

Analysis of Modern and Ancient Artifacts for the Presence of Corn Beer; Dynamic Headspace Testing of Pottery Sherds from Mexico and New Mexico

**Materials Research Society
Symposium Y, Materials Issues in Art and Archaeology VIII
November 2007**

**Theodore Borek*, Curtis Mowry
Materials Characterization, Department 1822
Sandia National Laboratories**

**Glenna Dean
Archeobotanical Services, Inc.**



Hypothesis

- Did historic cultures of the American Southwest have fermentation practices that pre-date the European conquest of the New World?
- Is it possible to detect marker compounds for a fermented beverage?
- What would these compounds be? Organic? Volatile?





How this started

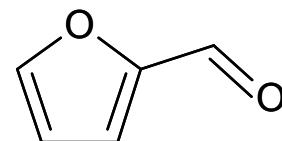
Did the residents at Chaco Canyon brew beer from Corn?

Can you do the spot test for furfural, as this would indicate if fermentation using corn was present?

Spot test (Anger and Ofri, 1964)

Phloroglucinol/HCl

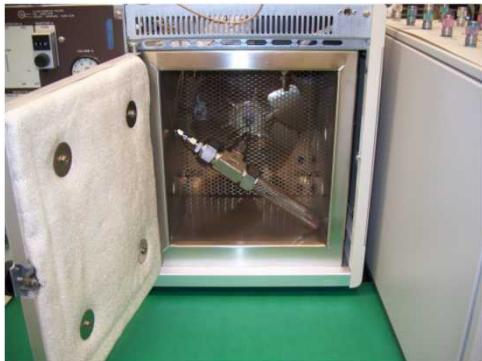
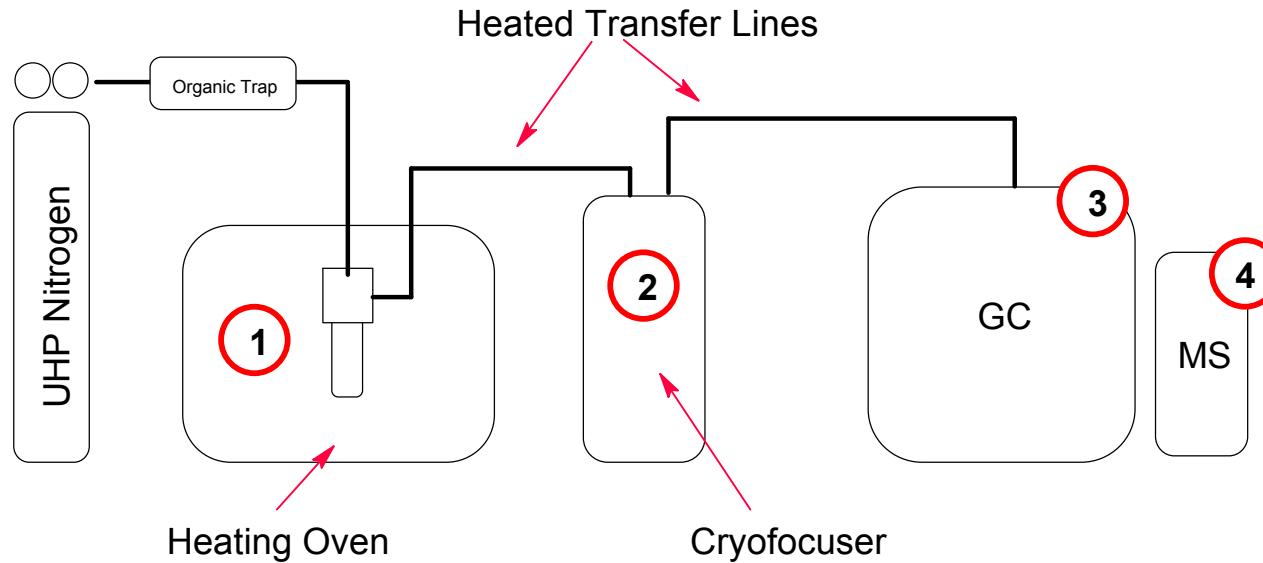
- Don't really want to put a concentrated acid solution onto a historical artifact.
- Is there an alternative to this wet chemical method, some instrumental method that will have minimal impact on the article to be tested?



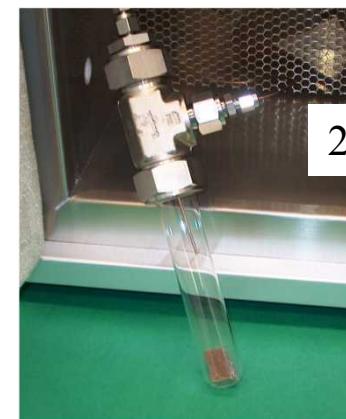
MW 96.09
bp 167°C



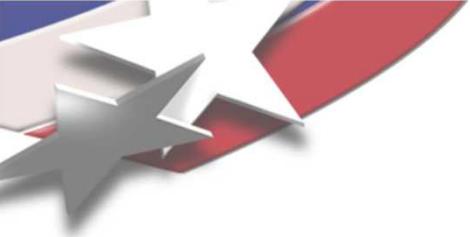
Dynamic Headspace Sampling



1. Heat
2. Trap/focus
3. Separate
4. Detect/identify



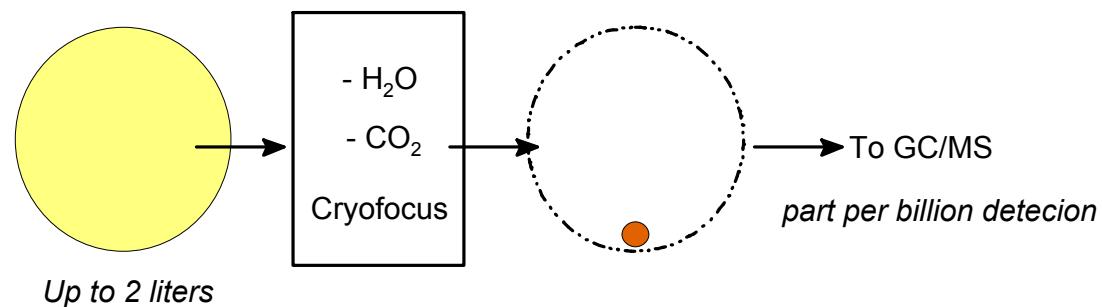
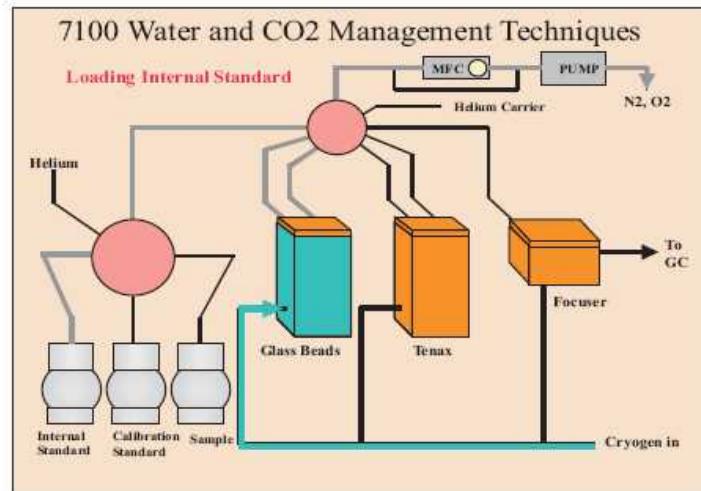
25 x 150mm



Cryofocusing Inlet System



Entech Instruments, Inc.
Model 7100A Cryofocuser
Model 7032A-L Autosampler





Why is this an attractive option?

1. We have had success using this method to determine trace organics on solid materials.
2. Solvents not used; no need to worry about selective extraction.
3. Ultimate temperature may be selected to minimize thermal stress on articles tested. Here we selected 190°C.
4. If necessary, further testing on the same article may be performed without too much concern for this method altering nonvolatile residues.
5. Nondestructive!



What does a corn beer volatile signature look like?

Progression of Analysis

- Analysis of modern vessels used for intentional fermentation of corn; with this, we can vary how the fermentation is approached.
- Analysis of fermentation vessels from the Tarahumara, a tribe native to Mexico that brews corn beer for ceremonial purposes.
- Analyze sherds from Chaco Canyon National Historic Park, if available.
- Examine the data for similarities.

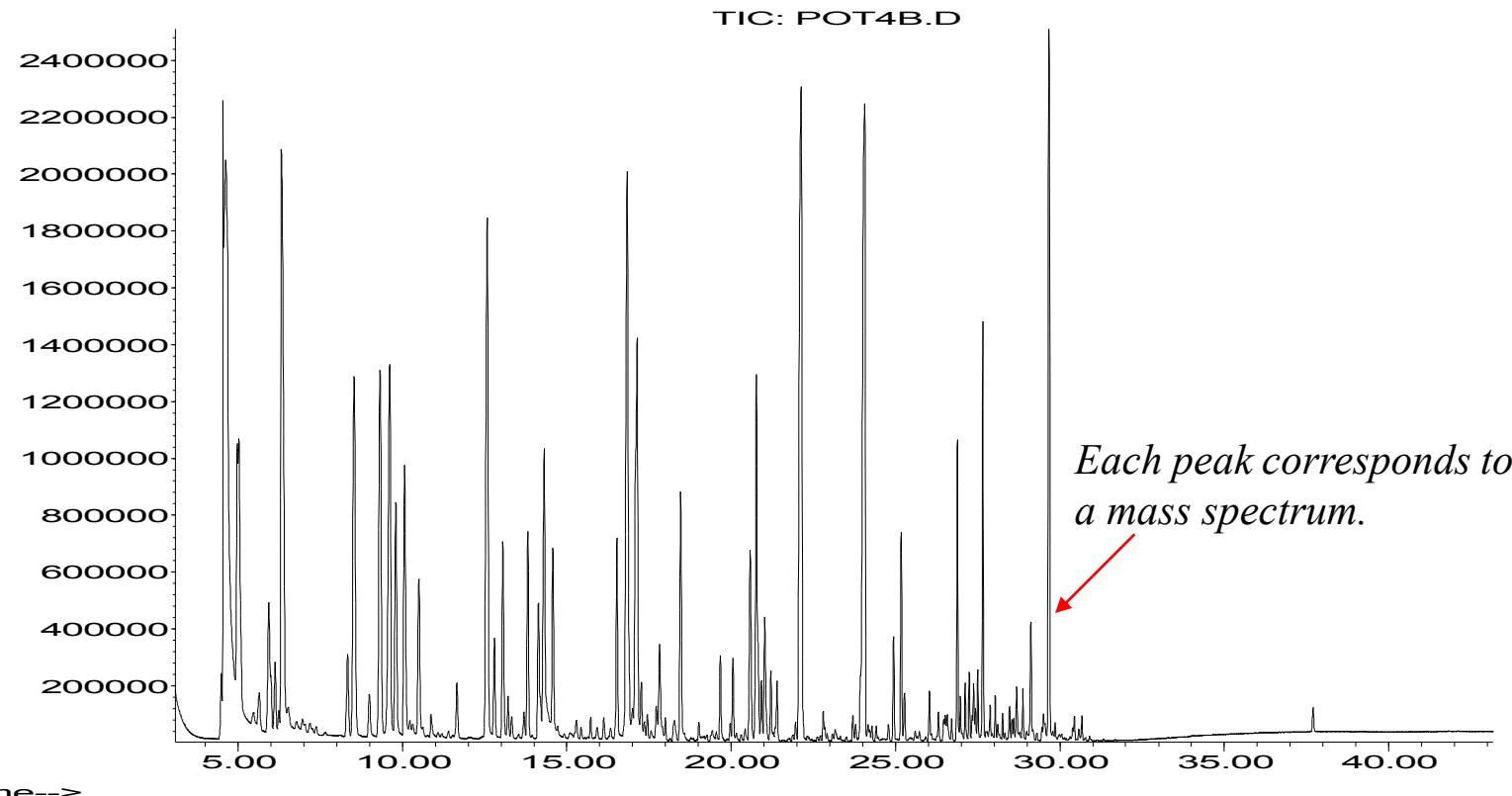


Intentional Fermentation with Modern Vessels



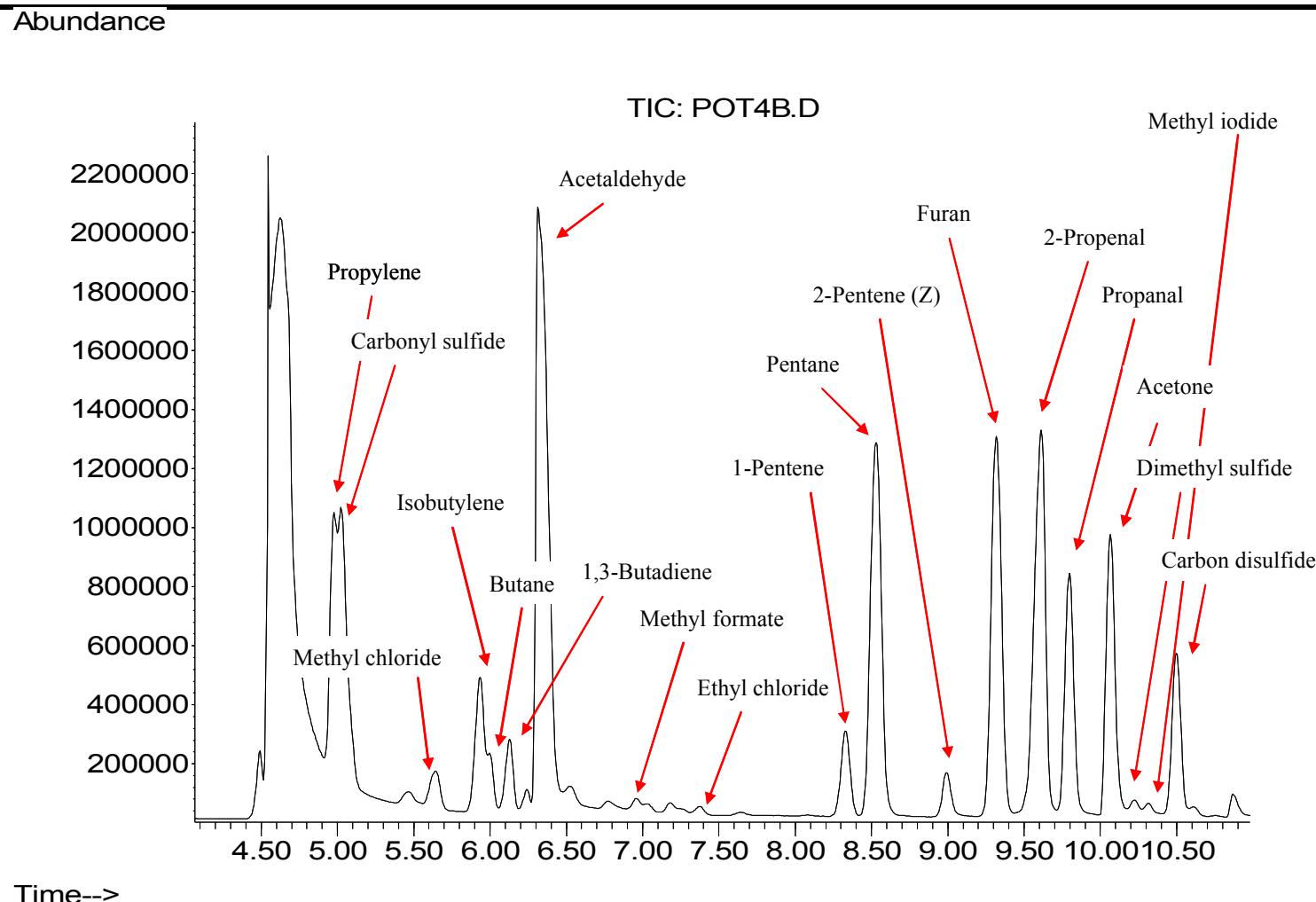
Typical Result

Abundance



We can then perform library matching to determine what these species might be.

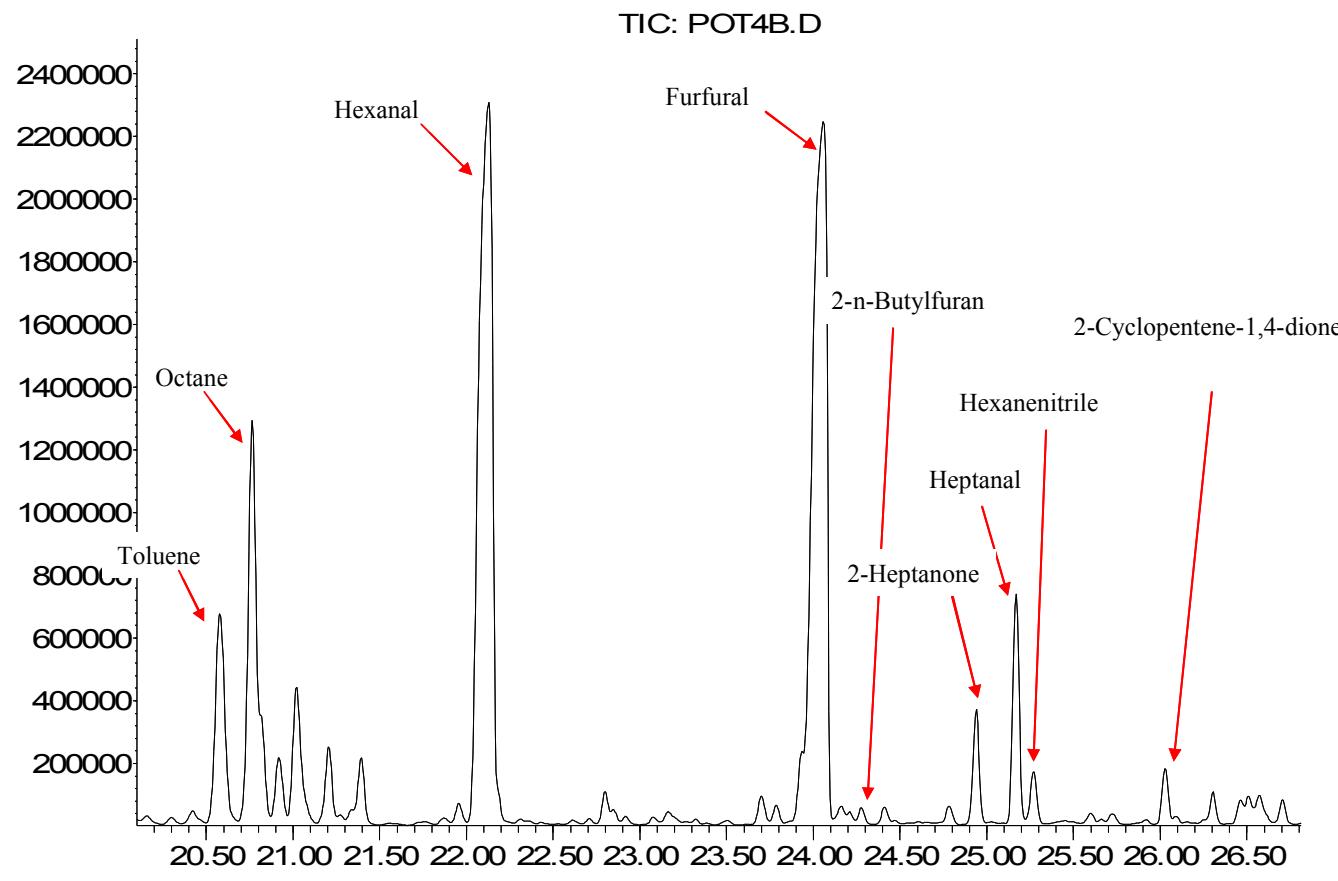
Mass Spectral Library Matching

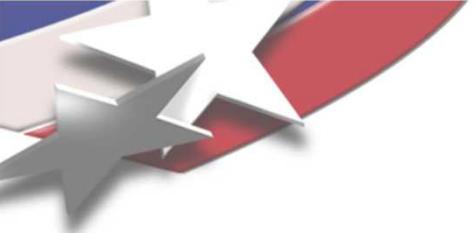




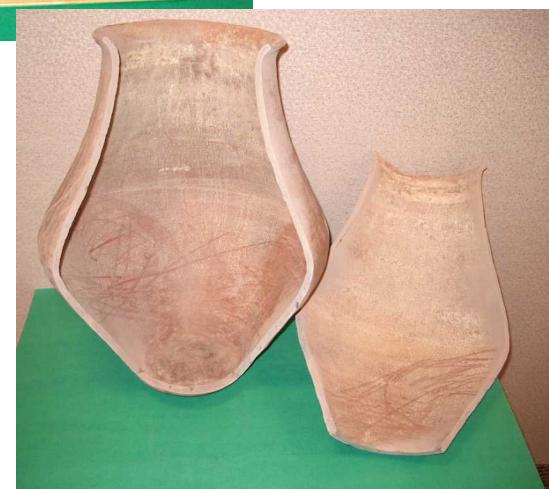
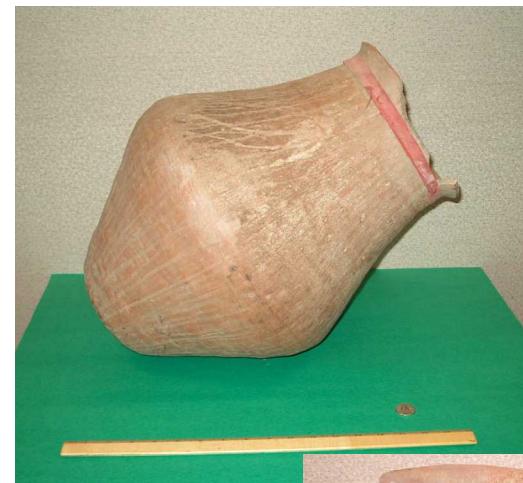
Mass Spectral Library Matching, cont.

Abundance



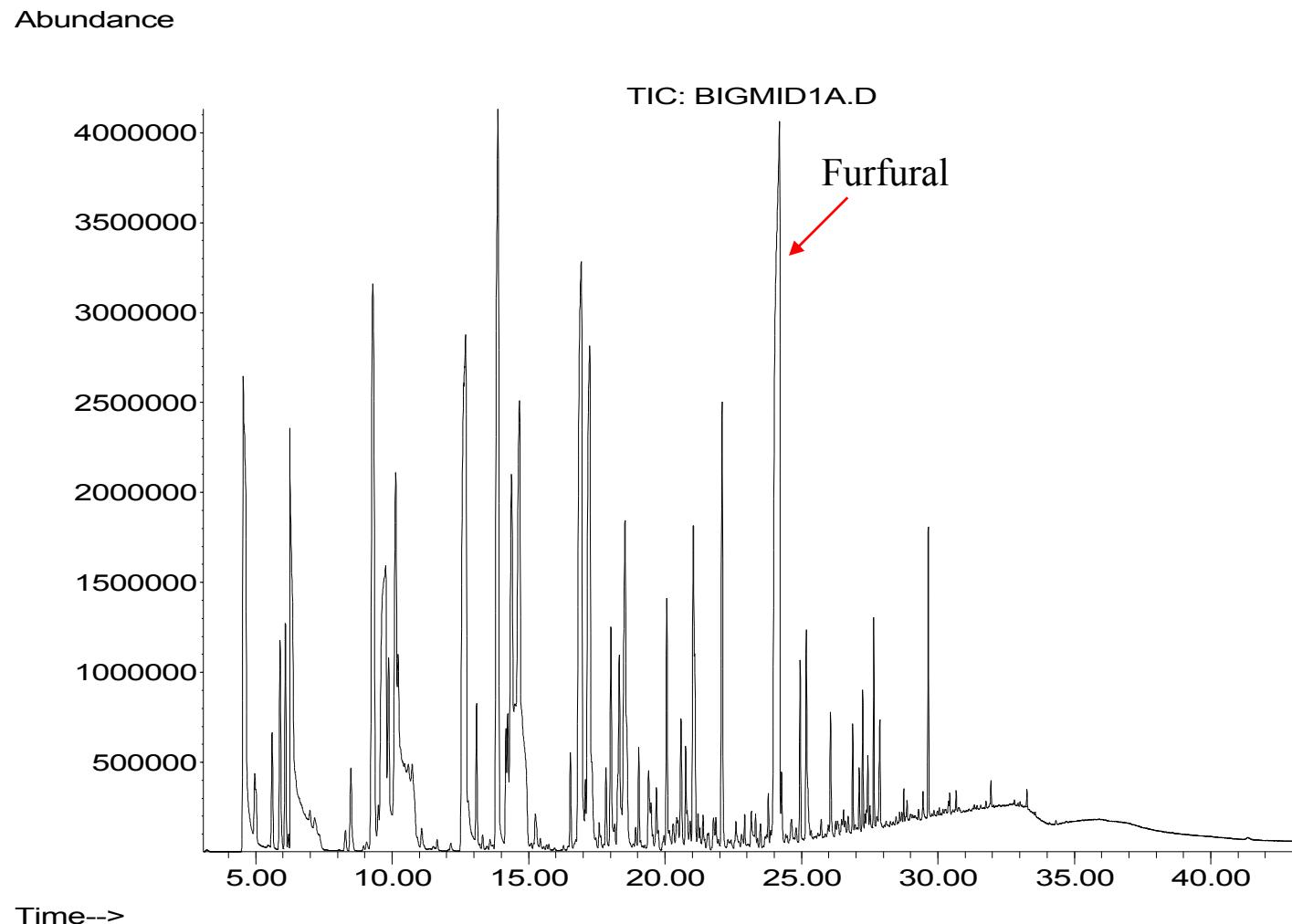


Tarahumara Brew Pots





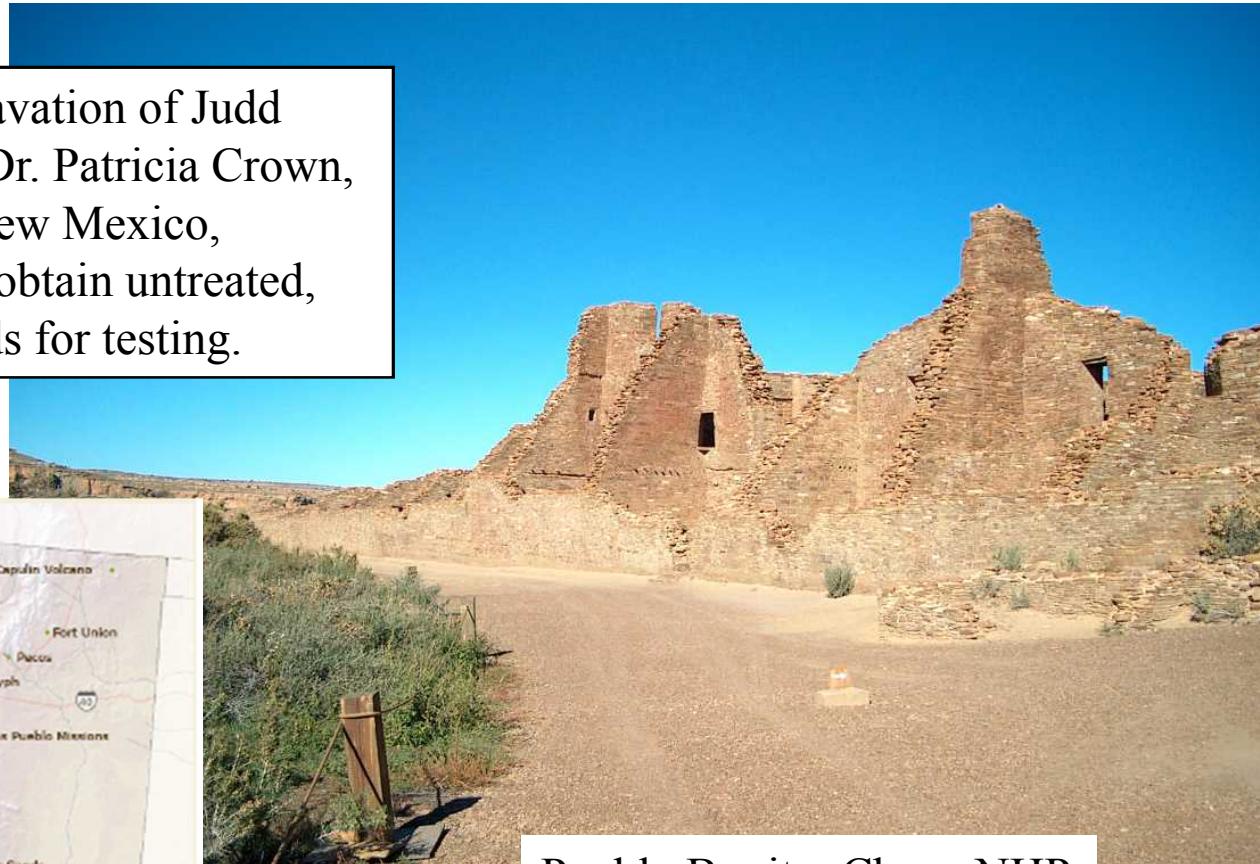
Typical Tarahumara Result





Chaco Culture National Historical Park

In 2006, re-excavation of Judd Excavation by Dr. Patricia Crown, University of New Mexico, permitted us to obtain untreated, uncleaned sherds for testing.



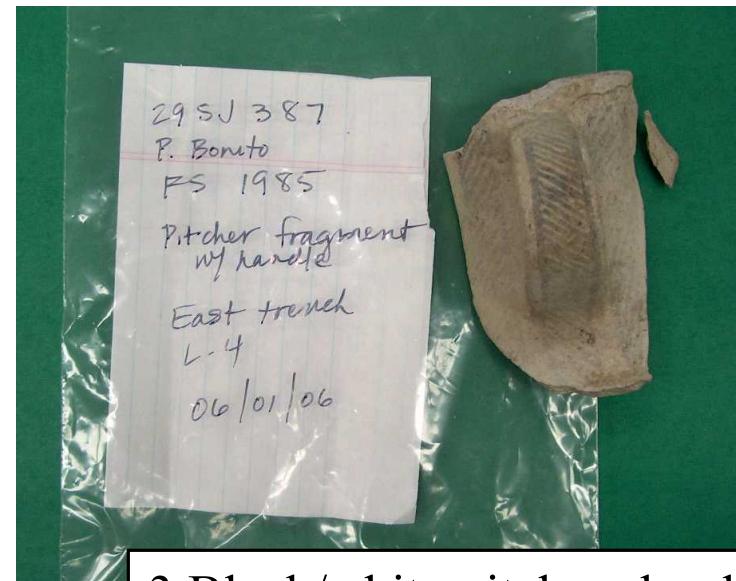
Pueblo Bonito, Chaco NHP



Chaco Sherds



3 possible cylinder jar sherds

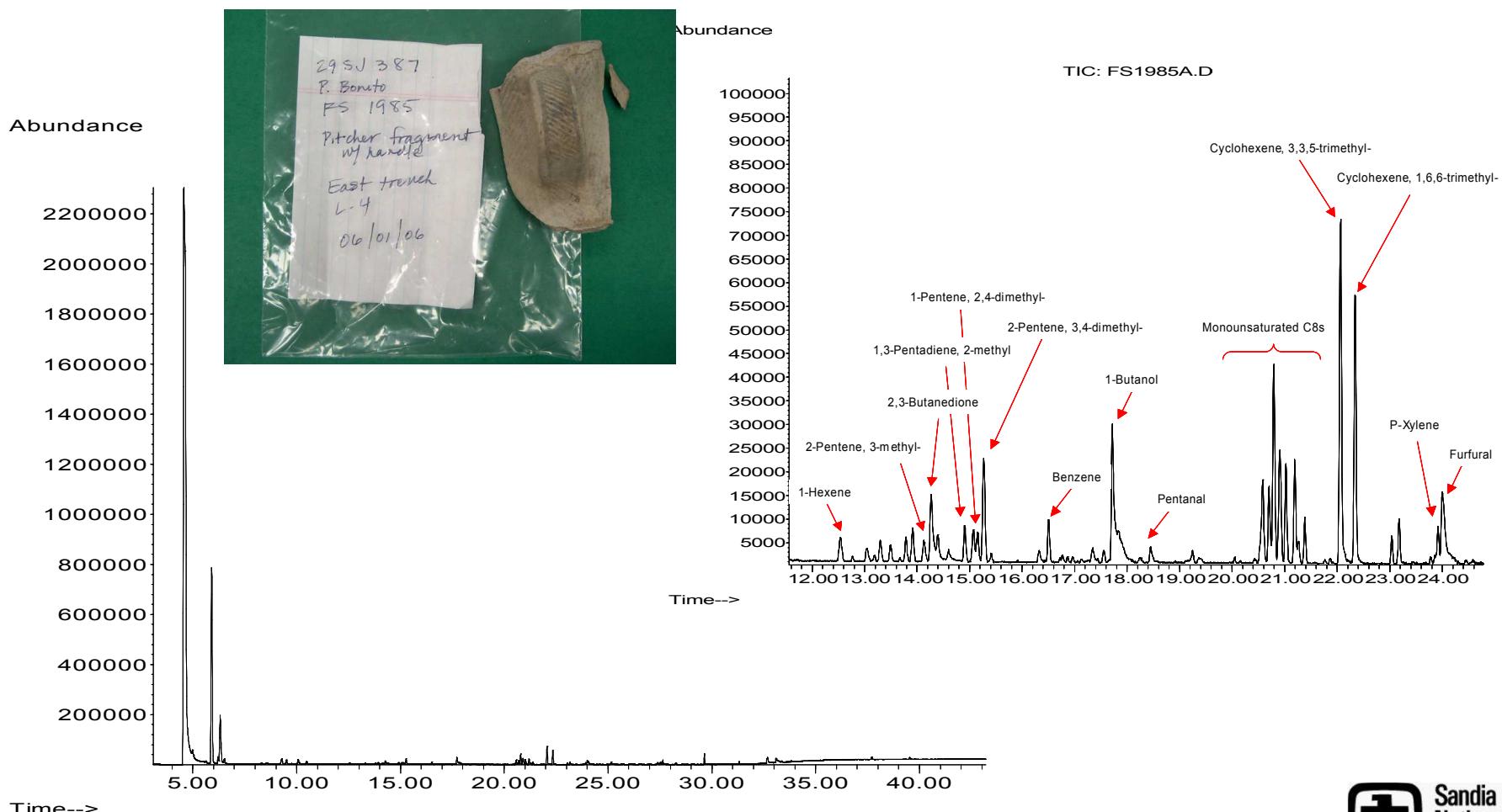


3 Black/white pitcher sherds



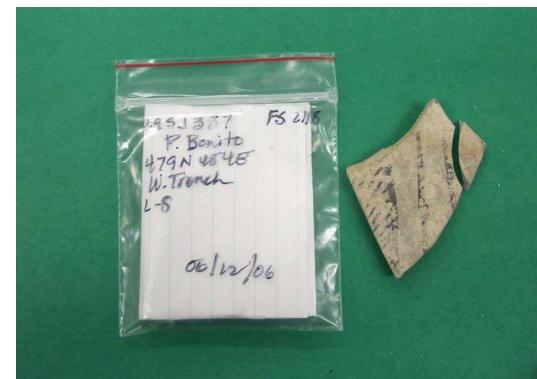
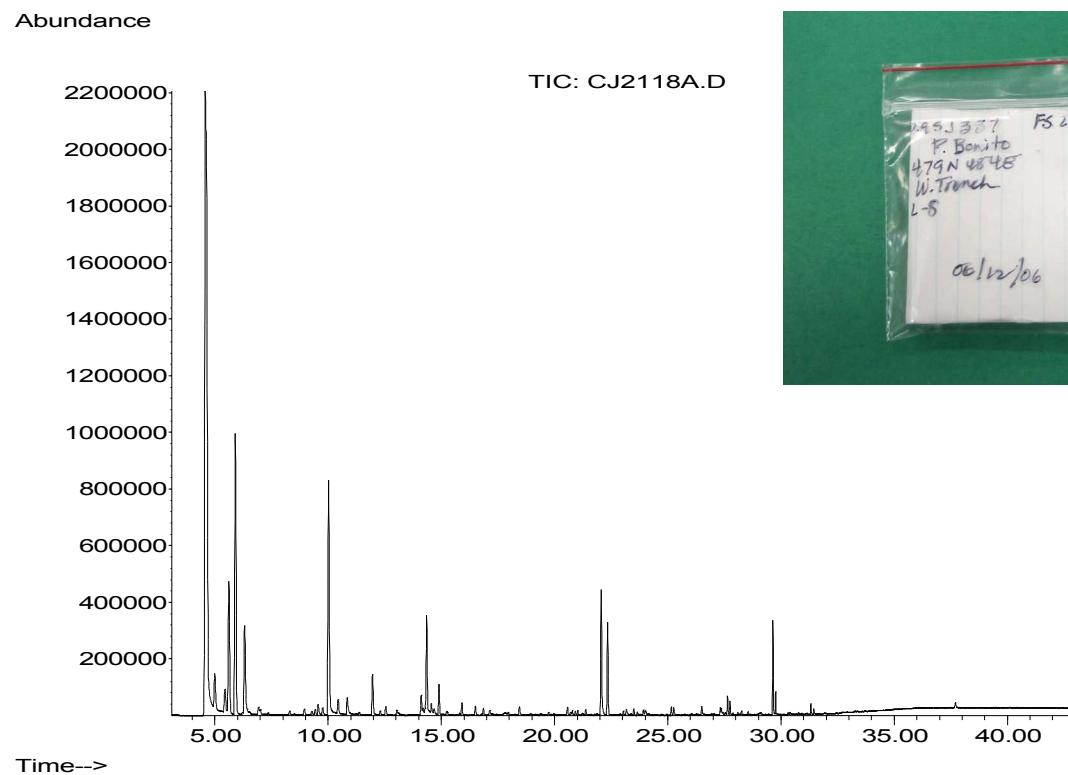
3 Mogollon smudged bowl sherds

Results, Chaco Pitcher Sherd



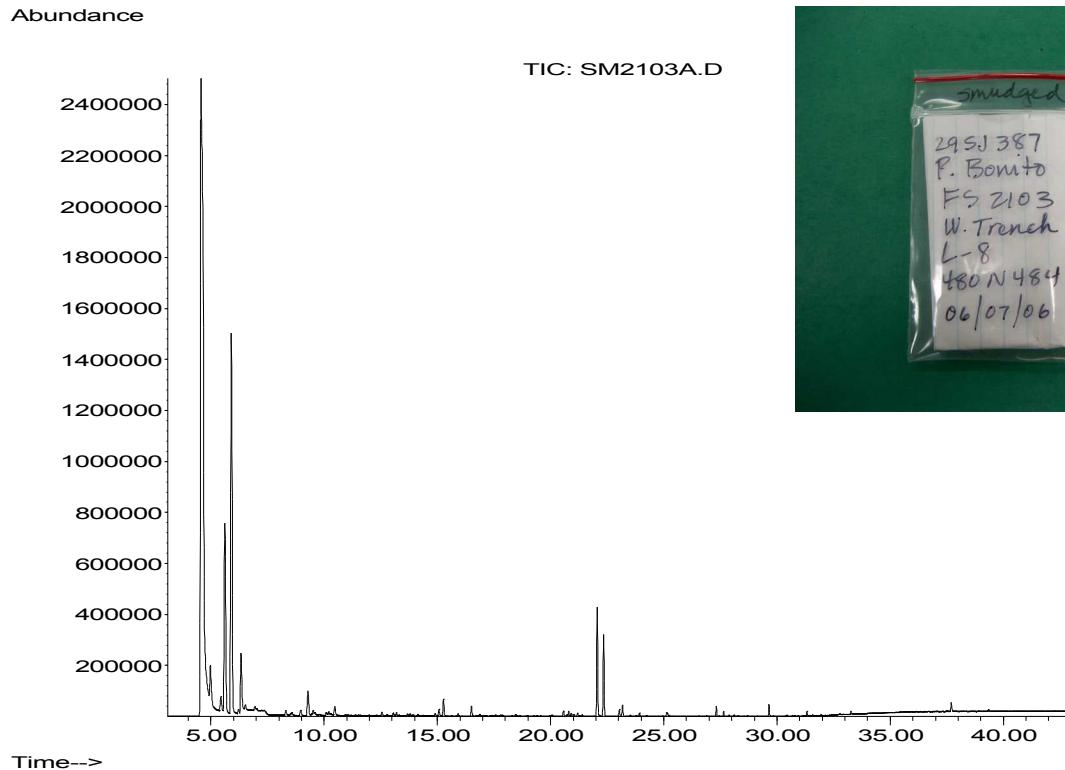


Results, Chaco Cylinder Jar





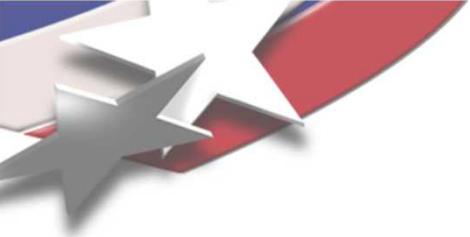
Results, Chaco Smudged Bowl



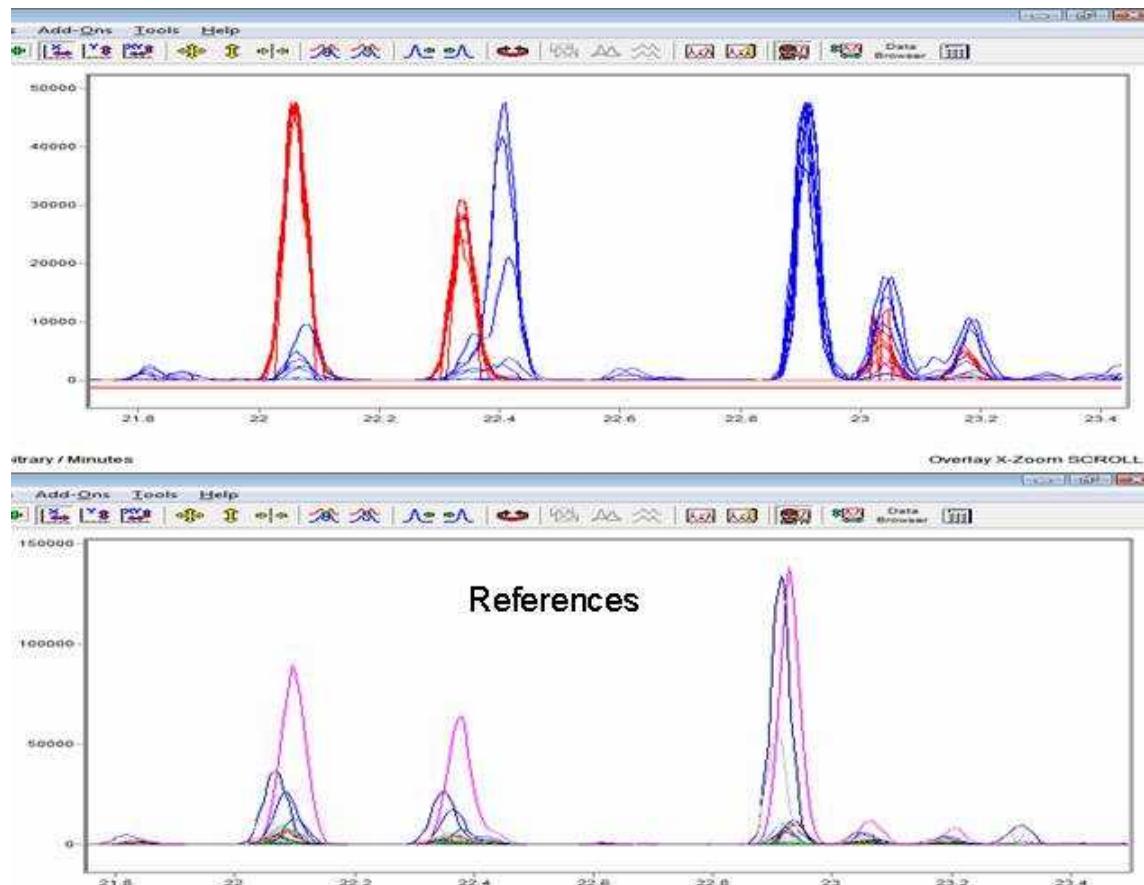


Correlation of the Data

- 1. Account for subtle shifts in chromatographic retention time.**
- 2. Compare peaks across the data set.**
- 3. Look for markers and similarities.**

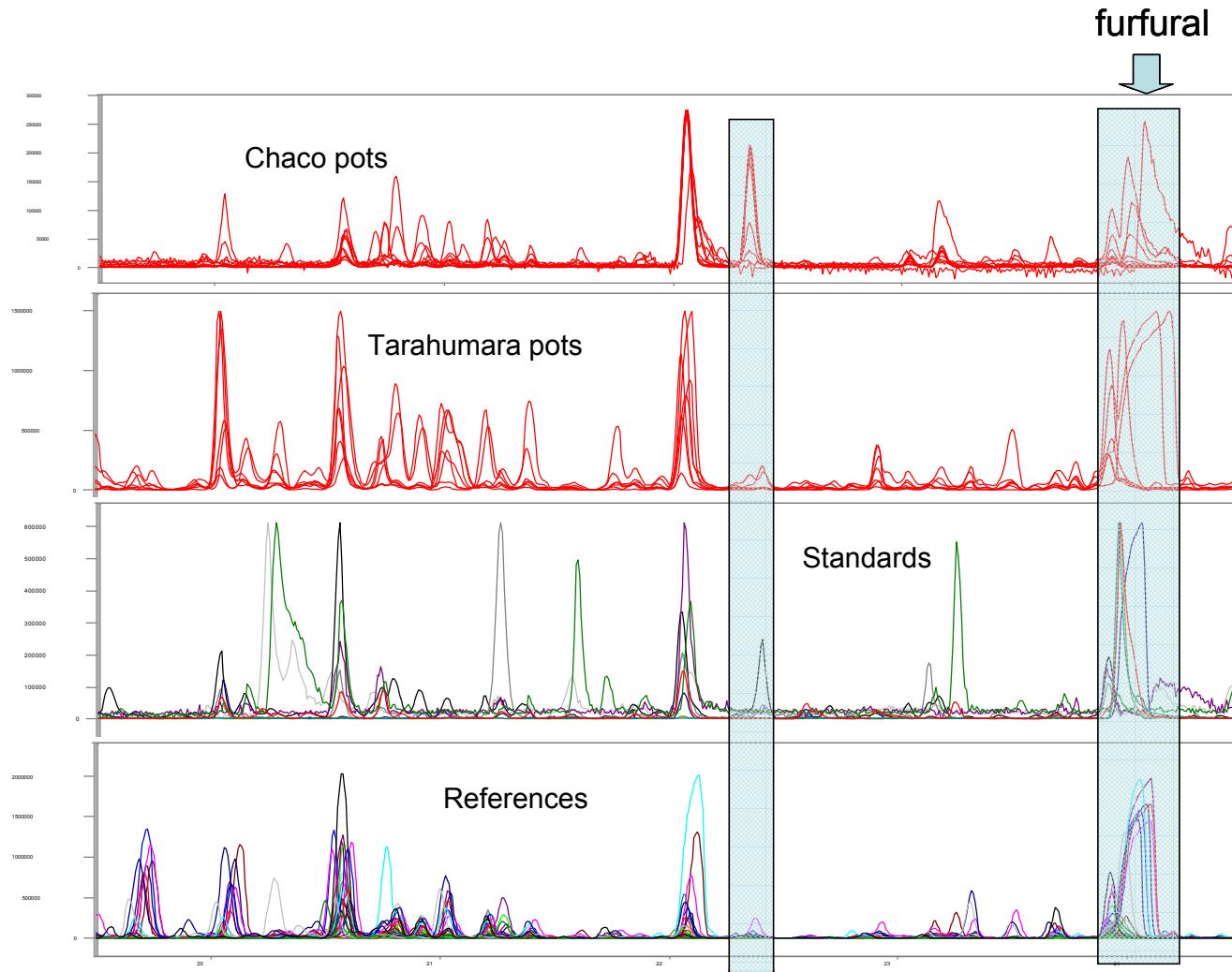


Correlation of the Data



109 plots, chaco=red tarahumara=blue

Data from 19.5 to 24.5 minutes





Other samples analyzed

- Soil samples from Chaco Culture NHP
- Artifacts that have been washed to determine if museum collections may provide useful information using this method.
- Grain 'storage' vessels
- Corn gruel in modern vessels
 - Corn gruel intentionally left to spoil.
- Samples from a 'chicha' brewery excavation in Peru.



Conclusions

- It is possible to use the 'dynamic headspace sampling' technique to observe volatile organic species on modern and ancient articles.
- There appear to be consistencies across the modern homebrew and Tarahumara pots.
- We are currently examining all of the data to look for markers that would indicate intentional fermentation occurred on Chaco Cultural articles.



Acknowledgement



Fajada Butte

The authors would like to acknowledge the contributions of:

**Dr. Patricia Crown,
University of New Mexico**

Chaco Culture NHP