A proposal to quantify trace levels of hexachlorobenzene in fireworks

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Abstract: *Hexachlorobenzene, a persistent organic pollutant, may be present in firework compositions from four sources. This paper makes a proposal to determine what "trace" quantities of hexachlorobenzene may be found in firework compositions, particularly those originating in the Far East where HCB usage was common and contamination still exists. Proposals are made to discriminate between deliberate use of HCB as an additive in firework compositions, as a deliberate "let down" agent in other colour enhancers and as an unintended trace contaminant.*

We propose a cut-off limit of 50 ppm in a coloured star composition at which level analysis can conclude that the HCB has not been added deliberately.

Furthermore the destruction of HCB in the normal functioning of the fireworks is considered and shown to reduce any residual amounts of HCB to extremely low levels.

Keywords: *HCB, Hexachlorobenzene, contamination*

Introduction and background

Hexachlorobenzene, C_6Cl_6 (HCB), also known as benzenehexachloride, phenylhexachloride and a variety of proprietary names, is a persistent organic pollutant regulated by international agreements[1] that ban its production and use. In recent years there has been considerable concern that HCB is being used in firework compositions imported into the EU and seizures of such goods have led to legal action being taken against the companies concerned and destruction of the fireworks by incineration.

This paper looks at the reasons why HCB has been used in firework compositions, the deliberate and accidental presence of HCB, and the likely fate of HCB in compositions that are functioned as fireworks.

HCB has been used in Far-Eastern manufacture of fireworks (despite China being a signatory to the Stockholm convention) and significant quantities of HCB have been found in Chinese fireworks imported into the EU in recent years. We are not aware of HCB being used in any European manufacture of fireworks.

The presence of HCB now

There are four possible mechanisms by which hexachlorobenzene could be present in firework compositions.

Although there have been some high profile cases where HCB has been found in specific firework compositions to about 6% extent, we believe that the deliberate use of HCB as a chlorine donor has effectively been stopped in all but a handful of cases.

However there remain four main possible sources of HCB in firework compositions:

- From its presence as a softening agent in some samples of PVC
- From the deliberate using up of HCB by firework manufacturers as a minor component of another chlorine donor. We believe that this is done primarily to use up stocks without having to pay high costs for destruction of

Article Details	*Article No: - 0092*
Manuscript Received:-10/11/2011	*Final Revisions:- 19/12/2011*
Publication Date:-20/12/2011	*Archive Reference:-1400*

Table 1. *Properties of chlorine donors*

Let down ratio	ppm in final star
1 : 1	50 000–150 000
1 : 10	5000–15 000
1 : 100	500–1500
1 : 1000	50–150
1 : 10000	5–15

HCB and because HCB is cheap. However it is unlikely that it would be practical to "let down" HCB into other chlorine donors in a ratio of less than 1 : 100 as the practical difficulties of so doing would outweigh the desire to use up HCB in this way;

- From trace contamination of other materials by HCB that has been used previously;
- As a result of HCB still being sprayed as a fungicide onto crops surrounding firework factories in China.

We believe that the first of these is rapidly diminishing as stocks are depleted, but that the second and third are impossible to prevent and the second mechanism will also be diminishing.

Deliberate "letting down" of other chlorine donors would typically lead to HCB concentrations as shown in Table 1.

For ease we shall consider the two mechanisms of unintentional trace contamination together.

Hence, by accidental contamination small quantities of HCB may still be found in firework compositions, in addition to the increasingly rare occurrences where it is apparent that HCB has been added deliberately in significant quantities to colour compositions.

Recent information from Denmark appears to highlight these extremes[2] – the Danish authorities are still finding some fireworks which contain HCB at levels which demonstrate that HCB must have been used deliberately as a chlorine donor in 5–10% of the relevant colour composition (usually green, blue or purple). The Danish authorities also identify another group where the levels are some 1000 times less in concentration – which appear to be those compositions where accidental contamination has occurred.

The historic use of HCB in firework compositions

Coloured firework compositions usually contain a "colour enhancer", added to the basic pyrotechnic composition, to increase the intensity of the coloured flame production by maximising the concentration of desirable coloured species (usually metal–halogen species) in the flame whilst minimising the production of undesirable species (i.e. ones that produce unwanted colours). For instance the copper–chlorine species produces a blue flame, whilst a copper–oxygen species produces a yellow/green colour.

Colour enhancers are usually chlorine rich organic compounds which decompose at the pyrotechnic burning surface (ca. 2000 °C) to produce chlorine radicals, hydrogen chloride and chlorine gas in the flame. Such "chlorine donors" include the following compounds as shown in Table 2.

For instance, for blue and green light colour production using copper carbonate (adapted from ref. 3) the reaction scheme to produce colour emitters is shown in Figure 1.

The simplified reaction mechanism for a firework composition for coloured light production has the

Table 2 *Properties of chlorine donors*

Chlorine donor	Formula	%Cl	Comments
Hexachlorobenzene (HCB)	C_6Cl_6	74	
Polyvinylchloride (PVC)	$(C_2H_3Cl)_n$	57	
Saran	$(C_2H_2Cl_2)_n$	73	
Parlon	$(C_5H_6Cl_4)_n$	68	
Hexachlorocyclohexane	$C_6H_6Cl_6$	73	Benzene hexachloride (BHC)
Dechlorane	$C_{10}Cl_{12}$	78	Poor fuel

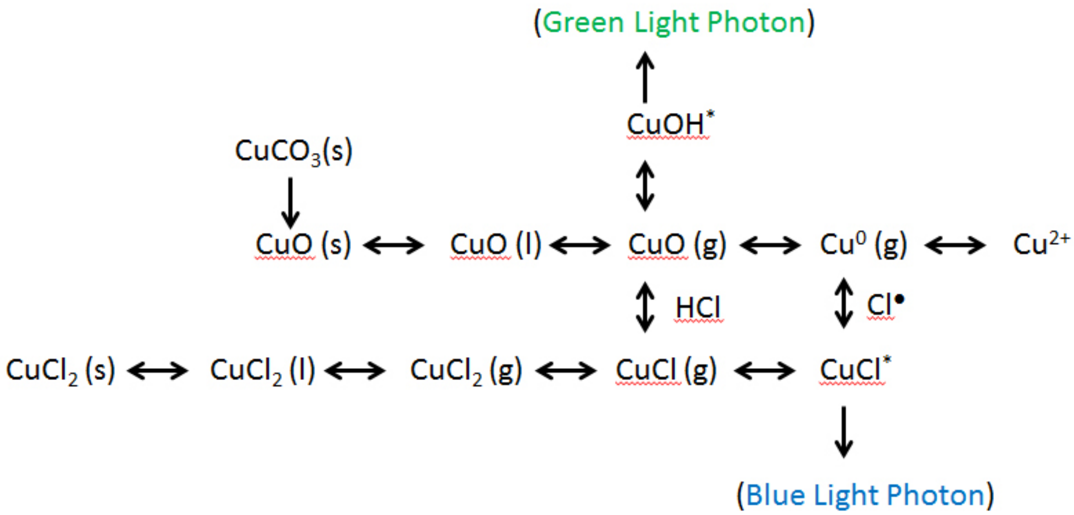

Figure 1. *Typical reaction scheme to give coloured light.*

form:

Oxidant + fuel → products + heat

Heat + coloured species in the flame → excited coloured species → light emission

The excited coloured species is normally shown thus: CuCl*.

A variety of oxidants have been used, but coloured light production appears only to be efficient if the flame temperature is above 2000 °C. The flame temperatures for a variety of common oxidants are shown in Table 3.

Hence the most common and most efficient (and relatively safe) oxidant used is potassium perchlorate ($KClO_4$).

The fuels used vary depending on the desired effect and the intensity and duration of the flame but typically include

- Aluminium
- Magnalium (a Mg/Al alloy)
- Red gum
- Shellac

Colour agents are added to the basic pyrochemical composition to produce metal–X species in the flame which emit colour at the flame temperature. These include the following metal salts:

- Copper oxide or copper carbonate – blue
- Strontium carbonate – red
- Barium carbonate – green
- Cryolite (sodium aluminium fluoride) – yellow

It is important to realise that it is not these compounds themselves which cause emission of coloured light. Instead it is the production of other metal containing species in the flame which are excited and subsequently emit coloured light.

Table 3. *Flame temperatures for compositions.*

Oxidant	%	Fuel	%	Flame temperature (C)	Comments
$KClO_4$	74	Shellac	16	2247	Most common oxidiser for colour compositions
NH_4ClO_4	76	Shellac	14	2207	Little used in fireworks
$KClO_3$	77	Shellac	13	2177	Sensitive compositions
KNO_3	72	Shellac	18	1697	Does not produce adequate colour

Colour enhancers and other additives

In addition to the base composition, typically 5–15% of a colour enhancer (chlorine donor) is added to the composition to enhance the production of the desirable metal–chlorine species as shown in Figure 1. Maximisation of this desirable copper–chlorine species (CuCl*) is required to produce blue light of high colour purity.

Note that Figure 1 shows the production of another excited copper species in the copper flame – the excited copper–hydroxy species CuOH* which emits green/yellow light on relaxation. It is essential in the generation of a pure blue colour to minimise the production of this species as blue and green/yellow lie on opposite sides of the emission chromaticity diagram and too much production of the latter colour will "wash out" the desired blue flame.

Lastly gums or resins are added to permit consolidation of the composition into stars.

Table 4 illustrates some typical coloured firework compositions for a variety of coloured stars.

Destruction of HCB by fire

The normal means[4] of destroying HCB containing items (including fireworks) is by controlled incineration at >1100 °C at which temperature the destruction of HCB is at least 99.99% efficient. As coloured firework compositions burn at >2000 °C we believe there will be an effective destruction of HCB in the coloured flame of a burning firework. It is the destruction of the chlorine donor to create chlorine radicals ($Cl^{\bullet}$) and hydrogen chloride (HCl) which leads to the generation of the desired excited metal–chlorine species in the flame (MCl*) which ultimately relaxes to give coloured light.

Calculations on trace HCB levels

We have made the following calculations for a variety of firework types containing blue stars contained within a multitude of other effects and as blue effects "alone". We have calculated the possible "worst case" release levels of HCB to the environment from the firework types shown in Table 5.

The weights and numbers of stars and resulting concentrations of HCB are shown in the following tables (Table 6 and Table 7).

We have made the following assumptions and conclusions from our calculations:

- That an HCB level of 50 ppm in the blue star composition is an acceptable "cut off" to prevent deliberate use or "letting down" of HCB as a chlorine donor in such compositions.
- That destruction of HCB in a firework flame is 100 times less efficient than in deliberate incineration – this is a very pessimistic viewpoint as the temperature of a burning firework composition exceeds the temperature used for incineration considerably.

The resulting maximum concentrations of HCB present in combustion by-products of these

Table 4. *Typical colour compositions.*

Component	Red star	Green star	Blue star	Yellow star	Purple star
Barium nitrate		50			
Potassium perchlorate	66	10	55	55	55
Copper oxide			15		11
Strontium carbonate	12				4
Cryolite				15	
Magnalium		13	6	6	
Charcoal	2				
Shellac/accaroid resin	13	7	9	9	9
Generic Chlorine donor	5	15	15	15	15
Generic Binder	5	5	5	5	5

These compositions are illustrative only and numbers do not refer to % values. Chlorine donors and binders may vary.

Table 5. *Description of firework articles*

Item #	Type	Category	Calibre (mm)	Contents
1	Cake	F3	20	Some blue stars
2	Cake	F3	30	Some blue stars
3	Cake	F4	30	Some blue stars
4	Cake	F4	45	Some blue stars
5	Rocket	F3	11	Some blue stars
6	Rocket	F3	19	Some blue stars
7	Shell	F4	75	Some blue stars
8	Shell	F4	150	Some blue stars
9	Cake	F3	20	All blue stars
10	Cake	F3	30	All blue stars
11	Cake	F4	30	All blue stars
12	Cake	F4	45	All blue stars
13	Rocket	F3	11	All blue stars
14	Rocket	F3	19	All blue stars
15	Shell	F4	75	All blue stars
16	Shell	F4	150	All blue stars

"Some blue stars" means typically a multi-coloured firework in which there is a proportion of blue stars. "All blue stars" means a firework whose primary effect is blue

Types and categories are as defined in EU Directive 2007/23/EC and Standards being derived from this Directive..

Table 6. *Analysis of "some blue stars" articles*

Item #	1	2	3	4	5	6	7	8
No of shots	16	50	100	200	1	1	1	1
Gross weight (Kg)	0.8	5	10	15	0.2	0.5	0.3	1.2
NEC (Kg)	0.15	0.8	2.5	4	0.05	0.3	0.15	1.0
Shots with blue stars	4	5	10	20	1	1	1	1
No of blue stars/shot	4	12	12	12	5	10	30	80
Number of stars per shot	8	12	20	15	20	50	50	100
Weight of individual star (g)	0.8	0.8	0.8	1.0	1.5	3.0	2.0	6.0
Total HCB per item (mg)	0.6	2.4	4.8	12.0	0.4	1.5	3.0	24.0
ppm HCB (overall NEC)	4.3	3.0	1.9	3.0	7.5	5.0	20.0	24.0
ppm HCB (overall – gross)	0.8	0.5	0.5	0.8	1.9	3.0	10.0	20.0

NEC = Net explosive content – the weight of pyrotechnic composition (including blackpowder) in a firework. Gross weight – the total weight of a firework including inert materials and tubes, but not including external packaging. Assumes 50 ppm HCB in blue star composition.

Table 7. *Analysis of "all blue stars" articles.*

Item #	9	10	11	12	13	14	15	16
No of shots	16	50	100	200	1	1	1	1
Gross weight (Kg)	0.8	5	10	15	0.2	0.5	0.3	1.2
NEC (Kg)	0.15	0.8	2.5	4	0.05	0.3	0.15	1
Shots with Blue stars	16	50	100	200	1	1	1	1
No of blue stars/shot	8	12	20	15	20	50	50	100
Number of stars per shot	8	12	20	15	20	50	50	100
Weight of individual star (g)	0.8	0.8	0.8	1.0	2.0	2.0	2.0	5.0
Total HCB per item (mg)	5.1	24.0	80.0	150.0	2.0	5.0	50.0	25.0
ppm HCB (overall NEC)	34.1	30.0	32.0	37.0	40.0	16.7	33.3	25.0
ppm HCB (overall – Gross)	6.4	4.8	8.0	10.0	10.0	10.0	16.7	20.6

NEC = Net explosive content – the weight of pyrotechnic composition (including blackpowder) in a firework. Gross weight – the total weight of a firework including inert materials and tubes, but not including external packaging. Assumes 50 ppm HCB in blue star composition.

examples are shown in Table 8 (Note – in parts per billion (ppb) of composition).

These concentrations are extremely pessimistic, and the following variations will all lead to significant reduction in potential HCB release:

- Increasing the efficiency of the destruction of HCB in a firework flame to that of an incinerator would reduce each by 100 fold.
- We have over-estimated the quantity of blue containing stars in the firework types (note use of HCB in stars other than blue is less likely).
- Concentrations of <50 ppm HCB are most likely from accidental contamination – the figure has been set as an upper limit which is easily determined by analytical means but which precludes the deliberate use of HCB. Contamination at single figure ppm levels would result in the final concentrations being reduced by a factor of at least 100.

Hence for typical fireworks, with only trace contamination of HCB the final concentration of HCB in combustion by-products is likely to be in the region 0.003 ppb to 0.06 ppb (Table 8).

Dispersion issues

The normal functioning of fireworks in open spaces leads to very high dilution of combustion by-products. The likely residual concentration of HCB into the local or remote environment is likely to be very significantly lower that the preexisting background levels[5] of up to 0.35 ng g^{-1} (= ppb).

EU harmonised standards for fireworks

Following the publication of Directive 2007/23/EC on the placing on the market of pyrotechnic articles, the EU Commission gave a mandate to CEN to produce harmonised standards for pyrotechnic articles, including fireworks. One such standard has been published, EN15947 for Categories 1, 2, and 3 fireworks; the harmonised standard for Category 4 fireworks (prEN16261 part 1 to 4) is expected to be published in the next few months. The Directive requires all fireworks to comply with an essential safety requirement, and for this to be confirmed by a Notified Body, prior to placing the fireworks on the market. Compliance with a harmonised standard is the usual method against which compliance with the essential safety requirement is determined.

Fireworks containing hexachlorobenzene are specifically excluded from the scope of EN15947 and prEN16261, and accordingly its presence or not is likely to be verified by Notified Body testing as part of the approval process and any fireworks containing HCB will not be authorised for placing on the market.

Table 8. *Residual HCB after firework functioning*

Item #	Maximum residual HCB (ppb) Pessimistic calculations	Maximum residual HCB (ppb) Realistic calculations
1	6.4	0.006
2	4.5	0.005
3	2.9	0.003
4	4.5	0.005
5	11.2	0.011
6	7.5	0.007
7	30.0	0.030
8	36.0	0.036
9	51.2	0.051
10	45.0	0.045
11	48.0	0.048
12	56.8	0.057
13	60.0	0.060
14	25.0	0.025
15	50.0	0.050
16	37.5	0.038

Realistic values allow for destruction of HCB in the flame.

Regulations on persistent organic pollutants

Regulation (EC) No 850/2004 on Persistent Organic Pollutants and Regulation (EC) No 1195/2006[6] amending Annex IV to Regulation (EC) No 850/2004[7] are the Regulations which control the use of HCB in the European Community. The relevant parts are:

Article 3. 1. which states:

"The production, placing on the market and use of substances listed in Annex I, whether on their own, in preparations or as constituents of articles, shall be prohibited."

Annex I lists hexachlorobenzene as a prohibited substance.

Article 4. 1. **(b)** exempts

"a substance occurring as an unintentional trace contaminant in substances preparations or articles."

However there is no definition of what level may be regarded as "trace", but Article 7, through Annex IV (as amended by Regulation No 1195/2006), exempts waste containing less than 50 ppm of hexachlorobenzene from the usual disposal requirements for HCB.

We propose therefore to use 50 ppm as the trace threshold in Article 4.1.(b).

Proposals

We propose the following:

Concentrations of HCB in individual coloured firework compositions of less than 50 ppm of the coloured star composition can be considered as trace or accidental contamination. This level equates to 0.8ppm - 20ppm by gross mass for fireworks containing "some blue stars" and 4.3ppm - 20.0ppm for fireworks containing "all blue stars" - hence we propose that 25ppm of the gross weight of the firework would be an appropriate cut off level for ease of carrying out the test.

Concentrations over 100 ppm of the gross weight of the firework should be subject to the same controls as at present and be regarded as deliberate use of HCB as a chlorine donor, or the deliberate "letting down" of HCB into other chlorine donors to diminish stocks.

Concentrations of between 25 ppm and 100 ppm of the gross weight of the firework should be subject to further investigation before action is taken.

Thus a crude test could be to examine the total HCB per gross mass of the firework. In terms of % HCB per gross mass of the overall firework these limits are obviously reduced significantly but the extent depends on the exact type and colour/effect of the relevant firework.

In cases where accidental contamination of equipment, non-explosive parts (e.g. cases) and other, non-colour, compositions has occurred these are likely to be below the 50 ppm limit imposed by the POP waste provisions. We are not aware of any evidence at present to suggest this is a significant contributor to HCB content in fireworks.

Conclusions

We have proposed a cut-off for the distinction between the deliberate use of HCB in firework compositions and the deliberate "letting down" of HCB into other chlorine donors, and the accidental presence of HCB in firework compositions from contamination. We suggest that the proposed limit is a sensible and pragmatic solution to the problem of accidental contamination and should be adopted across the EU.

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