CHEMICAL ENGINEERING TRANSACTIONS

VOL. 30, 2012

Guest Editor: Renato Del Rosso
Copyright © 2012, AIDIC Servizi S.r.l.,
ISBN 978-88-95608-21-1; **ISSN** 1974-9791

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at: www.aidic.it/cet

DOI: 10.3303/CET1230051

Test Procedure to Determine Material Specific VOC Emission Rates and Prediction Model of VOC-levels in Controlled Production Environments

Markus Keller*[a], Udo Gommel[a], Alexander Verl[a]

[a]Fraunhofer Institute for Manufacturing Engineering and Automation IPA, 70569 Stuttgart, Germany
markus.keller@ipa.fraunhofer.de

Volatile organic compounds (VOC) are an increasing concern in contamination-sensitive manufacturing sites. For the assessment and classification of VOC emissions from building products, a standardized fast screening procedure for classifying materials regarding VOC outgassing is developed to permit specific reduction of indoor airborne molecular contamination. It describes sample preparation and storage prior sampling followed by micro-chamber sampling and analysis via thermodesorption coupled with gas chromatography and mass spectrometry (TD-GC/MS). Knowing the active surface area, sampling time and emitted VOC mass measured, the material specific surface emission rate SER_a and classification number can be determined. The standardized method allows a faster material screening compared to existing large chamber measurement methods. Material screening results are entered into the database www.ipa-csm.com to allow the tested products to be directly compared with one another. Therefore, a material selection already in the planning phase of a controlled environment becomes possible. Based on SER_a values, an experimental proven simulation model enables the calculation of the expected ISO-AMC-class of the controlled environment to be constructed according to ISO 14644-8.

1. Introduction

Airborne molecular contamination (AMC) is defined as the presence in the atmosphere of a controlled environment of molecular substances in the gaseous or vapour state that may have a deleterious effect on the product, process or equipment. Toxicity or odour effects are not considered (ISO, 2006b). AMC can be categorized in the following substance groups: acids, bases, biotoxins, condensable contaminants, corrosive contaminants, dopants and VOC (JACA, 2003). A definition of VOC is given in ISO 16000-6 (ISO, 2006a). Emissions from building materials play a major role regarding the amount of VOC in a controlled environment regarding risk for the process or material (Bürgler et al., 2001). VOC can induce various damage scenarios. The lifetime of lithographic masks in semiconductor settings is shortened dramatically if VOC deposition occurs (Peters et al., 2007; Johnstone et al., 2003). Critical VOC compounds include siloxanes, phthalates, amines, ammonia, acids, organophosphates and doping materials (Shiramizu, 2010). Several studies demonstrated the VOC emission potential from building materials (De Bortoli et al., 1999; Yu and Kim, 2010). Sensitive manufacturing environments require a controlled low level of VOC in the ambient air. To reduce unwanted airborne VOC, cost-intensive technologies can be applied (Kennes and Veiga, 2010). Alternatively, low-VOC emitting building materials can be used (Keller and Gommel, 2012a). For material selection, laborious large scale test methods are already established (Umweltbundesamt,

Please cite this article as: Keller M., Gommel U. and Verl A., 2012, Test procedure to determine material specific voc emission rates and prediction model of voc-levels in controlled production environments, Chemical Engineering Transactions, 30, 301-306
DOI: 10.3303/CET1230051

2010). Different VOC labeling systems regarding VOC-emissions from building materials are developed (Maronai and Lundgren, 1998) but lack in comparable classification, harmonization and suitability for the selection of low VOC emission materials. Using different emission chamber geometries, a variation of the results of up to 60 % is reported (De Bortoli et al., 1999). Variations in air exchange rate can lead to different results (EC, 1991; Knudsen et al., 1999). Therefore, there is a need for an easy-to-use standardized method with a comparable classification system only focusing on process-critical contaminations, such as VOC. Established emission chamber methods are cost- and time consuming and therefore not useful for a fast material screening (ISO, 2006c). Several authors report a cost-effective micro chamber which fulfills the defined requirements and is comparable to large scale chamber methods or FLEC-cell method (Schripp et al., 2007; Lor et al., 2010). A standardized guideline describes the usage of small-scale emission cells (ASTM, 2010). The quantity of emitted VOC from materials is dependent upon surface area, sampling time, age and test temperature. The SER_a value is determined by collecting the emitted VOC on sorbent tubes and subsequent analysis using TD-GC/MS. A calculation model enables estimation of AMC level in controlled environments by using the determined emission rates of all major AMC-emitting materials.

2. Methods

2.1 Preparing samples

Ideally, flat samples with a homogenous surface prepared into VOC-free carrier materials (glass dishes, stainless steel) should be used. In multiple layer applications, layer composition must correspond to the planned usage. The cut edges of solid samples which should not be considered as being part of the active surface area need to be covered appropriately, e.g. with an aluminum cutting ring or with aluminium foil (Figure 1, upper left). Reactive hardening material samples need to be pre-conditioned over a period of 30 days at 23 °C and 45 % relative humidity. Samples may not become contaminated during pre-conditioning by storing them in a VOC-reduced environment (M+W Products GmbH, Stuttgart, see Figure 1, middle).

Figure 1: Upper left: Representative material sample with a sampling chamber and overlying ring for determining the surface-specific emission rate of the material sample. Lower left: Material samples in micro-chamber with one cover lid opened and other lid closed with an adsorption tube attached on the outlet of the closed chamber. Middle: storage environment with VOC filtration. Right: setup for experimental prove of the calculation model

2.2 Micro Chamber Measurement and Analysis

Defined material samples (A = 10 cm^2) are placed in a micro chamber (µCTE, Markes International, Llantrisant, see Figure 1: lower left) under atmospheric pressure at a standardized temperature of 23 +/-1 °C (VDI, 2012). After an equilibration time of 6 min, the VOC-sampling takes place over a period of 60 min. As rinsing gas, ultrapure nitrogen is used with a flow rate of 100 mL/min. The VOC emitted from the material are collected onto a Tenax-TA sorption tube. Sorption tubes are analyzed by TD-GC/MS according VDA 278 (VDA, 2002). Other established methods can be used as well (Benzo and Gilardoni, 2008). A six-point calibration from 10^{-9} g to 10^{-6} g total mass of hexadecane is performed, loaded onto the tubes using a Calibration Solution Loading Rig (Markes International, Llantrissant) with a flow of 100 mL/min ultrapure nitrogen for 5 min. For each analyzed set of tubes, a standard tube dotted with hexadecane was analyzed as well to determine the response factor. For each detected VOC-compound, the quantification is done using the response factor in correlation to hexadecane.

2.3 Determining the standardized material classification number AMC_m

Materials are classified based on tests performed at room temperature. A possible second analysis at an elevated temperature can be done to gain further outgassing information, in particular critical substances in the material sample. The mass of all VOC m_{VOC} is related to the sample surface area A and the sampling time t to calculate the material surface specific emission rate SER_a (Equation 1).

$$SER_a = \frac{m_{TVOC}}{A \cdot t} \tag{1}$$

The SER_a, expressed in grams per square meter and second is normalized to the surface area A_{norm} = 1 m^2, the reference volume V_{norm} = 1 m^3 and a normed air exchange rate n_{norm} = 1 s^{-1}. After being logarithmized in a decadal way, the normed material-specific airborne molecular contamination class regarding the outgassing from materials (AMC_m) class is obtained (Equation 2).

$$AMC_m = \log\left[\frac{SER_a \cdot A_{norm}}{V_{norm} \cdot n_{norm}}\right] \tag{2}$$

According to VDI 2083 part 17, the material classification is expressed as follows: AMC_m class N (VOC) with a value lying between 0 and -12 with 0.1 as lowest permissible increment of N. The SER of a material with an AMC_m class = -6 is ten times less than the SER of a material with AMC_m class = -5. The term “VOC” defines the volatile organic compounds as contaminant group. For VOC, the actual method detection limit is m_{TVOC} = 1 ng or AMC_m class = -9.6 (VOC). The classification procedure can be done for all other AMC contaminant groups as well.

2.4 Estimation of the ISO-AMC class of a real scenario controlled environment

The described calculation model enables estimation about the ISO-AMC class of a controlled environment with defined air intake and exhaust. ISO-AMC class 5 (x) equals an AMC concentration of 10^{-5} g/m^3 for the contaminant group x (ISO, 2006b). Regarding all relevant major AMC mass flows in a controlled environment m_{ges} (material emission and intake air) with a room volume V and the ventilation rate F, the resulting ISO-AMC class (x) in the controlled environment can be calculated as follows over time (equation 3):

$$ISO - AMC\,class(x) = \log\left(c_0 - \frac{\dot{m}_{ges}}{F}\right) e^{\left(-\frac{F}{V} \cdot t\right)} + \frac{\dot{m}_{ges}}{V} \tag{3}$$

Relevant materials to be considered for the ISO-AMC class estimation are materials with large surface area (flooring and wall systems, ceiling, filter systems) and with high molecular emission (sealants, adhesives and lubricants). The temperature and humidity inside most controlled environments equals the chamber measurement parameters with 23 °C and 45 % relative humidity, so these parameters are comparable. The calculated value ISO-AMC class (x) reflects the situation for materials with age 30 days. As AMC outgassing from materials reduces over time, the ISO-AMC class will lower accordingly. Therefore, this represents a good estimation of the ISO-AMC class after completion of the setting.

2.5 Experimental prove of the model

A calibrated cavity ringdown spectrometer was used for fast response water vapour measurements; see figure 1 right (Picarro G1114, Picarro Inc, Sunnyvale). Glass dishes (A = 0.0001 m^2) filled with 2 ml water were placed as AMC emission source into a polyamide chamber with V = 0.0015 m^3. For the simulation of increasing mass flows, the mass flow of water vapour was increased by increasing the numbers of glass dishes. The housing inlet was open to laboratory air. Ventilation rate was fixed to the suction of the mass spectrometer. The different mass flows of water vapour were calculated from the steady-state values using following parameters: F = ventilation rate: gas flow through chamber; r = measured volume fraction of water vapour in air; c = concentration of water in a saturated atmosphere at 20 °C (calculated with the Magnus formula); $x_{Saturation}$ = volume fraction of water vapour in saturated air; see Equation 4:

$$F \cdot r = \frac{c_{Saturation}}{x_{Saturation}} \tag{4}$$

In a second experiment, the ventilation rate F was varied using different inlet flow rates of ultra pure air. The spectrometer was attached in bypass mode to the outlet of the chamber. This setup can only be seen as first evaluation of the model as water vapour may differ from various specific VOC in emission feature. More tests with different VOC may be useful for the general evaluation the developed model.

3. Results

3.1 Outgassing measurements

The excellent reproducibility of the method is previously shown (Keller and Gommel, 2012b). In Figure 2, the displayed selection of investigated epoxy flooring materials demonstrate a huge difference in classification. For some materials, no VOC outgassing could be detected at all, so these materials are classified with AMC_m class = 9.6 (VOC), the best possible classification value based on the actual lower detection limit (LDL) of the method.

Flooring material	Sikafloor-269 CR	Sikafloor-269 ECF CR	Sikagard-183 CR	Sikafloor-381	Sikafloor-381 AS	Sikafloor-390	Sikafloor-390 AS	Sikaflex Wallcoat N	StoPox WL 100	Sikafloor-266 CR	Sikafloor-266 ECF CR	Sikafloor-325	Sikafloor-235 ESD	Sikaflex Pro 3 (i-Cure)	StoPox BB OS	StoPox WHG Deck 100	Sikafloor-264	Sikafloor-263 SL	Sikaflex PRO 3 WF	Sikaflex AT Connection
AMC_m class	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-9.6**	**-7.8**	**-7.7**	**-7.1**	**-6.8**	**-6.8**	**-6.6**	**-6.6**	**-6.5**	**-6.5**	**-4.8**	**-4.6**

Figure 2: AMC_m class (VOC) of different epoxy flooring systems according to VDI 2083 part 17

3.2 Experimental prove of the model

The obtained experimental data fit to the simulation using the described calculation model, see figures 3a and 3b. The corresponding mass flows of water vapour and ventilation rates F are mentioned directly in the figures.

4. Conclusions

The use of a suitable emission chamber test method and corresponding analytics enables the determination of the SER_a value of VOC emitted from a material sample. Through appropriate standardization, a comparable material class can be calculated based on this value. The standardized material classification permits a direct comparison of the tested materials to be made with regard to the emission of VOC. The calculation model enables an ISO-AMC class estimation of a controlled environment already during planning. Therefore, a systematic building material selection will improve VOC-levels not only of controlled environments but for all indoor areas.

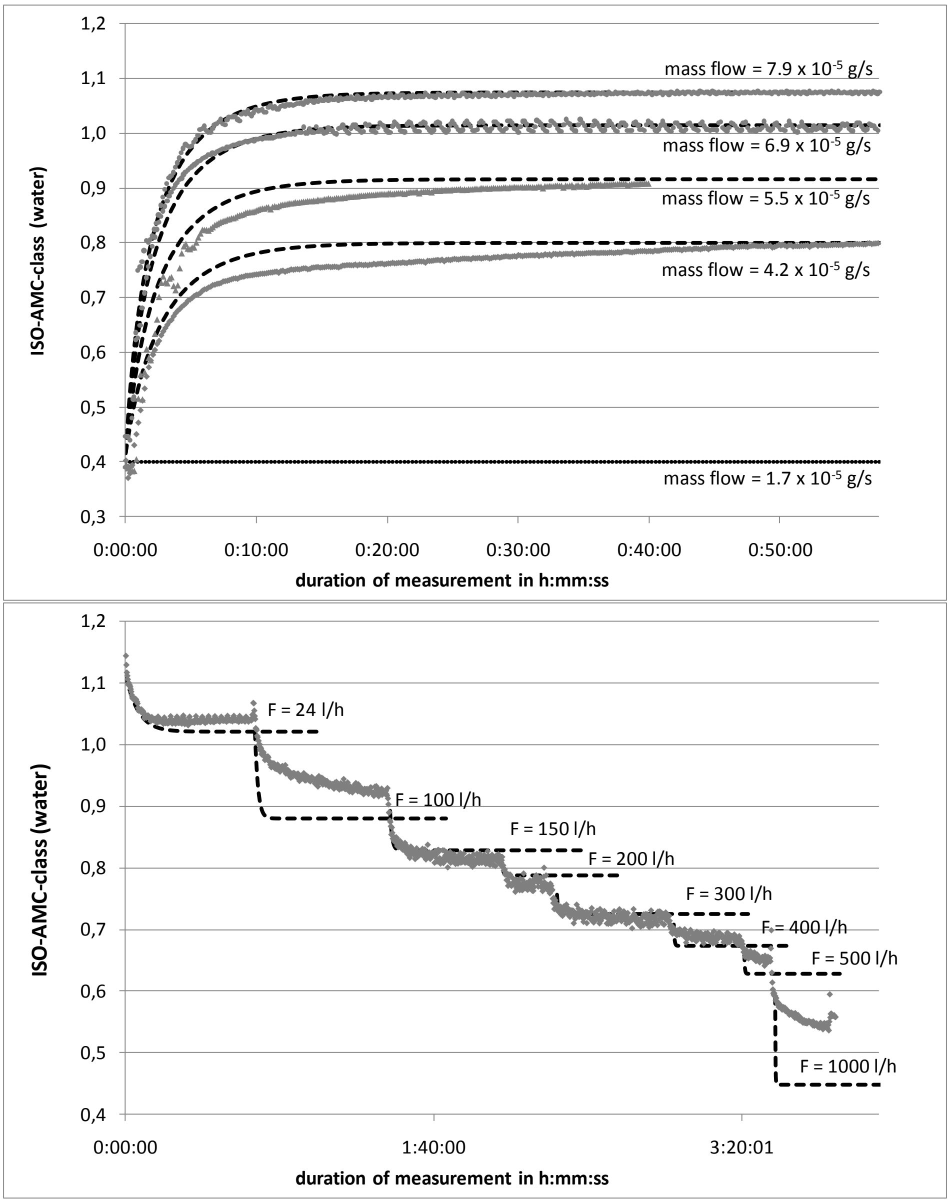

Figure 3 (upper): Fit of experimental data (grey) and model (black) for varying mass flow of water vapor. (lower): Fit of experimental data (grey) and model (black) for varying ventilation rates F.

References

ASTM, 2010. ASTM D5116-10. Standard Guide for Small-Scale Environmental Chamber Determinations of Organic Emissions from Indoor Materials/Products. In: ASTM Volume 11.07 Atmospheric Analysis, ASTM International,, West Conshohocken, United States.

Benzo M., Gilardoni G., 2008. Succesful application of Thermal Desorption-Gas Chromatography/Olfactometry/Mass Spectrometry technique to the indentification of main odorants in complex mixtures of volatile compounds. Chemical Engineering Transactions, 15, 199-206.

Bürgler J., Frickinger J., Zielonka G., Pfitzner L., Ryssel H., Schottler M., 2001. Control of Organic Contamination in CMOS Manufacturing. In G. Kissinger, L. H. Weiland, Proceedings of SPIE, 4406.

EC, 1991. Effects of Indoor Air Pollution on Human Health, EUR 14086 EN, 1991. Commission of the European Communities, Brussels, Luxembourg.

De Bortoli M., Kephalopoulos S., Kirchner S., Schauenburg H., Vissers H., 1999. VOC Emitted from Building Products: Results of European Interlaboratory Comparison. Indoor Air, 103-116.

ISO, 2006a, ISO 16000-6. Determination of VOC in indoor and test chamber air by active sampling on Tenax TA sorbent, thermal desorption and gas chromatography using MS/FID. International Organization for Standardization, Geneva, Switzerland.

ISO, 2006b, ISO 14644-8. Cleanrooms and associated controlled environments - Part 8: Classification of airborne molecular contamination. International Organization for Standardization, Geneva, Switzerland.

ISO, 2006c, ISO 16000-9. Determination of the emission of VOC from building products and furnishing - Emission test chamber method. International Organization for Standardization, Geneva, Switzerland.

JACA, 2003, Classification of Air Cleanliness for Airborne Molecular Contamination Level in Cleanrooms and associated controlled Environments and its Measurement Methods. Japan Air Cleaning Association, JACA method 35 A.

Johnstone E., Dieu L., Chovino C., Reyes D., Hong P., Krishnan P., 2003, 193 nm Haze Contamination: A close relationship between mask and its environment. SPIE USE, 2, 5256-5258.

Keller M., 2010, Emissions from cleanroom suitable materials. Reinraumtechnik, 3/2010, 14-17 (in German).

Keller M., Gommel U.,2012a, Research on cleanroom flooring systems. TechnoPharm, 2, 31-41 (in German).

Keller M., Gommel U., 2012b, Comparable measurement of VOC-emissions from building materials followed by a standardized classification system. Journal of Japan Air Cleaning Association JACA, 5 (49), 44-53.

Kennes C., Veiga M., 2010, Technologies for the abatement of odours and volatile organic and inorganic compounds. Chemical Engineering Transactions, 23, 1-6.

Knudsen H., Kjaer U., Nielsen P., Wolko P., 1999, Sensory and chemical characterization of VOC emissions from building products: impact of concentration and air velocity. Atmospheric Environment 33, 1217-1230.

Lor M., Vause K., Dinne K., Goelen E., Maes F., Nicolas J., Romain A.-C., Degrave C., 2010, Horizontal Evaluation Method for the Implementation of the Construction Products Directive, Final Report. Belgian Science Policy TAP 2, Brussels, Belgium.

Maronai M., Lundgren N.D., 1998, Assessment of the Health and Comfort Effects of Chemical Emissions from Building Materials: the State of the Art in the European Union. Indoor Air (Supplement 4), 26-31.

Peters L., 2007, Haze Defects Limit Life of Photomasks. Semiconductor International, 32.

Schripp T., Nachtwey B., Toelke J., Salthammer T., Uhde E., Wensing M., 2007, A microscale device for measuring emissions from materials for indoor use. Journal of Analytical and Bioanalytical Chemistry, 5, pp. 1907-1919.

Shiramizu Y., 2010, Monitoring for Molecular Contaminants in Semiconductor Production Lines. Journal of Japan Air Cleaning Association, 48 (4), 53-57.

Umweltbundesamt, 2010, AgBB scheme - Committee for Health-related Evaluation of Building Products. Umweltbundesamt, Dessau, Germany.

VDA, 2002, VDA 278. Thermo desorption analysis of VOC emissions for the characterization of non-metallic materials for automotive industries. VDA-QMC, Berlin, Germany.

VDI, 2012, VDI 2083 Part 17. Cleanroom Technology - Cleanroom Suitable Materials. Verein Deutscher Ingenieure, Beuth Verlag, Berlin, Germany.

Yu C. W., Kim Y. T., 2010, Building Pathology, Investigation of Sick Buildings – VOC Emissions. Indoor Built Environ, 19 (1), 30-39.