10.15 Lachrymator Analysis

10.15.1 Introduction

Lachrymator definition: A substance that irritates the eyes and produces tears

Three types of lachrymators can be found in chemical sprays:

1. CS = O-Chlorobenzalmalononitrile (2-chlorobenzalmalononitrile) Tear gas
2. CN = Chloroacetophenone(2-chloroacetophenone) - Mace / Chemical Mace
3. OC = Oleoresin Capsaicin (Trans-8-methyl-N-vanillyl-6-nonenamide) - Pepper spray

Lachrymator examination involves chemical analysis of the contents from an aerosol dispenser or the identification of lachrymator(s) from a stain on clothing or any other item.

Laboratory Sample Collection:

Product dispenser (known) - The dispenser can be evaluated by depressing the trigger to determine if it is operational. The aerosoldispenser may be inoperable if any part of it is damaged, or if the solvent or propellant used in the dispenser is spent. The contents of an aerosol dispenser are analyzed using FTIR or Gas Chromatography/Mass Spectrometry (GC/MS). The concentration of the lachrymator in an aerosol dispenser is not determined during analysis.

Questioned stains - Items such as clothing or swabs that may contain a lachrymator are examined for staining. Most commercially available pepper sprays leave orange-brown stains however, some lachrymators are colorless and leave no visible spray pattern. The stains may be cut out and extracted using a solvent, or the whole item can be extracted if appropriate. If an entire garment or large item is examined without finding stains, the examination can be concluded, or areas of probable/possible contact could be sampled.

10.15.2 Minimum Standards of Analysis

Identification by infrared spectroscopy or mass spectrometry. This procedure is for qualitative analysis only (quantitation not performed in FSD laboratories on this evidence type). Treat the questioned samples and any submitted control/standard samples in the same manner.

When performing extractions also analyze a blank of the extraction liquid and an unstained portion of the substrate, if possible. If an unstained portion of the substrate is not possible, analyze the extraction solvent as the negative control.

Fourier Transform Infrared Spectrometer (FTIR)

- **See Trace Procedures/Training Manuals 7.2 Instrument Standards and Controls for FTIR Verification**

- Run a polystyrene verification standard each day the instrument is used for casework.
- Blanks: A blank of any cell or salt plates used will be run before each sample.
- IR spectra and/or case record notes must include case number, exhibit number, date, analyst's initials, resolution, number of scans, sample type (KBr pellet, liquids, vapor, etc.), frequency range and mode (absorbance or %T).
- IR spectra of case exhibits must be preserved in the case record.

Gas Chromatograph/Mass Spectrometer (GC/MS)

- **See Trace Procedures/Training Manuals 7.7 Instrument Standards and Controls for Gas Chromatography - Mass Spectrometer**
- Run a function verification test sample each day a case is worked (example: ASTM - Instrument Sensitivity Test Mixture).
- Blanks will be run at the same conditions as the samples.
- All GC and GC/MS data (hard copies or digital files) generated from case exhibits must be properly identified and put into the case record object repository.
- The instrument parameters used for an analysis must be documented in the procedures manual or in the case record.

Chemical Identification and Documentation

- Identifications made by comparison to other than in-house standards must be noted in the case record (i.e. published data or library database).
- Identification made via computer search must be confirmed by visual comparison to computer's standard and noted in the case record.
- Identification can be made by comparison to extracts of known commercial products, labeled as containing, or known to contain, these chemicals, that also compare to published data.

10.15.3 Safety Considerations

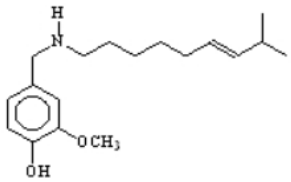
Tear gas products are irritants, by definition, and will cause physical discomfort if inhaled. If working with spray products or highly concentrated clothing items, perform analysis in a fume hood.

Avoid contact with skin and eyes.

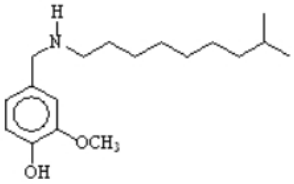
This protocol involves hazardous materials, operations, and equipment. This protocol does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this protocol to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use. Proper caution should be exercised and the use of personal protective equipment should be considered to avoid exposure to dangerous chemicals. Consult the appropriate MSDS for each chemical prior to use.

10.15.4 Oleoresin Capsicum

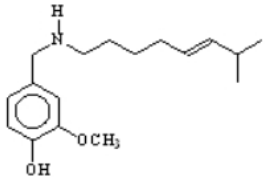
Oleoresin capsicum is the extract from capsicum (various peppers) obtained using either acetone or ether as the solvent. It is an irritant used in certain chemical weapons and is legal only if the oleoresin capsicum concentration is no greater than 2%. It is not difficult to show the presence of capsaicinoids, the active ingredients of oleoresin capsicum. It is not, however, possible to quantitate the oleoresin capsicum because the amounts of the active ingredients differ according to the solvent used in the extraction, the type of peppers used, and even among peppers of the same type.
There are a number of capsaicinoids that differ in the length and saturation of the carbon chain. The capsaicins have a double bond and the dihydrocapsaicins are saturated. The norcapsaicins have 1 less and the homocapsaicins have one more carbon than capsaicin.



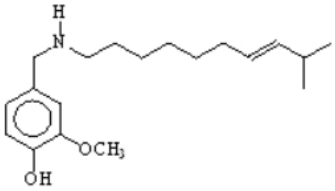
Capsaicin



Dihydrocapsaicin



Norcapsaicin



Homocapsaicin

10.15.4.1 Extraction of capsaicin for GC-MS:

From a canister device:

- In a fume hood, spray a sample from the canister into a watch glass and evaporate the volatile solvents. A red/orange colored oil will remain.
- Extract the capsaicin using methanol.

From Fabric (or other surfaces):

- Remove stained area and place into a glass beaker - Extract the stained area with methanol
- Remove the extracted solution onto a watch glass and evaporate if necessary to concentrate the sample

10.15.4.2 Extraction for TLC Purification:

- Dissolve about 5ml of sprayed liquid in hexane (a trace of $CHCl_3$ may be needed to completely dissolve the sprayed liquid).
- Extract several times with 5% aqueous NaOH.
- Wash combined extracts with hexane.
- Acidify aqueous solution with H_2SO_4.
- Extract several times with $CHCl_3$.
- Evaporate $CHCl_3$ to give oily residue.
- Run TLC on Silica Gel GF plates using 75:24:1 benzene:ethyl acetate: formic acid.
- Visualize with UV short wavelength, then spray with Chloranil spray (0.1g chloranil in 10ml CH_3OH). Ammonia vapors are then carefully blown over the plate and color development is observed.
- Isolate the spots from the TLC plate.
- Dissolve in dilute aqueous Na_2CO_3 and filter.
- Acidify to pH 1 - 2 with H_2SO_4.
- Extract with $CHCl_3$ and evaporate.

10.15.4.3 FTIR:

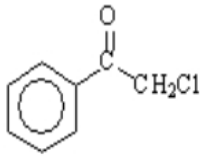
Use normal procedures

10.15.4.4 GC-MS:

Use normal procedures

10.15.5 2-Chloroacetophenone – CN

2-Chloroacetophenone
MW= 154.6
C_8H_7ClO



2-Chloroacetophenone (CN tear gas) is a lachrymator used in certain chemical weapons.

In Michigan, CN tear gas weapons are illegal regardless of the amount or concentration of CN tear gas.
2-Chloroacetophenone (C_8H_7ClO, MW = 154.6)

10.15.5.1

UV Analysis: Maximum at 247nm in methanol.

10.15.5.2

GC Analysis: Use normal procedures. CN tear gas requires low column temperatures of 130 - 160°C.

10.15.5.3

Extraction of 2-Chloroacetophenone for GC-MS analysis:

- If particles of possible CN are observed, in a fume hood, place a few particles into an autosampler vial and add approximately 1 – 2 ml of pentane or hexane, then cap.
- If no particles are observed, in a fume hood, rinse the canister/container with pentane or hexane and collect the rinse onto a watch glass. Evaporate to concentrate the sample. After the extract evaporates to dryness, scrape a portion of crystal residue from the periphery and place into an autosampler vial. To the vial add 1 – 2 ml of pentane or hexane and cap.

Note: Sometimes there will be a carrier oil present which may remain after the clean-up procedure. While in these cases it may not be possible to obtain an infrared spectrum, the residue will still be suitable for mass spectrometry.

Evaporation of solvent:

- If an intact canister is submitted, utilizing a fume hood, spray the canister directly onto a watch glass. Extract with pentane or hexane. After the extract evaporates to dryness, scrape a portion of crystal residue from the periphery and place into an autosampler vial. To the vial add 1 – 2 ml of pentane or hexane and cap.

10.15.5.4

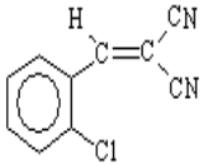
FTIR Analysis: Use normal procedures.

10.15.5.5

GC-MS Analysis: Use normal procedures.

10.15.6 Orthochlorobenzalmalononitrile (2-chlorobenzalmalononitrile) - CS

Orthochlorobenzalmalononitrile
MW=188.5
$C_{10}H_5ClN_2$



Orthochlorobenzalmalononitrile (CS tear gas) is a lachrymator used in certain chemical weapons.

It is legal to carry for self-defense only if it is in a device capable of carrying and releasing not more than 35 grams of any combination of CS tear gas and inert ingredients. Orthochlorobenzalmalononitrile ($C_{10}H_5ClN_2$, MW = 188.5)

10.15.6.1

UV Analysis: Maximum at 297 nm in methanol

10.15.6.2

GC-MS Analysis: Use normal procedures. CS tear gas requires column temperatures of 150 - 180 degrees C.

10.15.6.3

Extraction

Note: Sometimes the carrier oil remains after extraction. While in these cases it may not be possible to obtain an infrared spectrum, the extract will still be suitable for mass spectrometry.

Methanol Extraction:

- same as 10.15.4.1

Hexane-Acetonitrile Extraction:

- Add 20ml acetonitrile (bottom layer) and 10ml hexane (top layer) to a separatory funnel.
- Spray the CS canister directly into the separatory funnel. The CS will go to the acetonitrile layer and the oil will go to the hexane.
- Mix gently (DO NOT SHAKE) and invert gently a couple of times. If the mixture is shaken, oil will contaminate the acetonitrile layer because hexane and acetonitrile are partially miscible.
- Allow layers to separate and draw off the acetonitrile.
- Evaporate under stream of air with acetonitrile and wash with hexane.

- Draw off the acetonitrile and evaporate. This time an oily, crystalline residue should be present.
- Spread the crystals out on a watch glass and wash them with cold hexane. Be careful not to wash too much, because CS is somewhat soluble in hexane.

10.15.7 References

Link to the Michigan Legislature page pertaining to the penal code for self-defense spray or foam devices: http://www.legislature.mi.gov/(S(k0knvziswbbs0445a5vjzl45))/mileg.aspx?page=GetObject&objectname=mcl-750-224d

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