Characterization of a Non-radioactive Electron Capture Detector Based on the Dielectric Barrier Discharge Plasma

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Introduction

- Discussion of the radioactive ECD
- DBD-ECD
    - Principle of operation
    - Advantages of the DBD
- Data from the DBD-ECD
- Exemplary applications
- Future work
- Conclusions

The ECD Detector

- Derived from Lovelock's argon ionization detector
- Uses radioactive source emitting high energy Beta
  - Typically Ni-63 or Tritium
- Beta particles collide with heavier gas generating "thermalized" electrons
- Electrons in detector set up a standing current
  - High background signal
- Constituents of interest enter detector and capture electrons
  - Results in a decrease in standing current forming the basis of the chromatographic response

The ECD Detector: Advantages

- Highly sensitive to some constituents
  - Halogenated hydrocarbons, especially multiply substituted (CT, some pesticides, PCBs), predominant application
  - Nitro compounds, especially multiply (DNT, TNT, etc....)
  - Disulfides, diketones
- Selective
  - Take advantage of differences in sensitivity to simplify the chromatography
- Can be very stable
  - A bit of explanation is in order here... (HID, comparison to TCD?, routine production)

The ECD Detector: Disadvantages

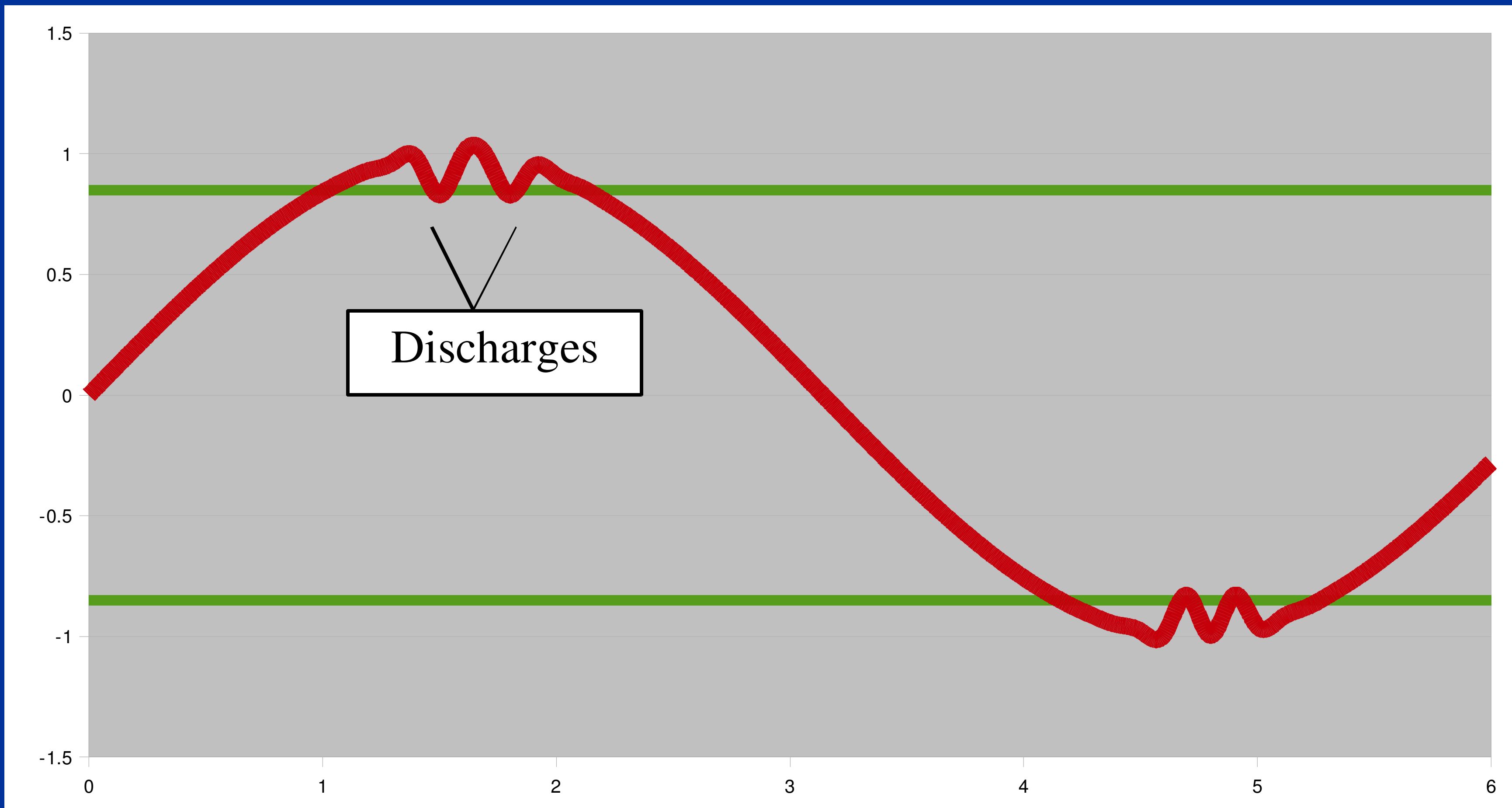
- Needs high purity gases/no leaks
  - Oxygen and water suppress signal
- Limited linear range
- Widely varying responses (CF vs CT)
- Radioactive source:
  - Subject to licensing requirements/shipping restrictions
  - In US, subject to annual monitoring for escape
  - Prevent thermal runaway: migrate Ni into foil
  - Hydrogen exchange (for tritium foils)
  - Long term liability (custody, disposal, etc...)
  - Difficult to get it clean

Dielectric Barrier Discharge (DBD)-ECD detector: use DBD to 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
  - Low valve disturbance, packed column compatible

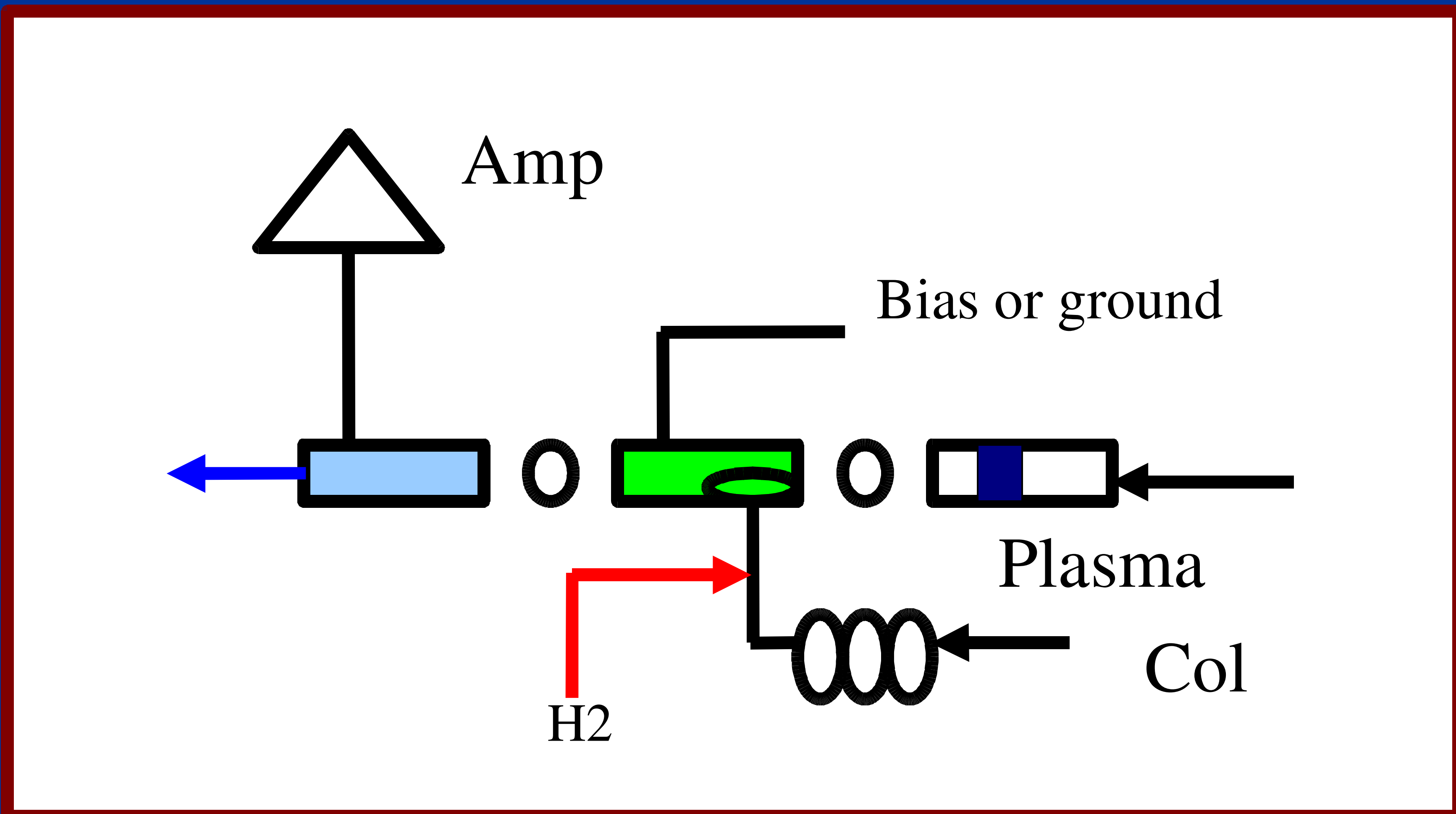
Dielectric Barrier Discharge is key

Discharge Cycle

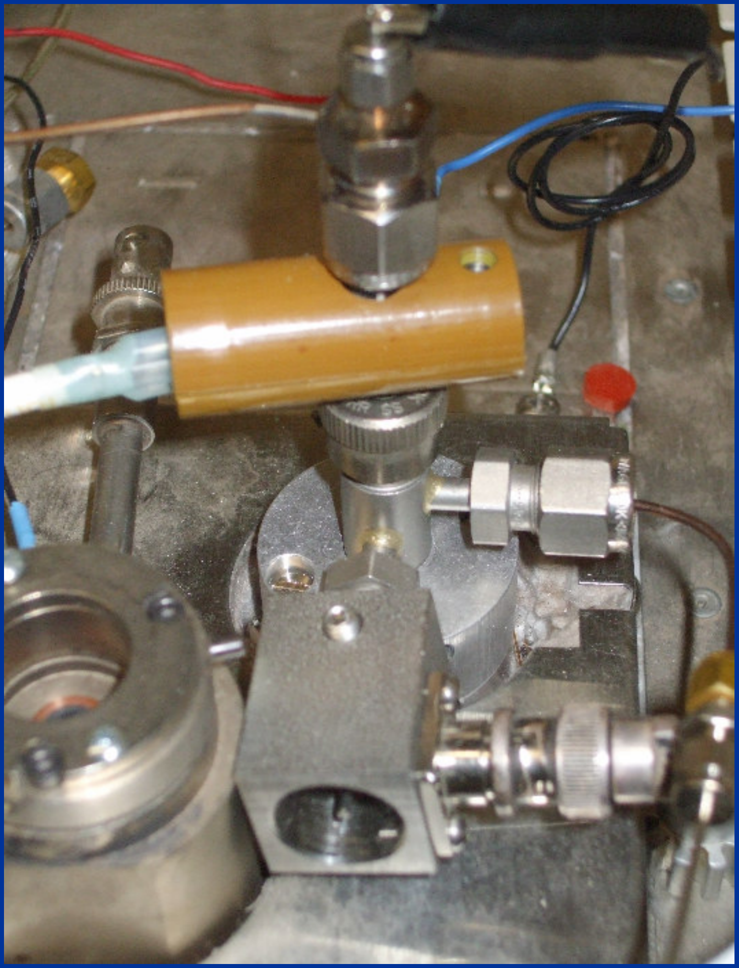


Multiple discharges per ½ cycle; operating at ~30 kHz

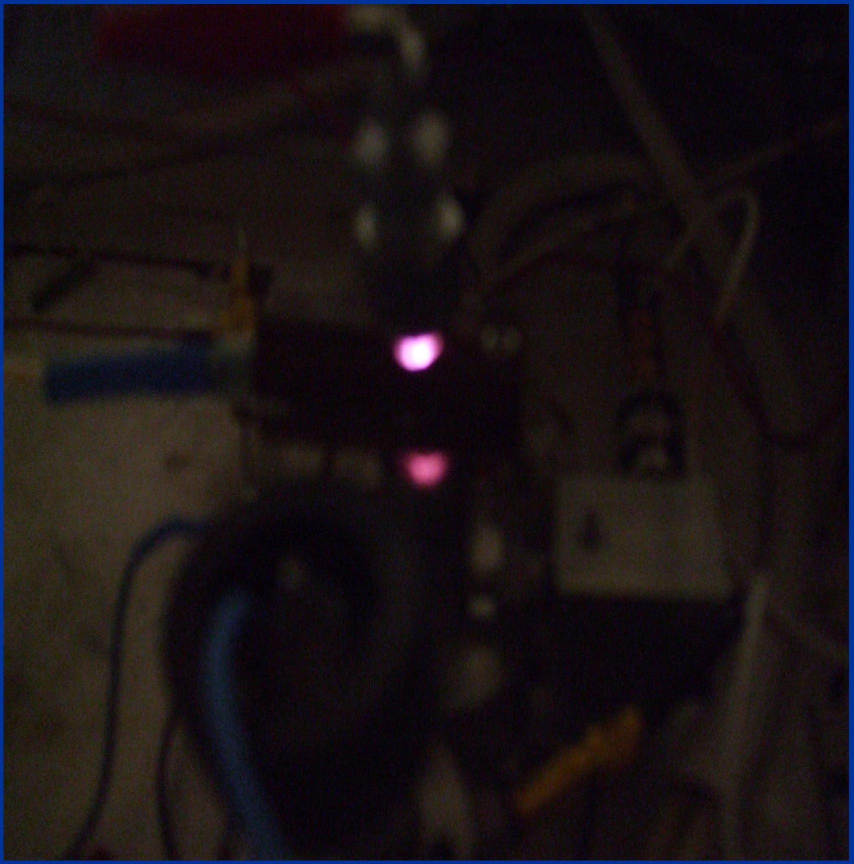
ECD Schematic



Detector Picture



Installed on Varian 3400



Helium plasma color

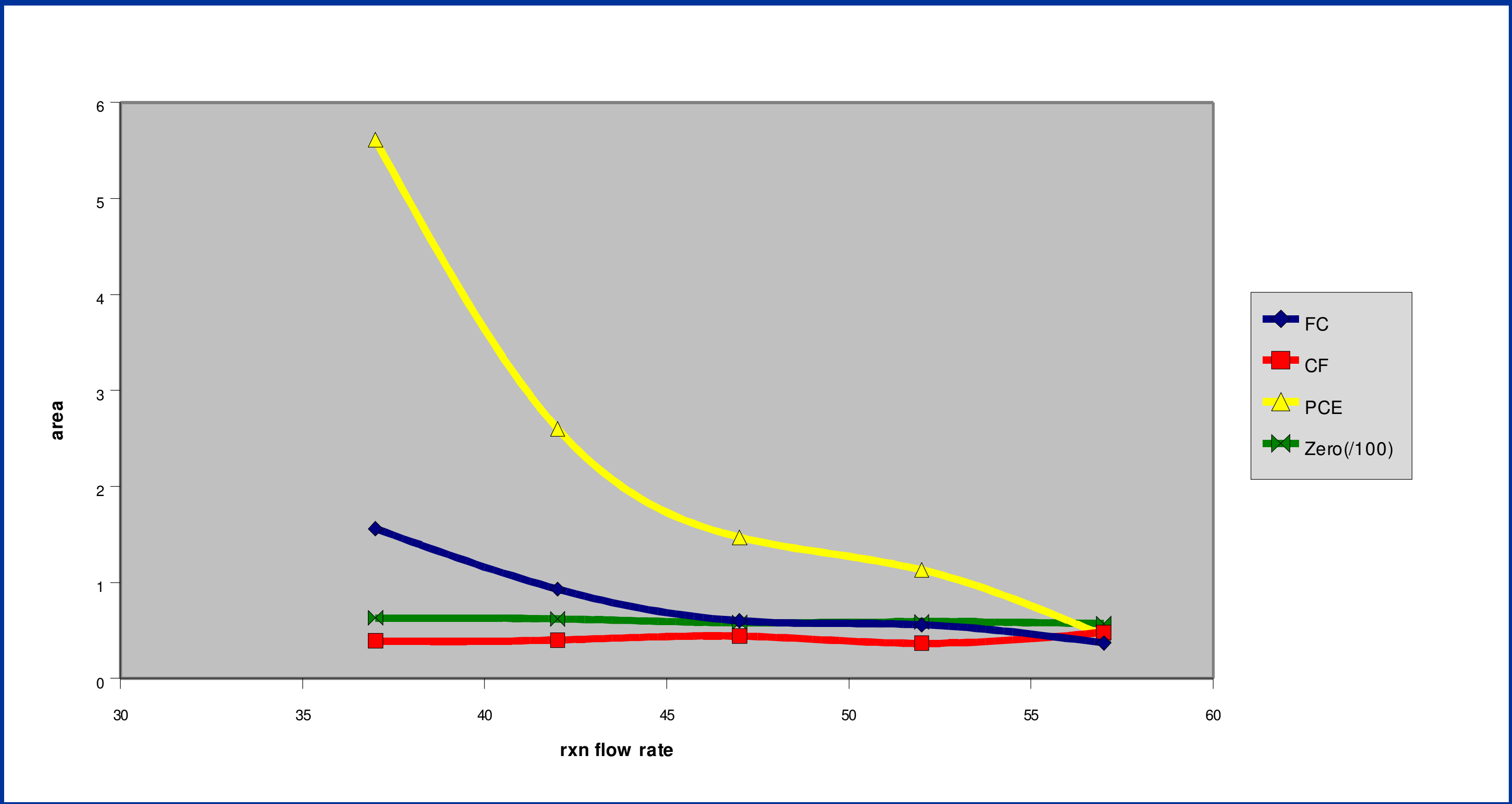
DBD-ECD Evaluation Set Up

- HP 5890 GC:
    - 6 port injection valve 250 ul loop
    - 30 m X 0.25 RTX-VMS, 1.4 film, helium carrier
    - Temp. programmed oven (35-105C)
- Detector
    - DBD-ECD in constant current mode
        - Standard DBD power supply
    - Standard HP 5890 ECD electrometer
    - Helium reaction gas, hydrogen dopant
- Evaluation Standard
    - F113 (50ppb), Chloroform (80ppb), PCE (60ppb) in compressed air

DBD-ECD data, or "Being aggressive does not always help."

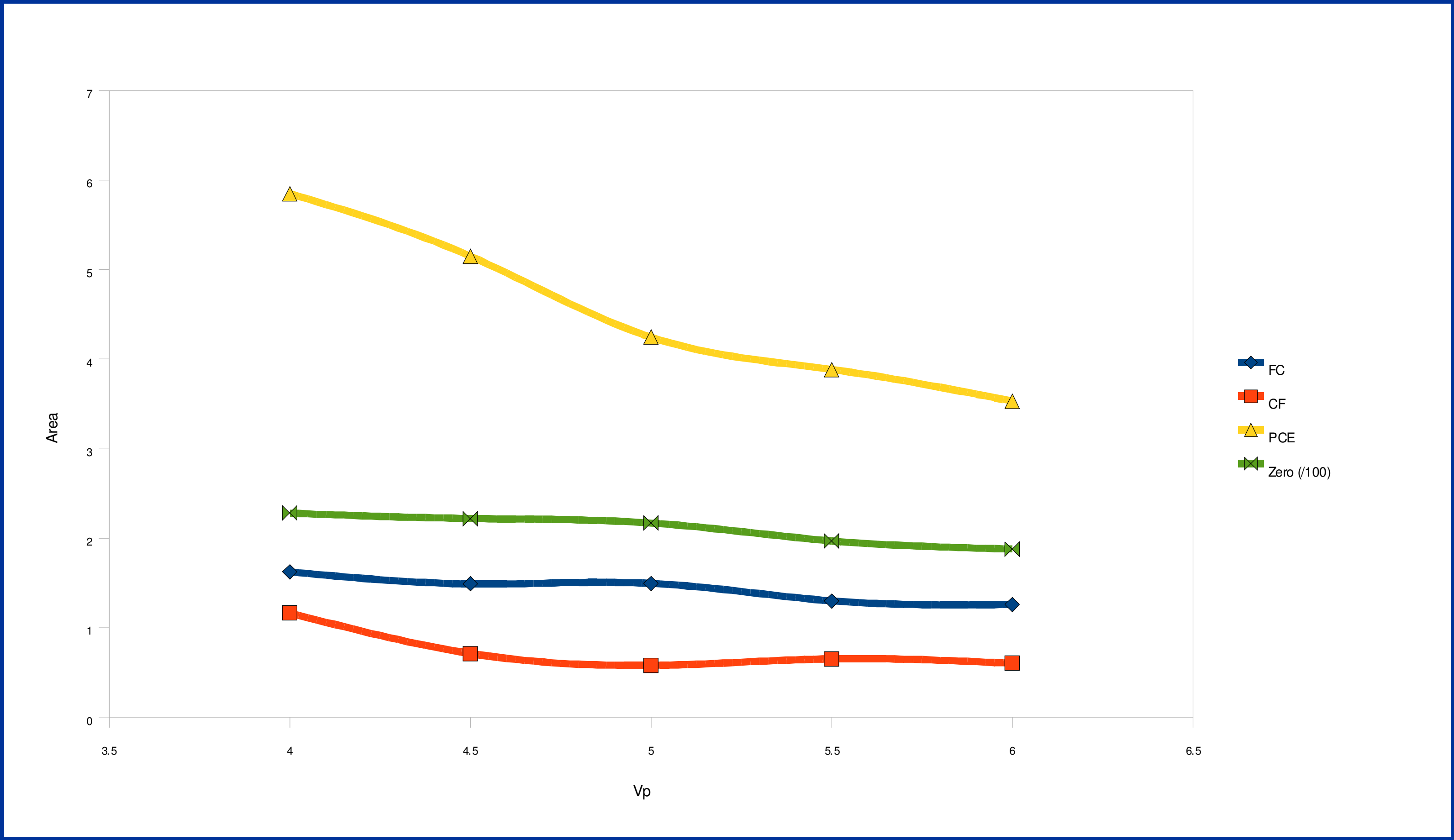
- Can take the standing current anywhere we want to
  - Does not necessarily help the sensitivity
- PCE considered a dissociative component
  - Most susceptible to changes in conditions?
- For me, easiest to understand to most difficult

Effect of helium flow rate (reaction gas)



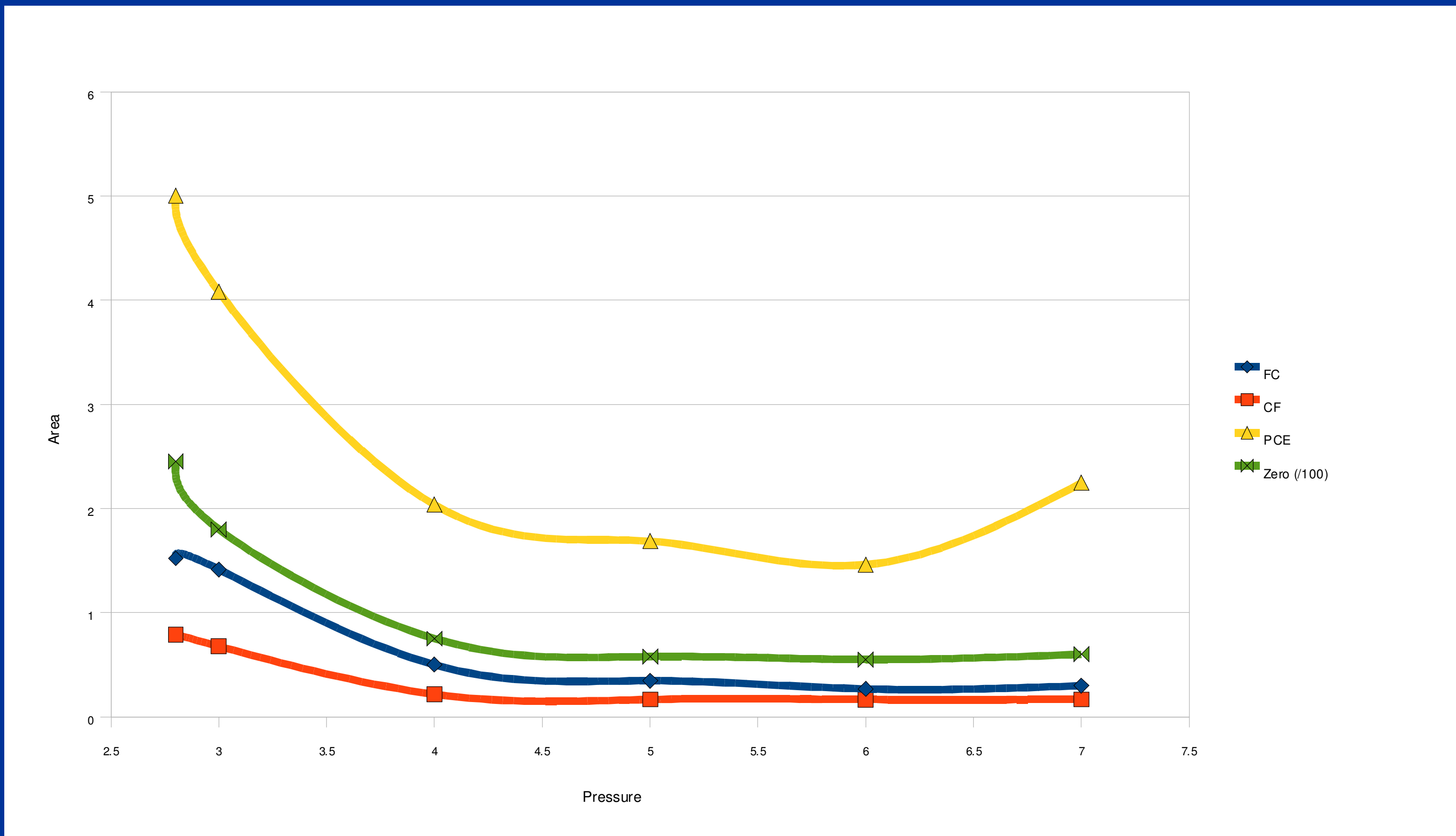
ECD concentration dependent detector; nitrogen incursion

Effect of primary power



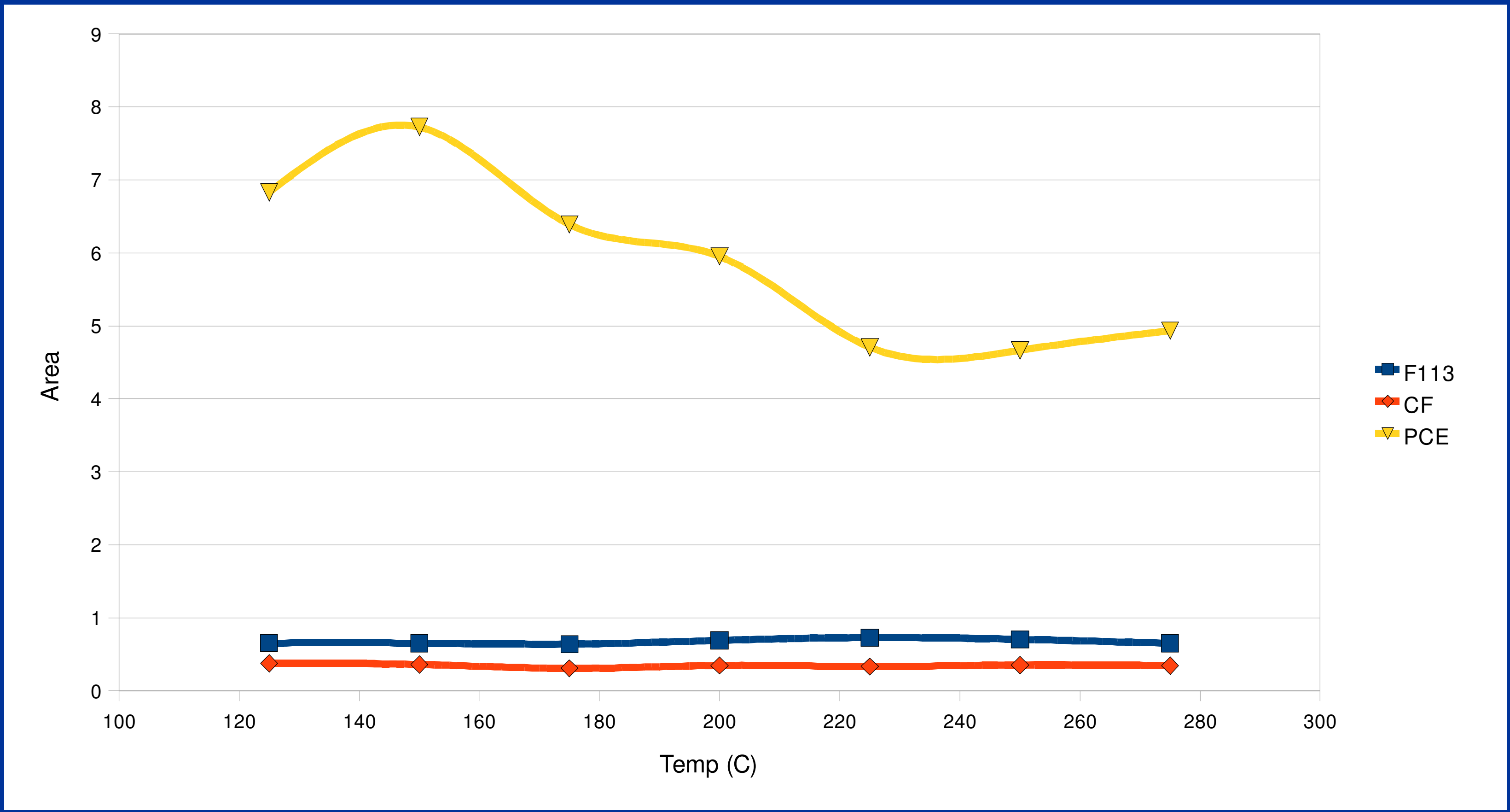
Ionization; non-thermal electrons?; off axis plasma

Effect of dopant gas



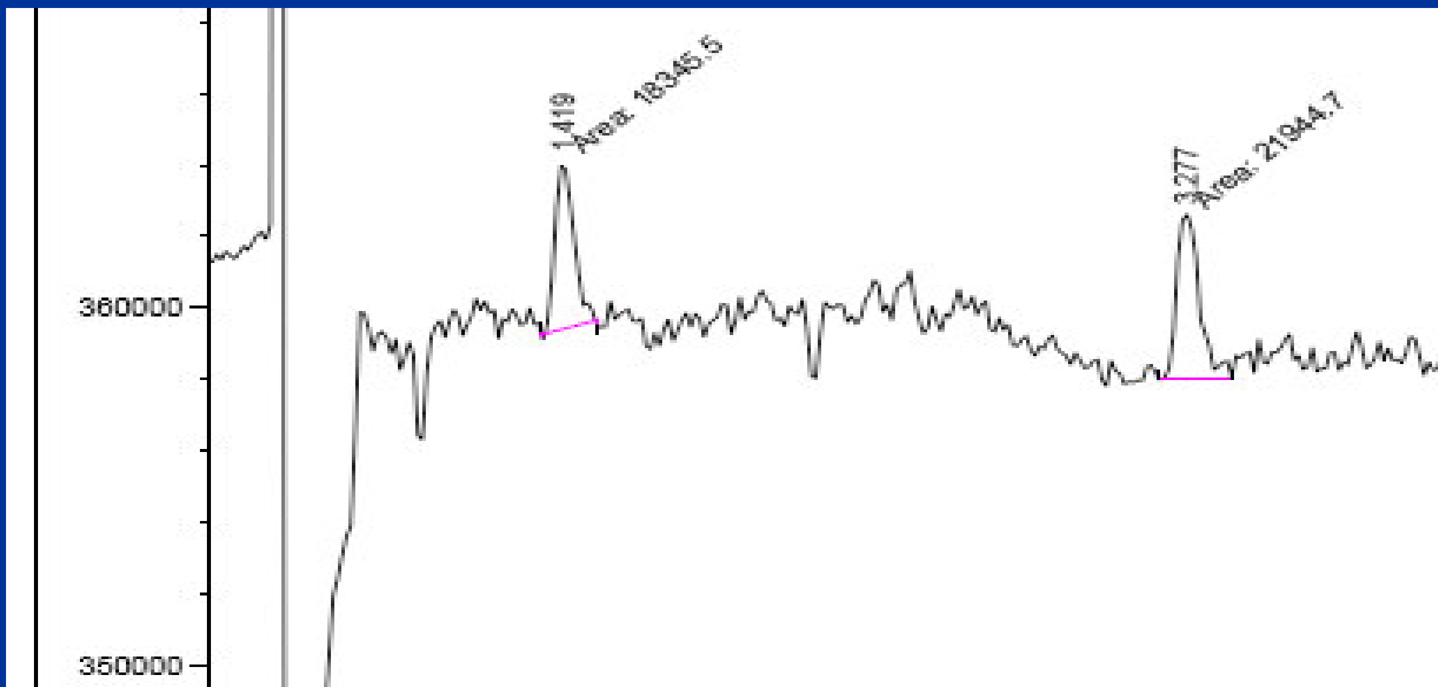
Change in 0; so much i(standing);fundamental difference with Wentworth; tight control of dopant

Effect of temperature



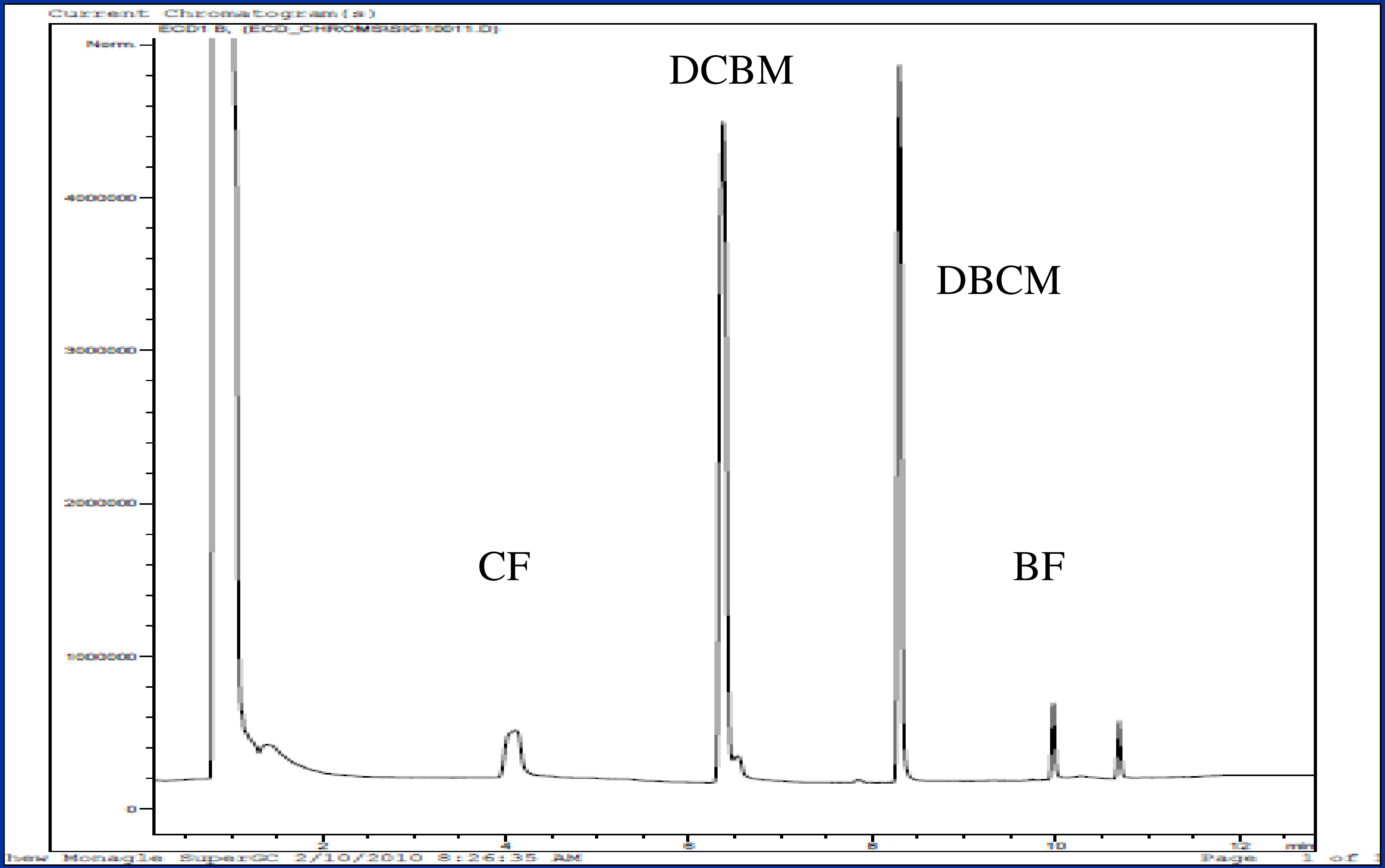
Most puzzling; dissociative (II); follows trend of Wentworth

First look at detection limits; 0.5 pg on column, FC and CF

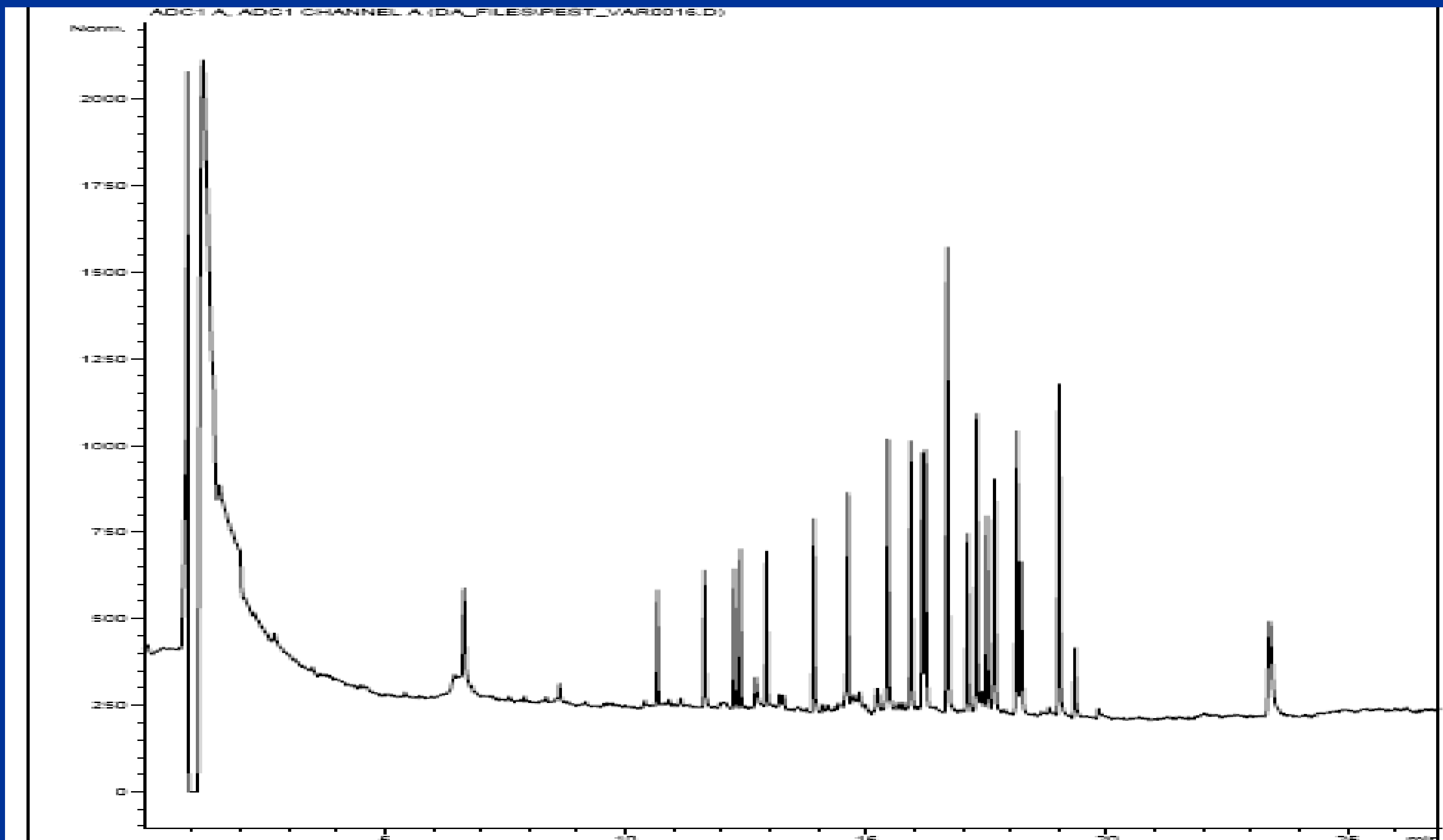


Looked at PCE; want to look at nitrogen dopant

Trihalomethanes in Drinking Water headspace extraction

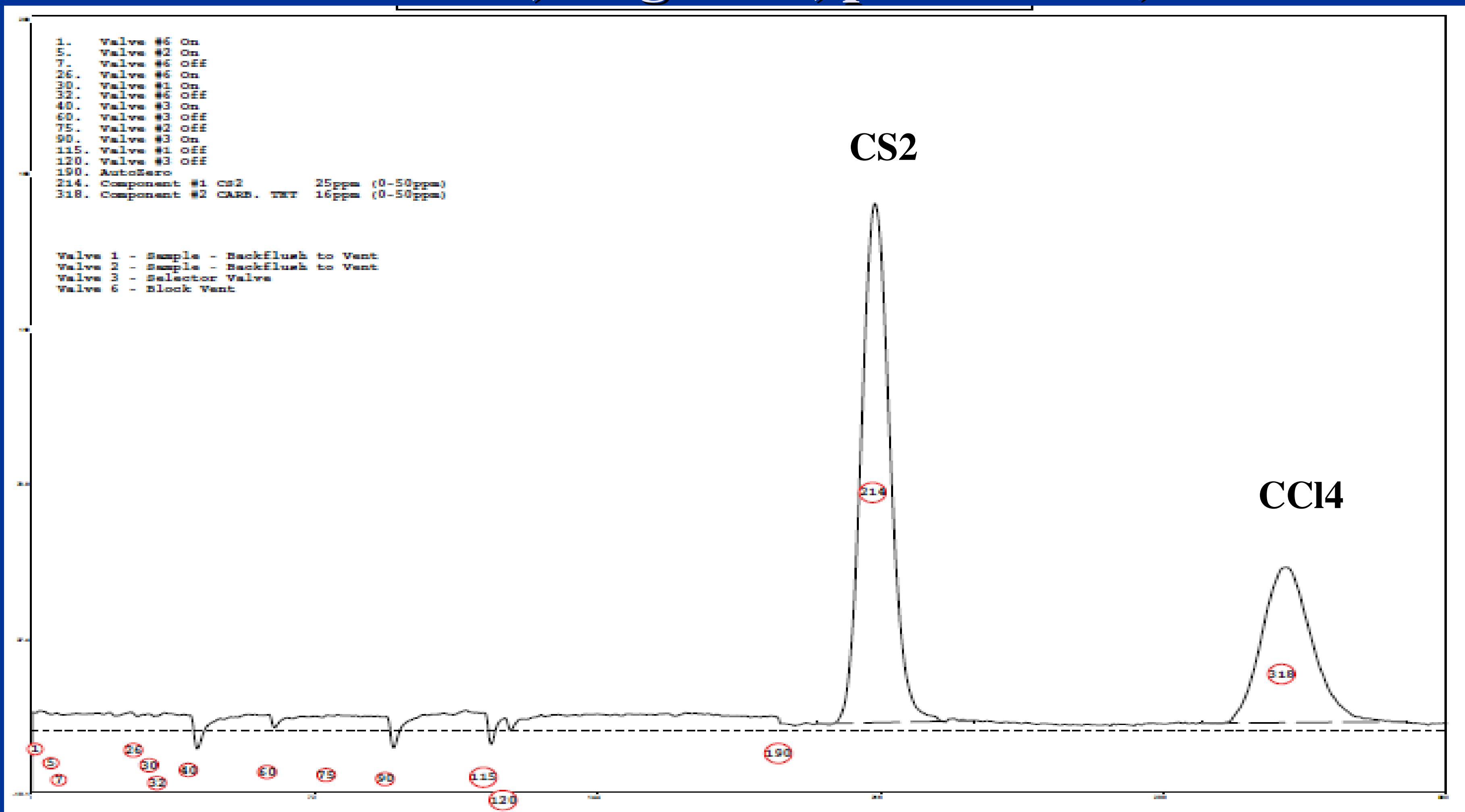


40 ppb pesticide standard; Varian 3400; HP-1, 30 m X 0.32 X 0.25 film, 250/275 65/1/14/125/10/265/10



Carbon Disulfide and Carbon Tetrachloride in air

(packed columns, multiple valves, 70:1 split, 2 loop volumes, no getters, process GC)



Further Work

- Nitrogen as a dopant source
  - Compare linearity and detection limits to hydrogen
- Continued exploration of physical design
- Application to heavier components
  - In particular, Pesticides and PCBs
- Beta prototype in commercial laboratories

DBD-ECD effective substitute for radioactive ECD

- Large/Stable/Non-radioactive Metastable Source
- Able to use common laboratory gases
  - Helium and hydrogen/nitrogen
  - No extra purification required (no getters)
- Able to use existing electrometers
  - Simple to implement
  - Able to take advantage in software integration
- Disadvantages
  - Basically the same as a radioactive ECD (varying sensitivity, two gas supplies, limited linearity, clean gases, leak free system) except,
  - Tight control of dopant necessary