Is there still a need for selective GC detectors?

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Outline

GC Detectors Available from Agilent
Electron Capture Detector (ECD)
Nitrogen Phosphorus Detector (NPD)
Flame Photometric Detector (FPD)
Sulfur and Nitrogen Chemiluminescence Detectors (SCD/NCD)
Inductively Coupled Plasma/Mass Spec as a GC Detector (ICP-MS)
GC Detectors Available Through Agilent

Thermal Conductivity Detector (TCD)

Flame Ionization Detector (FID)

Micro Electron Capture Detector (µECD)

Nitrogen Phosphorus Detector (NPD)

Flame Photometric Detector (FPD)

Sulfur Chemiluminescence Detector (SCD)

Nitrogen Chemiluminescence Detector (NCD)

Inductively Coupled Plasma-Mass Spec (ICP-MS)

Mass Selective Detector (MSD)

Triple Quadrupole MS (QQQ-MS)
Typical Detector Operating Ranges

- TCD
- FID
- AED
- NPD (P)
- NPD (N)
- MSD
- FPD (S)
- FPD (P)
- SCD (S)
- PFPD (S)
- HID
- ICP-MS

- ppt
- fg
- ppb
- pg
- ppm
- ng
- 0.1\(\mu\)g
- µg
- mg
Analysis of PCBs in Fish Oil Using GC with Dual ECD Detectors - Background

Fish are an excellent source of omega-3 fatty acids (DHA & EPA)

American Heart Association recommends eating fatty fish at least two times per week or taking a daily fish oil supplement

0.5-1.8 g of DHA + EPA /day “significantly reduces deaths from heart disease and all causes”

But fish and fish oil may contain pollutants:

PCBs, PBDEs, PCDDs, PCDFs, & heavy metals

American Heart Association (http://www.americanheart.org/presenter.jhtml?identifier=4632)
PCB Analysis: Agilent 7890A with Deans Switch for Heart Cutting and Backflushing

No Cut

- ECD 1
- S/S Inlet 41.040 psig
- DB-XLB
- ECD 2
- DB-200
- PCM 20.160 psig

Restrictor
Solenoid valve (off)
Heart Cutting with the Deans Switch to Isolate Target PCBs from Fish Oil Spiked with Aroclor 1260

Column 1: DB-XLB
P/N 121-1232

Column 2: DB-200
P/N 122-2033

Heart Cuts 28 52 101 118 153 138 180
GC-FID Chromatogram of Fish Oil with No Backflushing

1-µL splitless injection of 10% fish oil without backflushing. GC oven was held at 290 °C for 30 min at the end of the run.

Highlighted areas are backflushed
Deans Switch in Backflush Mode

Backflushing Column (3 min @ 295 °C)

- ECD 1
- S/S Inlet (1.000 psig)
- DB-XLB
- restrictor
- solenoid valve (off)
- PCM (80.000 psig)
- ECD 2
- DB-200
Retention Time Precision Column 1 with and without Backflushing

10 Runs with Backflushing

10 Runs without Backflushing
Retention times shift ~4-5 sec during 10 runs
Comparing Area Count Stability on Secondary Column for 2 PCBs – With and Without Backflushing

Comparing PCB Area Counts on Column 2 With and Without Backflushing in a 10-Injection Series

- PCB 118
- PCB 153
- 118 No BF
- 153 No BF

Raw Area Counts vs. Injection number
NPD: Blos Bead ➔ Better Results, Longer Lifetime

• Longer bead lifetime (2–3X)

• More stable operation throughout the bead’s lifetime

• For nitrogen containing compounds – similar sensitivity and selectivity specifications

• For phosphorous containing compounds – superior sensitivity and selectivity specifications

• Superior resistance to ambient humidity and moisture

The Blos bead is available as an aftermarket consumable (part number G3434-60806) to retrofit into existing 6890 and 7890 NPDs.
What’s better about the Blos bead NPD (vs today’s white ceramic bead NPD)

Agilent’s Blos NPD bead performance

- **Nitrogen** containing compounds specs:
  - Similar* sensitivity (pg/s)  
    - Blos: 0.4*  
    - Ceramic: 0.4  
  - Similar selectivity (gN/gC)  
    - Blos: 25,000  
    - Ceramic: 25,000

  * some users got 2-3X improvement in N signal/noise

- **Phosphorous** compounds specs:
  - Superior sensitivity (pg/s)  
    - Blos: 0.06  
    - Ceramic: 0.2  
  - Superior selectivity (gP/gC)  
    - Blos: 200,000  
    - Ceramic: 75,000
NPD Jets, Standard vs Extended Tip

NPD Jet Tip extends ~ 9mm beyond old one
Analytes are positioned closer to the bead, minimizing tailing.
Drug Standard by NPD using Different Jets

Blue is Extended Tip, less tailing

Red is Standard Tip, more tailing
Extended NPD Jet For Improved Nitrogen

Extended Jet Part Numbers are the same for 6890 and 7890:

- G1534-80580 NPD Jet Capillary Detector
- G1534-80590 NPD Jet Universal Detector

The extended jet comes installed in all 7890 NPDs (with a the standard jet in the ship kit for legacy SOP requirements)

The standard jet came installed in all 6890 NPDs (with a the extended jet in the ship kit for last ~year of 6890s shipped)
Tox Screen of Whole Blood, GC/NPD/MSD

1. Nicotine
2. Nicotinamide
3. Carisoprodol artifact
4. Cotinine
5. Meprobamate
6. Caffeine
7. Carisoprodol
8. Methadone
9. Cyheptamide (ISTD)
10. Oxycodone
11. Cholesterol

Column effluent split between NPD and MSD
## Improvements to Agilent’s Flame Photometric Detector (FPD) for P and S

<table>
<thead>
<tr>
<th></th>
<th>Sulfur Sensitivity (pg/sec)</th>
<th>Phosphorus Sensitivity (fg/sec)</th>
<th>Sulfur Selectivity (gS/gC)</th>
<th>Phosphorus Selectivity (gP/gC)</th>
<th>Maximum Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Previous Agilent FPD</td>
<td>20</td>
<td>900</td>
<td>1.00X10^5</td>
<td>1.00X10^6</td>
<td>250</td>
</tr>
<tr>
<td>Enhanced Agilent FPD</td>
<td>3.6</td>
<td>60</td>
<td>1.00X10^6</td>
<td>1.00X10^6</td>
<td>250</td>
</tr>
</tbody>
</table>

New optics include both a lens and wide-band optical filter set
New transfer line design eliminates leaks

Upgrade kits available for 6890 & 6850 FPDs
Pesticides: Three Way Splitter with Makeup

1X method with 1:1:1/10 split FPD:MSD:ECD

Auto-sampler

Phosphorus FPD

AUX EPC
3.8 psig

μECD

3-Way Splitter with Makeup

5975C MSD

Column

30 m X 0.25 mm id X 0.25 um HP-5MS

7890 GC
Milk Extract (1 injection)

- Full scan TIC
- SIM
- µECD
- FPD(P)
Nitrogen and Sulfur Chemiluminescence Detectors

- Acquired by Agilent in December 2006 from General Electric
- Primarily applied in the energy and petrochemical industries.
- Sulfur chemiluminescence detection growing use corresponds to increasing regulation of sulfur monitoring in fuels worldwide.
- Nitrogen chemiluminescence detection is complementary to the sulfur detector in both technology and application.

**Chemistry Behind Detector Operation**

**Nitrogen (NCD)**

\[ R-N + O_2 \rightarrow NO \]
\[ NO + O_3 \rightarrow NO_2^* \rightarrow NO_2 + h\nu \text{ (800-3200 nm)} \]

**Sulfur (SCD)**

\[ R-S + O_2 \rightarrow SO \]
\[ SO + O_3 \rightarrow SO_2^* \rightarrow SO_2 + h\nu \text{ (300-400 nm)} \]
Key Attributes of NCD and SCD

- **High Selectivity**: Highest selectivity for Nitrogen and Sulfur over Carbon
- **No Quenching**: Detector response not inhibited by hydrocarbons
- **Equimolar**: Simplifies quantification of unknowns
- **Linear**: Simplifies calibration
- **Fast**: Options for fast GC or comprehensive 2D GC
- **Complimentary**: NCD and SCD complement other Agilent detectors, such as NPD, FPD, FID and MS (e.g. for nitrosamines)
## Sulfur Selective Detector Comparison

<table>
<thead>
<tr>
<th>Detector</th>
<th>Sensitivity (pg S/sec)</th>
<th>Selectivity (g S/g C)</th>
<th>Other Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>FPD</td>
<td>3.6</td>
<td>$10^6$</td>
<td>Nonlinear, quenching</td>
</tr>
<tr>
<td>PFPD</td>
<td>&lt;1</td>
<td>$\geq10^6$</td>
<td>Nonlinear; quenching not as bad, less repeatable</td>
</tr>
<tr>
<td>AED</td>
<td>~1</td>
<td>$10^5-10^6$</td>
<td>Linear, equimolar, true multielement</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>~1</td>
<td>$\sim 10^9$</td>
<td>Linear, equimolar, expensive</td>
</tr>
<tr>
<td>SCD*</td>
<td>&lt;0.5</td>
<td>$&gt;10^7$</td>
<td>Linear, equimolar</td>
</tr>
</tbody>
</table>

*SCD*: Selective Chemical Detectors
Example of Sensitivity and Selectivity - SCD

- Carbon disulfide
- Ethylmethyl sulfide (Toluene Solvent 99.9% Virtually No Response)
- Thiophene 1.8 ppm S
- 30 ppb Sulfur 3-methiophene
- Baseline expanded

Our measure is your success.
Key Points

SCD

• Highest sulfur selectivity over carbon
• Very little or no quenching
• Linear and equimolar response
• Simultaneous FID SCD Signals are possible

NCD

• Highest nitrogen selectivity over carbon
• Very little or no quenching
• Linear and equimolar response
• Most stable nitrogen detector
• Designed with selective nitrosamines mode
Sulfur Determination in Fresh and Roasted Garlic by Static Headspace GC Sulfur Chemiluminescence

Fresh Garlic

Roasted Garlic

16
S
32.07
Selected Nitrosamines by GC/NCD
1 µL injection of a 2.0 µg/mL standard, 10:1 split

200 pg each on column

<table>
<thead>
<tr>
<th>Peak</th>
<th>Compound</th>
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<tr>
<td>1</td>
<td>N-Nitrosodimethylamine</td>
</tr>
<tr>
<td>2</td>
<td>N-Nitrosomethylethylamine</td>
</tr>
<tr>
<td>3</td>
<td>N-Nitrosodiethylamine</td>
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<tr>
<td>4</td>
<td>N-Nitrosopyrrolidine</td>
</tr>
<tr>
<td>5</td>
<td>N-Nitrosomorpholine</td>
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<tr>
<td>6</td>
<td>N-Nitrosodi-n-propylamine</td>
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<tr>
<td>7</td>
<td>N-Nitrosopiperidine</td>
</tr>
<tr>
<td>8</td>
<td>N-Nitrosodi-n-butylamine</td>
</tr>
<tr>
<td>9</td>
<td>N-Nitrosodiphenylamine</td>
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The Inductively-Coupled Plasma
The Domain of ICP-MS

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<th>1</th>
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<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
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</table>

Element Groups (Families)

<table>
<thead>
<tr>
<th>Alkali Group</th>
<th>Alkaline Earth</th>
<th>Transition Metals</th>
<th>Rare Earth</th>
<th>Other Metals</th>
<th>Metalloids</th>
<th>Non-Metals</th>
<th>Halogens</th>
<th>Noble Gases</th>
</tr>
</thead>
</table>

Traditional Elements

Non-Traditional Elements

Impossible Elements
6890 GC coupled to 7500 ICP-MS

Silcosteel® lined heated transfer line and heated ICP torch injector both under 6890 control (Aux heated zones)

Bidirectional communication between GC and ICP-MS via APG remote

GC control via GC LUI or co-resident GC chemstation
Where would you use it instead of other “element specific” detectors?

Need to measure multiple **elements** simultaneously (**universal and specific at the same time**)

Need better **selectivity** than ECD or ELCD (**comparable sensitivity for Cl, better for heavier halogens**)

Need better sensitivity than FPD or PFPD

Need isotopic information (IDMS)

Need larger dynamic range (**larger than any other GC detector**)

Our measure is your success.
Sulfur in CARB Low Sulfur Reformulated Gasoline

Sulfur 32 elemental chromatogram on top, Carbon 13 chromatogram inverted below

Abundance

Ion 32.00 (31.70 to 32.70): GAS02.D
Ion 13.00 (12.70 to 13.70): GAS02.D (*)

S 32.07
Why ICP-MS as a GC detector for PBDEs?

**Sensitive** (low fg sensitivity, reduced need for pre-concentration or large volume injections)

**Specific** (no interference from other halogenated compounds)

Wide linear range

**Compound independent response** (can quantify without standards)

Tolerant of **wide range of GC gases and flows**

**MS confirmation of Bromine isotope ratios**
Low fg Sensitivity for PBDEs with No interference from other halogens

Extracted ion chromatogram, m/z 79 (Br) and 35 (Cl, inverted) of mixture of 50 ppb PBDE mix spiked into 500 ppm total PCB as Aroclors 1016 and 1260 (hydrogen carrier)
Organotins in marine sediment CRM

GC-ICP-MS chromatograms of $^{118}\text{Sn}$ and $^{120}\text{Sn}$ obtained for spiked PACS-2 extract

Data kindly provided by Dr. Kazumi Inagaki, National Metrology Institute of Japan

DL ~ 0.03pg as Sn
Iodophenols in river water by SPME/GC/ICP-MS

Data kindly provided by Rodolfo Wuilloud et. al. University of Cincinnati

DL ~ 0.1 ppb
P, S, Cl, Br and I containing pesticides
GC-ICP-MS

DL ~ 0.02 - 2 ppb

Dichlobenil, 2,4,6-TBA, DBOB, Phorate, PCNB, Terbufos, Diazinon, Malathion, Dursban, Ioxynil
The End

coolfreeimages.net

Thank You!
References – Element Selective GC Detectors

ECD

NPD
Sindy Zhou and Han-wen Wang, “Improving your NPD System Efficiency,” Agilent Application Note 5989-1511EN, October 2004
Bruce Quimby, “Improved Forensic Toxicology Screening Using A GC/MS/NPD System with a 725-Compound DRS Database,” Agilent Application Note 5989-8582EN, May 2008

FPD
Chin-Kai Meng, “Improving Productivity and Extending Column Life with Backflush,” Agilent Application Note 5989-6018EN, December 2006
Chin-Kai Meng and Mike Szelewski, “Replacing Multiple 50-Minute FPD/ELCD/SIM Analyses with One 15-Minute Full-Scan Analysis for 10x Productivity Gain,” Agilent Application Note 5989-7670EN, November 2007
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SCD/NCD


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“Nitrosamine Analysis by Gas Chromatography and Agilent 255 Nitrogen Chemiluminescence Detector (NCD),” Agilent Technical Overview 5989-6773EN, August 2007

ICP-MS

Raimund Wahlen, “A Comparison of GC-ICP-MS and HPLC-ICP-MS for the Analysis of Organotin Compounds,” Agilent Application Note 5988-6697EN, August 2002