

FORMATION AND SOURCES I -POSTER

FORMATION OF PCDD/PCDF AND PCBs BY IR ACTIVE SMOKE SCREEN GRENADES AND HUMAN EXPOSURE ASSESSMENT

Michael Oehme^{*}, Edo Kruslin[#] and Klaus Hieke⁺

^{*}Organic Analytical Chemistry, University of Basel, Neuhausstr. 31, CH-4057 Basel, Switzerland

[#]Toxicological Institute Basel, Offenburgerstr. 21, CH-4007 Basel, Switzerland

⁺Buck System GmbH, DE-79395 Neuenburg, Germany.

Introduction

Smoke screen ammunition is an important part of defensive warfare. It has two major functions: to hide aims and staff and/or to mislead aim searching detectors of missiles or other devices from a target. For the first purpose, a dense fog-like smoke is generated while an IR-absorbing curtain is required for the second one. Sometimes both principles are combined. The earlier applied ZnCl₂ based smokes were formed by ignition of a mixture of Zn-powder with polychlorinated compounds such as CCl₄ or chlorinated aromates. Though never properly investigated, it can be assumed from observed toxic effects that highly toxic aromatic compounds such as PCDD/PCDF were formed as by-products. For example, more than eleven thousands cows were poisoned in the Central part of Switzerland due to the application of smoke grenades containing hexachloronaphthalene¹. Nowadays, fogs based on phosphorous acid are widely applied. However, the IR-absorbing fraction is still generated by mixtures containing chlorides and organic compounds. Therefore, the risk of formation of undesired chlorinated aromatic compounds of high toxicity cannot be excluded. The aim of this work was to evaluate the possible formation of PCDD/PCDF and PCB when using IR active smoke screen grenades as well as to estimate roughly the exposure of military personal in the terrain.

Methods and Materials

Composition of smoke screen grenade: The IR-deflecting smoke is formed from a mixture of an oxidised aromatic compound, magnesium, a fluorinated polymer and chloroparaffins. Information about further details is restricted. The reaction heat of magnesium with the halogenated compounds generates a temperature up to 2000 °C which transforms the aromatic substance into soot particles. The soot screen is stable for about 40 to maximum 90 s.

Sample collection: About 20 g of the mixture were ignited in a smoke chamber of 1 m³ volume. Totally four experiments were carried out. Particle size measurements showed that only the inhalable particle fraction of ≤ 10 µm diameter was present after 1 h waiting time. This fraction was collected on a glass fibre filter of 40 mm diameter and the gas phase adsorbed on two polyurethane foam plugs of 2 cm diameter and 5 cm length. The sampling volume was ca. 1.2 m³ at a sampling rate of 15-20 l/min. Due to the observed dilution effect, this corresponded to 60 % of the overall sample amount in the chamber. If necessary the glass fibre filter was changed. Around

FORMATION AND SOURCES I -POSTER

100 mg of soot were collected per experiment. In addition, the soot deposited on an aluminium foil after a waiting time of 3-4 h was collected. About 4 g soot were generated from 20 g material. Roughly, about 5 % of the totally formed soot had a size $\leq 10 \mu\text{m}$.

Extraction and analysis: Soxhlet extraction with toluene was carried out of both the filter and the PUR foams according to a standard procedure by ERGO (Hamburg, Germany)². Isotope-labelled internal standards were added prior to extraction as required by these methods. Blanks samples and the PUR back-up foam were analysed separately as a quality control measure. Levels found in these samples were far below 1 % of the measured concentrations. Sample clean-up, separation and quantification were carried out at the same laboratory according to standardised procedures published elsewhere². In brief high resolution gas chromatography was used combined with low or high resolution mass spectrometry. All samples fulfilled the quality control requirements (e.g. recovery rates of added standards, >85-90 %). Table 1 lists the quantified compounds.

Estimation of exposure: The estimation of exposure of persons was based on a similar study carried out for smoke screen grenades in Norway³. The dispersion parameters applied there, were adapted to this study. Based on field experiments in the Norwegian study, it was concluded that the method of Briggs⁴ was best suited for a simulation of such an emission assuming that the emitted soot is in thermal equilibrium about 20 m from the source and that the wind speed does not exceed 3 m/s. Based on a totally produced amount of 400 g soot per grenade, an emission rate of 8 g/s and a reaction time of 40-50 s, the soot concentrations given in Table 2 were estimated.

Results and Discussion

PCDD/PCDF levels: The results summarised in Table 1 show similar levels in the fine soot fraction and the totally deposited soot. The concentrations are comparable to those found in slag of municipal incinerators before any emission control measures was carried out⁵. The collected gas phase contained less than 2 % of the fine soot fraction (1.6 $\mu\text{g}/\text{m}^3$ I-TEQ). The congener pattern was not typical for a pure combustion process. It resembled partly that of a metallurgical process due to much higher PCDF concentrations contributing more than 90 % to the I-TEQ.

PCB concentrations: Six standard PCB were present in ppb amount in the soot fraction. Sum concentrations are given in Table 1. Levels in the gas phase were comparable to those of the blank values (ca. 1-5 ng/m^3) due to the low sampling volume and were not further evaluated. The sum concentrations of the co-planar PCB 77, 126 and 169 were about 1 % of the sum of the six standard PCB. Their contribution to the I-TEQ was negligible.

Estimation of PCDD/PCDF exposure: The following assumptions were made to estimate the exposure of a person by the IR active smoke. The concentration found in the fine soot fraction was used together with the modelled soot concentrations given in Table 2 to calculate the I-TEQ levels in air at different distances (see Table 2). A person inhale about 20-50 l/min air when walking and 50-120 l/min when running. A stand time of the screen of 90 s and an inhaled volume of 100 l was selected, and a complete of the PCDD/PCDF in the soot was assumed. This resulted in a maximum exposure of 3.4 μg I-TEQ at a distance of 20 m. However, only a fraction of the total

FORMATION AND SOURCES I -POSTER

soot amount can be considered as inhalable. This is far below the recommended tolerable uptake rate according to the World Health Organisation (WHO) which has recently been decreased from 10 to 1-4 pg I-TEQ per kg body weight and day corresponding to 75-300 pg I-TEQ for a person of 75 kg weight⁶. At present the uptake from food is about 50-100 pg I-TEQ per day for adults⁷.

Table 1: Levels of PCDD/PCDF and selected PCB in the fine soot fraction and deposited soot. Concentrations in pg/m³ are given in parentheses. Observe that ΣPCB levels are given in ng/g.

Congener	Deposited soot [pg/g]		Fine soot fraction [pg/g]
	Sample 1	Sample 2	
2,3,7,8-TCDD	29	18	50 (3.7)
ΣTCDD	490	523	843 (62)
1,2,3,7,8-PeCDD	30	28	69 (5.1)
ΣPeCDD	291	349	1000 (74)
1,2,3,4,7,8-HxCDD	14	13	32 (2.4)
1,2,3,6,7,8-HxCDD	17	17	42 (3.1)
1,2,3,7,8,9-HxCDD	15	15	37 (2.7)
ΣHxCDD	171	195	217 (45)
1,2,3,4,6,7,8-HpCDD	40	48	396 (29)
ΣHpCDD	74	89	703 (52)
OCDD	55	49	815 (60)
2,3,7,8-TCDF	1120	791	2930 (215)
ΣTCDF	27900	34300	32500 (2400)
1,2,3,4,7,8-PeCDF	1310	1510	2070 (152)
2,3,4,7,8-PeCDF	581	764	801 (59)
ΣPeCDF	12700	20800	14200 (1040)
1,2,3,4,7,8,9-HxCDF	1300	1340	1510 (110)
1,2,3,6,7,8-HxCDF	911	1140	1000 (73)
1,2,3,7,8,9-HxCDF	92	107	124 (9.2)
2,3,4,6,7,8-HxCDF	375	476	487 (36)
ΣHxCDF	8280	12400	9570 (705)
1,2,3,4,6,7,8-HpCDF	1470	2040	1480 (109)
1,2,3,4,7,8,9-HpCDF	313	433	363 (27)
ΣHpCDF	2620	3700	2690 (199)
OCDF	758	1180	812 (60)
I-TEQ (PCDD/PCDF)	802	906	1230 (91)
Σ PCB ^a [ng/g]	86	70	380 (28)
PCB 77	12.4	11.6	i
PCB 126	0.83	0.80	4.2 (0.32)
PCB 169	0.06	0.07	0.2 (0.02)
I-TEQ (PCB)	90	87	44

^a Sum of PCB 28, 52, 101, 138, 153 and 180; i: Interference

FORMATION AND SOURCES I -POSTER

Table 2: Estimated dispersion of soot produced by one IR-smoke screen grenade according to the model of Briggs and the parameters given under experimental

Compound	Distance from emission point [m]					Wind [m/s]
	20	100	150	200	250	
Soot [mg/m ³]	27	1.9	1.0	0.69	0.5	3
Soot [mg/m ³]	13.5	0.98	0.51	0.35	0.26	6
PCDD/PCDF: I-TEQ [pg/m ³]	34	2.5	1.2	0.87	0.65	3
ΣPCB ^a [ng/m ³]	17	1.2	0.62	0.43	0.31	3
Total PCB ^b [ng/m ³]	85	6	3.1	2.2	1.6	3

^a Sum of PCB 28, 52, 101, 138, 153 and 180; ^b estimated by multiplying ΣPCB by a factor of 5

Estimated PCB exposure: The estimated PCB concentrations given in Table 2 are far below tolerable maximum values for indoor air which are e.g. in Switzerland and Germany 500 µg/m³⁸. Even the much lower limit in Norway of 10 µg/m³ is still far away from the levels found⁹.

References

- [1] Gruppe für Rüstungsdienste (1977). Note: Rauchvergiftung im Aktivdienst 1939/45. 28. 11. 1977. AC-Laboratorium, Wimmis Switzerland.
- [2] Gaus C., Pöpke O., Brunskill G.J. and Müller J.F. (2000) *Organohalogen Compd.* 46, 15.
- [3] Tønnesen D., Mikalsen A. and Schlabach M. (1994) Hazard evaluation of infrared smoke grenades based on the dispersion and the composition of the smoke (*NILU report OR 69/94*), Norwegian Institute for Air Research, N-2007 Kjeller, Norway.
- [4] Briggs G.A. (1974) Diffusion estimation for small emissions. Atmospheric turbulence and diffusion laboratory (*NOAA, Report ATDL-106*), Oak Ridge, TE, USA.
- [5] Bröker G. and Quaß U. (1998) in *Handbuch Dioxine* (Oehme, M., Ed.), Spektrum Verlag, Heidelberg, ISBN 3-8274-0126-7, p 77.
- [6] Van Leeuwen F.X.R., Feeley M., Schrenk D., Larsen J.C., Farland W. and Younes M. (2000), *Chemosphere*, 40, 1095
- [7] Fürst P. (1998) in *Handbuch Dioxine* (Oehme, M., Ed.), Spektrum Verlag, Heidelberg, ISBN 3-8274-0126-7, p 262.
- [8] Direktoratet for arbeidstilsynet (1990). Administrative normer for forurensning i arbeidsatmosfære. Bestellnr. 361, Oslo, Norwegen.
- [9] Suva (1999) Grenzwerte am Arbeitsplatz 1999. Suva, Abt. Arbeitsmedizin, Luzern, Switzerland.