THE ANALYSIS OF TEAR GAS IN HONG KONG

The Review of Dioxins in Tear Gas

Abstract

Recently, more and more people discuss whether the tear gas, especially made in china will decompose into any dioxins under the high heating temperature. As the discussion is highly controversial, we have studied several research papers and consulted the scholars in order to provide the literature review plus the technical and professional comments first on the further studies due to the limited laboratory equipment, so that our teams or someone can try the suggestion to find out more answer on this in the future.

HKGETV (Chinese Name: 香城教育電視)

Facebook, Instagram, Twitter, Telegram: @HKGETV

November 28, 2019 | HKGETV

Introduction

Dioxins and dioxin-like compounds (DLCs) are the chemicals that are highly toxic environmental persistent organic pollutants (POPs), some of those compounds such as 2,3,7,8-Tetrachlorodibenzodioxin (TCDD) which can let people suffer from Chloracne or Cancer due to the long-term exposure with certain concentration. Dioxins and DLCs are mostly come from municipal waste combustion, metal smelting, oil refining and process. Sometimes the forest fire can emit dioxins. There's a rumor saying that when Hong Kong Police Force fires the tear gas, the Dioxins and DLCs will be produced due to the decomposition of 2-Chlorobenzalmalononitrile (CS) under high temperature. Furthermore, one reporter also claimed he was diagnosed with Chloracne by a Chinese medicine practitioner. Generally, Chloracne results from over-exposure to certain halogenated aromatic compounds, such as polychlorinated biphenyls (PCBs), polychlorinated dibenzofurans (PCDFs) and Dioxin.

Literature reviews

Dioxins and DLCs are a group of compounds. The most dangerous compound is 2,3,7,8-Tetrachlorodibenzodioxin (TCDD). According to the technical support documents of World Health Organization (WHO) about 'cancer potency factors, appendix C- Use of the Toxicity Equivalency Factor (TEFWHO-97 and TEFWHO-05) Scheme for Estimating Toxicity of Mixtures of Dioxin-Like Chemicals', TCDD is the most dangerous compound (The highest TEF mean highest dangerous, maximum is 1).

Dioxin samples:				San Bernardino 11/27/88 (a)				Marion Co. incinerator (b)			
Congener	I-TEF	WHO-97 TEF	WHO-05 TEF	pg/m^3	I-TEQ	WHO-97 TEQ	WHO-05 TEQ	pg/m^3	I-TEQ	WHO-97 TEQ	WHO-05 TEQ
2,3,7,8-TCDD	1	1	1	0.0106	0.0106	0.0106	0.0106	81	81	81	81
1,2,3,7,8-PeCDD	0.5	1	1	0.048	0.024	0.048	0.048	9	4.5	9	9
1,2,3,4,7,8-HxCDD	0.1	0.1	0.1	0.076	0.0076	0.0076	0.0076	7	0.7	0.7	0.7
1,2,3,6,7,8-HxCDD	0.1	0.1	0.1	0.063	0.0063	0.0063	0.0063	8	0.8	0.8	0.8
1,2,3,7,8,9-HxCDD	0.1	0.1	0.1	0.066	0.0066	0.0066	0.0066	8	0.8	0.8	0.8
1,2,3,4,6,7,8-HpCDD	0.01	0.01	0.01	0.429	0.00429	0.00429	0.00429	138	1.38	1.38	1.38
OCDD	0.001	0.0001	0.0003	0.93	0.00093	0.000093	0.000279	184	0.184	0.0184	0.0552
2,3,7,8-TCDF	0.1	0.1	0.1	0.024	0.0024	0.0024	0.0024	168	16.8	16.8	16.8
1,2,3,7,8-PeCDF	0.05	0.05	0.03	0.035	0.00175	0.00175	0.00105	10	0.5	0.5	0.3
2,3,4,7,8-PeCDF	0.5	0.5	0.3	0.035	0.0175	0.0175	0.0105	15	7.5	7.5	4.5
1,2,3,4,7,8-HxCDF	0.1	0.1	0.1	0.081	0.0081	0.0081	0.0081	4	0.4	0.4	0.4
1,2,3,6,7,8-HxCDF	0.1	0.1	0.1	0.035	0.0035	0.0035	0.0035	4	0.4	0.4	0.4
2,3,4,6,7,8-HxCDF	0.1	0.1	0.1	0.033	0.0033	0.0033	0.0033	5	0.5	0.5	0.5
1,2,3,7,8,9-HxCDF	0.1	0.1	0.1	0.033	0.0033	0.0033	0.0033	5	0.5	0.5	0.5
1,2,3,4,6,7,8-HpCDF	0.01	0.01	0.01	0.404	0.00404	0.00404	0.00404	7	0.07	0.07	0.07
1,2,3,4,7,8,9-HpCDF	0.01	0.01	0.01	0.086	0.00086	0.00086	0.00086	10	0.1	0.1	0.1
OCDF	0.001	0.0001	0.0003	0.252	0.000252	0.0000252	0.0000756	36	0.036	0.0036	0.0108
Total TEQ (pg TCDD equiv/m^3)					0.105322	0.1282582	0.120795		116.17	120.472	117.316

(a) Ambient dioxin data. From: letter from ENSR to Mr. R. Propper, CARB, 5/16/1989. In: CARB, 1990. Many of the entered levels are based on detection limit. (b) Flue gas emissions, municipal waste/power generation facility, Marion Co., OR. From: Dioxin Emissions from Resource Recovery Facilities: a review of the existing data base. CAPCOA/ARB/USEPA, 1989.

Neither of these sources reported measuring any levels of PCBs. Any such additional contaminants, if present, would add to the total TEQ observed by the WHO-97 TEF or WHO-05 TEF method, but not by the I-TEF method.

As per the recent rumor that as 2-Chlorobenzalmalononitrile will decompose into Chlorobenzene during high heating temperature, Chlorobenzene will convert into Dioxin under high temperature with the presence of Aluminum oxide (Al2O3) and the link shown as below,
https://www.facebook.com/story.php?story_fbid=10157566163037158&id=11383432157&sfnsn=mo

However, our Chemistry team and a group of professors in Taiwan had reviewed the paper quoted by recent rumor with the topic of 'Formation of Dioxins in the Catalytic Combustion of Chlorobenzene and a Micropollutant-like Mixture on **Pt/γ-Al2O3**' and discovered that if the Dioxins are formed from Chlorobenzene, the situation must require **2 wt% of Platinum and Aluminum Oxide in a controlled environment**. If 2-Chlorobenzalmalononitrile inside the tear gas can decompose into Dixons, the tear gas inside must contain Aluminum Oxide and Platinum. After checking the MSDS of tear gas from Nonlethal Technologies, their tear gas products do not contain Platinum. Therefore, the possibility of Dioxins produced after the firing of tear gas including those made in China is very low that in other words, the dioxins produced by this catalytic combustion of Chlorobenzene is **nearly impossible.**

3 Composition/information on ingredients

· **Chemical characterization: Mixtures**

· **Components:**

2698-41-1	[(2-chlorophenyl)methylene]malononitrile Acute Tox. 3, H301; Acute Tox. 2, H330 Resp. Sens. 1, H334 Acute Tox. 4, H312; Skin Irrit. 2, H315; Eye Irrit. 2A, H319; Skin Sens. 1, H317; STOT SE 3, H335	>80%
1309-48-4	magnesium oxide	<10%
546-93-0	Magnesium carbonate	<2%
7778-74-7	potassium perchlorate Ox. Sol. 1, H271 Acute Tox. 4, H302	<2%
10294-40-3	barium chromate Acute Tox. 4, H302; Acute Tox. 4, H332	<1%
7429-90-5	aluminium powder (pyrophoric) Pyr. Sol. 1, H250; Water-react. 2, H261	<1%
7440-02-0	nickel Carc. 2, H351; STOT RE 1, H372 Skin Sens. 1, H317	<1%
7440-67-7	zirconium powder (pyrophoric) Pyr. Sol. 1, H250; Water-react. 1, H260	<1%

· **Additional information:**
For the wording of the listed Hazard Statements refer to section 16.
For the listed ingredient(s), the identity and/or exact percentage(s) are being withheld as a trade secret.

· **Notable Trace Components (< 0.1% w/w)**

15245-44-0	lead 2,4,6-trinitro-m-phenylene dioxide/ lead styphnate Unst. Expl., H200 Repr. 1A, H360; STOT RE 2, H373 Acute Tox. 4, H302; Acute Tox. 4, H332

We also discovered that the Hong Kong government responded the rumor later and claimed that the reason why excess Dioxins are formed and existed at the environment, came from the waste burnt by the protesters on the street.

According to the research from B.R. Stanmore with the topic of 'The formation of dioxins in combustion system', the dioxins can be produced from the combustion of

Municipal solid waste (MSW) such as trashes and garbage on the gas or solid phase and under the temperature between 200^{0}C and 800^{0}C. Also, the research shows that the concentration of Chlorine in the MSW didn't have any correlation or relationship of the amount of Dioxins formation.

Analyses of MSW and sinter flyashes

Sample	Size range	Elemental composition (mass%)				PCDD/F	
	(μm)	C	Cl	Cu	Fe	$ng\,g^{-1}$	$\mu g\,m^{-2}$
MSW1	> 800	30.4	1.8	0.06	1.78	115	30.7
MSW2	300–150	5.2	4.5	0.11	2.79	170	12.5
MSW3	38–20	2.5	8.65	0.16	1.6	1217	12.2
MSW4	–	2.2	9.1	0.1	1.0	554	–
MSW5	–	1.1	4.5	–	–	–	–
Iron sinter	72.5% < 40 μm	3.3 (2.7)[a]	9.5	–	49.9	667	4.5

Prof. Liao from the Department of Environmental and Occupational Health in National Cheng Kung University raises out that **every combustion of the organic substances, including tear gas or MSW, has the chance to produce trace amount of Dioxins and the difference is the amount of Dioxins formation and the types of dioxins produced. The high chlorine content of the organic chemical is NOT the necessary condition of dioxins formed during the combustion.**

Moreover, **the carbon content inside the fuel do NOT have any relation to the flame temperature**. The carbon content of the fuel is related to the difficulty of complete combustion of the fuel. The more carbon content inside the fuel is, the more difficult to have the complete combustion of chemical. The oxygen content in the air or controlled environment is the factor of flame temperature and according to the book named as 'The Color of the Smoke', the list of flame temperature is shown as below:

Material burned	Flame temperature
Charcoal fire	750–1,200 °C (1382-2192 °F)
Methane (natural gas)	900–1,500 °C (1652-2732 °F)
Bunsen burner flame	900–1,600 °C (1652-2912 °F) [depending on the air valve, open or close.]
Candle flame	≈1,100 °C (≈2012 °F) [majority], hot spots may be 1300–1400 (2372-2552 °F)
Propane blowtorch	1,200–1,700 °C (2192-3092 °F)
Backdraft flame peak	1,700–1,950 °C (3092-3542 °F)
Magnesium	1,900–2,300 °C (3452-4172 °F)
Hydrogen torch	Up to ≈2,000 °C (≈3632 °F)
MAPP gas	2,020 °C (3668 °F)
Acetylene blowlamp/blowtorch	Up to ≈2,300 °C (≈4172 °F)

According to the research from Christopher W. Schmidt and Steve A. Symes (2008). About 'The analysis of burned human remains', the table of flame temperature about organic chemical is shown as below:

Material burned	Flame temperature
Animal fat	800–900 °C (1472-1652 °F)
Kerosene	990 °C (1814 °F)
Gasoline	1,026 °C (1878.8 °F)
Wood	1,027 °C (1880.6 °F)
Methanol	1,200 °C (2192 °F)
Charcoal (forced draft)	1,390 °C (2534 °F)
Animal fat	800–900 °C (1472-1652 °F)

Prof. Liao also mentioned when the temperature of environment is high enough, **the higher the temperature is, the lower concentration of Dioxins formed and eventually all dioxins can be broken down**. Most of incinerators were designed to the combustion process under the nearly 1000 °C operation temperature in order to greatly reduce from the emission of dioxins. According to the European Waste Incineration Directive, incineration plants must be designed to ensure that the flue gases reach a temperature of at least 850 °C (1,560 °F) for 2 seconds in order to ensure proper breakdown of toxic organic substances.

Experiment Design and Further Study.

In order to understand whether the tear gas produce the Dioxins under the high temperature, the Professor from the Department of Applied Chemistry in National Chiao Tung University suggested the experiment about the collection of 3 types of samples for measuring the concentration of dioxins.

- First experiment: Collection of the air sample after firing tear gas and then measuring the concentration and types of Dioxins formation
- Second experiment: Collection of the air sample after burning MSW and then measuring the concentration and types of Dioxins formation.
- Third experiment: Collection of the air sample at the scene including the above 2 situations in the same time and then measuring the concentration and types of Dioxins formation.

These experiments can solve the doubt of both side. However, we have the difficulty to collect those samples and measure the concentration of the Dioxins. Therefore, we hope other public organizations or international parties can join together to conduct these experiments to solve the recent public concerns about the Dioxins.