Comparison of Non-radioactive Electron Capture Detector versus a Photoionization Detector for the Measurement of Diacetyl in Food

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Introduction

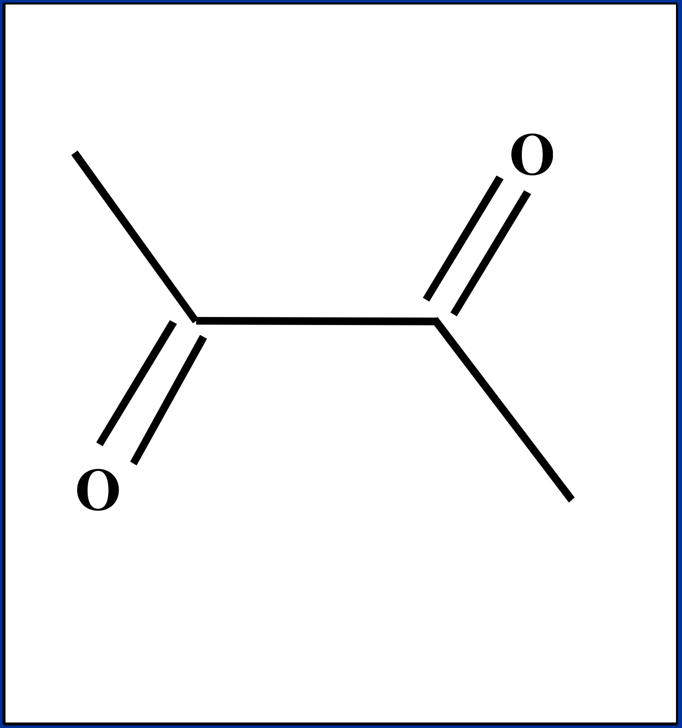
- Objective
- Characteristics of compound
    - Why we measure it
- DBD-ECD
- Analytical set up
- Chromatograms from food stuffs
- Lessons learned/conclusions

Objectives

- Diacetyl is a compound of concern
- Test non-radioactive ECD in real-world application
    - Identify issues with detector in use
- Evaluate the option of using PID or ECD to measure diacetyl
- Both ECD and PID detectors are AIC design
- Identify issues in measuring diacetyl in foodstuffs

Diacetyl: 2,3-butanedione

- Yellow liquid with butter like odor
- Found in butter*
- Also found in beer
- Added to margarine and popcorn as flavoring



* At least that is what I had read

Why would we want to measure it?

- In beer
  - Control/monitor the beer flavor
  - Identify problems with batch
- As a flavoring
  - Margarines
  - Popcorn
- Regulatory/Health and Safety
  - NIOSH investigation of popcorn manufacturing process
  - Method 1012, Method 2557

Diacetyl, Characteristics:

- MP; -4 to -6 C
- BP; 88 C
- MW; 86 g/mole
- Density; 0.99 g/mL
- IP; 9.3 eV
- Viscinal diketone
- Kovats: DB-1 ~560, DB-Wax ~ 975

Ideal GC candidate

Two detector alternative; ECD or PID?

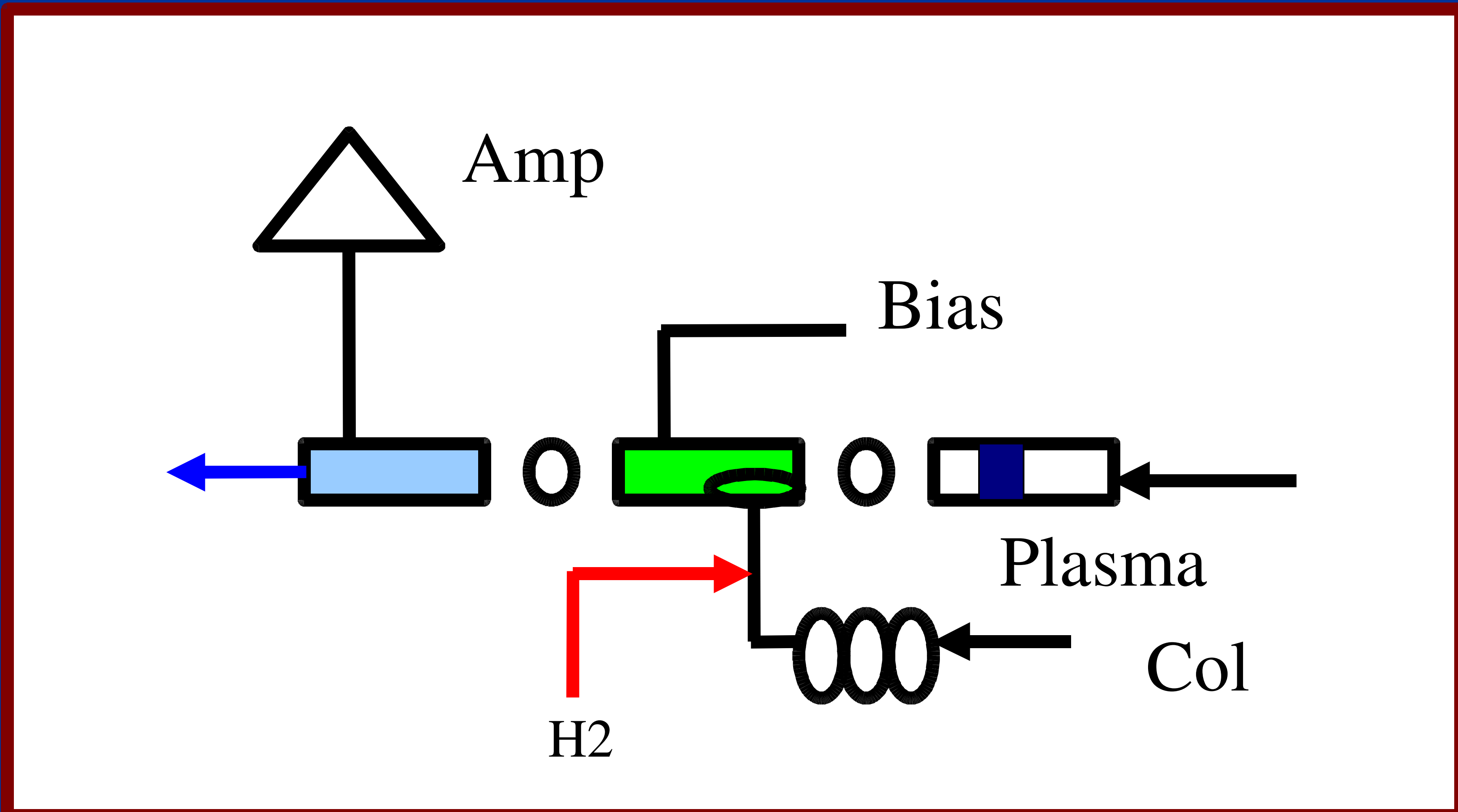
- ECD:
  - Advantages: highly sensitive, somewhat selective
    - Disulfides, diketones good ECD candidates
  - Disadvantages: requires clean operating system (gases, no leaks), limited linear range, **radioactive source**
- PID:
  - Advantages: highly sensitive, somewhat selective; only one gas required
  - Disadvantages: limited linear range, not as selective as ECD, lamp window may need cleaning.

One better than the other?

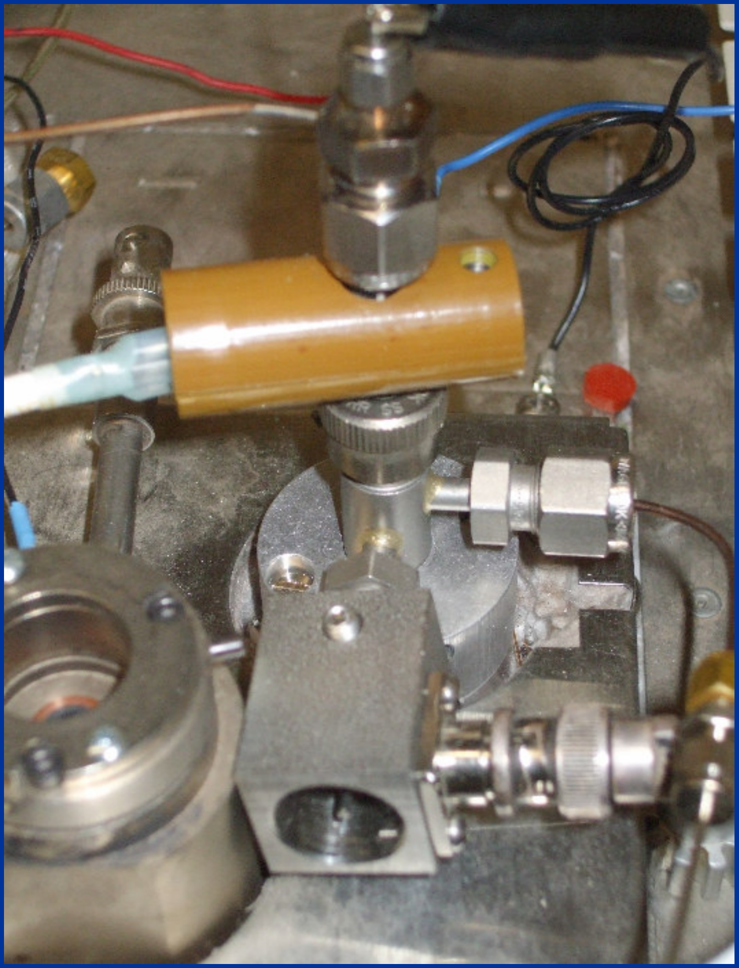
DBD-ECD eliminates biggest disadvantage of ECD detector: replace radioactive source

- DBD = Dielectric Barrier Discharge plasma
  - AC discharge across a dielectric barrier
  - Non-thermal discharge
  - Low electrode wear/large electrode surface
  - Ability to operate without getters/purging
- Simple design
  - Non-radioactive, windowless
  - Simple, robust power supply
  - Conventional electrometers

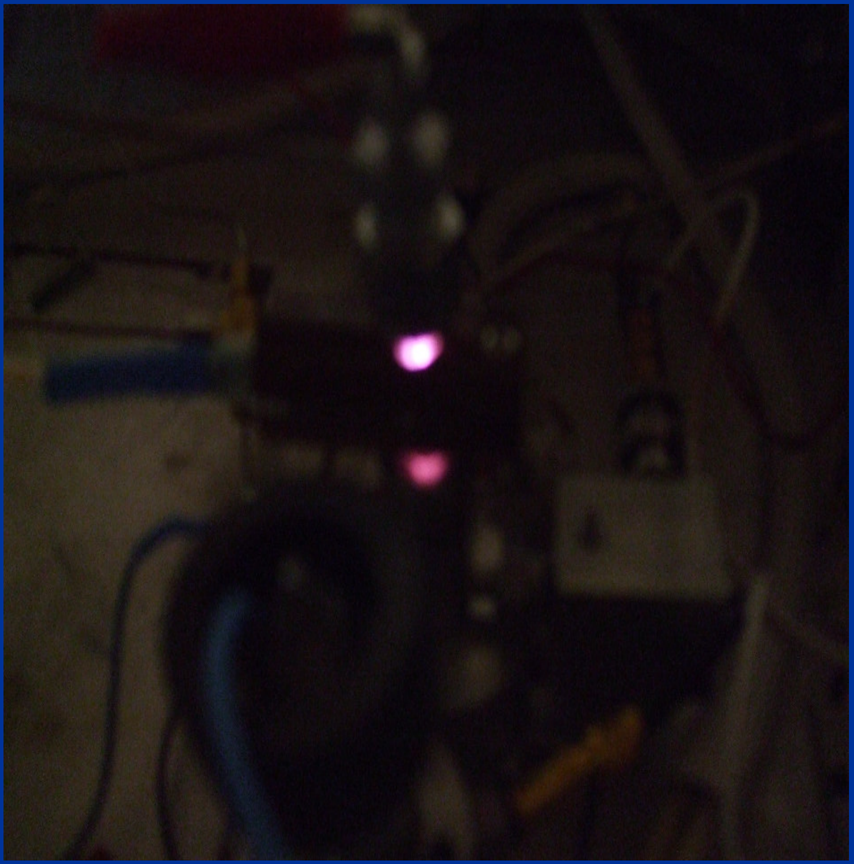
DBD-ECD Schematic:



Detector Picture



Installed on Varian 3400



Helium plasma color

Analytical set up: extraction

- Headspace Extraction (beer, butter, margarine)
  - Sample material into 20 mL VOA vial
  - 3 grams butter or margarine, 15 mL beer
  - Heated for 10 min at 50C in GC oven
  - 4 mL room air into vial, 3 mL vial air out
  - Aliquot transferred to GC using warm syringe
- Popcorn
  - Un-popped and microwave popped
  - From the bag, syringe into bag to withdraw sample
- Standards prepared in warmed static dilution bulb

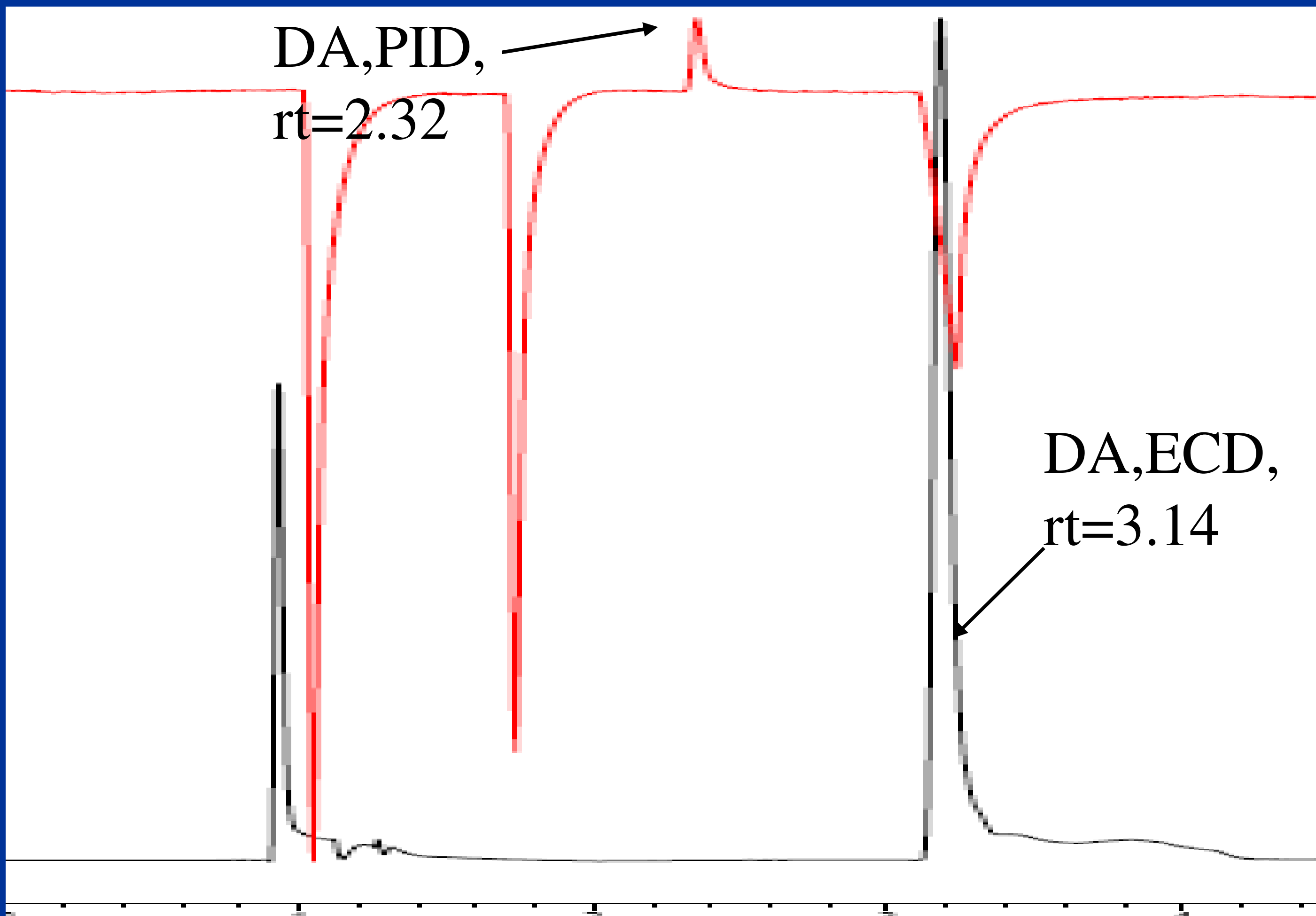
Analytical set up: instrumental

- HP 5890 A
  - 6-Port sample valve, 0.1 mL loop (65C)
  - Dual column configuration; Valco T inside oven
  - 30 meter RTX-VMS, 0.25 id X 1.4 film to ECD
  - 30 meter RT-Stabiliwax, 0.25 id X 0.5 film to PID
  - Flow rate: 6 mL/min (split to both columns)
  - Oven program: 55C/6 min/14C/min/95 C/1 min
- Dual column configuration
  - Allows for confirmation (unsure of early interferences)
  - Real time, direct comparison of detectors (same sample to both)
  - Allows evaluation of ECD selectivity

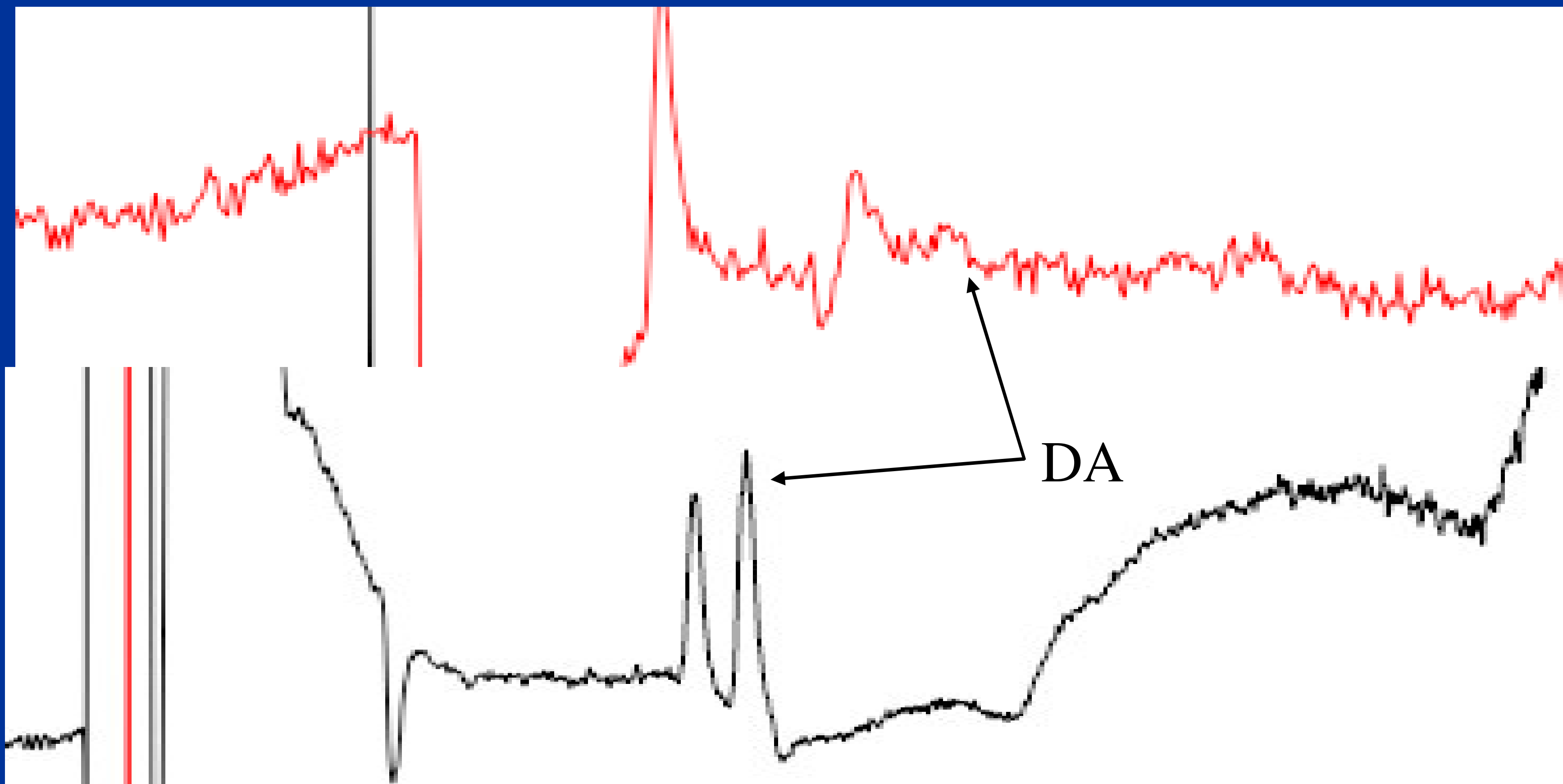
Instrumental set up; Dual Detectors

- DBD-ECD
  - Non-radioactive source (dielectric barrier discharge)
  - Uses helium reaction gas (five 9's), hydrogen dopant
  - Copper plumbing, no extra purification, typical GC flow controllers
  - Stacked electrode configuration
  - Uses HP 5890 ECD electrometer (N2 mode)
- In-house PID Detector
  - 10.2 eV lamp
  - Stacked electrode configuration
  - Use HP 5890 FID electrometer
  - Hydrogen sweep gas (10 mL/min)

Standard chromatogram both channels; 800 pg/column

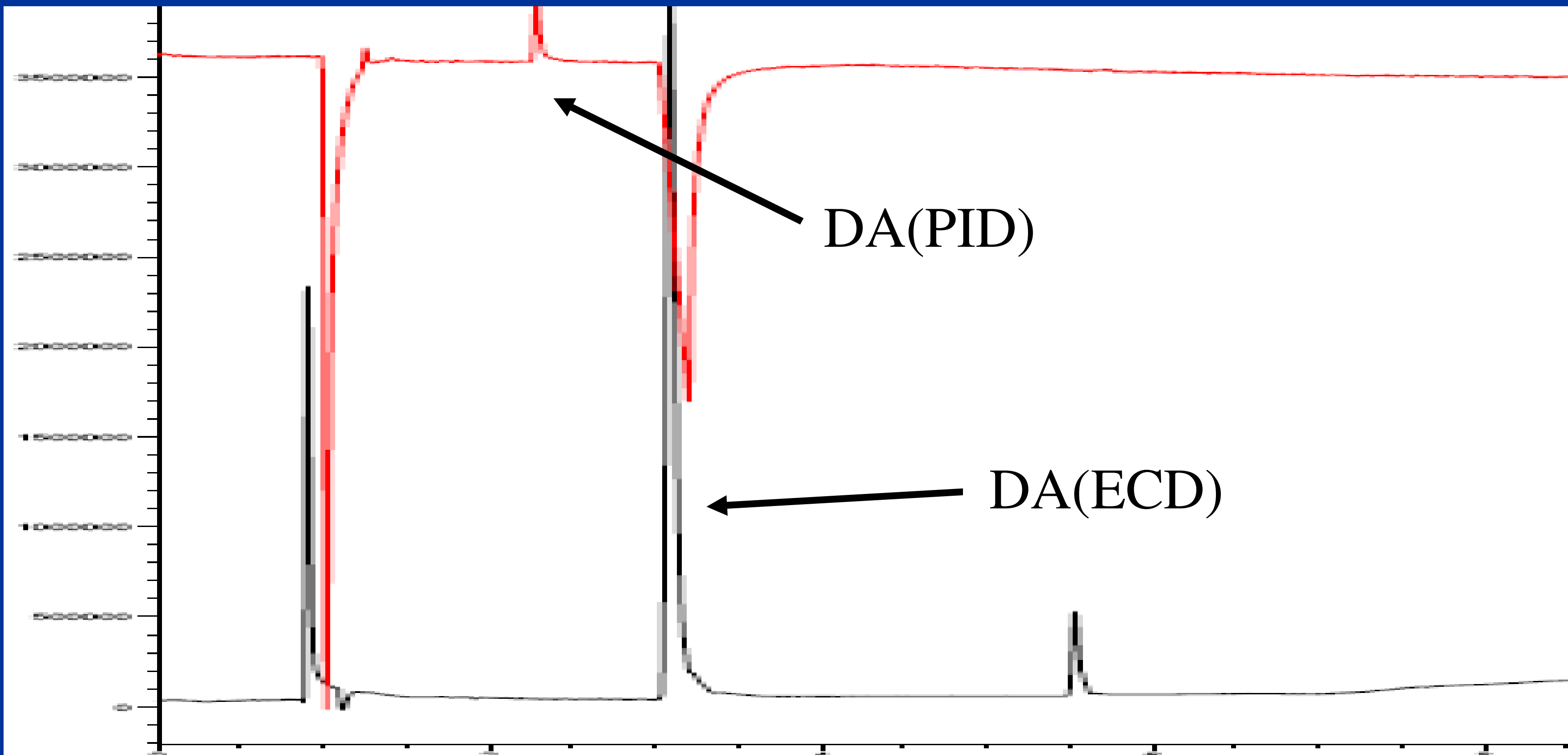


Butter (3 gram extraction)



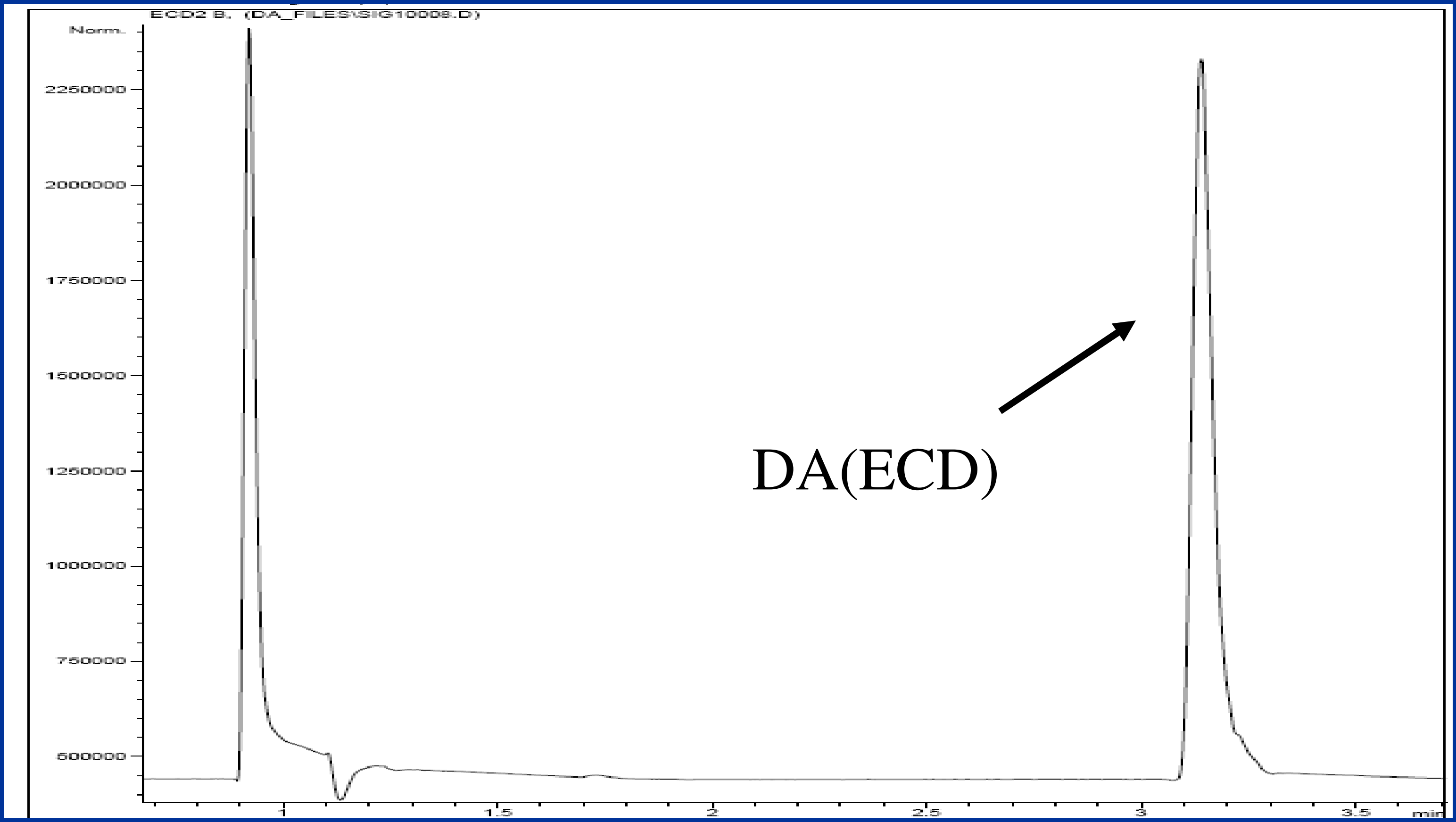
DA not detected (PID); very low on ECD*

Margarine; both channels



Much higher levels than butter

Margarine; ECD channel

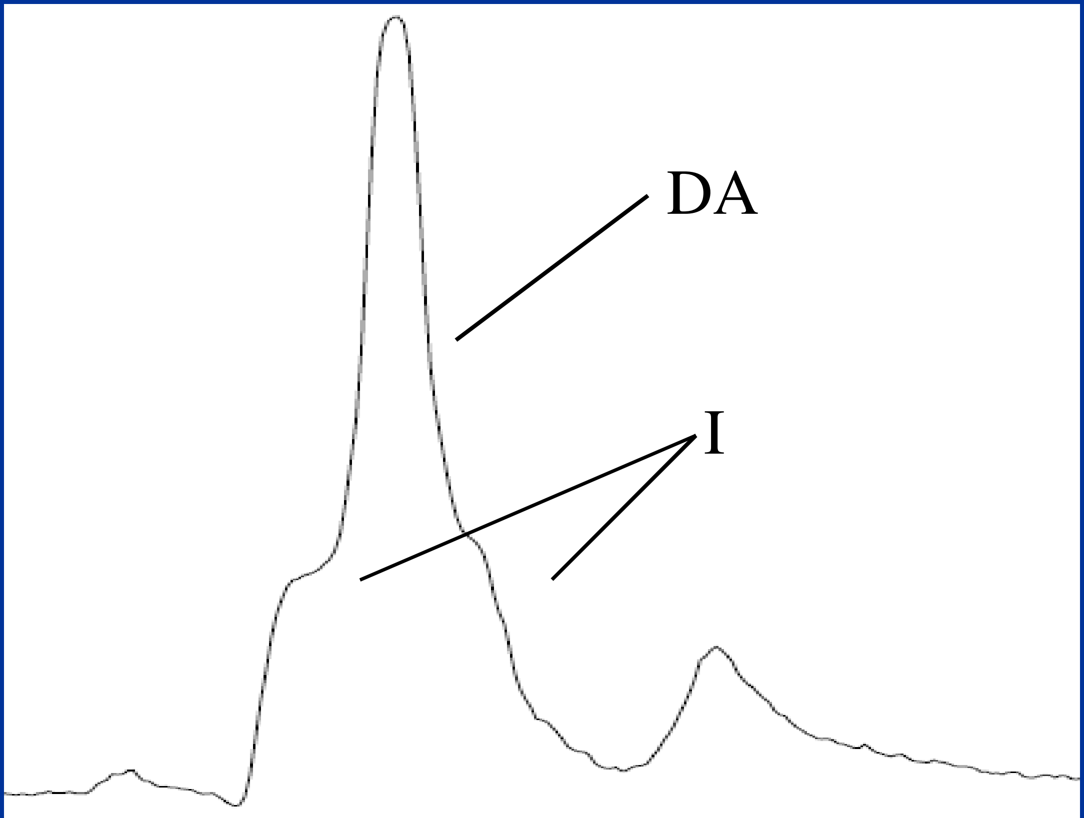


No significant interferences

Comparison of two margarines and agreement between ECD and PID

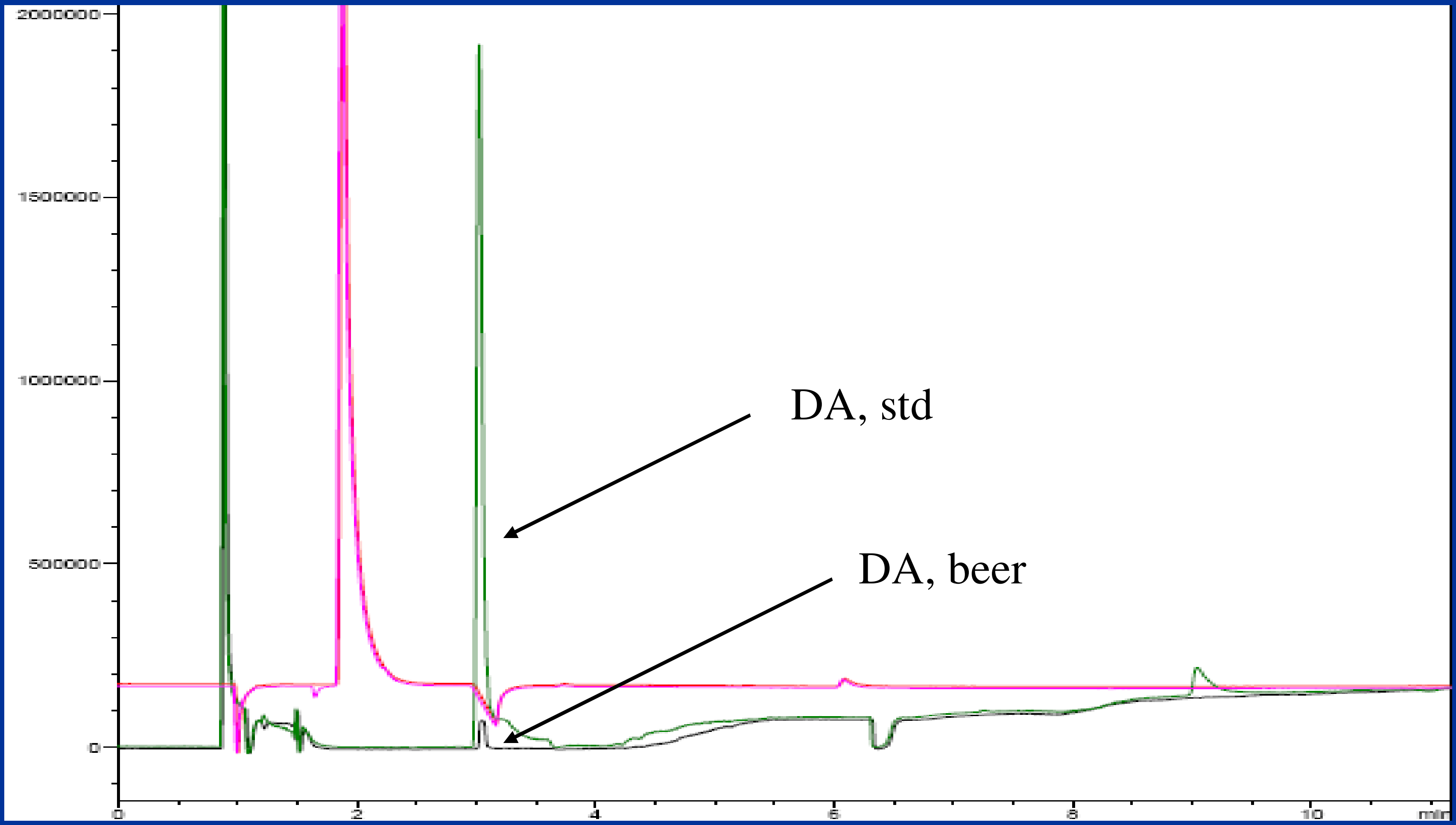
	DA PID	DA ECD	PID/ECD	ng/g (ECD)
M1	5.89	7.07	0.83	58.88
M1 xt	9.72	10.29	0.94	85.78
M2	13.97	13.32	1.05	111.02
M2 xt	18.37	16.42	1.12	136.81

Chromatogram from freshly opened stout

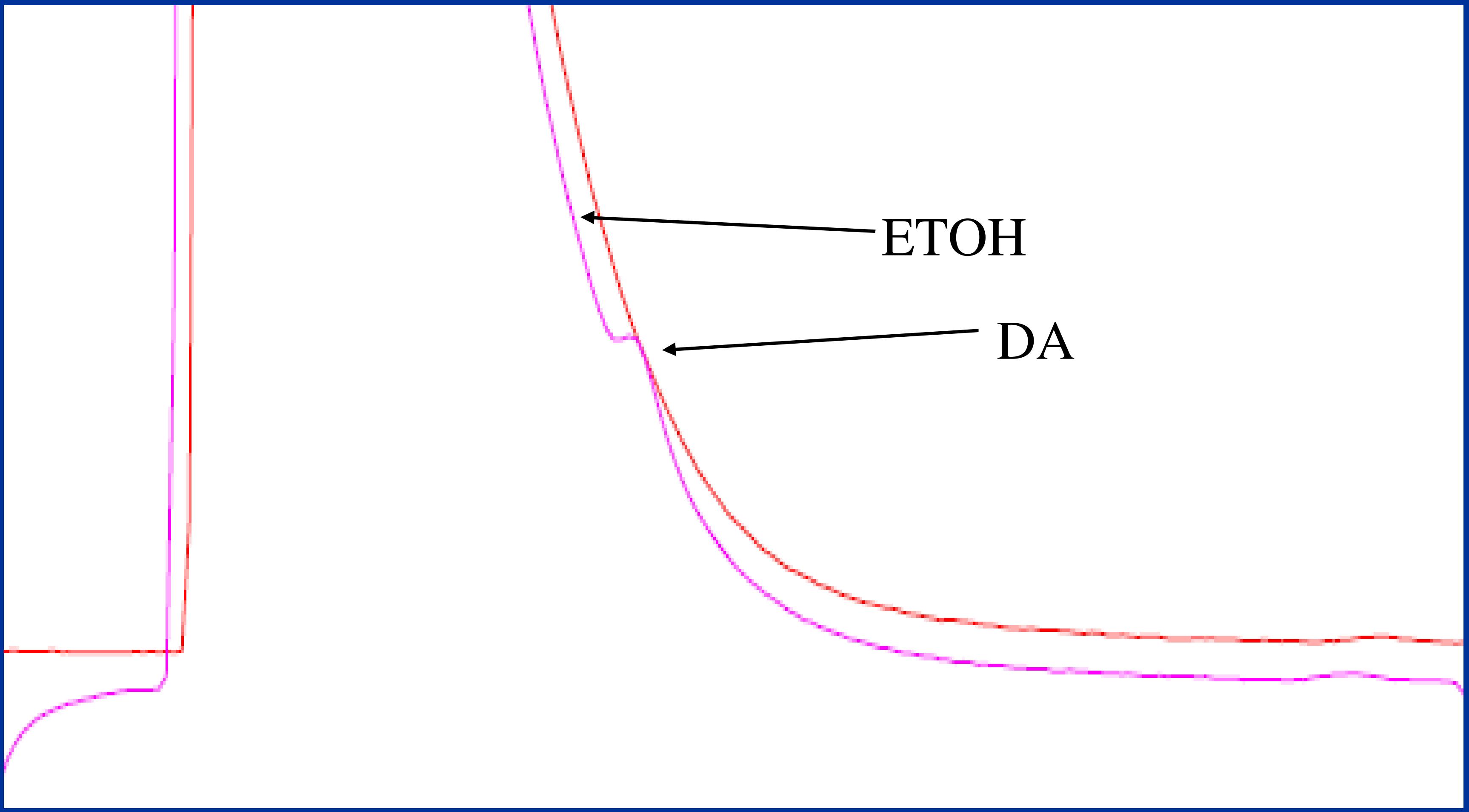


Even ECD subject to some interferences

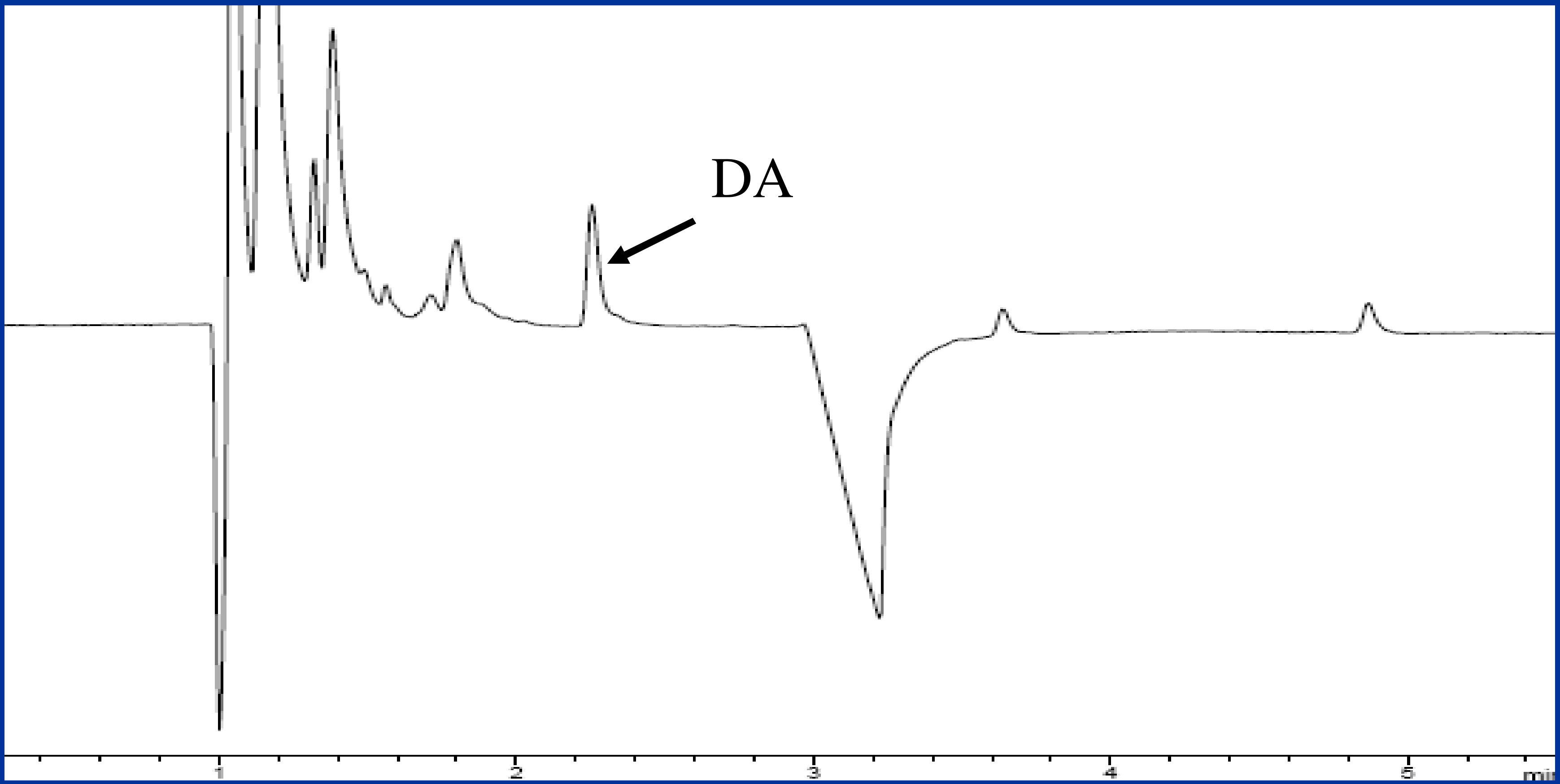
Chromatogram from flat beer co-injection, both channels: ECD clear of interferences



Chromatogram from flat beer co-injection: PID channel subject to interference



Chromatogram from freshly popped popcorn (PID)



Significantly less on second analysis (sample cooled)

Lessons leaned or,

"If you want to do Diacetyl in food..."

- Headspace optimization advisable
    - Longer incubation yields more sensitivity
    - Carbonation not an issue under these conditions
- Need a better way to sample popcorn
    - Sample portion of a bag
    - Should be microwave safe
    - Sample very wet directly after popping
    - Sampling immediately after popping
- Dual column configuration advantageous
    - Especially if using PID's or FID's
    - Subject to interferences (especially ethanol)

Conclusion, Diacetyl in food stuffs

- Clearly evident in margarine, beer, popped popcorn
- Levels much lower than expected when starting out
  - Could be a function of headspace conditions
  - Lower levels in the flat beer than the fresh beer
- Very low concentration in butter (??)
  - Much higher levels in margarine than butter
- Difference in levels between two margarines
  - But is it significant?

Conclusion, ECD vs. PID

- Both ECD and PID can be used to measure Diacetyl
  - Depends on the levels you need to measure
- ECD
  - Much, much better detection limit
  - More selectivity
- PID
  - Sensitive enough for some samples (margarines)
  - Subject to interferences (i.e. ethanol)
  - Able to detect other constituents (see beer and popcorn)
- Good agreement between two detectors when free of interferences

Conclusion, DBD-ECD

- Dielectric Barrier Discharge can be used as a source for ECD
  - Stable plasma source, using five 9's helium
  - Does not require getters or specialized plumbing
  - Uses conventional ECD electrometers
- DBD-ECD very sensitive to viscinal diketones
- DBD-ECD selective
  - Absence of significant ethanol peak in beer analysis
- DBD-ECD non-rad source eliminates ownership issues
  - No licensing, swiping, custody issues
  - Can be easily dis-assembled and cleaned