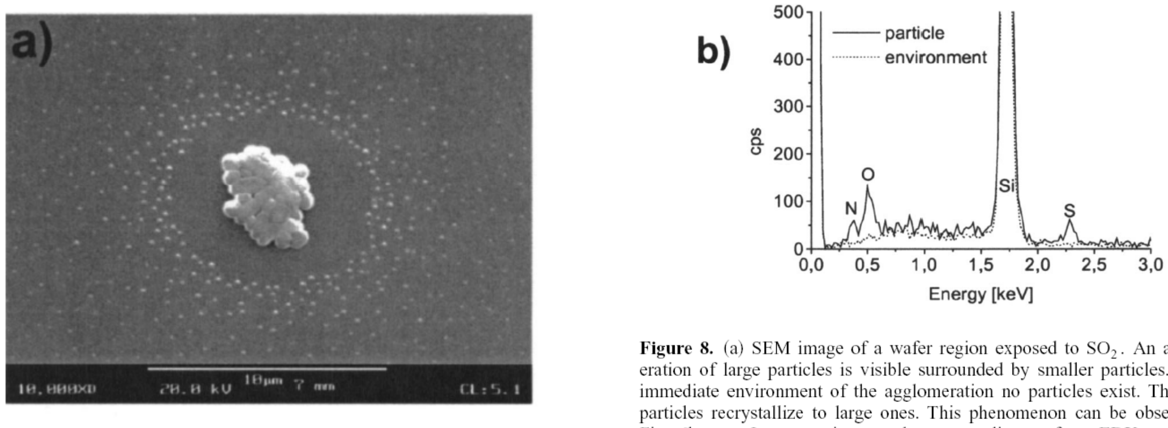
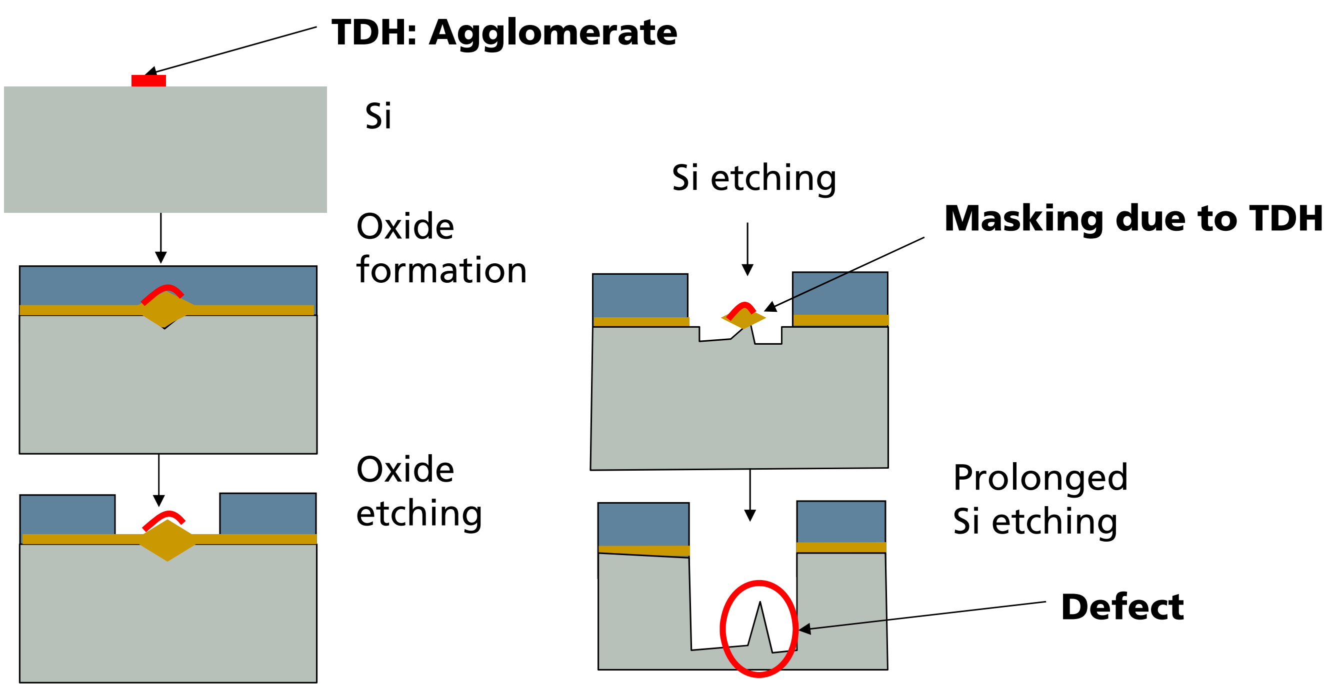


Figure 8. (a) SEM image of a wafer region exposed to SO_2. An agglomeration of large particles is visible surrounded by smaller particles. At the immediate environment of the agglomeration no particles exist. The small particles recrystallize to large ones. This phenomenon can be observed in Fig. 6b, too. In comparison to the surrounding surface, EDX spectra of particles indicate the elements sulfur, nitrogen, and oxygen (b).

N. Münter, W. Storm, T. Müller, B. O. Kolbesen "Analysis of Time-Dependent Haze on Silicon Surfaces" Journal of The Electrochemical Society, **150**(3) G192-G197 (2003)

Example: Waferprocessing und TDH – Possible defects



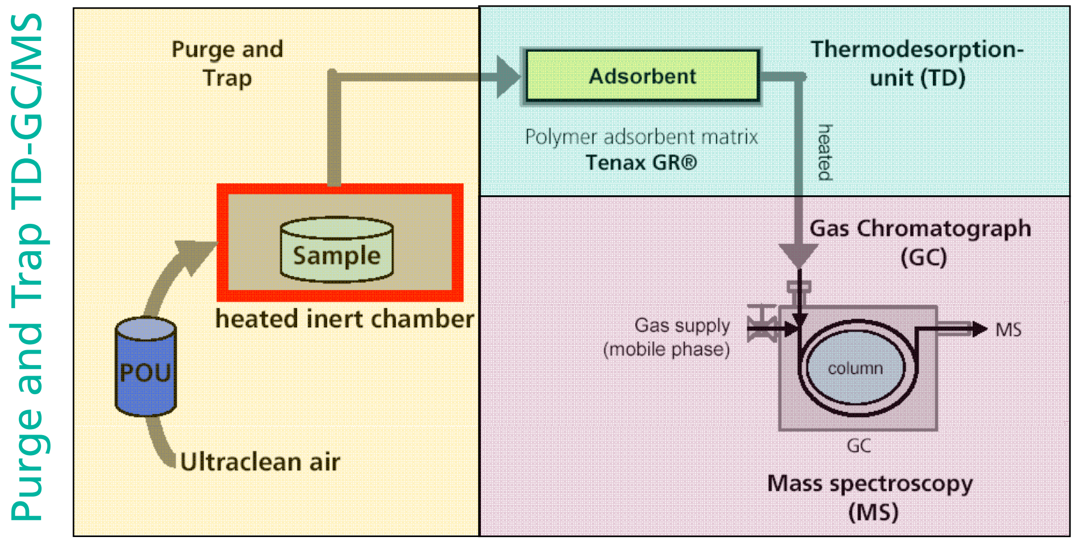
Source: Gregor Reeske, Georg Hohl, Klaus Schober und Robert Brause: KONTAMINATIONEN AUS DER REINRAUMLUFT UND IHR EINFLUSS AUF SILIZIUMWAFER BEISPIEL: TIME DEPENDENT HAZE; Process Technology, Engineering, Metrology, Siltronic AG, 2011.

Fundamentals in VOC-measurements
– General aspects

- Outgassing from materials is a **surface phenomenon.**
- There are **controlled environmental conditions** in the regarded surroundings (ex. temperature = 23 °C and rel. humidity = 45 %).
- Knowing the **specific material emission rate SER** [g/m²s], a statement about the emission properties of the tested material can be given.
- The SER is dependent on the **age of the material.**
- Knowing the SER, the age and the proportionate surface area of the material, its **theoreic ISO-AMC$_m$(or)-class** can be calculated.
- For a **qualitative statement about the presence of critical contaminants** (Semiconductor: phthalates, siloxanes, amines, organophosphates) the material sample is heated for total outgassing analysis at **90 °C.**

Fundamentals in VOC-measurements
– Emission chamber measurements by TD-GC/MS

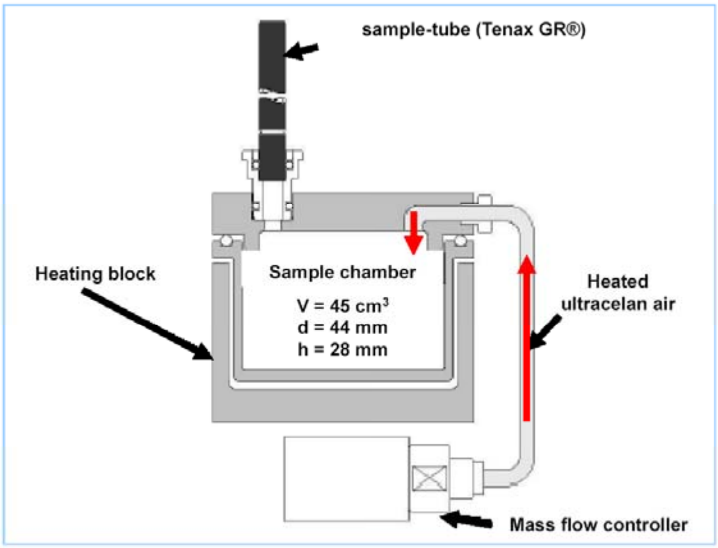
- Purge and Trap TD-GC/MS:
  Thermo desorption coupled with gas chromatography and mass spectrometer, emission chamber and adsorbent tubes:



Fundamentals in VOC-measurements
– Technical implementation of the chamber measurements

Requirements

- No temperature sinks
- No dead spaces
- Simple chamber cleaning
- Very good recovery rate
- Small sample chamber volume results in a high gas exchange rate



Source: MARKES International

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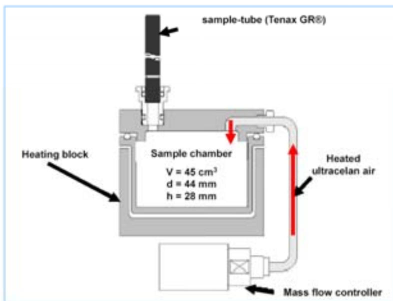
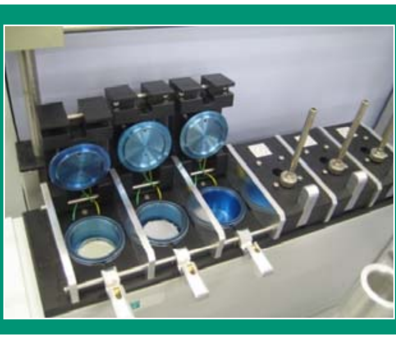
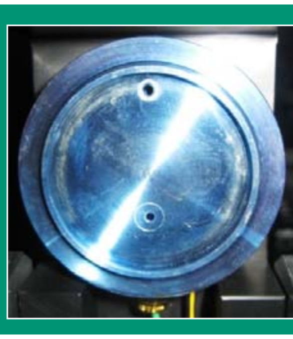
Fundamentals in VOC-measurements
– Technical implementation of the chamber measurements

Solution

- No temperature sinks: whole chamber is heated
- Simple “VOC-cleaning” by heat (120 °C)
- Small chamber volume: empty approx. V = 45 cm^3
- Solution: µCTE micro-chamber from MARKES International







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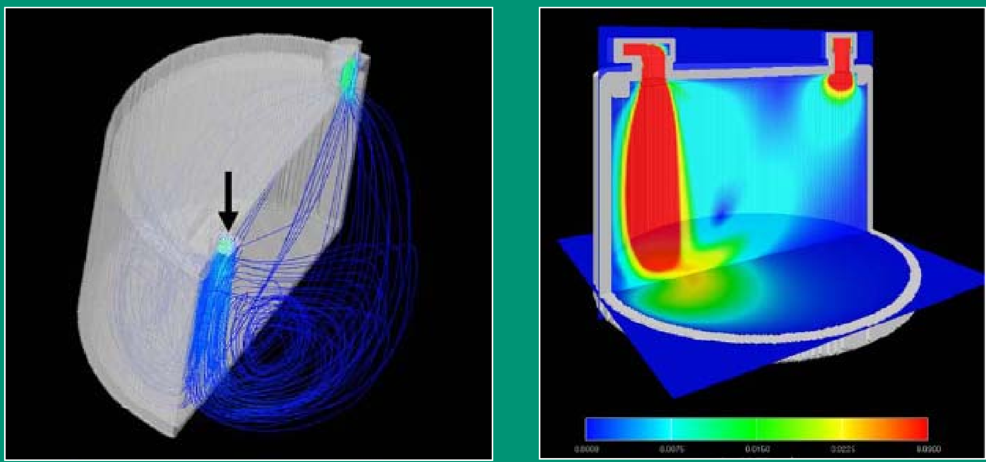
Fundamentals in VOC-measurements
– Technical implementation of the chamber measurements

No dead spaces: optimized airflow design

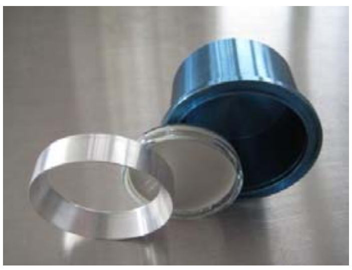


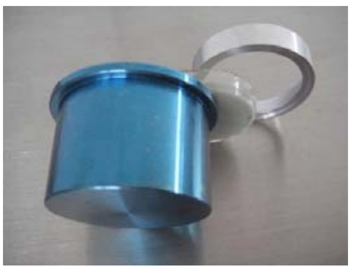
Source: MARKES International

Sample preparation and -storage
– Technical implementation

No open cutting edges: aluminum ring to cover potential **cutting edges** or standardized borosilicate glass Petri dish for **reactive samples**

- Reactive samples (Epoxy, Sealants, paint, …) are stored in a VOC-filtered minienvironment for 30 days after preparation (23 °C und 45 % rel. humidity)





Sample preparation and -storage
– Preparation of the samples

Preferred Sample holder (as applicable):

- borosilicate glass Petri dish (inert)
- Cleaning with Isopropanole and baking out at 250 °C for several hours

Diameter: d = 35,7 mm   Surface: A = 10 cm^2
Height: h = 7 mm   Max. Volume: V = 7 cm^3

Sample preparation and -storage
– Preparation of the samples

- Liquids are dosed at 4 ml in the glass petri dish.
- Cut goods are placed with the aluminum sample ring into the emission chamber

Sample preparation and -storage
– Measurement parameter: CSM-Standard

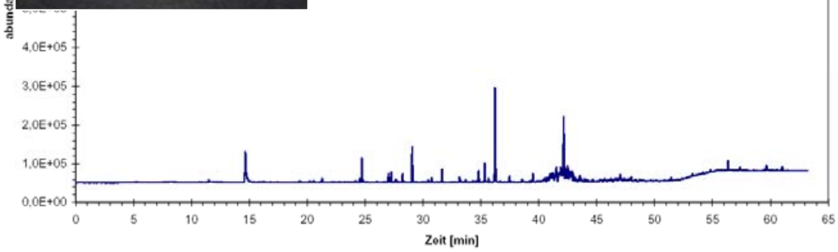
Set of parameters:

Parameter	23 °C	90 °C
Purge time	60 min	10 min
Purge gas flow (fix)	100 ml/min	
Surface (fix)	10 cm^2	
Microchamber volume (fix)	45 cm^3	
Measurement start after sample transfer into chamber (fix)	15 min	
Age of reactive samples after preparation at start of measurement (fix)	30 days	

The measurement at 90 °C is not used for later classification and gives only a qualitative information about the precence of critical contaminants.

Results of the TD-GC/MS measurements
Example: representative material sample at 23 °C

Through TD-GC/MS-analysis determined mass of organic contamination: (TVOC): $m_{TVOC} = 306$ ng



	CAS-No.	RT	Value
)		[min]	Mass [ng]
	111-71-7	24,54	4
C6)	111-76-2	24,72	25
	108-95-2	27,24	11
	124-13-0	28,23	8
	104-76-7	29,07	34
	124-19-6	31,64	12
	112-31-2	34,8	11
panon	621-87-4	35,21	17
1 164)		35,65	4
n-2-ol	770-35-4	36,21	88
n-1-ol	4169-04-4	36,28	12
	629-50-5	37,48	5
)	112-42-5	39,49	8
1-Dodecanol (C11)	112-53-8	42,14	67
		Total	**306**

Material classification acc. to VDI 2083-17 (draft)

Example: representative material sample at 23 °C

A_m = 0,001 m²
t = 60 min
m_{TVOC} = 306 ng

A = 0,001 m²
t = 1 s
m_{TVOC} = 0,085 ng

A = 1 m²
t = 1 s
SER_m = 8,5 * 10^{-8} g/m²s

$$SER_m = \frac{m_{TVOC}}{A_m \cdot t}$$

Hereby applied:
SER_m = surface specific material emission rate at room temperature 22 +/- 1 °C in g/(m²•s)
m_{TVOC} = mass of the total volatile organic contamination of the material sample in g
A_m = surface of the material sample m in m²
t = duration of the sampling in s

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Material classification acc. to VDI 2083-17 (draft)

Example: representative material sample at 23 °C

The material classification in **AMC_m(or)-classes** is done by using the value $TVOC_{norm}$ based on the ISO-AMC classes according to ISO 14644-8:

$$TVOC_{norm} = \frac{SER_m \cdot A_{norm}}{V_{norm} \cdot n_{norm}}$$

Hereby applied (see also previous slides):
V_{norm} = standardized theoretical chamber volume of 1 m³
A_{norm} = standardized material surface area of 1 m²
n_{norm} = standardized purge gas flow of1/s
$TVOC_{norm}$ = standardized TVOC in g/m³

$$AMC_m(or) = \log(TVOC_{norm})$$

SER_m = 8,5 * 10^{-8} g/m²s
↓
$TVOC_{norm}$ = 8,5 * 10^{-8} g/m³
↓
AMC_m (or) = -7,1

ISO-AMC Class	Concentration in g/m³
0	10^{0}
-1	10^{-1}
-2	10^{-2}
-3	10^{-3}
-4	10^{-4}
-5	10^{-5}
-6	10^{-6}
-7	10^{-7}
-8	10^{-8}
-9	10^{-9}
-10	10^{-10}
-11	10^{-11}
-12	10^{-12}

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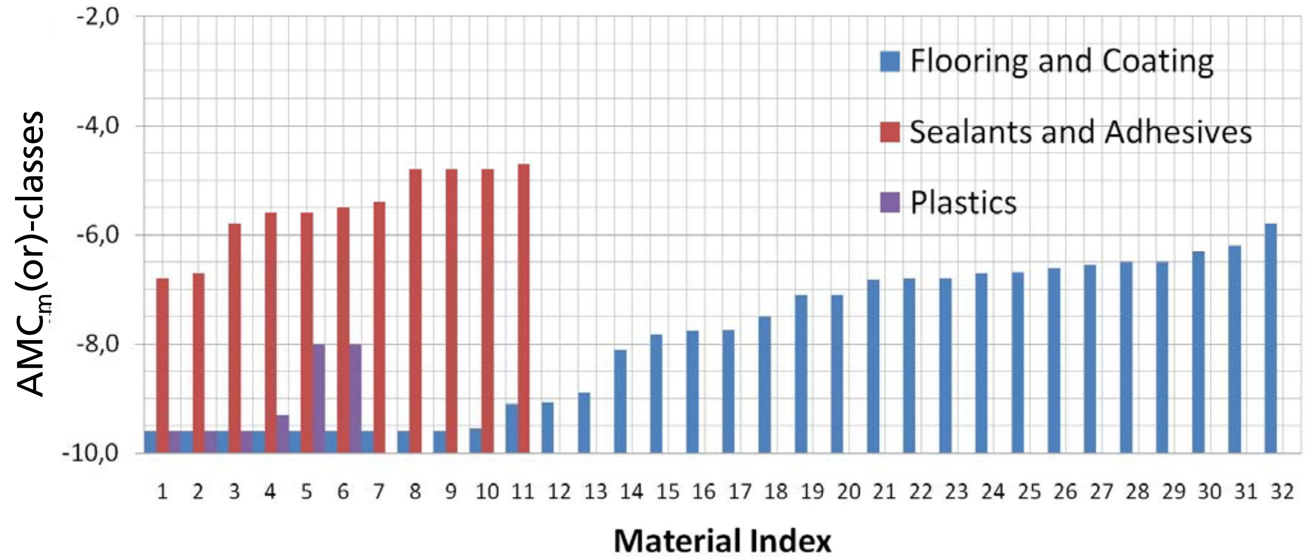
Material classification acc. to VDI 2083-17 (draft)

Comparable material classifications



Conversion of the material-specific ISO-AMC$_m$-class into the ISO-AMC$_{CR}$-class of real cavities (clean rooms etc.)

The proportionate material surface area and materials with a high TVOC emission play the major relevance regarding the SER$_m$-values for the ISO-AMC-class assessment. Most notably relevant are:

Large surface areas

- Flooring systems
- Wall
- Ceiling (filter systems)
- Air conditioning technology

Possible high TVOC-sources:

- Sealants
- Adhesives
- ...

Conversion of the material-specific AMC_m-class into the ISO-AMC-class of real cavities (clean rooms etc.)

Regarding all relevant VOC-emitting materials in a clean room (CR), the resulting ISO-AMC_{CR}-class in the cavity can be calculated as follows:

$$TVOC_{CR} = \frac{\sum (SER_m \cdot A_{CR})}{V_{CR} \cdot n_{CR}}$$

$$n_{CR} = LWR_{CR} \cdot FLA_{CR}$$

Hereby applied (see also previous slides):

$TVOC_{CR}$ = calculated TVOC of all relevant VOC-emitting materials in g/m^3
A_{CR} = material surface area in m^2
V_{CR} = clean room volume in m^3
n_{CR} = VOC-free air exchange rate in 1/s
LWR_{CR} = total air exchange rate in 1/s
FLA_{CR} = fraction of VOC-free fresh air supplied to the total air exchange rate
assumption: VOC-free air supply

$TVOC_{CR} = 5{,}7 \cdot 10^{-4} g/m^3$

↓

ISO-AMC (or) = -5,7

Example values:
A_{CR} = 100 m^2
V_{CR} = 300 m^3
LWR_{CR} = 0,15 1/s
FLA_{CR} = 0,1
n_{CR} = 0,015 1/s

ISO-AMC Class	Concentration in g/m³
0	10^{0}
-1	10^{-1}
-2	10^{-2}
-3	10^{-3}
-4	10^{-4}
-5	10^{-5}
-6	10^{-6}
-7	10^{-7}
-8	10^{-8}
-9	10^{-9}
-10	10^{-10}
-11	10^{-11}
-12	10^{-12}

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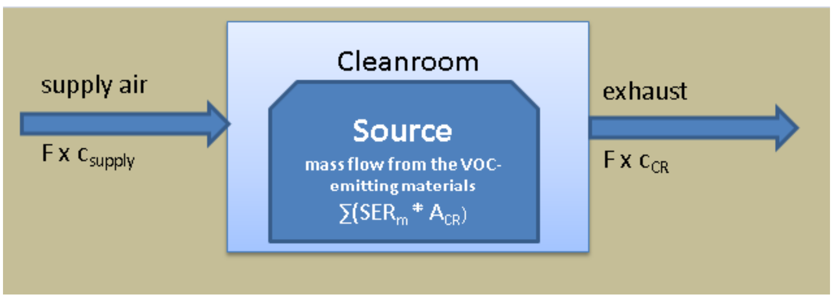
Conversion of the material-specific AMC_m-class into the ISO-AMC-class of real cavities (clean rooms etc.)

Theoretic background: mass flow equilibrum at the stationary phase:

$$0 = \text{source} + \text{supply air} - \text{exhaust air}$$
$$0 = \sum(SER_m \bullet A_{CR}) + F \bullet c_{supply} - F \bullet c_{CR}$$
$$F \bullet (c_{CR} - c_{supply}) = \sum(SER_m \bullet A_{CR})$$
$$c_{CR} - c_{supply} = \sum(SER_m \bullet A_{CR}) / F$$
$$\mathbf{c_{CR} = [\sum(SER_m \bullet A_{CR}) / F] + c_{supply}}$$

Hereby applied (see also previous slides):
C_{supply} = TVOC-value of the supply air in g/m^3
F = VOC-free air exchange rate in 1/s (F = V/n)
c_{CR} = $TVOC_{CR}$-value of the cavity in g/m^3



Remark:
For the determination of the total mass flow of the source $\sum(SER_m \bullet A_{CR})$, the single mass flows from all relevant materials $SER_{m1} \bullet A_{CR1}$; $SER_{m2} \bullet A_{CR2}$;… have to be summed-up.

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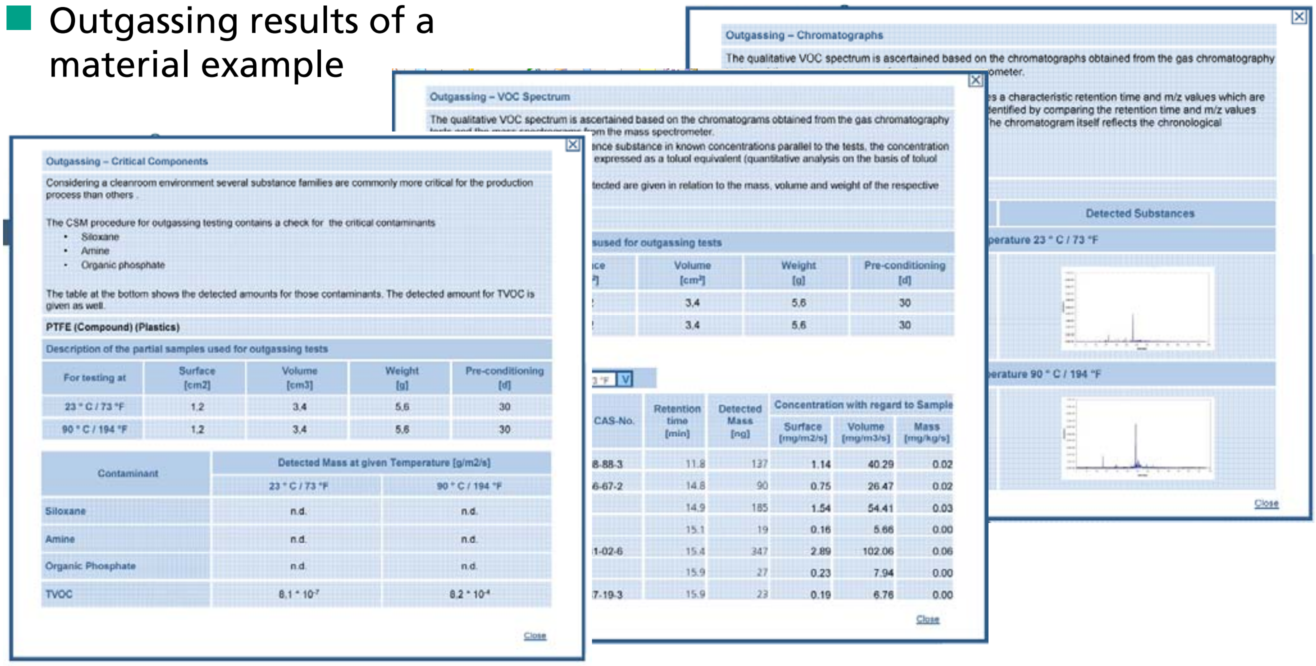
CSM-industrial alliance www.ipa-csm.com

Exclusive database for materials

- Outgassing results of a material example



Summary

- The guideline VDI 2083-17 (draft) allows standardized material classification regarding VOC emissions by:
  - Correct sample preparation and –storage
  - VOC-sampling using micro-chambers
  - Analysis using TD-GC/MS
  - AMC_m (or) material classification using the measured material specific emission rate SER_m
- Possible assessment of ISO-AMC (or)-level of real cavities
- All measurements can be done at the Fraunhofer IPA and implemented in the database www.ipa-csm.com
- Fraunhofer IPA conducts on-site VOC and TVOC-measurements

Contact Information

Fraunhofer Institute for Manufacturing Engineering and Automation IPA
Ultraclean Technology and Micromanufacturing

Head of Department
Dr. Udo Gommel | Phone +49 711 970-1633 | udo.gommel@ipa.fraunhofer.de

Project Manager
Markus Keller | Phone +49 711 970-1560 | markus.keller@ipa.fraunhofer.de

ADDRESS:
Nobelstr. 12, 70569 Stuttgart, Germany

INTERNET:
www.ipa.fraunhofer.de/cleanroom
www.ipa-qualification.com
www.tested-device.de