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Using the Dielectric Barrier Discharge Detector in an Electron Capture Mode

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The ECD Detector

- Uses radioactive source emitting high energy Beta
 - Typically Ni-63 or Tritium
- Beta particles collide with detector gas generating “thermalized” electrons
- Electrons in detector set up a standing current
 - Generally 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 selective constituents
 - Halogenated hydrocarbons, especially multiply substituted
 - Nitro compounds, especially multiply (DNT, TNT, etc....)
 - Disulfides, diketones
- Selective
 - Take advantage of differences in sensitivity to simplify the chromatography
- Can be very stable
 - Constant temperature/flow conditions

The ECD Detector: Disadvantages

- Radioactive source:
 - Subject to licensing requirements/shipping restrictions
 - In US, subject to annual monitoring for escape
 - Long term liability (custody, disposal, etc...)
 - Very difficult to get it clean without sending it in, cannot clean in the field
 - Prevent thermal runaway: migrate Ni into foil
 - Hydrogen exchange (for tritium foils)
- Limited linear range, widely varying responses
- Needs reasonably high purity gases/no leaks
 - Oxygen and water suppress signal

DBD-ECD detector: use DBD plasma to replace radioactive source

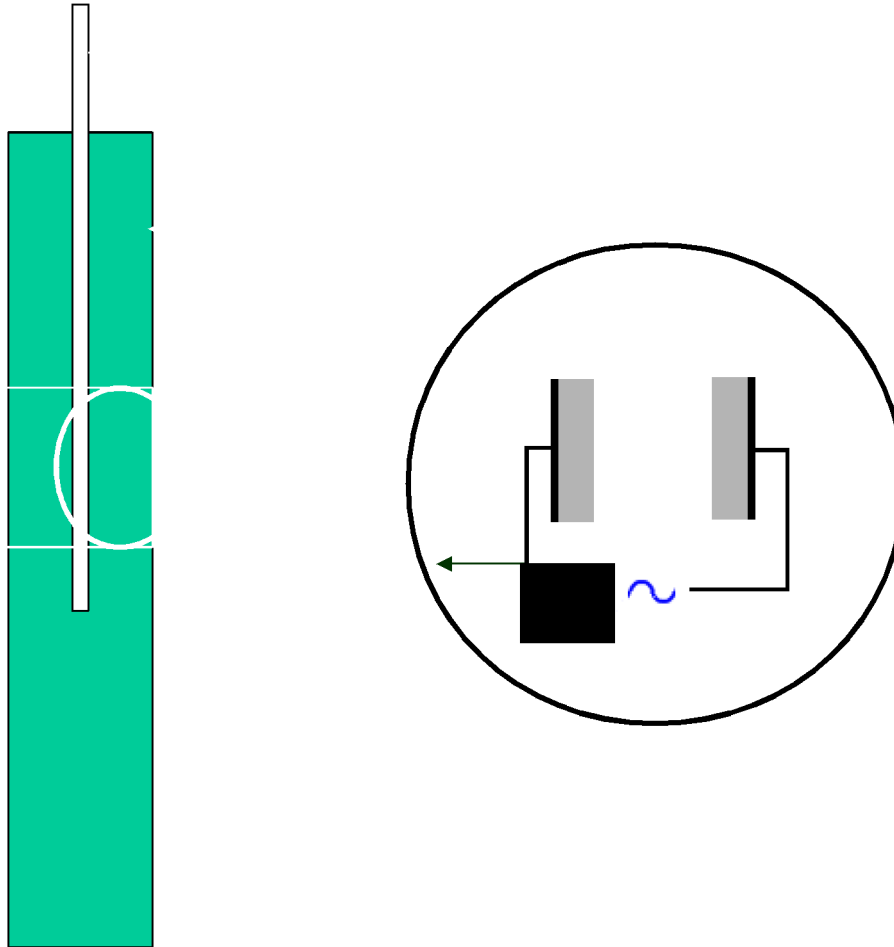
- **DBD = Dielectric Barrier Discharge plasma**
 - **A/C discharge across a dielectric barrier**
 - **Non-thermal discharge**
 - **Low electrode wear**
 - **Ability to operate without getters/purging**
- **Simple design**
 - **Non-radioactive, windowless**
 - **Simple, robust power supply**
 - **Conventional (modified) electrometer**
 - **Low valve disturbance, packed column compatible**

Principle of Operation

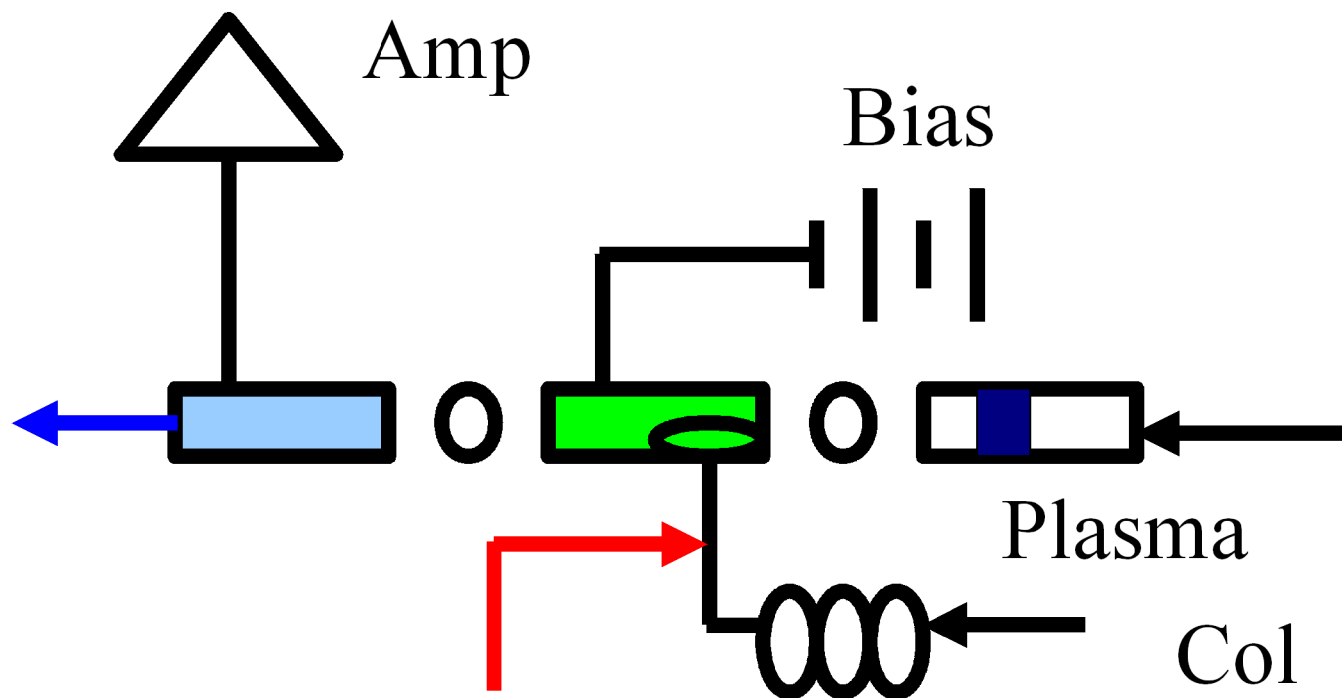
- **Helium mode discharge in DBD tube**
- **Small stream of dopant hydrogen as electron source**
- **Stacked electrode configuration**
 - **Constant bias applied to “upper” electrode**
 - **Collect electrons at “lower” electrode with modified FID electrometer**
- **Constituents of interest capture electrons, yields a negative peak in the data system**

Discharge on a Detector

Side View Cross Section



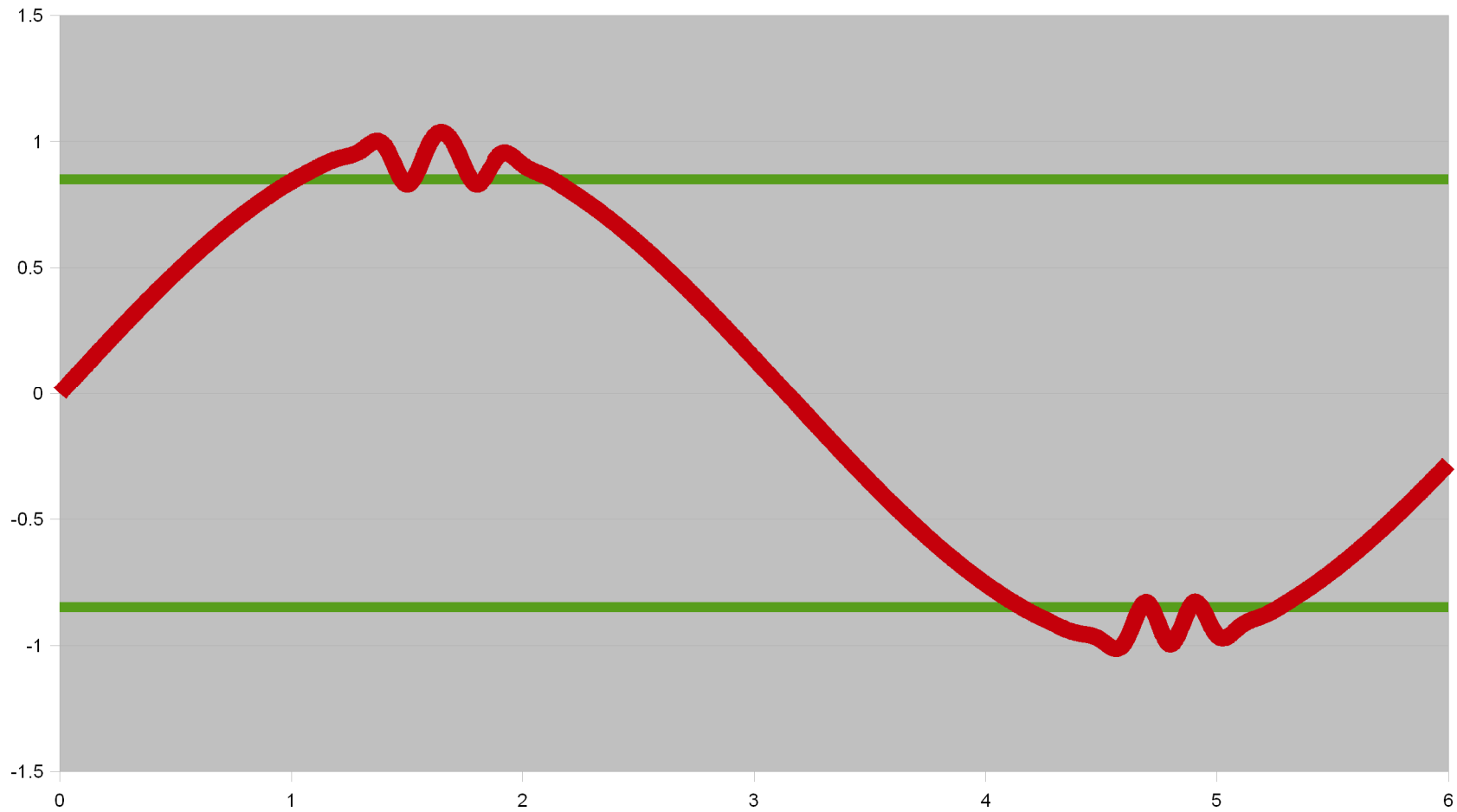
ECD Schematic



DBD-ECD Advantages/Disadvantages

- **Advantages:**
 - **Non-radioactive**
 - **Highly sensitive**
 - **Can be stable (less fussy than Helium mode -large standing current)**
- **Disadvantages**
 - **Widely varying sensitivity**
 - **Requires two gas supplies (helium and very low flow hydrogen)**
 - **Limited linearity**
 - **Clean gases, leak free**

Discharge Cycle

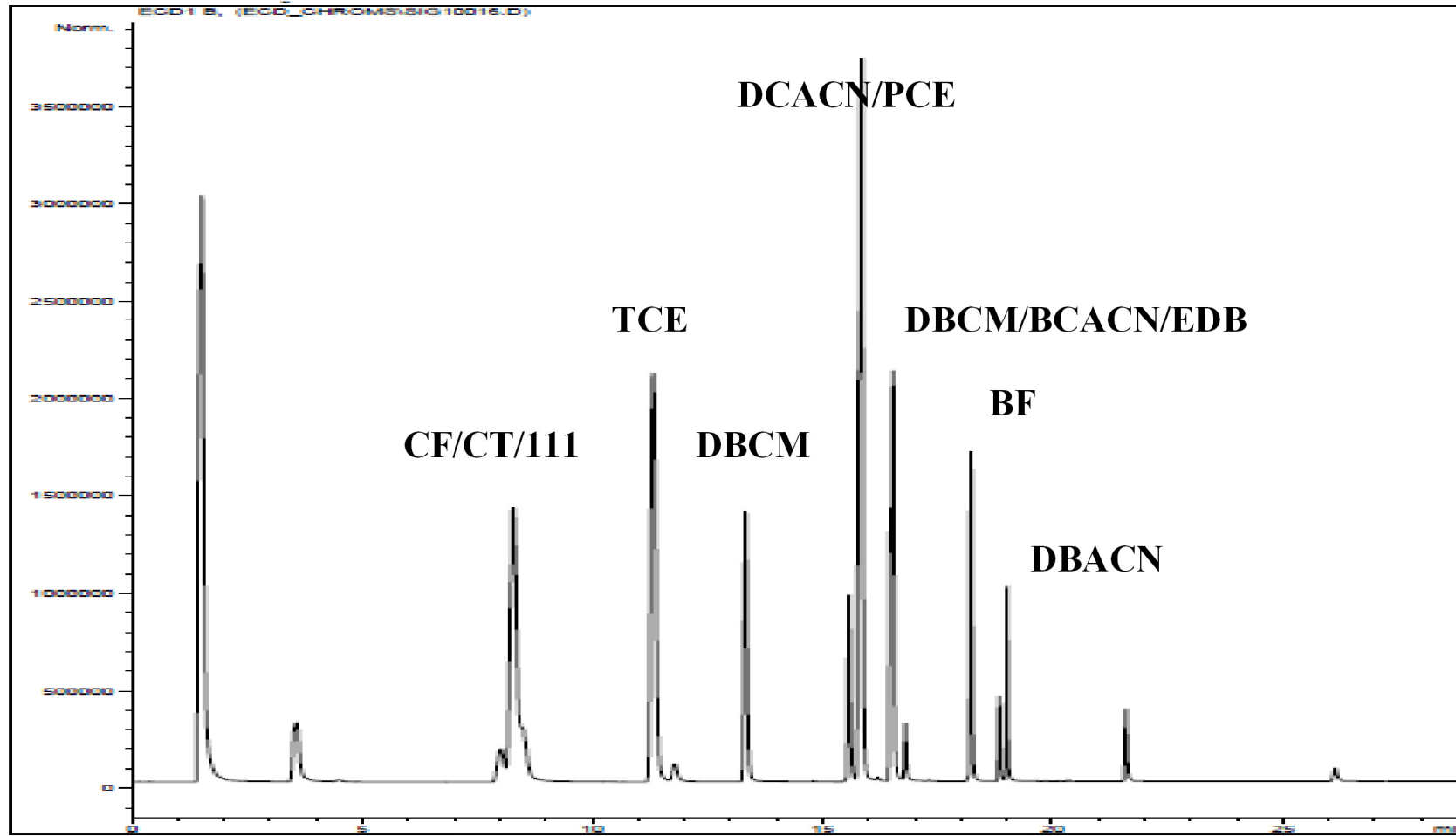


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EC Detector Mechanism's

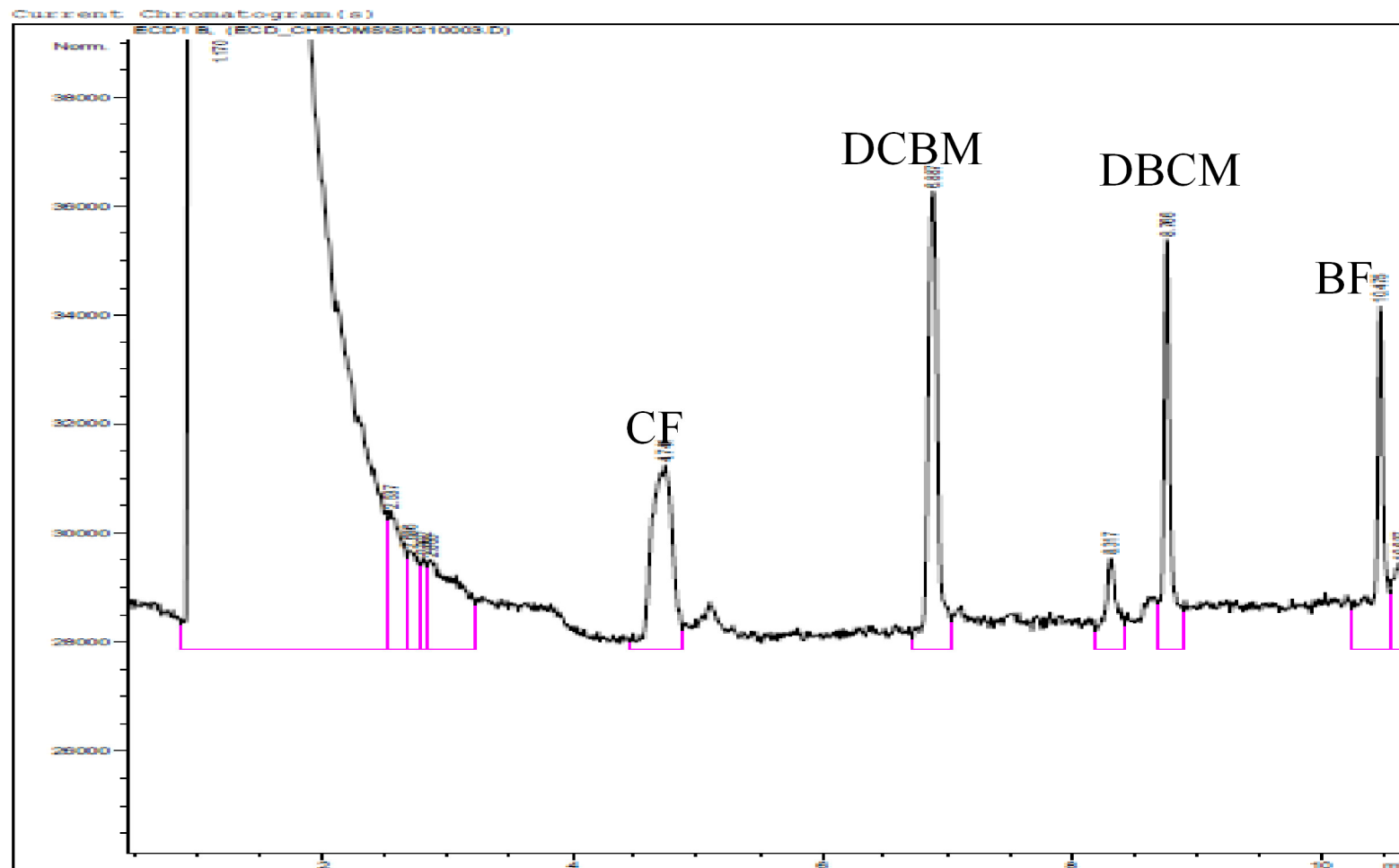
- **Associative electron capture:**
 - $AB + e(-) \rightleftharpoons AB(-)$
 - Response decreases with temperature (subject to TED)
 - Example: Azulene (C₁₀H₈)
- **Dissociative electron capture:**
 - $AB + e(-) > A + B(-)$
 - Response for some compounds will increase with temperature, i.e. Chloroform
 - Up to a maximum, i.e. Carbon tetrachloride

Haloacetic acids in air (evidence of difference in sensitivities)



Trihalomethanes in Water

(2 ppb by headspace)

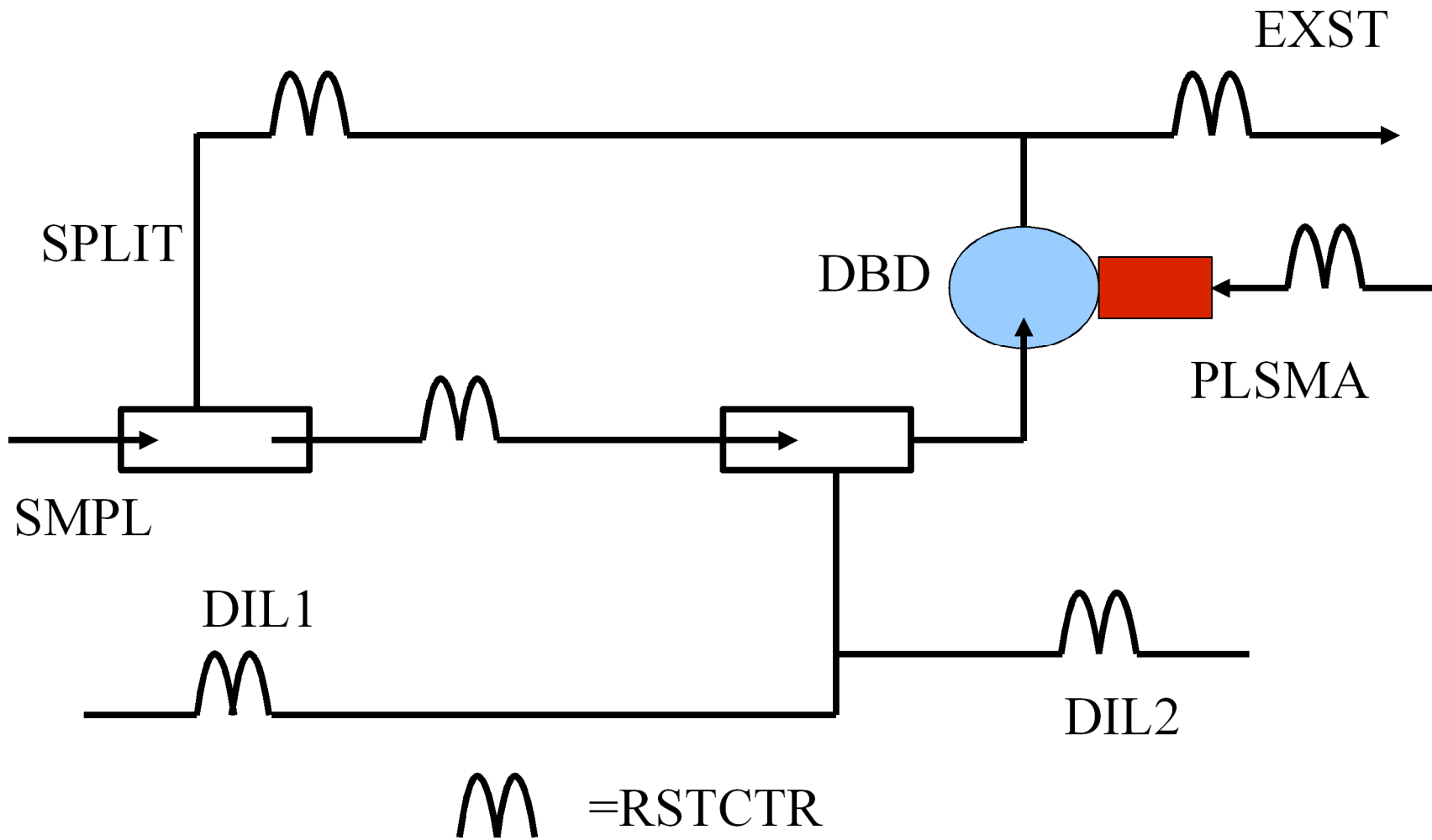


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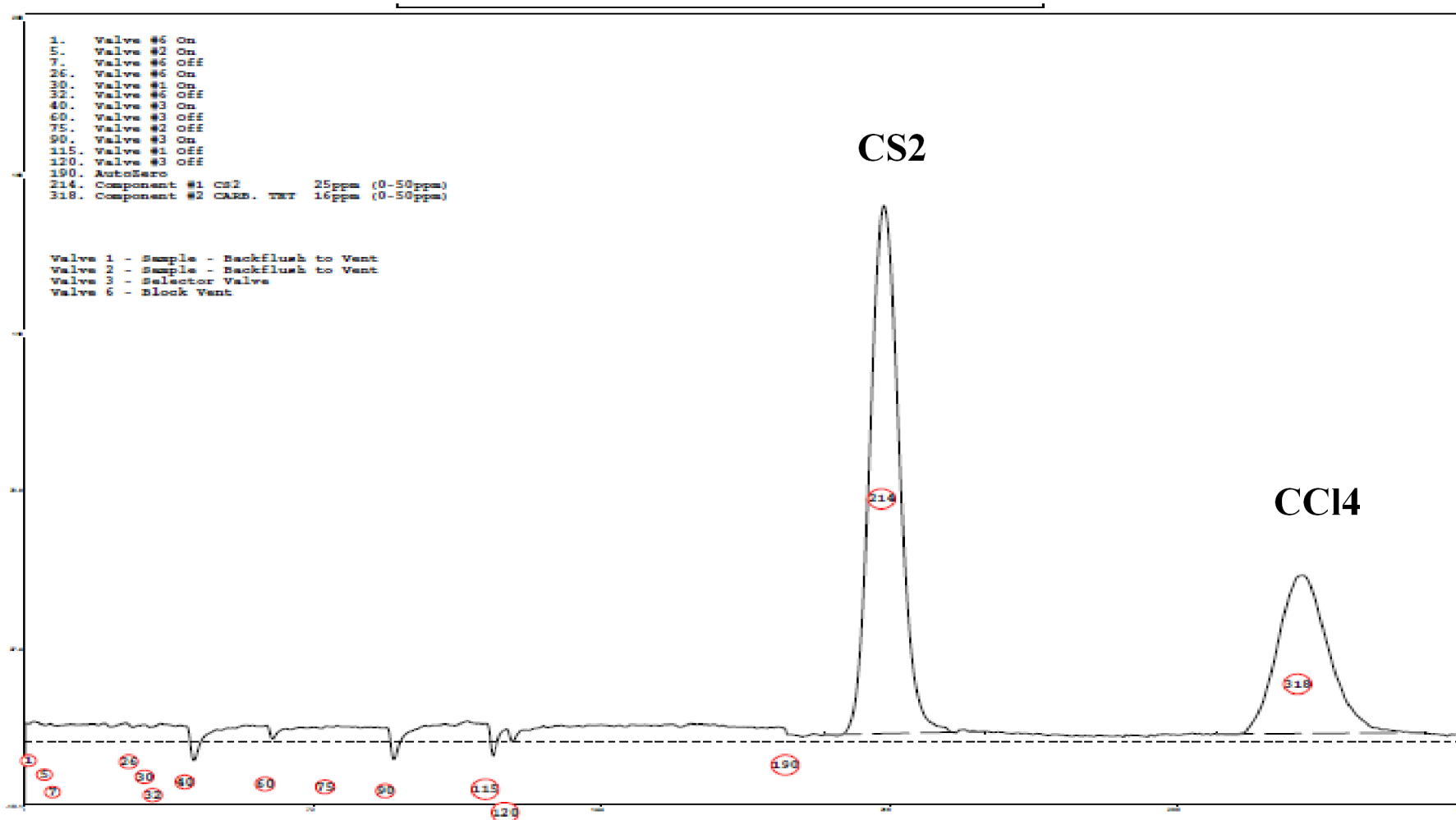
Compound ID's

- **Trihalomethanes:**
 - **CF, chloroform; DCBM, dichlorobromomethane, DBCM, dibromochloromethane, BF, bromoform**

Splitter for CS₂/CCl₄



Carbon Disulfide and Carbon Tetrachloride in air (using variable dilution, 2 loop volumes)



Questions?