Development of new element recipes for the GC-AED

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Abstract

The Atomic Emission Detector for Gas Chromatography (GC-AED) is a true multi-element detector for GC. The AEDs sensitivity and selectivity arise from its ability to use real-time spectral data from a photodiode array to enhance elemental signal response and suppress background interference. Element recipes define how this spectral information is collected, processed, and saved into raw data files. Although the AED ships with a large number of element recipes, there is still a need to be able to create new recipes for elements not included in the standard configuration, or to optimize existing recipes for different background interferences.

Creating a new element recipe requires careful selection of standard compounds, GC conditions, spectral emission wavelengths, and the specific diodes that are used to generate the signal and background chromatograms. In addition, software optimization of diode weighting factors is used to enhance the selectivity and sensitivity of the resulting recipe. This presentation will describe the experimental techniques used to generate element recipes for the AED using a new Copper recipe as an example.

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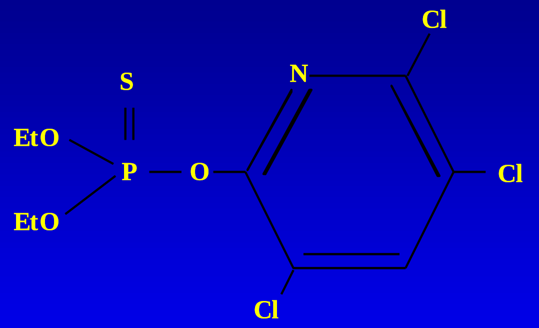
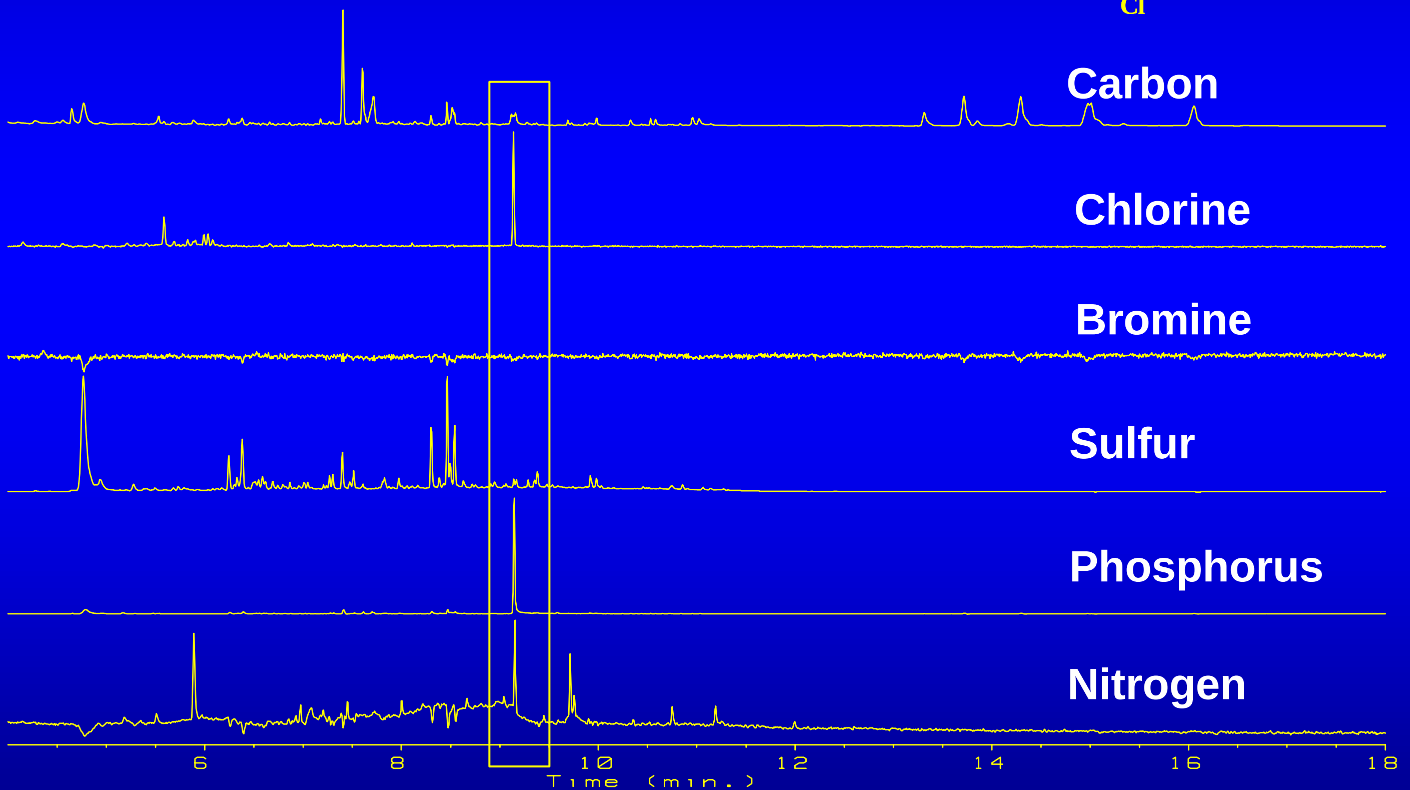
GC-AED Overview

Chlorpyrifos by GC-AED





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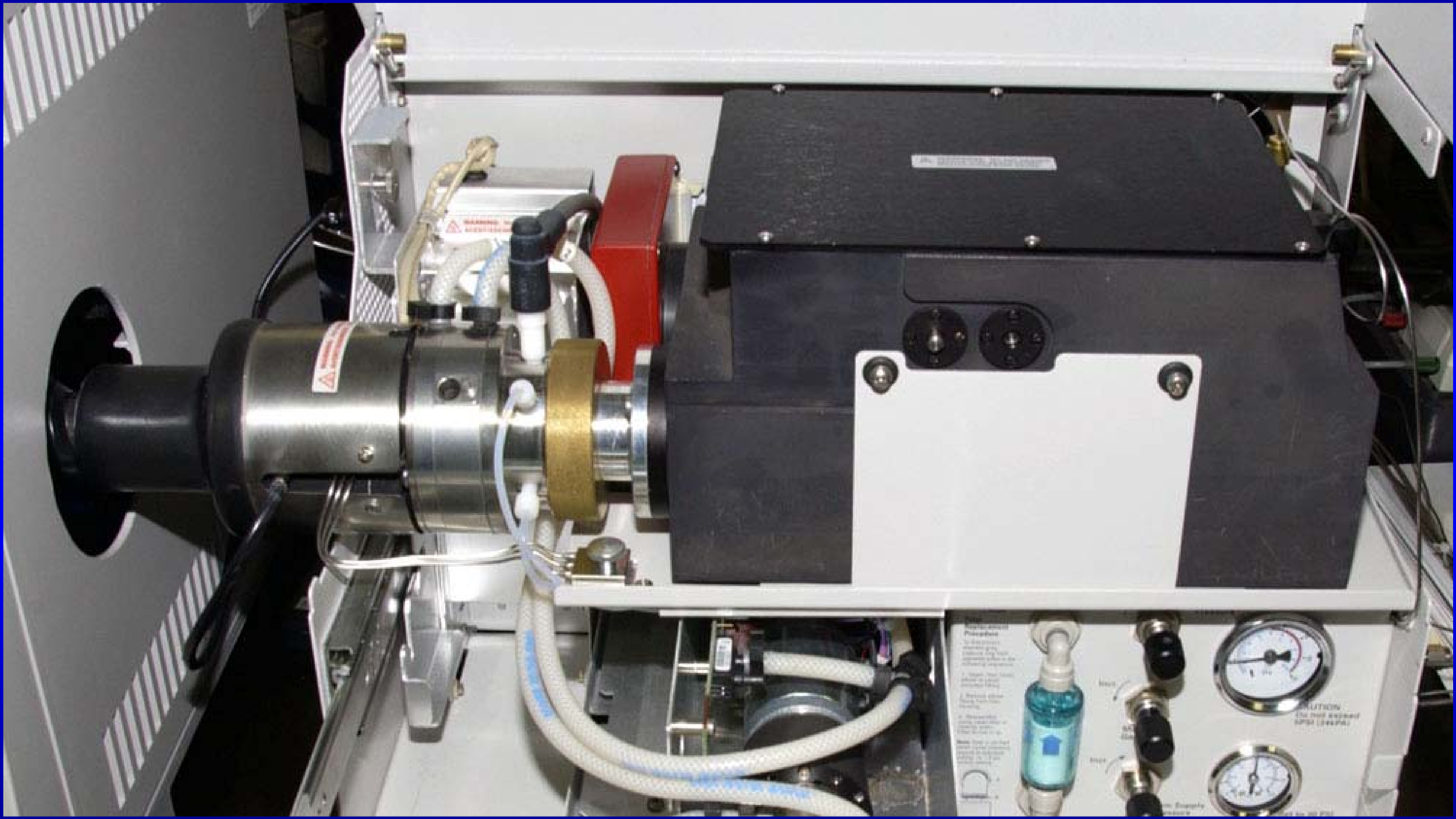
GC-AED History

- Commercialized by Hewlett Packard / Agilent Technologies
  - 1989: HP5921A Atomic Emission Detector
  - 1996: HP G2350A Atomic Emission Detector
- Licensed to Joint Analytical Systems
  - 2002: JAS G2370AA Atomic Emission Detector

Agilent G2350A AED



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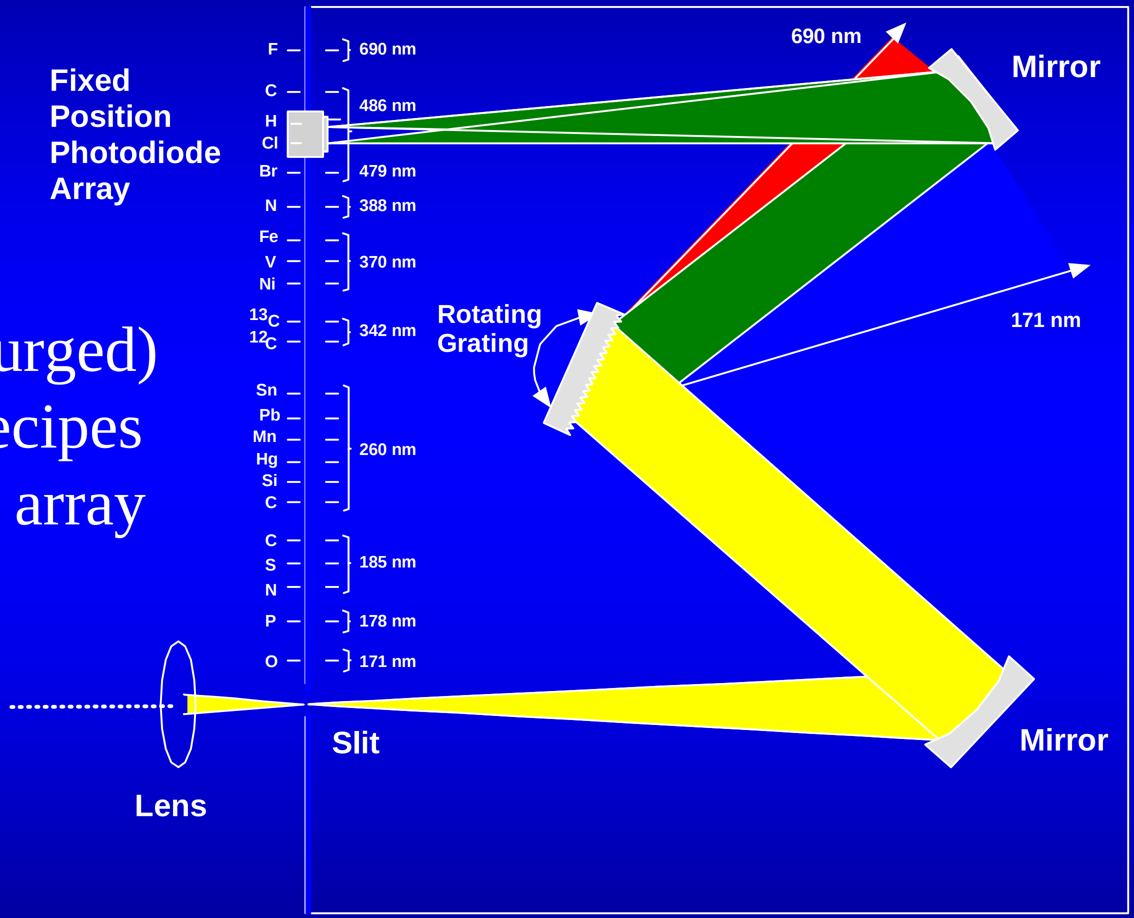
Spectrometer and Diode Array



- ~170 to 800 nm (N2 Purged)
- 329 Diodes Used in Recipes
- 20-26 nm imaged onto array

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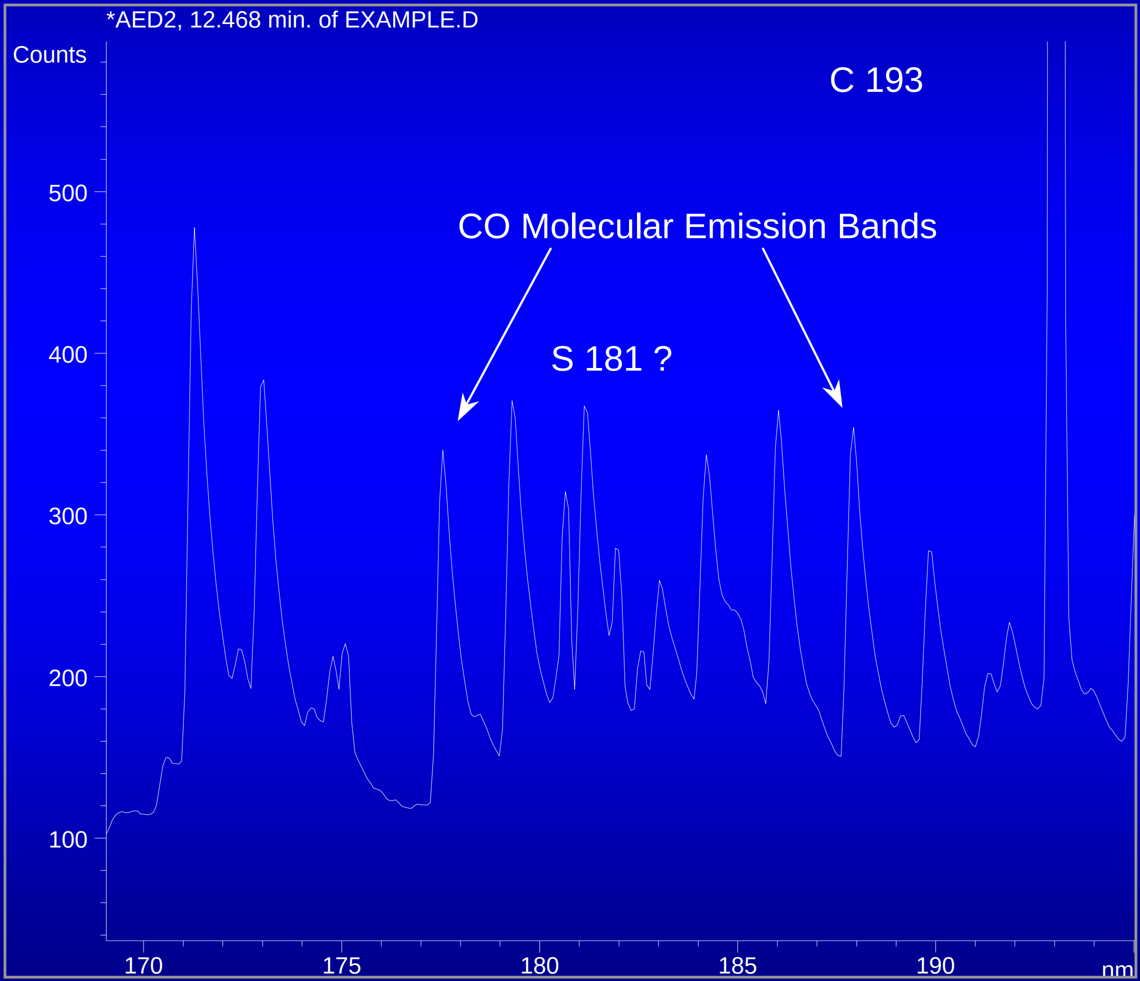
AED Signal Generation

AED Spectrum of Hydrocarbon Sample



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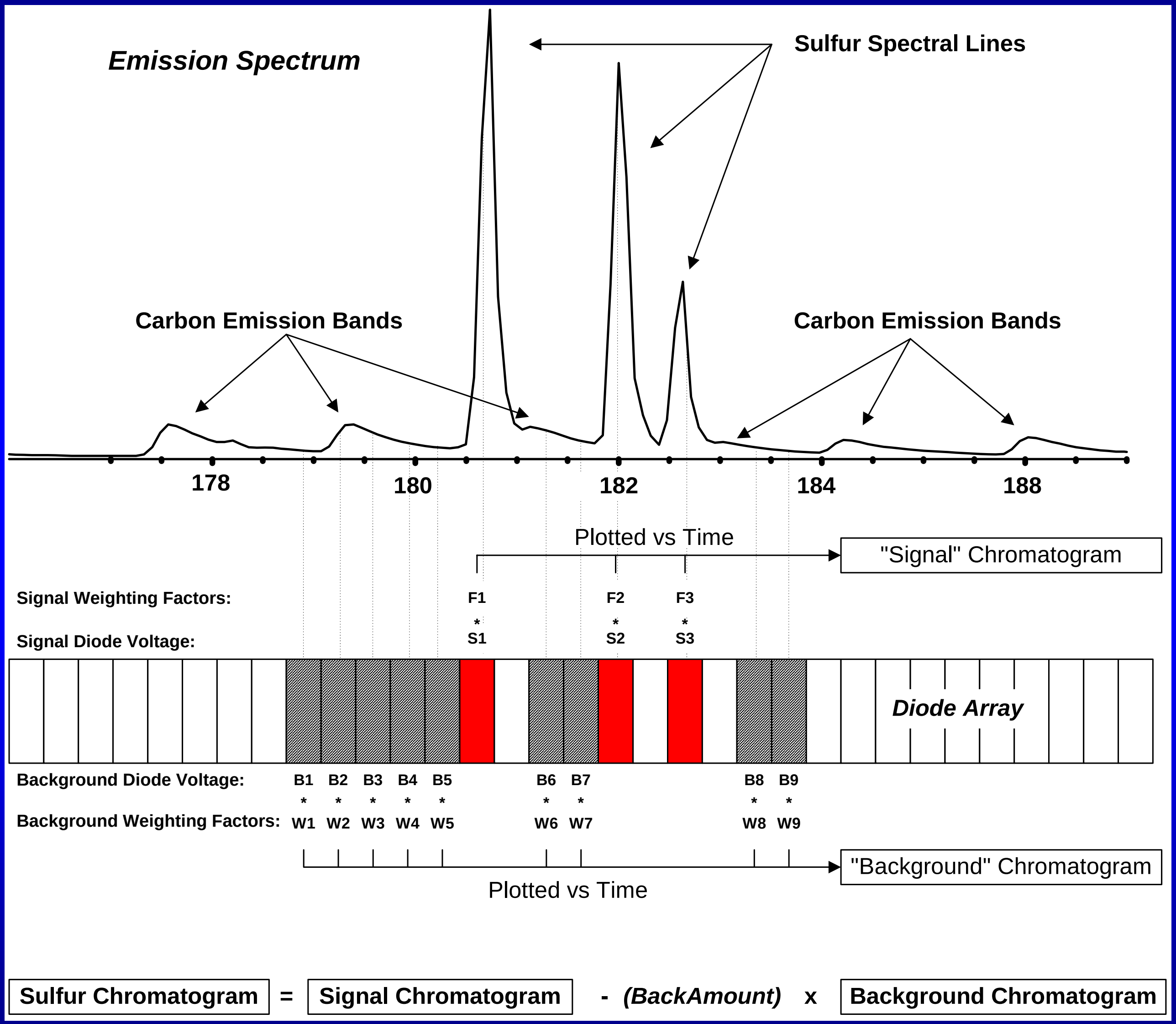
AED Signal Generation



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AED Element Recipes

- Named based on the element plus approximate wavelength (*e.g.* C 193)
- Defined by:
  - Array/Spectrometer position (FrameRef)
    - 20-26 nm “window” on array
    - +/- 164 Diodes around center diode of frame
  - Signal Diodes and Weighting Factors
  - Background Diodes and Weighting Factors
- Recipes must use the same FrameRef in order to be acquired in the same chromatographic run
  - Reagent gases and makeup gas flow rate must also be compatible

G2350A AED Standard* Recipes

Carbon 179, 193, 248, 264, 496, 834	**Hydrogen** 486, 656	**Nitrogen** 174, 388	**Oxygen** 171	**Sulfur** 181	**Chlorine** 479, 837
Bromine 478, 827	**Fluorine** 690	**Iodine** 183, 206	**Phosphorus** 178, 186	**Boron** 250	**Selenium** 196
Arsenic 189	**Germanium** 265	**Lead** 261, 406	**Manganese** 259	**Mercury** 254	**Silicon** 252
Tin 271, 301, 303, 326	**Iron** 302	**Nickel** 301	**Vanadium** 292	**Antimony** 218	**Tellurium** 208

*** Excludes stable isotope recipes**

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Why are Custom Recipes Needed?

- Add new element capability
- Extend existing element to alternate wavelength – compatibility with other recipes
- Re-optimize for sensitivity / selectivity / linearity
- Different background/matrix
  - All of the “normal” AED recipes were optimized for selectivity against ***carbon*** interference
  - Water in headspace GC
  - Silicon and Oxygen in Siloxanes

AED Recipe Creation

- HP 5921A AED
  - Simple recipes
  - Custom recipes could be created by the end user
  - Included as Part of AED "Pascal" ChemStation
- G2350A/G2370AA AED
  - Much more sophisticated recipe creation
  - Undocumented "Windows" GC ChemStation Recipe Creation Macro
  - Not distributed to end users

Overview of Process

Use Creation of a New Copper Recipe to Illustrate

- Select wavelengths
- Select standards
- Develop chromatographic conditions
- Acquire chromatogram with spectra
- Select signal and background diodes
- Optimize
- Evaluate recipe – sensitivity and selectivity
- Create element set and element group file

Selecting Wavelengths

- Wavelength tables
  - NIST Handbook of Basic Atomic Spectroscopic Data:

    http://physics.nist.gov/PhysRefData/Handbook/
  - "Persistent" Lines
  - High intensity
  - Emission is between ~ 170 nm and 800 nm
  - Coincides with an existing "FrameRef" allowing other elements to be analyzed in the same injection (and making recipe creation much easier)
- Molecular Bands?
  - Use reagent gases to form molecular species
  - O 171 (CO), N 388 (CN), C179 (CO)

Copper Recipe Example

Persistent Lines of Neutral Copper (Cu I)

Intensity	Wavelength (Å)	A_{ki} ($10^8 s^{-1}$)	Energy Levels (cm^{-1})	Configurations	Terms	*J*	Line Ref.	A_{ki} Ref.
100	2441.64	0.0201	0.000 40943.73	$3d^{10}(^1S)4s$ $3d^9(^2D)4s4p(^3P°)$	^2S $^4P°$	1/2 1/2	S48	M03
200	2492.15	0.0279	0.000 40113.99	$3d^{10}(^1S)4s$ $3d^9(^2D)4s4p(^3P°)$	^2S $^4P°$	1/2 3/2	S48	M03
1000	3247.54	1.37	0.000 30783.686	$3d^{10}(^1S)4s$ $3d^{10}(^1S)4p$	^2S $^2P°$	1/2 3/2	S48	M03
1000	3273.96	1.36	0.000 30535.302	$3d^{10}(^1S)4s$ $3d^{10}(^1S)4p$	^2S $^2P°$	1/2 1/2	S48	M03
150	5105.54	0.020	11202.565 30783.686	$3d^9 4s^2$ $3d^{10}(^1S)4p$	^2D $^2P°$	5/2 3/2	S48	FW96
200	5153.24	0.60	30535.302 49935.200	$3d^{10}(^1S)4p$ $3d^{10}(^1S)4d$	$^2P°$ ^2D	1/2 3/2	S48	FW96
250	5218.20	0.75	30783.686 49942.057	$3d^{10}(^1S)4p$ $3d^{10}(^1S)4d$	$^2P°$ ^2D	3/2 5/2	S48	FW96

NIST Handbook of Basic Atomic Spectroscopic Data

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Selecting Standards

- Standard must be able to pass through the GC inlet, column, and elute as a reasonable peak into the AED plasma.
- Thermal stability
  - Significant issue for organometallic compounds
- Synthesize?
- Purchase – may be limited options
- Solvent choice can impact stability of metal complexes

Copper Recipe - Standards

Copper Standard Compounds Considered:

- Copper Naphthenates
- Copper (III) ethylacetoacetate
- Copper (III) trifluoroacetylacetonate (Cu TFA)

Interference Compounds:

nC10, nC12, nC14, nC16 Paraffins

Standard Mixture Used:

- Cu TFA + Paraffins in Methylene Chloride

Chromatographic Conditions

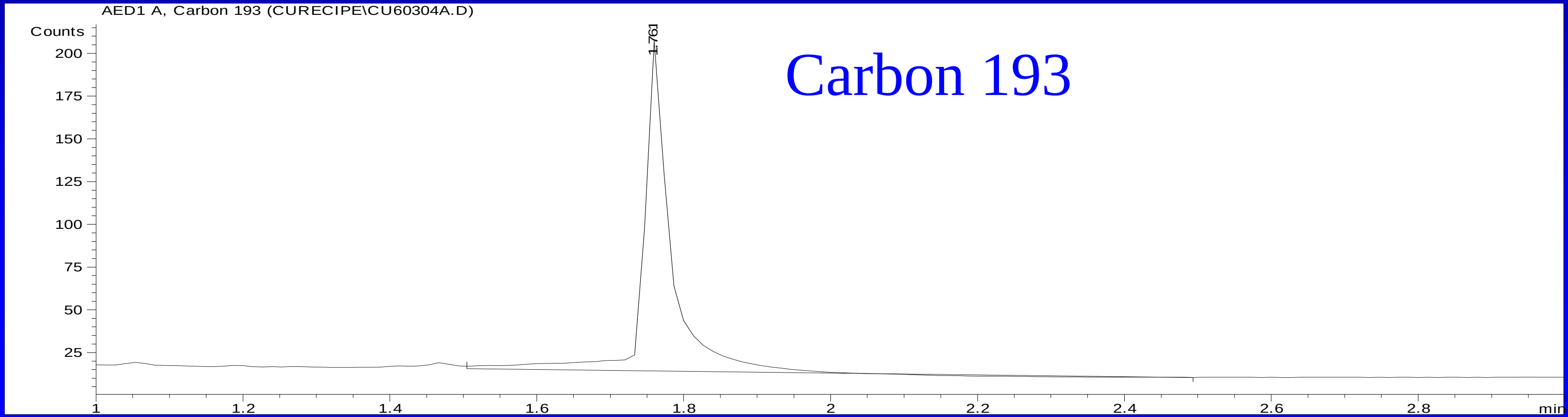
- Select chromatographic instrumentation and conditions to ensure standard elutes as a "peak"
  - PTV or On-column Inlet
  - Short column, high flow rates
- Need to be able to separate standard from "interference" peaks (usually hydrorcarbons)

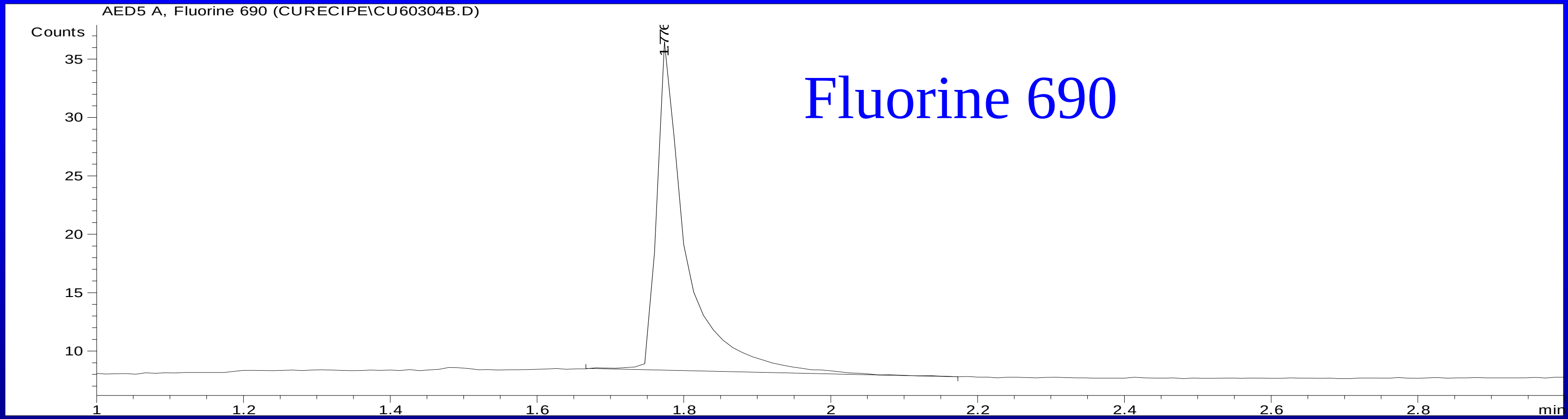
Copper Recipe
Running Standard Mixture

- You start out “blind” (recipe doesn’t exist)
- Include Carbon recipe (or other element in standard) in method to help determine retention time of standard – C 193 and F 690 for Cu TFA
- Acquire chromatogram and spectra using another element recipe from the same FrameRef – Sn 326
- Confirm copper spectrum exists at retention time of copper complex (decomposition?)
- Make initial “rough” recipe to aid with subsequent experimental optimization

Cu TFA Standard

Carbon 193 and Fluorine 690 Chromatograms





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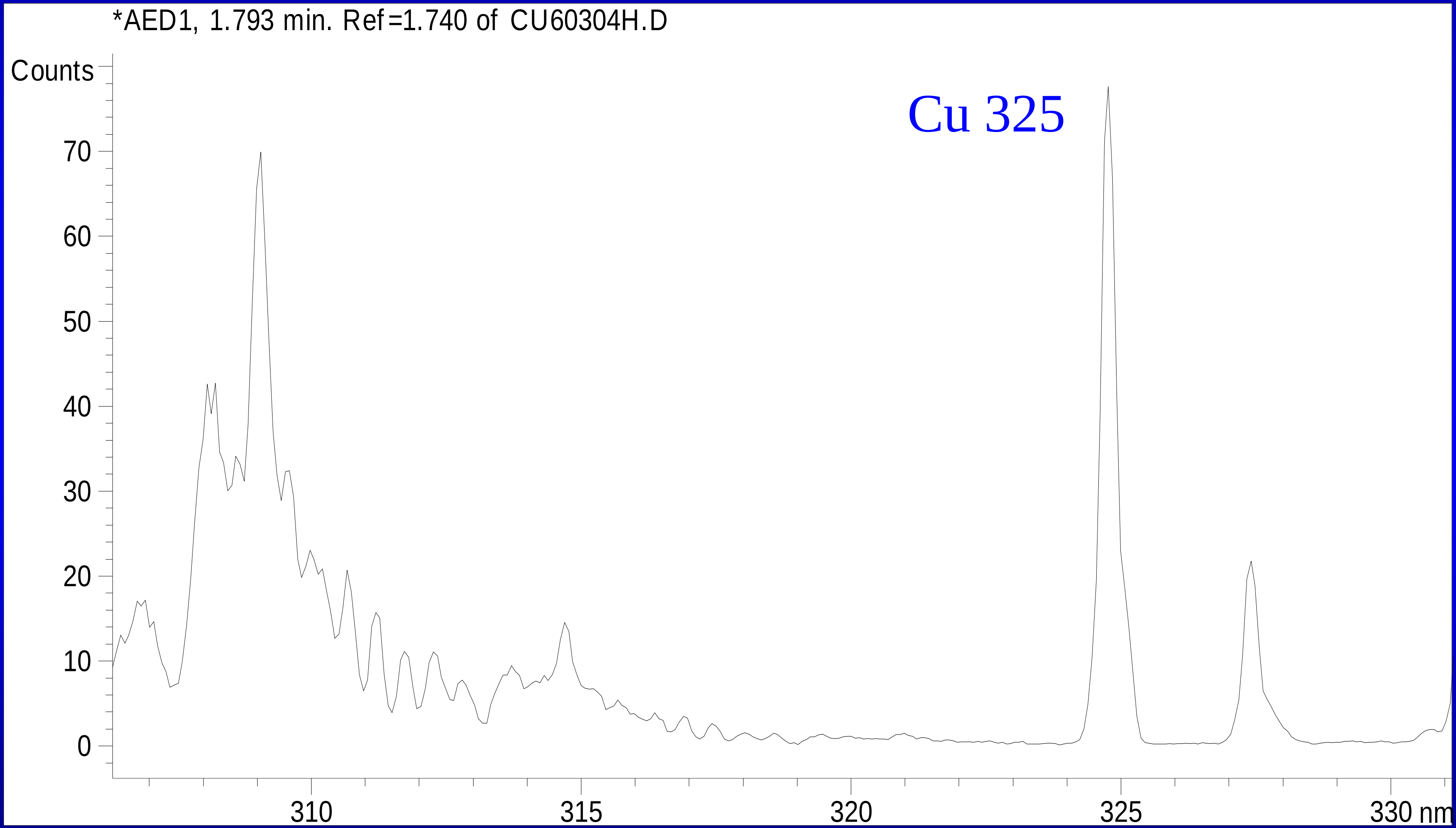
Spectrum of Frame 318 at Cu TFA Ret. Time



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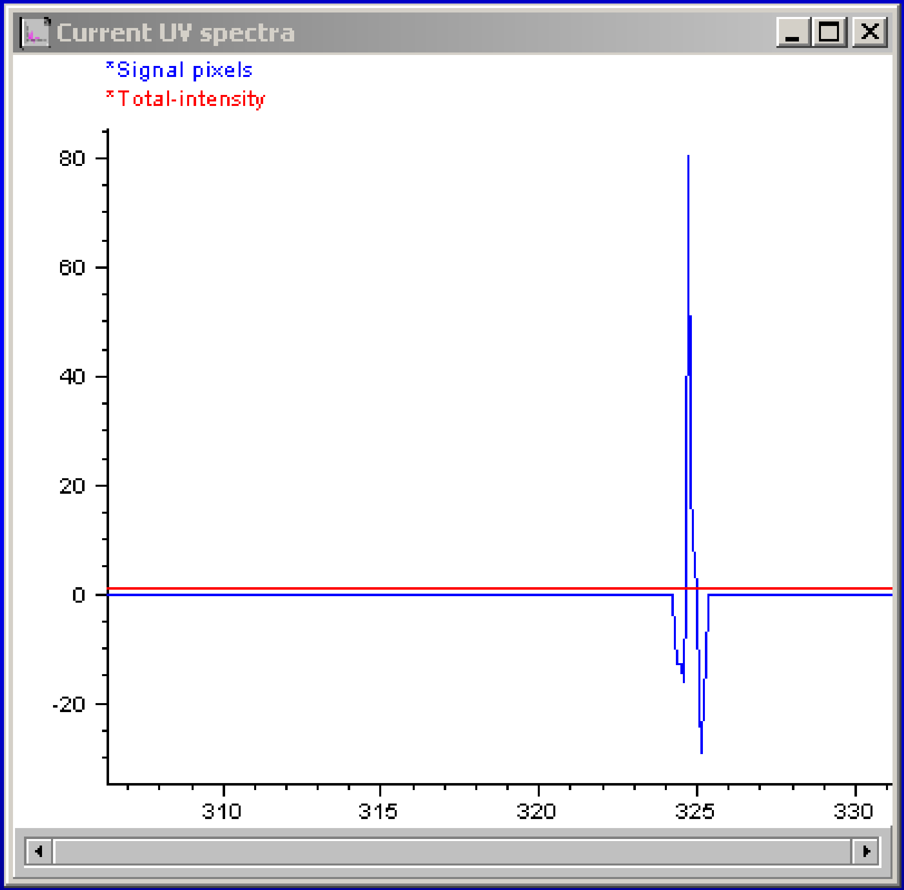
Run Recipe Macro

- Load data file containing the standard + interference chromatogram and spectra
- Specify Signal, Background, and Interference retention time ranges
  – Signal and Background Ranges used to optimize S/N
  – Signal and Interference Ranges used to optimize Selectivity

Select Signal and Background Diodes



Pixel	Wavelength	Factor
234	324.012	0.00
235	324.088	0.00
236	324.163	0.00
237	324.239	0.00
238	324.314	-7.61
239	324.390	-12.65
240	324.465	-12.65
241	324.541	-16.25
242	324.616	0.00
243	324.692	80.46
244	324.767	22.30
245	324.843	9.26
246	324.918	6.35
247	324.994	0.00
248	325.069	-19.61
249	325.145	-29.21
250	325.220	-17.43
251	325.296	-13.55
252	325.371	0.00
253	325.447	0.00
254	325.522	0.00
255	325.598	0.00

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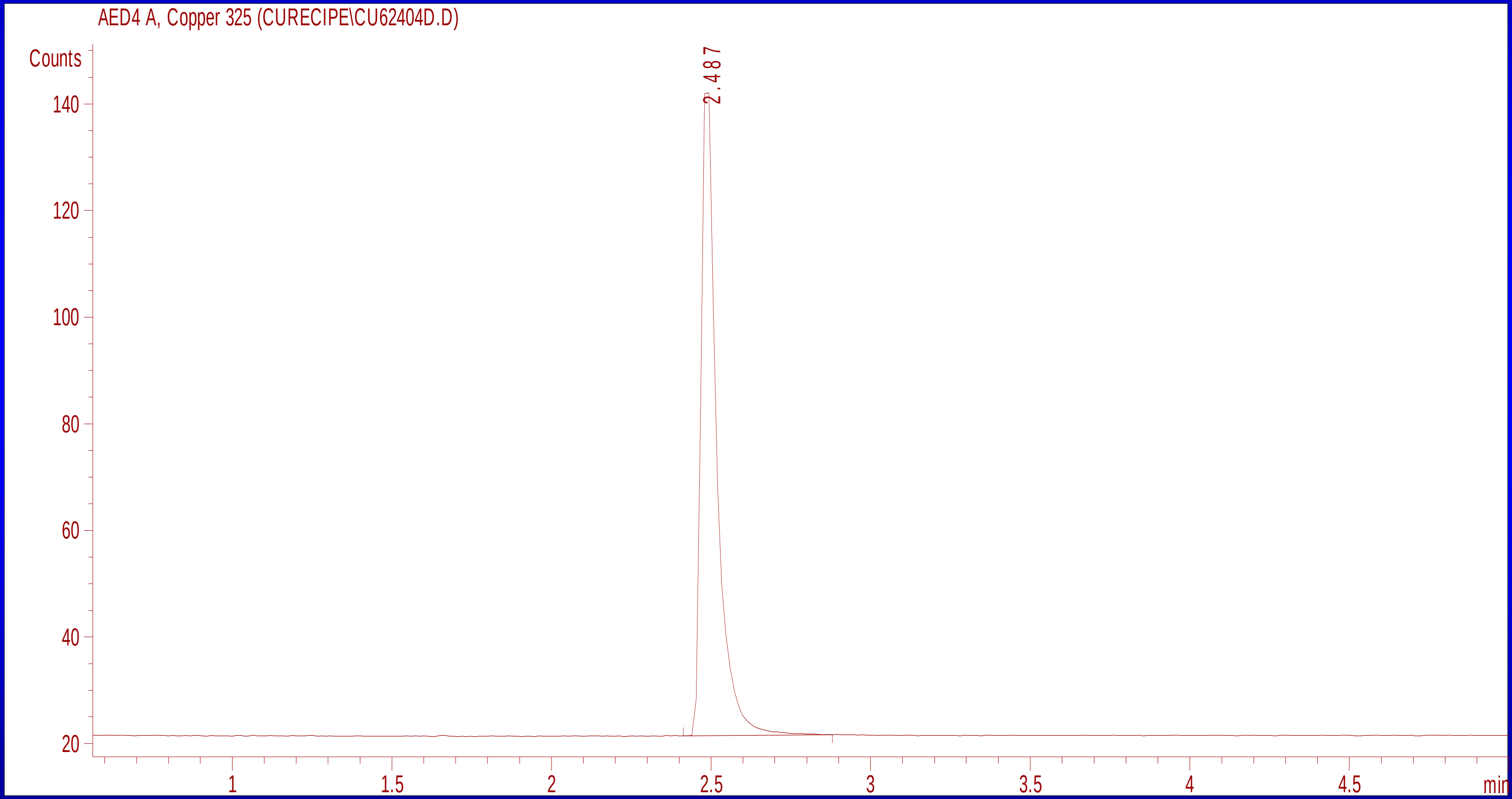
Optimizing the Recipe

- Recipe macro has optimization routine
  - Optimize for Selectivity
  - Optimize for Sensitivity
  - Optimize for Selectivity and Sensitivity
- Try different combinations of Signal and Background Diodes
- When finished, create the recipe file and test performance
  - Selectivity (inject interference mixture at high levels)
  - Linearity
  - Sensitivity

Copper 325 Chromatogram

Cu TFA Standard



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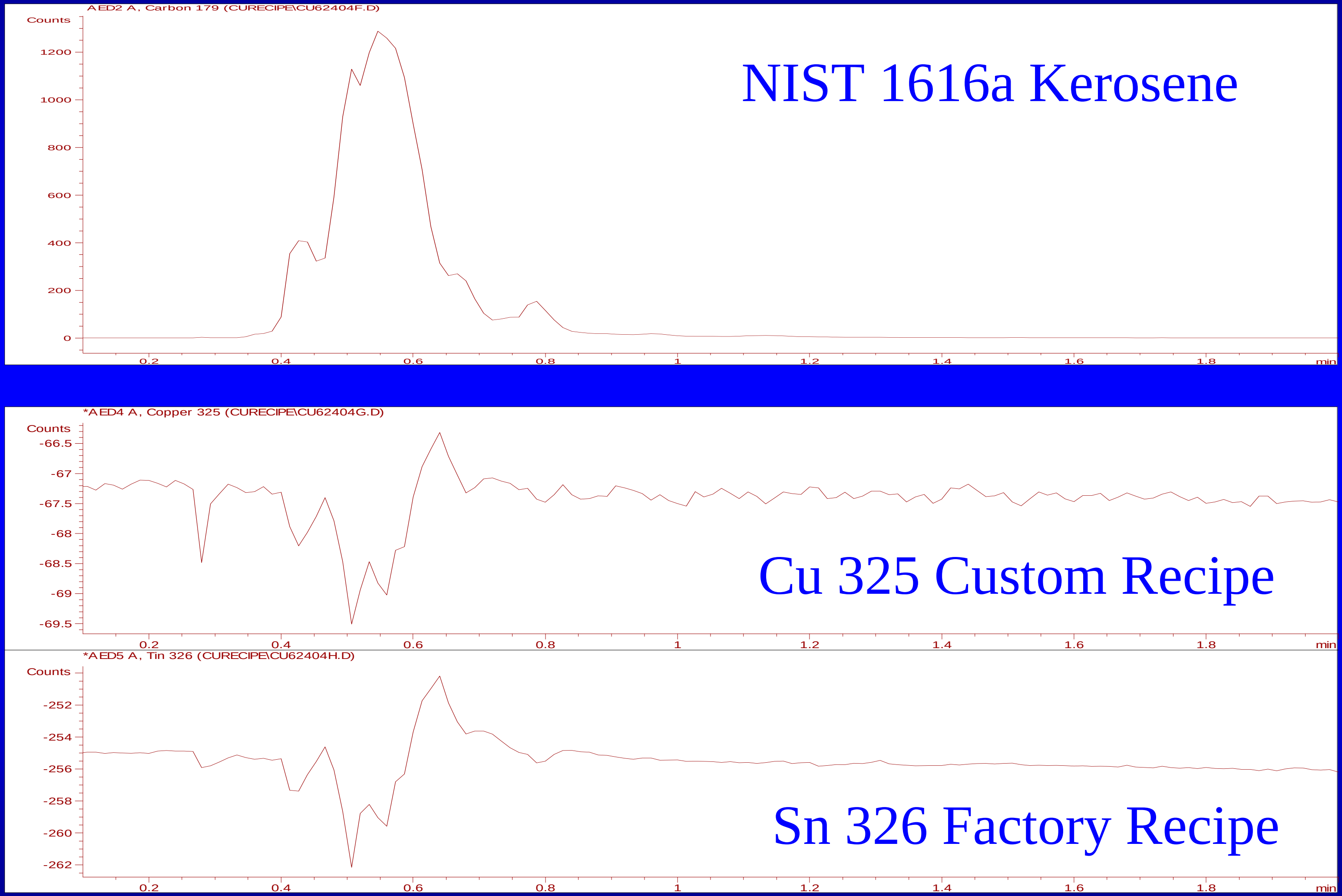
Selectivity Check



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Custom Recipe Disclaimer

- Factory recipes have undergone extensive performance tests on multiple instruments to establish specifications for sensitivity, selectivity, and linearity.
- It is impractical to perform similar levels of testing on custom recipes. Consequently recipe performance and applicability should be evaluated for each particular application.

Conclusion

Although not a trivial process, it is possible to create new recipes for the GC-AED to increase its flexibility and expand its usefulness.

Acknowledgements

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