Screening of hexachlorobenzene (HCB) contents in fireworks

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Abstract: *This paper gives a brief overview of the findings of hexachlorobenzene (HCB) in fireworks compositions observed within EC type-examinations according to Module B (as set out in the annex II of the Directive 2007/23/EC) of the notified body BAM. In this work, roughly 220 samples were analysed, originating from 49 consumer fireworks articles of the category F2, such as batteries, combinations, fountains and rockets. It was found that the vast majority of samples showed concentrations below 5 mg HCB/kg. However, in three cases concentration values between 5 mg HCB/kg and 50 mg HCB/kg were observed, and in a further four cases extreme values of up to 8046 mg HCB/kg were detected. The results of this study are compared with published HCB findings originating from market surveillance activities in Europe.*

Introduction

Hexachlorobenzene (HCB, sum formula C_6Cl_6) is a toxic, carcinogenic, persistent and bio-accumulative compound. Due to its highly persistent and lipophilic properties HCB degrades slowly and accumulates preferentially in fatty tissue. Therefore, HCB is categorized as a so-called persistent organic pollutant (POP substance).

In Europe HCB has not been used or intentionally produced for many years. However, the use of HCB in the past was manifold. The widest use was probably within the agriculture and farming industry, as a fungicide or pesticide, as well as for seed treatments. In addition, it was widely used as a softener for polyvinylchloride (PVC) and fire protection agents in plastic materials. To a minor extent HCB was used as a chlorine donor, color enhancer and smoke intensifier in pyrotechnic compositions. Currently, HCB is an unintentional by-product of several industrial sectors where both chlorine and carbon are present. The concentration in the environment is mainly due to historical pollution and accumulation.[1] Further continuative information on the historic use, properties, and typical reaction schemes of HCB was recently published by Smith and Guest.[2]

HCB is controlled by a number of European regulations. The placing on the market and use of HCB as a plant protection product has been forbidden in the European Union since 1981 by the Council Directive 79/117/EEC prohibiting the placing on the market and use of plant protection products containing certain active substances.[3] The import and export of HCB was restricted by the Council Regulation (EEC) No 2455/92 of 23 July 1992 [4] and by the Regulation (EC) No 304/2003 of the European Parliament and of the Council of 28 January 2003.[5,1]

Advanced legislation on HCB was achieved, within the framework of the United Nations Environment Programme (UNEP), by the Aarhus Protocol (1998) to the 1979 Convention on long-range transboundary air pollution on POPs and the Stockholm Convention (2001) on POPs.[6] These international agreements establish a global regime for controlling POPs, including HCB, and aim at eliminating or reducing their use. They were implemented at the European level in 2004 by Regulation 850/2004,[7] which prohibited, among others, the production, placing on the market and use of HCB.

The Stockholm Convention sets out measures for the minimization and elimination of unintentional HCB emissions and was implemented at the European level by the Regulation (EC) 850/2004.[7,1]

At last HCB is totally banned (except for research) in Europe but can still be found as unintentional release or unintentional trace contaminant in products.

Within the scope of CLEEN – Chemicals Legislation European Enforcement Network – the project EUROPOP was launched in 2010 with the aim of investigating the content of HCB in fireworks (mostly imported from China). Within the EUROPOP project a threshold limit value of 50 mg HCB/kg was stated. This value is based on the waste provisions following Article 7 of the POPs regulation.[8] Some further information about a reasonable measurement threshold value of HCB in fireworks was recently published by Smith and Guest.[2] They also proposed a cut-off limit of 50 ppm (which corresponds to 50 mg kg^{-1}) in a colored star composition at which level analysis can conclude that the HCB has not been added deliberately. This value seems to be broadly accepted and applied by the market surveillance authorities and testing institutes in Europe.

The latest standardization developments in Europe have taken this issue into account. According to the Directive 2007/23/EC of the European Parliament and of the Council on the placing on the market of pyrotechnic articles[9] (article 8), European standardization bodies are requested to draw

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up or revise European standards in support of this Directive. Therefore, the European Committee for Standardization (CEN) set up the Technical Committee CEN/TC 212. This technical committee consists of five Working Groups (WGs), each corresponding to the different pyrotechnic categories. With regard to fireworks articles, working groups 1 (consumer fireworks of the categories 1–3) and 2 (display fireworks of category 4 for persons with specialist knowledge only) were established. Up to this date, the following standard series were published:

- "EN 15947 Pyrotechnic articles – Fireworks, Categories 1, 2, and 3[10]" consisting of 5 parts: 1—Terminology, 2— Categories and types of firework, 3— Minimum labelling requirements, 4—Test methods and 5—Requirements for construction and performance.
- "EN 16261 Pyrotechnic articles – Fireworks, category 4[11]" consisting of 4 parts: 1—Terminology, 2—Requirements, 3—Test methods and 4—Minimum labelling requirements and instructions for use.

In both relevant standard parts – EN 15947-5[10] and EN 16261-2[11] – the scopes are defined and it is stated that both standards do "not apply for articles containing pyrotechnic compositions that include any of the following substances": hexachlorobenzene and polychlorobenzene, respectively (amongst others). These lists of substances are not exhaustive and these substances are often referred to as "forbidden substances" in fireworks. Due to the fact that the absence of HCB is not explicitly given as a requirement in the subsequent chapters of these standard parts, connected with a specific test method or procedure, the experimental proof of the absence within conformity assessment procedures

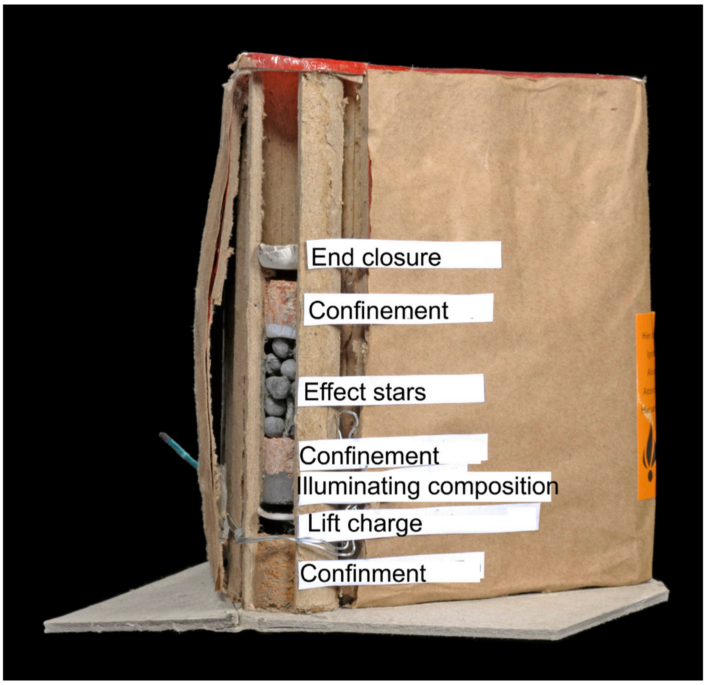

Figure 1. *Dismantled fireworks combination of category F2 (photo: BAM).*

Figure 2. *Dismantled fireworks rockets of category F2 (photo: BAM).*

applying these standards is not mandatory. However, some notified bodies under the Directive 2007/23/EC[9] carry out tests regarding HCB within EC type-examination procedures of fireworks. BAM as one of the notified bodies saw the need to implement a screening procedure for HCB within the type tests of fireworks. An analytical method for the quantification of HCB was developed and different pyrotechnic compositions of 49 firework articles have been tested to date. Figure 1 and Figure 2 show examples of dismantled fireworks articles during the type examination procedures at BAM.

This paper presents the main relevant results of the HCB screenings and gives comparison with results of other published studies.

Experimental set up

Fireworks articles

During a period of two years about 220 pyrotechnic compositions were analysed for HCB in the BAM laboratory. The samples were taken randomly from 49 firework articles. The fireworks articles belonged to the category F2 potentially presenting a low hazard and low noise level and which are intended for outdoor use in confined areas. Within this category the following fireworks types according to EN 15947-2[10] were part of this investigation:

- Batteries of shot tubes (various numbers of tubes),
- Batteries of fountains,
- Combinations of various types (e.g. shot tubes and mines),
- Fountains, and
- Rockets.

Analytical procedure

An analytical method was developed for the determination of HCB in fireworks on the basis of the procedures proposed by the CLEEN project EUROPOP[8] and the Austrian

Environmental Agency.[12] The procedure is described as follows.

Sample preparation

Depending on availability of the substance, masses of the pyrotechnic compositions of approximately 2 g to 7 g are weighed into a beaker. Distilled water is added to dissolve water-soluble compounds or to soften any starch based binder. Thereby, the subsequent crushing of larger composition particles is easier and safer. The water phase is separated by filtration and then discarded. During the developing of the analytical procedure the HCB content in the water phase was checked several times; HCB was not detected. After drying of the composition residue, an extraction with a mixture of hexane and acetone (1 : 1 v/v; approx. 50 mL) follows. The solvent is separated again by filtration.

Analytical measurement

For analytical measurement gas chromatography combined with mass spectrometry (GC-MS) was applied.

The prepared sample solution, as described above, is used for a first screening of the HCB amount. 50 µL of it are dissolved in 1 mL of a solvent mixture of hexane and acetone (1 : 1 v/v) and measured by GC-MS in SCAN-mode. If an HCB peak is detected in this first test, the assumption can be made that the HCB content of the pyrotechnic composition exceeds the threshold value of 50 mg kg^{-1} (considering the above mentioned sample mass and the volume of the prepared sample solution).

For quantification in SIM-mode the previously prepared sample solution must be diluted in an appropriate way to fit the concentration range, which is described by an HCB-calibration. HCB concentration lay between 0.1 µg HCB/mL and 2.5 µg HCB/mL for calibration. Six calibration levels were set. HCB with a purity of 99.8 area percentage GC (analytical standard) was used. As internal standard lindane ($C_6H_6Cl_6$, γ-hexachlorocyclohexane, analytical standard, 99.8 area percentage GC) was selected. It was dissolved in hexane to get a concentration of about 20 µg lindane/mL. An amount of 50 µL of the internal standard solution was added to the individual HCB solution.

The same amount of internal standard solution was added to the eventually diluted sample solution for the final quantification measurements. The measuring process was run in cycles, where each cycle consists of analysis of the pure solvent mixture (hexane : acetone, 1 : 1 v/v), threefold measurement of the sample solution, followed by analysis of the pure solvent mixture again. After 20 measuring cycles an already used calibration solution had to be analysed again. When a deviation of 10% or more was observed a new calibration had to be done. Method parameters are given below. The SCAN- and SIM-modes differed only in detection of selected ions. Whereas in SCAN-mode ions in the range of 20 amu to 550 amu were detected, in SIM-mode only the target and qualifier ions of HCB and lindane were of interest.

A typical GC-chromatogram with MS spectrum in SIM-mode is displayed in Figure 3.

According to the selected method parameters HCB was detected at a retention time at about 11.8 min, and the internal standard at about 12.7 min.

The limit of detection is lower than 5 mg HCB/kg pyrotechnic composition. The limit of quantification is generally lower than the limit value of 50 mg kg^{-1}.

For the determination of the recovery rate several pyrotechnic compositions, which were probably clear of HCB, were spiked with different HCB concentrations. The spiked samples were run through all steps of the procedure. A recovery rate of around 70 % was determined.

Table 1. *Method parameters of GC-MS*

Gas chromatograph (HP 6890 GC)	
Inlet conditions	230 °C, split-mode 100 : 1, sample volume 1 µL
Oven program	100 °C (hold time 2 min)
1st heating rate	15 K min^{-1} to 160 °C (holding time 0 min)
2nd heating rate	5 K min^{-1} to 280 °C (holding time 10 min)
Flow	Constant, 1 mL min^{-1} (carrier gas He)
Column	Nonpolar ((5%-phenyl)-methylsiloxane), length 30 m, ID 0.25 mm, film thickness 0.25 µm
Transfer line	300 °C

Mass spectrometer (HP 5973 MSD)	
Ion source	Electron impact ionization (70 eV), 230 °C
MS quadrupol	150 °C
SIM-mode	HCB target ion 284, qualifier 249, 282, 286
	Lindane (int. standard), target ion 181, qualifier 183, 217, 219

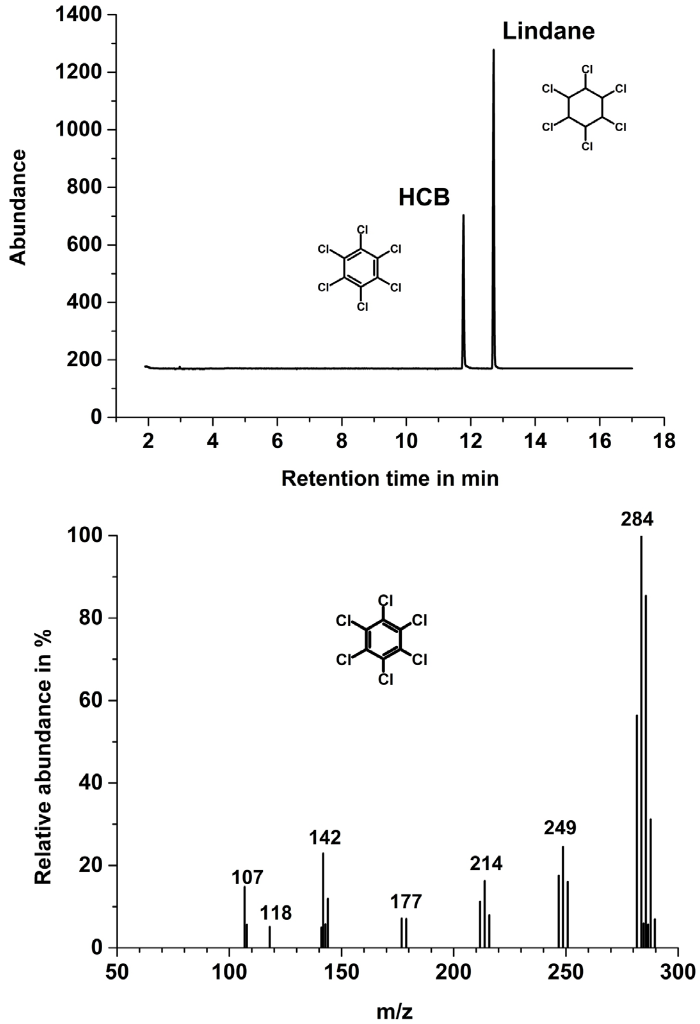

Figure 3. *Gas chromatogram of HCB and lindane (SIM-mode) and MS spectrum of HCB (SCAN-mode).*

Results and discussion

Within the EC type-examination procedures of fireworks according to the Directive 2007/23/EC[9] a screening for the so called "forbidden substances" was established at BAM. As well as some heavy metals or certain substance combinations with chlorates, HCB is among this group. For the EC type-examination the manufacturer provides a sample representative of the production envisaged. Mainly the effect charges (e.g. stars) were analysed in each article due to the enhanced probability of finding HCB, potentially added as a chlorine donor and color intensifier. Besides the effect charges also other parts of the firework articles were investigated, e. g. priming composition, bursting and lift charges. The main results are presented in Table 2, the detailed single values are illustrated in Figure 4.

As shown in Table 2 and Figure 4, HCB could only be detected for the effect charges. HCB was not found in primer, bursting or lift charges, as expected.

Detectable HCB concentrations could be analysed in less than 4% of the effect charges. Only four samples had HCB contents above the threshold value of 50 mg HCB/kg. Although the overall detection rate of this value of 1.5% is low, the observed overstepping of the threshold value was found to be very dramatic in these cases (2000 mg HCB/kg up to 8046 mg HCB/kg). These high concentrations indicate an intentional addition of HCB to the effect charge. As a consequence of this the respective EC type-examinations were refused for the articles concerned. The newly requested types have not shown any relevant HCB contamination.

In Table 3 the results for HCB in fireworks analysed within the scope of the EUROPOP project[8] are shown. The samples for this investigation were taken within the scope of market surveillance activities from fireworks articles which were already placed on the market, i.e. having been already type and batch tested by notified bodies and manufacturers/ importers in Europe.

The percentage of samples in which the limit value of 50 mg HCB/kg was exceeded was found to be 10% on average. The observed violations ranged from 62 mg HCB/kg up to 27 000 mg HCB/kg. The EUROPOP report[8] remarks that in only 13 cases was a legal action (e. g. product warning within the RAPEX notification system) taken.

The findings of the EUROPOP project differ strongly in comparison with the results of this work. The violation rate observed in the BAM survey (1.5%) is much lower than the violation rate observed in the EUROPOP project (10%). One reason for this is maybe the different sources of fireworks which were investigated. For the BAM screening fireworks articles were investigated which were subjected to EC type-examination procedures, and which might have been specially manufactured or selected for this examination and the addition of HCB was avoided. In contrast to this, the EUROPOP project investigated only firework articles which were already placed on the European market after being type and batch tested by either notified bodies or

Table 2. *Main HCB concentration results of the BAM screening*

Pyrotechnic composition	HCB concentration ranges		
	<5 mg HCB/kg	5 to 50 mg HCB/kg	>50 mg HCB/kg
Effect charges (total number of samples = 201)			
Number of samples matching the HCB ranges	194	3	4
Percentage	96.5 %	2.0 %	1.5 %
Priming composition, bursting charges, lift charges (total number of samples = 20)			
Number of samples matching the HCB ranges	20	0	0

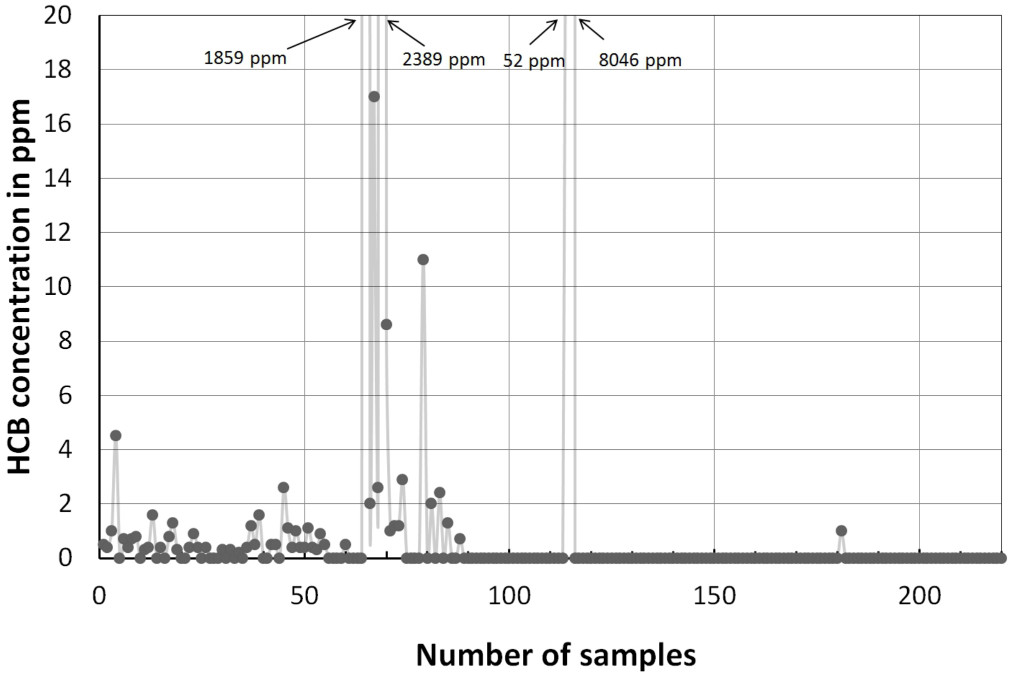

Figure 4. *HCB concentrations measured during the BAM screening.*

manufacturers/importers. One has to consider the fact that within batch test procedures no dismantling or chemical analysis is mandatory. A deliberate addition of HCB to the pyrotechnic compositions is likely to remain undetected during batch testing according to the current requirements as set out in the respective standard part EN 15947-5.

Taking the findings of this work and the referenced market surveillance activities into account, it might be worthwhile for the experts in the CEN/TC 212 (such as manufacturers, enforcement and notified bodies, market surveillance institutions), to reconsider if the experimental proof of the absence of some "forbidden" chemicals listed in the scope of the European EN 15947-5 like HCB should be included as a specific requirement for EC type-examinations and, more importantly, for batch tests performed within quality systems of the manufacturers and importers in Europe. Especially the inclusion within batch testing procedures would require significantly more efforts compared to the current situation, as dismantling of an article would be a necessary step before the actual screening could be carried out. However, these additional measures for consumer safety must be carefully weighed against the possible unnecessary burden for all included parties (economic operators and notified bodies). Future developments and market surveillance results in this field should therefore be carefully observed and assessed.

Table 3. *HCB contents in fireworks tested within the EUROPOP project*[8]

	Total number of samples	<5 mg HCB/kg Number	5 to 50 mg HCB/kg Number	>50 mg HCB/kg Number
Austria	22	18	4	—
Belgium	11	9	—	2
Denmark	74	41	24	9
Estonia	10	10	—	—
Finland	18	14	2	2
Germany	182	126	38	18
Iceland	22	17	1	4
Netherlands	3	2	1	—
Sweden	40	28	2	10
Switzerland	51	46	5	—
UK	6	6	—	
∑	439	317	77	45
Percentage		72.2%	17.5%	10.2%

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