Real-Time Detection of Safety-Related Substances in Dust Particles using a Single Particle Mass Spectrometer

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OUTLINE

+ OBJECTIVE & BACKGROUND

+ METHODOLOGY & EXAMPLES
  • Single Particle Mass Spectrometers (SPMS)
  • Example particle
  • Data Evaluation

+ OUTLOOK & SUMMARY

FKZ: 13N15567
Realtime Detection of Hazardous Dust Particles

- Worldwide transport of hazardous compounds
- Illegal transport of explosives and drugs
- Some of the compounds do not have enough vapor pressure, therefore they exist in form of particles/dust/aerosols
- Transport of synthetic and very toxic opioids, such as fentanyl and its derivates are increasing in the last years

Funded partners:
- ParteQ GmbH
- Photonion GmbH
- University Rostock
- German federal criminal police (BKA)

Associated partners:
- Airport Rostock
- DHL
- German customs

FKZ: 13N15567
R&D Project HazarDust

Goal: development of a detection technology for hazardous particles on **luggage**, transport **containers**, or even **envelopes** based on Single Particle Mass Spectrometry.
Non-volatile Hazardous Compound

- Common military and industrial explosives: NO₂ compounds, often low vapor pressure
- Home made explosives: peroxides, middle to high vapor pressure
- Drugs (Fentanyls), very low vapor pressure

<table>
<thead>
<tr>
<th>Name</th>
<th>Molecular Weight</th>
<th>Density [g/cm³]</th>
<th>Vapor Pressure</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMX (Octogene)</td>
<td>296</td>
<td>1.91</td>
<td>~ 1 ppq (25°C) Particle</td>
<td></td>
</tr>
<tr>
<td>RDX (Hexogene)</td>
<td>222</td>
<td>1.83</td>
<td>6 ppt ... 30 ppt (25°C)</td>
<td>Particle</td>
</tr>
<tr>
<td>PETN (Pentrite)</td>
<td>316</td>
<td>1.78</td>
<td>18 ppt (25°C) Particle</td>
<td></td>
</tr>
<tr>
<td>TNT (2,4,6-Trinitrotoluene)</td>
<td>227</td>
<td>1.65</td>
<td>7.7 ppb (25°C) Particle/Vapor</td>
<td></td>
</tr>
<tr>
<td>HMTD (Hexamethylene triperoxide diamine)</td>
<td>208</td>
<td>0.88</td>
<td>1.7 ppb (22°C) Particle/Vapor</td>
<td></td>
</tr>
<tr>
<td>Fentanyl</td>
<td>336</td>
<td>1.1</td>
<td>~6 ppt (25°C) Particle</td>
<td></td>
</tr>
<tr>
<td>Carfentany (deadly conc.)</td>
<td>395</td>
<td>1.1</td>
<td>~0.3 ppt (25°C) Particle</td>
<td></td>
</tr>
</tbody>
</table>

**Bild:** Fentanyl | DEA.gov. Abgerufen am 2. Februar 2022.
Wipe Sampling: Problems……

- Desorption of a mixture, target compound could be suppressed
- Sampling and desorption is time consuming

→ Some minutes

Solution: Chemical analysis of each single particle, ideally in milliseconds !!!
1994 bipolar TOF with LDI of aerosols, using laser velocimetry for simultaneous detection of negative & positive ions (Hinz et al. 1994; Prather et al. 1994)

⇒ start of the modern ATOF, SPMS, SPAMS …
1) Particle inlet system

Formation of gas-free particle beam in vacuum (differentially pumped aerodynamic lens or jet expansion) → size depended particle velocity
2) Particle sizing system

Laser velocimetry:
Particle detection by cw-laser using light scattering
(size range: ~2.5 µm down to ~150 nm)
Nano Particles (30-150 nm): Free running LDI laser @ 100 to 2000 Hz
(Excimer Laser only)
SPMS with LDI ionisation

3) Laser Desorption Ionization

Laser Desorption/Ionization: ➔ Formation of Plasma
4) Dual ToF-MS

Dual, bipolar TOFMS: Detects anionic and cationic LDI species from the individually ionized particles → Broad coverage of chemical species
Health Relevant Ambient Particles

Pollutants and parameters we need to detect at a single-particle level:

- Transition metals (Fe, Ni, Cu, Zn …) and heavy metals (Pb …)
- Carbon fractions (Soot/EC or OC)
- Polycyclic Aromatic Hydrocarbons (PAH, carcinogens)
- Aging- and SOA-indicators (Oxalate, NO$_3^-$, SO$_4^{2-}$)
- Particle size in the high tissue delivered dose (TDD) size range (250-500 nm)
- Individual particle source apportionment by source markers
Health Relevant Ambient Particles

SPMS with LDI using optimized laser parameters detects:
• Toxic heavy metals (e.g. Pb)
• Transition metals with enhanced sensitivity (Fe, Ni, Cu, …)
• Carbonaceous soot (EC)
• Nitrate, sulfate, OC, other metals, some organics (e.g. oxalate)

However the health relevant carcinogenic Polycyclic Aromatic Hydrocarbons (PAH) are not detectable

➔ Resonance based two-step laser ionization schemes (REMPI) have been developed to sensitively detect important PAH-compounds together with the toxic metals by SPMS
➔ But: PAH need to be volatilized
Examples

Single Particle MS of a wood combustion particle

**LDI approach: Elements**

LDI-SP-TOFMS
single particle \(d_{ae} = 1.9 \, \mu m\)

- \(K^+\)
- \(Na^+\)
- \(Fe^+\)
- \(K_2CN^+\)

**Two-step LD-REMPI approach: PAH signature**

LD-REMPI-SP-TOFMS
single particle \(d_{ae} = 3.6 \, \mu m\)

- \(202\)
- \(178\)
- \(152\)
- \(165\)
- \(220\)
- \(234\)
- \(252\)


HazarDust
NEW: Combination of Simultaneous LDI & PAH-SPMS

Instrument with 3 big Lasers (IR & LDI & REMPI)??

Idea: Single UV-laser with spatially shaped pulse for combined LDI (cations/metals, anions) & REMPI excitation (PAH)
Examples

Single Particle MS of diesel & wood soot / tar balls

Simultaneous LDI & PAH-SPMS

Single Particle MS of ambient particles (transport over 100km!)

**Simultaneous LDI & PAH-SPMS**

- **a)** Aged particle with heavy metal (Pb)
  
  *East European coal power plant/heavy industry ash particle*

- **b)** Aged particle with organic (PAH)
  
  *East-European combustion particle/house heating*
Examples

Single Particle MS of Ambient Particles in Rostock

Simultaneous LDI & PAH-SPMS

LDI negative:
- sulphate lower than usual background
- CN⁻, phosphate indicate biomass (burning)

LDI positive:
- only fragments & potassium: wood/biomass
- no transition/alkali metals: no coal, industrial

REMPI:
- 228 & 252 dominate
- weak alkylated PAHs

Pattern of a local fire (easter fire!)
Currently also pattern of ship emissions are evaluated → tracking

https://www.flickr.com/photos/robven/1953413479
Examples

Single Particle MS of Compounds of Medical Use and Abuse

- Aspirin
- Ibuprofen
- Cannabidiol
Examples
Single Particle MS of drugs (First Results)

**Metamizol**

- m/z = 263
- m/z = 137
- m/z = 121

**Tramadol**

- m/z = 203.14
- m/z = 121
- m/z = 263
Examples
Single Particle MS of drugs/precursors (First Results)

4-anilino-\textit{N}-phenethylpiperidined (4-ANPP)

280 m/z

4-ANPP as fentanyl precursor
Examples
Single Particle MS of Explosives (First Results)

\(3,4\text{-DNT}\) with CO\(_2\) laser

\(m/z = -137\)

\([-62]\)

\([-46]\)

\([-26]\)

\(2,4\text{-DNT}\) with CO\(_2\) laser

\(m/z = -137\)

\([-97]\)

\([-62]\)

\([-46]\)

\([-26]\)

\(\leftarrow 3,4\text{-DNT}\)

(MW=182)

\(\leftarrow 2,4\text{-DNT}\)

(MW=182)
Examples

Single Particle MS of Explosives (First Results)

\[ \text{N-O-N} + \text{O}^- \]

\[ \text{C}_6\text{H}_3\text{N} + \text{O}^- \]

\[ \text{C}_6\text{H}_2\text{N} + \text{O}^- \]

\[ \text{m/z} = -210 \]

\[ \text{m/z} = -226 \]

\[ \text{m/z} = -197 \]

\[ \text{m/z} = -181 \]

\[ \text{m/z} = -137 \]

\[ \text{TNT-fragments} \]


\[ \text{2,4,6-TNT} \]

\[ \text{3,4,5-TNT} \]
Software integration & data evaluation

User-friendly GUI

Control

Data-acquisition

Data-processing

Feedback
Data-evaluation

supervised

Goal

Non-supervised

Expert judgement

Machine learning algorithm
Creation of database and pattern recognition routines

Realtime 'intelligent' data-evaluation

ART 2-A theory (Adaptive Resonance Theory)
• Real-time method for particle classification
• ART is an architectural concept for neural networks
• Particles are either assigned to existing clusters or a new cluster is created.
• Cluster centers are readjusted with each assigned particle (self-learning)
• Later, if necessary, definition of cluster centers from example spectra of target substances.

Adapted ART 2-A theory (Adaptive Resonance Theory)
• Clusters are checked in parallel
• Second ART run only for the cluster centers or a DBSCAN (Density-Based Spatial Clustering of Applications with Noise: Density-Based Spatial Clustering of Applications with Noise).
• Expert Judgement

Punkte bei A sind Kernpunkte. Punkte B und C sind dichterreichbar von A und dadurch dichteverbunden und gehören zum selben Cluster. Punkt N ist weder ein Kernpunkt noch dichterreichbar, also Rauschen (Wikipedia)
Creation of database and **pattern recognition routines**

- **DeepLearning data evaluation**
  - Simple access using APIs
  - Machine learning, AI, neuronal networks …
  - Example: Keras is an open source deep learning library, written in Python, based on TensorFlow
Field tests and optimisation

- Application under realistic/real conditions
- Optimisation
Summary & Outlook

- Single particle analysis is an interesting solution for detection of hazardous particles → fast (up to 100Hz!)
- An unique laser desorption and laser ionization method allows simultaneous LDI and REMPI ionization → hard & soft ionization methods for inorganic and organic compounds
- Environmental applications show the potential of the technology
- First spectra of drugs and explosives are shown from the R&D project **HazarDust**
- Parameters for laser based ionization of target compounds have to be optimized
- Further measurements, also with fentanyl and other explosives are planned for the next future
Thank you!

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Photonion GmbH was founded in 2009 in Schwerin, Germany

Photonion is a Spin-Off company of the Analytical Group of Prof. Zimmermann

Producing **customized mass spectrometers** for chemical analysis of complex gas mixtures, aerosol application and process control

Specialized on soft ionization techniques in mass spectrometry especially photoionization

Performing contract research