

Validation of control guidance sheets for filling of containers with organic solvents

R. Hebisch, J. Karmann, J. Fritzsche, N. Fröhlich, A. Baumgärtel

Abstract A new measurement strategy has been developed for validation studies of Control Guidance Sheets (CGS) in the framework of control banding. It consists of simultaneous stationary measurements at the local exhaust ventilation (LEV) and in the working area accompanied by personal air sampling at the worker during his activities. This strategy has been applied for validation of CGS for filling of organic solvents into jerrycans, drums and intermediate bulk containers. For assessment of the airborne concentration the stationary measurement at the LEV is most suitable, showing the strongest influence of its incorrect use and inadequate configuration. Workplace measurements performed using this strategy show good agreement between predicted exposure bands according to CGS and measured airborne concentrations of the filled solvents when using appropriate LEV. Additionally, the measurements indicate, that miscellaneous configurations of technical protection measures assure workers' protection when filling organic solvents into containers. Therefore, several CGSs for the same activity may be established according to the validation study which enables an expanded use of control banding tools.

Validierung von Schutzleitfäden für das Befüllen von Behältern mit organischen Lösemitteln

Zusammenfassung Es wurde eine neue Messstrategie zur Validierung von Schutzleitfäden für Tätigkeiten mit Gefahrstoffen entwickelt. Diese umfasst simultane ortsfeste Messungen unmittelbar an der Absaugvorrichtung und im Tätigkeitsbereich der Beschäftigten sowie eine personengetragene Messung während der Tätigkeiten. Mithilfe dieser Messstrategie wurden Schutzleitfäden für das Befüllen von Kanistern, Fässern und Intermediate Bulk Containern validiert. Die stationäre Messung direkt an der Absaugvorrichtung erwies sich dabei als am besten geeignet, um die unzureichende oder unkorrekte Verwendung der Absaugung zu zeigen. Arbeitsplatzmessungen mittels dieser Messstrategie zeigten eine gute Übereinstimmung zwischen den vorhergesagten Expositionsbändern für die Schutzmaßnahmen entsprechend den Schutzleitfäden und den gemessenen Luftkonzentrationen der umgefüllten Lösemittel bei korrektem Einsatz der Absaugvorrichtungen. Weiterhin veranschaulichten die Messungen, dass verschiedene technische Gestaltungen der Absaugvorrichtungen den Schutz der Arbeitnehmer beim Befüllen von Behältern mit organischen Lösemitteln sicherstellen. Auf der Grundlage dieser Ergebnisse werden daher für derartige Umfülltätigkeiten weitere Schutzleitfäden entwickelt. Mehrere gleichwertige Schutzleitfäden können somit zu höherer Akzeptanz in den Betrieben führen.

Dr. rer. nat. Ralph Hebisch, Dipl.-Ing. (FH) Jörg Karmann, B. Sc. Jörg Fritzsche, Dipl.-Ing. (FH) Norbert Fröhlich, Dr. rer. nat. Anja Baumgärtel, Federal Institute for Occupational Safety and Health (BAuA), Hazardous Substances Laboratory, Dortmund, Germany.

1 Introduction

The British COSHH Essential scheme was published in a series of papers in 1998 [1 to 3]. This scheme is intended as a tool for risk assessment and risk management in small and medium-sized enterprises (SME). Control strategies are derived based on considered toxicological hazards and the exposure potential of chemicals. Chemical substances are allocated to the five hazard bands of this scheme according to the R-phrases in Annex 1 of Council directive 67/548/EEC [4]. For each of these hazard bands, target airborne concentrations are derived.

The exposure potential of chemical substances has been characterized by inherent physical properties and operational factors [3]. As our investigation only deals with liquids, further considerations are restricted to liquid substances. For liquids, volatility is the relevant physical property which may be described by the boiling point or the vapour pressure. According to their volatility liquids are classified into those with low, medium and high volatility. At room temperature liquids with a boiling point between 50 and 150 °C are considered to have a medium volatility. When the boiling point is < 50 °C the volatility is defined to be high and for boiling points above 150 °C it is low. The operational factor in this scheme is the volume of liquid per container which also results in three categories. Small scale operations include a batch of less than 2.5 l. For medium and large scale operations the volume for one operation (according to one container) is 2.5 to 1,000 l and more than 1,000 l, respectively. Based on these allocations, four exposure predictor bands for liquids (EPL) have been derived.

Four control strategies (CS) are considered [1]. CS1 is general ventilation, CS2 refers to engineering control, CS3 is containment of handled substances and CS4 requires special expert advice. When combining these control strategies with EPL different concentration ranges are expected, each covering one order of magnitude in concentration. If these concentration ranges are combined with the target concentration of the five hazard bands a control can be assigned to each substance accounting for the physical properties and the amount used [3]. To enable the appropriate use of COSHH Essentials, so-called „Control Guidance Sheets“ have been established which describe good practice [1].

The use of control banding tools, such as COSHH Essentials, is becoming more widespread due to their generic character. The Federal Institute for Occupational Safety and Health (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin, BAuA) has adopted and advanced this approach which is available as “Easy-to-use workplace control scheme for hazardous substances” (EMKG) in version 2.2 in 2012 [5]. In this version also chemicals with a legal occupational exposure limit value (OELV) are covered. The EMKG approach is comparable with control banding according to COSHH Essentials, but notable differences exist due to several different allocations of R-phrases. Furthermore, the upper limit for

Table 1. List of investigated substances and their relevant parameters and allocations according to the EMKG.

Substance	Boiling point in °C	R-phrases	Occupational exposure limit in Germany [11]		Assignment according to [5]		
			in ppm	in mg/m ³	Volatility	Exposure predictor band for litre quantities	Hazard band
Acetone	56	11-36-66-67	500	1,200	medium	EPL 3	A
Butanone (Methyl ethyl ketone)	79	11-36-66-67	200	600	medium	EPL 3	A
Amyl acetate	149	10-66	50	270	medium	EPL 3	B (*)
Cyclohexane	81	11-38-65-67-50-53	200	700	medium	EPL 3	A
Cyclohexanone	156	10-20	20	80	low	EPL 2	B
Ethanol	78	11	500	960	medium	EPL 3	A
Ethyl acetate	77	11-36-66-67	400	1,500	medium	EPL 3	A
n-Hexane	69	11-38-48/20-51/53-62-65-67	50	180	medium	EPL 3	B (*)
Isopropyl acetate	89	11-36-66-67	100 [12]	420 [12]	medium	EPL 3	A
Isopropyl alcohol (2-propanol)	82	11-36-67	200	500	medium	EPL 3	A
Methanol	65	11-23/24/25-39/23/24/25	200	270	medium	EPL 3	A (*)
1-Methoxy-2-propanol	120	10-67	100	370	medium	EPL 3	A
Methyl acetate	57	11-36-66-67	200	610	medium	EPL 3	A
Methyl tert-butyl ether (MTBE)	55	11-38	50	180	medium	EPL 3	B (*)
Methyl isobutyl ketone (MIBK)	116	11-20-36/37-66	20	83	medium	EPL 3	B
1-Propanol	96	11-41-67	–	–	medium	EPL 3	B
Toluene	111	11-38-48/20-63-65-67	50	190	medium	EPL 3	B (*)
Xylene	138	10-20/21-38	100	440	medium	EPL 3	A

(*) Hazard band assigned according to the OELV [11]

small scale operations is 1 l, and the allocation to hazard bands is according to the OEL instead of R-phrases.

From the beginning, different attempts have been performed to validate the EMKG and the corresponding generic control guidance sheets. First of all, data from different BAuA field studies and existing substance exposure data have been used for validation of control banding [6]. One of the problems with this study was obtaining exposure data for pure control strategies. Some other validation studies have been confronted to a comparable situation: existing data from workplace measurements have been used [7 to 9]. In a second BAuA study Monte Carlo simulations have been performed for mixtures of substances [10]. These simulations showed that such a probabilistic model reproduces the empirical determined level of protection with satisfactory precision.

The present study was designed to continue the validation of the EMKG. Thus, all measurements have been carried out for this purpose. Therefore, an activity which is widely used was chosen for the measuring program. Filling of containers with liquids is such an activity, for which generic control guidance sheets already exist in the framework of EMKG. The control guidance sheets according to EMKG are No. 211 “IBC filling and emptying” and 212 “Drum filling” [5]. In COSHH Essential these control guidance sheets have the same numbers and titles.

To establish a suitable measurement approach, filling of organic liquids has been investigated in different chemical trade companies. Mainly, these companies fill organic solvents into jerrycans, drums and intermediate bulk containers (IBC). Accordingly, the investigations were restricted to the medium scale operation factor corresponding to litre amounts per each filled container. The investigations have been performed to show whether this newly developed measurement strategy as described below is appropriate for

the validation study. Also, it was aimed to draw conclusions concerning the validity of control guidance sheets and their further development.

2 Materials and Methods

2.1 Description of the enterprises and the investigation program

All measurements have been performed in chemical trade companies. In these companies organic solvents are filled into containers, such as drums, jerrycans and IBCs. Normally, underground tanks are used for storing the organic solvents from which they are transferred with systems consisting of pumps and transfer lines into the containers. In all cases the filling stations were equipped with local exhaust ventilations (LEV) in different configurations. In all enterprises several solvents have been filled into different kinds of containers. All containers have been filled with litre amounts in the range from about 3 l for jerrycans up to 970 l for IBCs. Independent of the hazard, the physical properties and the amount of the solvent used LEV was applied in all cases. Therefore, no measurements have been performed in cases where only control strategy 1 was implemented. Since all solvents covered merely the hazard bands A and B, the filling process did not require containment according to control strategy 3 in any case [2; 5].

For the filling of all types of containers, different modes have been used:

- below level or below bunghole filling with filling pipes surrounded by an extraction hood (different configurations),
- filling gun with integrated or external extraction hood,
- filling gun with extraction tube.

Normally, the filling process was semi-automatic. The employee started the filling which was controlled using a balance or mass flow controlled. Depending on the density of



Figure 1. Different technical configurations for drum filling. Top left: according to existing control guidance sheet, top right: delivery tube surrounded by a trapezoidal extraction hood, bottom left: delivery pistol integrated into an extraction cup with exhaust ventilation, bottom right: manual filling pistol and external extraction hood (all photographs show sampling position 1 immediately at the LEV; additionally the photo at the bottom right shows the position 2 for personal air sampling).

the organic solvents the resulting maximum amounts were 45 kg for jerrycans, 190 kg for drums and 900 kg for IBCs. After manual closing of filled containers they were transported by a conveyor belt or on pallets using a forklift. As can be seen from **Table 1** – with the exception of cyclohexanone (low volatility) – all solvents exhibit a medium volatility. Therefore, measuring results for cyclohexanone were mainly used for plausibility check.

2.2 Measurement strategy

During all activities simultaneous measurements of the solvent concentrations in workplace atmosphere have been performed both stationary and personal air sampling. At each of these sampling positions two samples have been collected. Generally, six concentration values have been obtained for each filling process under investigation. For data assessment the mean of the parallel measurements at each position was used.

Position 1 in this measuring strategy (**Figure 1**) was a stationary measurement immediately at the LEV, normally at the edge of the extraction hood or the filling system on the side faced to the worker. The result of this measurement was used for characterization of the performance of the LEV. The obtained concentration value was the decision criterion if the expected exposure band was hit or not. At position 2 per-

sonal air sampling (see also **Figure 1**, bottom right) was carried at the employee running the filling device. This result was used for exposure assessment and comparison with the OELV. Position 3 was a stationary sampling in the vicinity of the filling device inside the working area of the employee. Typically, this position was about 2 m away from the filling device. This measurement provides information about the expansion of the solvent in the work environment.

2.3 Sampling and analytical determination

For personal air sampling SENSYDINE LFS 115 low flow samplers have been used connected with PerkinElmer thermal desorption tubes filled with Chromosorb 106®. The duration of sampling was 30 to 60 min with an air flow of 10 ml/min. During sampling the filling process has been repeated several times, e. g. about 20 drums in 30 min. Approximately, the measured concentration over all filled containers during this period was considered to be the same concentration as for filling of one container.

The collected samples were analysed after thermal desorption using a PerkinElmer TurboMatrix 650 thermal desorber in combination with a PerkinElmer Clarus 680 gas chromatograph equipped with a Clarus 600 S mass spectrometer. Additionally, a flame ionisation detector has been used for quantification.

Table 2. Results of the measurements at position 1 (LEV).

Container	Number of solvents according to table 1	Total number of measurements	Measured concentration met the expected exposure band (5 to 50 ppm) or was lower				
			Number of measurements	range in ppm	mean in ppm	median in ppm	95-percentile in ppm
Jerrycans	8	12	8	12.8 to 45.0	26.8	19.1	44.8
Drums	12	34	19	3.2 to 46.2	14.8	10.4	33.7
IBCs	12	24	22	0.44 to 49.1	16.2	15.1	39.2
total	17	70	49	0.44 to 49.1	17.4	13.2	44.8

Table 3. Classification of measurements into HIT (exposure band met or lower when measuring at LEV) and FAIL (exposure band exceeded when measuring at LEV).

	HIT			FAIL		
	at the LEV in ppm	personal air sampling in ppm	in the vicinity of the filling station in ppm	at the LEV in ppm	personal air sampling in ppm	in the vicinity of the filling station in ppm
Mean	17.4	5.0	3.74	738	31.8	9.60
Median	13.2	2.29	1.64	356	16.0	4.36
95-percentile	44.8	9.84	13.5	1,840	108	26.7

Before performing analytical determination, all companies provided samples of the solvents to be investigated. These chemicals were run through a chromatographic system to determine contaminants. In almost all cases these solvents were found to be free of contaminants which could influence the analytical results. Cyclooctane was used as internal standard for calibration.

3 Results and discussion

The investigations were intended to check if the expected exposure according to EMKG [5] will be met when fulfilling the protective measures according to the corresponding control guidance sheet. Immediately after starting the investigation program it was obvious that there exist different configurations of the technical devices which are in wide-spread use for filling of jerrycans, drums and IBCs. In Figure 1, as an example, some devices for drum filling are represented. Therefore, some modifications were made to the investigation program. The expected exposure band was used as a target for the exposure measured at different filling devices. For all these measurements the technical parameters were documented, especially the air flow and the geometry of the LEV and their distance from the bunghole of the filled containers.

Overall, 70 measurements during filling have been carried out. An overview is given in Table 2. Of these measurements, 49 (70%) met the expected exposure band. Generally, for the remaining 30% the measured concentration at the LEV was much larger than the upper limit of 50 ppm for the expected exposure band (up to 5,000 ppm). For all of these measurements one or more of the following deficits have been observed during the measurement:

- incorrect positioning of the LEV (not form fitted or too far away),
 - no repositioning of the LEV when filling the next container on palletes,
 - air velocity of the LEV too small,
 - filling flow velocity too high (causing aerosols, splashes),
 - leakage in the transfer line or damaged extraction hood.
- Based on this information the measurement results at position 1 (immediately at the LEV) have been divided into two

groups: exposure band hit or lower concentration (HIT) and exposure band failed (FAIL), as an indicator for an efficient or non-efficient LEV, respectively. Accordingly, the FAIL data set includes all measurement results exceeding 50 ppm for the investigated solvents according to Table 1. The measured concentrations for position 2 (personal air sampling) and 3 (in the vicinity of the filling station) have been assigned to these groups in accordance with position 1.

The data sets for jerrycans, drums and IBCs which hit the expected exposure band of 5 to 50 ppm for organic solvents with a boiling point between 50 and 150 °C have been subject to statistical tests for variances and means [13]. No significant difference was detectable for the variances at 99% confidence level. As a consequence an overall variance and the corresponding standard deviation have been calculated for all data. In a second step, the mean values have been tested. Because there was no difference detected at the same confidence level the overall means for all solvents have been calculated for positions 1 to 3. In Table 3 these parameters are summarized together with those for the measuring results which exceeded the expected exposure band. Using data from Table 3 the ratio FAIL/HIT has been calculated for the statistical parameters derived for positions 1 to 3. Clearly, Figure 2 shows a strong decrease of this ratio from positions in close proximity to the LEV as compared to the vicinity of the filling station. As expected, the ratio for personal air sampling is closer to that in the vicinity of the filling station. This is in accordance with the activities of the employees who do their jobs at the filling station but also in the surrounding area. Consequently, measurements of substance concentrations directly at the LEV are a better indicator for assessing its efficiency in comparison to personal air sampling. Furthermore, the relationship between boiling point and measured concentrations for all filling processes which met the expected exposure band has been investigated. According to the findings described above this was reasonable only for the measurements performed at the LEV. Although the correlation is weak, Figure 3 shows a tendency towards reduced concentrations with increasing boiling point. Using the linear regression function for this relationship from Figure 3 for cyclohexanone, a concentration at the LEV was calculated to be about 2.4 ppm. This is in good agree-

ment with the expected exposure band of 0.5 to 5 ppm for EPL 2 (see Table 1). Additionally, two measurements during filling of cyclohexanone into drums and IBCs have been performed. The measured concentrations at the LEV were 3.9 and 1.1 ppm, respectively. Albeit, two measurements are only an indication, this finding supports our results for the validation of control guidance sheets.

The investigation has been performed for substances allocated to the hazards bands A and B. Normally, for substances allocated to the hazard band A, only general ventilation (control strategy 1) is demanded with an expected exposure band of 50 to 500 ppm, when filling of litre amounts into containers (see Table 1). Looking to the measured concentrations where LEV was incorrectly positioned or not adequate for seven cases, concentrations larger than 500 ppm (662 to 5,000 ppm; median 1,040 ppm) have been measured at position 1, when substances allocated to hazard band A were filled into jerrycans, drums or IBCs. This result suggests that a check-up is necessary to verify if the application of general ventilation alone is sufficient for workers' protection during filling of these substances into containers. At the moment the recommendation is to fill all organic solvents into containers using LEV for substances allocated to hazard band A and B according to EMKG [5].

4 Conclusion

A measuring strategy was developed which has proven to be useful for the validation of control guidance sheets. Measuring the concentration of substances immediately at the LEV enables a good assessment of the performance of the LEV applied. This measurement is more significant than personal air sampling because the employee filling the containers is also doing other jobs, during which he is away from the filling device.

The results obtained using this measuring strategy showed a good agreement with the predicted exposure for filling of organic solvents into jerrycans, drums and IBCs if adequate LEV is applied. LEV has to be used form fitted over the bung-hole of the container. Furthermore, the distance to the bung-hole has to be as small as possible, because the efficiency of LEV strongly decreases with increasing distance from the bung-hole.

Of the operations investigated, in only one case the configuration of the filling device was in accordance with the control guidance sheet. However, several other configurations met the expected exposure band. Therefore, our recommendation is to provide not only one control guidance sheet for such cases. As a result of this investigation the BAuA is generating

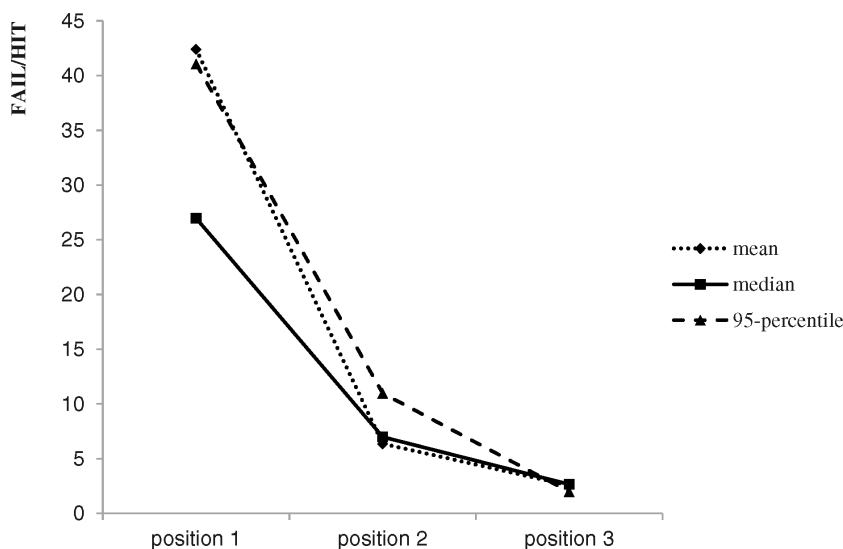


Figure 2. Relation FAIL/HIT for the statistical parameters mean, median and 95-percentile for the measurements at the LEV (position 1), personal air sampling (position 2) and in the vicinity of the filling device (position 3).

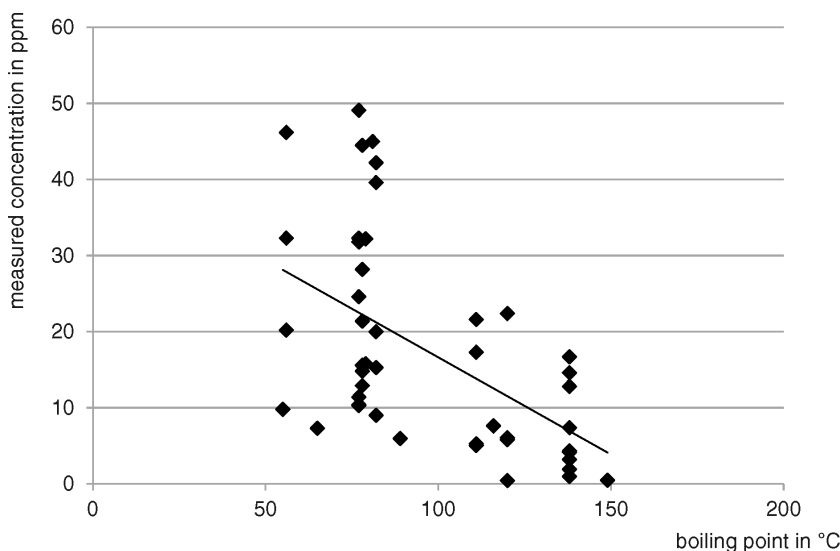


Figure 3. Graphical relationship between measured concentration and boiling during filling of containers with organic solvents; linear regression line: $y = 0.26x + 42$; coefficient of correlation: $r = 0.54$.

additional control guidance sheets for filling organic solvents into jerrycans, drums and IBCs, based on several effective technical configurations found in chemical trade companies. All of these control guidance sheets will be labelled as validated according to this investigation.

Acknowledgements

The authors are grateful to the VCH Verband Chemiehandel (Association of the Chemical Trade Companies in Germany) for providing the sampling opportunity in enterprises which are member of this association. Our special thank is given to the employees which appreciative enabled personal air sampling.

References

- [1] *Russell, R. M.; Maidment, S. C.; Brooke, I. M.; Topping, M. D.*: An introduction to a UK scheme to help small firms control health risks from chemicals. *Ann. Occup. Hyg.* 42 (1998) No. 6, p. 367-376.
- [2] *Brooke, I. M.*: A UK scheme to help small firms control health risks from chemicals: toxicological considerations. *Ann. Occup. Hyg.* 42 (1998) No. 6, p. 377-390.
- [3] *Maidment, S. C.*: Occupational hygiene considerations in the development of a structured approach to select chemical control strategies. *Ann. Occup. Hyg.* 42 (1998) No. 6, p. 391-400.
- [4] Annex I of Council Directive 67/548/EEC of 17 June 1967 on the approximation of law, regulations and administrative provisions relating to the classification, packaging and labelling of dangerous substances. Annex 1 was latest updated by ATP: 29-OJ No. L 152 of 30 April 2004; replaced by regulation EC 1272/2008.
- [5] *Kahl, A.; Wilmes, A.; Guhe, C.; Packroff, R.; Lotz, G.; Tischer, M.*: Easy-to-use workplace control scheme for hazardous substances. Version 2.2. Published by: Federal Institute for Occupational Safety and Health (BAuA), Dortmund 2012. www.baua.de/de/Publikationen/Fachbeitraege/Gd64.html
- [6] *Tischer, M.; Bredendiek-Kämper, S.; Poppek, U.*: Evaluation of the HSE COSHH Essentials exposure predictive model on the basis of BAuA field studies and existing substances exposure data. *Ann. Occup. Hyg.* 47 (2003) No. 7, p. 557-569.
- [7] *Lee, E. G.; Harper, M.; Bowen, R. B.; Slaven, J.*: Evaluation of COSHH Essentials: methylene chloride, isopropanol, and acetone exposures in a small printing plant. *Ann. Occup. Hyg.* 53 (2009) No. 5, p. 463-474.
- [8] *Hashimoto, H.; Goto, T.; Nakachi, N.; Suzuki, H.; Takebayashi, T.; Kajiki, S.; Mori, K.*: Evaluation of the control banding method – comparison with measurement based comprehensive risk assessment. *J. Occup. Health* 49 (2007) No. 6, p. 482-492.
- [9] *Lee, E. G.; Slaven, J.; Bowen, R. B.; Harper, M.*: Evaluation of the COSHH essentials model with a mixture of organic chemicals at a medium-sized paint producer. *Ann. Occup. Hyg.* 55 (2011) No. 1, p. 16-29.
- [10] *Tischer, M.; Bredendiek-Kämper, S.; Poppek, U.; Packroff, R.*: How safe is control banding? Integrated evaluation by comparing OELs with measurement data and using Monte Carlo simulation. *Ann. Occup. Hyg.* 53 (2009) No. 5, p. 449-462.
- [11] Technische Regeln für Gefahrstoffe: Arbeitsplatzgrenzwerte (TRGS 900). *BArbBl.* (2006) No. 1, p. 41–55; last rev. *GMBL.* (2014) No. 64, p. 1312-1313.
- [12] List of MAK and BAT Values 2014. Published by: Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe der Deutschen Forschungsgemeinschaft. Weinheim: Wiley-VCH 2014.
- [13] *Doerffel, K.*: Statistik in der analytischen Chemie. 3rd ed. Weinheim: Verlag Chemie 1984.