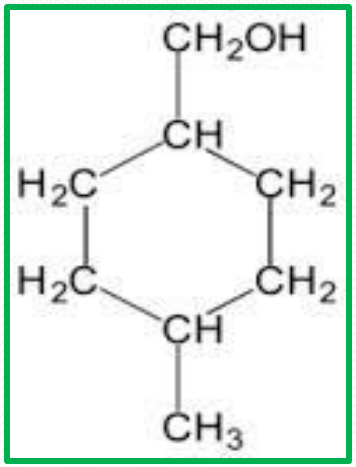
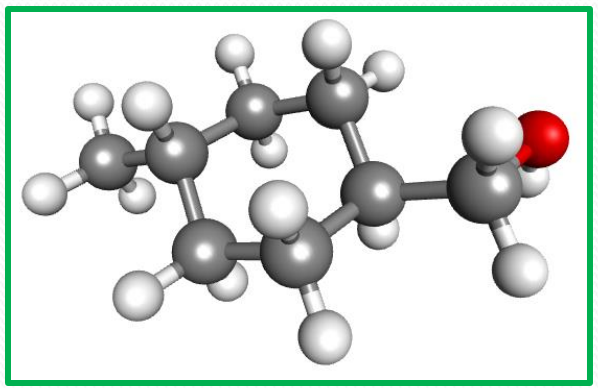
Analytical Method Development for MCHM Spill at Elk River (WV)



- May 15, 2014
- Niranjan Selar



GCWW in NBC News

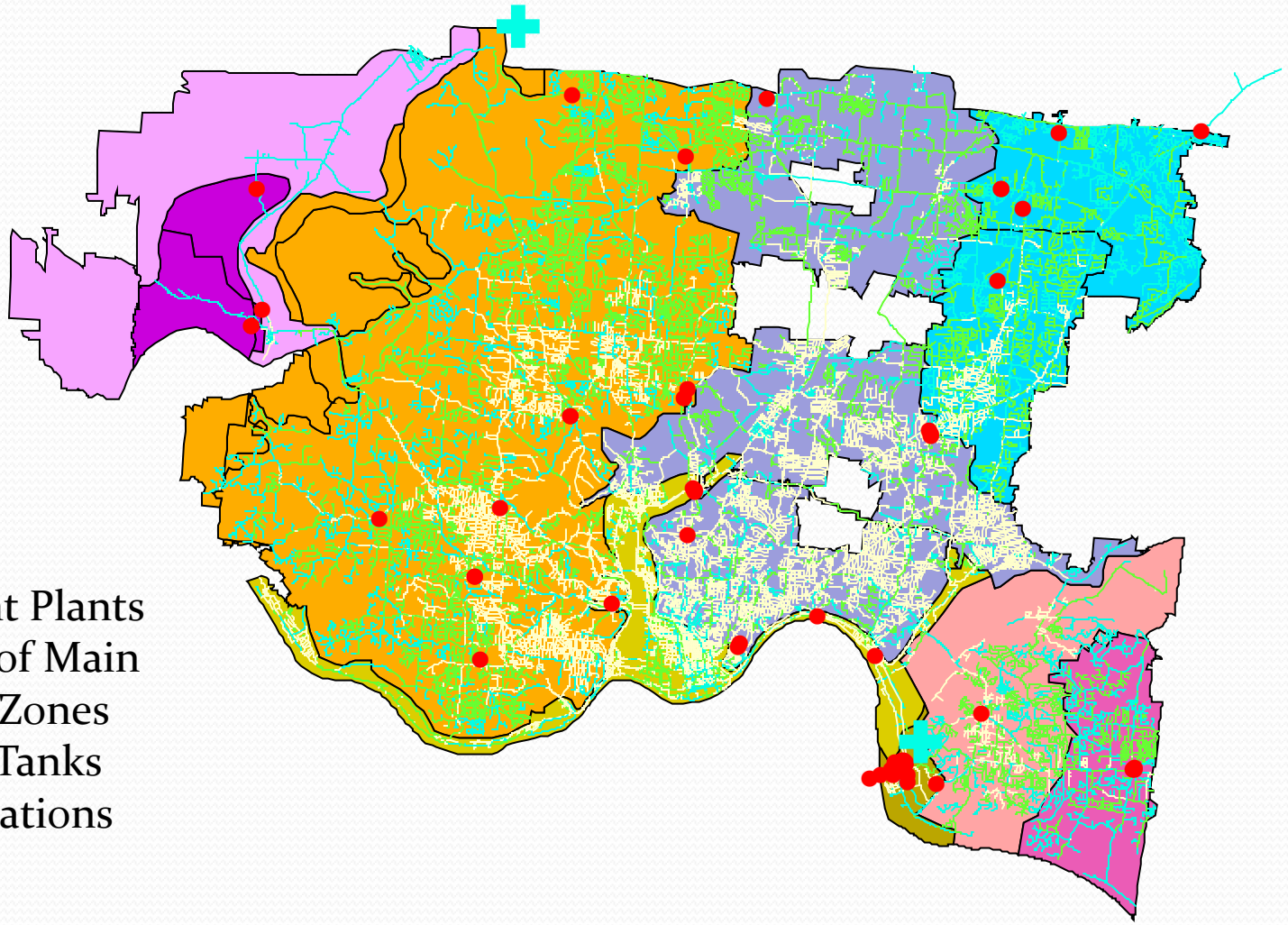
- http://www.nbcnews.com/video/nightly-news/54081819/#54081819

- http://www.nbcnews.com/video/nightly-news/54081819/#54081819

Presentation Overview

- GCWW Overview
- Spill Summary
- Lab Overview
- Research and Method Development for MCHM
- RMT Plant Samples
- Analytical Method for 4-MCHM (WV Spill)

Overview of GCWW System



- 2 Treatment Plants
- 3100 Miles of Main
- 11 Pressure Zones
- 27 Storage Tanks
- 19 Pump Stations

- Customers

Overview of GCWW System

- GCWW has two water treatment facilities
- The Richard Miller Treatment Plant (RMTP) which draws water from Ohio River (Surface Water). (240mgd Capacity)
- Charles M. Bolton Treatment Plant (CMBP) which draws water from the Great Miami River (Ground Water). (40mgd Capacity)

GREATER CINCINNATI WATER WORKS

RMTP

Intake Pier

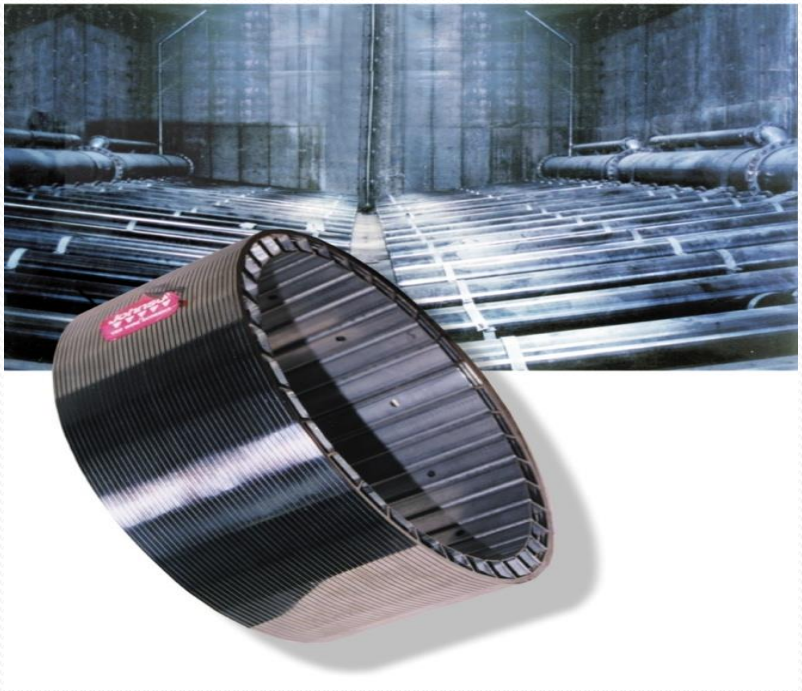
RAW Water PS

Sand Filtration

- 47 Rapid Sand Filters
- Filtration Rate @ 3.0gpm/ft^2
- Effluent Turbidity <0.3 NTU

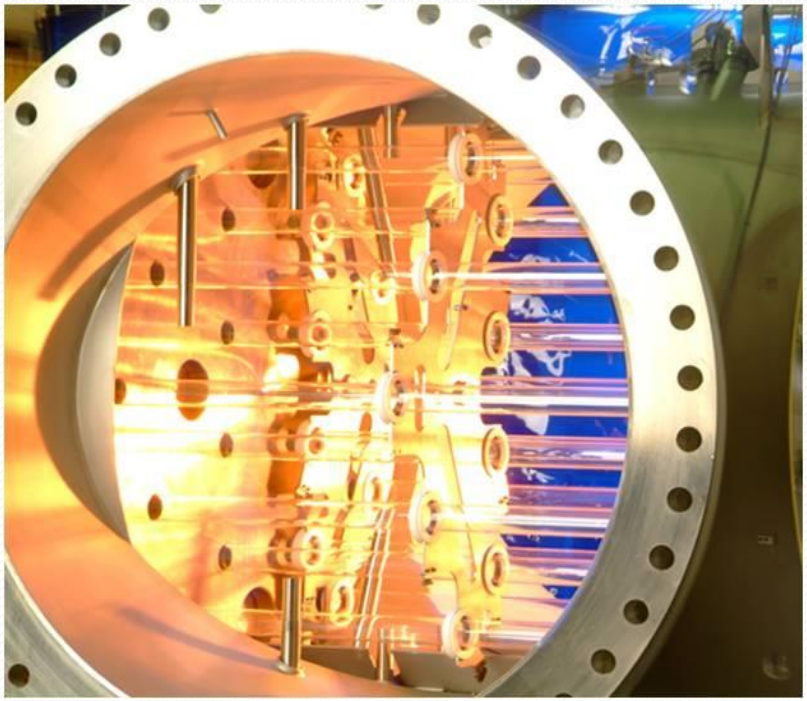
GAC Adsorption

Granular Activated Carbon (GAC):
Bituminous coal for natural and synthetic organics adsorption



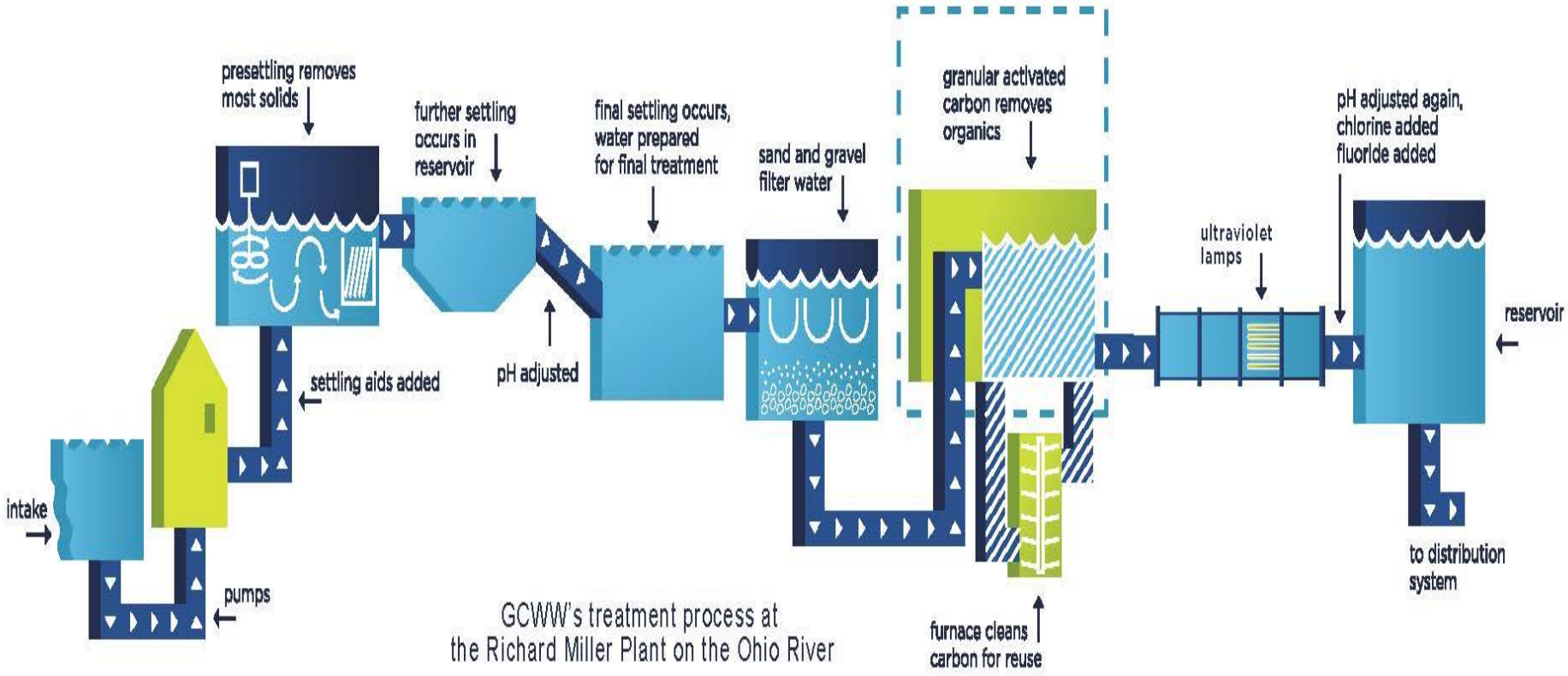
12 GAC contactors
Area: 1950 ft^2 each
Depth: 11.5 ft of carbon
EBCT: 15 min
Effluent TOC < 1.2 mg/L

UV Disinfection



- 8 UV Reactors
- Medium Pressure = Polychromatic UV Light
- Designed to disinfect up to 4-log Crypto, Giardia

Treatment Process at RMTP



Spill Summary

- January 9, 2014: At least 8000 gallons of an industrial chemical 4-Methylcyclohexanemethanol (MCHM) are spilled into the Elk River, a secondary tributary of the Ohio River
- Chemical is used for Coal Processing to separate impurities from the coal.
- The MCHM was taken into the Kanawha Valley Drinking Water Plant (1.5 miles downstream) where it is subsequently distributed to drinking water customers
- "Do Not Use" orders are issued for roughly 300,000 people
- Because of the Do Not Use order, media coverage was intense
- Spill Continued Downstream toward Cincinnati
- Spill Location was approximately 200 miles upstream of Richard Miller Treatment Plant


Cincinnati to
Beckjord – 10 miles
Meldahl – 25 miles
Huntington – 157 miles
Elk River - 200 miles
Ohio
West Virginia
Kentucky
Cincinnati, OH, USA
Beckjord Power Station
Meldahl Dam
Ohio River
Kanawha River
Huntington, WV
Elk River, Charleston, WV
© 2013 Google
Image Landsat
Google earth
Imagery Date: 4/9/2013 lat 38.622895° lon -82.886932° elev 710 ft eye alt 199.18 mi

More investigations launched as 180,000 West Virginians still told not to use water

By **Greg Botelho** and **Stephanie Gallman**, CNN
updated 9:30 PM EST, Tue January 14, 2014

How safe is West Virginia tap water, if pregnant women shouldn't drink it?

By **Catherine E. Shoichet**, **Jean Casarez** and **Ashley Fantz**, CNN
updated 11:00 PM EST, Thu January 16, 2014

Chemical spill brings W.Va. capital to standstill

Posted: Jan 10, 2014 4:41 AM EST
Updated: Jan 10, 2014 11:38 PM EST

Hospital admissions over W. Virginia chem spill double even after water declared safe

Get short URL

Published time: January 20, 2014 20:26
Edited time: January 20, 2014 23:34

West Virginia emergency declared after chemical spill leaves thousands without water

West Virginia chemical spill shines spotlight on loose regulation

By **Alexandra Field**, **Meridith Edwards** and **Catherine E. Shoichet**, CNN
updated 10:39 PM EST, Mon January 13, 2014

Cincinnati to shut intakes as a precaution

Jan. 14, 2014 | 0 Comments

Company in West Virginia chemical spill files for bankruptcy

January 17, 2014 | Tom Hals | Reuters

Thousands warned not to drink water after W. Va. spill

Jan. 10, 2014 | 0 Comments

Recommend Be the first of your friends to rec

Water Works says chemical plume has passed Cincinnati

Ohio River intake valves to open Thursday

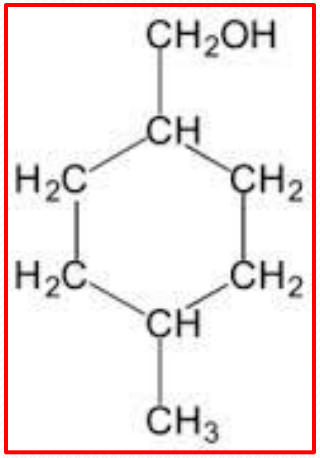
UPDATED 12:17 PM EST Jan 16, 2014

GCWW Response

- GCWW was notified by ORSANCO of the spill on the Evening of Thursday January 9 (the same day as the spill).
- On Friday morning an internal task team (Water Quality and Supply) was formed to respond.
  - **Analytical method development**
  - Water storage/pumping plan
  - Treatment adjustments/performance evaluation (jar tests)
  - ETA based on river flow & models = middle part of the following week
- We initiated further communication with ORSANCO and Northern Kentucky Water District.
- Michele Ralston coordinated interaction with the Media

Initial Research

- Chemical Properties, Health Effects, and Treatability
- Can we analyze for the compound
- Began multiple calculation techniques for Estimated Time of Arrival calculation
- Estimates of MCHM concentration
- Treatability of MCHM with PAC

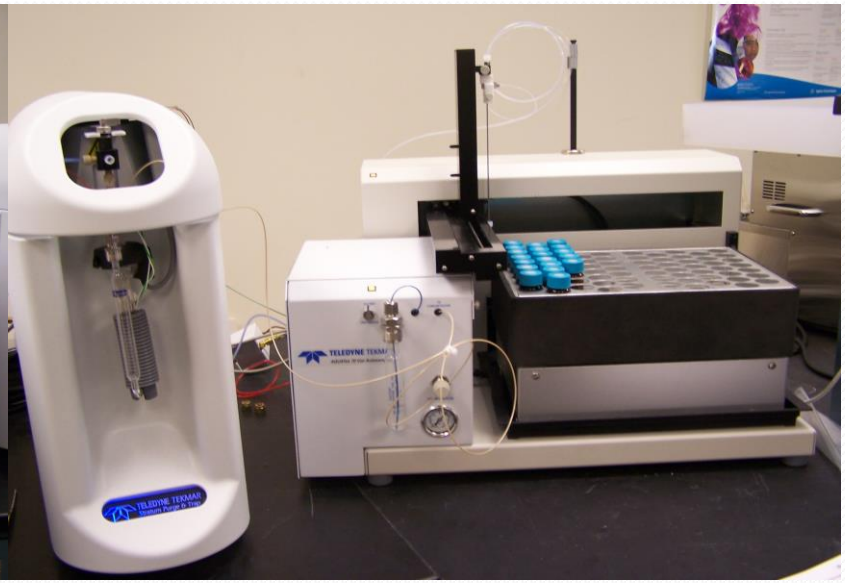


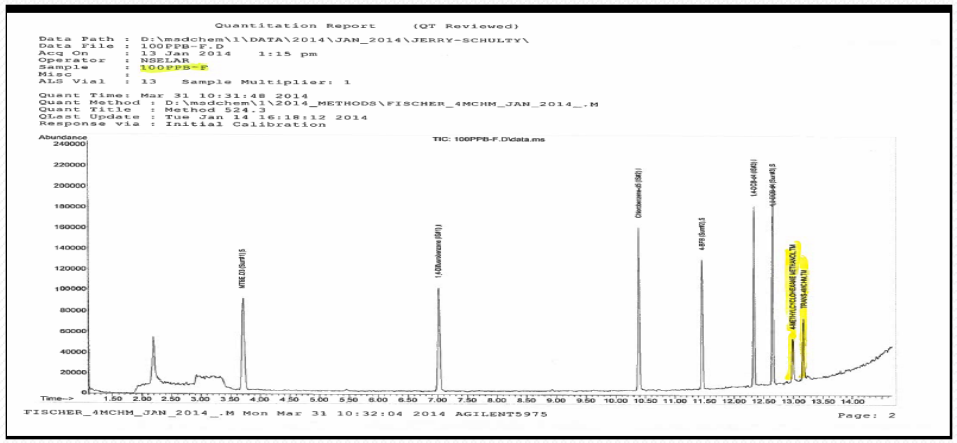
Planning for Intake Shutdown

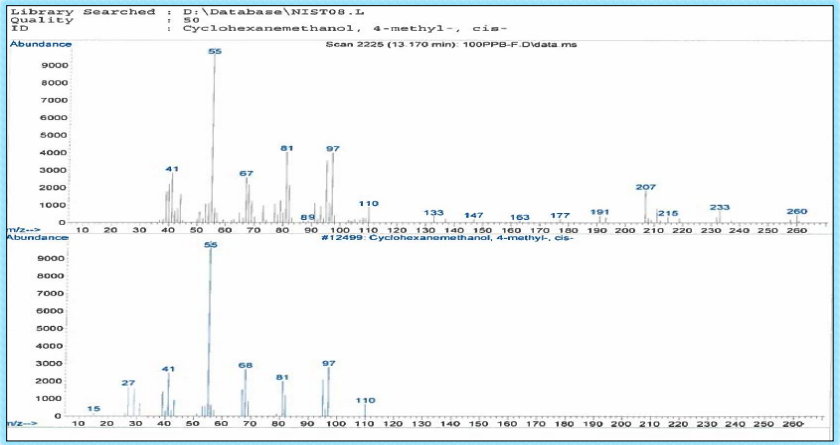
- WQM and Supply Divisions coordinated so Supply could fill storage tanks and the settling reservoirs to prepare for an extended intake shutdown
  - Preventative maintenance at RMTP was delayed to ensure we had full capacity to fill up before and after the spill
  - Additional GAC contactors were put in service to accommodate the unseasonal high pumping.
  - Production testing at Bolton was delayed to ensure capacity during the spill.

GC/MS for 524.3 Method

(VOCs, THMs, Gasoline)







Laboratory Analyses

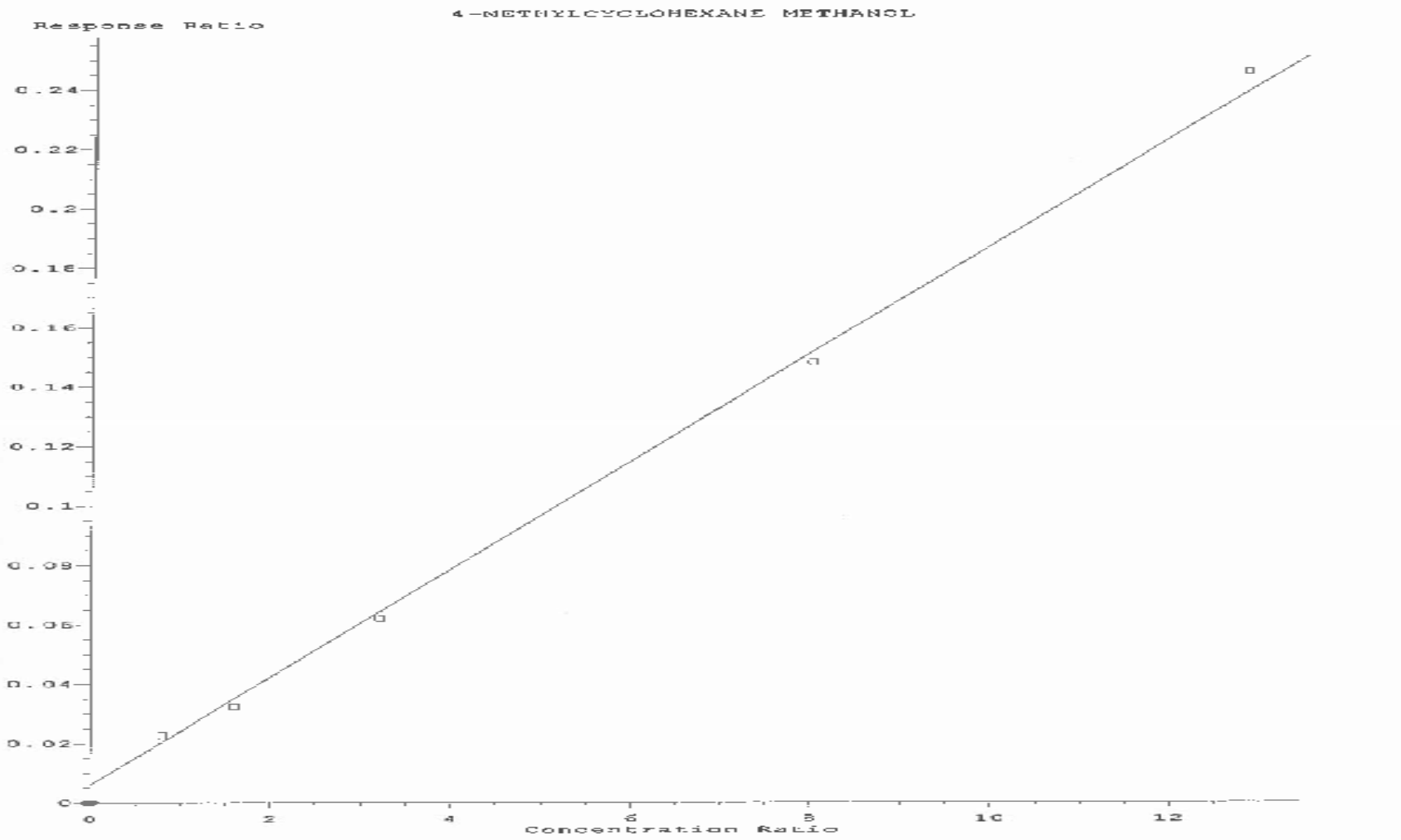
Method Development

- Limited information available on MCHM
  - No analytical method
- Crude MCHM sample received on Friday afternoon
- VOC – trial test with GC/MS
  - 100 ppb dilution in methanol
  - longer run (20-25 minutes)
  - higher purging temperature (50-60 C)
- Identified 2 peaks at GC/MS - Cis and trans isomers
  - Looked for additional peaks – none
- Made calibration curve with pure compound on Sunday
  - LOD = 4 ppb
- GC/MS analyses run 24/7 from Sunday - Thursday
- Odor threshold limit tests were employed in addition to GC/MS analyses with pure compound.
  - The odor analyses could detect the compound at lower concentrations (1 ppb).

Agilent 7890 GC/MS for MCHM Analytical Method Development

- The Calibration curve for MCHM using Agilent 7890 GC and 5875 MS with Teledyne Stratum purge and trap was 4ppb to 50ppb
- The Restek column 30m x 0.25mm ID x 1.4µm
- The oven program for GC: 45°c for 4.5 min then 12°c/min to 100°c for 0 min and 25°c/min to 240°c for 10 min.
- Total runtime is 25 min (changes made to the method 524.3) to optimize for MCHM
- Heating the water sample to 50°c while purging helped to achieve lower detection limit.
- This method resulted in 2 peaks indicating 2 different confirmations of MCHM (Cis and Trans).

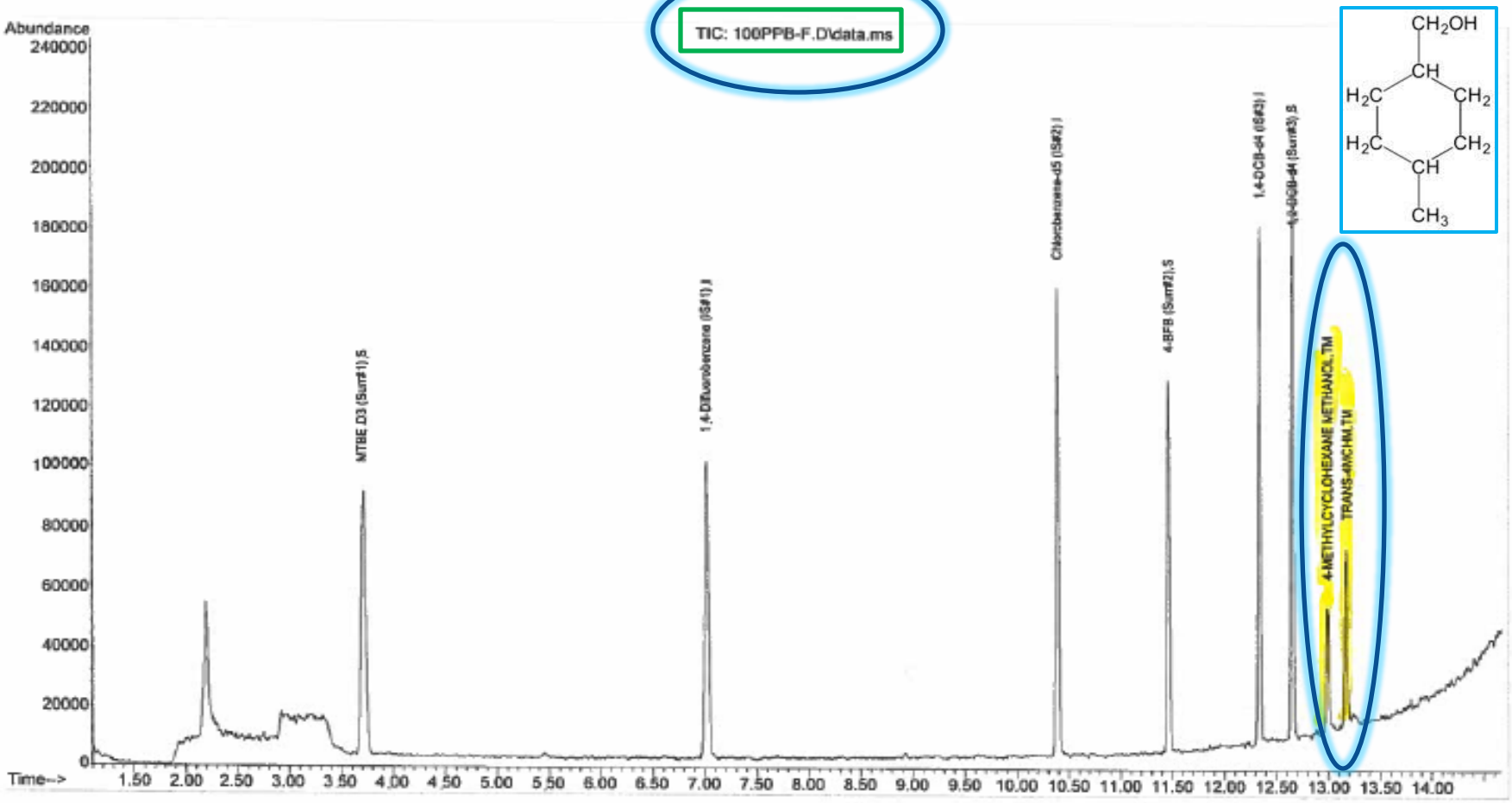
Calibration Curve for MCHM



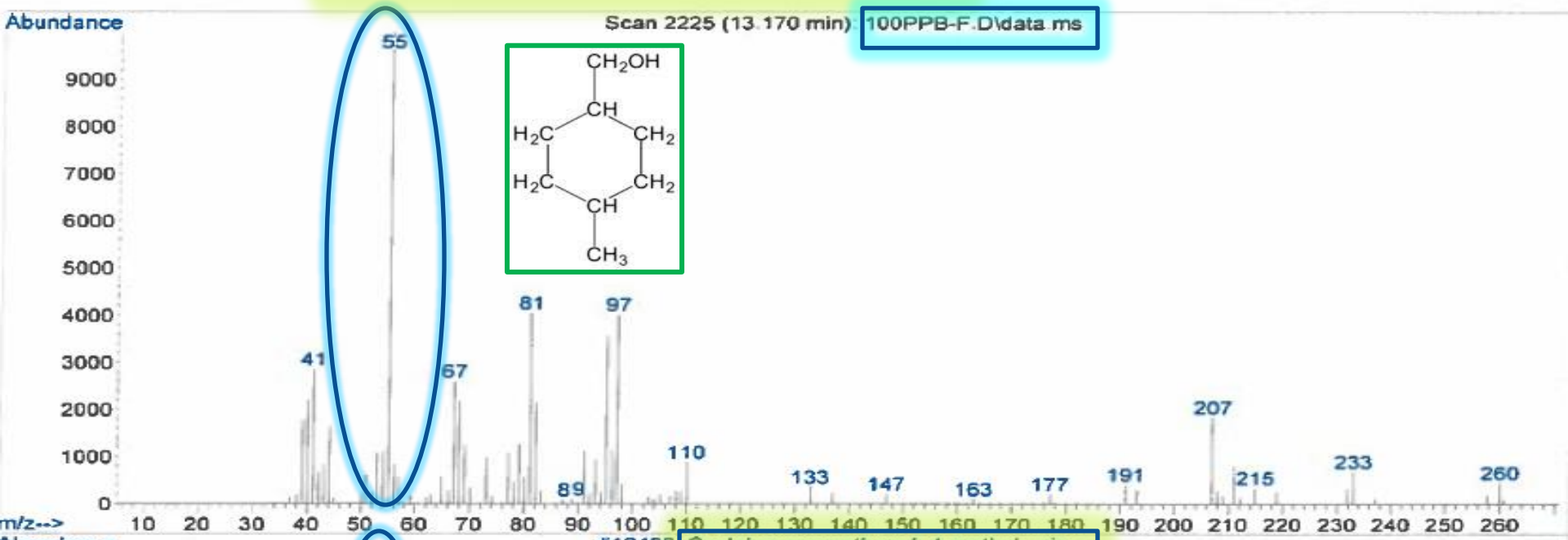
Quantitation Report (QT Reviewed)

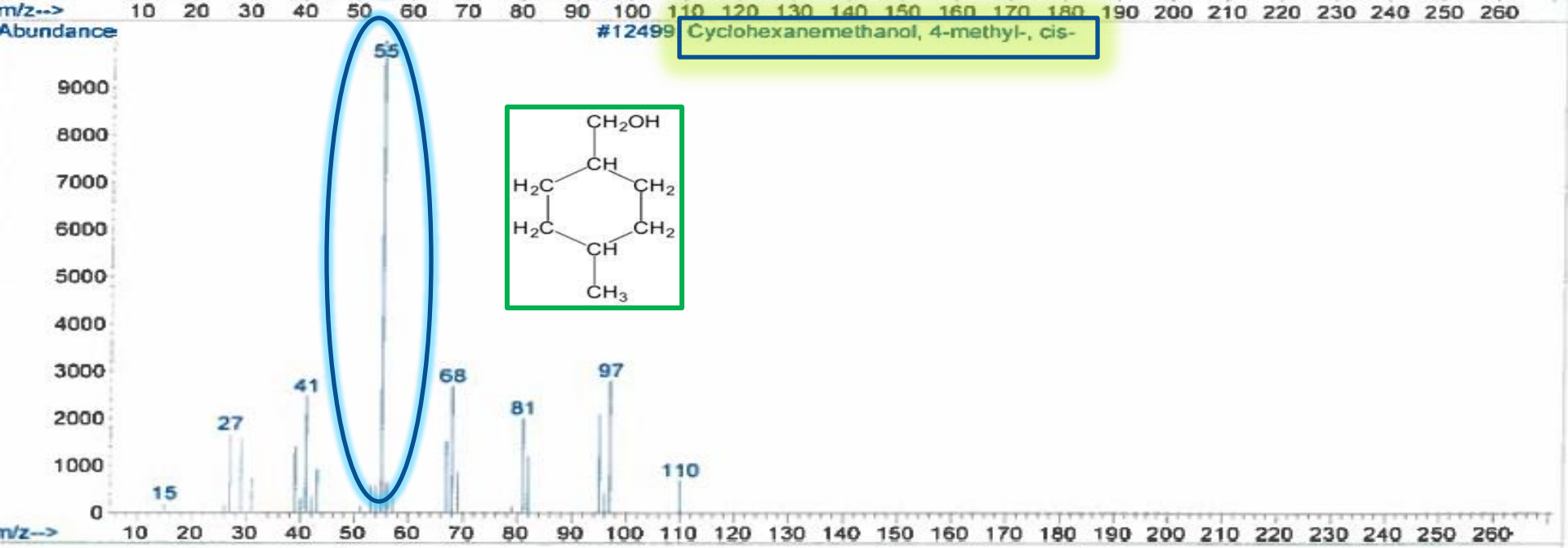
Data Path : D:\msdchem\1\DATA\2014\JAN_2014\JERRY-SCHULTY\
Data File : 100PPB-F.D
Acq On : 13 Jan 2014 1:15 pm
Operator : NSELAR
Sample : 100PPB-F
Misc :
ALS Vial : 13 Sample Multiplier: 1

Quant Time: Mar 31 10:31:48 2014
Quant Method : D:\msdchem\1\2014_METHODS\FISCHER_4MCHM_JAN_2014_.M
Quant Title : Method 524.3
QLast Update : Tue Jan 14 16:18:12 2014
Response via : Initial Calibration

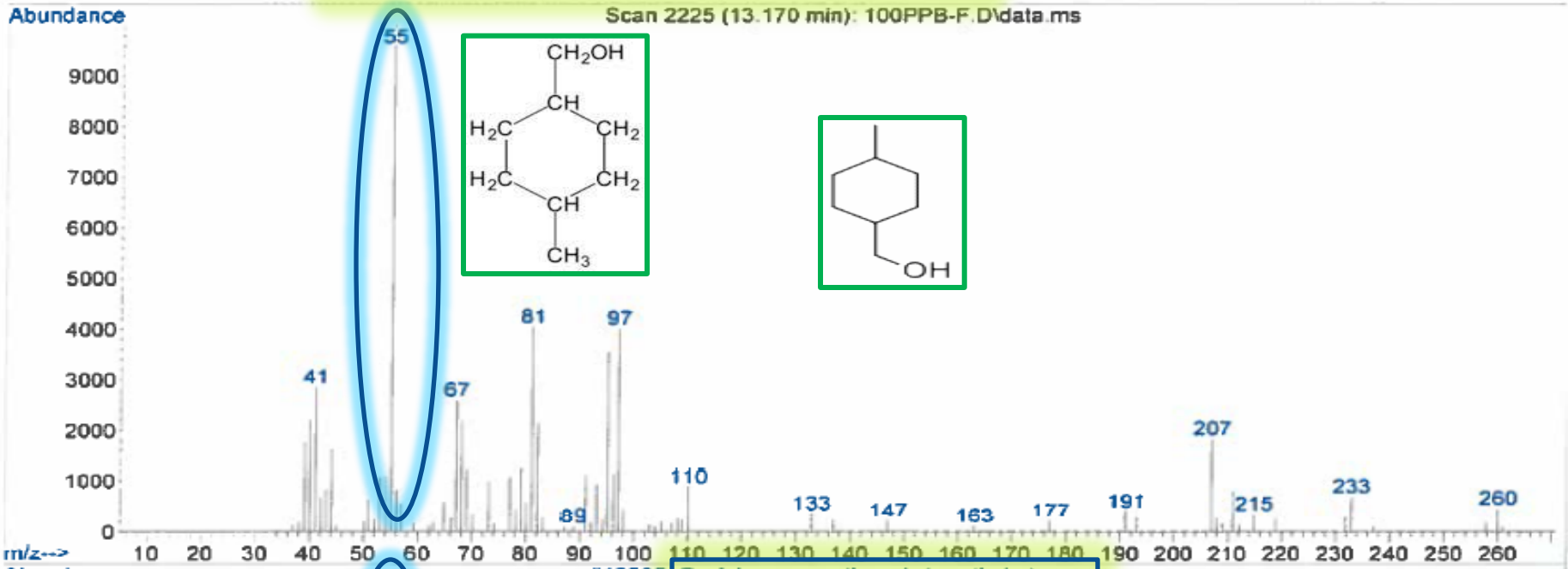


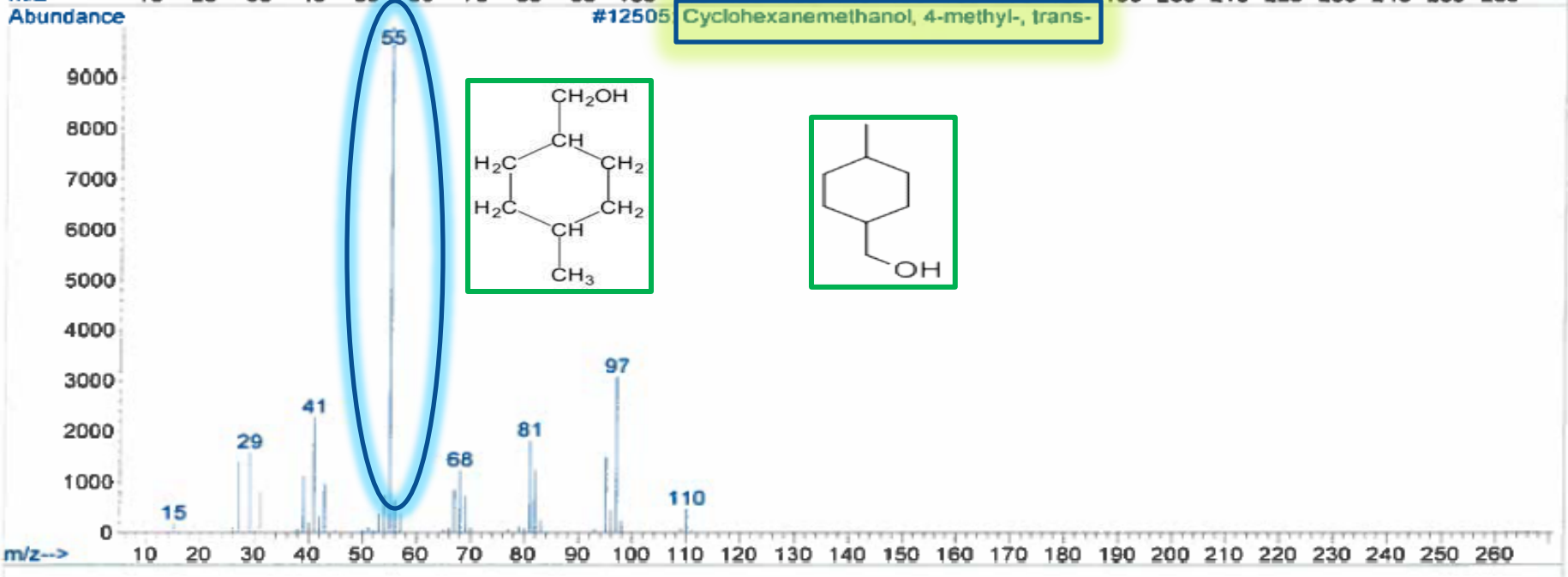
Library Searched : D:\Database\NIST08.L
Quality : 50
ID : Cyclohexanemethanol, 4-methyl-, cis-



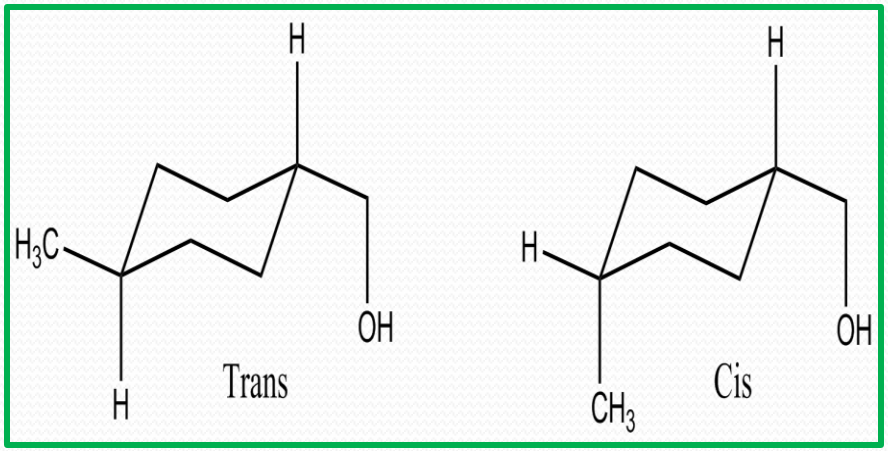


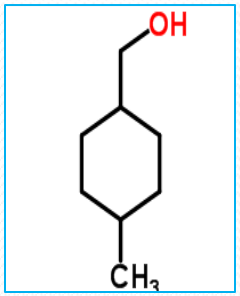
Library Searched : D:\Database\NIST08.L
Quality : 59
ID : Cyclohexanemethanol, 4-methyl-, trans-



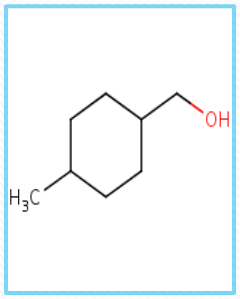


Chemical Structure of 4-MCHM

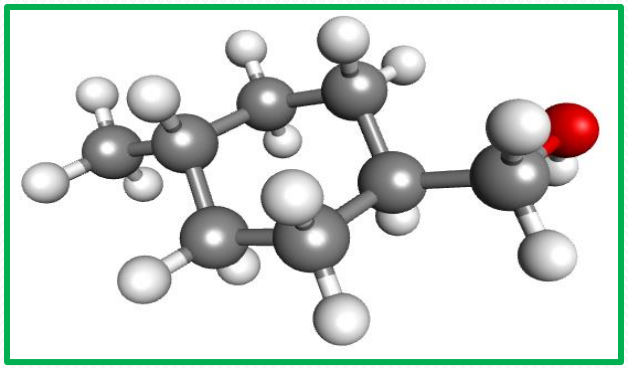




Trans-MCHM



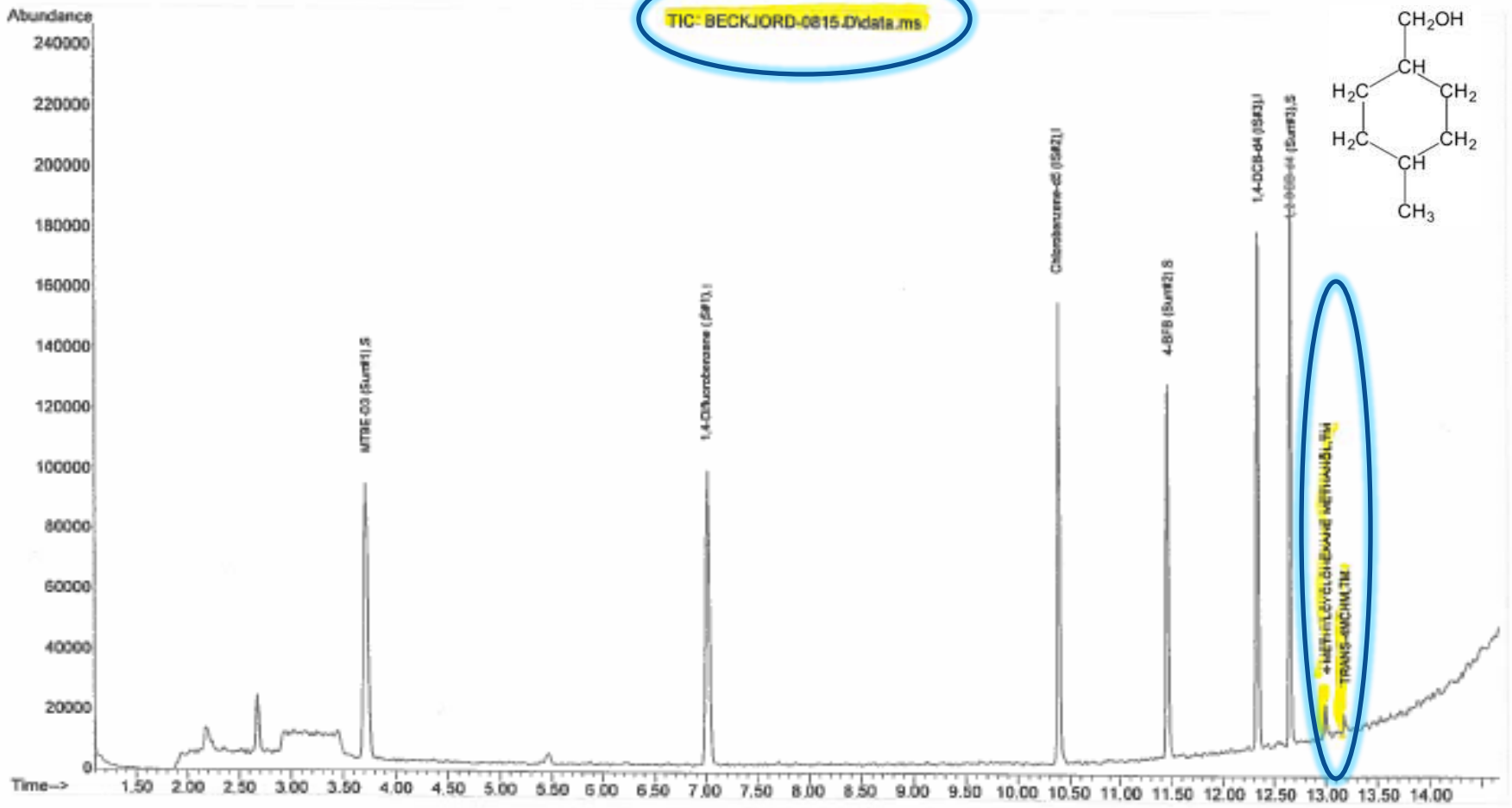
Cis-MCHM



Quantitation Report (QT Reviewed)

Data Path : D:\msdchem\1\DATA\2014\JAN_2014\RMTP_SPILL\
Data File : BECKJORD-0815.D
Acq On : 15 Jan 2014 9:04 am
Operator : NSELAR
Sample : BECKJORD-0815
Misc : 01/15/2014 008:15am
ALS Vial : 1 Sample Multiplier: 1

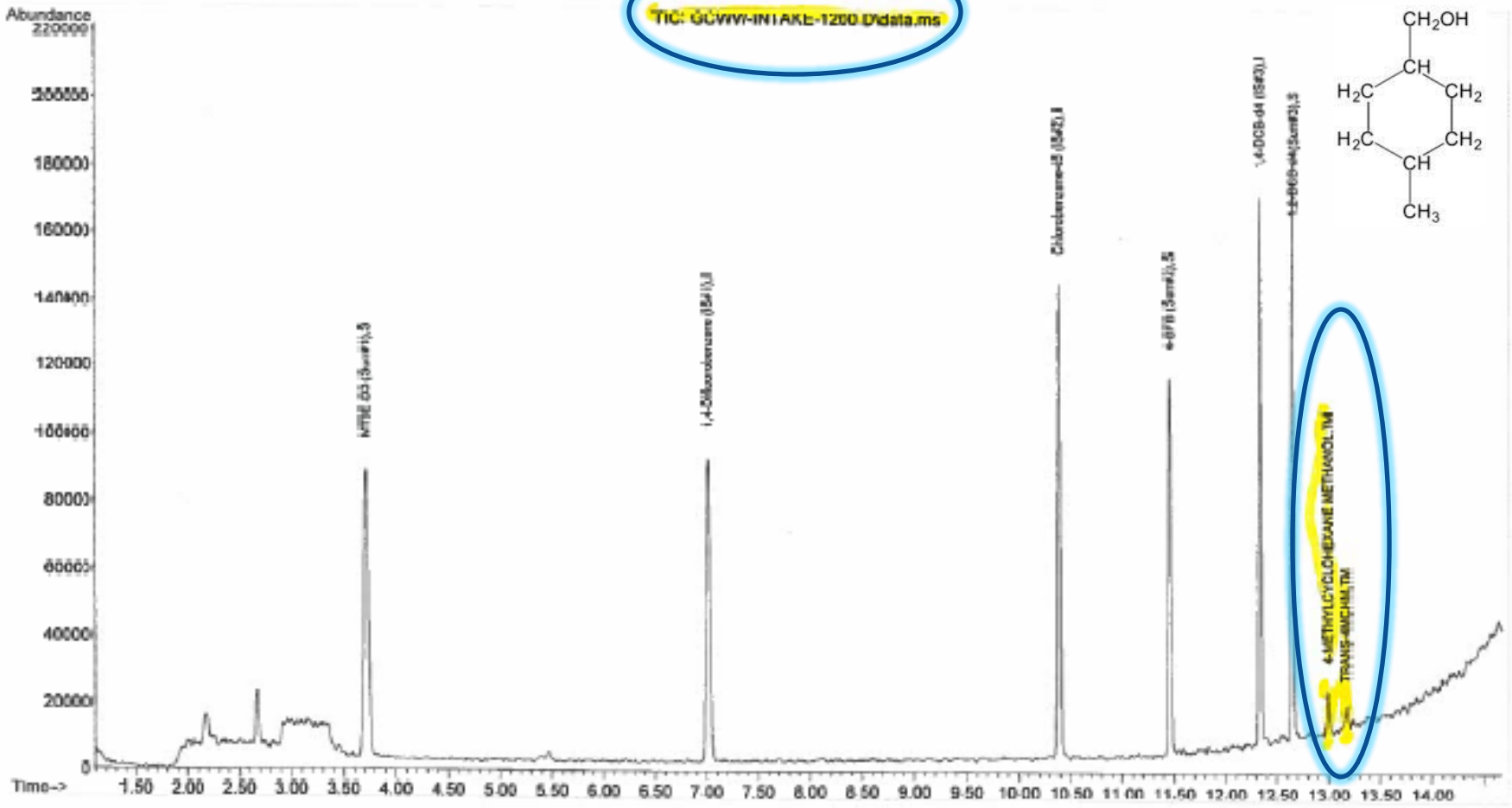
Quant Time: Feb 27 14:10:55 2014
Quant Method : D:\msdchem\1\2014_METHODS\FISCHER_4MCHM_JAN_2014_.M
Quant Title : Method 524.3
QLast Update : Tue Jan 14 16:18:12 2014
Response via : Initial Calibration



Quantitation Report (QT Reviewed)

Data Path : D:\msdchem\1\DATA\2014\JAN_2014\RMTP_SPILL\
Data File : GCWW-INTAKE-1200.D
Acq On : 15 Jan 2014 1:47 pm
Operator : NSELAR
Sample : GCWW-INTAKE-1200
Misc : 01/15/2014 812:00PM
ALS Vial : 3 Sample Multiplier: 1

Quant Time: Feb 27 14:07:58 2014
Quant Method : D:\msdchem\1\2014_METHODS\FISCHER_4MCHM_JAN_2014_.M
Quant Title : Method 524.3
QLast Update : Tue Jan 14 16:18:12 2014
Response via : Initial Calibration



Laboratory Analyses (cont.)

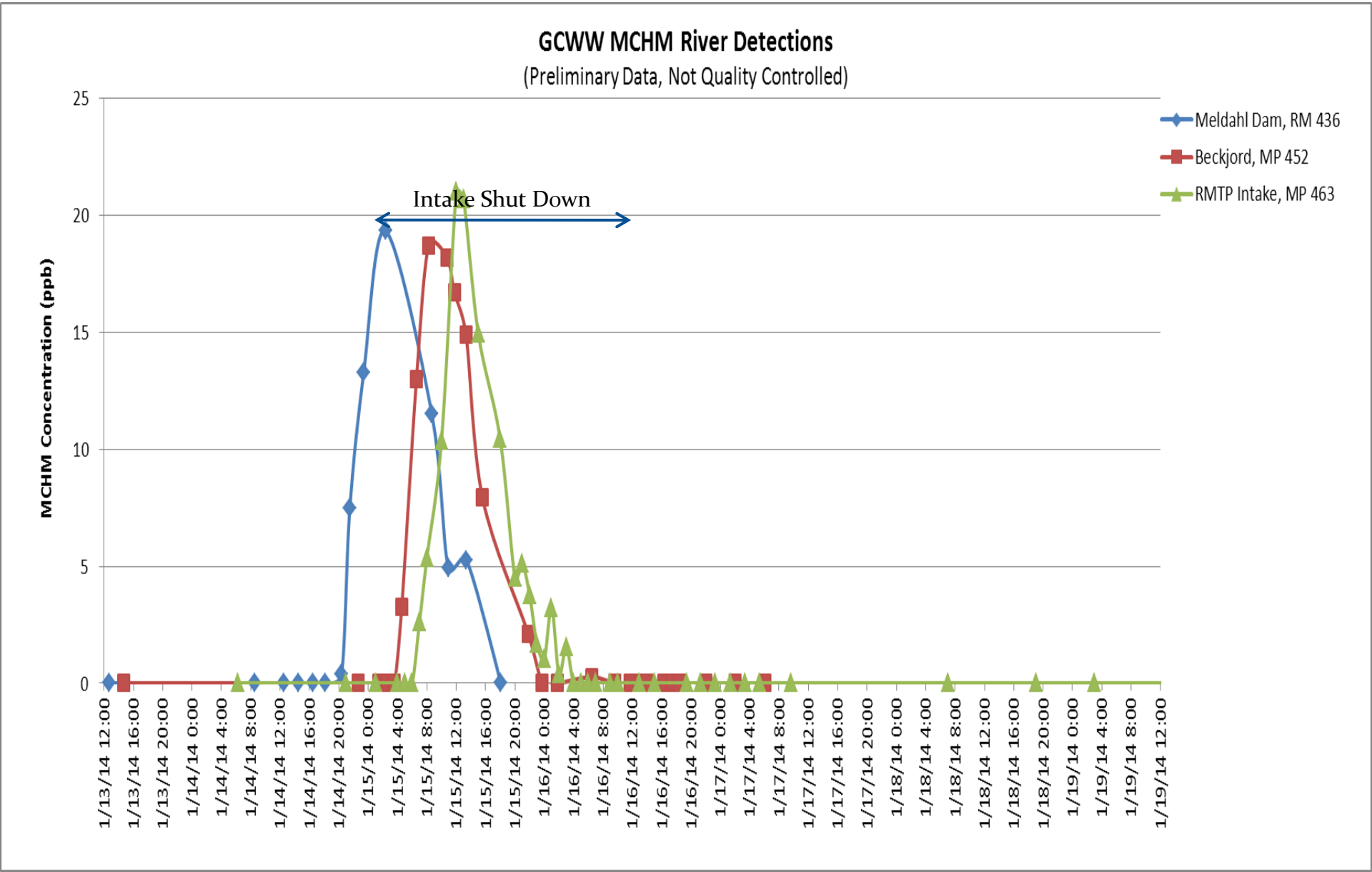
- Ordered consumables and chemicals!
- Worked with ORSANCO and Huntington WV to develop an in-house analytical method
- Provided laboratory standard and technical assistance to other agencies including NKWD, USEPA, Huntington, ORSANCO, Louisville, State of Indiana and State of Kentucky
- Analyzed samples from Huntington WV and from the Kanawha River over the weekend

Sampling Plan

- Developed cooperative sampling plan
  - Sample collection 24/7 Tuesday - Thursday
  - NKWD sampled our intake, their intake, delivered samples to us
  - GCWW/MSD sampled and analyzed samples upstream at Meldahl Dam and Beckjord Power Station (baseline and then around the clock)
    - Sample collection every hour.
    - Meldahl – 2 employees stationed at Dam, 1-2 drivers
    - Beckjord 1-2 employees
    - 12 hour shifts
  - ORSANCO collected samples further upstream
  - Upstream data from Huntington was shared with GCWW/NKWD
  - Utilized Staff from WQM, Supply, MSDGC

Treatment Response

- Extra contactor put into service for added capacity before the spill arrived
- Researched Treatability of the contaminant with PAC
- Performed Jar Tests to determine effective dose of powdered activated carbon
- Fed PAC for 5 hours prior to shutting down the intakes just in case something got by our early warning stations
- Intakes were shut down on January 14 at 11:45 PM and re-opened on January 16 at 2:00 PM
- From Thursday to Tuesday after the spill, PAC was fed to ensure any undetected trailing contaminants were treated.
- PAC cost approximately $26,000


GCWW MCHM River Detections
(Preliminary Data, Not Quality Controlled)
MCHM Concentration (ppb)
25
20
15
10
5
0
Intake Shut Down
Meldahl Dam, RM 436
Beckjord, MP 452
RMTP Intake, MP 463
1/13/14 12:00
1/13/14 16:00
1/13/14 20:00
1/14/14 0:00
1/14/14 4:00
1/14/14 8:00
1/14/14 12:00
1/14/14 16:00
1/14/14 20:00
1/15/14 0:00
1/15/14 4:00
1/15/14 8:00
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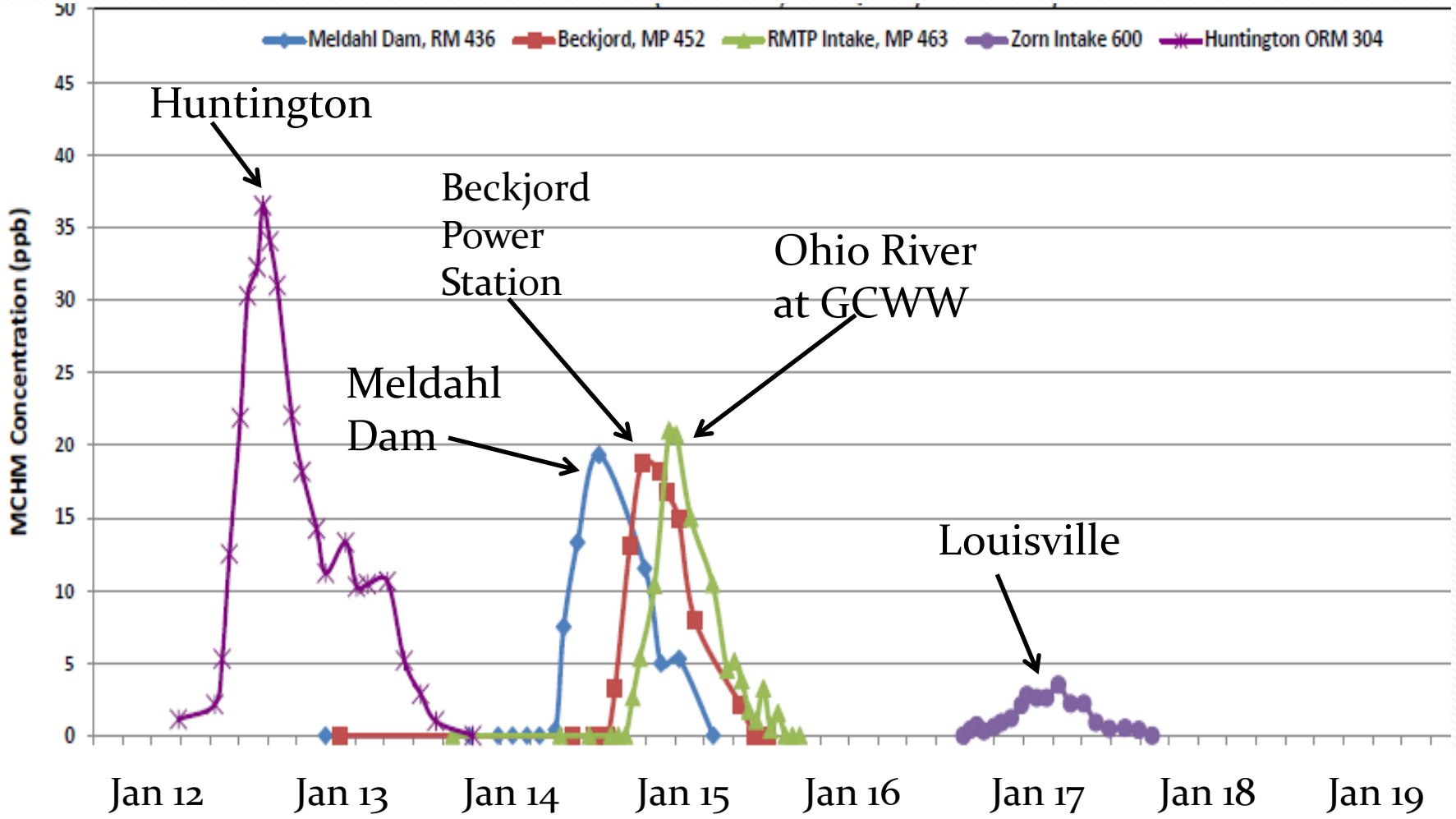
1/19/14 0:00
1/19/14 4:00
1/19/14 8:00
1/19/14 12:00

Ohio River Data



Some of the Agencies Involved

- The White House
- USEPA Region 3 (WV)
- USEPA Region 4 (KY)
- USEPA Region 5 (Ohio, IN)
- ORSANCO
- KDOW
- OEPA
- IDEM
- DEPT of Homeland Security
- WV DEP
- CDC
- Local/State Health Departments
- National Poison Control Center
- National Guard
- ACOE
- Duke Energy
- MSDGC
- NKWD and many other water utilities

End Result

- GCWW's spill response procedures proved to be effective
- Close coordination between Supply and WQM ensured that system had adequate water storage.
- The spill was effectively detected and tracked due to our in-house analytical and sampling capabilities
- Intakes were shut down to ensure no contamination reached our customers
- Coordination between GCWW/MSDGC, NKWD, ORSANCO, and other agencies was excellent
- Feedback on our response from outside agencies and customers has been positive