Report from the workshop on chemical forensics in Helsinki
Capabilities across the field and potential applications in the CWC Implementation
June 20-22, 2016
Helsinki
Dr Christopher Timperley
Dr Jonathan Forman
Professor Paula Vanninen
Workshop agenda

- Experiences and Perspectives on Investigations of Alleged Use, *moderated by dr Christophe Curty*
- Chemical forensics and chemical weapons: *moderated by dr Daan Noort*
- Chemical forensics in law enforcement: Crime laboratories, *moderated by mr Cheng Tang*
- Chemical forensics in law enforcement: Illegal drug attribution analysis, *moderated by professor Slawomir Neffe*
- Biomedical samples, *moderated by professor Slavica Vučinić*
- Other attribution analysis, *moderated by professor David Gonzalez*
- Reconstructing past events, *moderated by professor Ponnadurai Ramasami*
Mr Dominique Anelli, former head of the OPCW Demilitarisation branch

Working together for a world free of chemical weapons
Mr Dominique Anelli

Working together for a world free of chemical weapons

April
First mission of Declaration Assessment Team

23 June
Final CW shipment leaves Syria

31 August
OPCW-UN Joint Mission comes to an end

August
Reports of sulfur mustard use

10 September
Fact-Finding Mission confirms use of chlorine as CW

29 April
Fact-Finding Mission on chlorine attacks established

27 May
Fact-Finding Mission attacked

6 March
UNSCR 2209

7 August
UNSCR 2235 - establishment of JIM

December
Scheduled completion of all CW destruction

October
FFM confirms sulfur mustard use

November
Joint Investigative Mechanism fully operational

2014

2015

CWPF destruction operations
Mr Lennie Phillips, Team leader in the OPCW FFM

OPCW Fact Finding Mission

- Open source information
- Videos and photos supplied during interviews
- Interviews
- Number of incidents
- Spread of incidents
- Samples
Mr Lennie Phillips, Team leader in the OPCW FFM

OPCW Fact Finding Mission

Since 2013 almost 800 samples has been coordinated by the OPCW lab/ Hugh Gregg
OPCW Fact Finding Mission

Recommendation:
System for managing and collection of data should be established including collection of samples, analytical information and annotation.
A searchable collection of physical objects and information is valuable for retrospective review.

Since 2013 almost 800 samples has been coordinated by the OPCW lab/ Hugh Gregg.
Gaps relevant to IAU:

- Broad range of sample types and toxic chemicals (including non-scheduled chemicals)
- Biomedical samples
- Trace level analysis
- Availability of reference materials

Toxin analysis

Attribution analysis:

- Addressed only recently – lessons can be drawn from other fields of analysis (food/wine adulteration, counterfeit drugs, explosives)
- Based on impurity profiling, statistical analysis, isotope ratios – databases as a limiting factor

- More research is needed

S&T opportunities: HRMS
Recommendation:
Development of ROPs for the sampling of biomedical materials, and their handling and storage
Methods for TICs like chlorine
Abonded chemical weapons discovered in China

Types of chemical agents discovered

<table>
<thead>
<tr>
<th>Agent</th>
<th>Chemicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow Agent</td>
<td>✓ Mustard, ✓ Lewisites, ✓ Mixture of Mustard and Lewisites</td>
</tr>
<tr>
<td>Red Agent</td>
<td>✓ DA: Diphenylchloroarsine, ✓ DC: Diphenylcyanoarsine</td>
</tr>
<tr>
<td>Blue Agent</td>
<td>✓ Phosgene</td>
</tr>
<tr>
<td>White Agent</td>
<td>✓ Trichloroarsin (used in mixture with the Blue agent)</td>
</tr>
</tbody>
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Dr Zhanshang Zhao Ministry of National Defence and Mr Cheng Tang (OPCW SAB)
Source Attribution of Cyanides Using Anionic Impurity Profiling, Stable Isotope Ratios, Trace Elemental Analysis and Chemometrics

Nikhil S. Mirjankar, Carlos G. Fraga,* April J. Carman, and James J. Moran

Pacific Northwest National Laboratory, 902 Battelle Boulevard, Richland, Washington 99352, United States

DOI: 10.1021/acs.analchem.5b04126


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Carlos Fraga, PNNL
HCA Dendrogram using HPIC Peak Areas for unk5, SO$_4$, OX, and PO$_4$

- Area-normalized and auto-scaled HPIC data of 120 cyanide sample profiles.
- KCN and NaCN samples cluster into three groups: (1) US/UK/ES, (2) GE/BE, and (3) CZ.
- Each group corresponds to one solid cyanide factory: (1) US, (2) GE, and (3) CZ.

Carlos Fraga, PNNL
Recommendation:

- Methods using impurity profiling and isotopic ratio distribution for purposes related to determining responsibility for use of chemical weapons, for abandoned chemical weapons, or for clandestine chemical weapons production are valuable to develop
  - solvents, trace metals and inorganic elements

- Each group corresponds to one solid cyanide factory: (1) US, (2) GE, and (3) CZ.
Mr Jari Pukkila, National Bureau of Investigation Forensic Laboratory, Finland described the general principles of crime scene operations, evidence collection and sample handling.
evidence collection : strategy

1) rescue service

2) CBRNE -team

3) technical scene investigators
   - scene preservation
   - scene assessment
   - search and sampling strategy
   - documentation

Recommendation: Cooperative working relationships with organizations and network of experts relevant to forensics

Mr Jari Pukkila, National Bureau of Investigation Forensic Laboratory, Finland described the general principles of crime scene operations, evidence collection and sample handling.
Dr Michael Collins, Australian Forensic Drug Laboratory, National Measurement Institute, the illicit drug profiling programme
SAMPLING vs. TIME OF EXPOSURE

- Blood sampling by Syrian doctors
- Urine and 1st blood sampling by UN
- 2nd blood sampling by UN

Dr. Rudolf Johnson, CDC, “Measuring Human Exposure to Nerve Agents and Marine Toxins”
Provenance and Attribution

- **Attribution** means the authorship of a work of art.
- To determine the attribution it is necessary to study the following points:
  - Style
  - Subject
  - Provenance
  - Technique and materials
- Together all these help us to contextualise the work of art.
Material analysis

Pre-analysis
- Method selection

Analysis
- Light microscopy
- Sampling
- EDXRF
- PIXE
- EDXRF-SEM
- Raman/IR
- Polarized microscopy

Results
- Material analysis: Inorganic and Organic compounds

Professor Juhani Huuskonen, University of Jyväskylä and RECENART® Inc., Finland, chemical forensics and art.
Serlachius Fine Art Foundation: Claude Monet, ”A Haystack in the Evening Sun” 1891.

With hyperspectral camera RECENART team revealed a signature underneath the paint layers. The material analysis verified that the pigments used in the painting (also in the paint that covered the signature) were exactly the same that Claude Monet had used in his other Haystack paintings.

**Result:** The painting was attributed to Claude Monet.
Biomarkers in archaeology

Professor Evershed

Pistacia resin
Frankincense
Birch bark products
Coniferous resin
Heated resin product

Widely occurring sterol
Manure indicators in soils
Petroleum bitumen

Plant epicuticular waxes

Beeswax

Isoprenoid fatty acid
Common fatty acid

Oxidised fatty acid

Thermally altered fatty acids

Macromolecule building blocks: collagen, aDNA, carbohydrates, etc.

Natural dyes
Determining stable isotope values

Whole tissues or crude extracts → Sealed tube combustion and trapping of CO₂ (and N₂) → Isotope ratio MS → Bulk isotope values

Whole tissues or crude extracts → Combustion using an elemental analyser → GC separation of CO₂ and N₂ → Isotope ratio MS → Bulk isotope values

Isolate individual compound classes, e.g. amino acids or lipids → Separate compounds by GC (and now HPLC) → Combust or thermolyse eluting compounds → Isotope ratio MS → Compound-specific isotope values
Analysis of lipids in archaeological pottery

Professor Evershed

Surface residues

Archaeological potsherd

Analytical protocol

Solvent extraction

Total lipid extract

Fractionation

Saponification

Derivatisation

Trimethylsilyl derivatives

Fatty acid methyl esters

Gas Chromatography (GC)

→ Separation
→ Quantification

GC-combustion-isotope ratio –MS (GC-C-IRMS)

$\delta^{13}$C values

GC/mass spectrometry (GC/MS)

→ Structure elucidation

GC-thermal conversion IRMS

$\delta$D values

Absorbed residues
Linking of molecular structure-to-isotopic composition increases the diagnostic value of commonly occurring preserved biomarkers, such as lipids and proteins, allowing exploitation of previously inaccessible information relating to metabolism, digestive physiology, environment, climate and absolute age, thereby enhancing provenance assignments.
Archaeologic & forensic applications: provenance of (raw) materials

- stone, soil, metals & ore, vitreous materials, ceramics…
- plants, wine, paper, ivory, caviar…
- … people
Archaeologic & forensic applications: provenance of (raw) materials

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Professor Patric Degryse, Centre for Archaeological Sciences at the Katholieke Universiteit Leuven, on provenance, technology, on exchange and trade of inorganic materials in an archaeological context by examining isotopic evidence.
The provenance postulate

– the isotopic ‘fingerprint’ of a raw materials is inherited in the object
– Different raw materials can have different ‘fingerprints’
– Intra-source variability is (far) smaller than inter-source variability

Conclusions-Recommendations

- A Workshop or a temporary working group could be considered to develop forensic methods and capabilities for CWC verification.
- Appropriate functions within the OPCW could benefit from cooperative working relationships with organisations and networks of experts relevant to forensics.
- Establishing a system for the management of data is essential for use in a forensic capacity.
Conclusions-Recommendations

- A searchable collection of **physical objects and information** is valuable for retrospective review.
- For example, existing compiled data on abandoned chemical weapons and impurity **profiles** for known synthetic routes to nerve and vesicant agents could serve as a resource to those working in the field of chemical weapons related investigations.
Conclusions - Recommendations

- Methods using impurity profiling and isotopic ratio distribution for purposes related to determining responsibility for use of chemical weapons, for abandoned chemical weapons, or for clandestine chemical weapons production are valuable to develop

- **Autonomous systems** to support investigations of alleged use of chemical weapons could benefit investigators

- Forensic **training** will continue to be valuable for enhancing forensic awareness and forensic investigation capabilities