A Systematic Approach to the Analysis of General Unknowns

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New Jersey State Police
Office of Forensic Sciences
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General Unknowns

• Reasons for Submission:
  – Identification of contents
  – Determination if specific compound(s) is/are present
  – Determination if a questioned substance is comparable to a known
  – Routine case takes a turn
General Unknowns

• Role of Analyses:
  – Provide links between:
    • Victim & Suspect
    • Victim & Scene
    • Suspect & Scene
  – Provide proof of a criminal act.
  – Provide investigative leads.
  – Support or refute a story.
  – Provide information for reconstructions.
Common Submissions

• Unknown powders
• Unknown liquids
• Unknown mixtures
• Items with unknown residues
• Solids thought to contain adulterants
• Liquids thought to contain adulterants
Common Analytes

- Inorganic salts
- Building materials
- Acids
- Bases
- Greases
- Oils
- Cleaning products
- Bleach
- Volatile organics
- Solvents
- Pesticides
- Random schmutz
General Considerations

- Safety first
- Is there any background information?
- Analysis requires a well thought out approach
  - No single way to approach any given case
  - Experience and common sense are important
- Often utilize every available resource
- Can be literally anything, but often something common
Case Example

• Background:
  – Suspect is an illegal alien looking to purchase a large quantity of “Ammonium Nitrate”
  – White powder found in vehicle
  – Visual/Stereomicroscopic exam indicated powder was finely ground and uniform
  – Proceeded to use EDXRF for elemental analysis
Case Example
Case Example

- Elemental profile of sample indicated the presence of lime

- This was then confirmed using X-Ray Diffraction
Systematic Approach

• The Analytical Funnel:
  – Start with general approach and compile information
  – Narrow down possibilities with ultimate goal of identification
Systematic Approach

• Analytes can be broken down into solids, liquids, and gases
• Each of which may contain single components, homogenous mixtures (e.g. liquid solutions), or heterogeneous mixtures (e.g. mixed crystalline compounds)
Systematic Approach

• General Observations:
  – Packaging (commercial container, condition of container, listed ingredients, markings, etc.)
  – State of sample (solid, liquid, gas, mixture)
  – General amount of sample present
  – Obvious odor
Solids

• Visual/General Examination
  – Color
  – Consistency (e.g. metallic, powder, resin, polymeric, etc.)

• Stereomicroscopic Examination
  – Crystalline vs. Amorphous
  – Organic vs. Inorganic
  – Homogenous vs. Heterogeneous
    • Manual separation of particles
Solids

• Light Microscopy/Polarized Light Microscopy
  – Color with transmitted light
  – Homogenous vs. Heterogeneous
  – Isotropic vs. Anisotropic
  – Presence of pigments/fillers
  – General refractive index
  – Particle identification
Solids

- Ignition test (low explosives, improvised explosive mixtures)
- Chemical Tests
  - Solubility
  - Spot Tests/Color Tests
  - Crystal Tests
Solids

- **Instrumentation:**
  - Elemental Analysis: EDXRF, SEM-EDS
  - GC, GC/MS (Organics)
  - Pyrolysis GC, GC/MS
  - FTIR
  - XRD
Solids

- **General Approach:**
  1) Visual/General Examination
  2) Stereomicroscopic Examination
  3) PLM
  4) Elemental Analysis (organic vs. inorganic)
  5) Compound Identification
     a) FTIR
     b) XRD
     c) Mass Spectrometry (GC/MS, Py-GC/MS)
  6) Additional tests
     a) Chemical Tests
     b) Ignition Tests
Liquids

- Visual/General Examination
  - Color
  - Single vs. Multi Phase (organic/aqueous mix)
  - General viscosity
  - Presence of any precipitate or sediment
- pH
- Conductivity (Ionic Solution)
- Ignition Test (Ignitable Liquid)
Liquids

- Solid-Liquid Solution
- Liquid-Liquid Solution
- Extractions
  - Liquid-Liquid
  - Acid/Base
  - Solid Phase Extraction
  - Precipitation
  - Evaporation/Distillation
  - Heated and Passive Headspace (volatile organics)
Liquids

- Chemical tests
  - Precipitate Reactions
  - Spot Tests
  - Color Tests
  - Crystal tests

- Instrumental Analysis
  - Elemental Analysis
    - EDXRF (in absence of vacuum)
    - SEM-EDS (precipitates only)
Liquids

- Instrumental Analysis (cont.)
  - GC, GC/MS (organic solutions, extracts)
  - FTIR
    - Liquid samples (liquid cell, ATR)
    - Precipitates
  - XRD
    - Precipitates
Liquids

• General Approach:
  1) Visual/General Examination
  2) pH
  3) Conductivity
  4) Ignition Test
  5) Extraction/Solvent Dilution/Evaporation/Precipitation
  6) Sample Screening/Identification of Components
     a) FTIR
     b) Mass Spectrometry (GC/MS, Py-GC/MS)
     c) Elemental Analysis
  7) Chemical Tests
Elemental Analysis of Liquid (EDXRF w/o Vacuum)
Swab Blank (EDXRF w/o Vacuum)
Gases

- Rarely Encountered
- Safety Concerns
- Analysis
  - GC, GC/MS
  - FTIR via Gas Cell
Elemental Analysis

- Organic vs. Inorganic
- Elemental composition
- Preliminary information for screening purposes
- SEM-EDS vs. EDXRF
Special Considerations

- Consider any chemistry
- Controls and Comparisons
- Hydration States
  - Desiccation, Baking Out
- Hygroscopic Salts
  - Dry and coat with mineral/silicone oil
- Small amounts of analyte: scale down tests
- Rely on others
  - Ask questions
  - Make calls
- Sometimes it just doesn’t work out!
Case Examples
Beefcake 4000
A Cup of Joe
A Cup of Joe

• Suspect is accused of adding cupric sulfate to instant coffee
• Victim prepares a cup of joe that doesn’t taste so good
Cup of Joe
Cup of Joe
Cup of Joe
The Anarchist
The Anarchist

• Background:
• Suspect had an anarchist cookbook sampler
  – Plastic water bottle with white slurry and what appeared to be balls of aluminum foil
  – Gray powder (“Explosive Powder”)
  – Incendiary device (analyzed as fire debris)
EDXRF vs. SEM-EDS
EDXRF vs. SEM-EDS

<table>
<thead>
<tr>
<th>New Jersey State Police</th>
<th>Eagle III u-Probe</th>
<th>Operator: VJD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fsc: 56793</td>
<td>LSec: 200</td>
<td>04-Aug-2005</td>
</tr>
<tr>
<td></td>
<td>12:17 PM</td>
<td>kv: 20</td>
</tr>
<tr>
<td></td>
<td>uAmp: 1000</td>
<td>(Rh)</td>
</tr>
<tr>
<td></td>
<td>2000um-Spot</td>
<td>Atm: Vacuum</td>
</tr>
</tbody>
</table>

| B |

![Graph showing intensity vs. energy (keV) with peaks for Al, Cl, and Ca]
EDXRF vs. SEM-EDS

Label A: White Slurry
Gray powder ("Explosive Powder")

- Visual/Stereomicroscopic examination disclosed the presence of gray and beige granules as well as clear crystals
- Ignition test negative
- Proceeded to analyze using EDXRF and SEM-EDS
The Anarchist

Gray powder:
The Anarchist

Gray powder EDXRF:
The Anarchist

• Conclusions:
  – Gray Powder
    • Clear crystals had rhombohedral shape characteristic of sucrose. Confirmed sucrose using FTIR.
    • Mixture of arsenic and sugar indicated that this sample was rat poison.
Mmmm Lunch!
Mmmm Lunch

• Background:
  – Husband Suspects Wife of Poisoning His Prepared Lunch Consisting Of:
    • Buffalo Style Chicken Wings
    • Coffee
Mmmmm Lunch
Mmmm Lunch
Mmmm Lunch

Coffee Chromatogram

Coffee Aromatic Profile
Mmmmm Lunch

Coffee (Insecticide)

Coffee (Insecticide) Mass Spectrum
Mmmmm Lunch

Abundance

#146576: Permetrinic acid, methyl ester
Glade
• Background:
  – Partially decomposed female victim found in basement of boarding house covered with white powder
  – Victim’s husband was the main suspect
  – A sample of the white powder was collected at scene and submitted for identification
  – Prosecution theory: The husband killed his wife and hid her in the basement. Covered her with white powder to hide odor.
The white powder was received in the lab and opened.
A sweet, distinct odor was immediately noticed.
Analysis proceeded as follows: Visual/stereomicroscopic examination, elemental analysis, FTIR, XRD.
Results: Primarily inorganic, containing sodium sulfate.
• Background research indicated a possible carpet deodorizer
• Proceeded to reference collection
• Shop-Rite across the street
• Looked a bit crazy for a while in the cleaning supplies aisle looking at ingredients and sniffing various carpet deodorizer bottles
• Found one that had a comparable odor, purchased and brought it back to the lab for analysis
• Performed same analyses and observed comparable results
• Extracted both the unknown and reference sample for GC-MS analysis.
• Observed to contain similar components (Jasmine Oil)
• Report: The white powder contains sodium sulfate and a fragrance component. Substances which contain such mixtures include but are not limited to some carpet deodorizers.
Elemental Analysis

New Jersey State Police  Eagle III u-Probe  Operator: VJD

Fsc: 9345  LSec: 200  09-Aug-2005 9:42 AM  kV: 40  uAmp: 35 (Rh)  2000um-Spot  Atm: Vacuum

A  C:\Documents and Settings\Administrator\My Documents\Data\VJD\ Spec #13 White Powder.spc

B  C:\Documents and Settings\Administrator\My Documents\Data\VJD\ \Glade Carpet Deodorizer Std.spc  Glade

Intensity

Na  Si

Energy [keV]

0.50  1.00  1.50  2.00  2.50  3.00  3.50  4.00  4.50
FTIR
XRD
GC-MS

Glade Carpet Deodorizer

Unknown White Powder
In validation of the conclusion, after the report was issued, it was disclosed that the suspect admitted to his cellmate that he had sprinkled carpet deodorizer on the victim to hide the odor.
Resources
Resources

NIST Chemistry WebBook

NIST Standard Reference Database Number 69

View: Search Options, Models and Tools, Documentation, Changes, Notes

Show Credits

NIST reserves the right to charge for access to this database in the future.

Search Options top

General Searches
- Formula
- Name
- IUPAC identifier
- CAS registry number
- Reaction
- Author
- Structure

Physical Property Based Searches
- Ion energetics properties
- Vibrational and electronic energies
- Molecular weight
Resources

Search for Species Data by Chemical Formula

Please follow the steps below to conduct your search (Help):

1. Enter the desired chemical formula (e.g., C4H*Cl): [C7H8]
2. Select any desired options for the search:
   - [ ] Exactly match the specified isotopes. (Help)
   - [ ] Allow elements not specified in formula. (Help)
   - [ ] Allow more atoms of elements in formula than specified. (Help)
   - [x] Exclude ions from the search. (Help)
3. Select the desired units for thermodynamic data:
   - [ ] SI
   - [x] calorie-based
4. Select the desired type(s) of data:
   - Thermodynamic Data
     - [ ] Gas phase
     - [ ] Condensed phase
     - [ ] Phase change
     - [ ] Reaction
     - [ ] Ion energetics
     - [ ] Ion cluster
   - Other Data
     - [ ] IR spectrum
     - [ ] THz IR spectrum
     - [ ] Mass spectrum
     - [ ] UV/Vis spectrum
     - [ ] Gas Chromatography
     - [ ] Vibrational & electronic energy levels
     - [ ] Constants of diatomic molecules
     - [ ] Henry's Law
5. Press here to search: [Search]
Resources

Search Results

11 matching species were found.

For each matching species the following will be displayed:

- Chemical name
- Chemical formula
- Structure image (if available)

Click on the name to see more data.

1. Toluene (C₆H₅)

2. 1,3,5-Cycloheptatriene (C₇H₈)

3. 2,5-Norbornadiene (C₆H₈)

4. Quadricyclane (C₆H₄)

Toluene

- **Formula**: C₆H₅
- **Molecular weight**: 92.1384
- **IUPAC Standard InChI**: 1/C6H5/c1-7-5-3-2-4-6-7/h2-6H2,1H3
- **IUPAC Standard InChIKey**: VUYVABEYXQUJUBWUMSSA-N
- **CAS Registry Number**: 108-88-3
- **Chemical structure**: 

This structure is also available as a 2D Molfile or as a computed 3D Molfile.

- **Isotopomers**:
  - C₆D₅: C₆D₅
  - Toluene-d₆

- **Other names**: Benzene, methyl, Methyldiisopropylmethane, Methylbenzene, Methylphenylmethanol, Phenylethanol, Aromatic-Isolated, Toluene, Methane, methyl-NCI-C0772. Toluene, Toluol, Ecra waste number U220, Tolu-sol, DN 1294, Dracyl, Mesityl benzene, Benzenophene, Tol, methylbenzene (toluene)

- **Permanant link**: For this species. Use this link for bookmarking this species for future reference.

- **Information on this page**:
  - IE Specimen
  - Mass spectrum (electron ionization)
  - References
  - Notes / Error Report
Resources
## Resources

### SDBS Compounds and Spectral Search

<table>
<thead>
<tr>
<th>Compound Name:</th>
<th>Atoms:</th>
<th>Spectrum:</th>
</tr>
</thead>
<tbody>
<tr>
<td>*%, ** for the wild card.</td>
<td>C (Carbon), H (Hydrogen), N (Nitrogen), O (Oxygen), etc.</td>
<td>Check the spectra of your interest.</td>
</tr>
<tr>
<td>e.g., %benzene = ethylbenzene...</td>
<td></td>
<td>□ MS □ IR</td>
</tr>
<tr>
<td>Molecular Formula:</td>
<td></td>
<td>□ ¹³C NMR □ Raman</td>
</tr>
<tr>
<td>C, H, then the other elements are alphabetical order, %, ** for the wild card.</td>
<td></td>
<td>□ ¹H NMR □ ESR</td>
</tr>
<tr>
<td>Molecular Weight:</td>
<td></td>
<td>IR Peaks (cm⁻¹):</td>
</tr>
<tr>
<td>Up to the first place of a decimal point</td>
<td></td>
<td>Allowance ± 10</td>
</tr>
<tr>
<td>CAS Registry No.:</td>
<td></td>
<td>*;&quot; or space is the separator for multiple peaks.</td>
</tr>
<tr>
<td>*%, ** for the wild card.</td>
<td></td>
<td>Use &quot;;&quot;, to set a range: e.g., 550-750, 1650-3000.</td>
</tr>
</tbody>
</table>

| SDBS No.: | | Transmittance < 80% |
| *%, ** for the wild card. | | |

| | | ¹³C NMR Shift (ppm): |
| | | Allowance ± 2.0 |
| | | *;" is the separator for multiple shifts, e.g. |
| | | 129.3, 184,... |

| | | No shift regions: |
| | | Range defined by two numbers separated by a space, e.g., 110 78,... |

| | | ¹H NMR Shift (ppm): |
| | | Allowance ± 0.2 |
| | | No shift regions: |
Resources
Resources

### Chemical Information

- **Chemical Name:** Calcium chloride anhydrous
- **CAS Registry Number:** 010043-52-4
- **Synonyms:** Calcium chloride; Calcium chloride, dihydrate; Calcium chloride (CaCl2); Calcium chloride (anhydrous)

### Information from other National Library of Medicine databases

- **Health Studies:** Human Health Effects from Hazardous Substances Data Bank (HSDB)
- **Toxicity Information:** Search TOXNET
- **Chemical Information:** Search ChemIDplus
- **Biomedical References:** Search PubMed

### Products that contain this ingredient

<table>
<thead>
<tr>
<th>Brand</th>
<th>Category</th>
<th>Form</th>
<th>Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pakmix Fast Set Accelerator for Concrete</td>
<td>Home Maintenance</td>
<td>powder</td>
<td>15-25</td>
</tr>
<tr>
<td>MaryKate Moisture Absorber</td>
<td>Home Maintenance</td>
<td>pellets</td>
<td>90-97</td>
</tr>
<tr>
<td>2000 Flushes Automatic Bowl Cleaner</td>
<td>Inside the Home</td>
<td>granules</td>
<td>0-1.6</td>
</tr>
<tr>
<td>Seventh Generation, Natural Lavender Laundry Liquid</td>
<td>Inside the Home</td>
<td>liquid</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Seventh Generation, Sensitive Care Laundry Liquid</td>
<td>Inside the Home</td>
<td>liquid</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Seventh Generation, Free and Clear Laundry Liquid</td>
<td>Inside the Home</td>
<td>liquid</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Seventh Generation, Baby Laundry Liquid</td>
<td>Inside the Home</td>
<td>liquid</td>
<td>0.01-1</td>
</tr>
<tr>
<td>Zee Super D-Ice</td>
<td>Landscape/Yard</td>
<td>crystals</td>
<td>&gt;90</td>
</tr>
</tbody>
</table>
### Resources

#### Brand Information

<table>
<thead>
<tr>
<th><strong>Product Name:</strong></th>
<th>2000 Flushes Automatic Bowl Cleaner</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Form:</strong></td>
<td>granules</td>
</tr>
</tbody>
</table>
| **Product Category:** | Inside the Home » Bathroom » bowl cleaner  
                        Inside the Home » Toilet Bowl » cleaner |
| **Date Entered:** | 1996-08-21                          |
| **Related Items:** | Products with similar usage in this database |

#### Manufacturer

<table>
<thead>
<tr>
<th><strong>Manufacturer:</strong></th>
<th>WD 40 Company</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Address:</strong></td>
<td>1061 Cudahy Place</td>
</tr>
<tr>
<td><strong>City:</strong></td>
<td>San Diego</td>
</tr>
<tr>
<td><strong>State:</strong></td>
<td>CA</td>
</tr>
<tr>
<td><strong>Zip Code:</strong></td>
<td>92110</td>
</tr>
<tr>
<td><strong>Telephone Number:</strong></td>
<td>619-275-1400</td>
</tr>
<tr>
<td><strong>Fax Number:</strong></td>
<td>619-275-5823</td>
</tr>
<tr>
<td><strong>Toll Free Number:</strong></td>
<td>800-448-9340</td>
</tr>
<tr>
<td><strong>Date Info Verified:</strong></td>
<td>2008-01-09</td>
</tr>
<tr>
<td><strong>Related Items:</strong></td>
<td>Products by this manufacturer</td>
</tr>
</tbody>
</table>

The following information (Health Effects, Handling/Disposal, and Ingredients) is taken from the product label and/or the Material Safety Data Sheet (MSDS) prepared by the manufacturer. The National Library of Medicine does not test products nor does it evaluate information from the product label or the MSDS.

#### Health Effects

**Acute Health Effects:** From MSDS

- Inhalation: Irritating to the nose, mouth, throat, and lungs. May
References

- [http://riodb01.ibase.aist.go.jp/s dbs/cgi-bin/cre_index.cgi?lang=eng](http://riodb01.ibase.aist.go.jp/s dbs/cgi-bin/cre_index.cgi?lang=eng)
Acknowledgements

- Dr. Howard Baum
- Ajit Tungare
- Jacki Mancilla
- George W. Chin
- Melissa Balogh, Stew Hung, and Jayne DeMichelle
- Cassandra Burke and the Symposium Steering Committee
- Jocelyn Williams
- Katie Ballance and The Pink Gorilla Dude
Questions?
Questions?