A Systematic Approach to the Analysis of General Unknowns

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Office of Forensic Sciences

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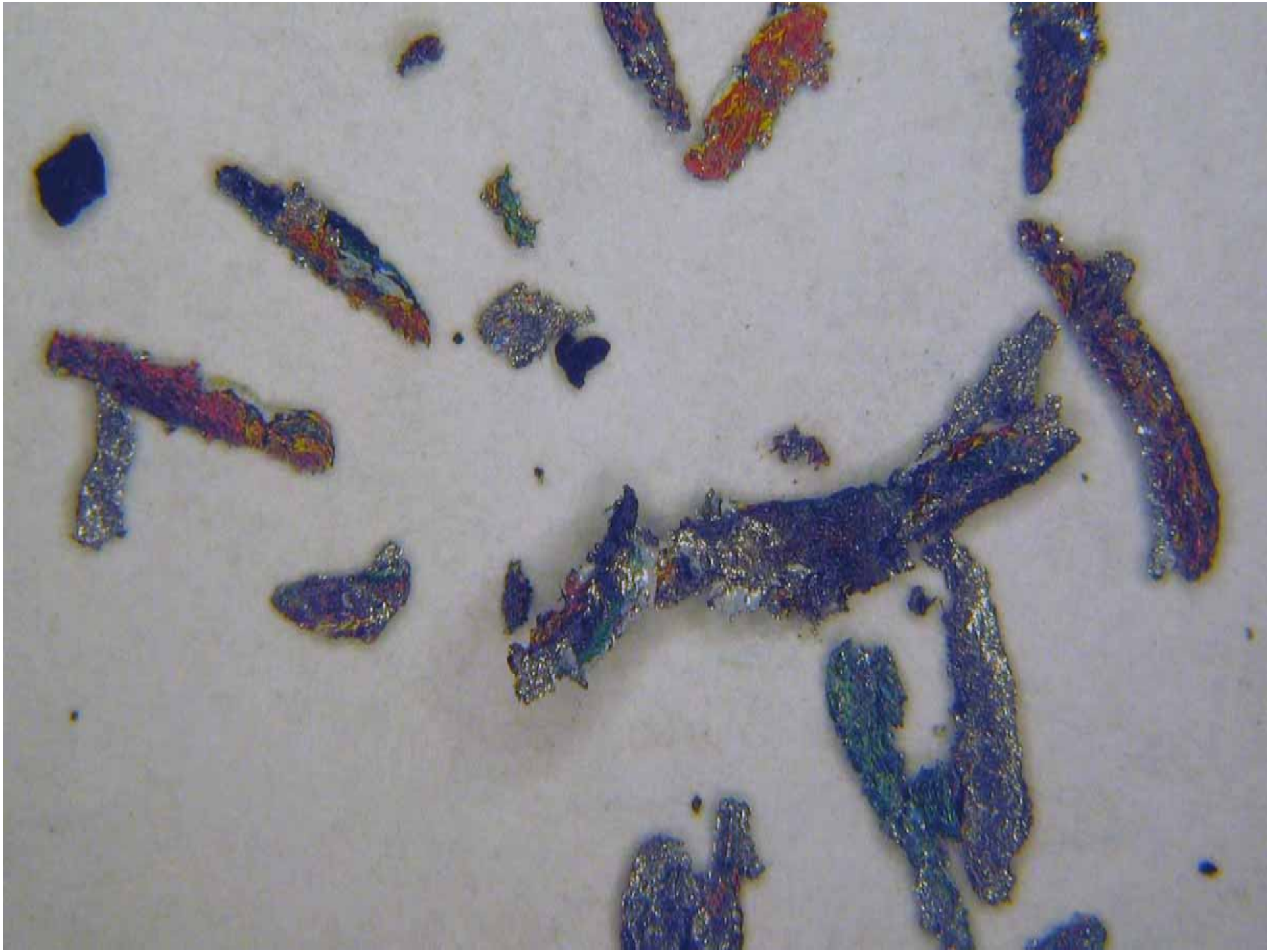
General Unknowns

- 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

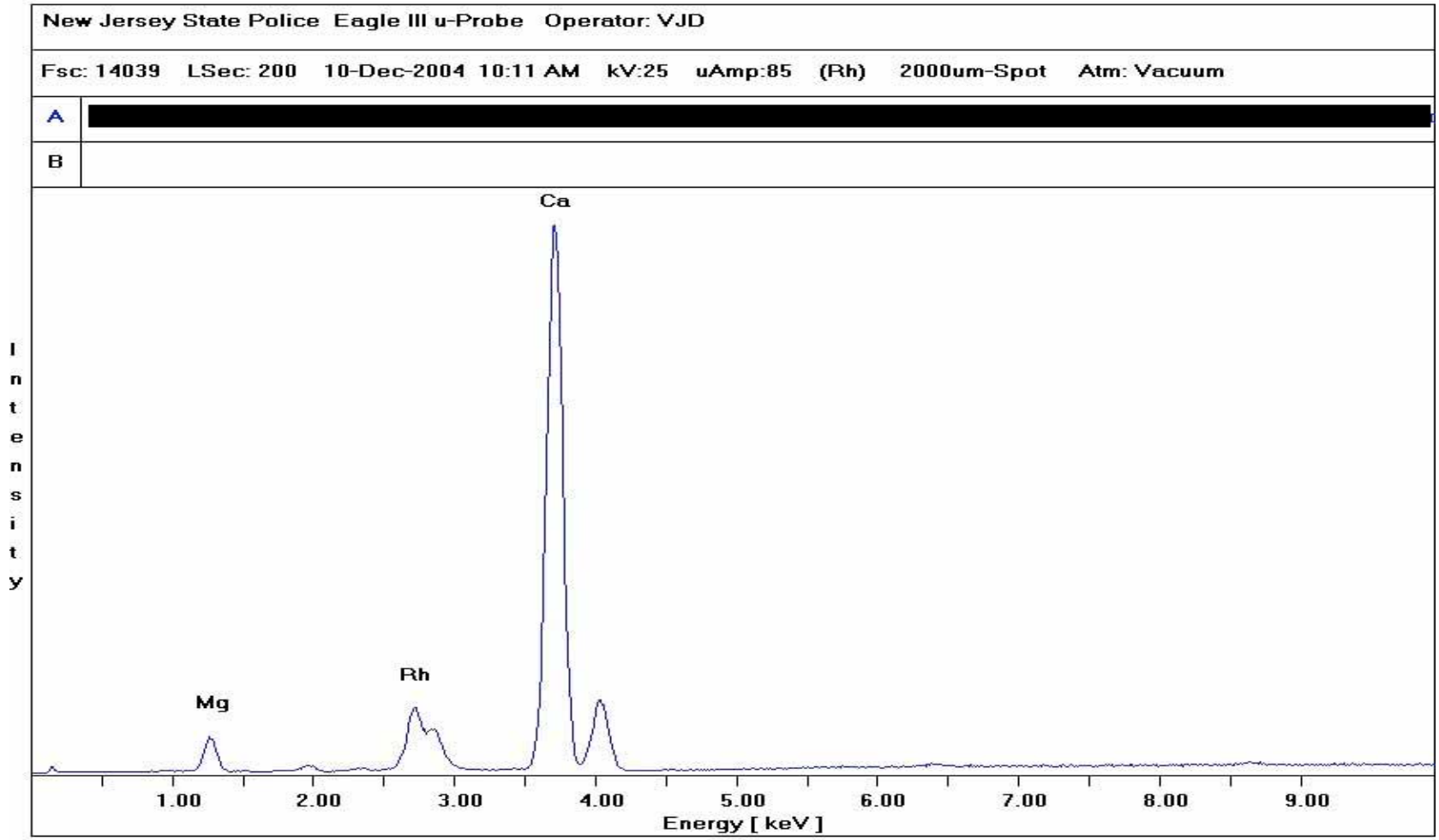
General Considerations

- 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



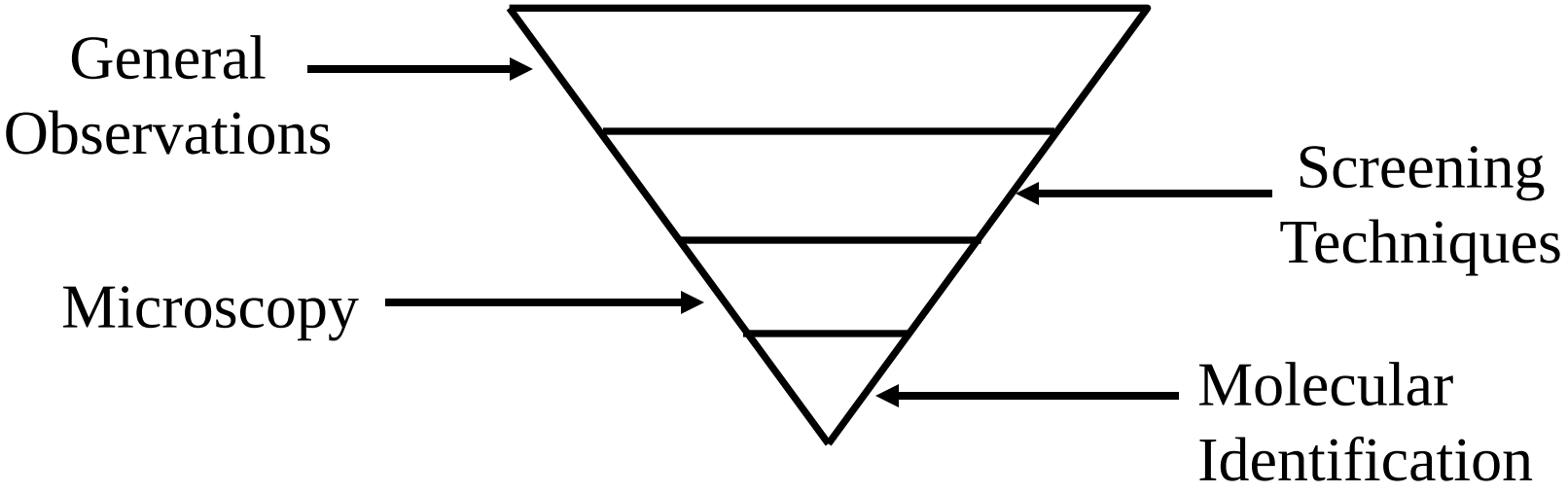
Case Example

- 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)

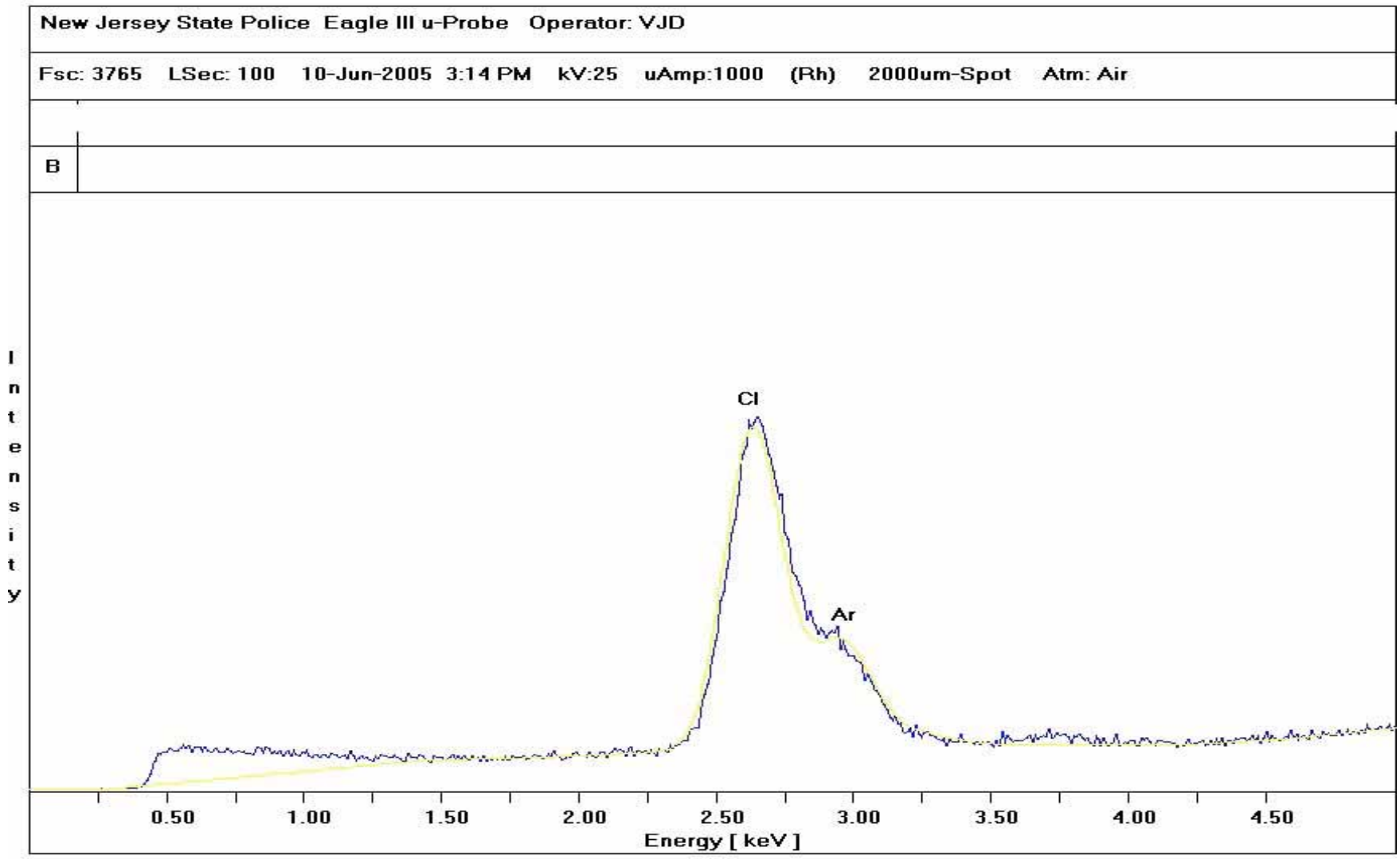
Liquids

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

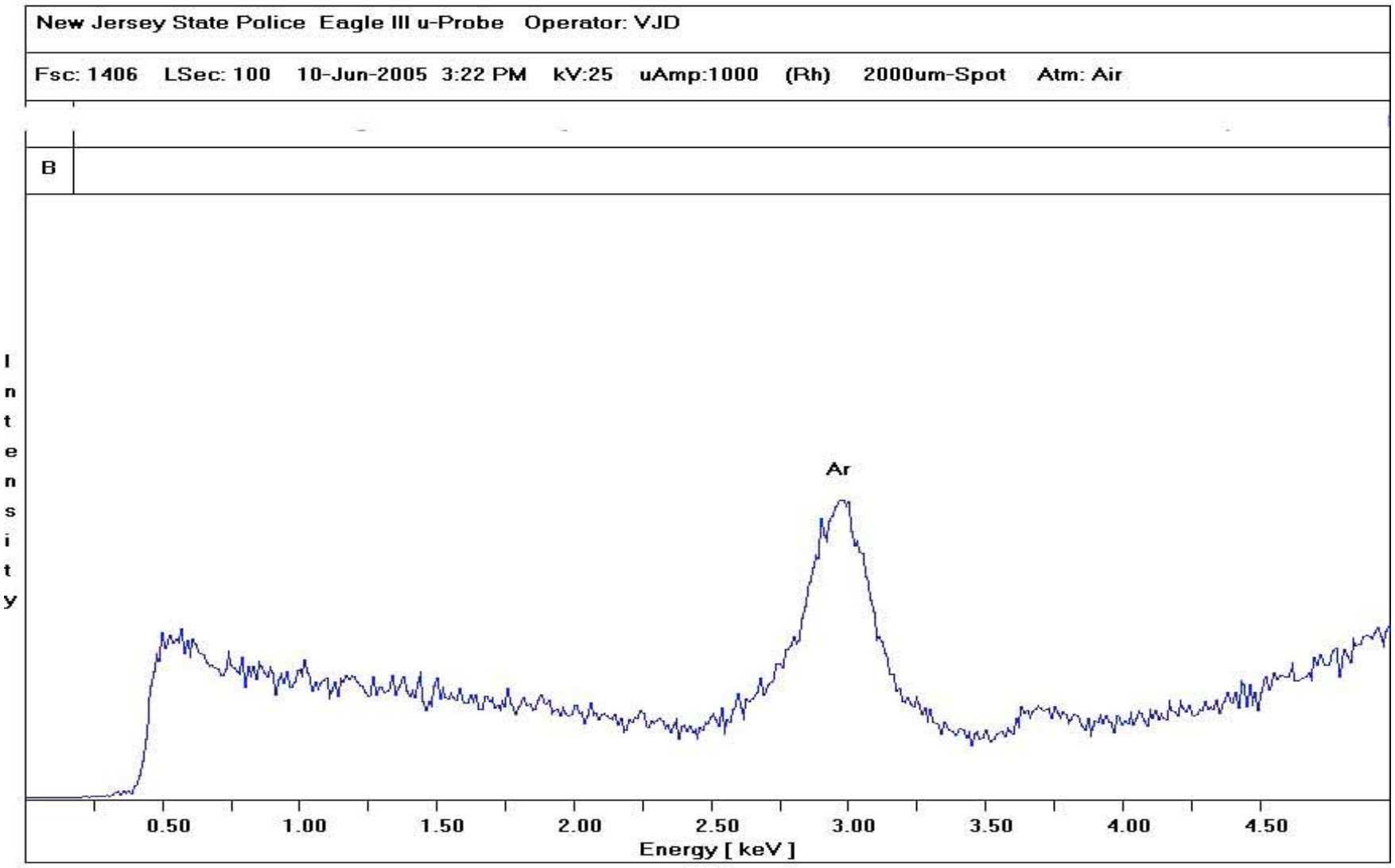
Liquids

- 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
- Hydroscopic 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

Beefcake 4000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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


NESCAFÉ
Taster's Choice
100% PURE INSTANT COFFEE
100% CAFÉ PURO INSTANTÁNEO
MAKES UP TO 105 CUPS
NET WT / PESO NETO 7 OZ (198 g)
LIGHT
MEDIUM
DARK

Cup of Joe

Cup of Joe

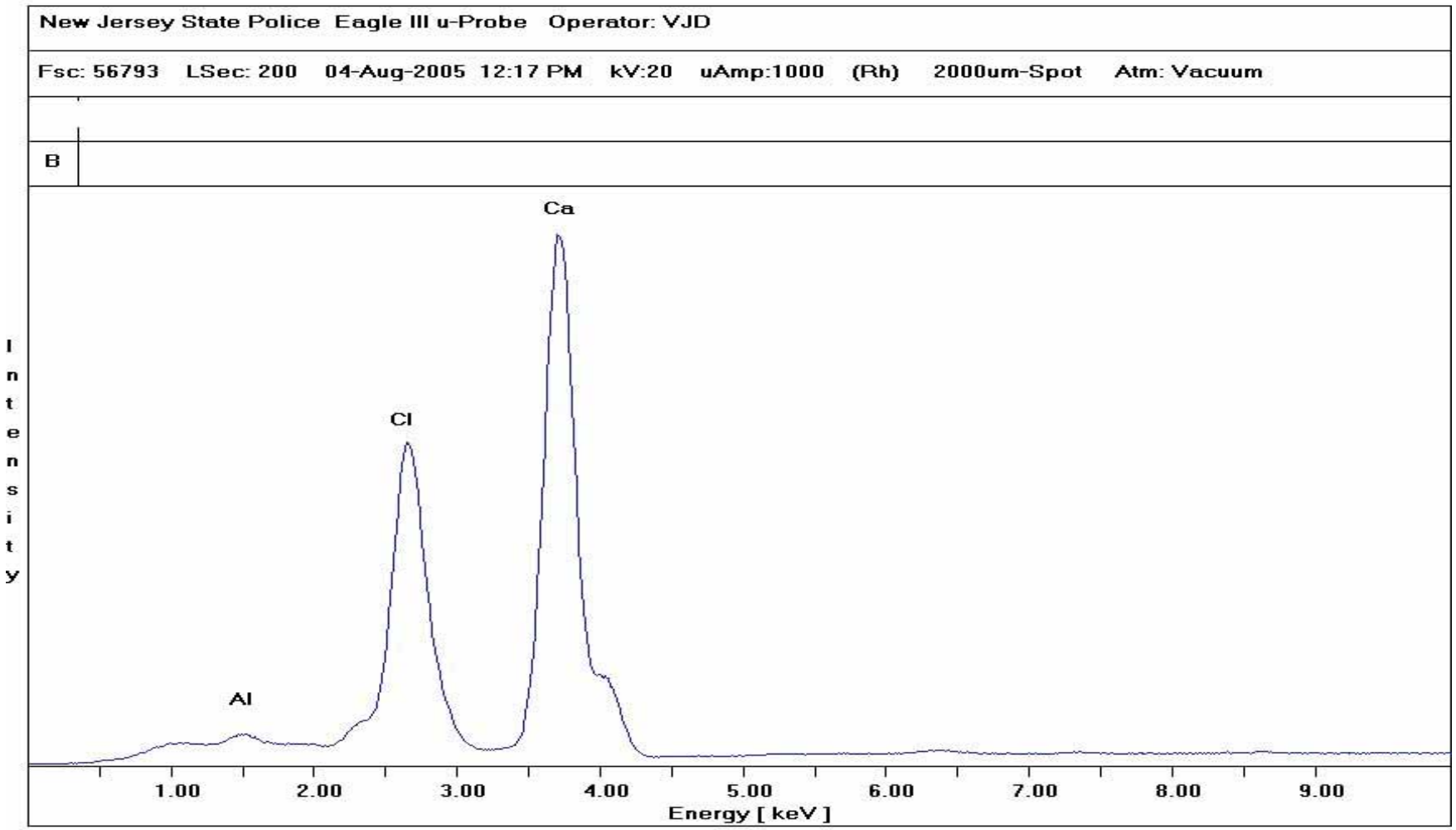
The Anarchist

The Anarchist

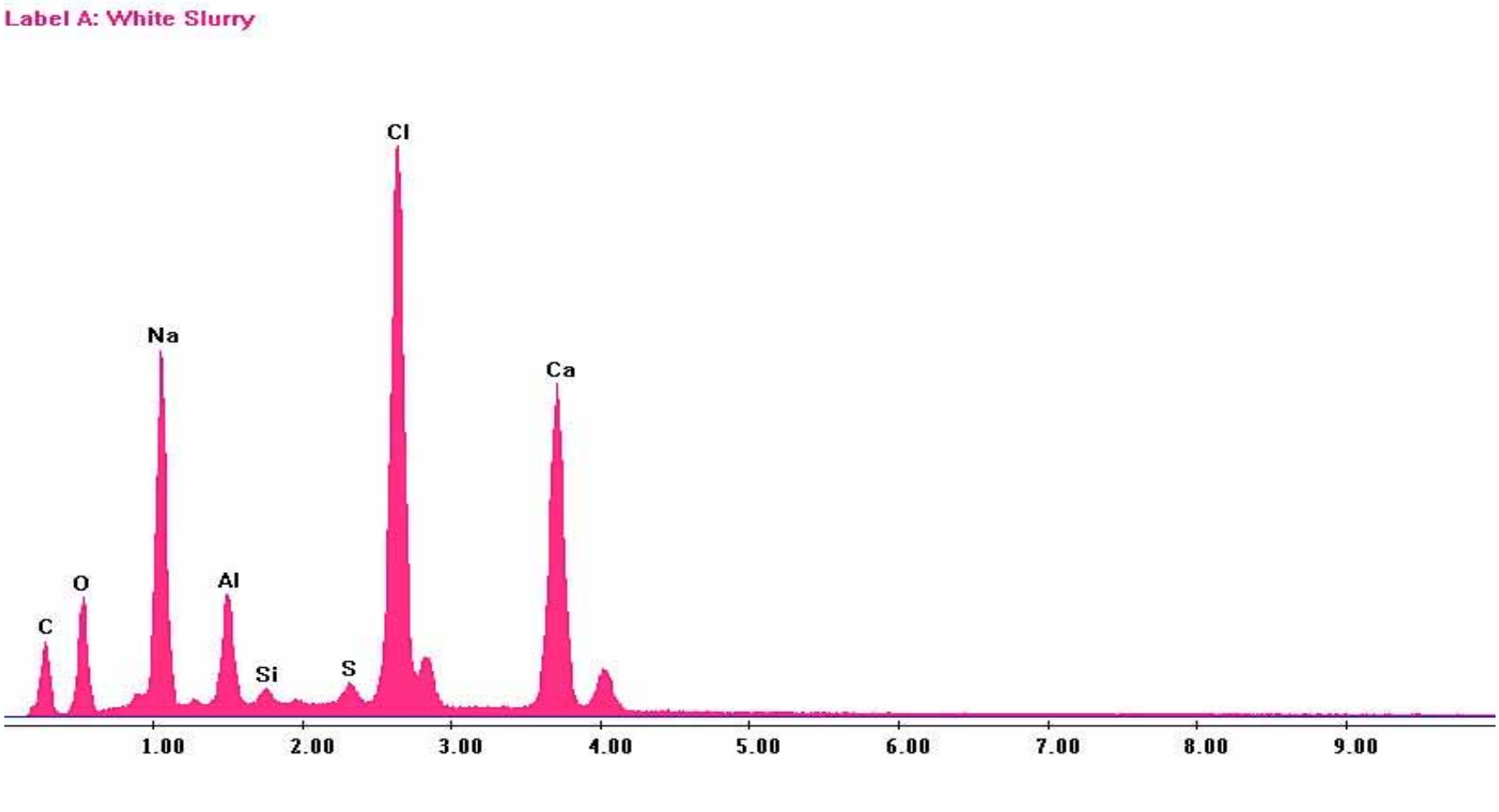
- Background:
- Suspect had an anarchist cookbook sampler
  - Plastic water bottle with white slurry and what appeared to be balls of aluminum foil
  - Gray powder (“Explosive Powder”)
  - Incendiary device (analyzed as fire debris)

EDXRF vs. SEM-EDS

EDXRF vs. SEM-EDS



EDXRF vs. SEM-EDS



The Anarchist

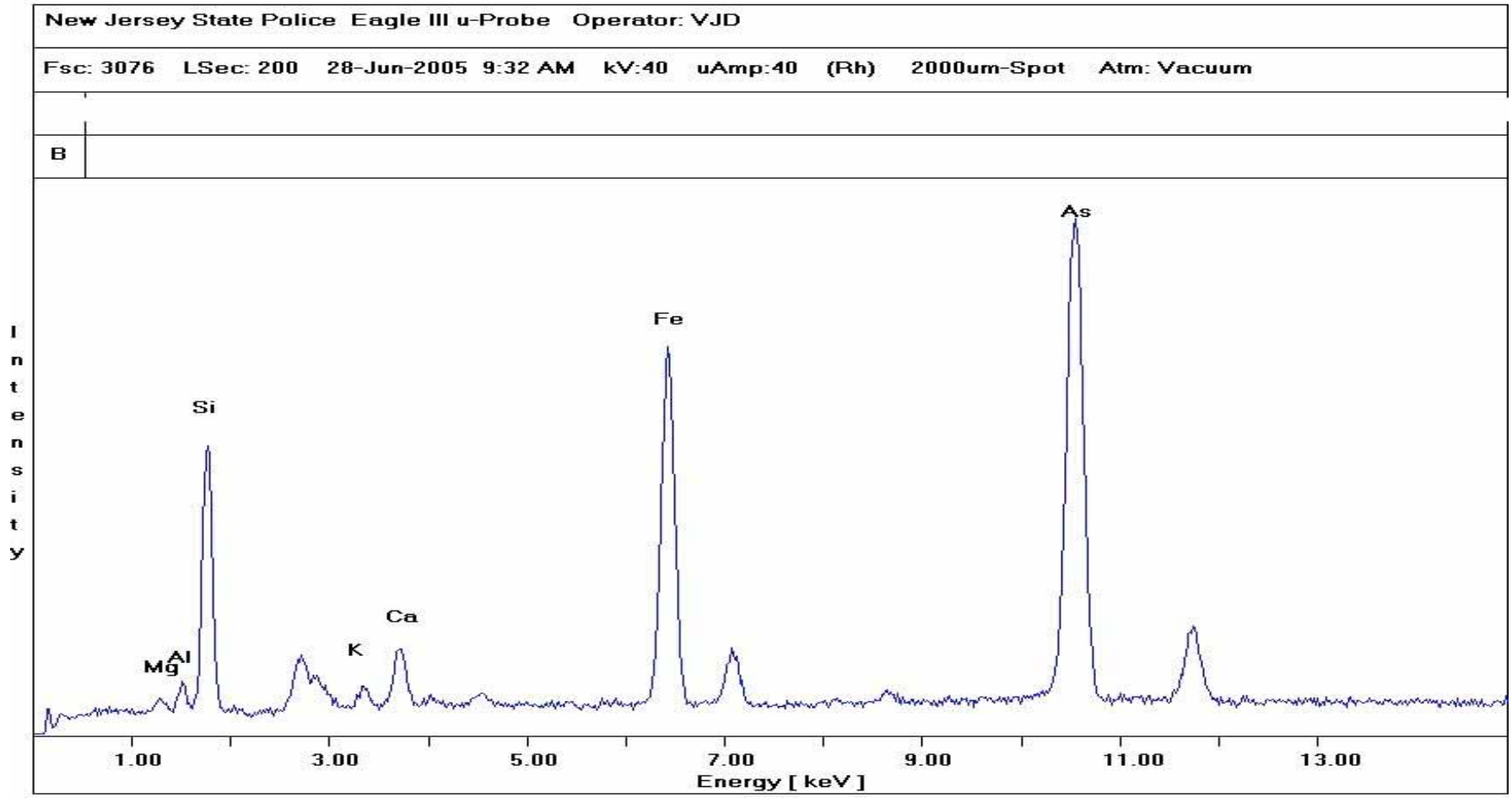
- Gray powder (“Explosive Powder”)
  - Visual/Stereomicroscopic examination disclosed the presence of gray and beige granules as well as clear crystals
  - Ignition test negative
  - Proceeded to analyze using EDXRF and SEM-EDS

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.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Mmmm Lunch!

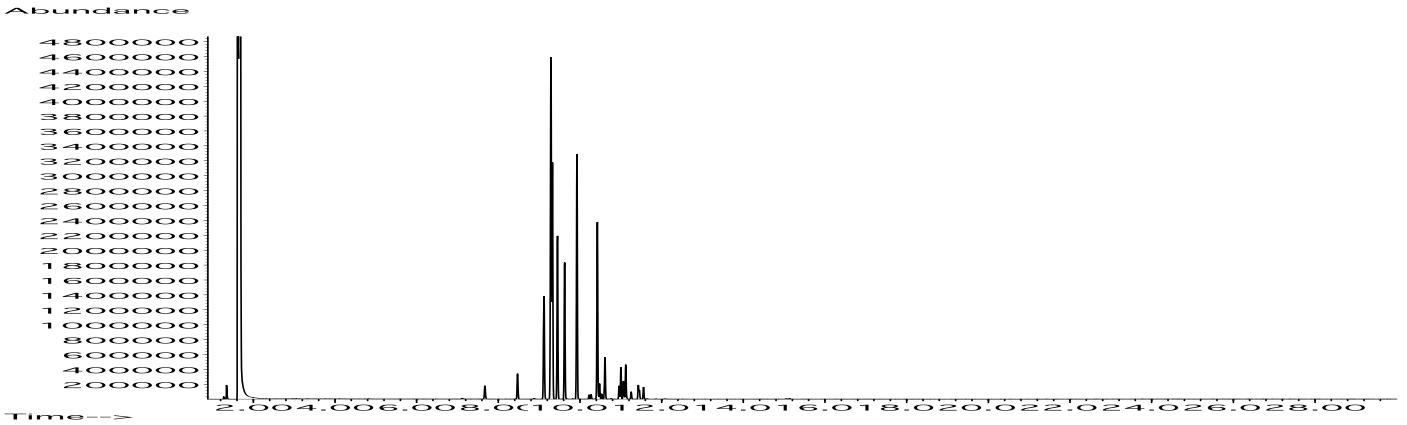
Mmmm Lunch

- Background:
  - Husband Suspects Wife of Poisoning His Prepared Lunch Consisting Of:
    - Buffalo Style Chicken Wings
    - Coffee

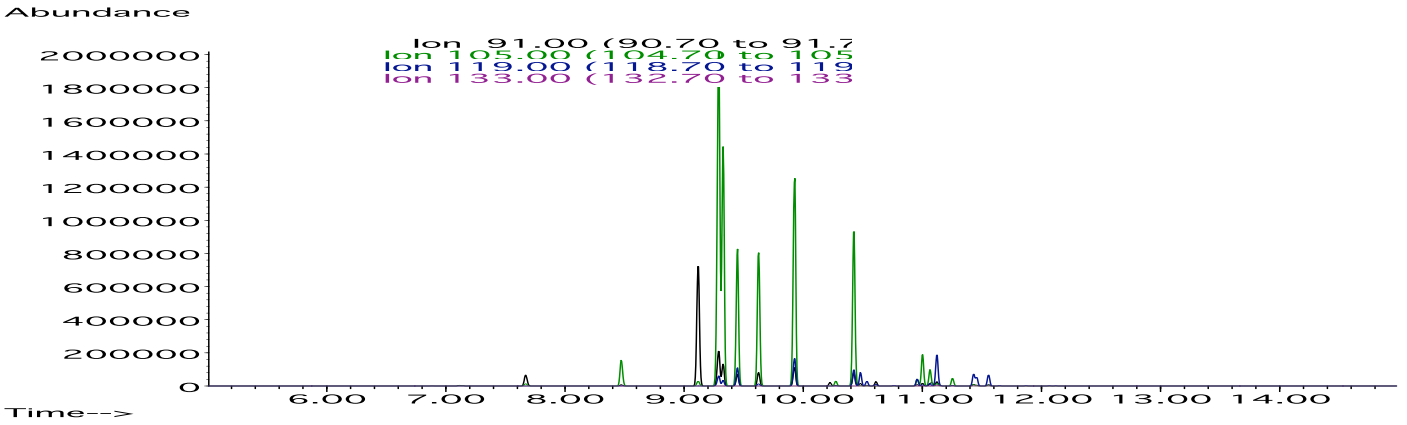
Mmmm Lunch

Mmmm Lunch

Mmmm Lunch

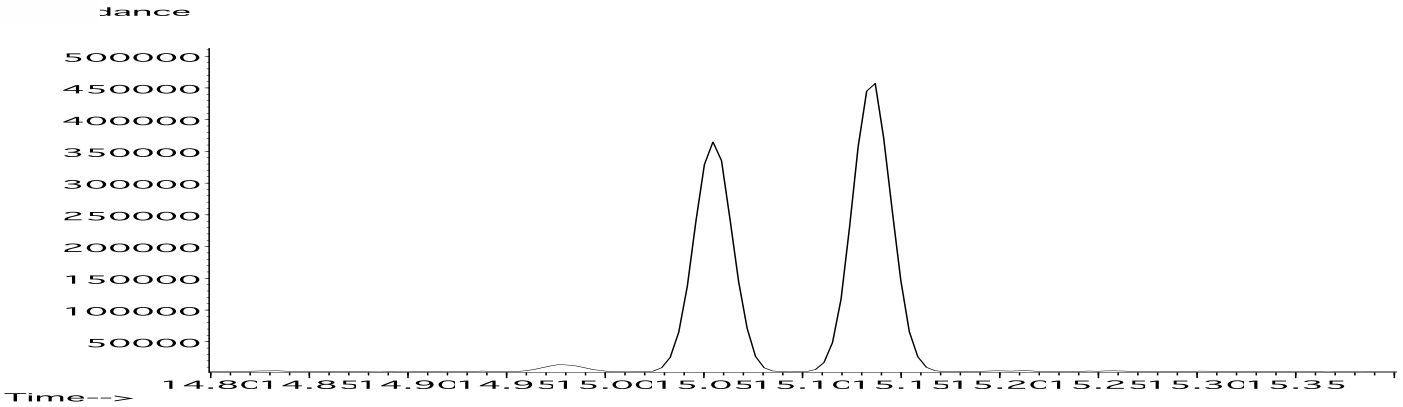


Coffee Chromatogram

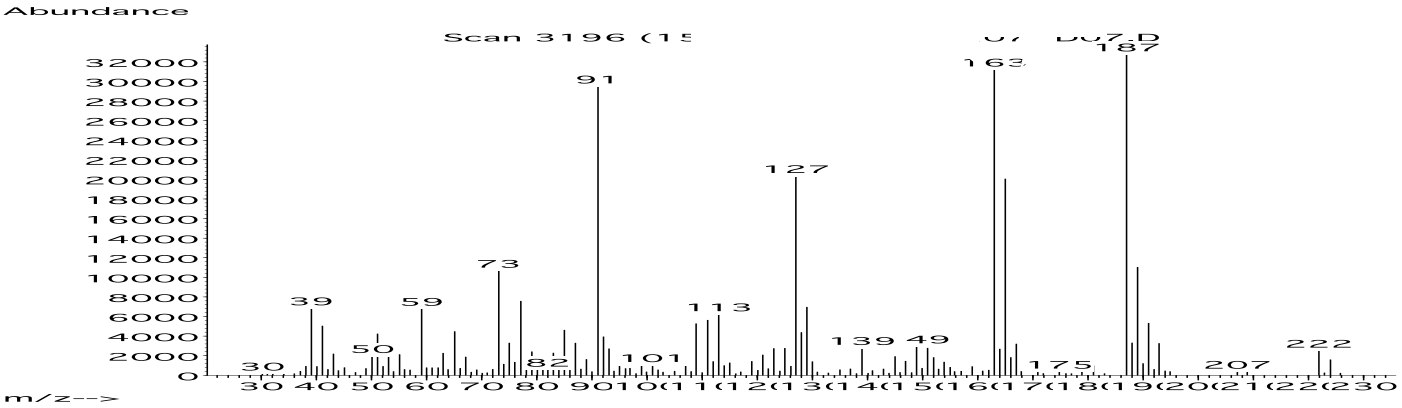


Coffee Aromatic Profile

Mmmm Lunch

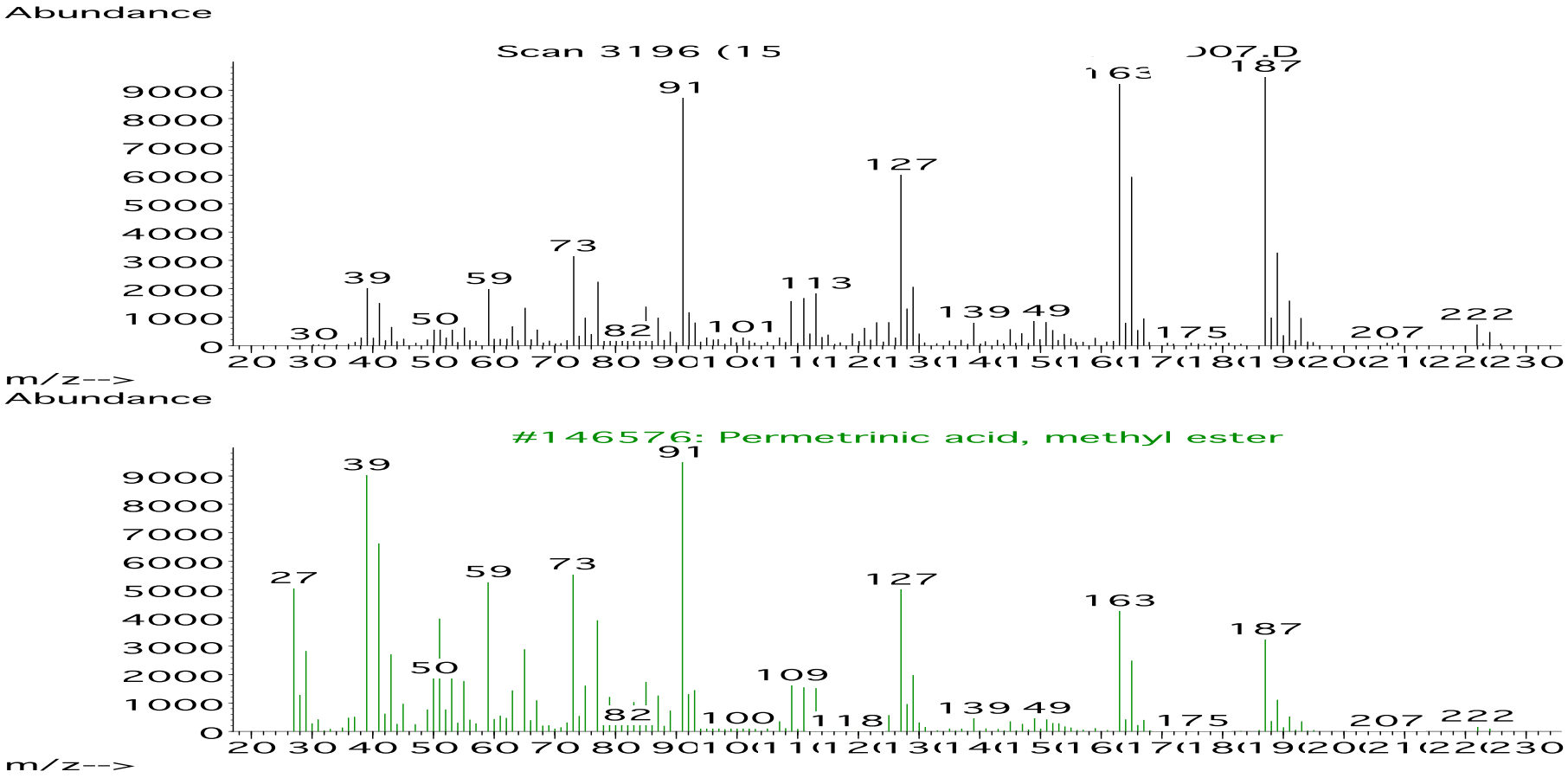


Coffee (Insecticide)



Coffee (Insecticide) Mass Spectrum

Mmmm Lunch


Abundance
Scan 3196 (15
007.D
91
163
187
127
73
39
59
113
30
50
82
101
139
49
175
207
222
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
m/z-->
Abundance
#146576: Permetrinic acid, methyl ester
91
39
27
59
73
127
163
187
50
109
82
100
118
139
49
175
207
222
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230
m/z-->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Glade

Glade

- Background:
  - Partially decomposed female victim found in basement of boarding house covered with white powder
  - Victim's husband was the 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.

Glade

- 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.

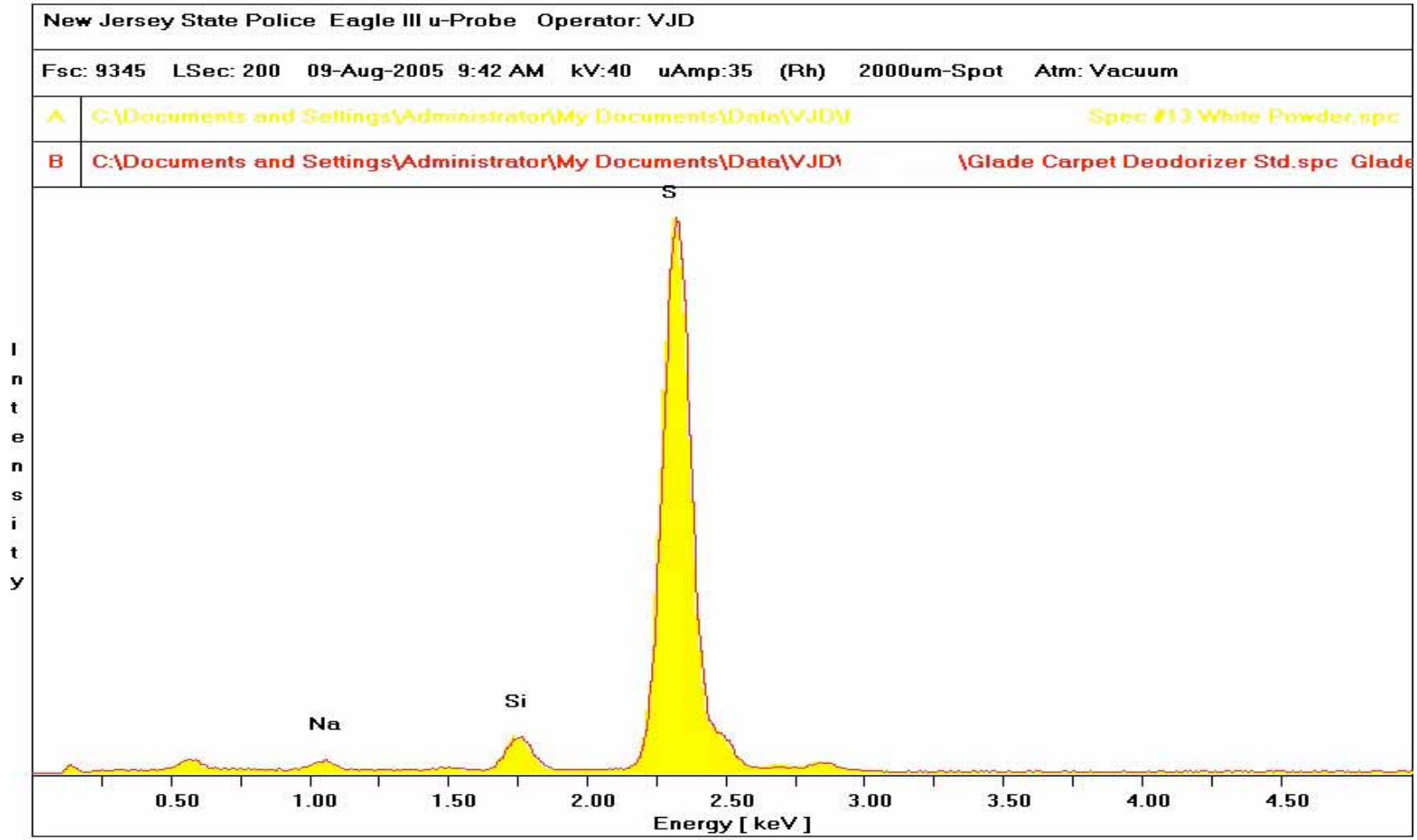
Glade

- 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

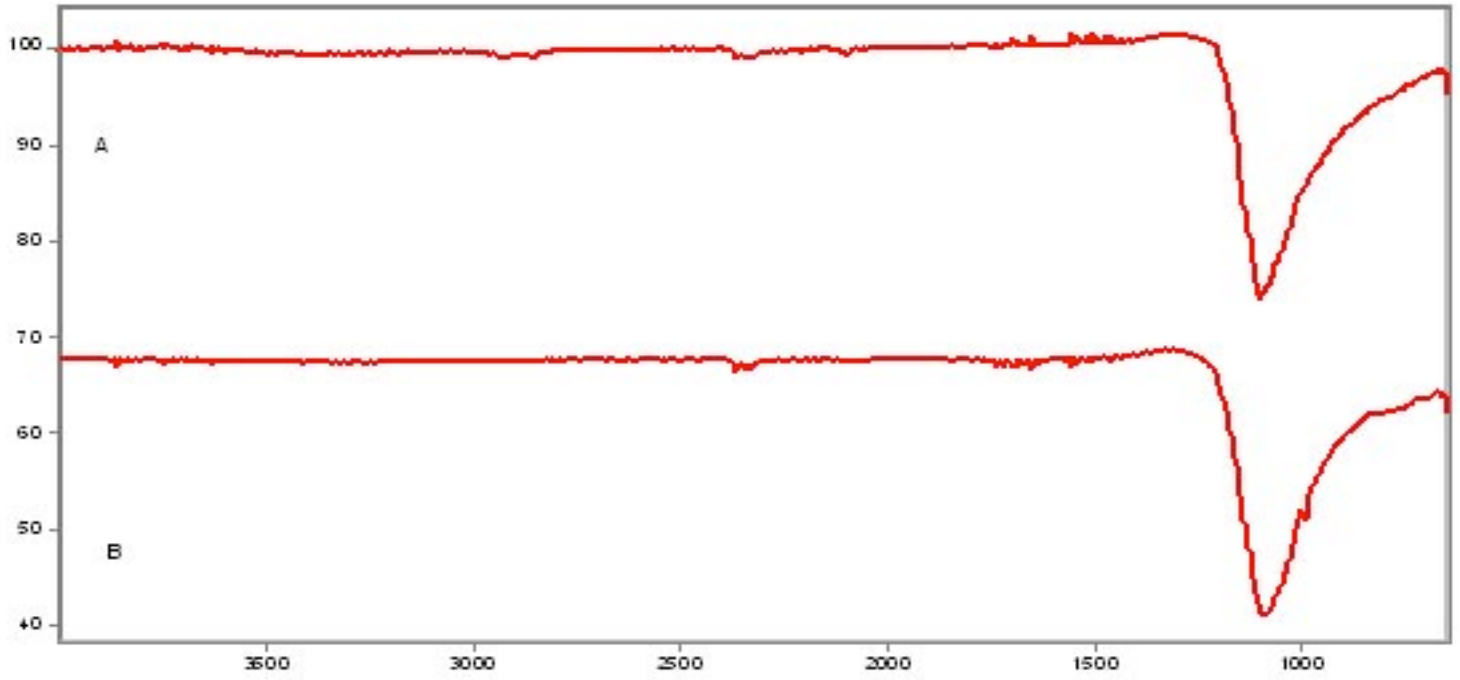
Glade

- 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



FTIR

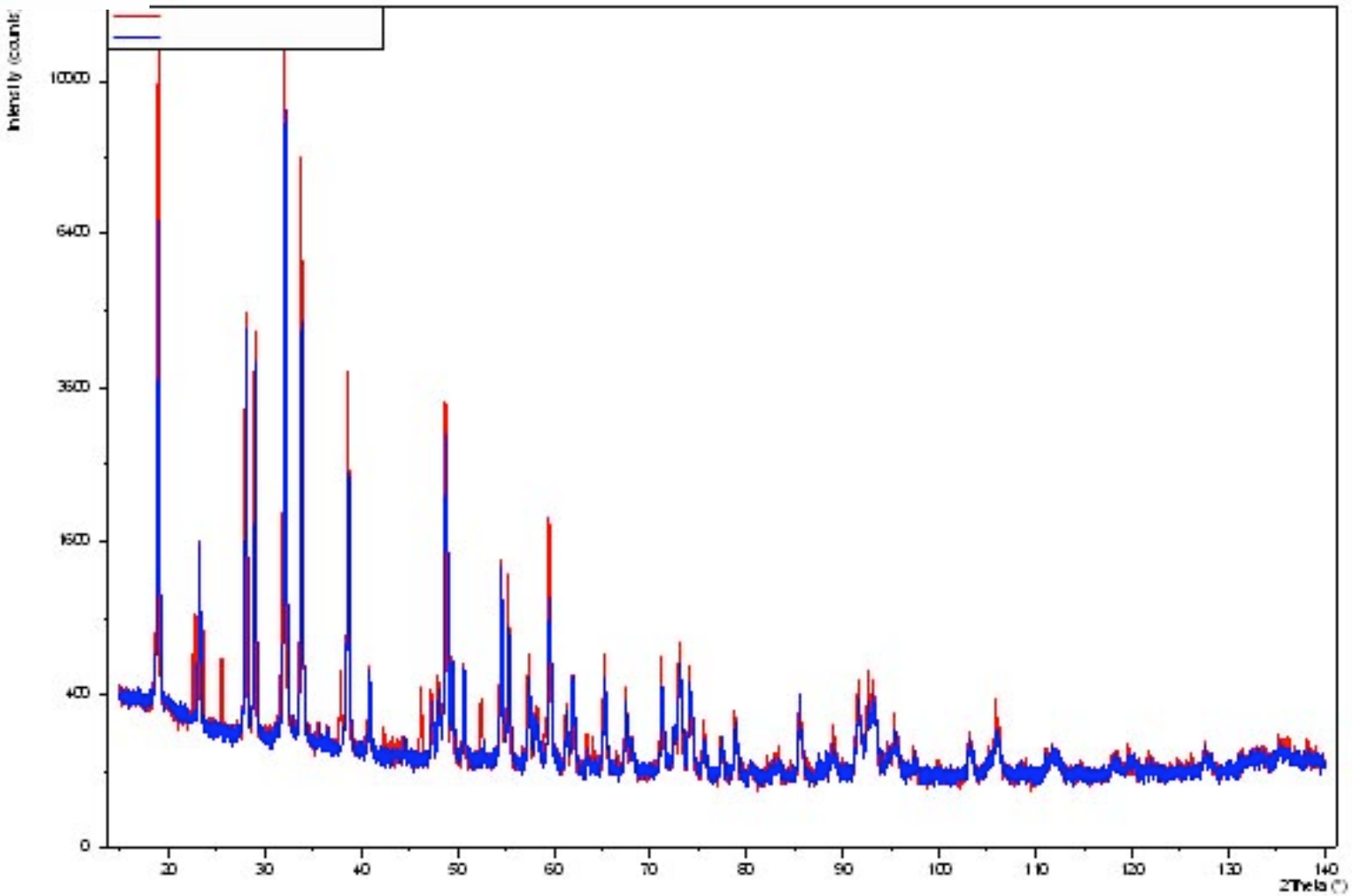


A
Resolution = 4 cm -1
Number of Scans: 32
User Initials: VJD
Sample Number: Specimen #13
Method: ATR
Case Number :
Comment: White Powder
Date: 8/9/2005

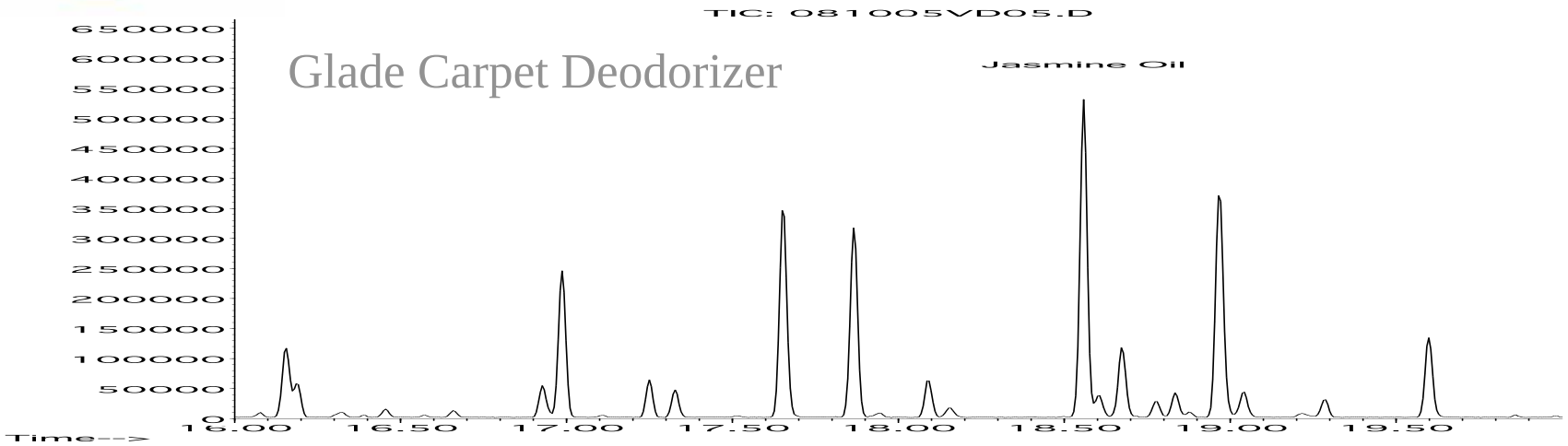
B
Resolution = 4 cm -1
Number of Scans: 32
User Initials: VJD
Sample Number: Glade Carpet Deodorizer Std
Method : ATR
Case Number :
Comment
Date: 8/9/2005

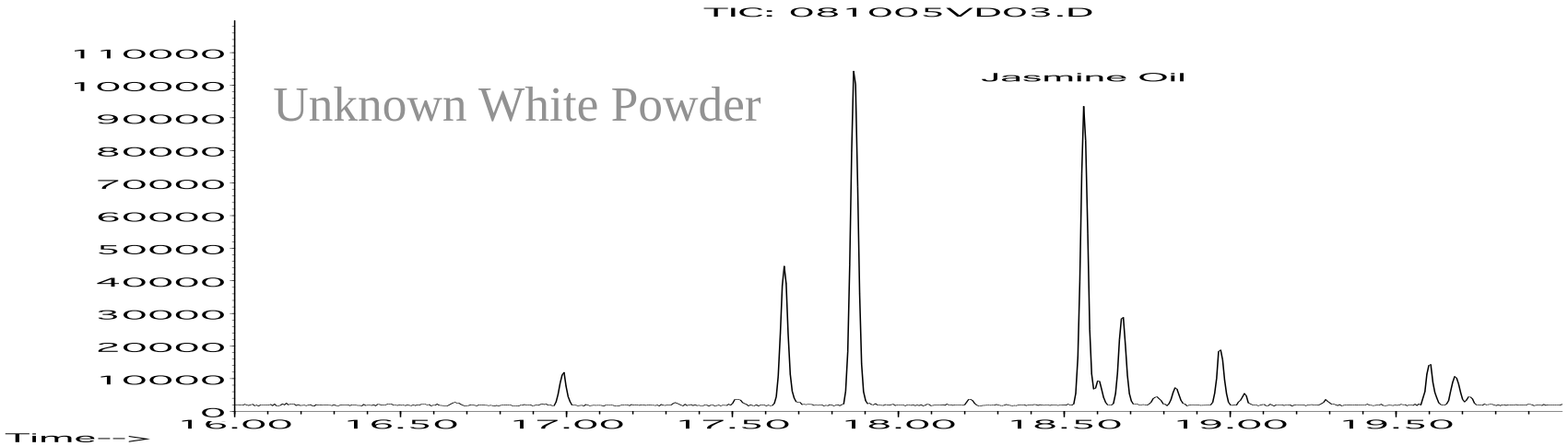
Illuminatir FTIR
New Jersey State Police
Central Laboratory
1200 Negron Road
Hamilton, NJ 08691

XRD


Intensity (counts)
10000
6400
3600
1600
400
0
20
30
40
50
60
70
80
90
100
110
120
130
140
2Theta (°)

GC-MS


TIC: 081005VD05.D
Glade Carpet Deodorizer
Jasmine Oil
Abundance
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
Time-->


TIC: 081005VD03.D
Unknown White Powder
Jasmine Oil
110000
100000
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
16.00
16.50
17.00
17.50
18.00
18.50
19.00
19.50
Time-->

Glade

- 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

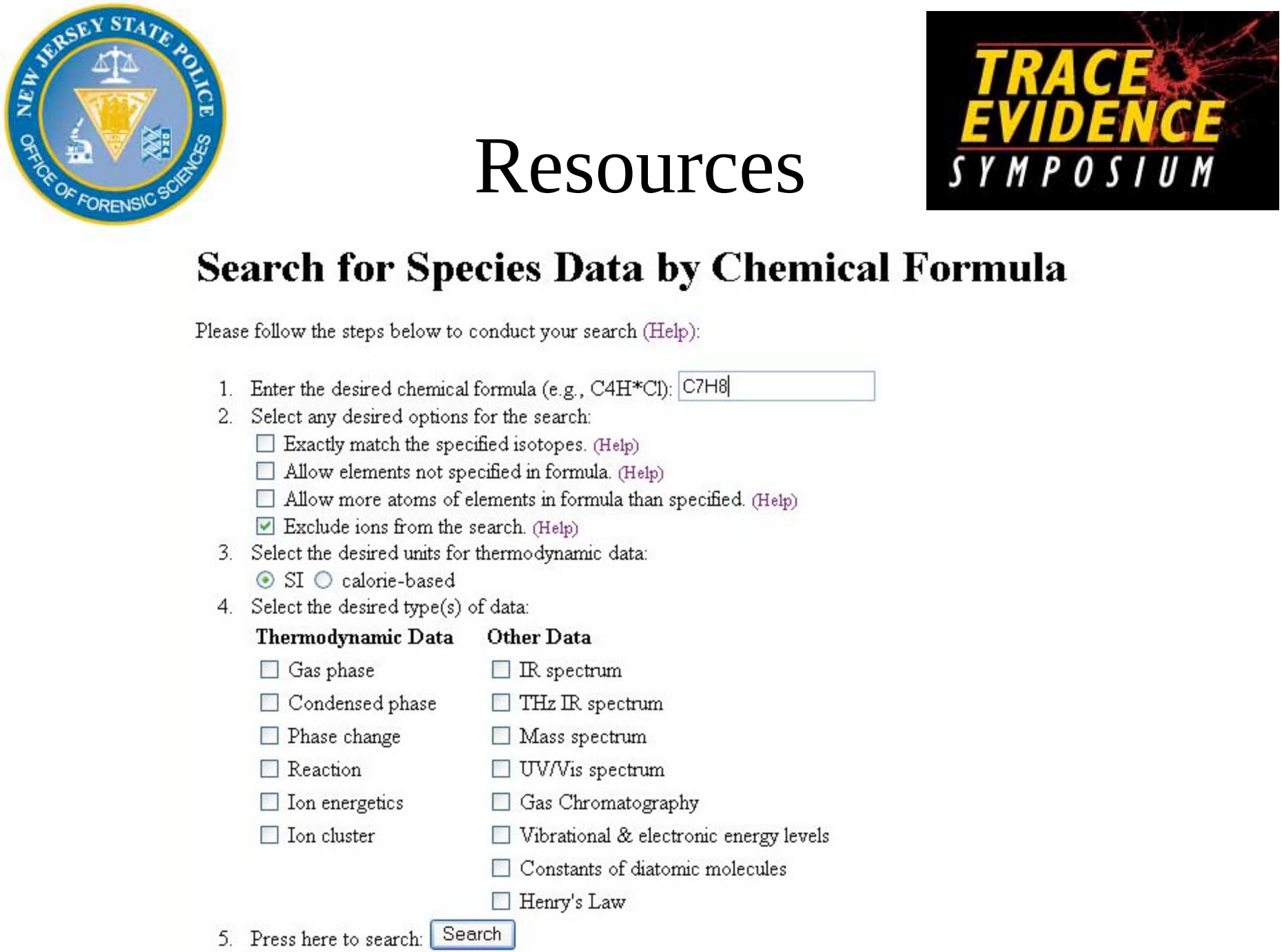
General Searches

- 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)
   - ☑ Exclude ions from the search. (Help)
3. Select the desired units for thermodynamic data:
   - ◉ SI ○ calorie-based
4. Select the desired type(s) of data:

Thermodynamic Data	Other Data
☐ Gas phase	☐ IR spectrum
☐ Condensed phase	☐ THz IR spectrum
☐ Phase change	☐ Mass spectrum
☐ Reaction	☐ UV/Vis spectrum
☐ Ion energetics	☐ Gas Chromatography
☐ Ion cluster	☐ Vibrational & electronic energy levels
	☐ Constants of diatomic molecules
	☐ Henry's Law

5. Press here to search: Search

Resources

Search Results

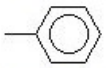
11 matching species were found.

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 (C_7H_8)



2. 1,3,5-Cycloheptatriene (C_7H_8)

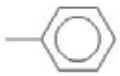
3. 2,5-Norbornadiene (C_7H_8)

4. Quadricyclane (C_7H_8)

NIST National Institute of Standards and Technology | Standard Reference Data Program | Data Gateway | Online Databases | Chemistry WebBook

Toluene

- **Formula:** C_7H_8
- **Molecular weight:** 92.1384
- **IUPAC Standard InChI:**
  - InChI=1S/C7H8/c1-7-5-3-2-4-6-7/h2-6H,1H3
  - Download the identifier in a file.
- **IUPAC Standard InChIKey:** YXFVVABEGXRONW-UHFFFAOYSA-N
- **CAS Registry Number:** 108-88-3
- **Chemical structure:**

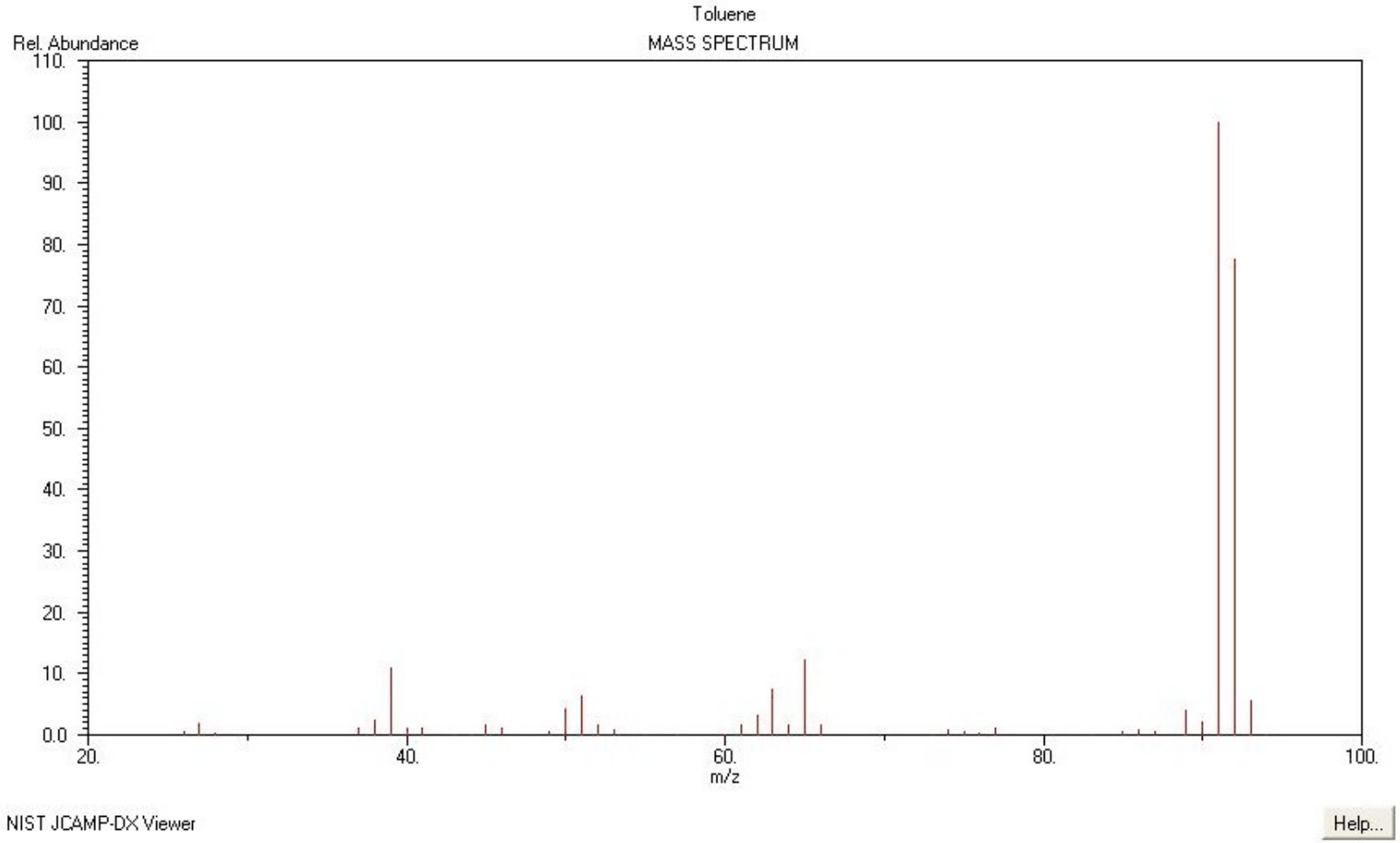


This structure is also available as a 2d Mol file or as a computed 3d Mol file.

- **Isotopomers:**
  - C6H5CD3
  - Toluene-d8
- **Other names:** Benzene, methyl; Methacide; Methylbenzene; Methylbenzol; Phenylmethane; Antisal 1a; Toluol; Methane, phenyl-; NCI-C07272; Tolueen; Toluen; Toluolo; Rcra waste number U220; Tolu-sol; UN 1294; Dracyl; Monomethyl benzene; Retinaphtha; Tol; methylbenzene (toluene)
- **Permanent link** for this species. Use this link for bookmarking this species for future reference.
- **Information on this page:**
  - IR Spectrum
  - Mass spectrum (electron ionization)
  - References
  - Notes / Error Report

Resources

Spectrum



Resources

Spectral Database for Organic Compounds SDBS

Japanese | Introduction | Disclaimer | HELP | Contact | What's New | RIO-DB | LINK | AIST

SDBS Compounds and Spectral Search

Compound Name:

"%,*"for the wild card.
eg. %benzene » ethylbenzene...

Molecular Formula:

C, H, then the other elements are alphabetical order, "%,*" for the wild card

Molecular Weight:

to

Numbers between left and right columns Up to the first place of a decimal point

CAS Registry No.:

"%,*" for the wild card.

SDBS No.:

"%,*" for the wild card.

Atoms:

C(Carbon)		to	
H(Hydrogen)		to	
N(Nitrogen)		to	
O(Oxygen)		to	
F(Fluorine)		to	
Cl(Chlorine)		to	
Br(Bromine)		to	
I(Iodine)		to	
S(Sulfur)		to	
P(Phosphorus)		to	
Si(Silicon)		to	

Numbers between left and right columns.

Spectrum:

Check the spectra of your interest.

☐ MS ☐ IR
☐ ^{13}C NMR ☐ Raman
☐ ^{1}H NMR ☐ ESR

IR Peaks(cm^{-1}): Allowance ± 10

"," or space is the separator for multiple peaks. Use "-", to set a range:. eg. 550-750,1650 3000-

Transmittance < 80 %

^{13}C NMR Shift(ppm): Allowance ± 2.0

"," is the separator for multiple shifts, eg. 129.3,18.4,...

No shift regions:

Range defined by two numbers separated by a space, eg. 110 78,...

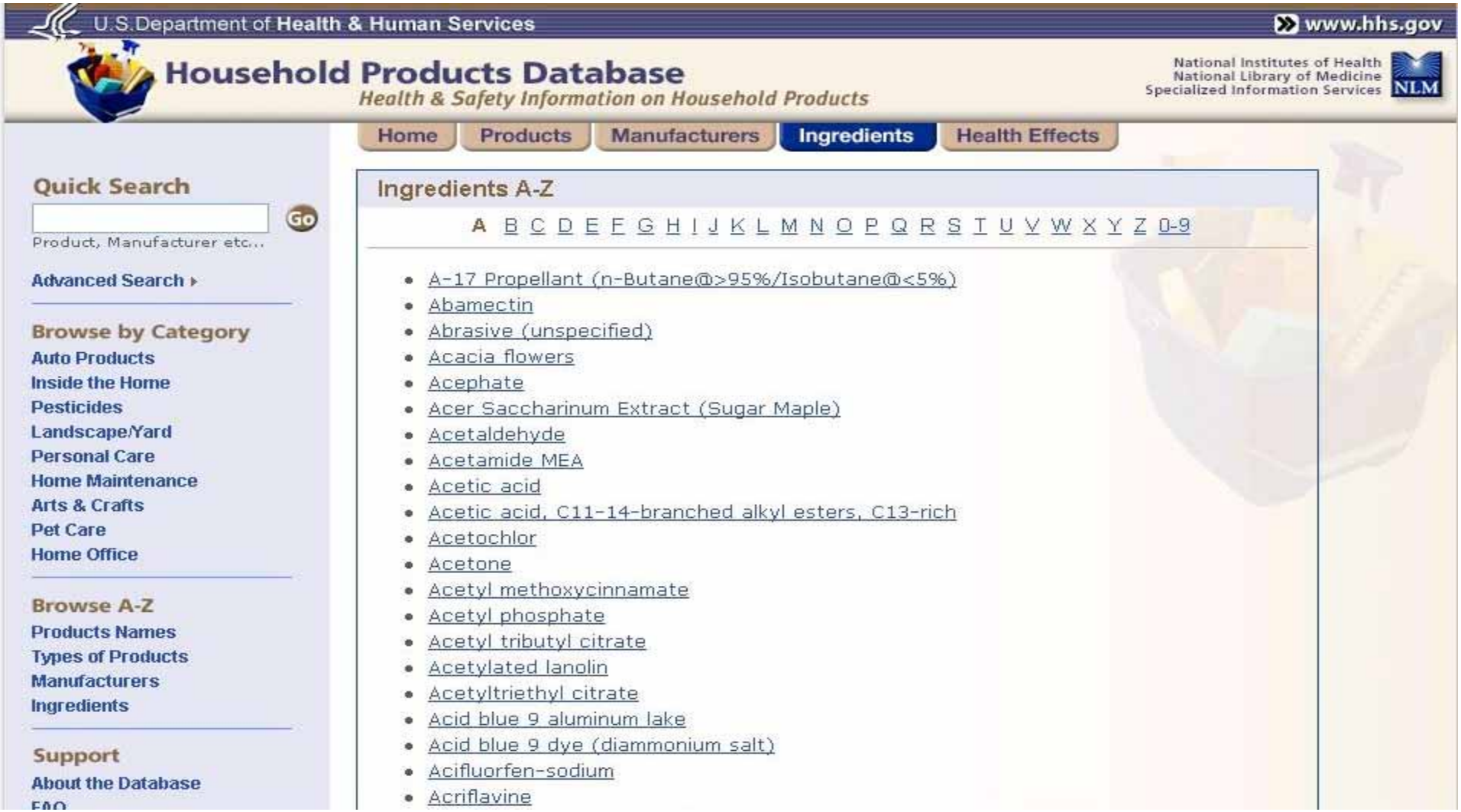
^{1}H NMR Shift(ppm): Allowance ± 0.2

No shift regions:

Resources


U.S. Department of Health & Human Services
www.hhs.gov
Household Products Database
Health & Safety Information on Household Products
National Institutes of Health
National Library of Medicine
Specialized Information Services
NLM
Home
Products
Manufacturers
Ingredients
Health Effects
Quick Search
Go
Product, Manufacturer etc...
Advanced Search
Browse by Category
Auto Products
Inside the Home
Pesticides
Landscape/Yard
Personal Care
Home Maintenance
Arts & Crafts
Pet Care
Home Office
Browse A-Z
Product Names
Types of Products
Manufacturers
Ingredients
Support
About the Database
What's under your kitchen sink, in your garage, in your bathroom, and on the shelves in your laundry room? Learn more about what's in these products, about potential health effects, and about safety and handling.
Auto Products
Brake Fluid, De-icer, Lubricant, Sealant, and more...
Inside the Home
Air Freshener, Bleach, Cleaners, Toilet Bowl Cleaner, and more...
Pesticides
Animal Repellant, Fungicide, Herbicide, Insecticide, and more...
Landscape/Yard
Fertilizer, Lawn Care, Swimming Pool Products, and more...
Personal Care
Antiperspirant, Hair Spray, Makeup, Shampoo, Soap and more...
Home Maintenance
Caulk, Grout, Insulation, Paint, Putty, Stain, and more...
Arts & Crafts
Adhesive, Glaze, Glue, Primer, Varnish, and more...
Pet Care
Flea & Tick Control, Litter, Stain/Odor Remover, and more...
Home Office
Ink, Toner, Correction Fluid, Electronics Cleaners, Pens and more...

Resources



U.S. Department of Health & Human Services

www.hhs.gov

Household Products Database

Health & Safety Information on Household Products

National Institutes of Health
National Library of Medicine
Specialized Information Services

NLM

Home | Products | Manufacturers | Ingredients | Health Effects

Quick Search

Go

Product, Manufacturer etc...

Advanced Search ▸

Browse by Category

- Auto Products
- Inside the Home
- Pesticides
- Landscape/Yard
- Personal Care
- Home Maintenance
- Arts & Crafts
- Pet Care
- Home Office

Browse A-Z

- Products Names
- Types of Products
- Manufacturers
- Ingredients

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- FAQ

Ingredients A-Z

A B C D E F G H I J K L M N O P Q R S T U V W X Y Z 0-9

- A-17 Propellant (n-Butane@>95%/Isobutane@<5%)
- Abamectin
- Abrasive (unspecified)
- Acacia flowers
- Acephate
- Acer Saccharinum Extract (Sugar Maple)
- Acetaldehyde
- Acetamide MEA
- Acetic acid
- Acetic acid, C11-14-branched alkyl esters, C13-rich
- Acetochlor
- Acetone
- Acetyl methoxycinnamate
- Acetyl phosphate
- Acetyl tributyl citrate
- Acetylated lanolin
- Acetyltriethyl citrate
- Acid blue 9 aluminum lake
- Acid blue 9 dye (diammonium salt)
- Acifluorfen-sodium
- Acriflavine

Resources

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Search calcium chloride as Ingredient in All Product Categories Go

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

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

Resources

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Advanced Search ▸

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Brand Information

Product Name:	**2000 Flushes Automatic Bowl Cleaner**
Form:	granules
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

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

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

Enter text or highlight term... Search TOXNET

Acute Health Effects: From MSDS
Inhalation: Irritating to the nose, mouth, throat, and lungs. May

References

- http://webbook.nist.gov/chemistry/
- http://householdproducts.nlm.nih.gov/
- http://riodb01.ibase.aist.go.jp/sdbs/cgi-bin/cre_index.cgi?lang=eng

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- Katie Ballance and The Pink Gorilla Dude

Questions?

Questions?