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RELEASE OF POLYCHLORINATED DIBENZO-P-DIOXINS AND DIBENZOFURANS BY SETTING OFF FIREWORKS

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ABSTRACT

Selected pyrotechnic articles were set off under laboratory conditions. Residues and vapors of smoke as well as unburnt charges were analyzed for polychlorinated dibenzo-p-dioxins, dibenzofurans (PCDD/F) and their precursors chlorinated benzenes and phenols. The contamination of the selected products with these organic xenobiotics proved to be very variable. Remains of fireworks contained octachlorinated dioxins and furans up to 142 ng I-TEQ/kg as well as hexachlorobenzene in the range of 0.05 to 1,400 mg/kg. The deflagration of detonating compositions usually resulted in a dispersion of contaminants, whereas continuously burning flare compositions partially led to a thermal decomposition of organic pollutants. A significant rate of formation of polychlorinated dioxins and furans was observed when setting off blue-lightning rockets and fountains. Further investigations revealed that even high temperatures during the deflagration of black powder charges could not suppress the formation of PCDD/F from appropriate precursors. © 1999 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Setting off fireworks during New Year's Eve is a widespread tradition. In Germany, approximately 30,000 tons of fireworks valued at about 80 million US\$ are set off annually. Nowadays, crackers, fountains and rockets do not only contain black-powder. To produce exciting effects and illuminations, modern

pyrotechnic compositions usually contain a great variety of admixtures. Among those are substances such as chlorine-based oxidizers, flame-colouring copper salts and pulverized polyvinylchloride, whose key positions in dioxin-forming processes are well known [1, 2]. Hitherto, due to high temperatures up to 2,500 °C accompanying the deflagration of pyrotechnic compositions, the formation of organic pollutants was considered to be unlikely. However, PCDD/F are mostly not generated in the centre of combustion zones but in adjacent areas of lower temperatures and longer dwell times. Therefore, the cooling period of the deflagration products has to be included in the theoretical considerations too, since smoke and ashes pass a temperature range in which dioxin formation is possible.

DYKE and COLEMAN [3] reported on a fourfold increase of PCDD/F concentration in ambient air during a celebration which was accompanied with fireworks and bonfires. The main objective of this work was to perform a laboratory-scale analytical investigation to find a relation between contamination of several pyrotechnic compositions and a possible environmental pollution by setting off fireworks.

EXPERIMENTAL

Seven different compositions were selected in order to cover the usual tender of articles. The selection was based on the kind of effect (e. g. crackers, light-rockets or sparkling fountains) besides the flame colour of light-rockets, which had influence on the content of de-novo-catalyst copper (Table 1). All fireworks, partly made in China and obtained from a German wholesaler were certified by German authorities.

Table 1. Selected pyrotechnic products with flame colour and copper content of the charge

Product	flame colour	Cu [mg/kg]
Firecracker	none	< 10
Cone Fountain	green / silver	23
Jumping Jack	none	28
Whistler	none	< 10
Sparkling Rocket	blue / gold	10,300
Roman Candle	green / red / yellow	21
Four-Colour Fountain	blue / green / red / yellow	up to 1,200

Unburnt products were manually separated into paper cartridges and charges. 1 to 10 specimen according to their masses were deflagrated in a 0,125 m³ steel chamber. Samples of gaseous emissions were taken using a rotary vane pump connected with a glass tube equipped with two polyurethane foam (PUF) plugs, which had been sequentially refluxed with methanol, dichloromethane, toluene and acetone and vacuum-dried before use. Solid residues (e.g. ashes and teared paper cartridges) were collected and wiping samples of the inside chamber surfaces were taken using toluene impregnated tissues. Blank samples of the chamber surface, the PUF plugs and the extraction equipment were taken for quality control.

All samples were analyzed for PCDD/F as well as for chlorinated benzenes and phenols. In order to determine PCDD/F and chlorinated benzenes the samples were extracted with toluene for 16 hours followed by a multicolun clean-up procedure described by HAGENMAIER et al. [4]. For determination of chlorinated phenols the unburnt samples were extracted with methanol for 12 hours and derivated with acetic anhydride [5]. The separation and quantification were carried out on a Hewlett-Packard 5890 II/5970 gaschromatograph / mass spectrometer using a J & W DB-5 capillary column. PCDD/F were quantified using ¹³C-labelled compounds (Promochem) as internal standards (isotope dilution method). External standards (Supelco, Riedel-de-Haën) were used for quantification of chlorobenzenes and chlorophenols. The determination of copper was carried out on a Jobin-Yvon JY 70 Plus ICP atomic emission spectrometer after acid digestion.

RESULTS

The contaminations of unburnt products are shown in Table 2 and 3. The reported PCDD/F concentrations are not converted into toxic equivalents. The only detectable congeners of PCDD/F were octachloro-dibenzo-p-dioxin and -furan as well as small amounts of heptachlorodibenzo-p-dioxin at strongly varying ratios. The detection limit for lower chlorinated PCDD/F was 10 ng/kg for each congener. Chlorobenzene pattern and concentrations were found to be variable too, whereas nearly no chlorophenols could be detected apart from pentachlorophenol in the cartridges in a range which is typical for paper products.

Table 2. Ranges of detected contaminations with chlorinated benzenes and pentachlorophenol in selected pyrotechnic products

	paper cartridges	charges
Chlorobenzenes (total)	< 5 ... 770 µg/kg	< 5 ... 52,000 µg/kg
Hexachlorobenzene	< 5 ... 770 µg/kg	< 5 ... 1,100 µg/kg
Pentachlorophenol	< 1.25 ... 219 µg/kg	< 1.25 µg/kg

Table 3. Residues of hepta- and octachlorinated dibenzo-p-dioxins and -furans in paper cartridges and charges of selected pyrotechnic products [ng/kg]

Product	paper cartridge			charge		
	HpCDD	OCDD	OCDF	HpCDD	OCDD	OCDF
Firecracker	16	322	79	< 10	535	26
Cone Fountain	111	384	22	< 10	< 10	< 10
Jumping Jack	< 10	33	24	< 10	28	< 10
Whistler	22	353	121	< 10	35	1,200
Sparkling Rocket	30	129	12	< 10	13	< 10
Roman Candle	< 10	426	39	< 10	< 10	22
Four-Colour Fountain	< 10	18	< 10	< 10	< 10	< 10

The results of the deflagration experiments show differences between the distinct types of products too. Detonating fireworks such as firecrackers or Jumping Jacks had nearly the same content of PCDD/F as before set off (Figure 1). Most of the impurities were detected in solid residues and only a smaller part was found on PUF plugs and in wiping samples indicating that pollutants were mostly not transferred into the

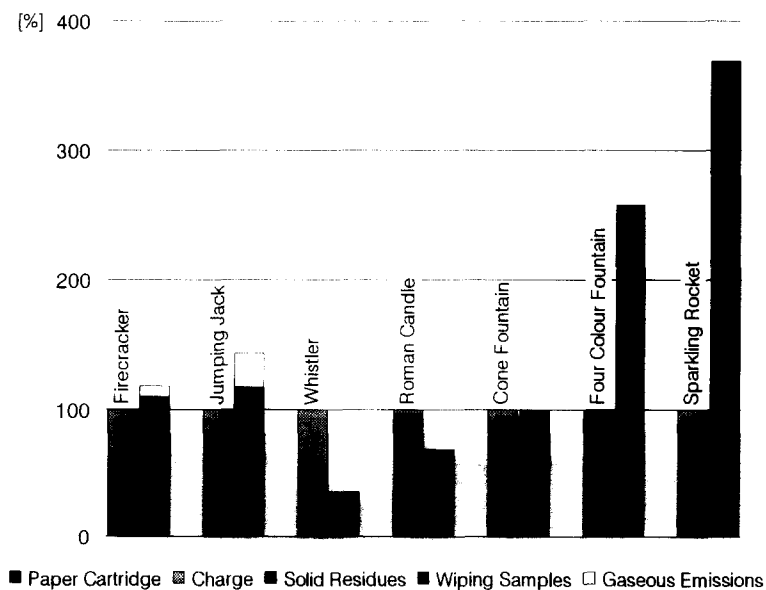


Figure 1. Residues of hepta- and octachlorinated dioxins and furans in pyrotechnic products before (100 %) and after set off

gaseous phase during explosion (Figure 2). Other fireworks like whistlers or roman candles, whose complete deflagration lasted several seconds, showed a decrease of contamination because of a decomposition of organic impurities in the charge. In this case the pollutants were transferred nearly quantitatively to solid residues. No PCDD/F could be measured in gaseous emissions (Figure 3), while chlorobenzenes showed a similar behaviour.

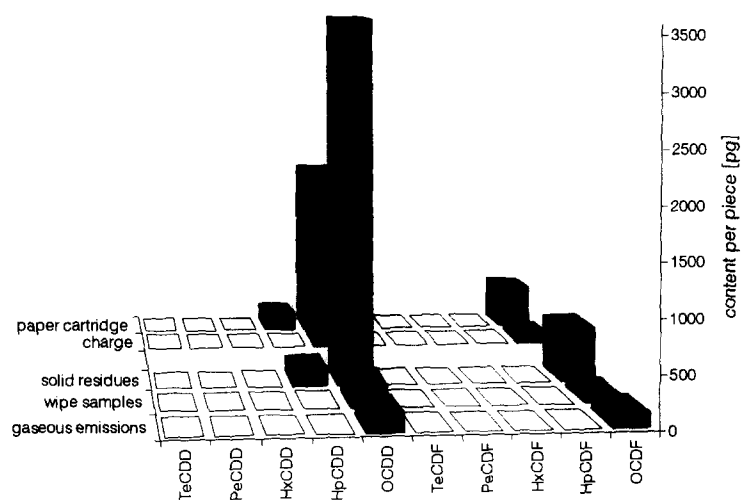


Figure 2. Characteristic congener pattern of detonating fireworks before and after set off (here: firecracker)

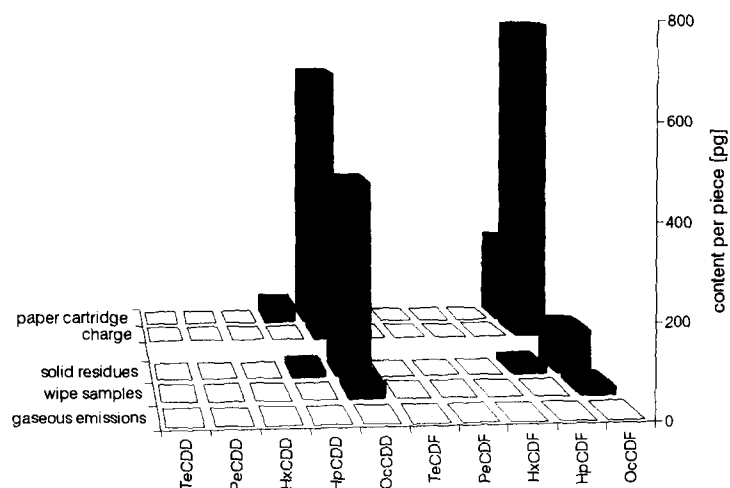


Figure 3. Characteristic congener pattern of continuously burning fireworks before and after set off (here: whistler)

A completely different effect was observed on deflagrating blue-lightning fireworks with a typical high copper concentration of the charge (Table 1). In contrast to the other described fireworks which showed no increase of PCDD/F contamination caused by deflagration, the set-off of the sparkling rocket resulted in a distinct increase of hepta- and octachlorinated congeners and detectable concentrations of the lower chlorinated ones (Figure 4).

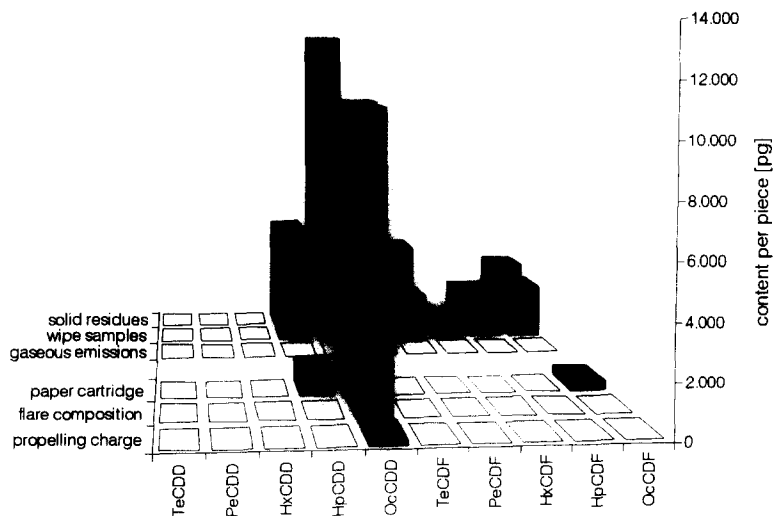


Figure 4. Distribution and congener pattern of a blue-lightning sparkling rocket before and after set off

In another experiment the charges of firecrackers were fortified with 500 $\mu\text{g/g}$ hexachlorobenzene or 500 $\mu\text{g/g}$ pentachlorophenol respectively. After removal of the injected solvent at 50 $^{\circ}\text{C}$ overnight the crackers were deflagrated. The residues were analyzed and the results were compared with those found in experiments with unfortified charges. Whereas no increase of PCDD/F content was observed by setting off crackers fortified with hexachlorobenzene, the presence of pentachlorophenol during deflagration led to a plain growth of dioxin content (Figure 5). An eightfold increase of OCDD and a more than 17-fold increase of HpCDD could be observed whilst the PCP reagent used for dotation was only contaminated with negligible amounts of OCDD.

The appearance of all three isomers of tetrachlorophenol in the residues of PCP treated crackers indicates the occurrence of dechlorination processes during deflagration. Neither residues of undotated charges nor pentachlorophenol used for dotation contained significant amounts of tetrachlorophenols. Condensation of tetrachlorophenols and PCP probably led to the formation of HpCDD.

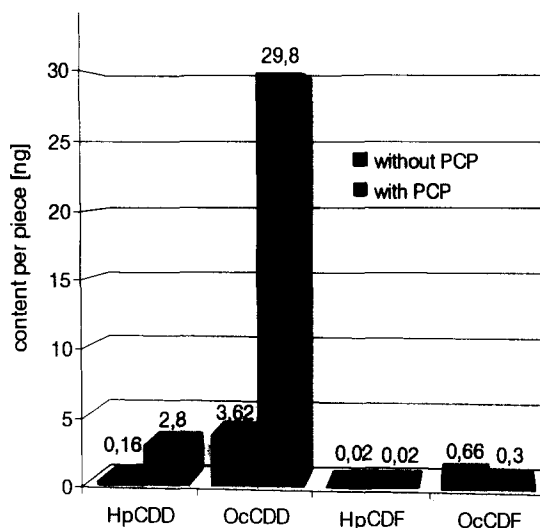


Figure 5. Concentration of several congeners after deflagration of unfortified and fortified firecrackers (500 µg/g PCP)

DISCUSSION

Concerning the emission of PCDD/F, the majority of the investigated pyrotechnic products proved to be harmless. The typically very small amounts of contaminations are only transferred from one sink (raw materials, paper) into another (ashes, residues). The extremely toxic 2,3,7,8-TCDD could not be detected in any of the samples. No indications were found that PCDD/F emissions from fireworks may cause air pollution. We expect that the increased background concentration detected by DYKE and COLEMAN [3] was mainly due to bonfires, not to fireworks.

Nevertheless, the increase of PCDD/F amounts following the deflagration of blue lightning articles indicates an influence of added copper salts for flame colouring upon the formation of PCDD/F. The major part of pollutants was found to be formed on ash particles as it is known from de-novo-synthesis [6]. By preparing several compositions with pentachlorophenol, it could be exemplified that even under extreme conditions at high temperatures and short reaction and cooling times PCDD/F can be formed from organic precursors. In contrast to PCP, hexachlorobenzene did not cause the formation of measurable traces of PCDD/F under comparable conditions. Chlorobenzenes can only combine to form PCDD/F after conversion to chlorophenols. This additional step might cause a lower conversion rate. Since the PCP content did not reach a level of 500 µg/g in any of the investigated products and the conversion ratio amounted to only 10^{-5} , these results are more of mechanistical rather than of environmental relevance.

However, one mixed sample representing typical pyrotechnical requisites that was collected in the streets of Hannover, Germany, on New Year's Day 1996, showed high concentrations of PCDD/F (104 µg/kg) and HCB (1,400 mg/kg). This single result shows that the control of product quality is still an important task to improve product safety on the one hand and waste disposal on the other hand.

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