



THE ANALYSIS OF TEAR GAS IN HONG KONG

1st Investigation of the 2- Chlorobenzalmalononitrile (CS) residue content inside the Tear Gas Canister from different manufacturers

Abstract

Hong Kong Police Force (thereafter called 'HKPF') is using a huge amount of tear gas since June 2019 for the crowd control. The press media found that the origin of tear gas's manufacturers chosen by HKPF included China and the United States.

As the design of heating temperature for CS Tear Gas should not be high enough to vaporize all CS particles, there're certain amount of CS remained in the used tear gas canister. Due to the legal restriction, the certified reference material of CS cannot be purchased, imported and used in Hong Kong. Our teams studied the several researches in order to confirm whether the active ingredient of tear gas is CS and develop the test method to find out the presence of CS on the sample. We would like to show our gratitude to Michael & his team of chemical Engineers and numerous scholars for the technical support provided. With their support, we can bring out the analysis and the unexpected result was found that the used canister of Jing An KF-302-20 CS Grenade did not have any CS residue.

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Objective

The Gas Chromatography–Mass Spectrometry is used to investigate the 2-Chlorobenzalmalononitrile (CS) residue content inside the different Tear Gas canister samples from different products used by Hong Kong Police Force (hereafter called 'HKPF') for comparison. The samples were included **Non-Lethal Technologies CS Multi-Smoke 5 Projectiles** with the product code of MP-6M5-CS (made in USA), **Jing An KF-302-20 CS Grenade** (made in China) (Pic.1) and **Norcino NF01 CS Smoke Projectile** (made in China) (Pic. 2) with the reference to the information from the internet.

Sampling

There were total 3 samples of the tear gas canister collected and the details as shown below:

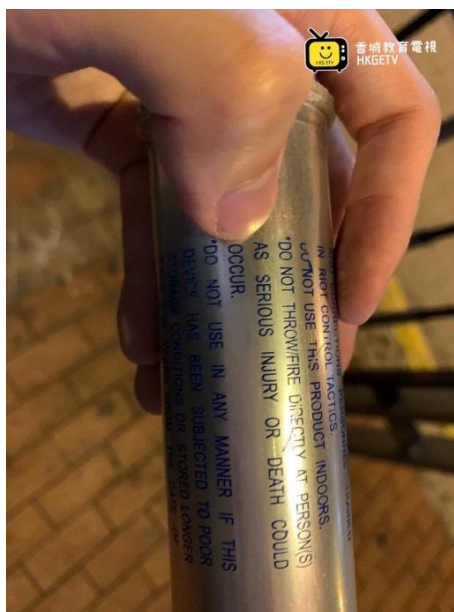
	Sample 1 (Refer to Pic. 1)	Sample 2	Sample 3 (Refer to Pic. 2)
Model of Tear Gas Canister	Jing An KF-302-20 CS Grenade	MP-6M5-CS	Norcino NF01 CS Smoke Projectile
Origin	China	United States	China
Collection Date	21 Oct 2019	29 Sep 2019	21 Oct 2019
Location	Yuen Long	Admiralty	Yuen Long

We assured that

1. The samples were dry (with no water poured by anyone at the scene) to affect their own mechanism inside.
2. There were no people stepped on the samples or trying to lower the temperature at the scene.
3. Sample 1 - 3 were stored in the dark place under room temperature between the collection and the test.



Pic 1. Jing An KF-302-20 CS Grenade



Pic 2. Norinco NF01 CS Smoke Projectile

Method

1. 40ml Methanol was added to each sample and all the samples are placed in an ultrasonic bath for 30 minutes (Pic. 3).
2. 1 ml of each sample solution was transferred to a centrifuge tube for 10 minutes of centrifugation with 3500 RPM.
3. Methanol was added and marked up to 20ml for dilution of each sample solution.
4. 10g of Magnesium Sulphate, MgSO₄ was added to each centrifuge tube.
5. The tube was then centrifuged again for 5 minutes.
6. 1 ml of the upper layer of each sample solution was transferred and evaporated.
7. All 3 sample solutions were finally reconstituted with 1ml Ethyl Acetate solution.



Pic 3. 40ml of Methanol was added to all samples and then put under 30 minutes of ultrasound extraction.

The configuration of GC-MS Analysis

The Gas chromatography–mass spectrometry was applied in this analysis. The parameters of the set up were listed as shown below:

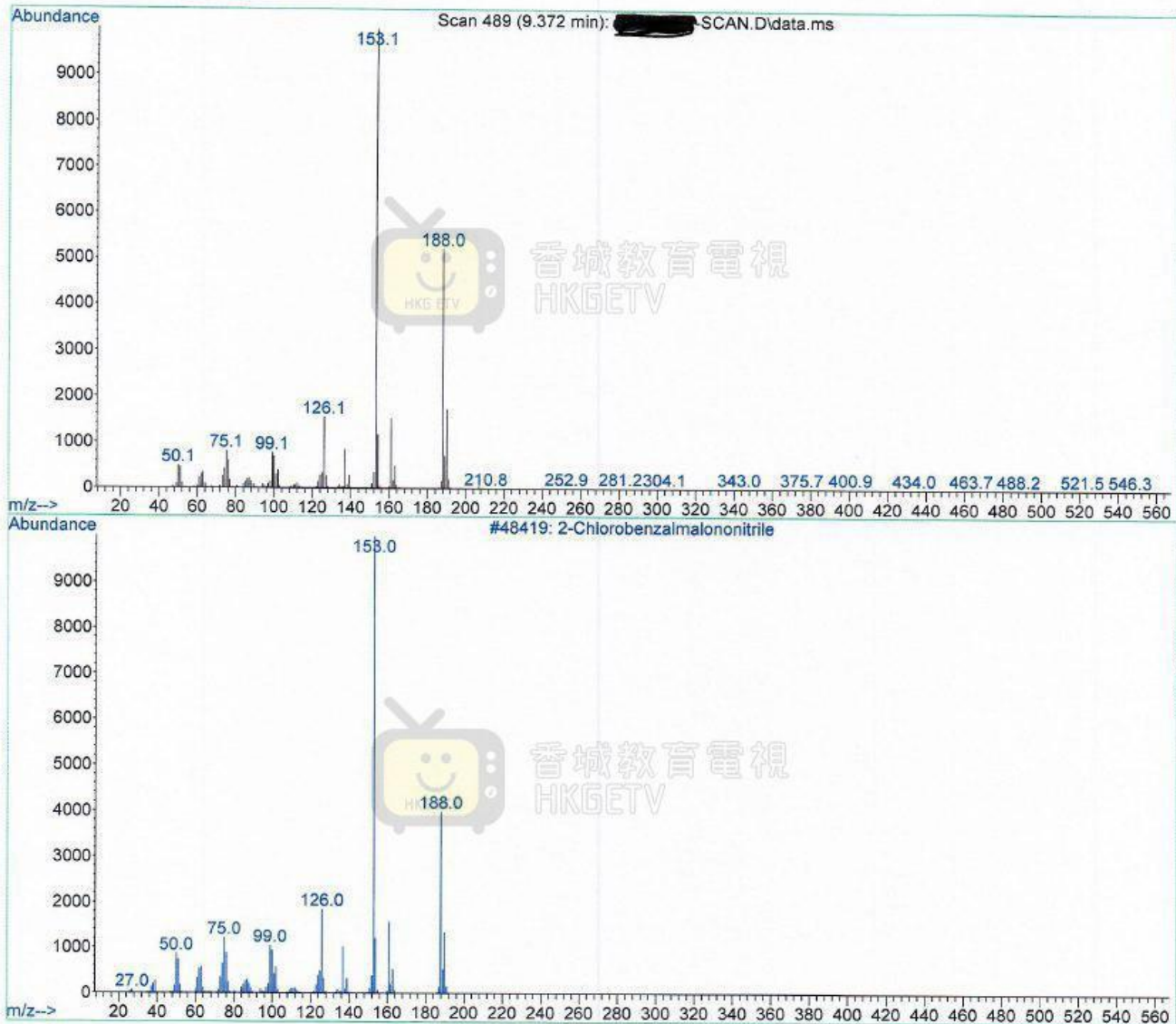
Column	HP-5MS 30m x 0.25mm x 0.25 um
Injection Temperature	250°C
Injection Mode	Splitless
Inlet Flow	1.0ml/min
Oven Temperature Program	90 °C 1min 10 °C/ min to 200 °C 30 °C/ min to 300 °C, Hold for 5min
Acq. Mode	Scan

Results and Findings

The analysis was performed on 22 October 2019.

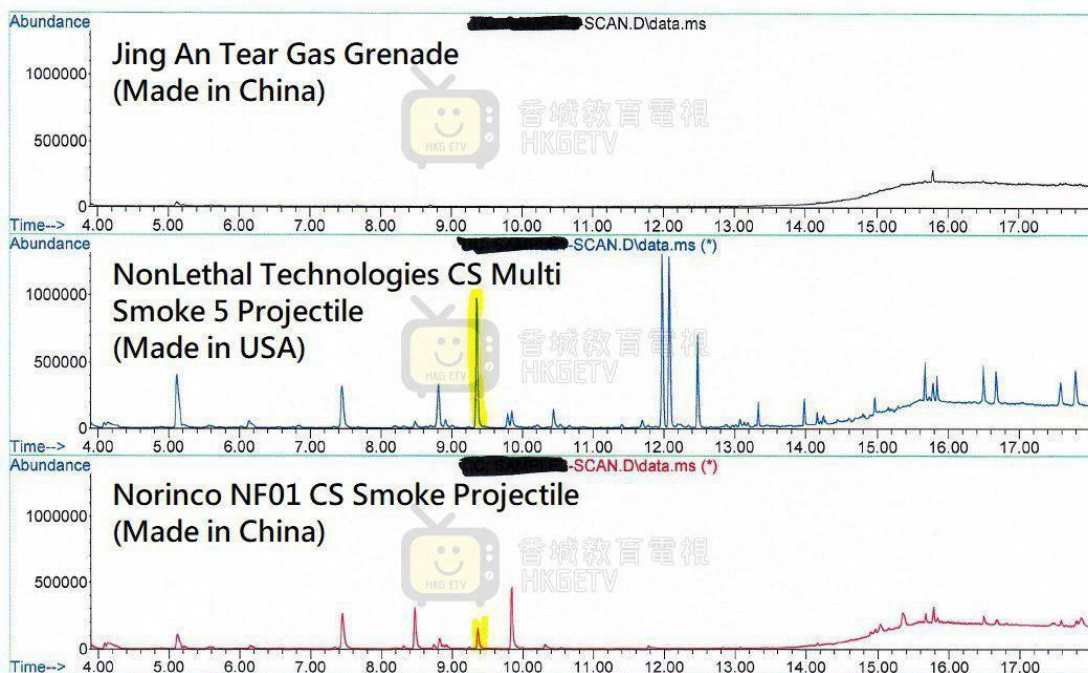
The total ion chromatograms (hereafter called 'TIC') of 3 samples were compared to the official total ion chromatogram of NIST library about CS. The retention time of CS is 9.372 minutes. The quality value was 97.

Library Searched : ██████████\NIST05a.L
Quality : 97
ID : 2-Chlorobenzalmalononitrile



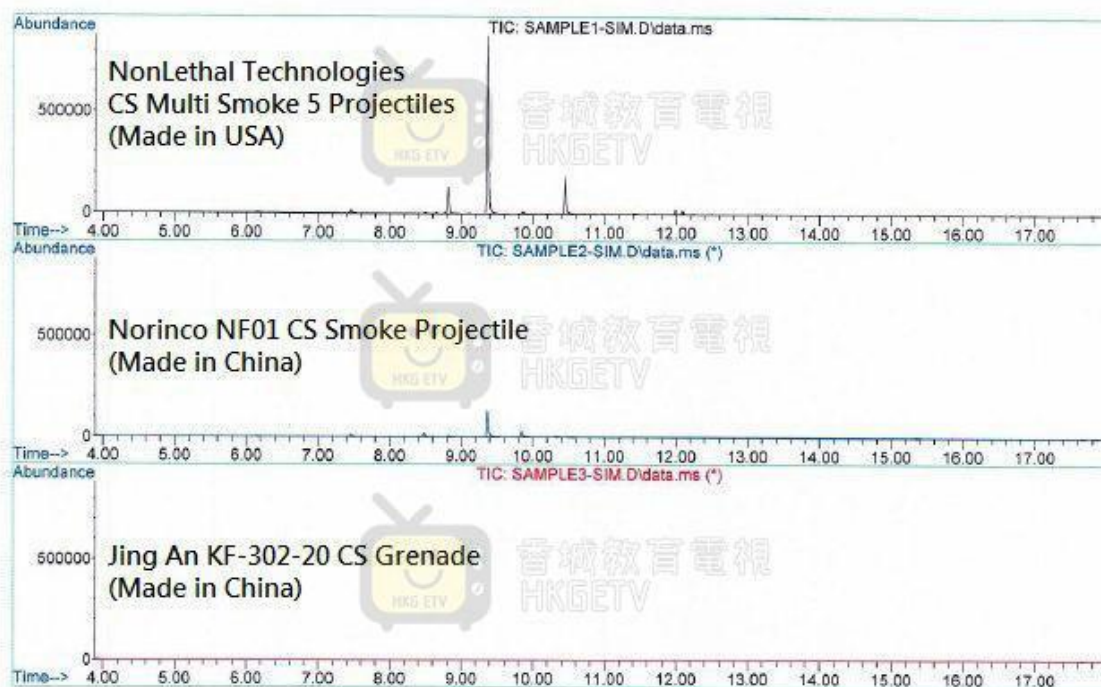
Pic 4 The Mass spectrum in comparison with the official spectrum in the NIST library

For the comparison of 3 TIC of the samples, the **peak area of CS in MP-6M5-CS was larger than that in Norinco NF01**, and **CS residue cannot be found in the Jing An KF-302-20** in Scan Mode.



Pic.5 TIC of those three samples as shown above.

The Ion 111, 153, 188, 126 and 140 were used in Select Ion Mode, the Result listed below:



At 9.372 min, the TIC of Jing An KF-302-20 CS Grenade cannot be found those target Ions (111, 153, 188, 126 and 140).

Conclusion

1. The peak area of 2-Chlorobenzalmalononitrile in MP-6M5-CS was the largest among 3 Total Ion Chromatograms, although the sample was collected earlier than the other 2 sample extracts from Chinese-made canisters.
2. Any residues of 2-Chlorobenzalmalononitrile cannot be found in the canister of Jing An KF-302-20 CS Grenade. The hypotheses of this result are shown as below:
 - A. There were no 2-Chlorobenzalmalononitrile in Jing An KF-302-20 CS Grenade.
 - B. The combustion temperature of Jing An KF-302-20 CS Grenade was too high which led to the complete decomposition of 2-Chlorobenzalmalononitrile.

Further Studies

If we have sufficient resources and manpower, we would like to make suggestions as below for further studies, which include but are not limited to the following items:

1. Increase the sample size in order to get more accurate results.
2. Try different extraction methods to improve the procedure of extraction.
3. Try different types of samples, such as food, textile or air samples.