Chemical Analysis of Consumer Fireworks

Per Alenfelt
Hansson PyroTech AB, Box 93, S-427 23, Billdal, Sweden
E-mail: p.alenfelt@hansson-pyrotech.com

ABSTRACT

A chemical analysis of a selection of fireworks has been made. The products were chosen to represent the typical use of consumer fireworks in Sweden 1998. The purpose of the assignment was to estimate to what extent consumer fireworks contribute to the total emission of some undesirable elements in Sweden.

Six consumer items were examined (two of them being multi item kits). Nineteen elements were analyzed, but focus was made on the environmentally undesirable elements arsenic, cadmium, lead and mercury.

The conclusion was that, as far as arsenic, cadmium and mercury are concerned, the contribution from consumer fireworks is insignificant compared with the total emission and deposition within the country.

The emission of lead, which is a well-known constituent in crackling fireworks effects, can at most be 0.8 % of the total emission and deposition in the country.

The figures in this paper do not provide any evidence in favor of restricting the lead content of fireworks.

Keywords: chemical analysis, fireworks, environment, pollutant, arsenic, cadmium, lead, mercury, crackling

Introduction

Fireworks and the Environment

Paracelsus (1493-1541) wrote[1] "What is there that is not a poison? All things are poison and nothing (is) without poison. Solely the dose determines that a thing is not a poison." This is the most fundamental and pervasive concept in toxicology.

When a fireworks composition is burned most of its ingredients react to produce energy and new solid and gaseous substances. The solid substances are spread in the air and will, sooner or later (depending on particle size and weather conditions), deposit on the ground. The actual bioavailability of elements from pyrotechnic emissions has not been determined and is not part of this study.

Focus was made on arsenic, cadmium, lead and mercury, since these elements are universally known to be the most toxic and most damaging of the environmental pollutants.

The Pyrotechnic Investigation

After years of lively debate concerning the connection between consumer fireworks and environmental problems the Swedish government started an official investigation[2] aiming to shed light on the subject. Hansson PyroTech AB got the assignment to estimate the total emission of some environmentally undesirable elements from consumer fireworks in Sweden during 1998.

The work was based on the following assumptions:

- Consumer fireworks were sold for 250 million SEK (about US$30 million) in Sweden during 1998[3].
- The consumer got 1 g of pyrotechnic composition per SEK.
- The chosen products were representative samples of what was typically being fired.

Table 1: Total Weight and Net Explosive Weight of Analyzed Consumer Fireworks Products.

No.	Total Wt. (g)	Net explosive Wt. (g)	Description
1	401	139.2	7 rockets (5 different types)
2	803	143.8	7 rockets (4 different types) + 2 mini cakes
3	652	180.0	25-shot cake
4	729	158.5	25-shot cake
5	4807	689.0	52-shot cake
6	2283	371.5	95 mm shell in mortar

Experimental

Elements

A standard package of 19 elements was chosen for quantitative analysis:

Aluminium (Al)	Lead (Pb)
Arsenic (As)	Magnesium (Mg)
Barium (Ba)	Manganese (Mn)
Boron (B)	Mercury (Hg)
Cadmium (Cd)	Nickel (Ni)
Calcium (Ca)	Phosphorus (P)
Chromium (Cr)	Potassium (K)
Cobalt (Co)	Strontium (Sr)
Copper (Cu)	Zinc (Zn)
Iron (Fe)	

Choice of Products

The products should represent what was typically being fired in Sweden during 1998. With support from representative sales figures, six popular consumer products were chosen for analysis, see Table 1.

All products were produced in China.

Sample Preparation

The items were dissected, and all pyrotechnic compositions were weighed and documented. See Table 2 for the rough distribution of pyrotechnic compositions in each item.

Table 2: Rough Distribution of Pyrotechnic Compositions. (Numbers in Weight Percent**.)**

Composition	1	2	3	4	5	6
Fuse powder	2	3	2	2	3	2
Motor powder	39	44	—	—	—	—
Lift charge	—	—	25	33	21	13
Burst charge	6	2	4	4	17	31
Blue	—	—	11	6	—	—
Crackling	24	—	—	—	—	—
Glitter	6	20	—	—	21	—
Gold	—	21	20	—	17	—
Green	13	—	22	—	—	—
Red	7	—	16	—	—	—
Silver	—	4	—	55	21	2
Strobe	—	6	—	—	—	52
White	3	—	—	—	—	—

The samples were representative mixtures of the total pyrotechnic content of each firework. The compositions from each product were prepared for analysis by grinding and were mixed by sieving.

Analysis

A certified analytic laboratory[4] analyzed the samples.

The method involved the following steps:

- Dissolution of the samples in concentrated nitric acid in a microwave oven.
- Removal of insoluble matter by filtration.
- Analysis by Inductive Coupled Plasma spectroscopy (ICP). For technical reasons

Table 3: Results of Chemical Analysis of Six Different Fireworks Products.
(Amounts in g per kg pyrotechnic composition.)

Element	1	2	3	4	5	6	Mean Value
Al	36	32	59	54	64	43	48
As	0.0024	0.044	0.013	0.010	0.046	0.0030	0.020
Ba	38	12	26	51	37	72	39
B	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10	<0.10
Cd	0.0032	0.020	0.0037	0.0044	0.021	0.0035	0.0093
Ca	2.4	3.4	0.85	0.72	0.88	0.57	1.5
Cr	0.028	0.95	0.0076	0.0078	0.5	0.0068	0.25
Co	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003	<0.003
Cu	10.9	0.75	23	10.4	0.77	0.31	7.7
Fe	1.3	9.2	0.58	0.57	0.25	1.4	2.2
Pb	46	3.2	6.8	2.5	5.3	0.037	11
Mg	21	22	27	30	32	42	29
Mn	0.23	0.5	0.099	0.11	0.25	0.12	0.22
Hg	0.00032	0.00044	0.00019	0.00027	0.00051	0.00018	0.00032
Ni	0.012	0.808	0.0086	0.0082	0.02	0.036	0.15
P	<0.10	<0.10	0.16	<0.10	<0.10	<0.10	<0.11
K	160	190	170	160	180	140	167
Sr	3.2	0.056	9.7	0.096	3.8	0.34	2.9
Zn	0.82	1.5	1.4	1.4	2.5	0.44	1.3

arsenic and mercury were determined by Atomic Fluorescence Spectroscopy (AFS).

General descriptions of the methods can easily be found in any book of analytical chemistry.[5]

Results

The results from the analysis are shown in Table 3. The amounts are shown as gram of pure element per kilogram of pyrotechnic composition.

Table 4: Estimated Discharge of Selected Elements from Consumer Fireworks in Sweden 1998.
(Amounts rounded off to one significant figure.)

Element	kg	Element	kg	Element	kg
Al	10,000	Co	<1	Ni	40
As	5	Cu	2000	P	<30
Ba	10,000	Fe	600	K	40,000
B	<30	Pb	3000	Sr	700
Cd	2	Mg	7000	Zn	300
Ca	400	Mn	60		
Cr	60	Hg	0.1		

Table 5: Estimation and Comparison of Discharge from Consumer Fireworks to Total Emission of Arsenic, Cadmium, Lead and Mercury in Sweden 1998.

	Arsenic	Cadmium	Lead	Mercury
To air[7]	1300 kg	780 kg	38,000 kg	880 kg
To water[8]	830 kg	1800 kg	13,000 kg	920 kg
Hunting[9]	—	—	164,000 kg	—
Deposition[10]	10–60,000 kg	10–20,000 kg	170–760,000 kg	10–30,000 kg
Consumer Fwks.	5 kg	2 kg	3000 kg	0.1 kg
Contribution from consumer fwks. in %	0.008–0.04 %	0.009–0.02 %	0.3–0.8 %	0.0003–0.0008 %

With support from the initial assumptions, the amount of consumer fireworks sold in Sweden during 1998 corresponds to a net explosive weight of 250,000 kg. Table 4 shows the calculated total amounts rounded off to one significant figure.

Discussion

Comparison with the Total Discharge in Sweden

To judge the impact of the discharge from consumer fireworks correctly, it is important to compare it with other sources of pollution. The emission of toxic metals is steadily decreasing. For example, the emission of lead has drastically decreased since lead-free gasoline was introduced. The problem is that Northern Europe receives enormous amounts from Middle and Southern Europe as deposition with rain and snow. In Table 5 the discharge from consumer fireworks is compared to the total emission and deposition of arsenic, cadmium, lead and mercury in Sweden.

The deposition in Sweden is very difficult to estimate due to uneven distribution of the fallout and because of the randomly spread control stations in the northern parts of the country.

Table 5 clearly shows that as far as arsenic, cadmium and mercury are concerned, the contribution from consumer fireworks is insignificant compared to the total emission and deposition within the country. The levels are so low that it is very doubtful that the elements are added to the fireworks on purpose. Most probably they are introduced inadvertently as impurities.

The emission of lead, which is a well-known constituent in crackling fireworks effects, can at most be 0.8 % of the total lead emission and deposition in the country.

The figures in this paper do not provide any evidence in favor of restricting the lead content of fireworks. If all lead from fireworks were eliminated, there would be no measurable difference in the lead pollution of Sweden's environment. There may well be very good reasons for not having lead in consumer fireworks, but, on the evidence of this paper, increased environmental pollution is not one of them.

Increased Sales during 1999

Since the sales probably were doubled during 1999 it is reasonable to believe that the emission of metals from the firing of consumer fireworks also was doubled. It is furthermore believed that at least half of the fireworks sold during 1999 were fired on New Years Eve. This could mean that 3000 kg of lead were discharged from consumer fireworks that single night. The emission from display shows was probably of the same magnitude.

Comments

Low Level Elements

Commercial pyrotechnic formulations seldom contain ingredients at levels below 1 weight percent. Some exceptions are stabilizers (boric acid, chromates) and free-flow agents (amorphous silica). The levels in table 3 imply that consumer fireworks from China do not contain ingredients based on As, P, Cd, Ca, Co, Hg, Mn, Ni or Zn. Metal powders used in pyrotechnics are often of low purity, which can explain the presence of Co, Mn, Ni and Zn, which all are common alloying additives.

Amounts of Barium and Strontium

In Table 4 the amount of strontium seems surprisingly low compared to the amount of barium. The distribution of red and green effects is usually equal in consumer fireworks, which implies that the amounts should be of the same magnitude. It is possible that the chosen products were not representative in the red/green distribution, but there are some other possible explanations of the difference. First of all, Chinese green stars are usually made with about 50 % barium nitrate whereas red stars are usually made with about 20 % strontium carbonate. Also taking in account of the difference in density (green stars are often a little heavier) the Sr/Ba ratio should be about 1/3. Furthermore barium nitrate is used for other effects than just green stars. Chinese recipes for glitter, silver, strobe and white stars also contain barium nitrate.[10]

Consumer fireworks in Sweden

Compared to other countries in the Northern Europe, Sweden has a rather liberal fireworks regulation. Anyone of at least 18 years of age can buy shells up to 100 mm, cakes with a net explosive weight up to 1000 g and rockets with a net explosive weight up to 250 g.

The reason for this is that most of the country is thinly populated, and, even in the bigger cities, open space is never far away. However, a special permit is required from the police when shooting inside city borders.

References

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