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

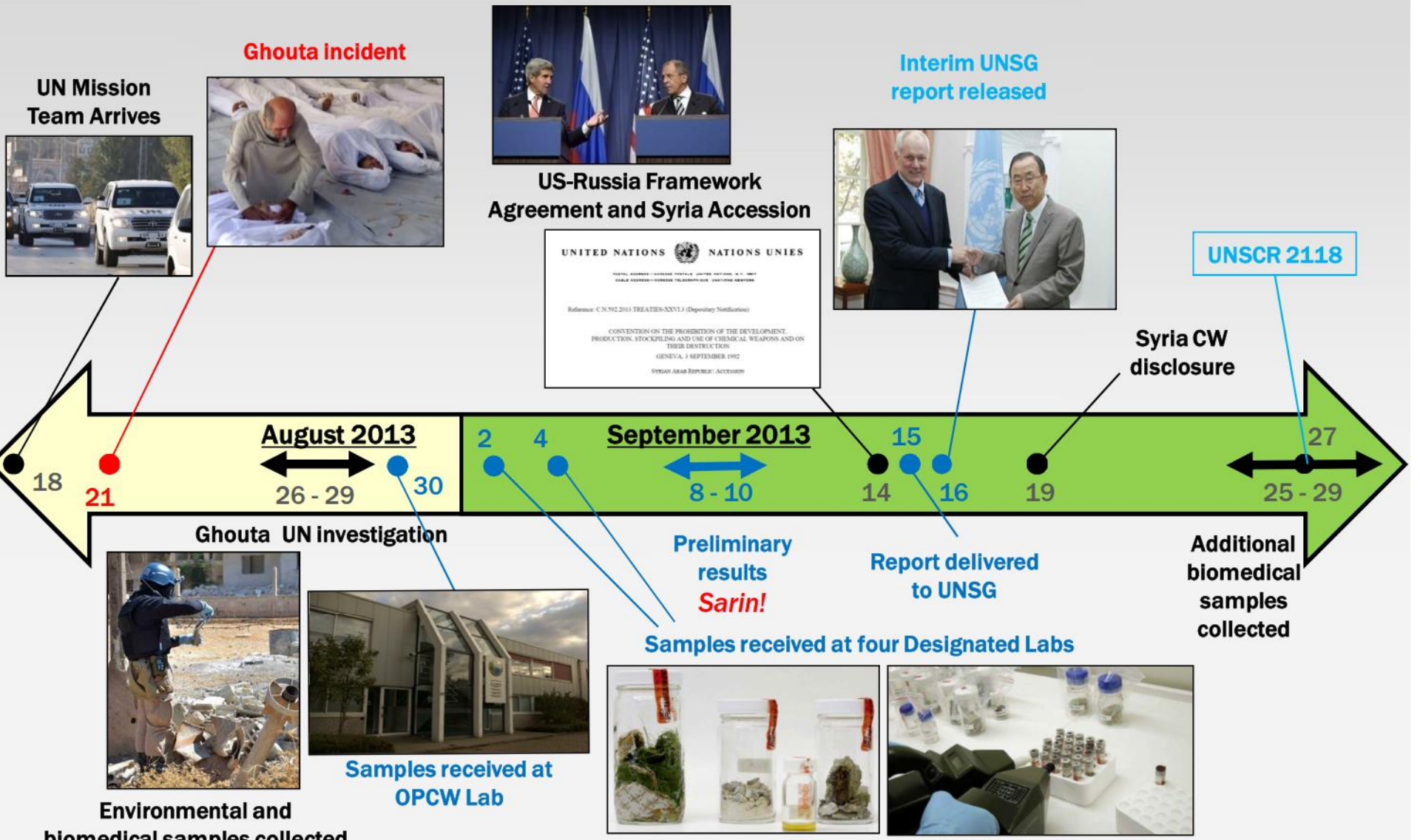
Dr Jonathan Forman

Professor Paula Vanninen

VERIFIN
HELSINGIN YLIOPISTO
HELSINGFORS UNIVERSITET
UNIVERSITY OF HELSINKI

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*


Ghouta Incident
UN Mission Team Arrives
US-Russia Framework Agreement and Syria Accession
UNITED NATIONS NATIONS UNIES
CONVENTION ON THE PROHIBITION OF THE DEVELOPMENT, PRODUCTION, STOCKPILING AND USE OF CHEMICAL WEAPONS AND ON THEIR DESTRUCTION
GENEVA, 3 SEPTEMBER 1992
Interim UNSG report released
Syria CW disclosure
UNSCR 2118
August 2013
September 2013
18
21
26 - 29
30
2
4
8 - 10
14
15
16
19
25 - 29
27
Ghouta UN investigation
Environmental and biomedical samples collected
Samples received at OPCW Lab
Preliminary results
Sarin!
Report delivered to UNSG
Samples received at four Designated Labs
Additional biomedical samples collected

Destruction of equipment commences

OPCW-UN Joint Mission announced
http://opcw.unmissions.org/

First shipment of chemicals loaded in Latakia

Destruction plan submitted to EC

Additional disclosures

October 2013

Syria 190th State Party

Functional destruction complete

22/23 CW sites verified

Unfilled munitions destroyed

January 2014

1 3 4 6 14 16 22 23 31 6 15 6 12 17 7

November 2013

December 2013

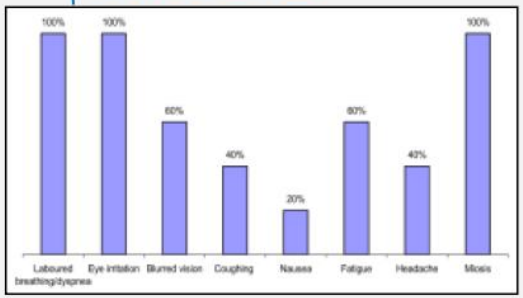
18/23 sites verified

Declaration under CWC Article III

Additional samples sent for analysis

Decision on destruction adopted

Final UNSG Report released



Advance team arrives

www.opcw.org

Mr Dominique Anelli

April
First mission of Declaration Assessment Team

23 June
Final CW shipment leaves Syria

31 August
OPCW-UN Joint Mission comes to an end

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

August
Reports of sulfur mustard use

7 August
UNSCR 2235 – establishment of JIM

October
FFM confirms sulfur mustard use

December
Scheduled completion of all CW destruction

2014

2015

29 April
Fact-Finding Mission on chlorine attacks established

27 May
Fact-Finding Mission attacked

August
Completion of Category 1 CW destruction

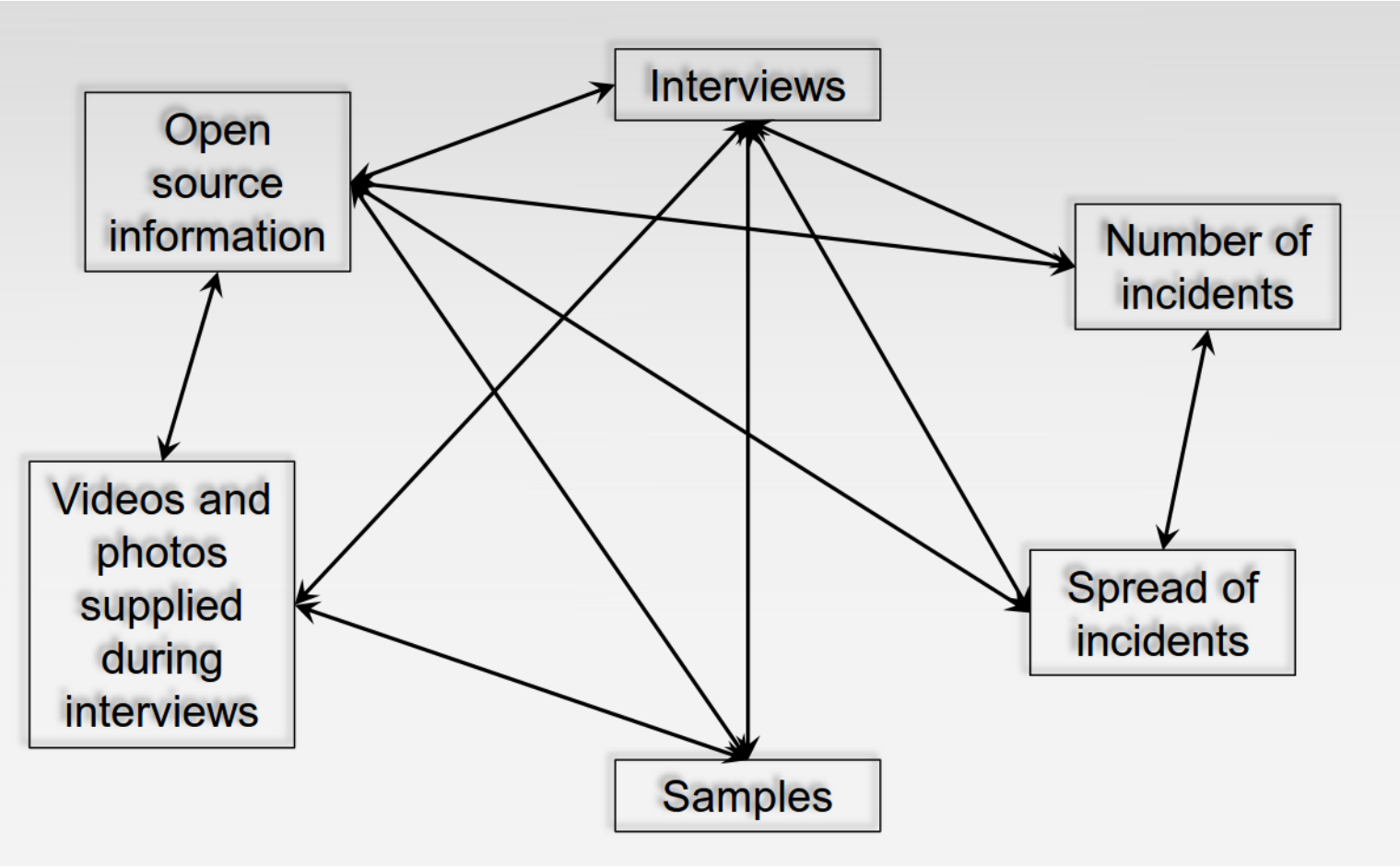
6 March
UNSCR 2209

CWPF destruction operations

November
Joint Investigative Mechanism fully operational

Mr Lennie Phillips, Team leader in the OPCW FFM

OPCW Fact Finding Mission



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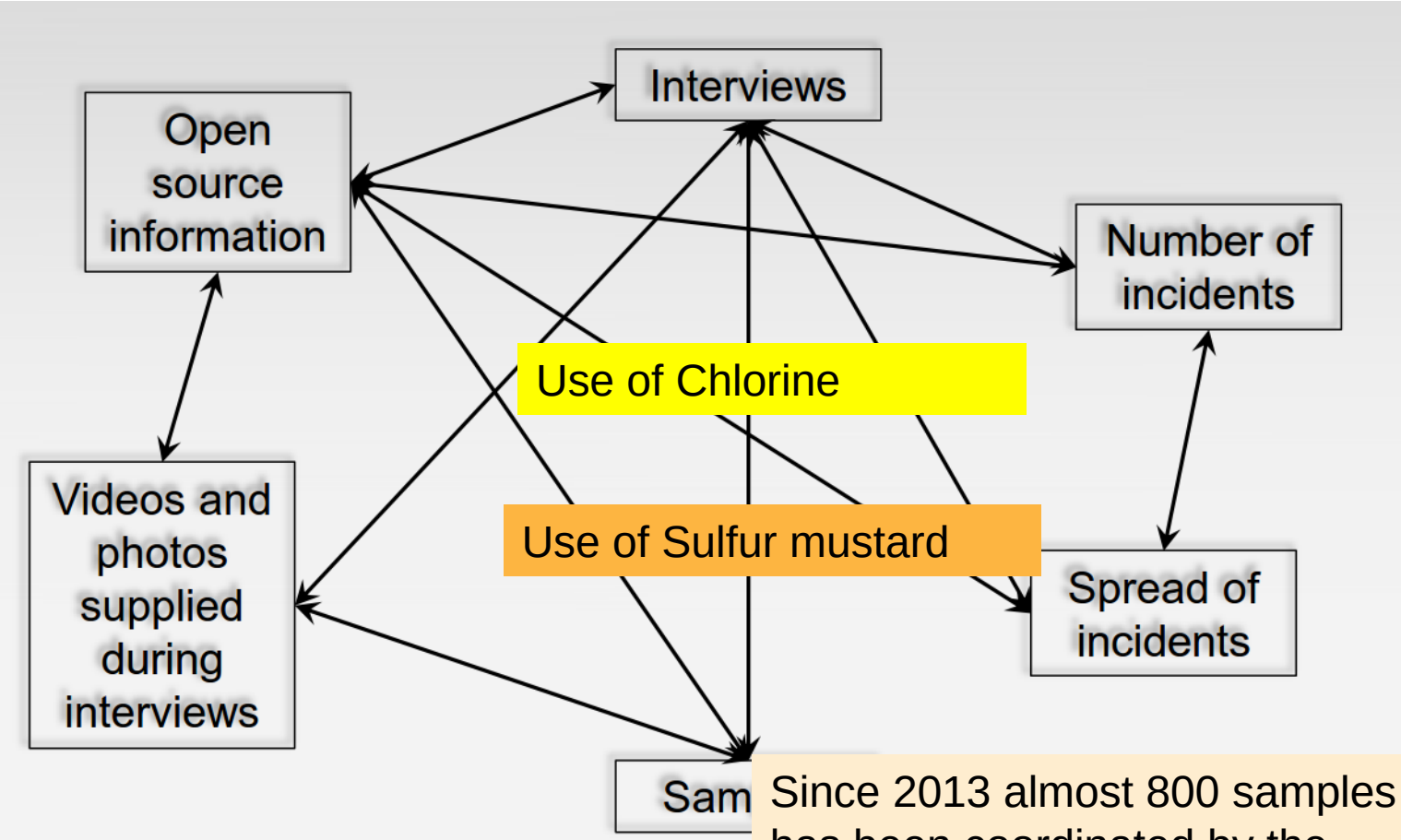
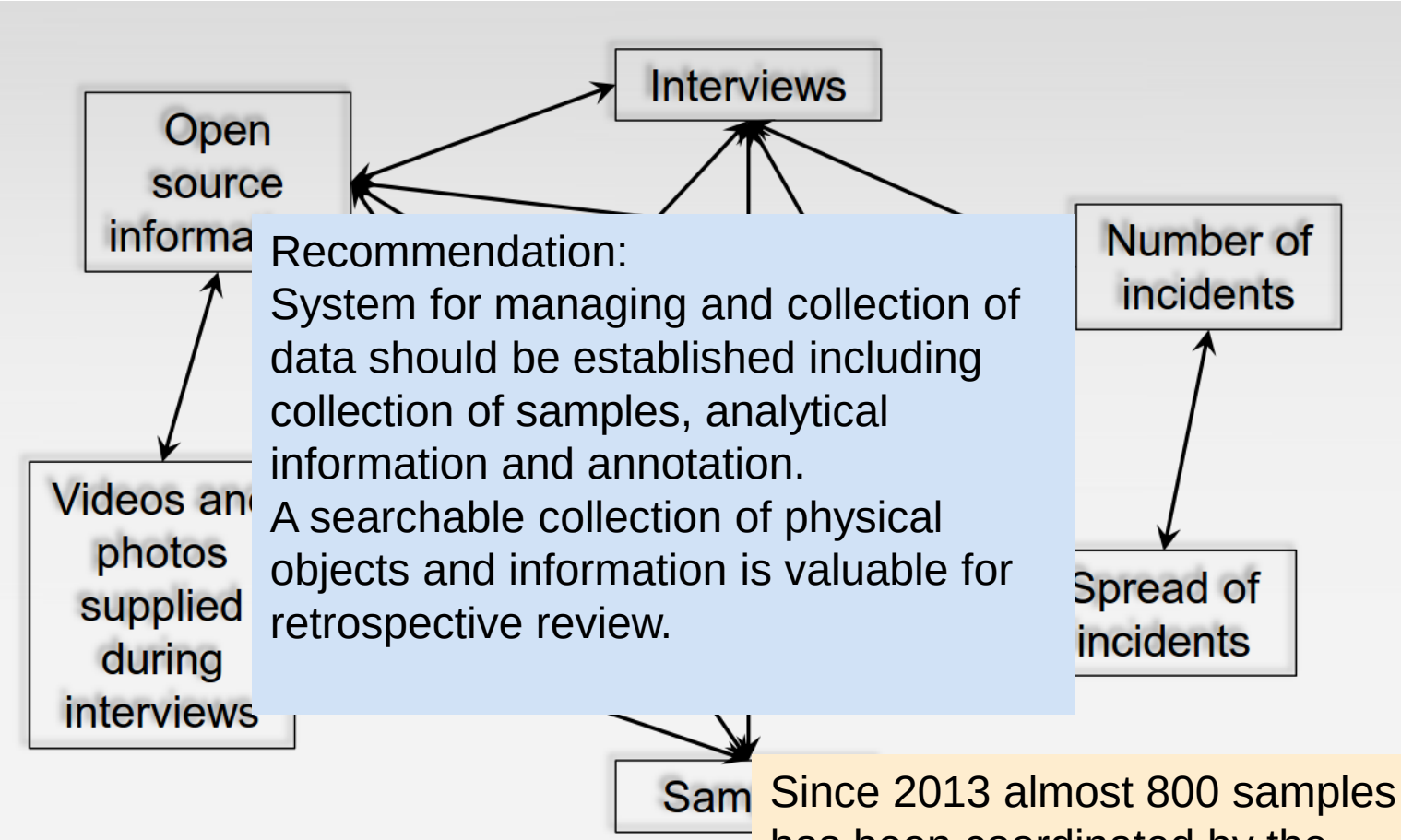
OPCW Fact Finding Mission



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

Mr Lennie Phillips, Team leader in the OPCW FFM

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

Dr Ralf Trapp

SAB TWG findings 2

- 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

Dr Ralf Trapp

SAB TWG findings 2

5

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- counterfeit drugs,
- d on impurity profiling, statistical analysis, isotope ratios – databases as a limiting factor
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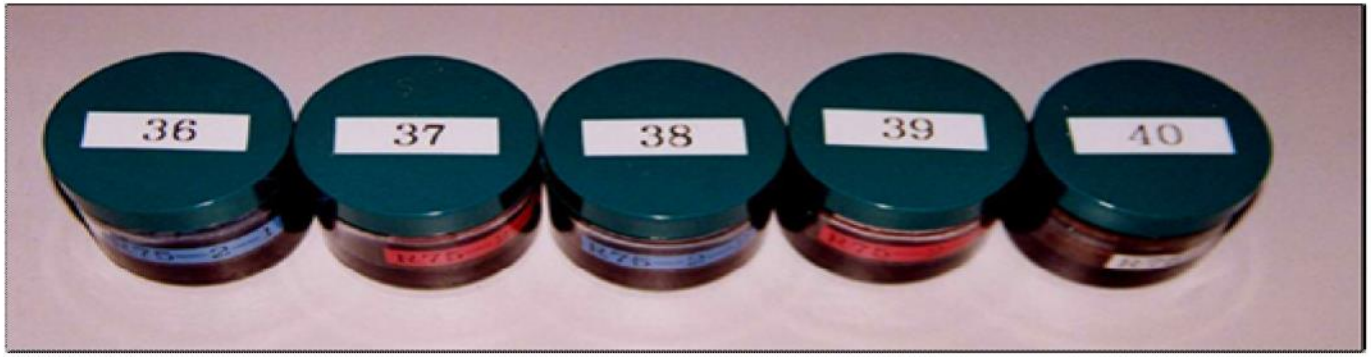
- S&T opportunities: HRMS

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

Yellow Agent	✓ Mustard ✓ Lewisites ✓ Mixture of Mustard and Lewisites
Red Agent	✓ DA: Diphenylchloroarsine ✓ DC: Diphenylcyanoarsine
Blue Agent	✓ Phosgene
White Agent	✓ Trichloroarsin (used in mixture with the Blue agent)



Dr Zhanshang Zhao Ministry of National Defence and Mr Cheng Tang (OPCW SAB)

analytical chemistry

Article

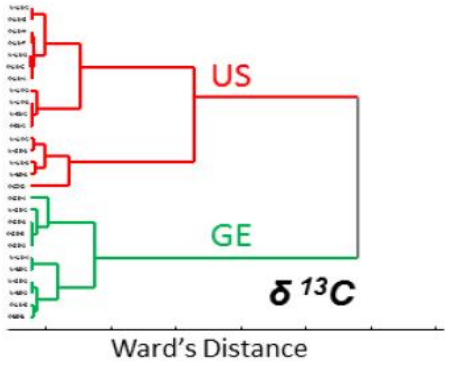
pubs.acs.org/ac

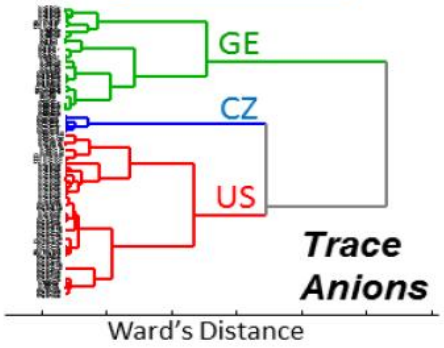
Source Attribution of Cyanides Using Anionic Impurity Profiling, Stable Isotope Ratios, Trace Elemental Analysis and Chemometrics

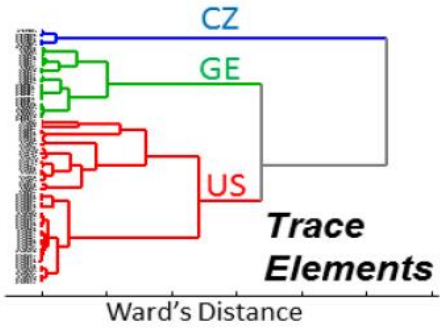
Nikhil S. Mirjankar, Carlos G. Fraga,* April J. Carman, and James J. Moran

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

DOI: 10.1021/acs.analchem.5b04126
Anal. Chem. 2016, 88, 1827−1834

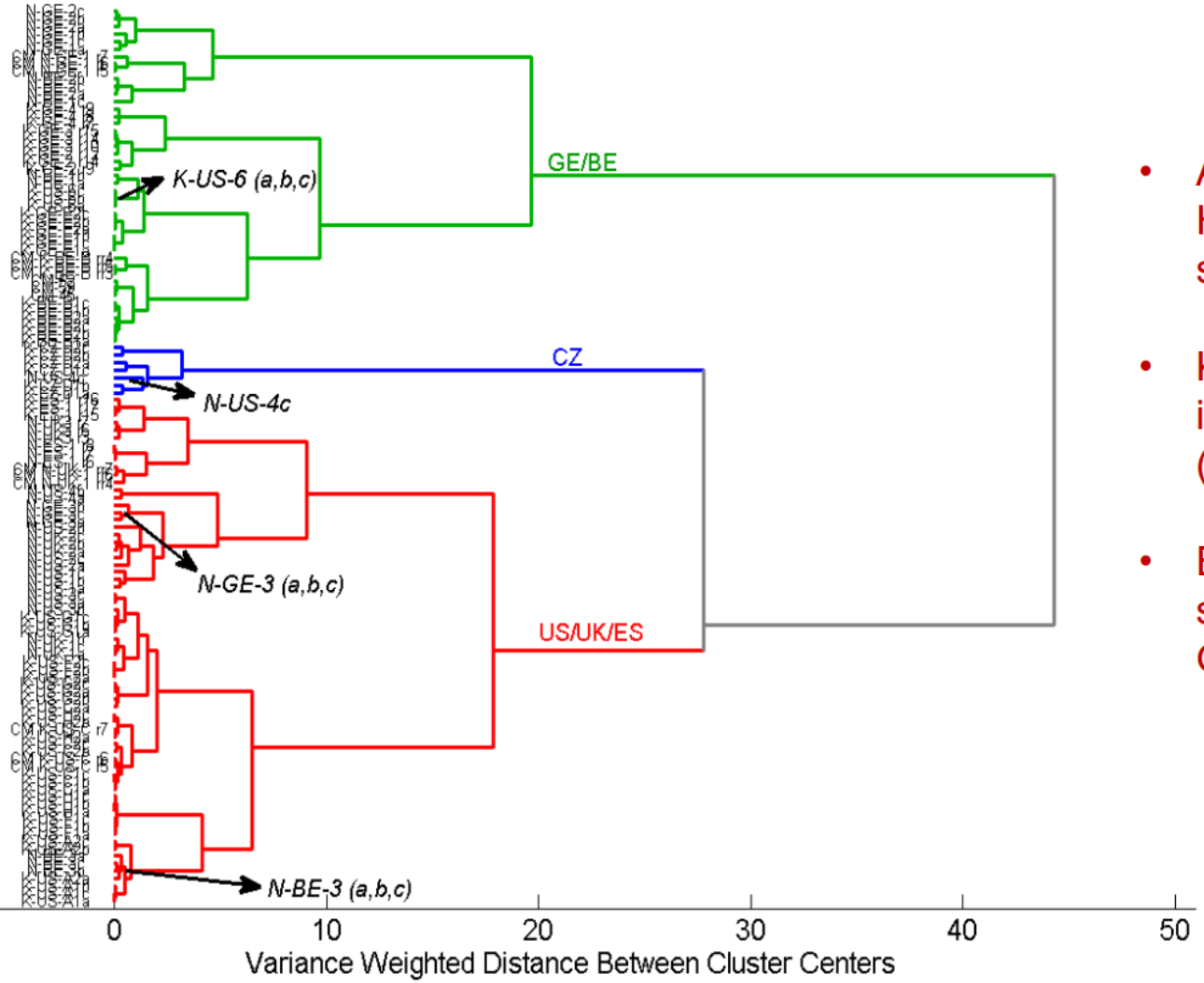






Pacific Northwest
NATIONAL LABORATORY

HCA Dendrogram using HPIC Peak Areas for unk5, SO_4, OX, and PO_4

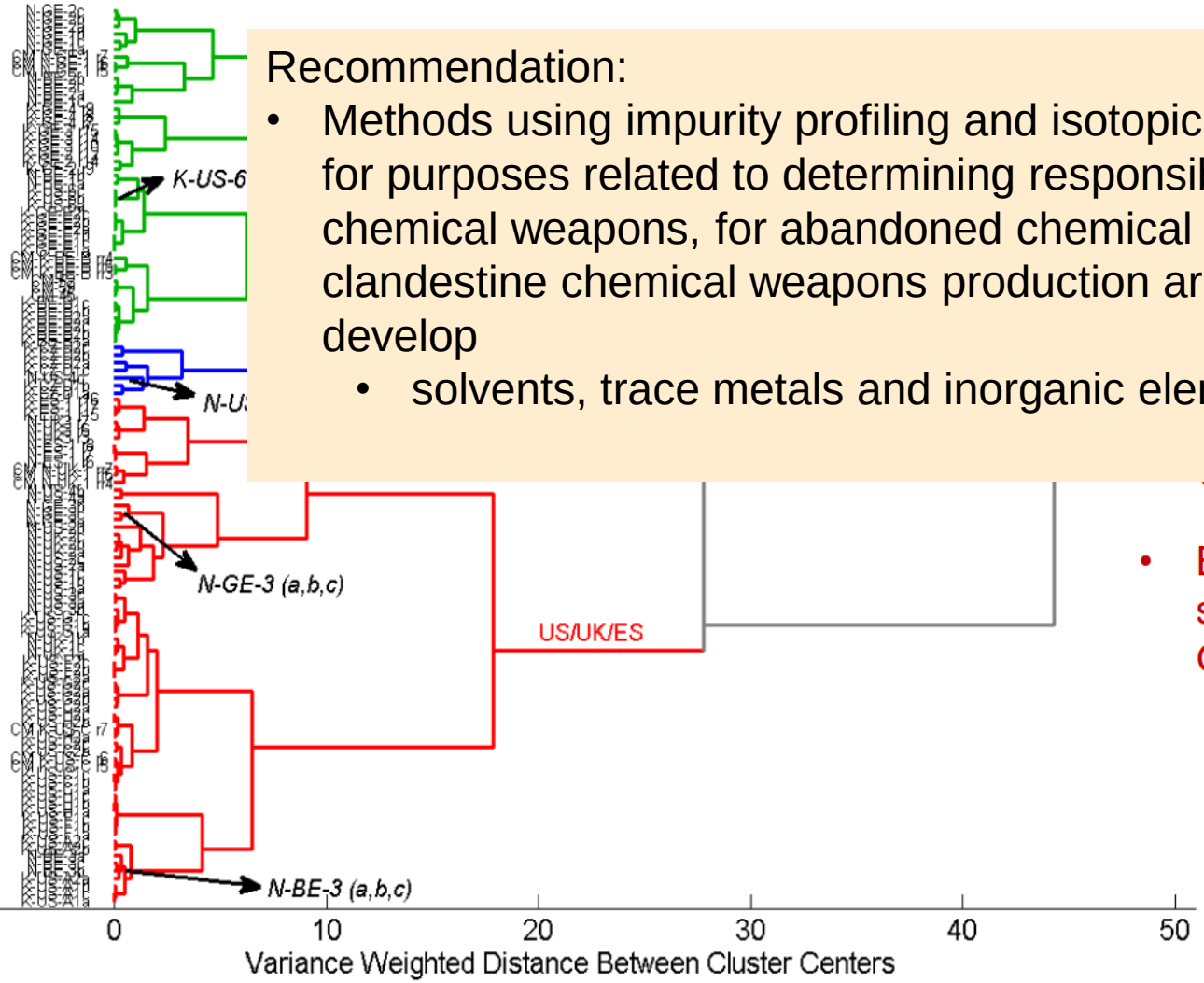


- Area-normalized and auto-scaled HPIC data of 120 cyanide sample profiles.
- KCN and NaCN samples cluster into three groups: (1) US/UK/ES, (2) GE/BE, and (3) CZ.
- Each group corresponds to one solid cyanide factory: (1) US, (2) GE, and (3) CZ.

Carlos Fraga, PNNL

Pacific Northwest

HCA Dendrogram using HPIC Peak Areas for unk5, SO_4, OX, and PO_4



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

auto-scaled

anide

ples cluster

US/UK/ES,

Z.

- Each group corresponds to one solid cyanide factory: (1) US, (2) GE, and (3) CZ.

Carlos Fraga, PNNL

Pacific Northwest

evidence collection : strategy

1) rescue service

2) CBRNE -team

3) technical scene investigators

- scene preservation
- scene assessment
- search and sampling strategy
- documentation

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

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- 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.

POLIISI
KESKUSRIKOSPOLIISI

Australian Government
National Measurement Institute

Heroin Signature Program

- HS 1 - Opiate Alkaloids (GC-MS)
- HS 2 - Manufacturing By-products
- HS 3 - Occluded Solvents
  - » Headspace GC-MS)

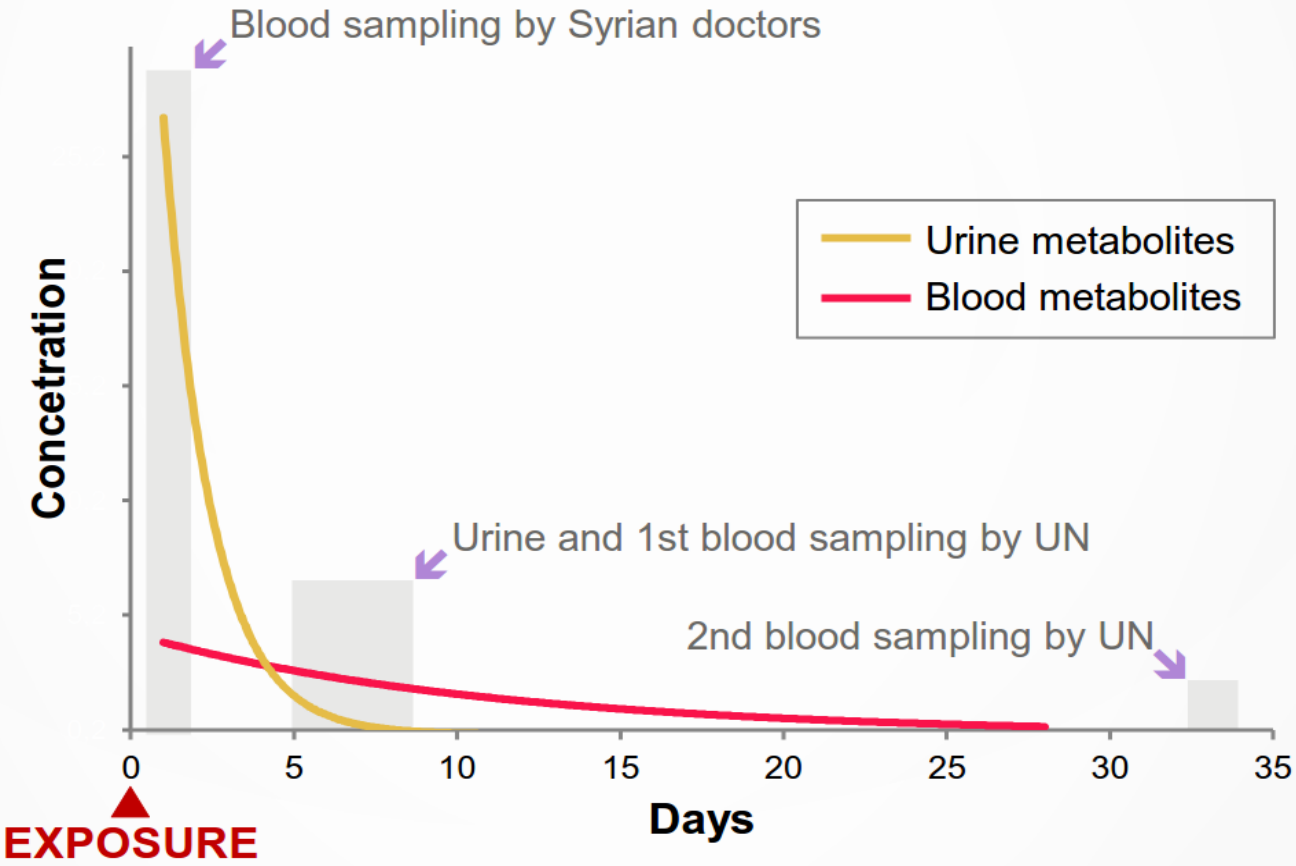
Geographical Origin

- HS 4 - Adulterants (CE)
- HS 5 - Diluents (LC-ELSD)
- HS 6 - Stable Isotope Ratios (IRMS)

Tactical Comparisons

Dr Michael Collins, Australian Forensic Drug Laboratory, National Measurement Institute, the illicit drug profiling programme

SAMPLING vs. TIME OF EXPOSURE



Sources: UN Reports in 2013 / T. Nakajima, *et al.*, *Arch. Toxicol.*, **72** (1998) 601–603 / M.I. Solano, *et al.*, *J. Anal. Toxicol.*, **32** (2008) 68–72.

CDC – Emergency Response Branch

Emergency Response Team

- Response 24-7
- Support collection, packing, storage and shipment

Rapid Toxic Screen

- 150 Chemical agents or metabolites in blood, urine, or plasma/serum

Laboratory Response Network

- Partnership between CDC and Public Health Laboratories

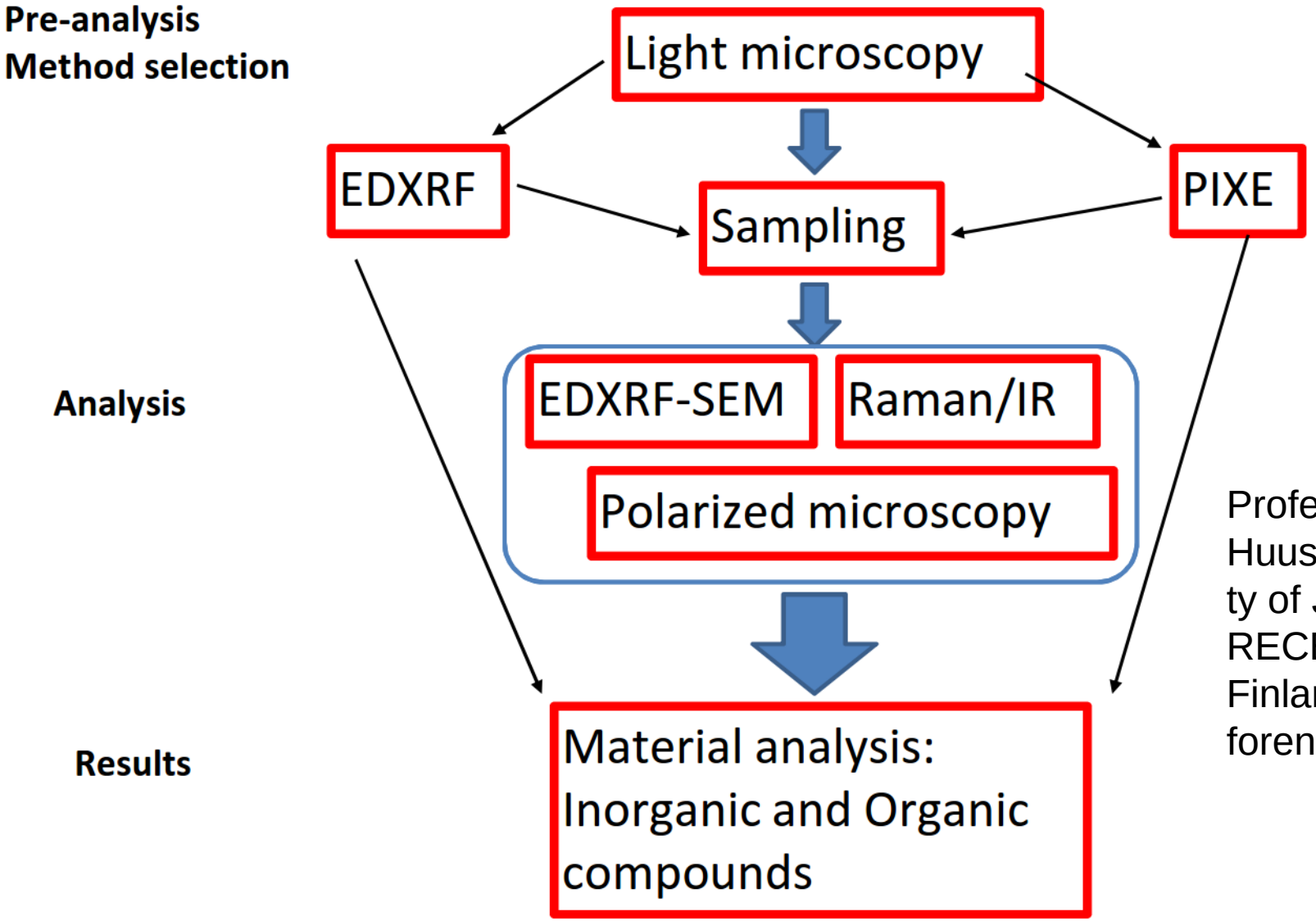
Dr. Rudolf Johnson, CDC, “Measuring Human Exposure to Nerve Agents and Marine Toxins”

Provenance and Attribution

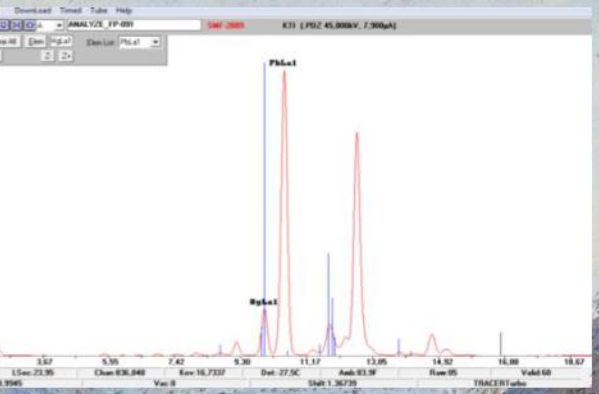
- **Attribution** means the authorship of a work of art.
- To determine the attribution it is necessary to study the following points:
  - **Style**
  - **Subject**
  - **Provenance**
  - **Technique and materials**
- Together all these help us to contextualise the work of art.

Professor Juhani Huuskonen,University of Jyväskylä and RECENART® Inc., Finland), chemical forensics and art

Material analysis



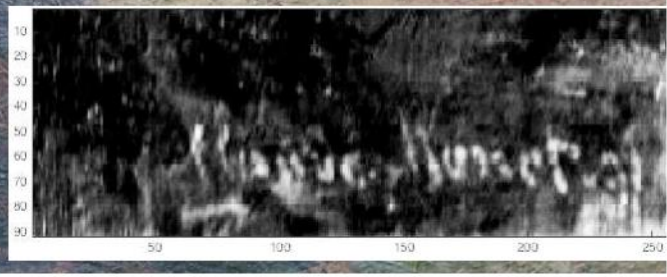
Professor Juhani Huuskonen,Univer ty of Jyväskylä an RECENART® Inc., Finland), chemical forensics and art



Serlachius Fine Art Foundation: Claude Monet, ”A Haystack in the Evening Sun” 1891.

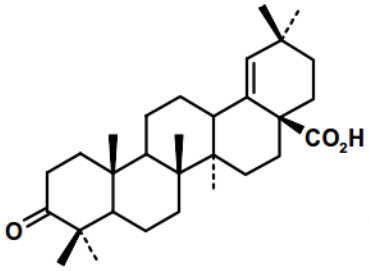
With hyperspectral camera RECENART team revealed a signature underneath the paint layers. The material analysis verified that the pigments used in the painting (also in the paint that covered the signature) were exactly the same that Claude Monet had used in his other Haystack paintings.

Result: The painting was attributed to Claude Monet.

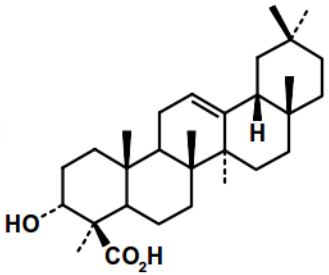


Biomarkers in archaeology

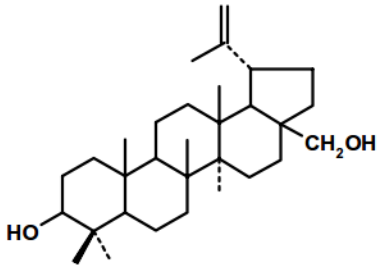
Professor Evershed



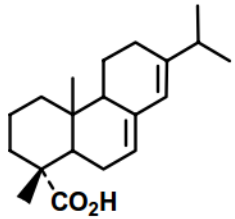
Pistacia resin



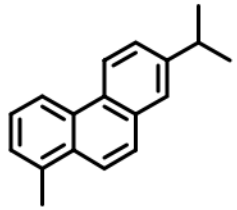
Frankincense



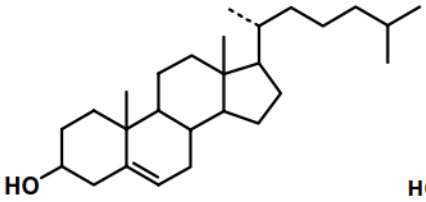
Birch bark products



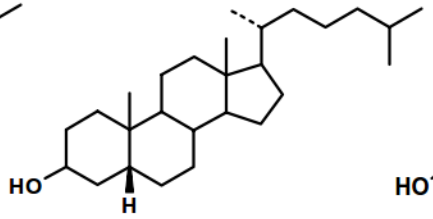
Coniferous resin

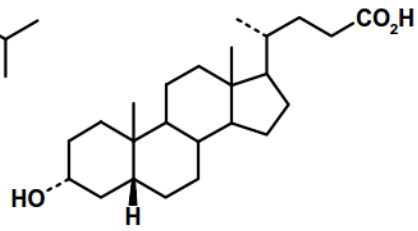


Heated resin product

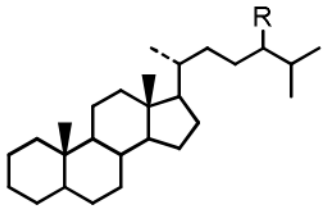


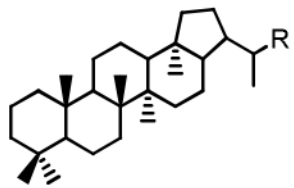
Widely occurring sterol



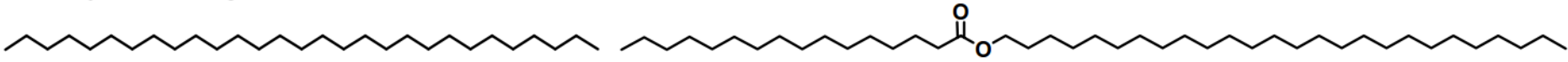


Manure indicators in soils

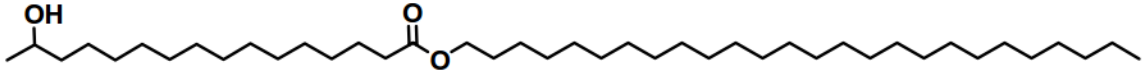




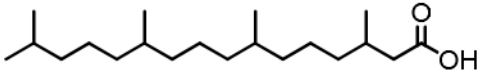
Petroleum bitumen



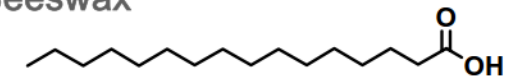
Plant epicuticular waxes



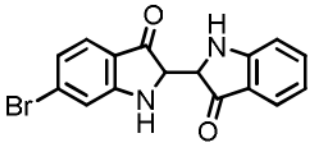
Beeswax

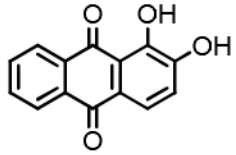


Isoprenoid fatty acid

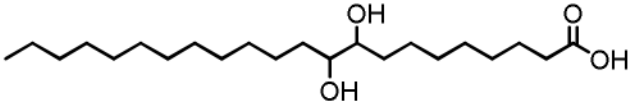


Common fatty acid

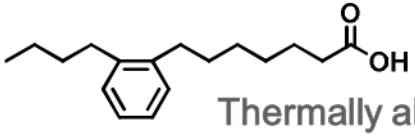




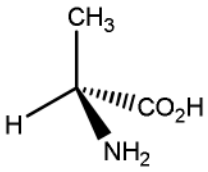
Natural dyes

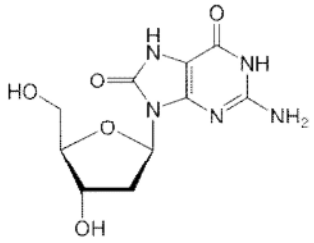


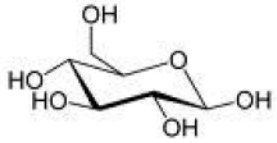
Oxidised fatty acid



Thermally altered fatty acids







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

Determining stable isotope values

Whole tissues or crude extracts

Sealed tube combustion and trapping of CO_2 (and N_2)

Isotope ratio MS

Bulk isotope values

Whole tissues or crude extracts

Combustion using an elemental analyser → GC separation of CO_2 and N_2 → 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

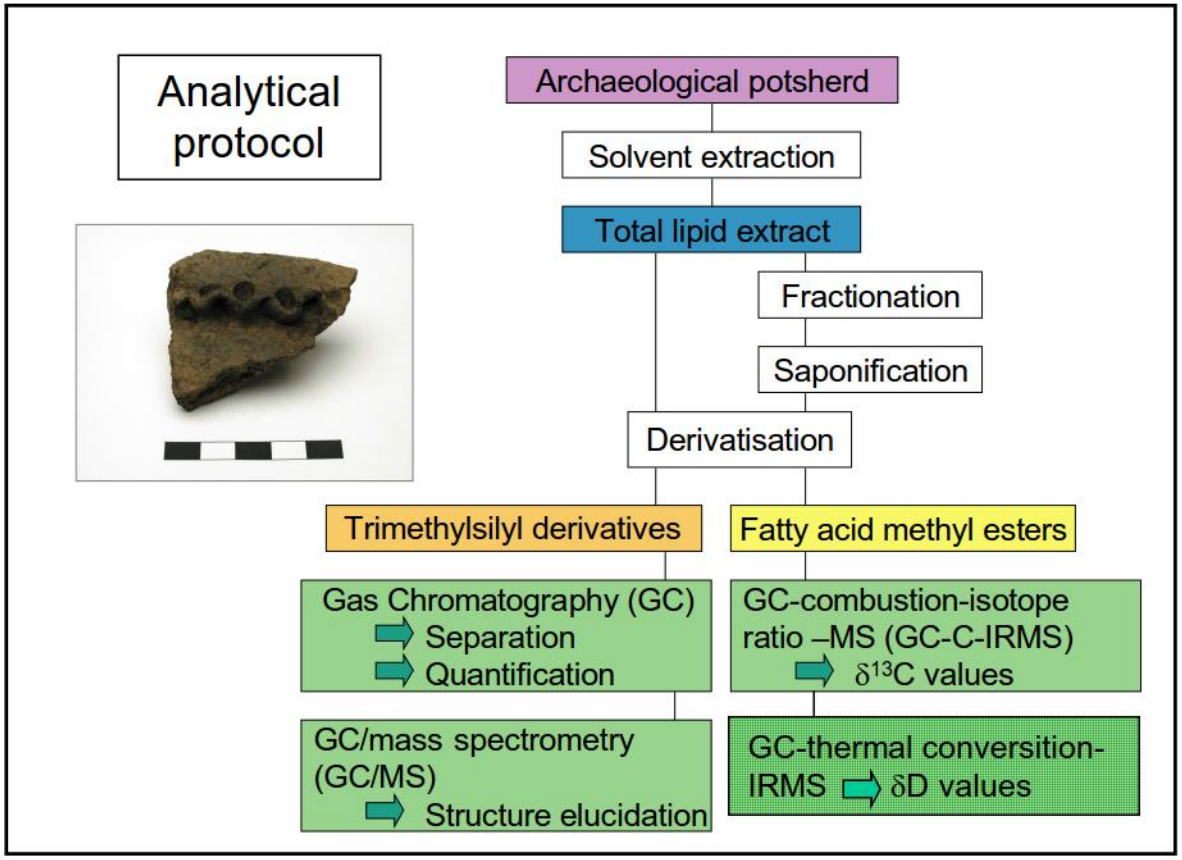
Compound-specific isotope values

Analysis of lipids in archaeological pottery

Professor Evershed

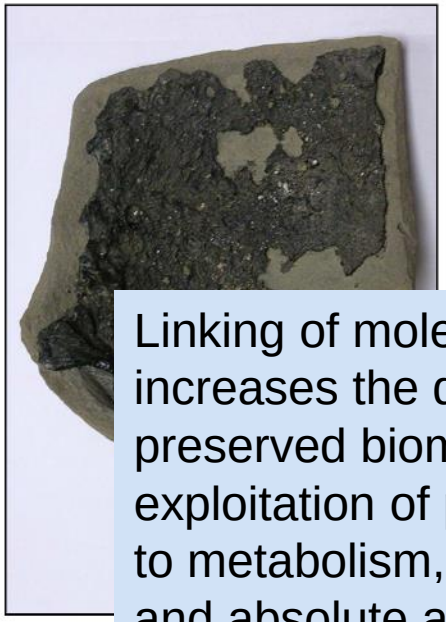
Surface residues

Absorbed residues



Analysis of lipids in archaeological pottery

Professor Evershed



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.

Surfa

Absorbed residues

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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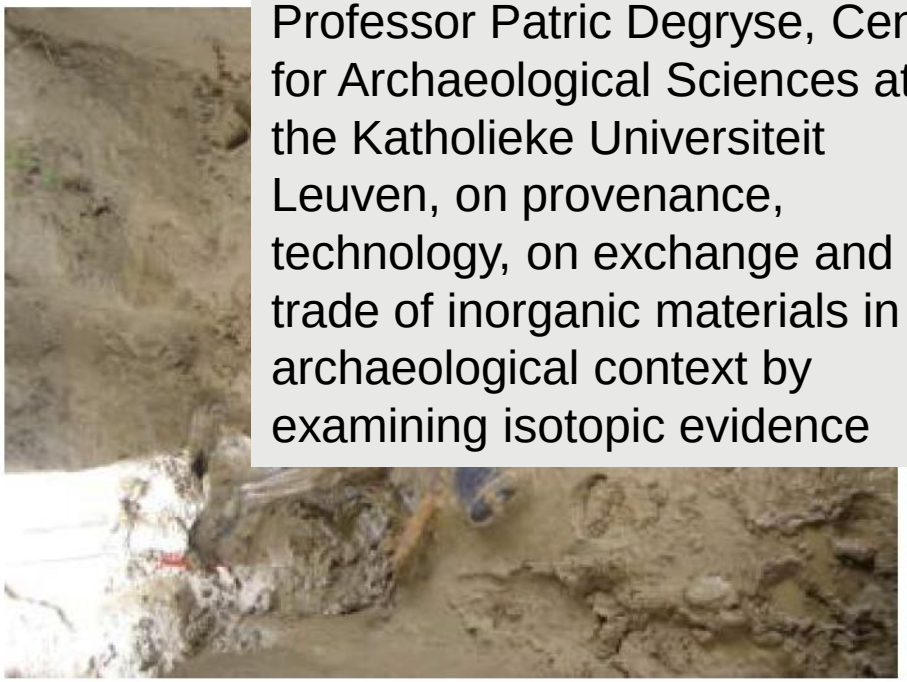

Professor Patric Degryse, Centre for Archaeological Sciences at the Katholieke Universiteit Leuven, on provenance, technology, on exchange and trade of inorganic materials in an archaeological context by examining isotopic evidence

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

Professor Patric Degryse

(Weigand PC, Harbottle G, Sayre EV (1977) Turquoise Sources and Source Analysis: Mesoamerican and the Southwestern U.S.A. In: Earle TK, Ericson JE (eds) Exchange Sytems in Prehistory, Academic Press New York, pp. 15-34)

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