Chemical Fingerprinting of California Methamphetamine

Jerry Massetti
Mark Kalchik
California State Department of Justice
Bureau of Forensic Services

Objectives of This Presentation

- Context of chemical fingerprinting project

  One part of CALMS

- To provide example of work in progress

Introduction: CALMS

- **CAL**ifornia **M**ethamphetamine **S**trategy
- CA State Department of Justice developed CALMS to address all facets of methamphetamine manufacturing and distribution in California.

Introduction: CALMS

- A response to rapidly increasing clandestine methamphetamine laboratory seizures.
- Federal grant received
- Based on many components of national methamphetamine strategy

CALMS Components (5)

- Law enforcement strike teams established
- Intelligence: strategic and tactical support
- Forensics
- Training and safety
- Prevention and community outreach

CALMS Forensic Component

- Field support
- Chemical signature analysis project

CALMS Chemical Signature Analysis Project

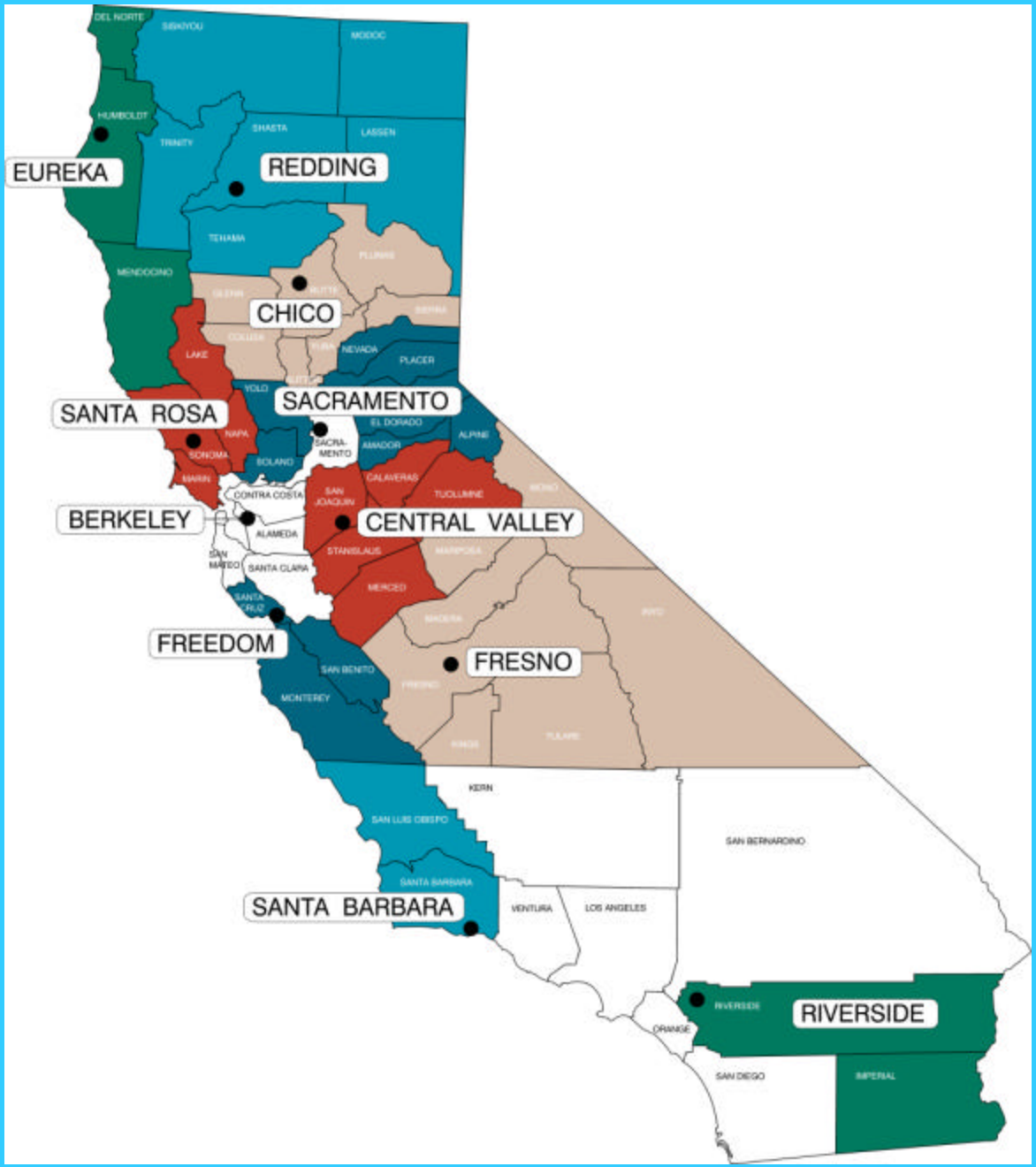
- Chemical analyses
- Interpretation and significance of chemical analysis results
- Database

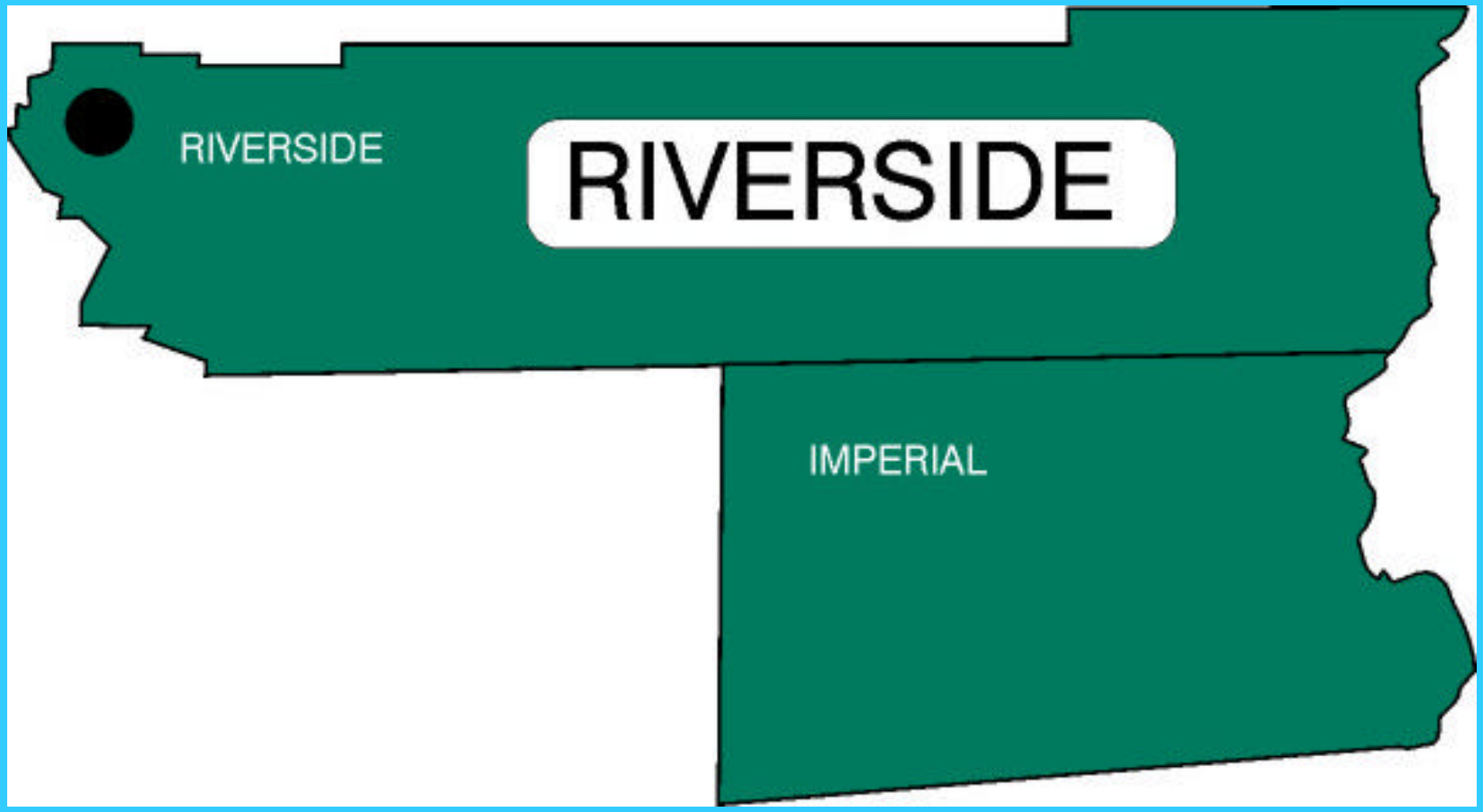
Chemical Analyses

- Quantitation
- Volatiles
- Profiling (“fingerprinting”)
  - Components detected by GCMS
  - Elemental

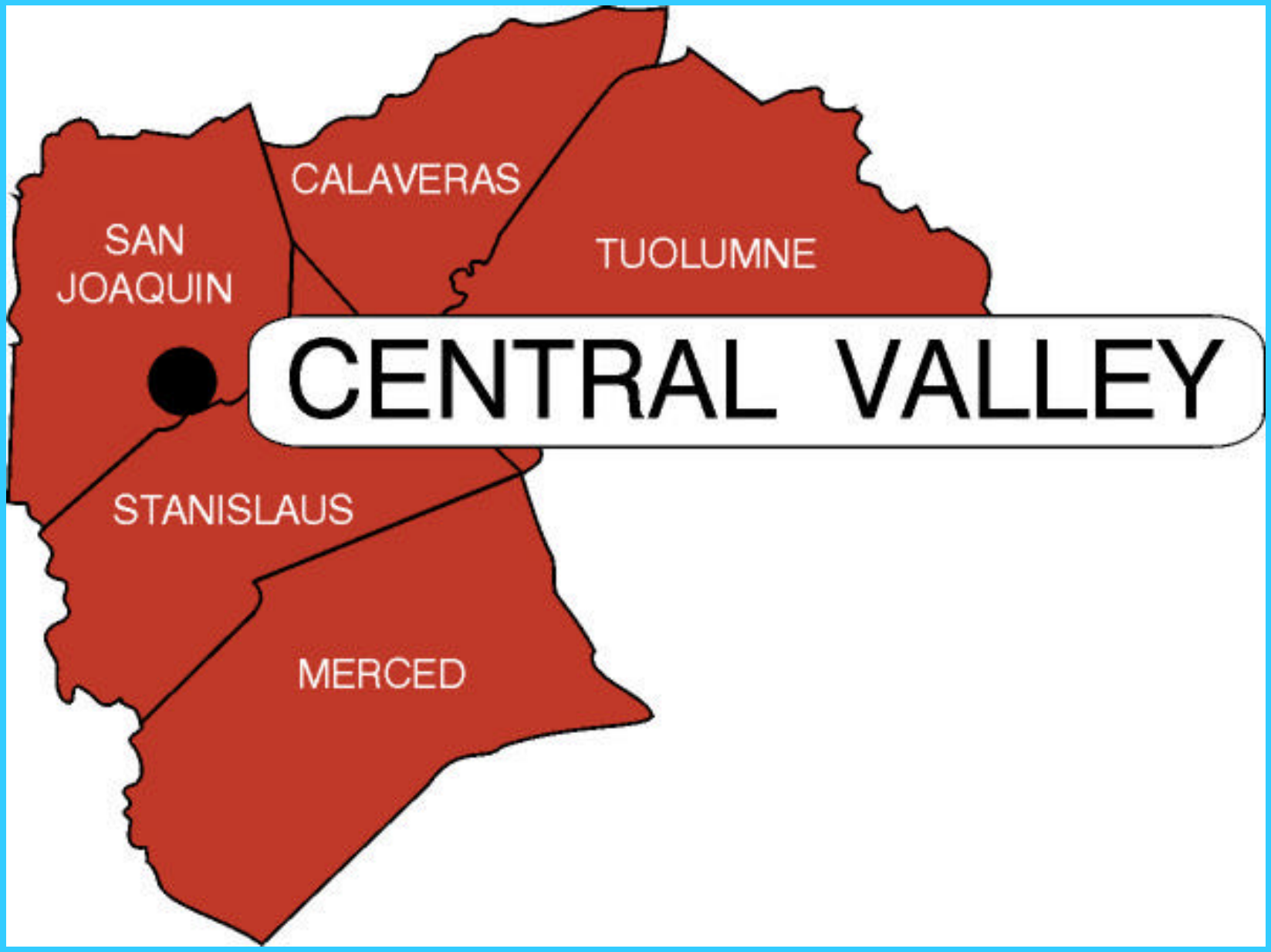
Significance

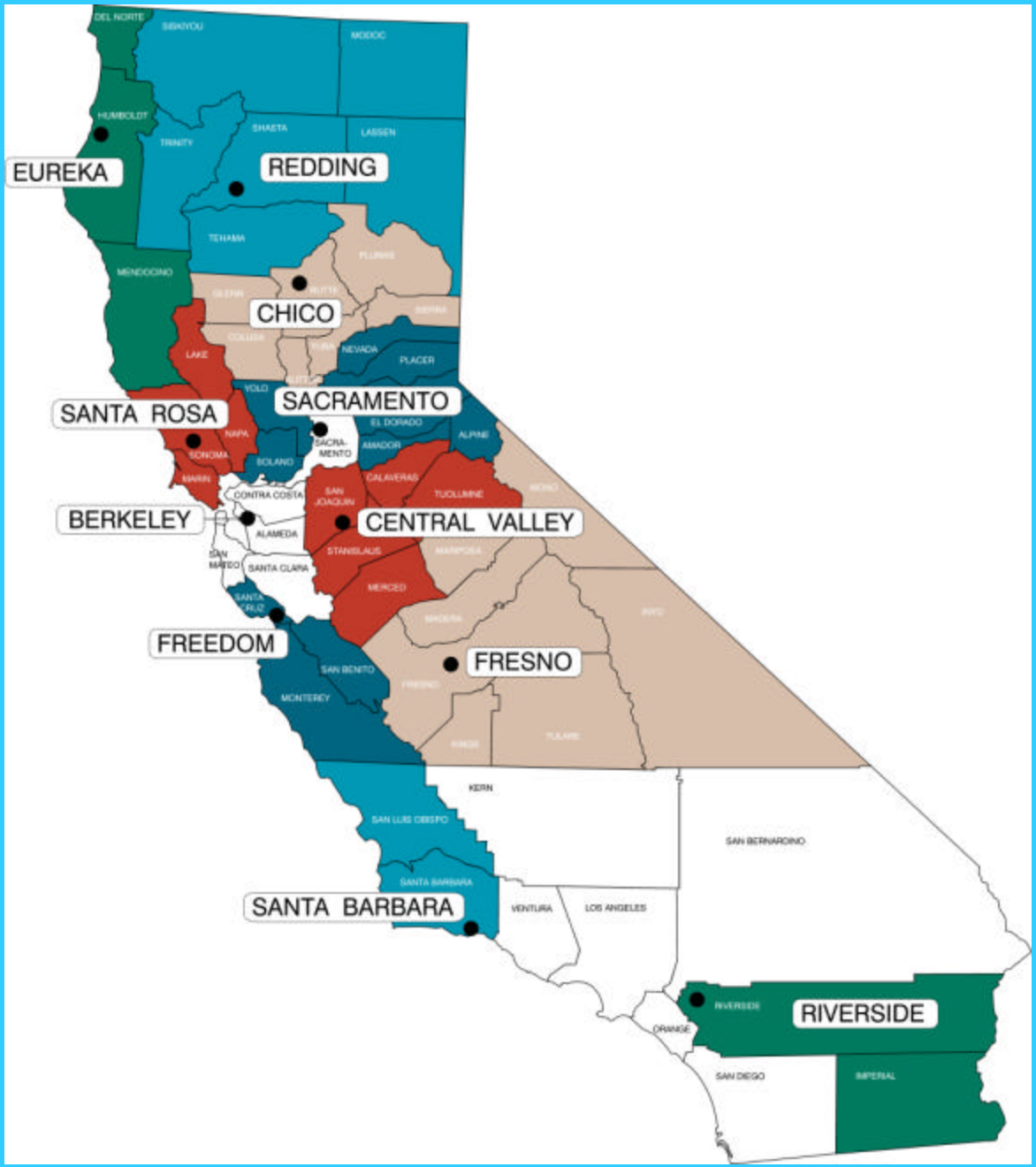
- Geographical
  - Indexing
  - Sourcing
- Manufacturer
- Reaction / storage conditions
  - Age
  - Temperature


EUREKA
REDDING
CHICO
SACRAMENTO
SANTA ROSA
BERKELEY
CENTRAL VALLEY
FREEDOM
FRESNO
SANTA BARBARA
RIVERSIDE
DEL NORTE
SISKIYOU
MODOC
HUMBOLDT
TRINITY
SHASTA
LASSEN
TEHAMA
PLUMAS
MENDOCINO
GLENN
BUTTE
SIERRA
COLUSA
LAKE
YUBA
NEVADA
PLACER
YOLO
SUTTER
EL DORADO
NAPA
SACRA-
MENTO
ALPINE
SONOMA
AMADOR
SOLANO
MARIN
CALAVERAS
CONTRA COSTA
SAN
JOAQUIN
TUOLUMNE
MONO
ALAMEDA
STANISLAUS
MARIPOSA
SAN
MATEO
SANTA CLARA
MERCED
SANTA
CRUZ
MADERA
INYO
SAN BENITO
FRESNO
MONTEREY
KINGS
TULARE
KERN
SAN LUIS OBISPO
SAN BERNARDINO
SANTA BARBARA
VENTURA
LOS ANGELES
ORANGE
SAN DIEGO
IMPERIAL


RIVERSIDE
RIVERSIDE
IMPERIAL

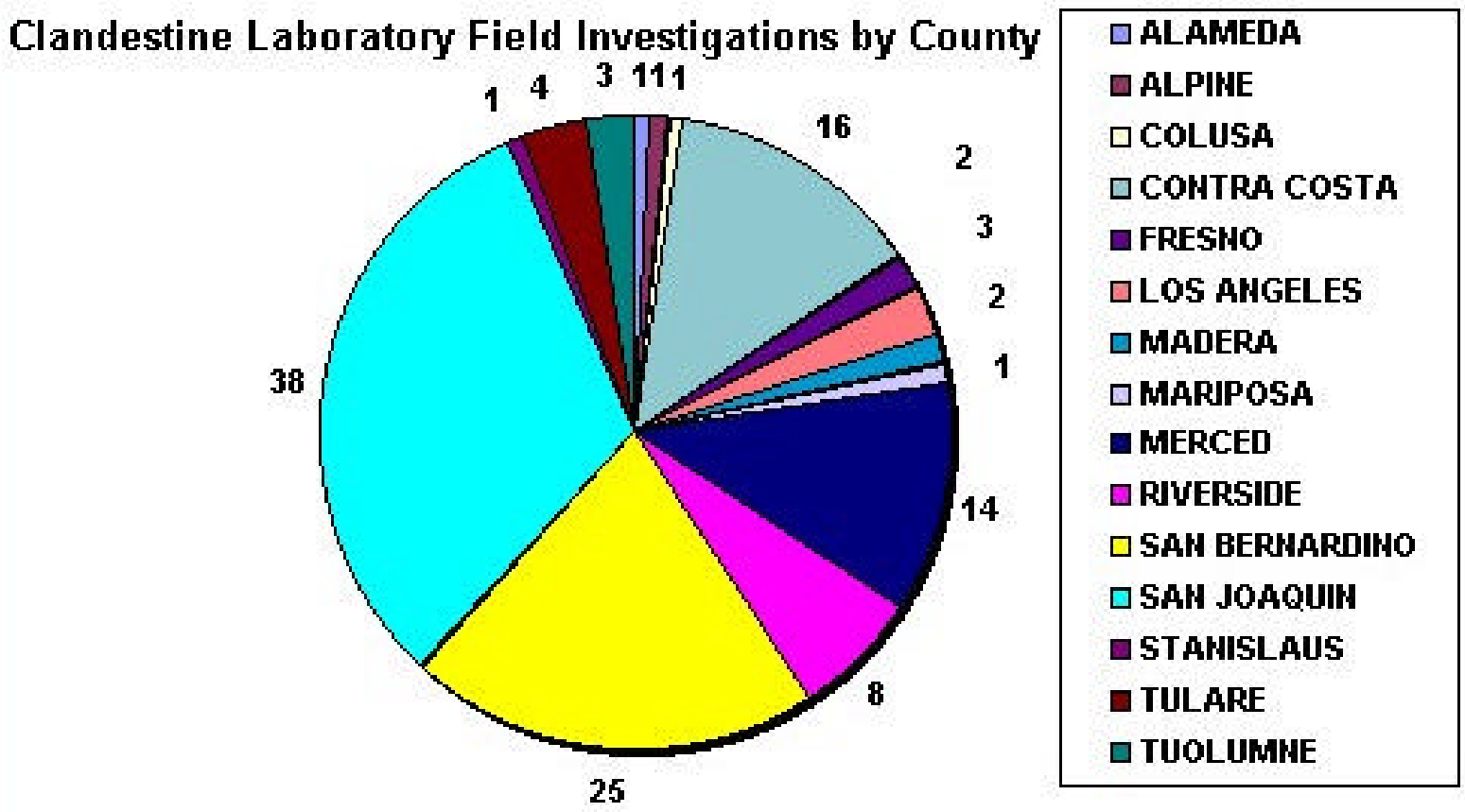
MONO
MARIPOSA
MADERA
INYO
FRESNO
FRESNO
KINGS
TULARE


CALAVERAS
SAN JOAQUIN
TUOLUMNE
CENTRAL VALLEY
STANISLAUS
MERCED

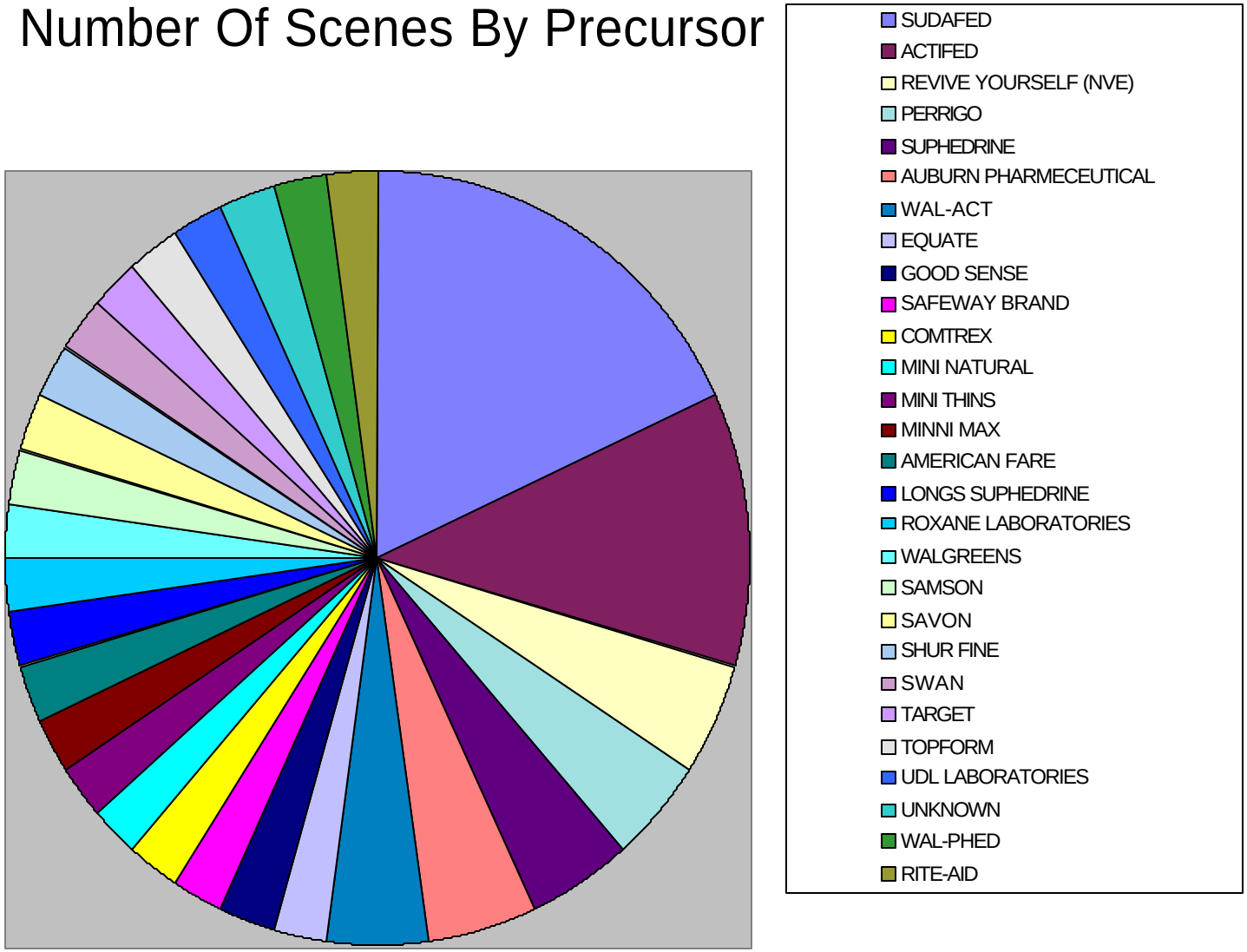

EUREKA
REDDING
CHICO
SACRAMENTO
SANTA ROSA
BERKELEY
CENTRAL VALLEY
FREEDOM
FRESNO
SANTA BARBARA
RIVERSIDE
DEL NORTE
SISKIYOU
MODOC
HUMBOLDT
TRINITY
SHASTA
LASSEN
TEHAMA
PLUMAS
MENDOCINO
GLENN
BUTTE
SIERRA
COLUSA
LAKE
YUBA
NEVADA
PLACER
YOLO
SUTTER
EL DORADO
NAPA
SACRA-
MENTO
ALPINE
SONOMA
AMADOR
SOLANO
MARIN
CALAVERAS
CONTRA COSTA
SAN
JOAQUIN
TUOLUMNE
MONO
ALAMEDA
STANISLAUS
MARIPOSA
SAN
MATEO
SANTA CLARA
MERCED
SANTA
CRUZ
MADERA
INYO
SAN BENITO
FRESNO
MONTEREY
KINGS
TULARE
KERN
SAN LUIS OBISPO
SAN BERNARDINO
SANTA BARBARA
VENTURA
LOS ANGELES
ORANGE
SAN DIEGO
IMPERIAL

Database

- Automated acquisition of analytical data
- From 10 regions within California


Clandestine Laboratory Field Investigations by County
1
4
3
1
1
1
16
2
3
2
1
14
8
25
38
ALAMEDA
ALPINE
COLUSA
CONTRA COSTA
FRESNO
LOS ANGELES
MADERA
MARIPOSA
MERCED
RIVERSIDE
SAN BERNARDINO
SAN JOAQUIN
STANISLAUS
TULARE
TUOLUMNE

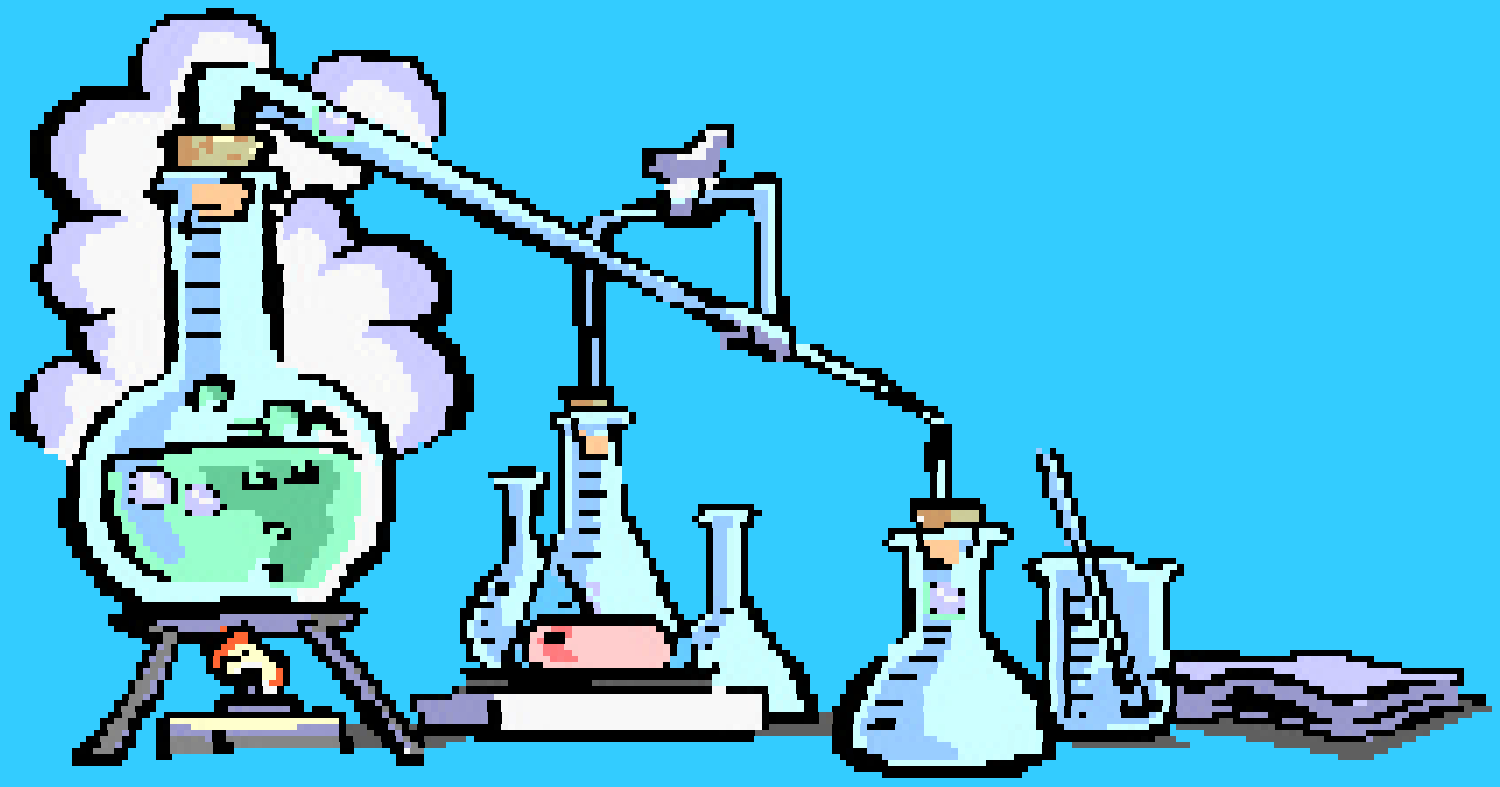
Number Of Scenes By Precursor



Summary of Context of Chemical Fingerprinting Project

- Signature analysis project is part of the forensic component of CALMS
- Several chemical approaches
- Automated acquisition of data
- Interesting geographical distribution of analytical laboratories within the “source country”

An Example of Work in Progress



DEA STRL - McLean VA

- Went for one week of training
- Went through procedures that DEA was using for quantitation, solvent analysis and impurity analysis
- We have moved away from their procedures due to the equipment we have available

Acidic Extract

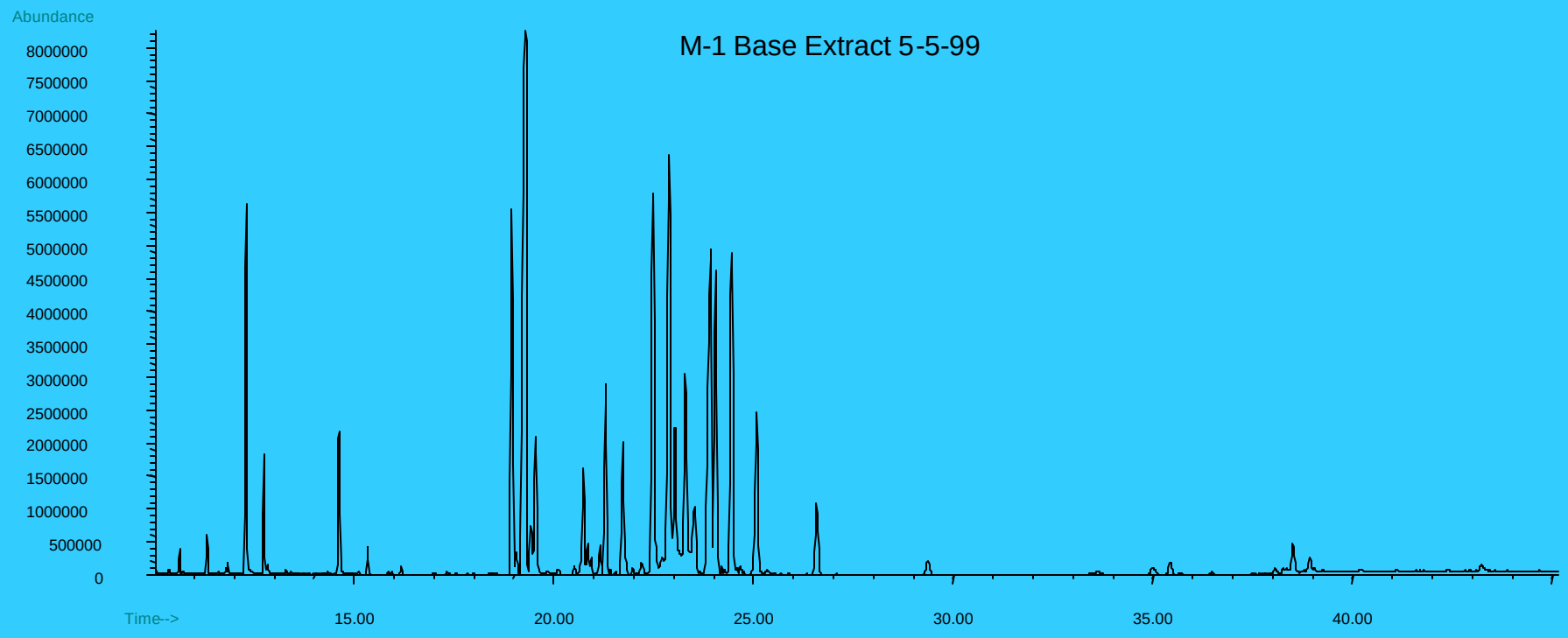
- Weigh approx. 100mg of sample into tube
- Dissolve in 1 ml acetate buffer
- Add 0.2 ml hexane and mix
- Place hexane in MS vial insert
- Analyze with GC/MSD

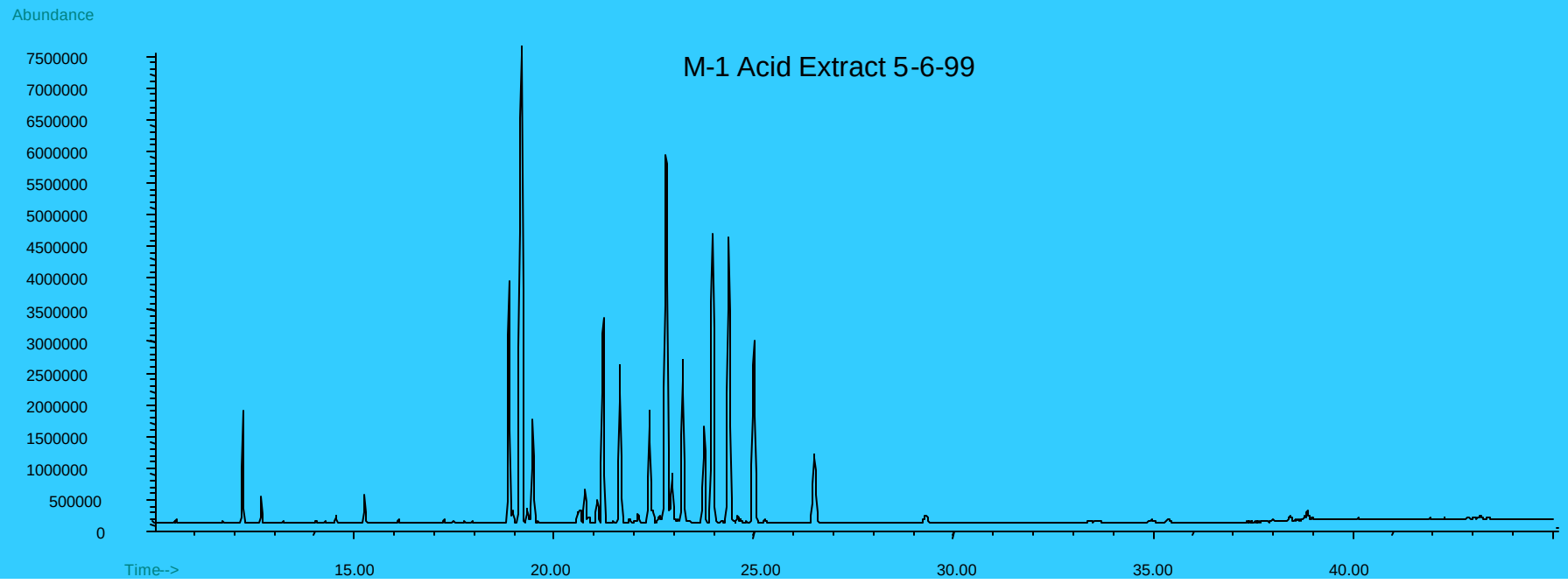
Basic Extract

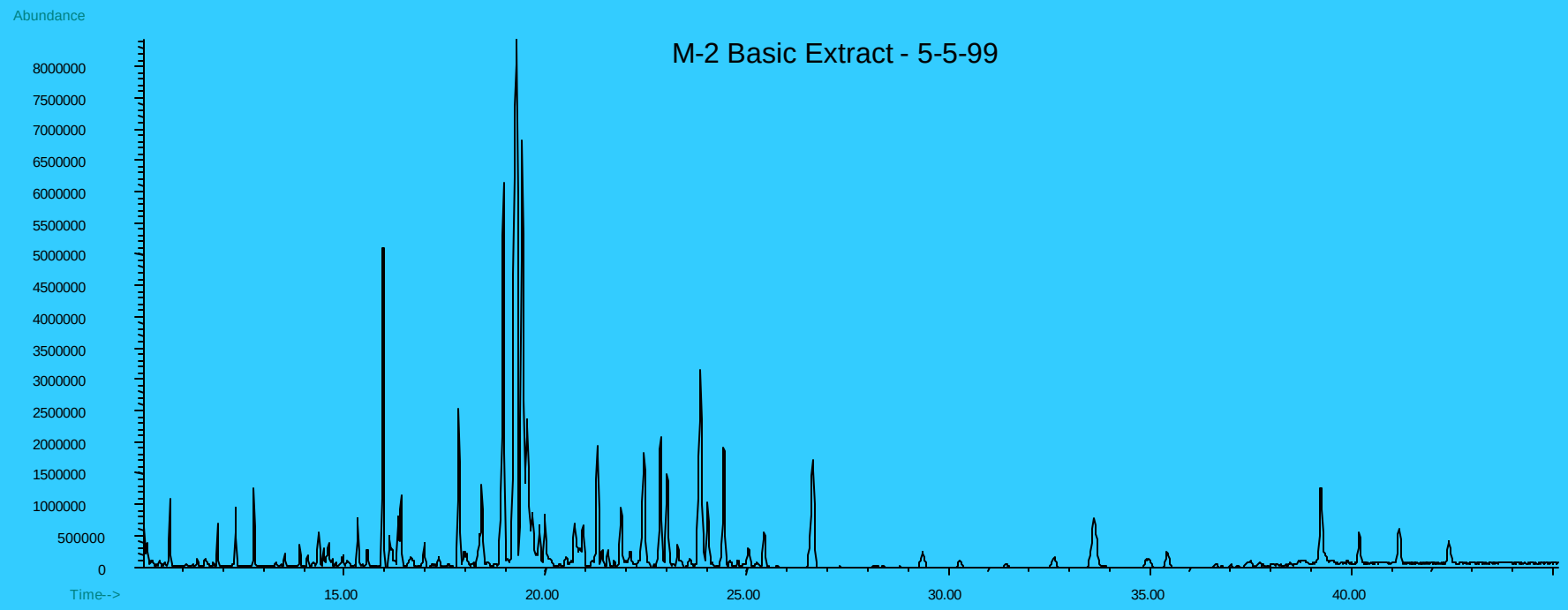
- Weigh approx. 100mg of sample into tube
- Dissolve in 1 ml phosphate buffer
- Add 0.25 ml 10% carbonate solution
- Add 0.2 ml ethyl acetate and mix
- Place ethyl acetate in MS vial insert
- Analyze with GC/MSD

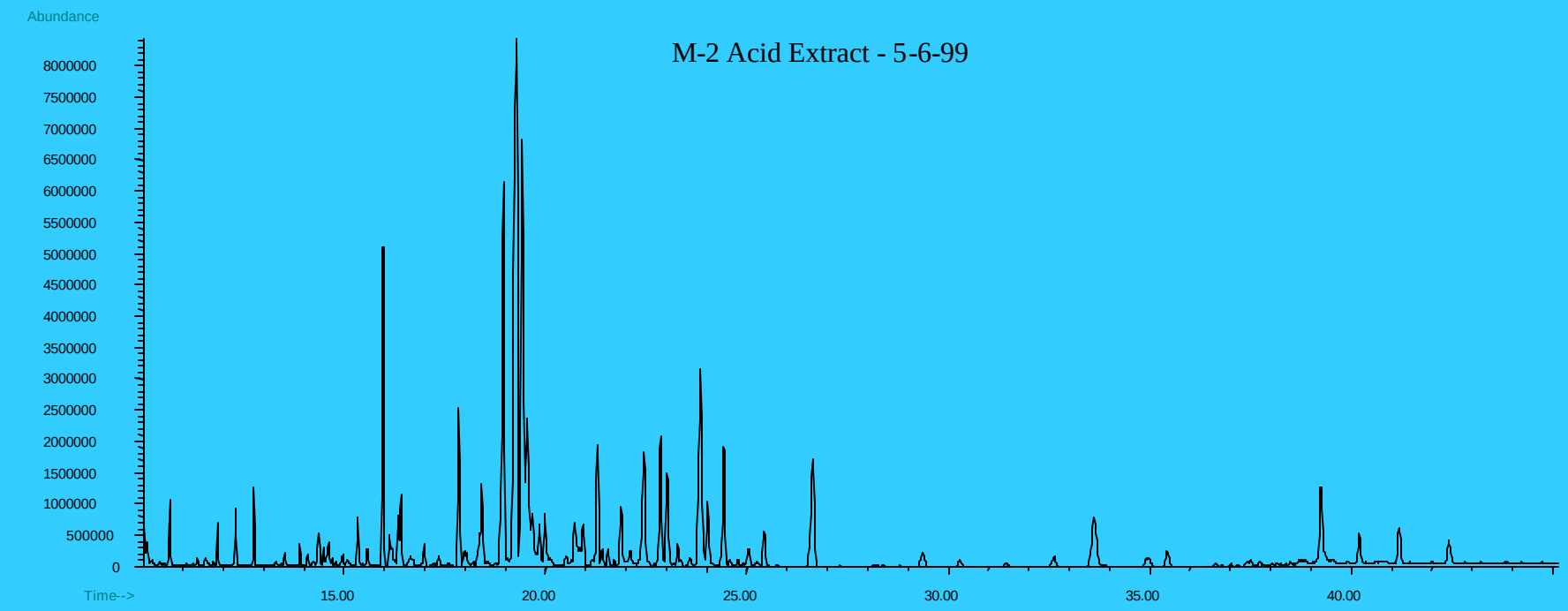
GC/MSD

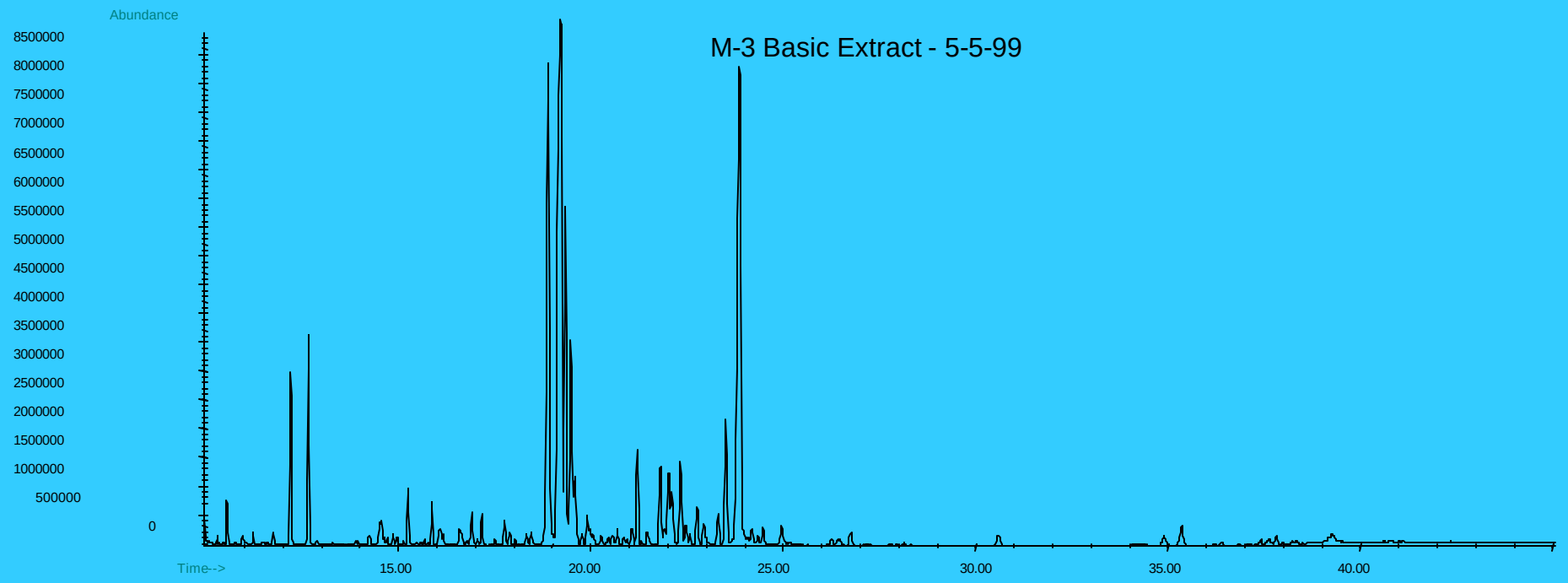
- The first portion of chromatogram is discarded
- Recording chromatogram after ephedrine
- Run is a 45 minute run
- Along with blank the turnaround time is approx. 1 hour

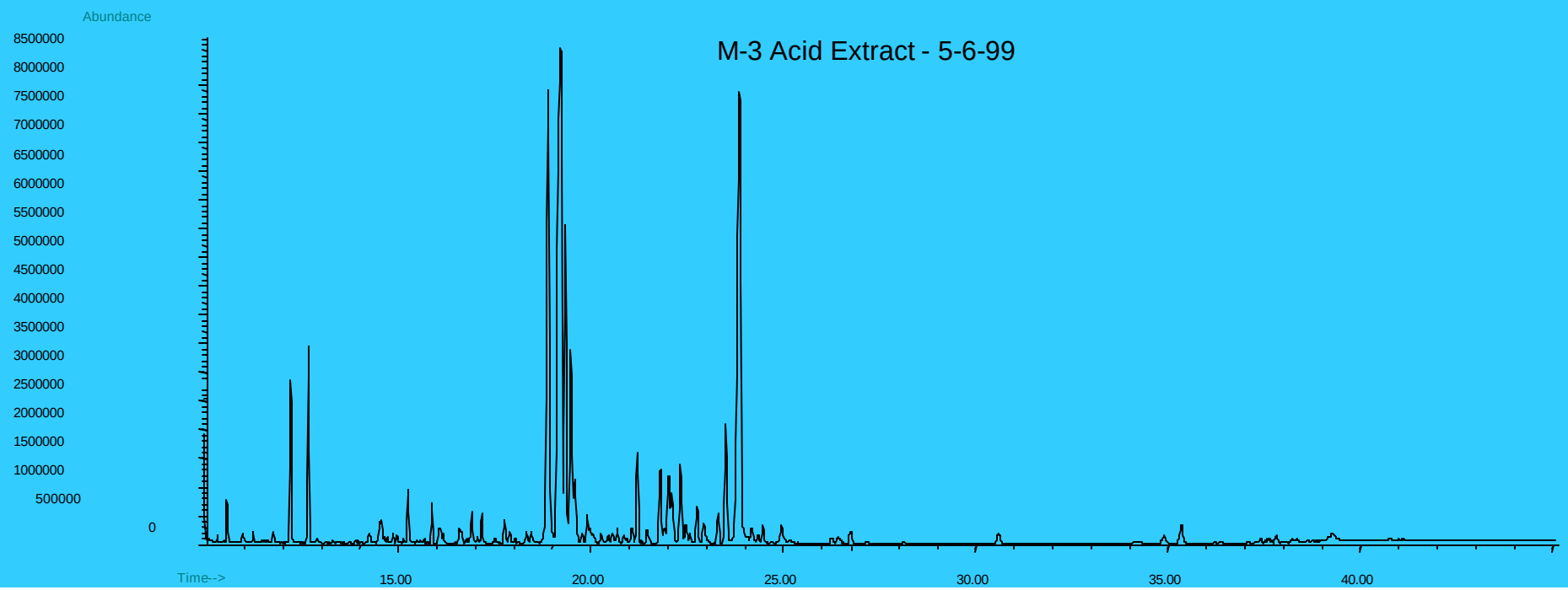

M-1 Base Extract 5-5-99
Abundance
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

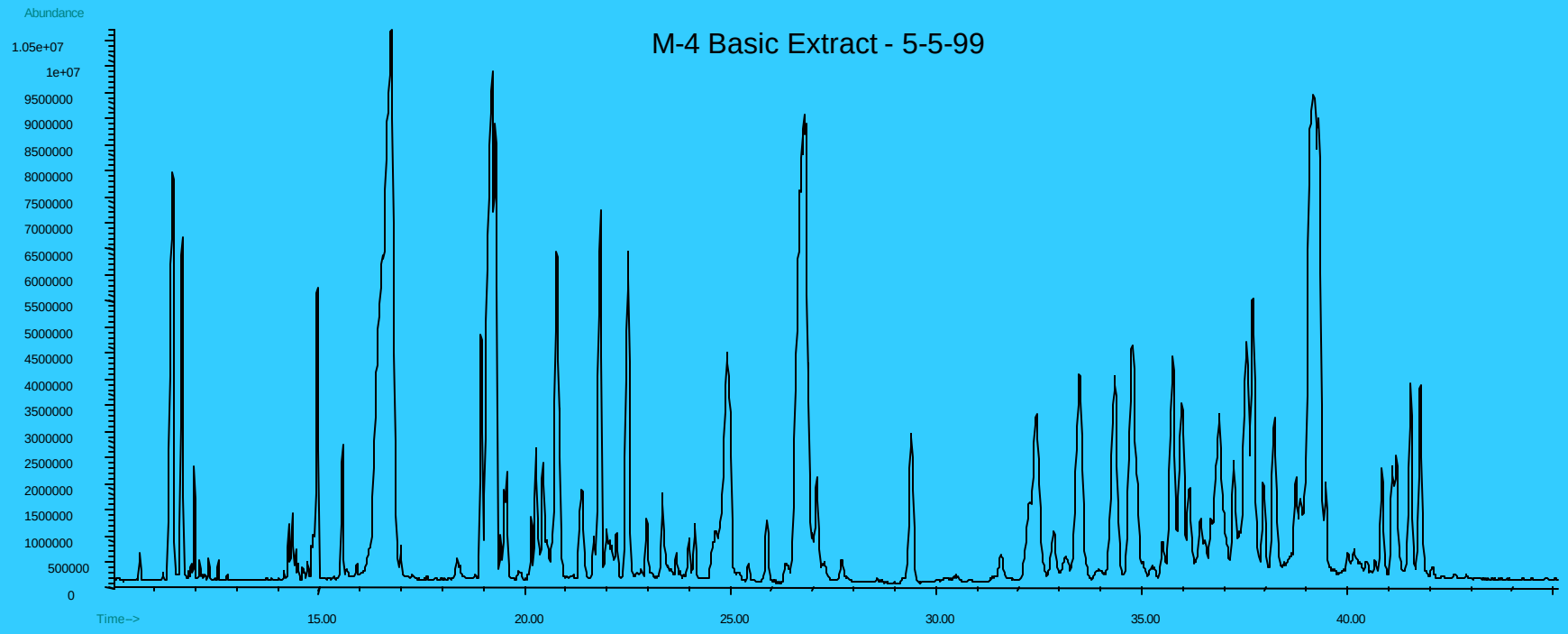

M-1 Acid Extract 5-6-99
Abundance
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

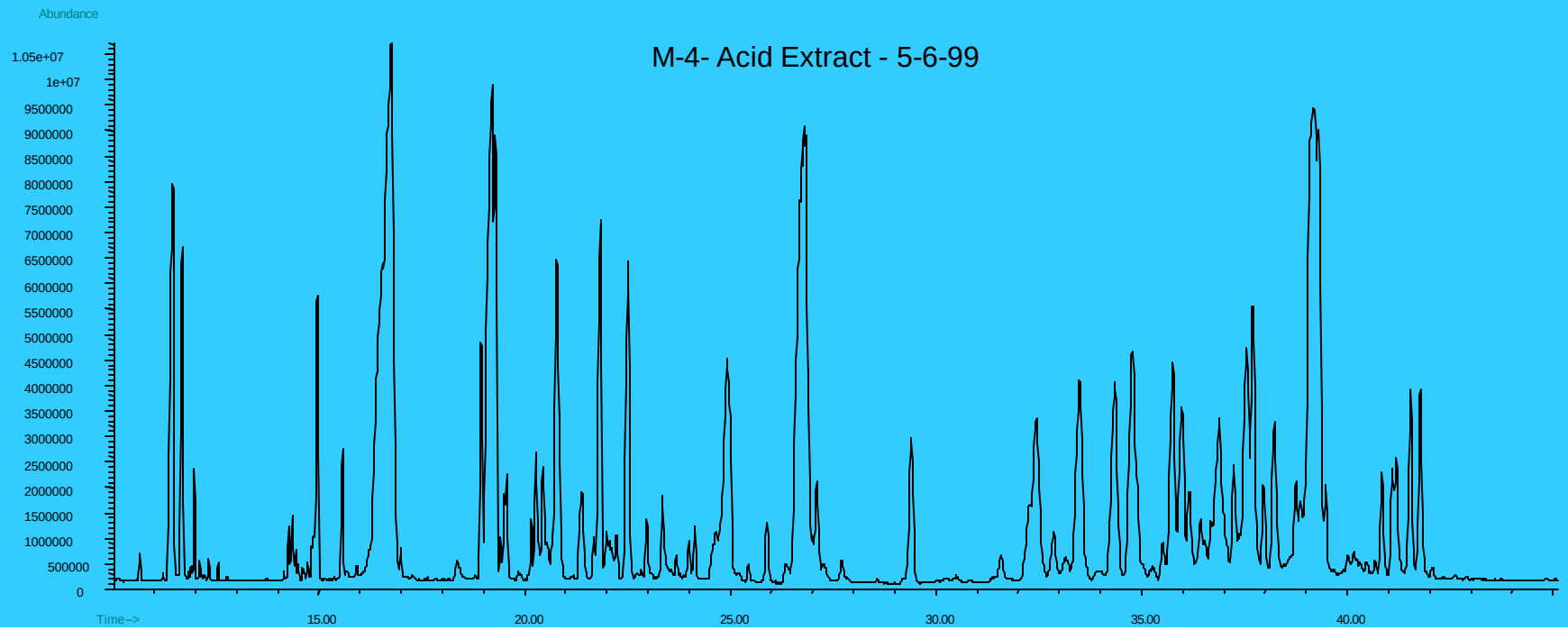

M-2 Basic Extract - 5-5-99
Abundance
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

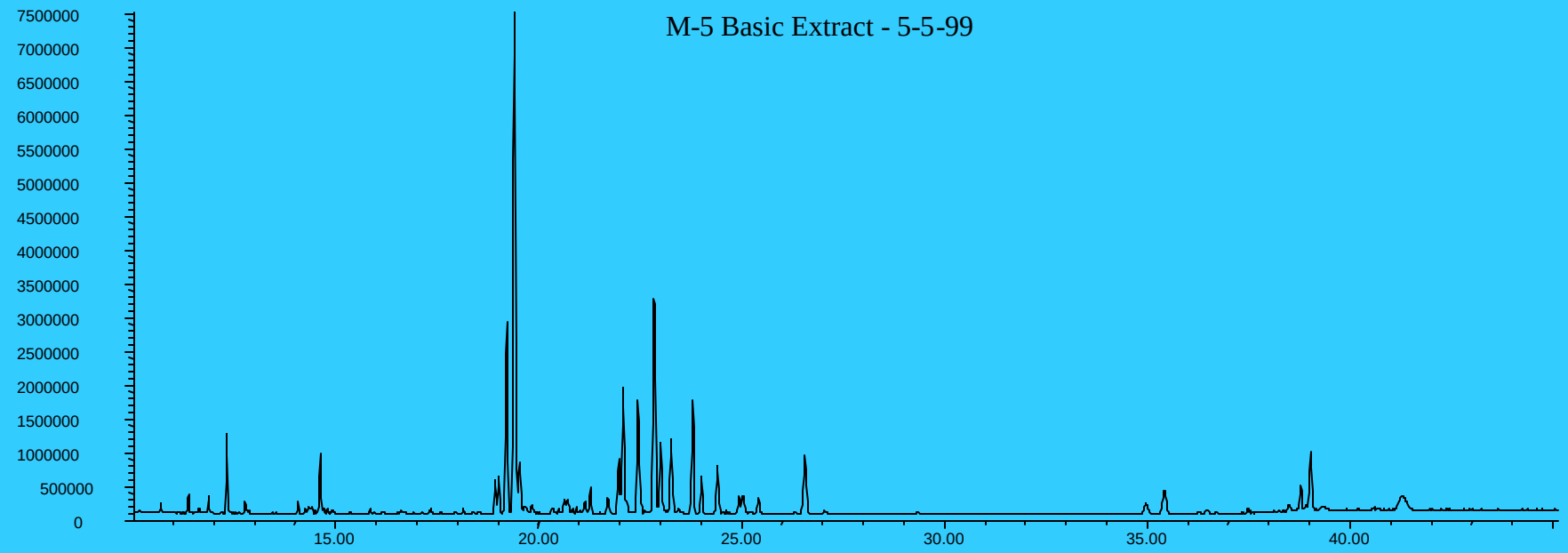

M-2 Acid Extract - 5-6-99
Abundance
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00


M-3 Basic Extract - 5-5-99
Abundance
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

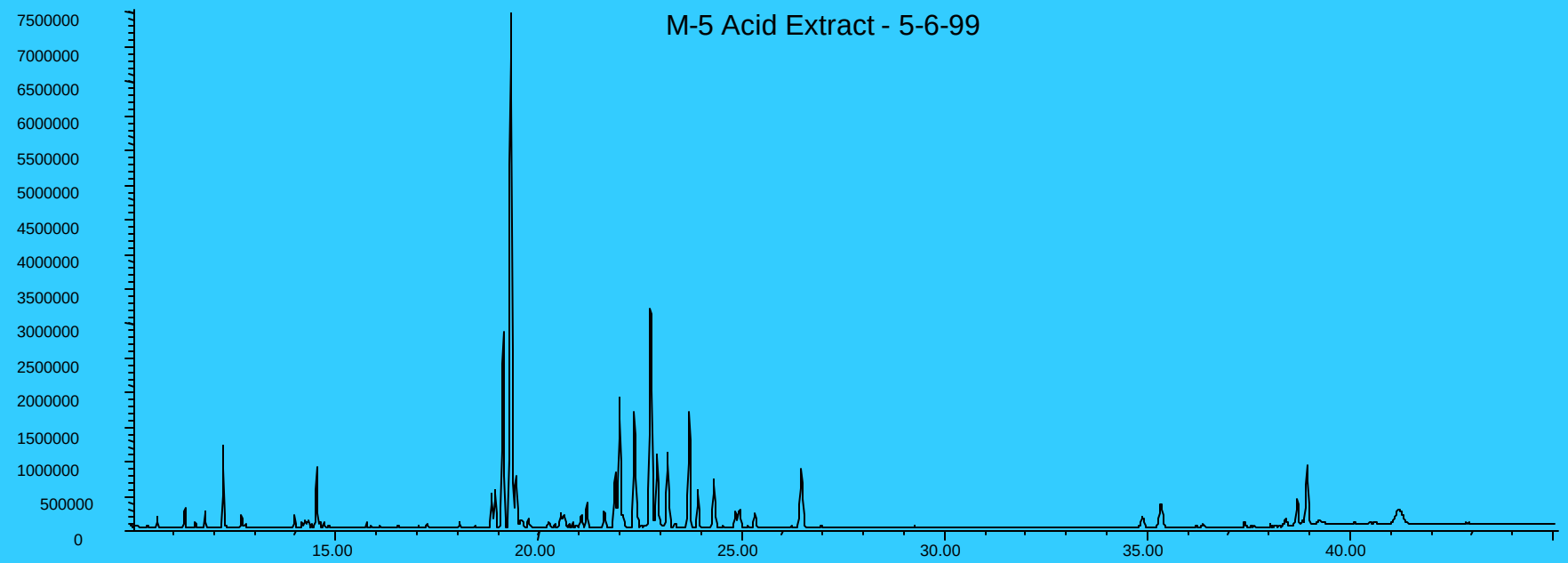

M-3 Acid Extract - 5-6-99
Abundance
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00


M-4 Basic Extract - 5-5-99
Abundance
1.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00


M-4- Acid Extract - 5-6-99
Abundance
1.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

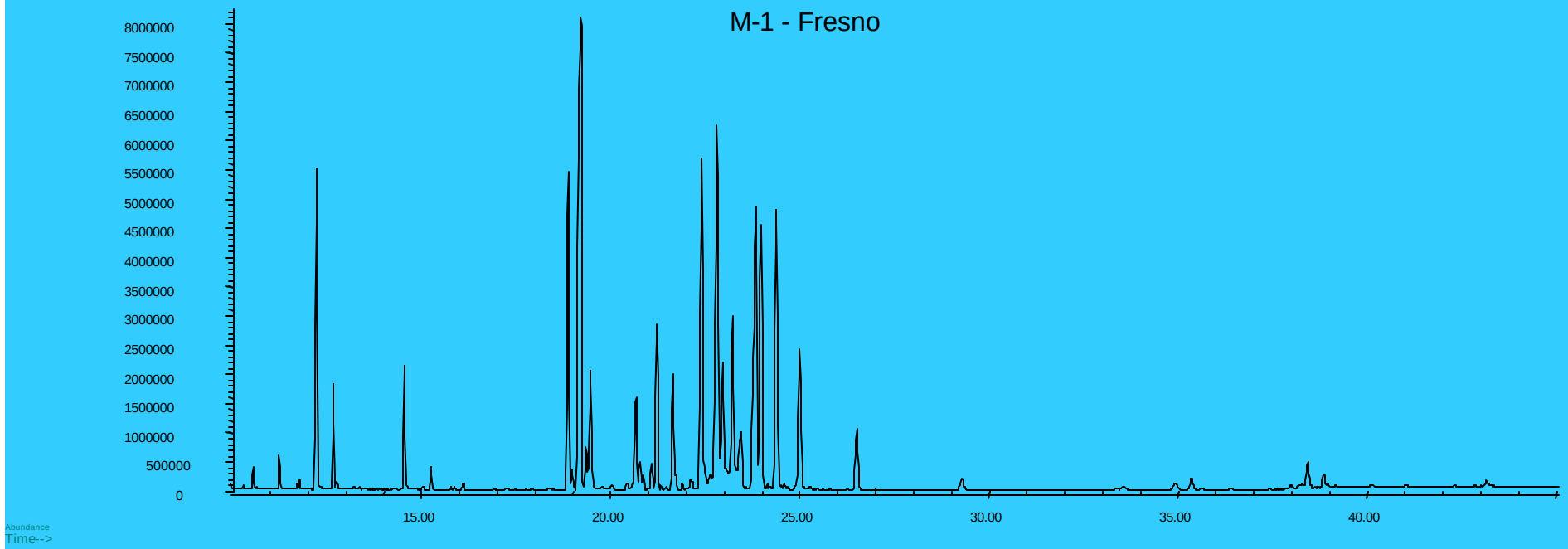


Abundance
Time-->



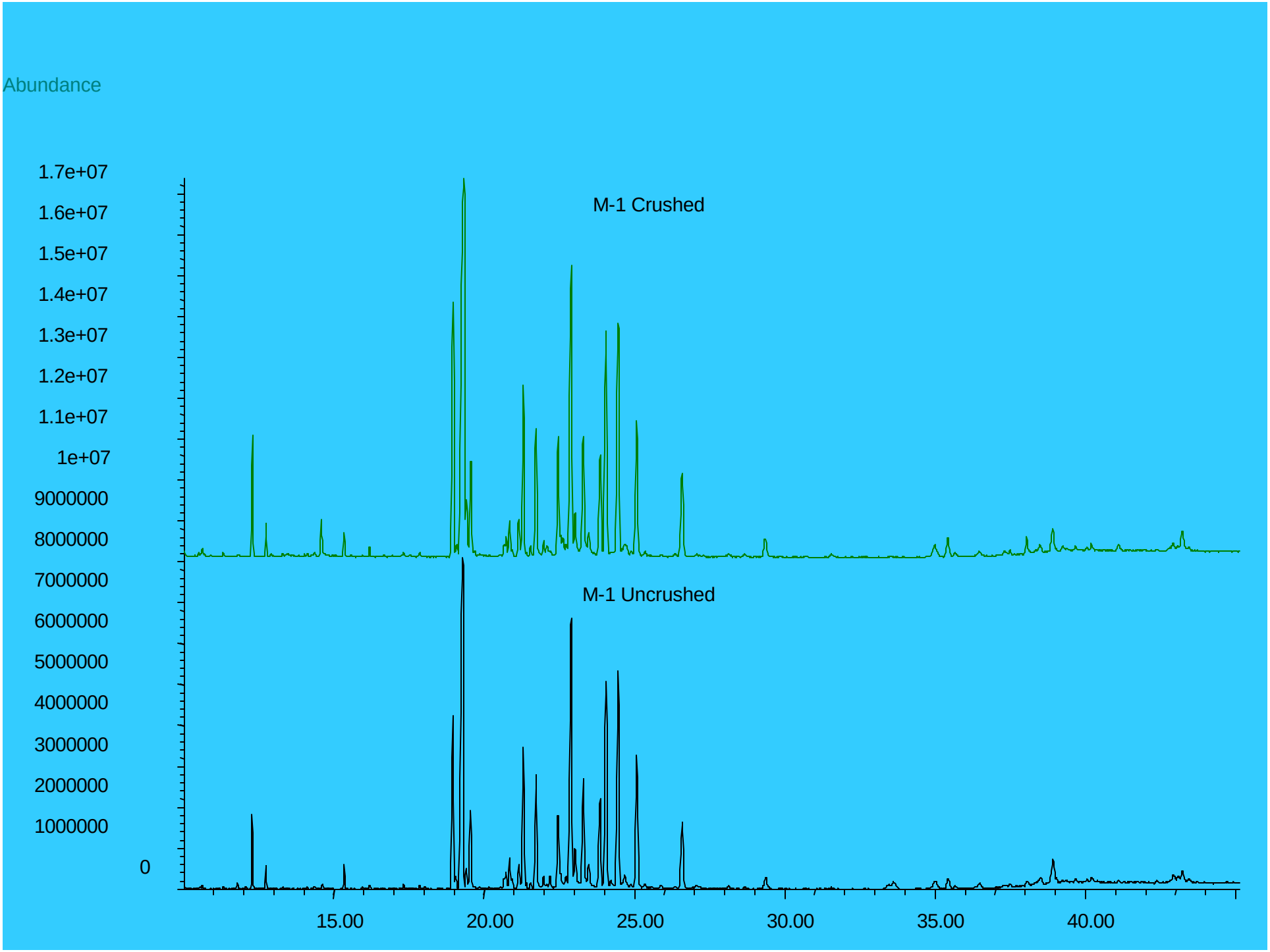
Interlaboratory Comparisons

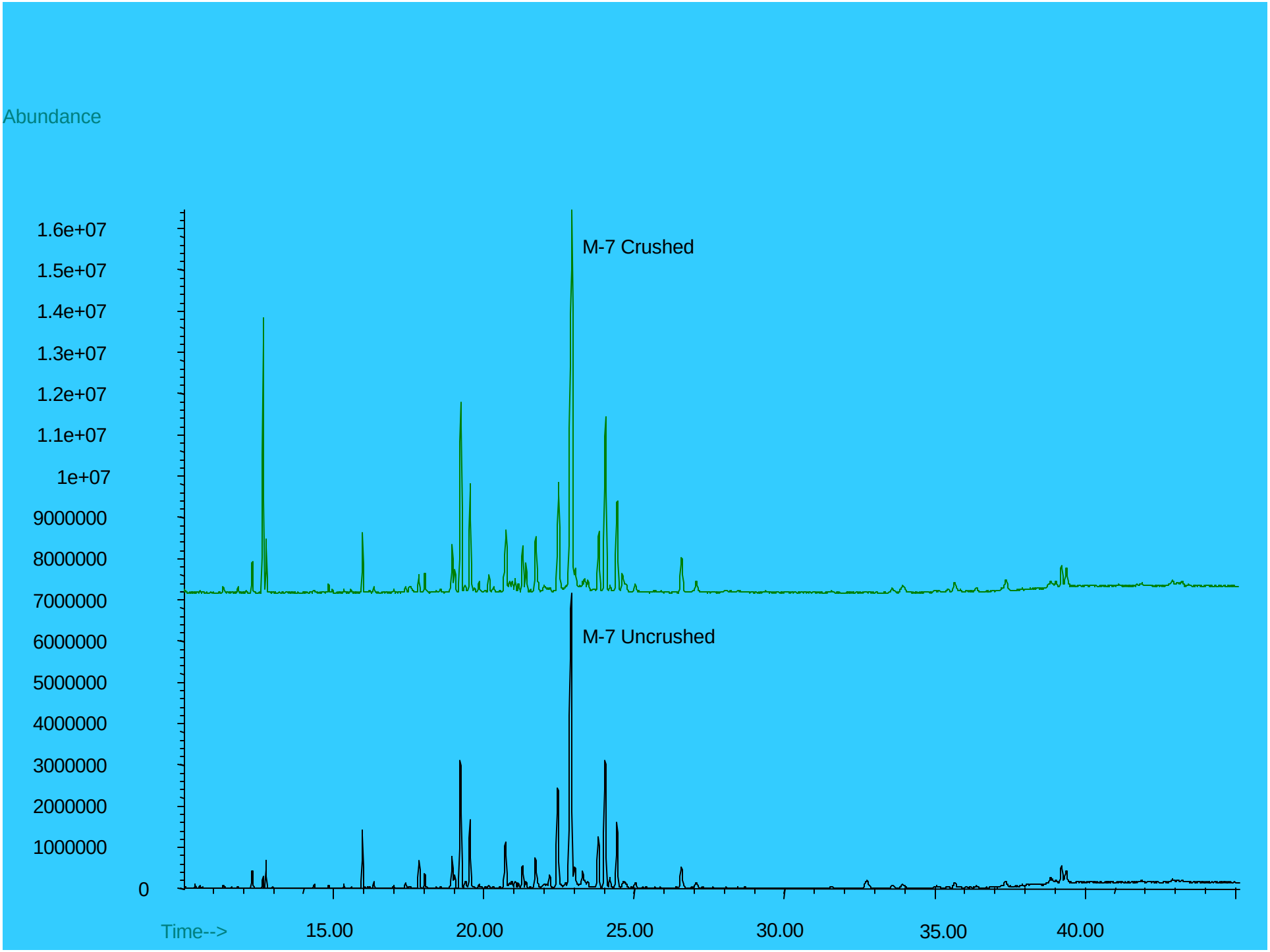
- We have tested some cases between Riverside and Fresno


M-1 - Fresno
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
15.00
20.00
25.00
30.00
35.00
40.00
Abundance
Time-->
M-1-Riverside
1.3e+07
1.25e+07
1.2e+07
1.15e+07
1.1e+07
1.05e+07
1e+07
9500000
9000000
8500000
8000000
7500000
7000000
6500000
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
15.00
20.00
25.00
30.00
35.00
40.00

Sample Preparation

- Looked at crushed versus uncrushed


Abundance
1.7e+07
1.6e+07
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
M-1 Crushed
M-1 Uncrushed
15.00
20.00
25.00
30.00
35.00
40.00


Abundance
1.6e+07
1.5e+07
1.4e+07
1.3e+07
1.2e+07
1.1e+07
1e+07
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
M-7 Crushed
M-7 Uncrushed
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

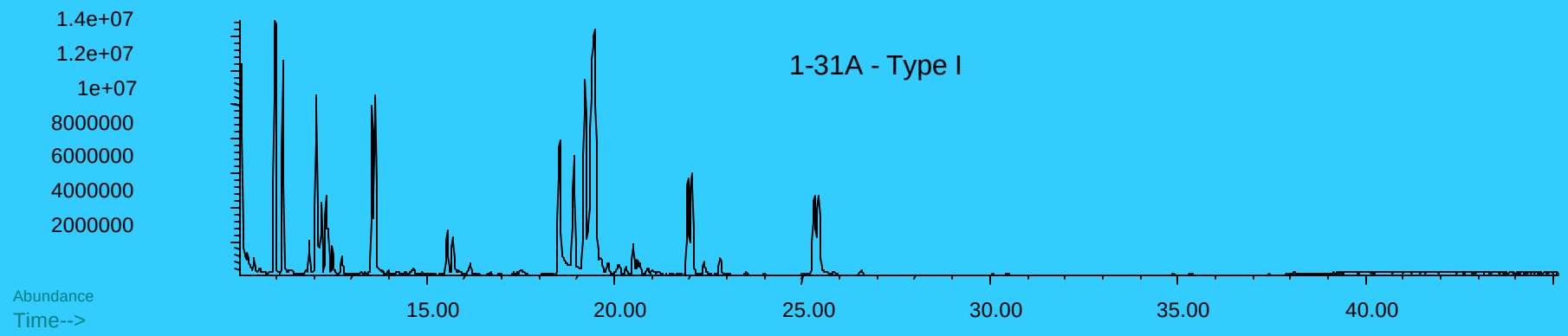
Comparison

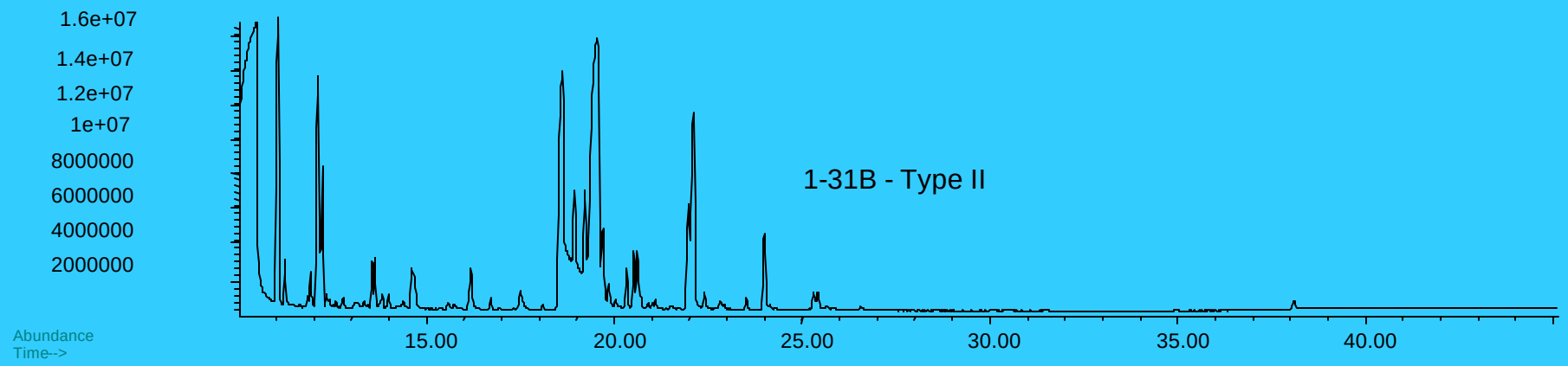
- At this time the chromatogram comparisons are by visual examination
- Developing automated comparison tools

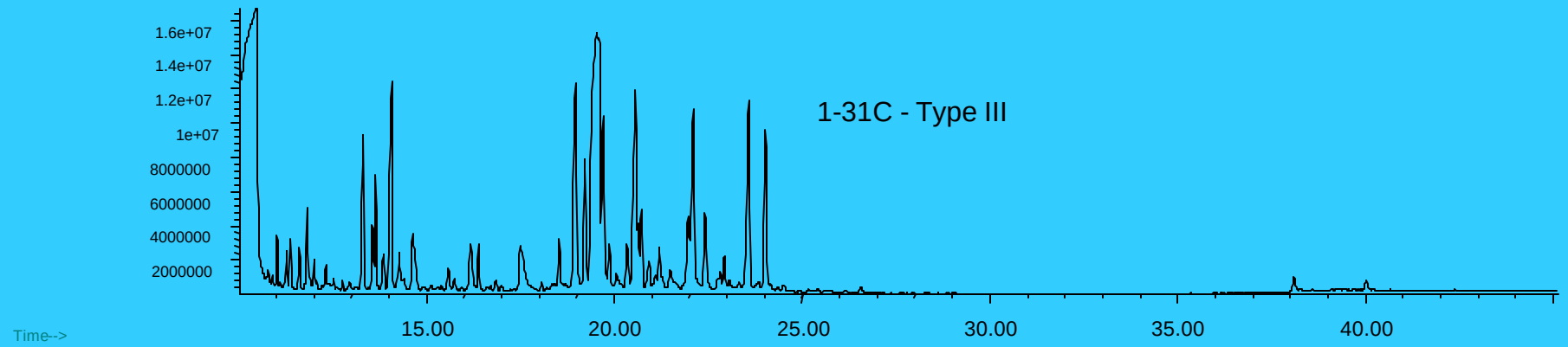
FR-99-000868

- From one lab site in Kings Co.
- 20 lbs of Methamphetamine in 18 packages
- Analyzed all 18 packages
- 3 heating mantles and 2 flasks at the scene

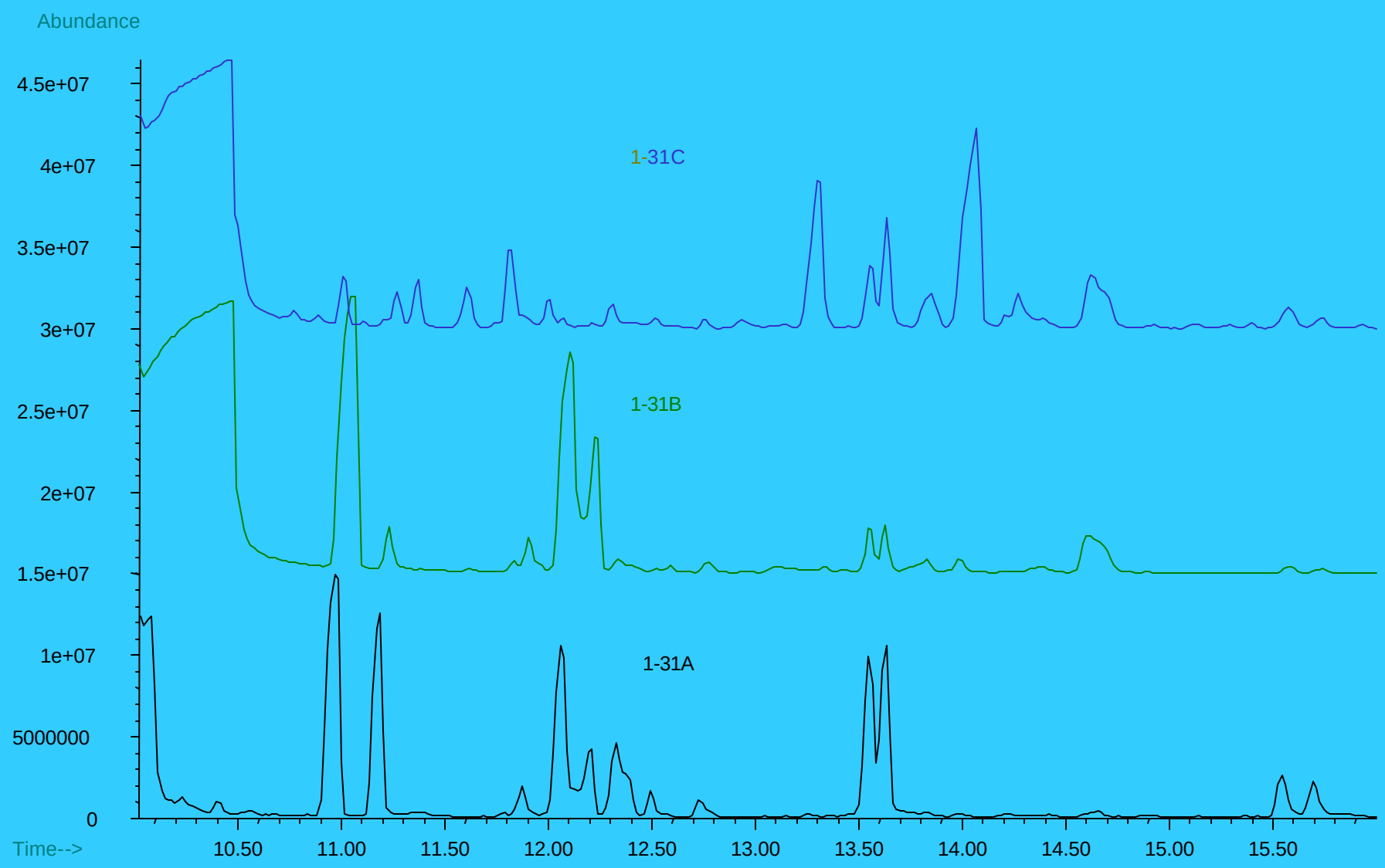
FR-99-000868


Abundance
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
1-31A - Type I
Abundance
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

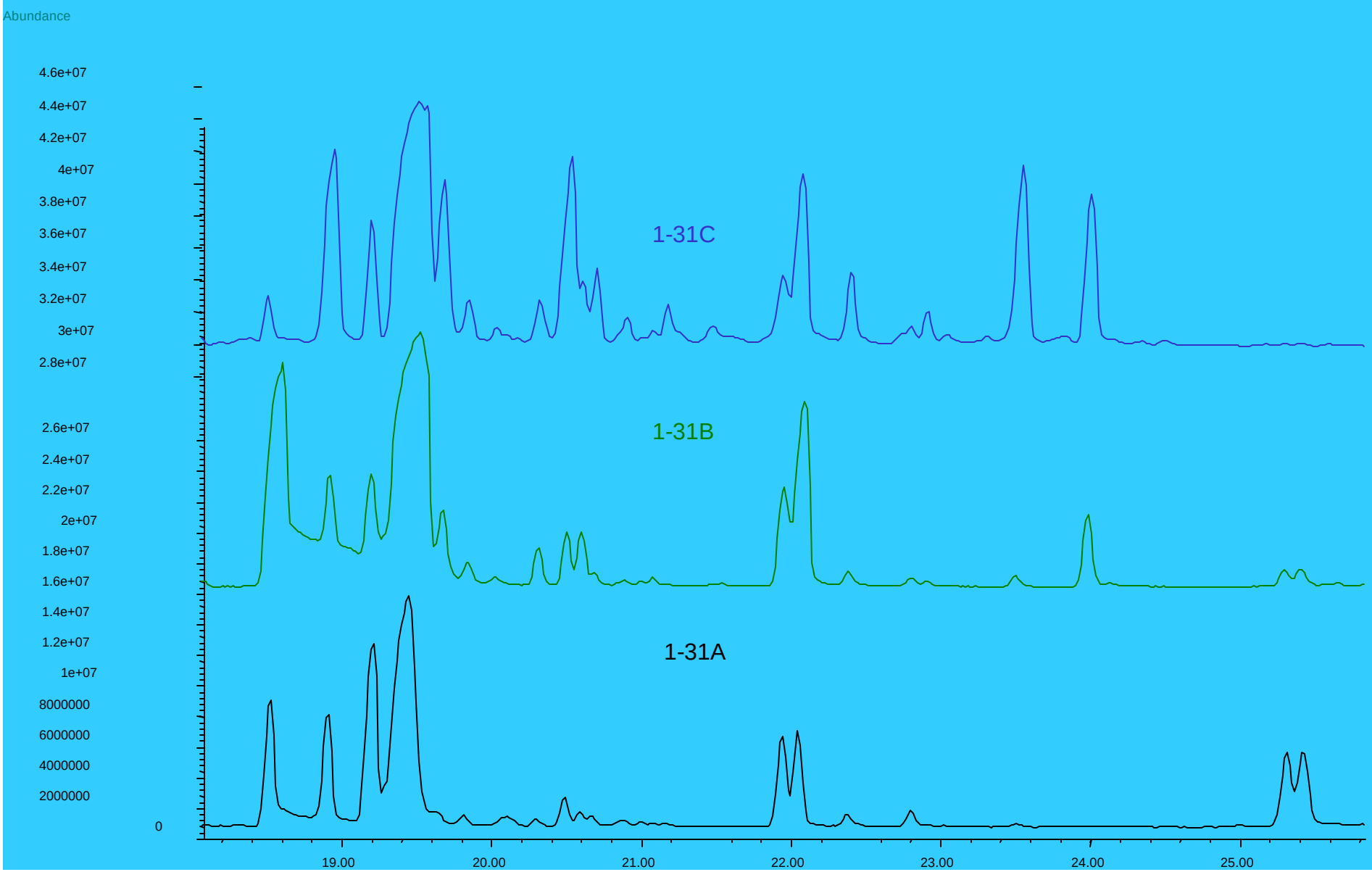

1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
1-31B - Type II
Abundance
Time-->
15.00
20.00
25.00
30.00
35.00
40.00


1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
1-31C - Type III
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

FR-99-000868

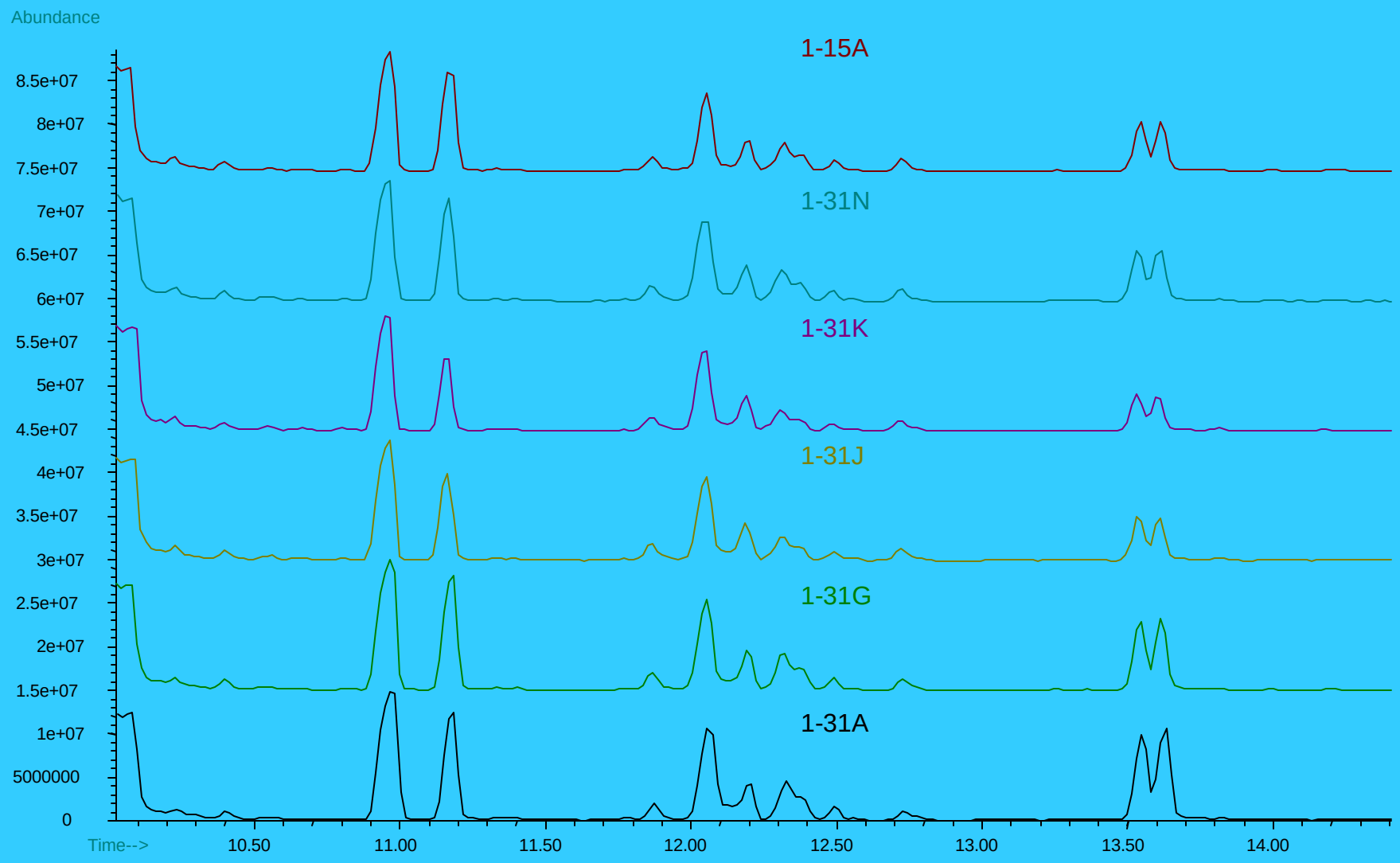

Abundance
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
Time-->
10.50
11.00
11.50
12.00
12.50
13.00
13.50
14.00
14.50
15.00
15.50
1-31C
1-31B
1-31A

FR-99-000868

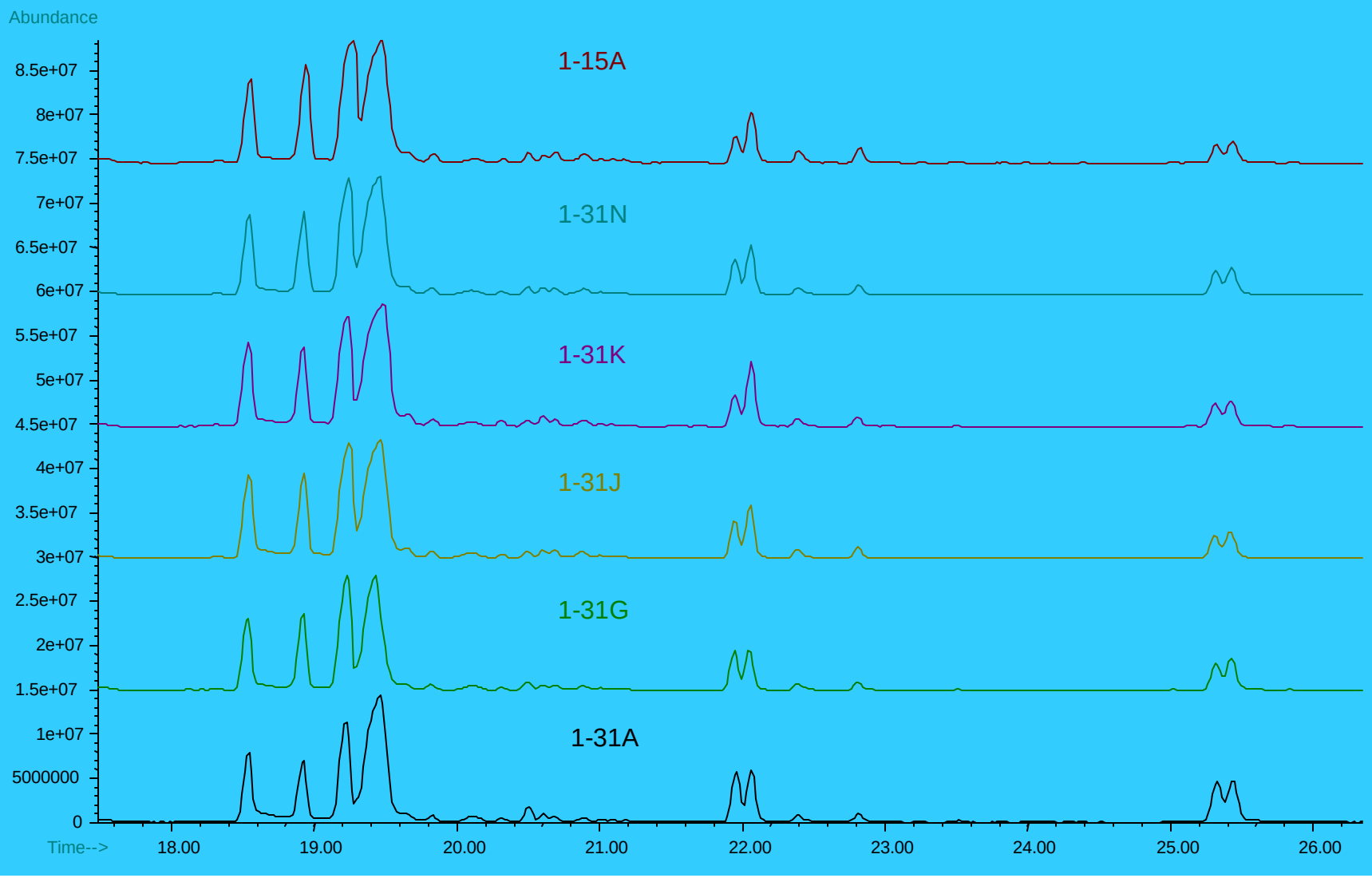

Abundance
4.6e+07
4.4e+07
4.2e+07
4e+07
3.8e+07
3.6e+07
3.4e+07
3.2e+07
3e+07
2.8e+07
2.6e+07
2.4e+07
2.2e+07
2e+07
1.8e+07
1.6e+07
1.4e+07
1.2e+07
1e+07
8000000
6000000
4000000
2000000
0
1-31C
1-31B
1-31A
19.00
20.00
21.00
22.00
23.00
24.00
25.00

Type I

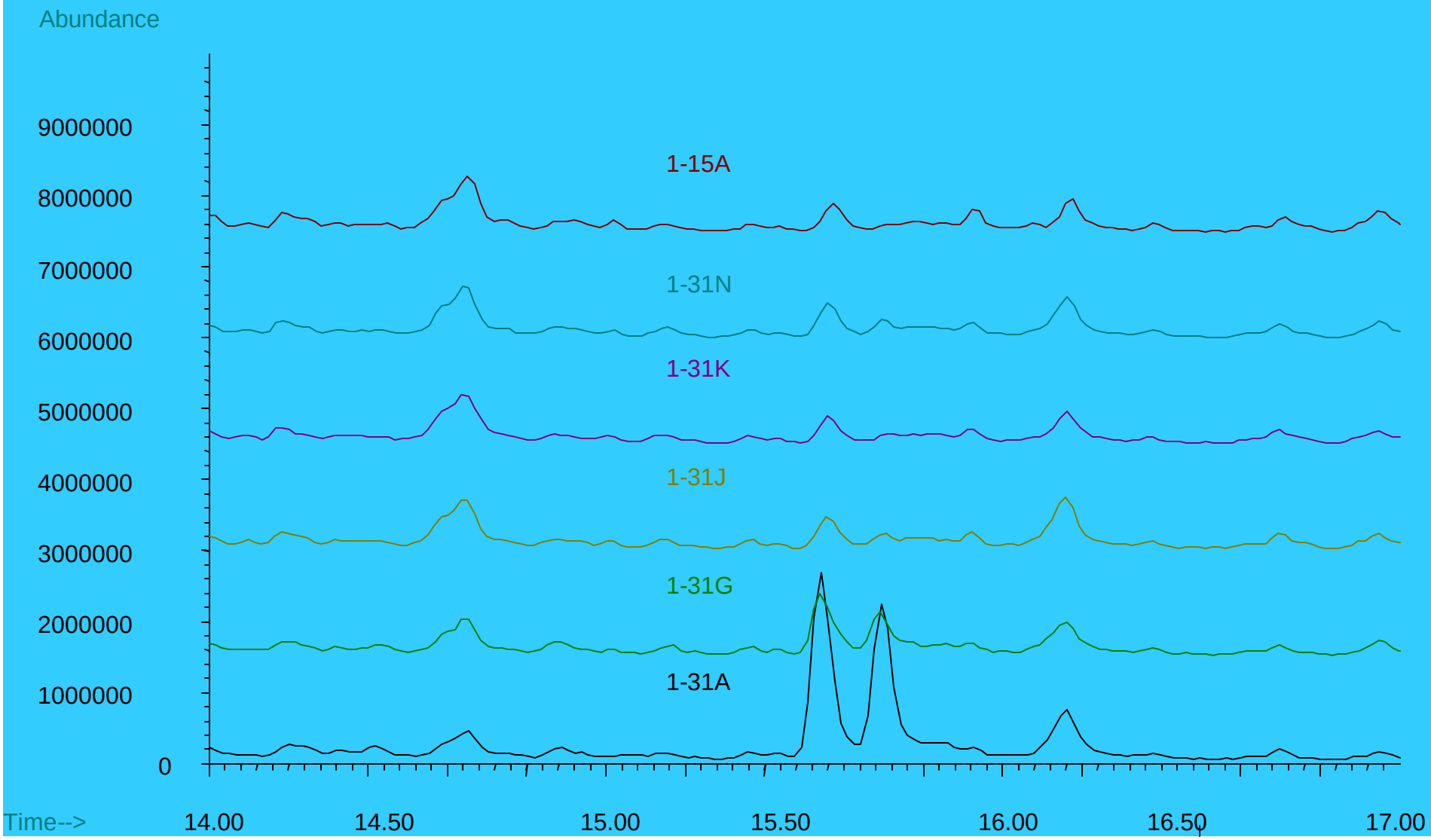
FR-99-000868


Abundance
1-15A
1-31N
1-31K
1-31J
1-31G
1-31A
8.5e+07
8e+07
7.5e+07
7e+07
6.5e+07
6e+07
5.5e+07
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
Time-->
10.50
11.00
11.50
12.00
12.50
13.00
13.50
14.00

FR-99-000868

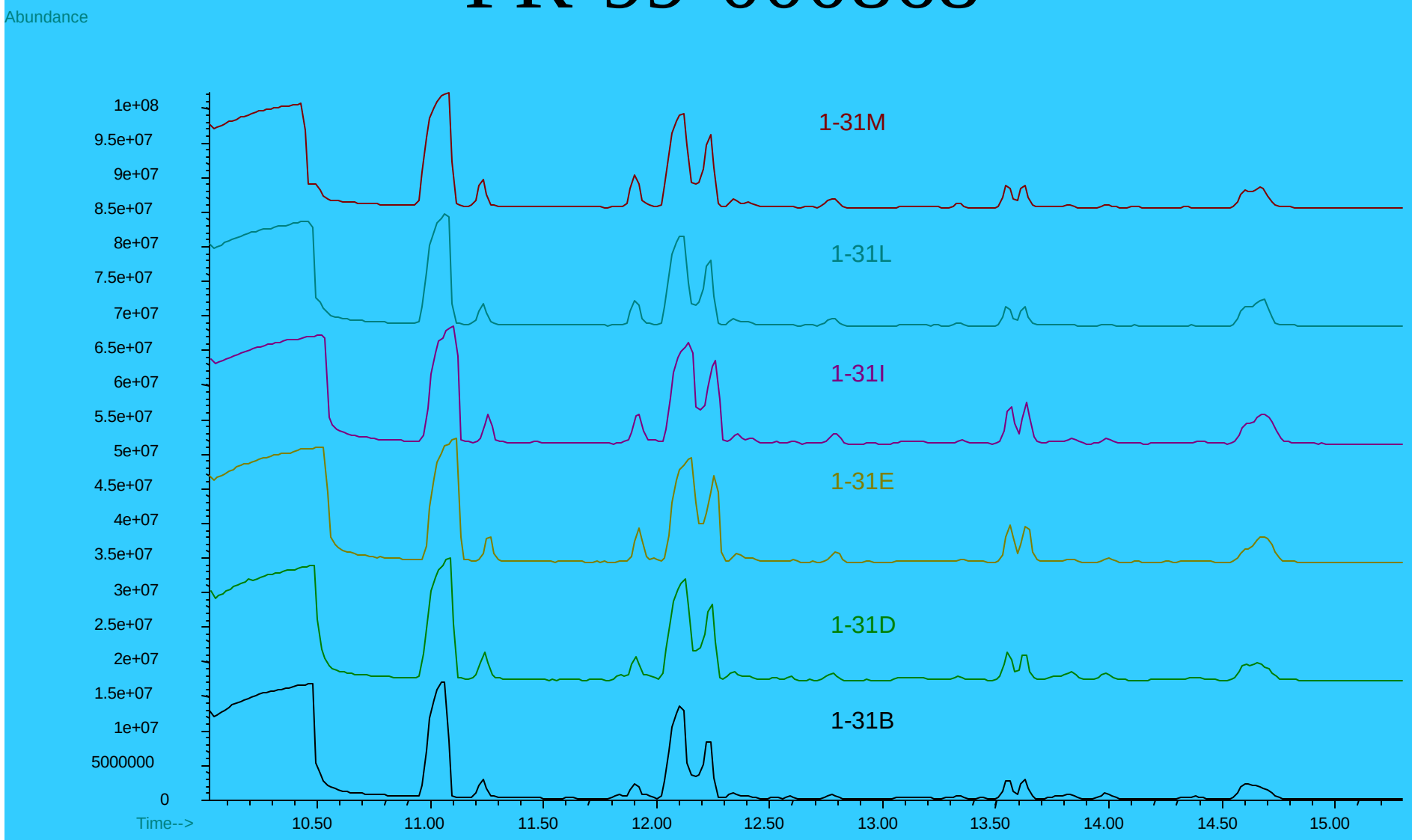

Abundance
8.5e+07
8e+07
7.5e+07
7e+07
6.5e+07
6e+07
5.5e+07
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
Time-->
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
1-15A
1-31N
1-31K
1-31J
1-31G
1-31A

FR-99-000868

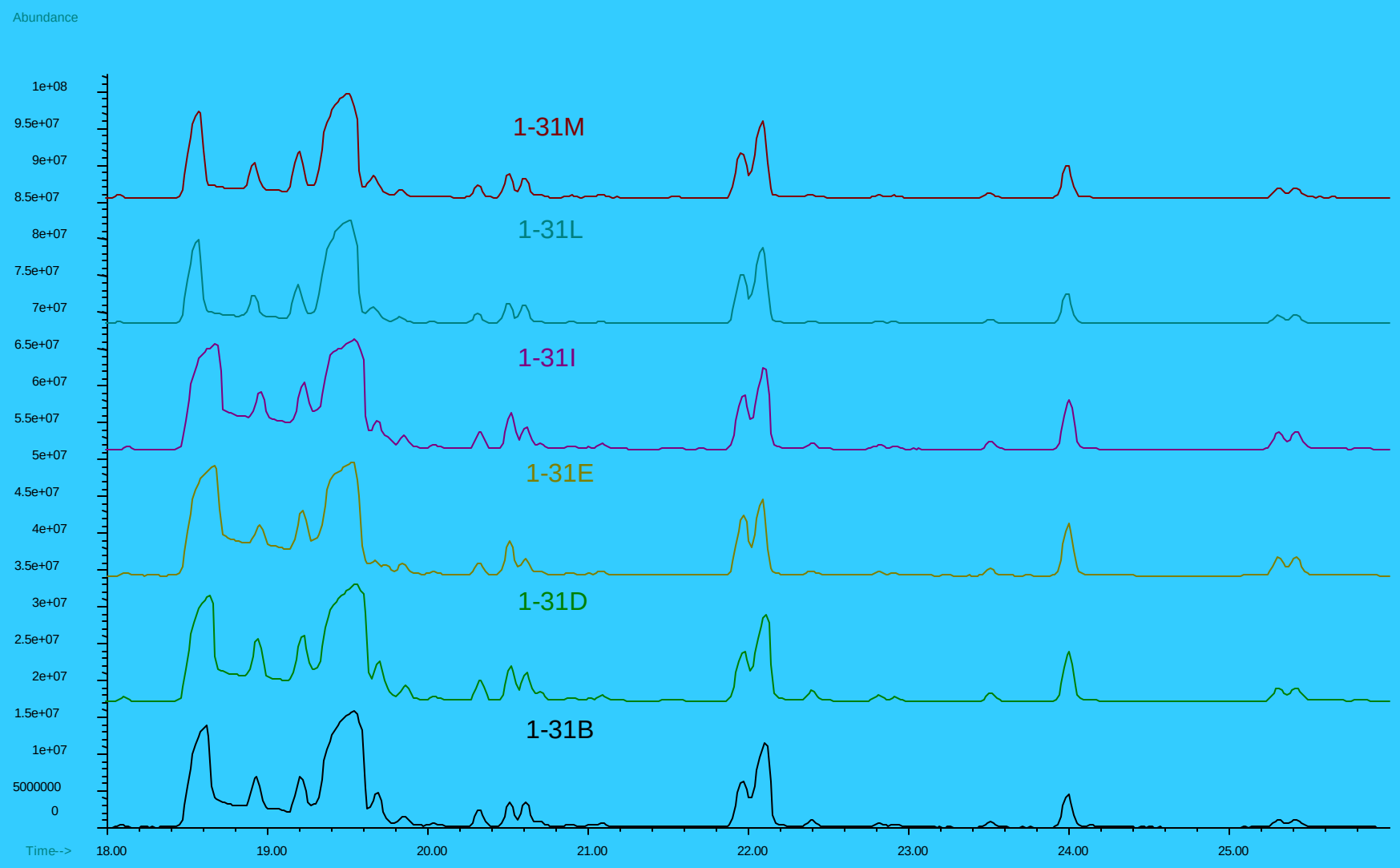

Abundance
9000000
8000000
7000000
6000000
5000000
4000000
3000000
2000000
1000000
0
1-15A
1-31N
1-31K
1-31J
1-31G
1-31A
Time-->
14.00
14.50
15.00
15.50
16.00
16.50
17.00

Type II

FR-99-000868


Abundance
1e+08
9.5e+07
9e+07
8.5e+07
8e+07
7.5e+07
7e+07
6.5e+07
6e+07
5.5e+07
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
Time-->
10.50
11.00
11.50
12.00
12.50
13.00
13.50
14.00
14.50
15.00
1-31M
1-31L
1-31I
1-31E
1-31D
1-31B

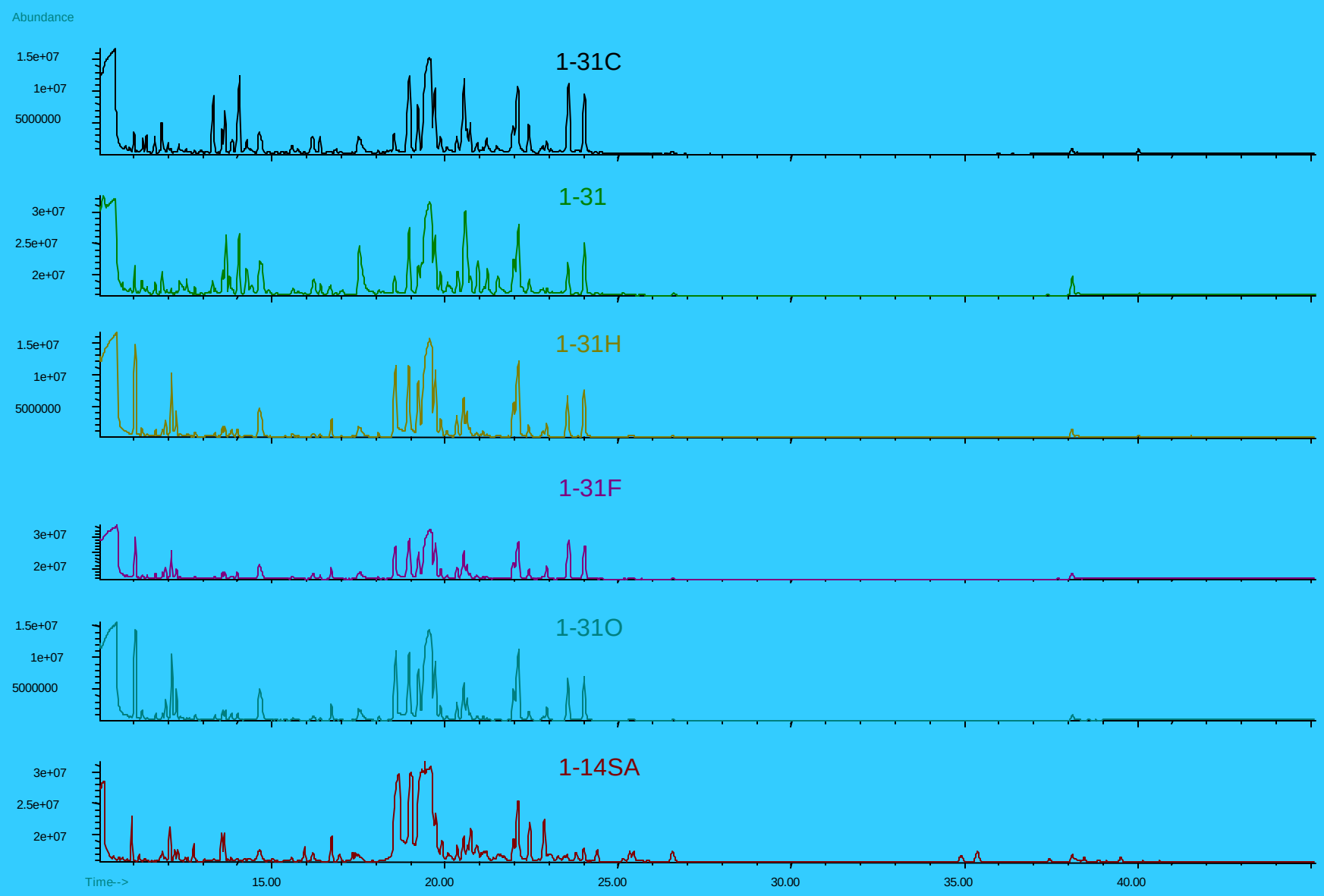
FR-99-000868


Abundance
1e+08
9.5e+07
9e+07
8.5e+07
8e+07
7.5e+07
7e+07
6.5e+07
6e+07
5.5e+07
5e+07
4.5e+07
4e+07
3.5e+07
3e+07
2.5e+07
2e+07
1.5e+07
1e+07
5000000
0
1-31M
1-31L
1-31I
1-31E
1-31D
1-31B
Time-->
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00

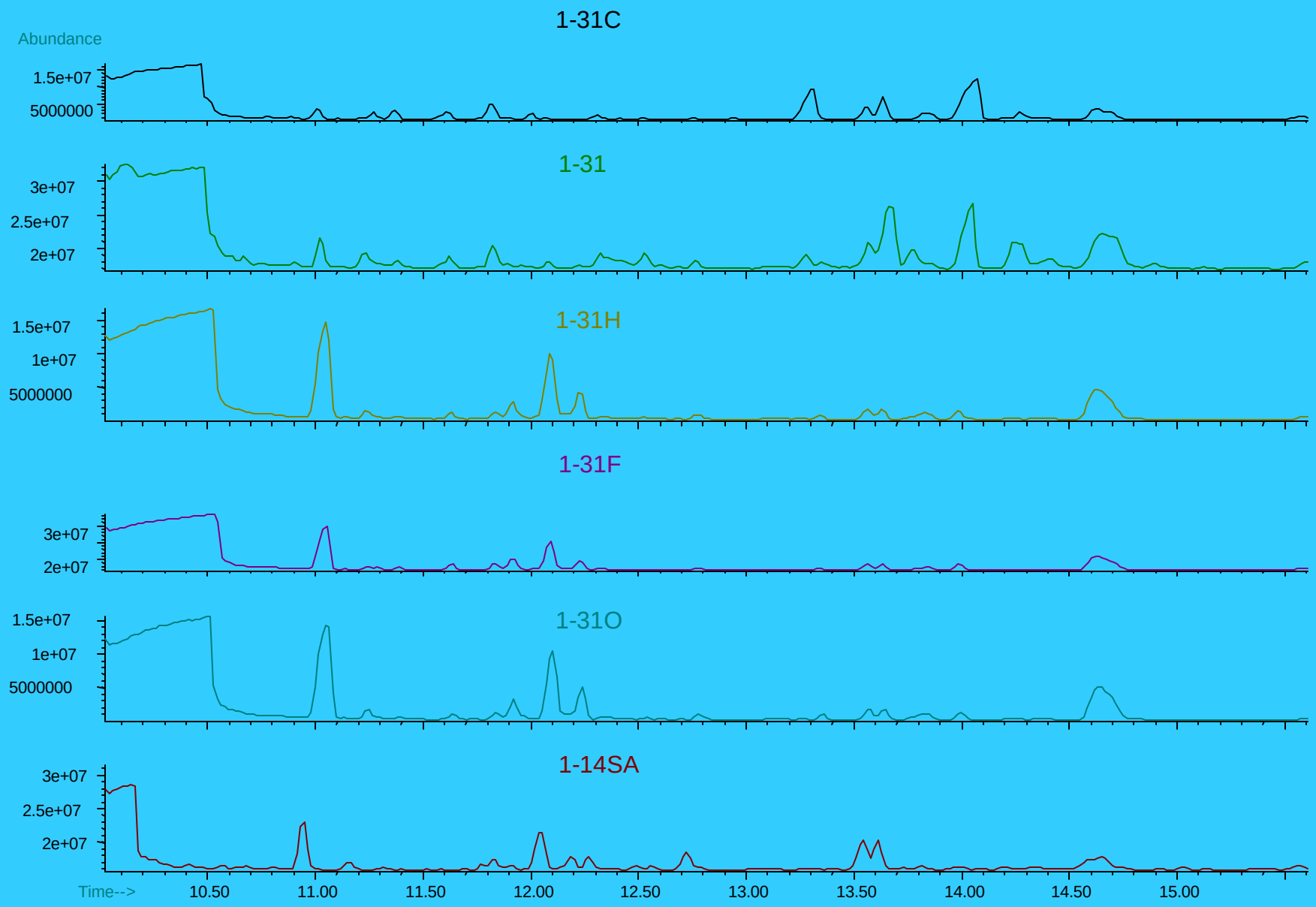
Type III

- Most variable
- Forms 3 subgroups of two each

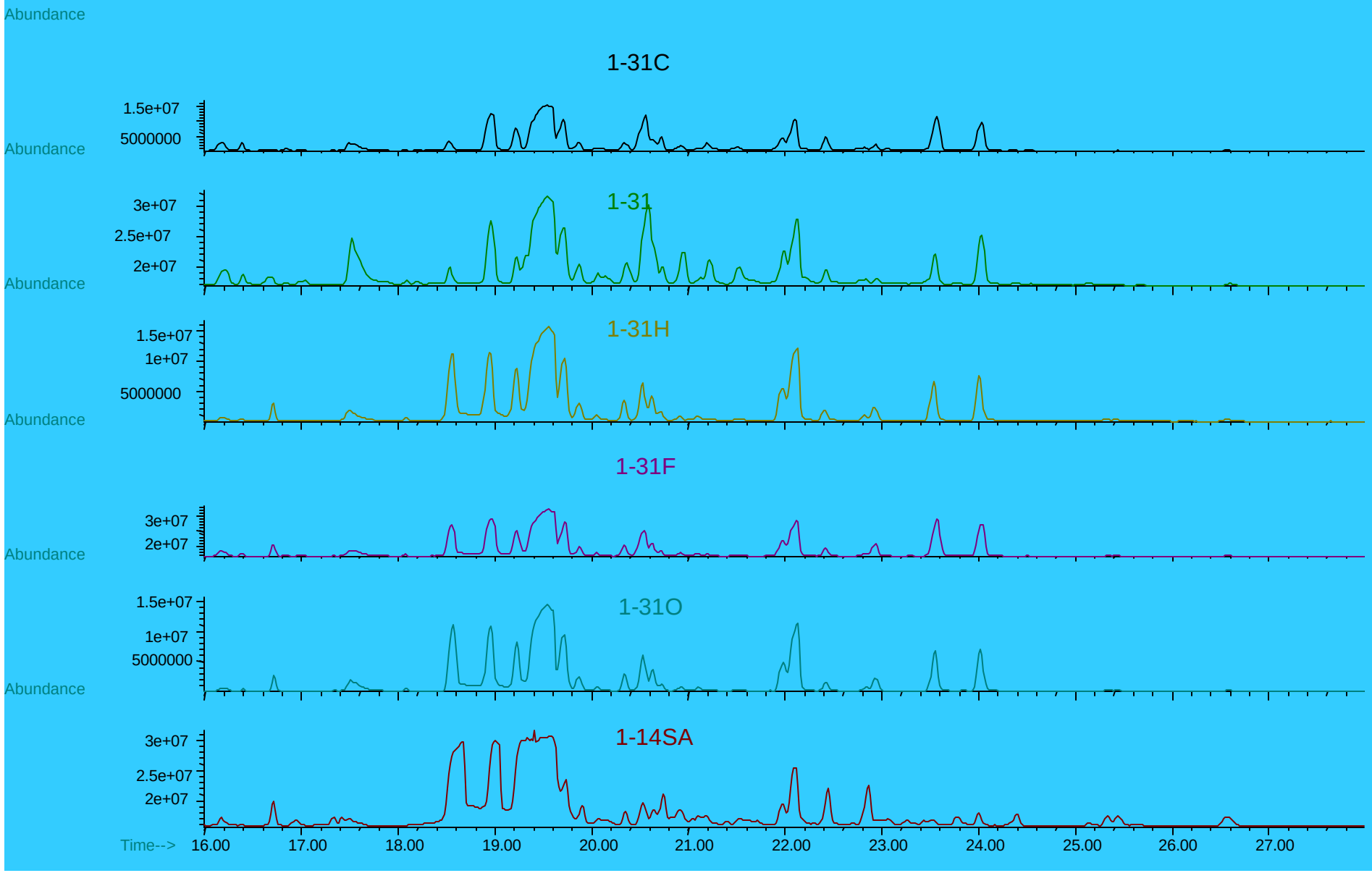
FR-99-000868


Abundance
1-31C
1.5e+07
1e+07
5000000
1-31
3e+07
2.5e+07
2e+07
1-31H
1.5e+07
1e+07
5000000
1-31F
3e+07
2e+07
1-31O
1.5e+07
1e+07
5000000
1-14SA
3e+07
2.5e+07
2e+07
Time-->
15.00
20.00
25.00
30.00
35.00
40.00

FR-99-000868


1-31C
Abundance
1.5e+07
5000000
1-31
3e+07
2.5e+07
2e+07
1-31H
1.5e+07
1e+07
5000000
1-31F
3e+07
2e+07
1-31O
1.5e+07
1e+07
5000000
1-14SA
3e+07
2.5e+07
2e+07
Time-->
10.50
11.00
11.50
12.00
12.50
13.00
13.50
14.00
14.50
15.00

FR-99-000868


Abundance
1-31C
1.5e+07
5000000
Abundance
1-31
3e+07
2.5e+07
2e+07
Abundance
1-31H
1.5e+07
1e+07
5000000
Abundance
1-31F
3e+07
2e+07
Abundance
1-31O
1.5e+07
1e+07
5000000
Abundance
1-14SA
3e+07
2.5e+07
2e+07
Time-->
16.00
17.00
18.00
19.00
20.00
21.00
22.00
23.00
24.00
25.00
26.00
27.00

Where we are

- The batches produced appear to be individual
- Need to look at the preparation procedures since crushing or grinding can change the chromatogram
- Extractions over time appear reproducible
- Quantitations are coming on line

Where we need to go

- We need to compare chromatograms across the three labs using the same extraction procedures
- We need to incorporate the chromatograms into the database

Summary

- This is a work in progress.
- Potential of setting up
  - Investigative trends
  - “Early warning system”
  - Index system
  - Sourcing capability

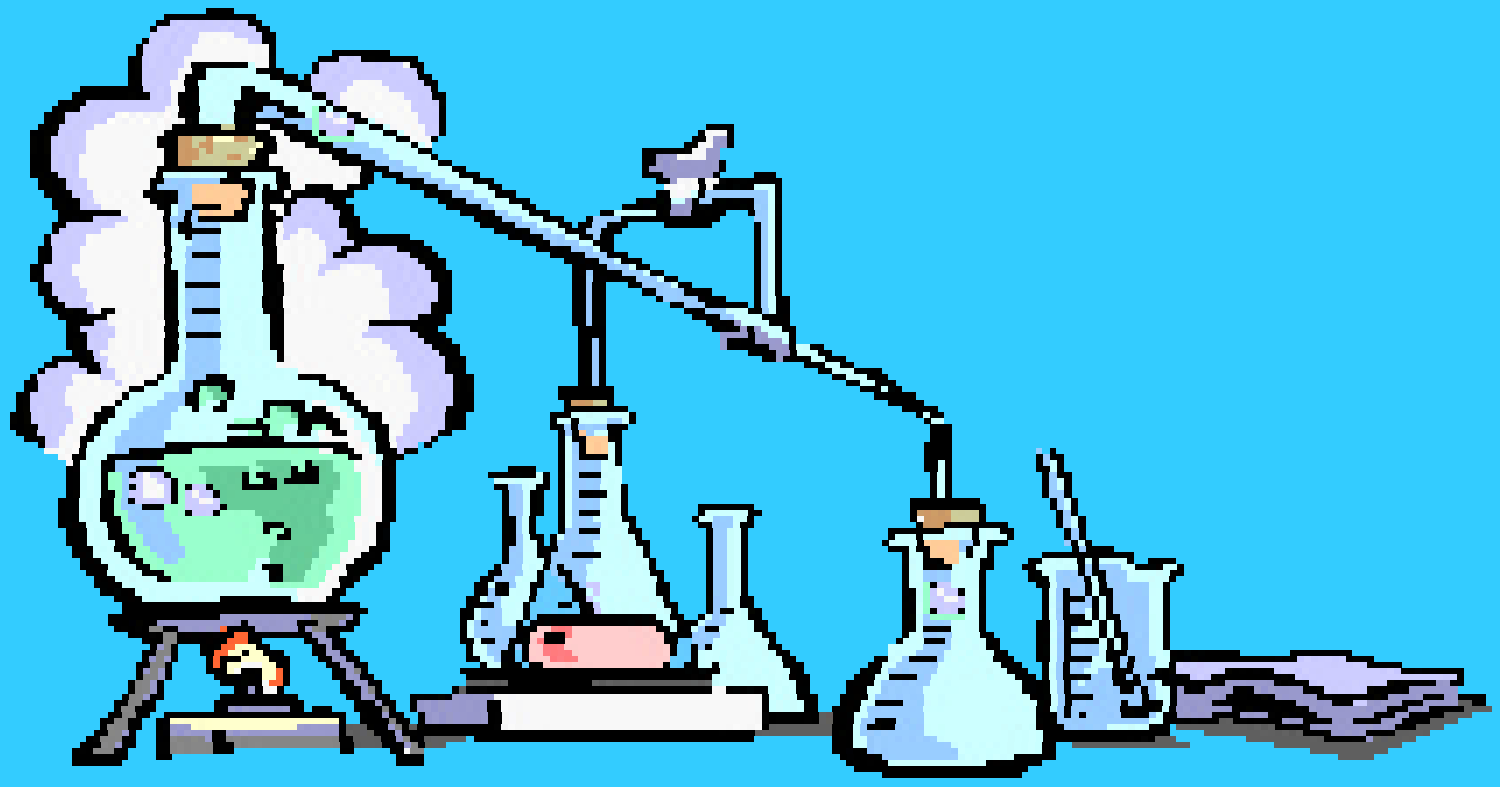
Summary

- Have accomplished placement of equipment into 3 BFS laboratories
- Have developed and compared quantitative methods using SIM
- Have improved cooperation between lab personnel and law enforcement

Acknowledgements

- Bureau of Forensic Services Group Effort

- G. Cortner, M. Vona, L. Melgoza,
  K. Ciula, M. Richardson, J. Yoshida,
  J. Jeffrey, K. Rager, J. Hamman,

Further Acknowledgements

- University of the Pacific
- Lawrence Livermore National Laboratory
- University of Utah