



**BUFFALO STATE**  
The State University of New York

# Crystallography Education for Non-Science College Students

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# **Professional Crystallographers**

(know physics, hardware and software,  
often write software and/or make new hardware)

# **Crystallography Users**

(know chemistry, maybe some physics;  
know how to use some software and hardware)

# **Analytical Lab Users**

(may know some chemistry, need analytical data,  
have little time to study theory)

***Our students:***

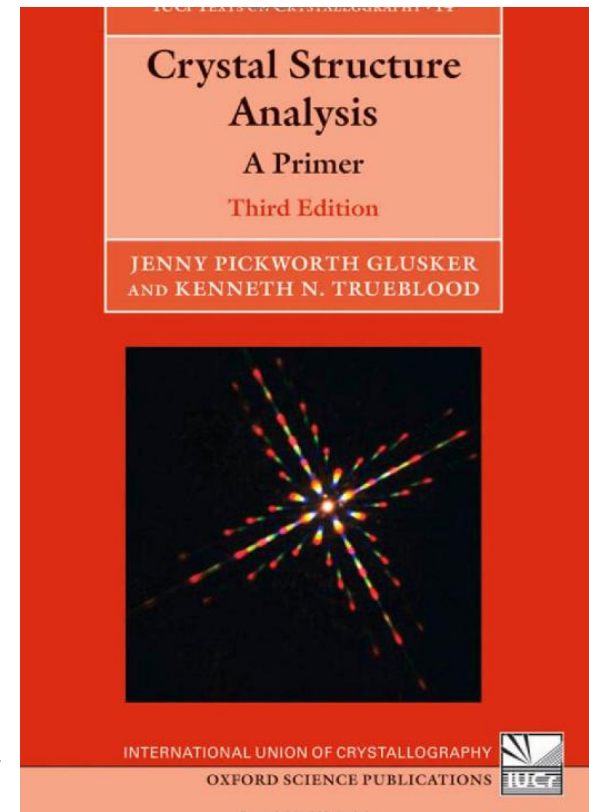
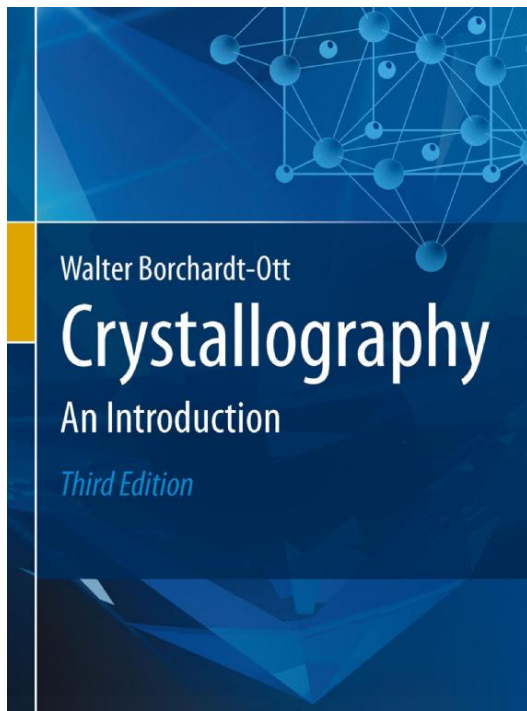
***High School and General Chemistry students***

***Forensic majors (undergraduate and graduate)***

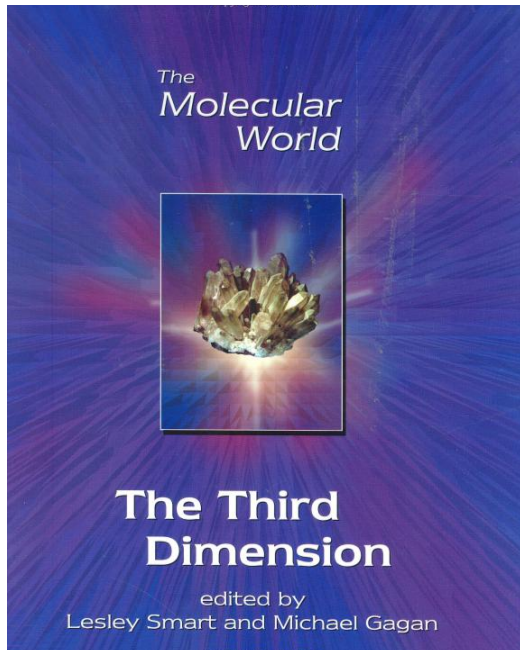
***Art Conservation Students (master program)***

***Timeframe: From 15 min demo to 5 week course***

350 pages!



230 pages



**Some very good textbooks  
- But little help for our students**

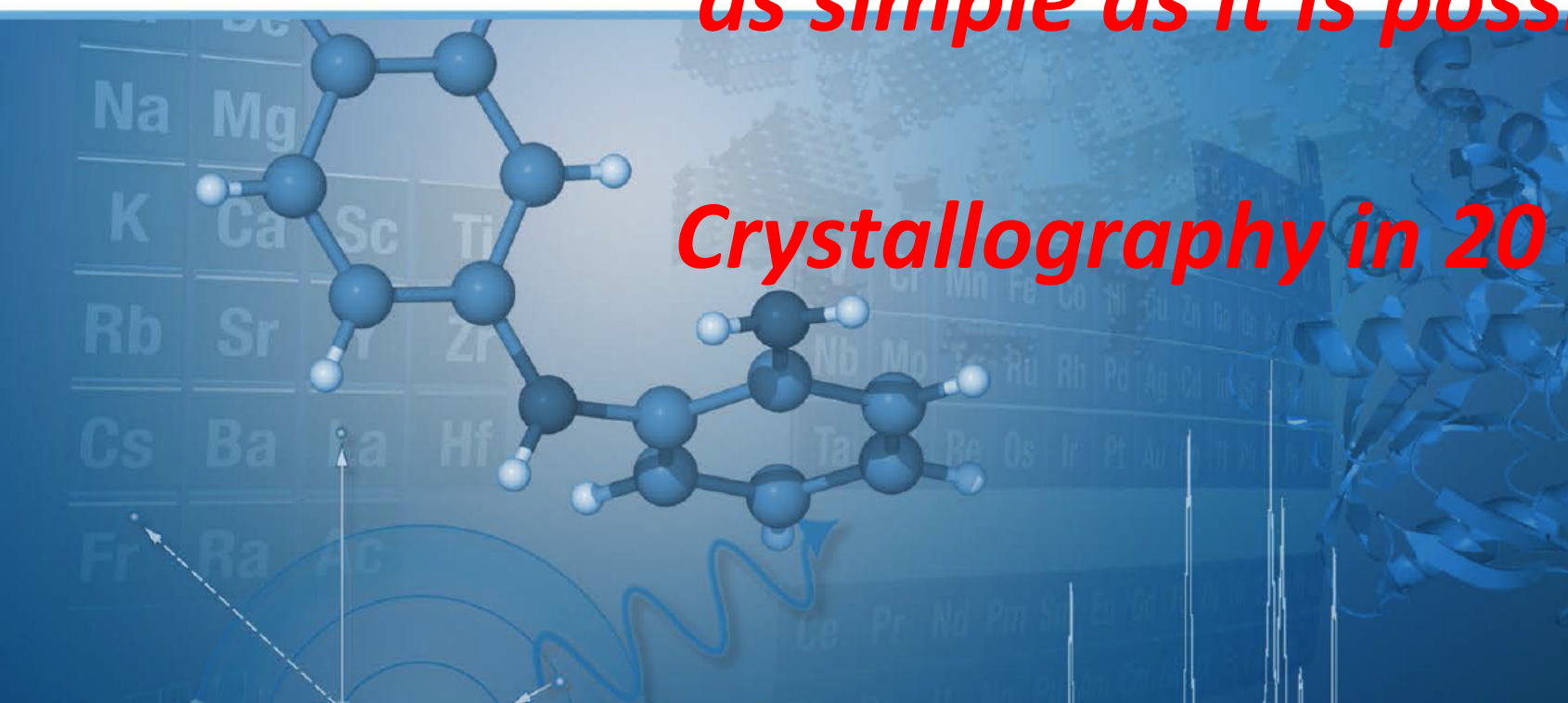
# Forensics Analysis with X-Ray Diffraction and X-Ray Fluorescence



Bruker AXS Inc., Madison, WI, USA  
April 16, 2013

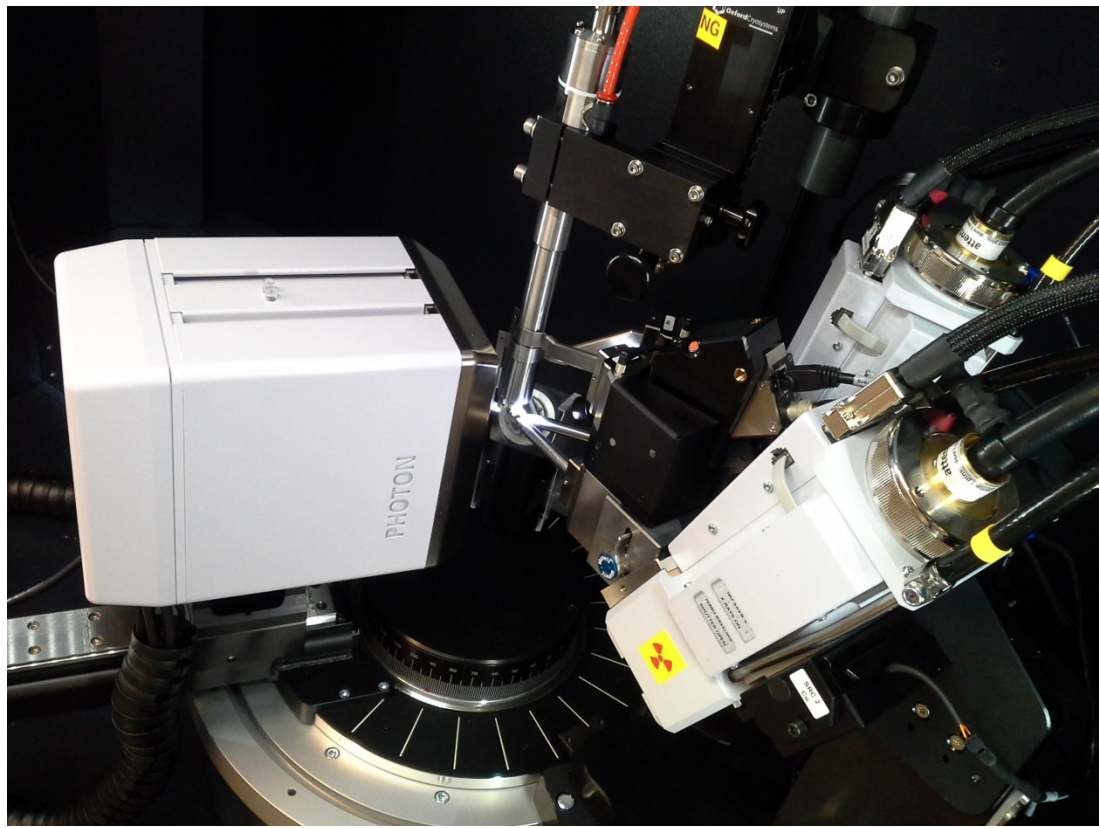
***Around 20 slides  
as simple as it is possible***

***Crystallography in 20 min!***



***Bruker webinar***





Our system:      Bruker D8 Venture  
                         Cu and Mo tubes  
                         Photon 100 CMOS detector

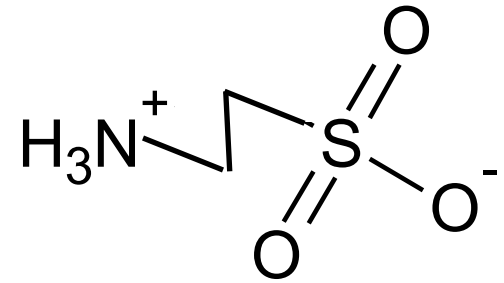
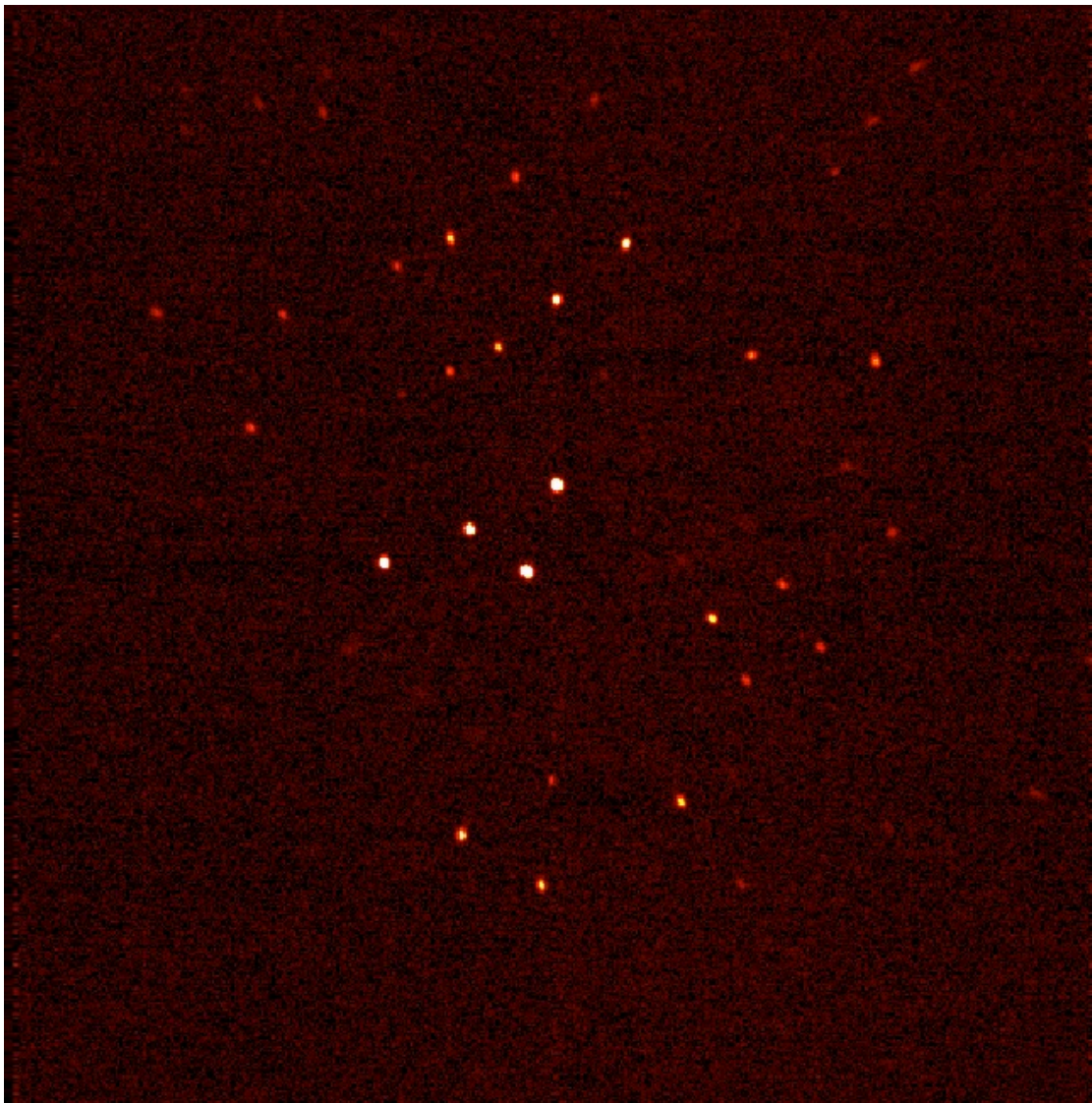
*We can do both single crystal and powder*

## **Solution No. 1**

A short demo for students  
who know practically nothing about X-ray  
and very little chemistry

Our goal:

To show where chemical formulas are coming from



Our best choice: Taurine



Can be crystallized  
by slow evaporation of energy drink

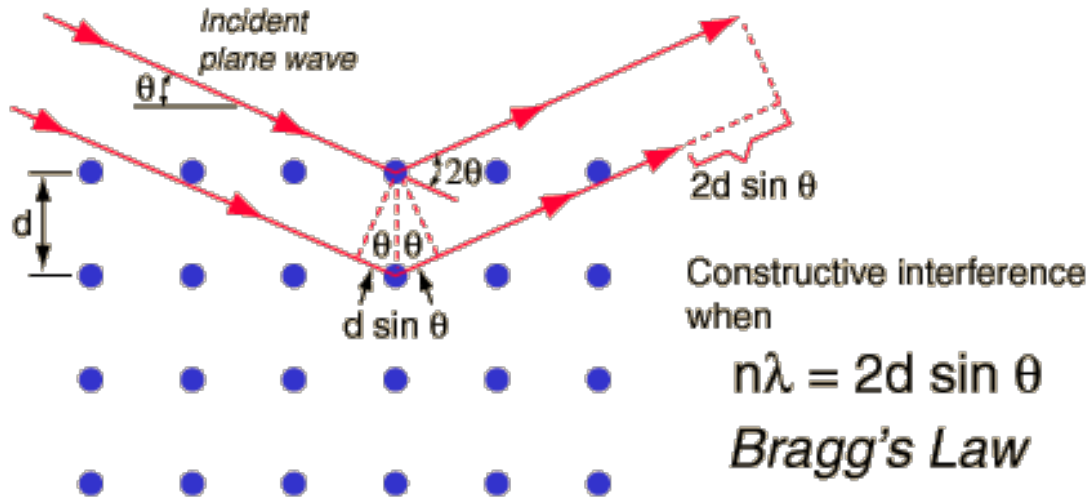
Small crystal cell, no chirality. Very rigid ionic crystal with multiple strong hydrogen bonds

**Data Collection:** 120 1 s phi-scans (3 degrees per second)  
Wide frame algorithm data processing

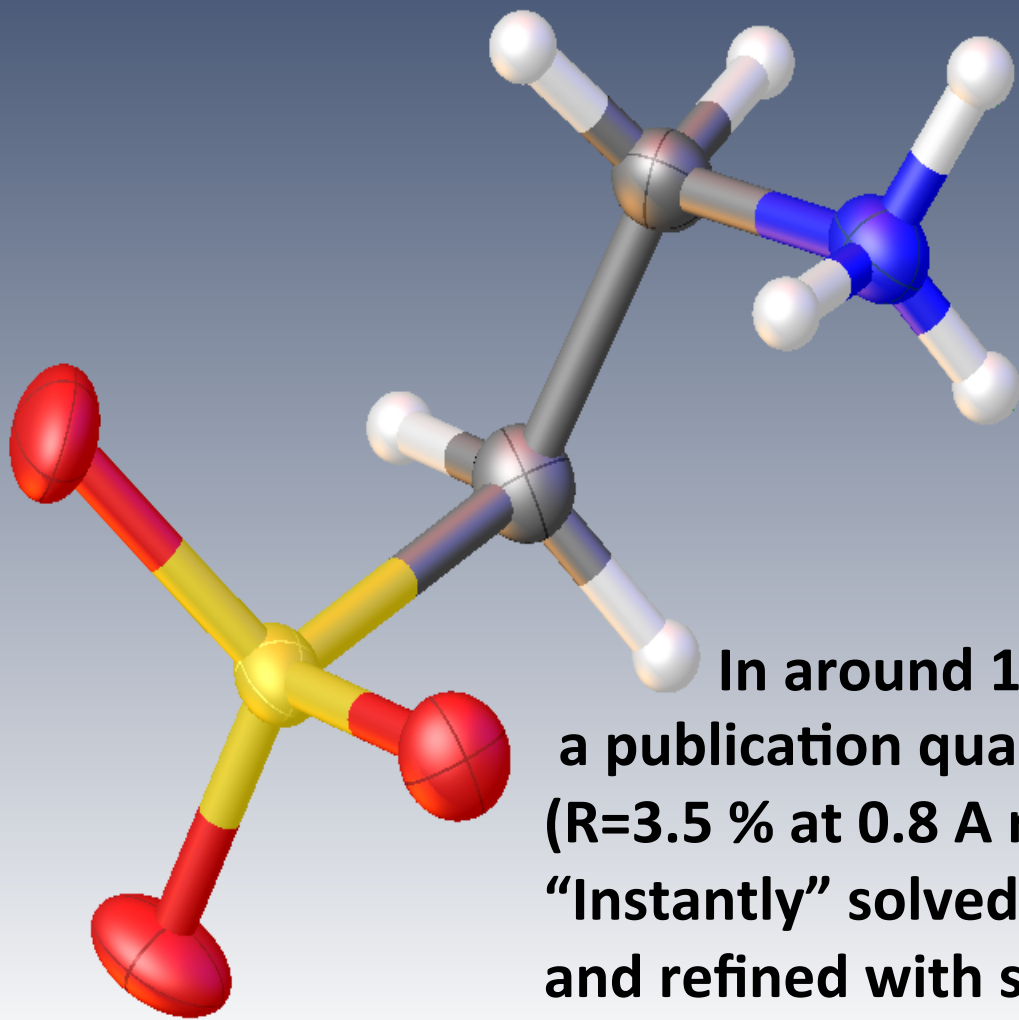


# The only “theory” we show:

Where the reflections on computer screen are coming from



When data are collected , we show this picture on another display and talk a little (5 min)



**In around 10-15 min we have  
a publication quality structure  
( $R=3.5\%$  at 0.8 Å resolution)  
“Instantly” solved with SHELXT  
and refined with several clicks using  
OLEX2 interface**

## SOLUTION No. 2

### For forensic students

(the same for anybody who is interested  
in an analytical aspect of X-ray crystallography)

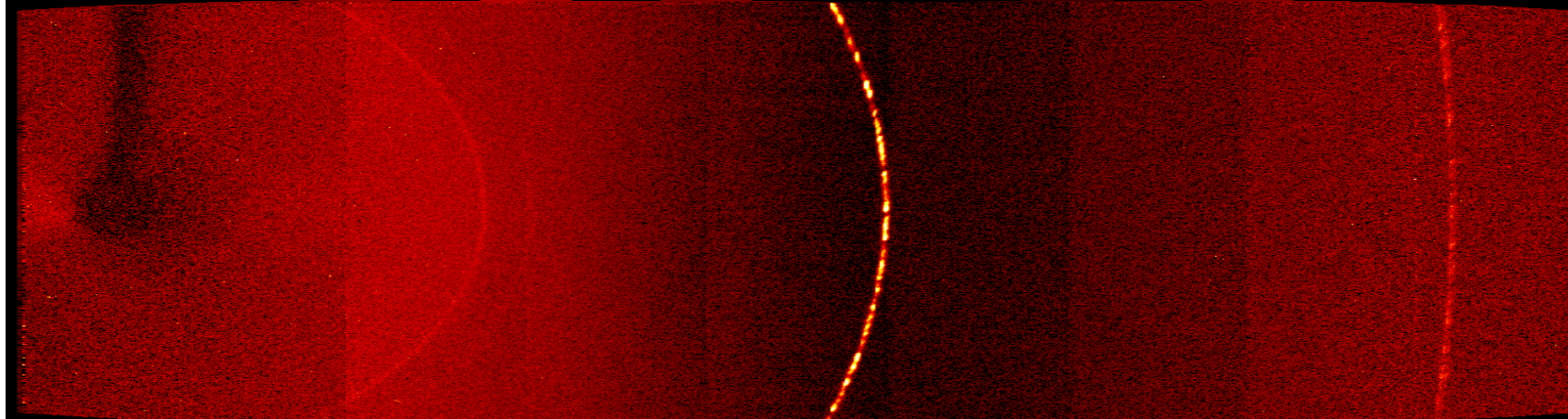
*A very practical approach, starting with polycrystalline samples  
and identification of crystalline solids*

*No symmetry teaching at all*

*Just empirical processing of diffraction data*

Samples are mounted using Mitagen loops  
using Apiezon



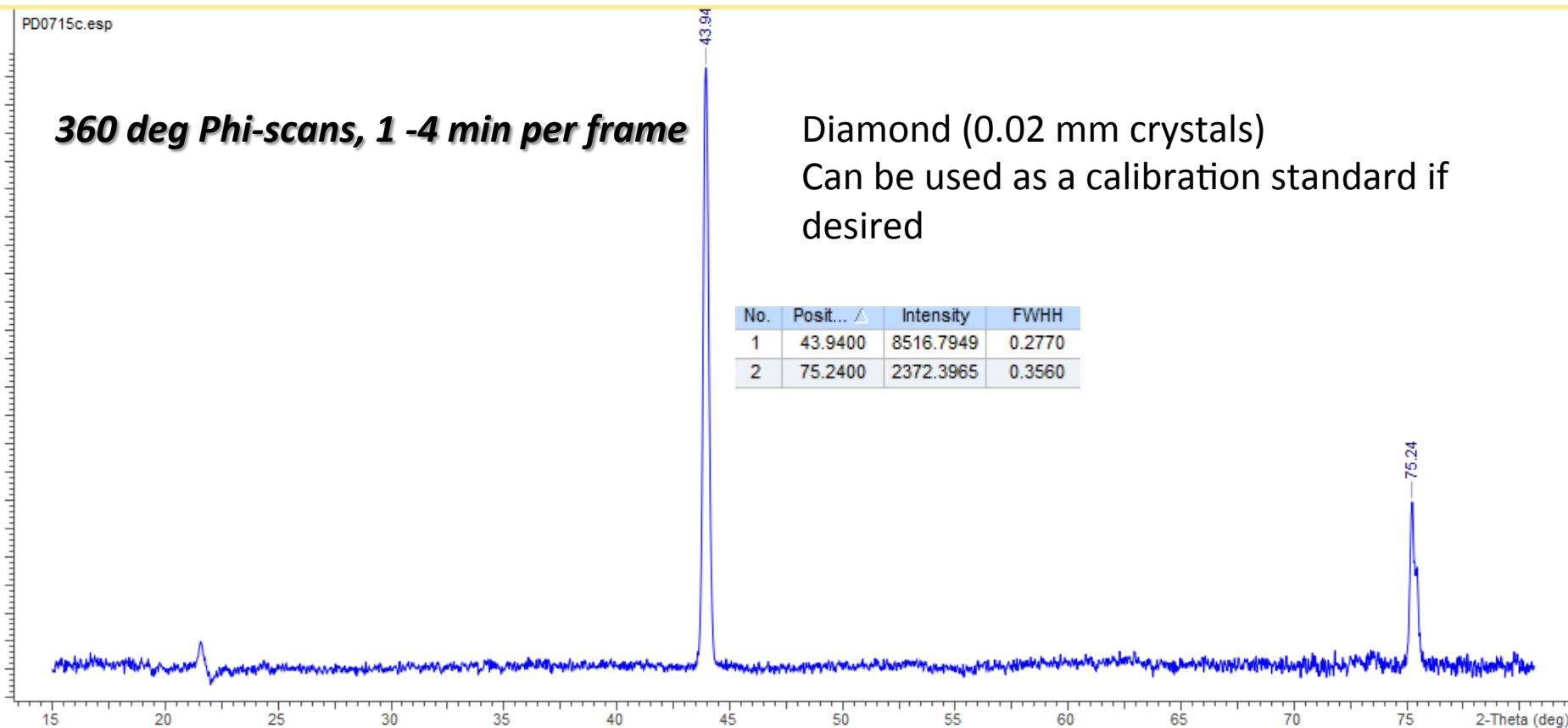


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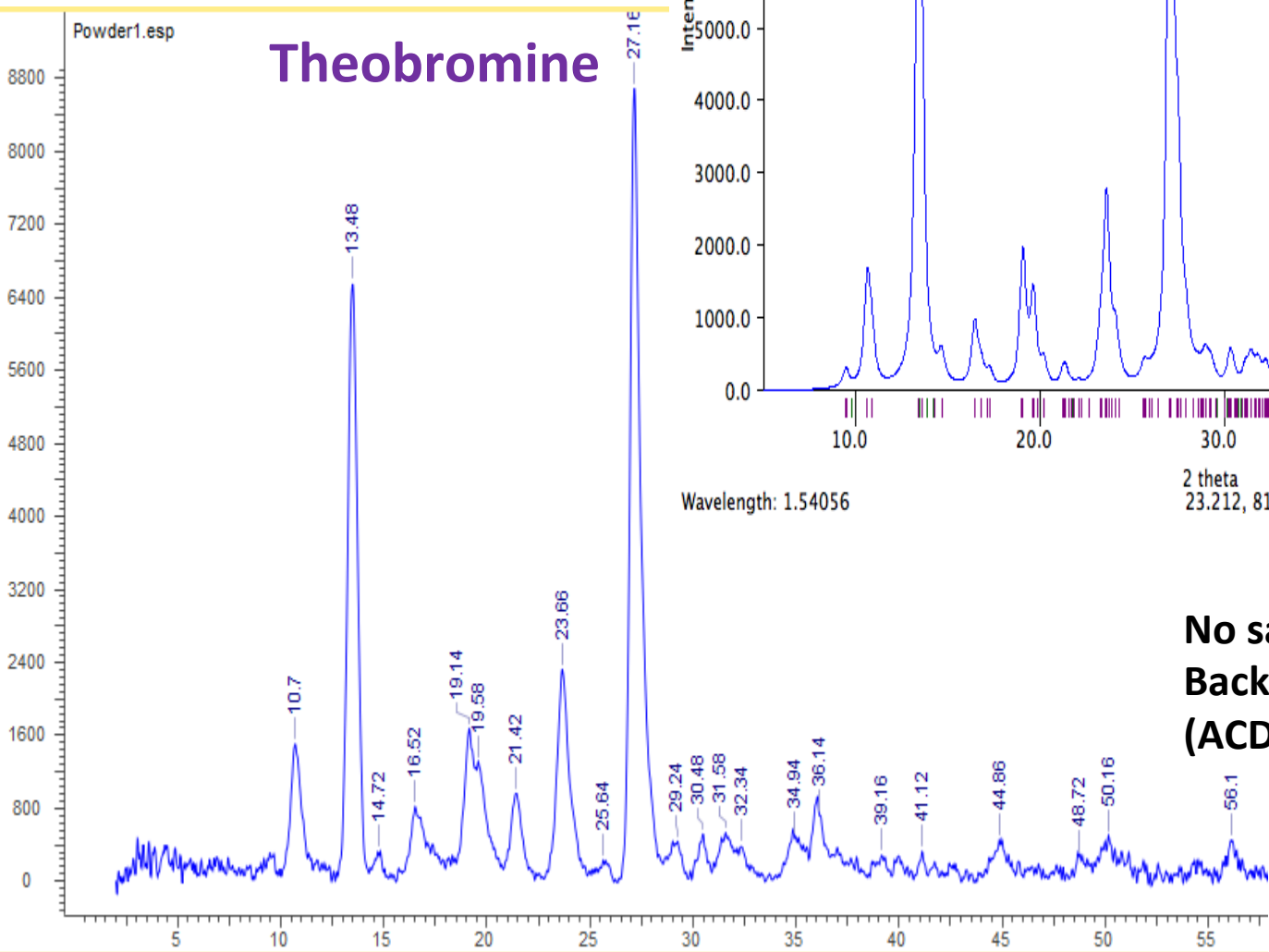
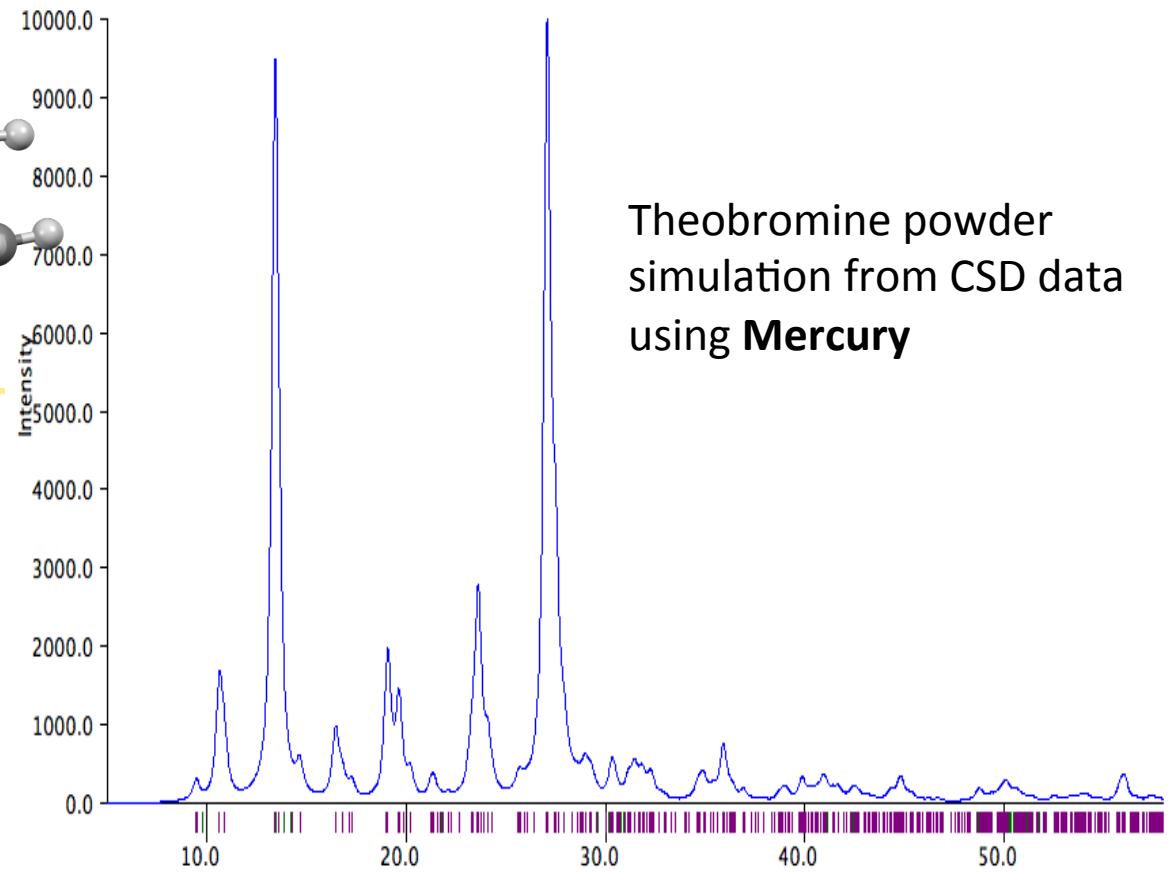
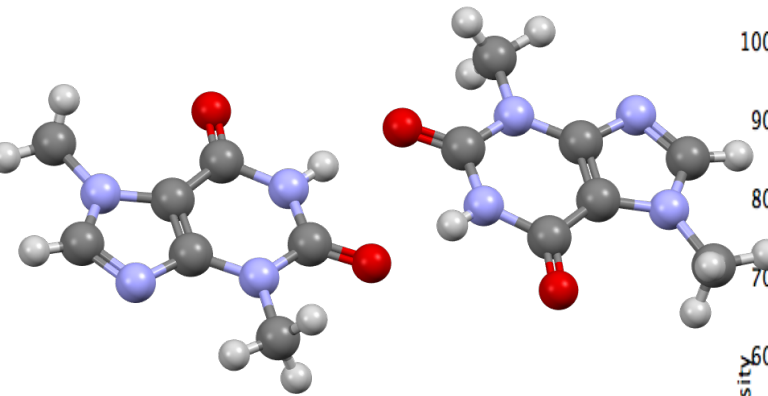
***360 deg Phi-scans, 1 -4 min per frame***

Diamond (0.02 mm crystals)  
Can be used as a calibration standard if  
desired

No.	Posit... / Δ	Intensity	FWHH
1	43.9400	8516.7949	0.2770
2	75.2400	2372.3965	0.3560







Wavelength: 1.54056  
2 theta: 23.212, 8166  
h, k, l = 2, 2, -1

**No sample prep**  
**Background subtracted**  
**(ACD Labs Spectra Processor)**



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Supplement Facts		
Serving Size: 20mg	Servings Per Packet: 500	
	Amount per serving	%DV
<b>Syneprine HCL</b>	<b>20mg</b>	*
*Daily Value not established		

*These statements have not been evaluated by the FDA. This product is not intended to diagnose, treat, cure or prevent any disease.*

Batch # \_\_\_\_\_ Expiration Date: \_\_\_\_\_

## From Bitter Orange Oil

DIETARY SUPPLEMENT



## synephrine hcl

99% Pure Bulk Powder

10 grams

**Directions:** Suggested serving is 20mg once daily. 1-2 rounded micro scoops.

**Ingredients:** Pure bulk powder.

**WARNING:** A scale is required to accurately measure. Do not take if you are under 18, or if you are pregnant or nursing. Do not take if you have high blood pressure or any medical complications. Always consult with your physician before taking any new dietary supplements.

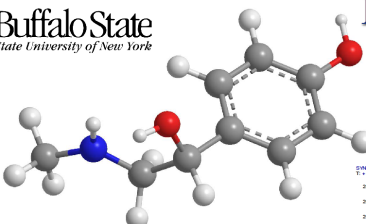


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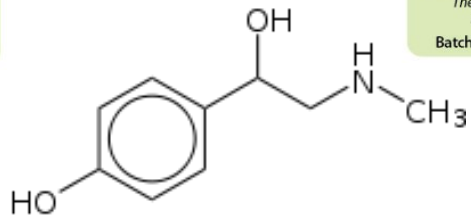
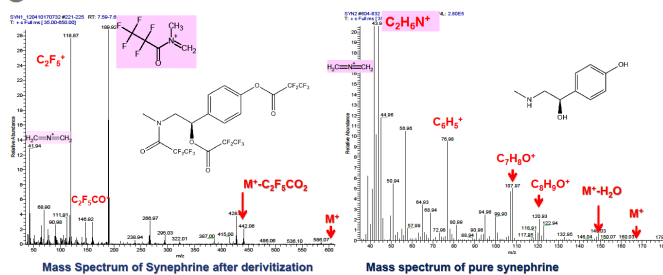
## Determination of Syneprine In Weight Loss Supplements

Anita McAndrew

Buffalo State  
 State University of New York

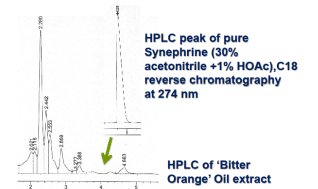


**Abstract**  
 Syneprine (4-[1-hydroxy-2-(methylamino)ethyl]phenol) is a natural monoamine alkaloid of phenylethylamine group, which is commonly used as a component in weight loss supplements, and is also a natural alkaloid present in bitter orange essential oil. We apply nuclear magnetic resonance and infrared spectroscopy for positive identification of synephrine after its isolation. Using varying methods of extraction we qualitatively and quantitatively determine the amount of synephrine in pharmaceutical and natural samples. Derivatization is necessary for analysis using gas chromatographic separation with consecutive determination using mass spectrometric detection. Because of phenyl group in synephrine molecule, high performance liquid chromatography with UV detection does not require derivatization and is therefore a natural alternative to GC/MS determination.



The synephrine sample analyzed was not a molecular synephrine but a protonated form crystallized as a chloride. The spectra of corresponding base, isolated from the chloride, were investigated. A sample of 'Bitter Orange' oil was examined and analyzed to determine the concentration of synephrine, using HPLC and GCMS

The sample of oil was run on HPLC after HCl extraction and there were no resulting peaks corresponding to the retention time of synephrine.



**Interpretation of Findings**  
 HPLC showed a very small concentration of Syneprine in the Bitter Orange Oil Sample. Analysis of the sample using GCMS indicated that limonene, a cheaper compound to isolate and extract for commercial use compared to synephrine, is the prevalent citrus component in the sample. The amount of limonene in the sample provided could be determined by preparing and analyzed using HPLC and compared to the value for the sample.

**Conclusions**  
 The synephrine sample purchase from Internet vendor appeared to be an almost pure synephrine hydrochloride. All parameters of a synephrine base isolated from this sample are in good agreement with known for natural p-syneprine.

The Bitter Orange Oil sample examined was determined to contain an inconsequential amount of synephrine, compared to what would be expected in a sample of bitter orange oil. With high probability it is a sweet orange oil.

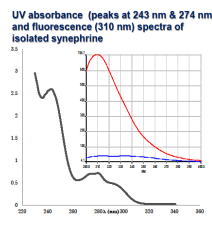
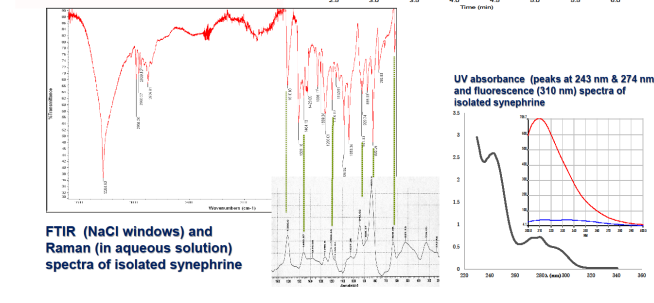
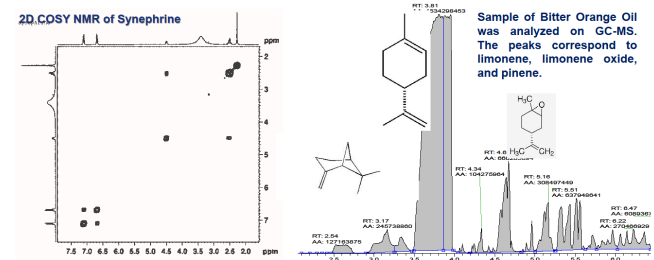
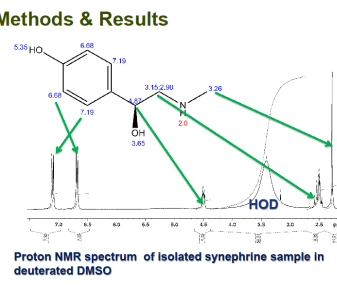
**References**  
 Andrade, A., Gas chromatographic method for analysis of p-syneprine in citrus aurantium l. products. *Chromatographie* 2009, 69, 225-29  
 Ivan Stewart, W. F. N., George J. Edwards, The isolation and identification of l-syneprine in the leaves and fruit of citrus". *The Journal of Biological Chemistry* 1964, 239 (3), 930-32  
 Marchel, E. A rapid and simple procedure for the determination of synephrine in dietary supplements by gas chromatography-mass spectrometry. *Journal of Pharmaceutical and Biomedical Analysis* 2006, 41, 1468-72  
 Santana, J., Determination of para-syneprine and meta-syneprine positional isomers in bitter orange-containing dietary supplements by LC/UV and LC/MS/MS. *Food Chemistry* 2007, 109, 675-82.

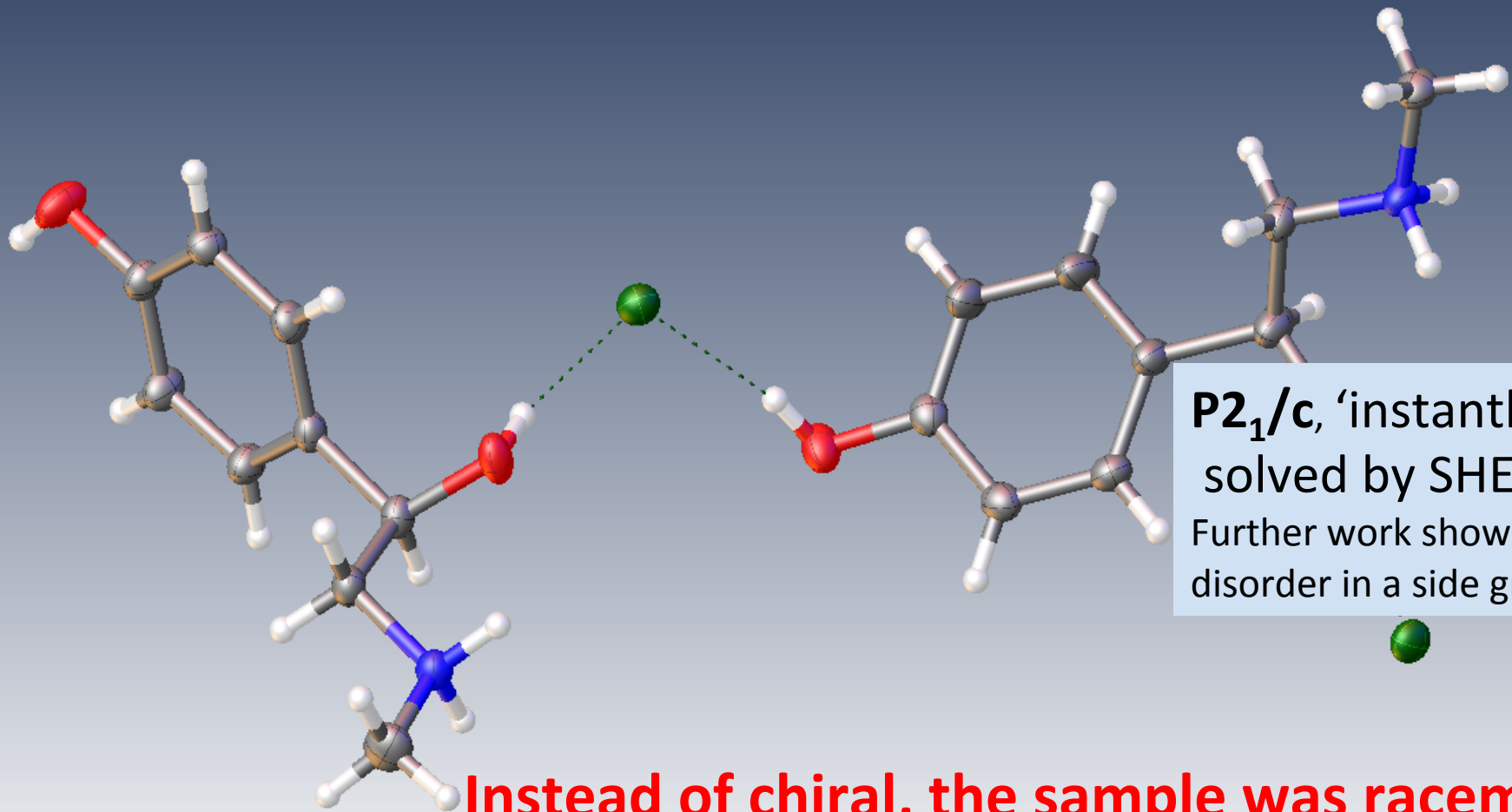
# Syneprine

was confirmed using Raman, FTIR, NMR, UV and MS

**But X-ray was wrong!!!**

**Background**  
 Syneprine is commonly used weight loss supplements, often as an alternative to ephedrine which is illegal or highly restricted in many areas. It is not reported as being a precursor to drug use, although there are some associated health risks. It is primarily derived from the immature fruit of *Citrus aurantium*, and has numerous common names such as Bitter Orange, Sour Orange, and Zhi shi. Dietary supplements contain an oral dose of 3-30mg, however as a pharmaceutical agent it is given orally or injected with dose of 20-100 mg.





**P2<sub>1</sub>/c**, 'instantly'  
solved by SHELXT  
Further work shows  
disorder in a side group

**Instead of chiral, the sample was racemic:  
was not in CSD**

# **Professional Crystallographers**

(know physics, hardware and software,  
often write software and/or make new hardware)

# **Crystallography Users**

(know chemistry, maybe some physics;  
know how to use some software and hardware)

# **Analytical Users**

(may know some chemistry, need analytical data,  
have little time to study theory)



# *Acknowledgements*



*IITG 2012*

*IITG 2013*

