A Presentation by OI Analytical

Analysis of Aldicarb, Methomyl, and Methiocarb by GC/PFPD in Under Five Minutes!

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A World of Solutions

Background

- Carbamates are among the most widely used pesticides in the world
- Shown by the USEPA to pose a human health risk
- Many are included in the USDA Pesticide Data Program (PDP)
- Because these compounds are thermally labile, they are traditionally analyzed by HPLC with post-column derivatization and UV fluorescence

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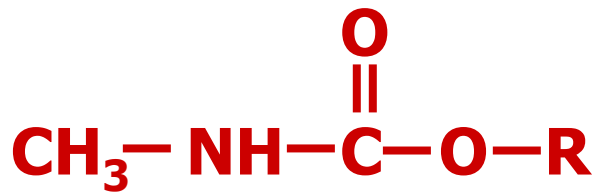
Chemical Structure

General structure for the
N-methyl-carbamates:



Where R is a functional group.
For the three carbamates analyzed here,
the R group contains at least one sulfur.

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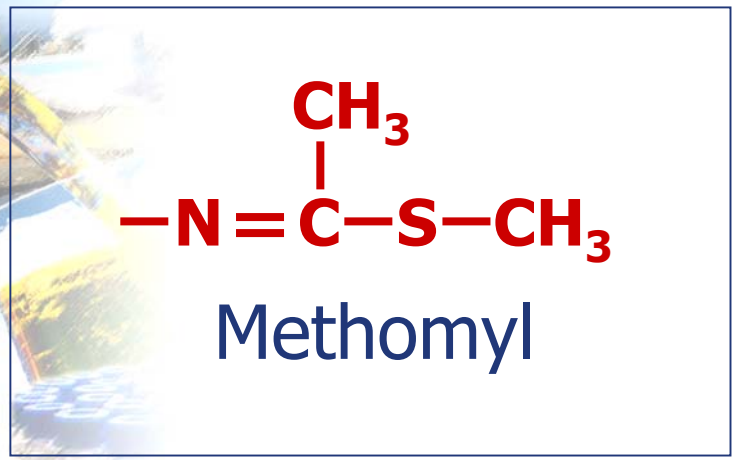
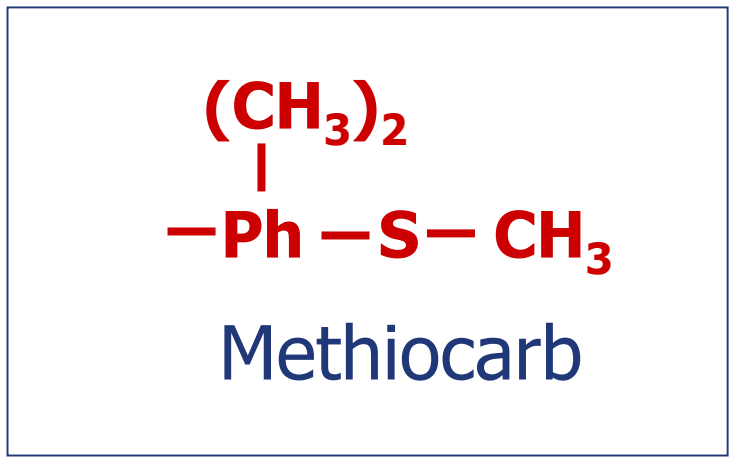
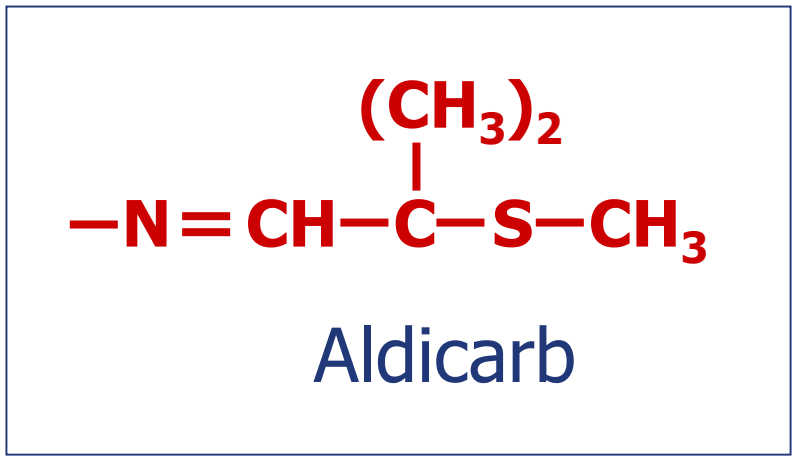
R-Group Structure



Methomyl



Methiocarb



Aldicarb

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HPLC Drawbacks

- Expensive and complex non-GC instrumentation
- Lower resolution

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Advantages of Using GC/PFPD

- Fast analysis time; <5 minutes
- Simple detector; readily available GC technology
- Improved resolution
- No derivitization necessary
- The GC-PFPD system can also be used for OP pesticide analysis (cost effective instrumentation)

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The Analytical Challenge

- Develop GC analytical configuration and conditions that will allow carbamate analysis at low GC temperatures
- Reduce thermal degradation at the column
- Reduce injector degradation
- Maintain sensitivity and repeatability

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The Analytical Approach

- Reduce residence time in a cooler injector via higher column flow rate
- Use a short GC column (4 meters), and high column flow rates (5 mL/minute)
- Compounds will elute at lower temperatures

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Theory

- Assume half the theoretical plates
  - *Shorter column*
  - *Faster column flow rate*
- Assuming constant elution time, analytes will spend twice the time at each adsorption site
- For each reduction in theoretical plates by half, double residence time is achieved by lowering column temperature by 20 °C
  - *Experimentally determined*

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Theory (cont.)

- Thus, each time the number of theoretical plates is divided by 2 the elution temperature is dropped by 20 °C
- For this case, using a 4-meter column and 5 mL/minute column flow, reduced the elution temperature by as much as 100 °C
  - *Compare to 30-meter column*
  - *Compare to 1 mL/minute column flow*

Theory (cont.)

- High column flow rate and low injection temperature also help to reduce compound degradation at the injector
  - *140 °C*
  - *Purge flow turned on at 0.2 minutes*
- Some loss in GC resolution compensated for by the PFPD sulfur selectivity (S/C 10^6 or better)
- Results in resolution and sensitivity better than or comparable to the LC method

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Project Goals

- Develop GC configuration that allows fast, low-temperature elution of aldicarb, methomyl, and methiocarb
- Demonstrate linearity of calibration
- Demonstrate repeatability
- Demonstrate performance in a matrix

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Sample Description

- Aldicarb, methomyl, and methiocarb
- Acetonitrile solvent
- Individual standards combined to make 10 ppm stock standard
- Dilutions to make six calibration standards, 50 ppb to 2,000 ppb
- Diluted to 100 ppb for repeatability study

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Instrument Conditions

Injector	Splitless, 140 °C, purge flow 20 mL/minute at 0.2 minutes, 4-mm single gooseneck liner without wool
Column	DB-5MS, 4 m x 0.25 mm I.D. x 0.25 µm film, 5 mL/minute column flow (He)
Oven	80 °C (no hold) 20 °C/minute to 180 °C, hold 1 minute Total run time 5 minutes or less
Detector	PFPD, 2-mm combustor, BG-12 optical filter, 200 °C, gases tuned for sulfur, 6–25 msec sulfur gate, linear mode

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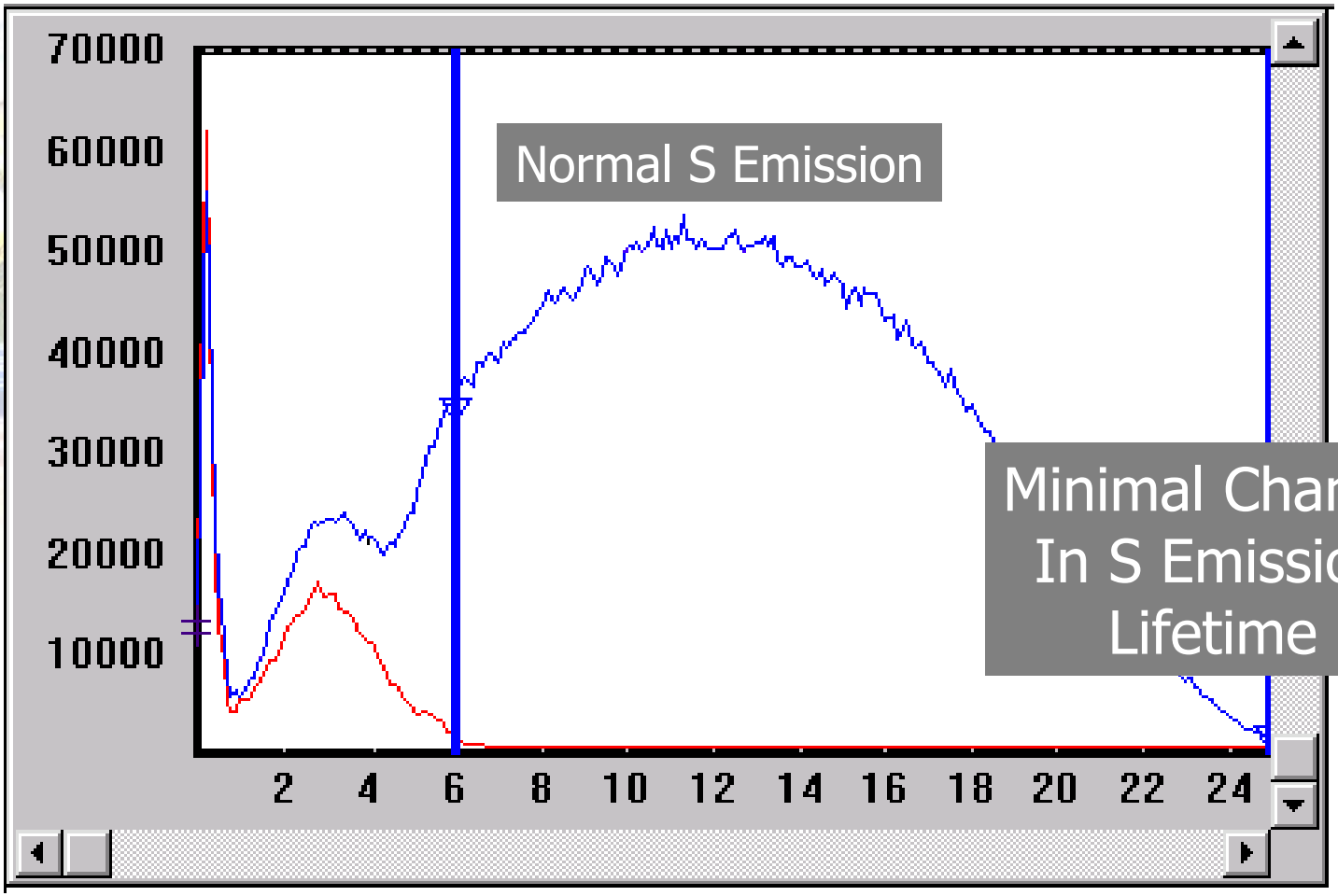
Sulfur Emission at 5 mL/min



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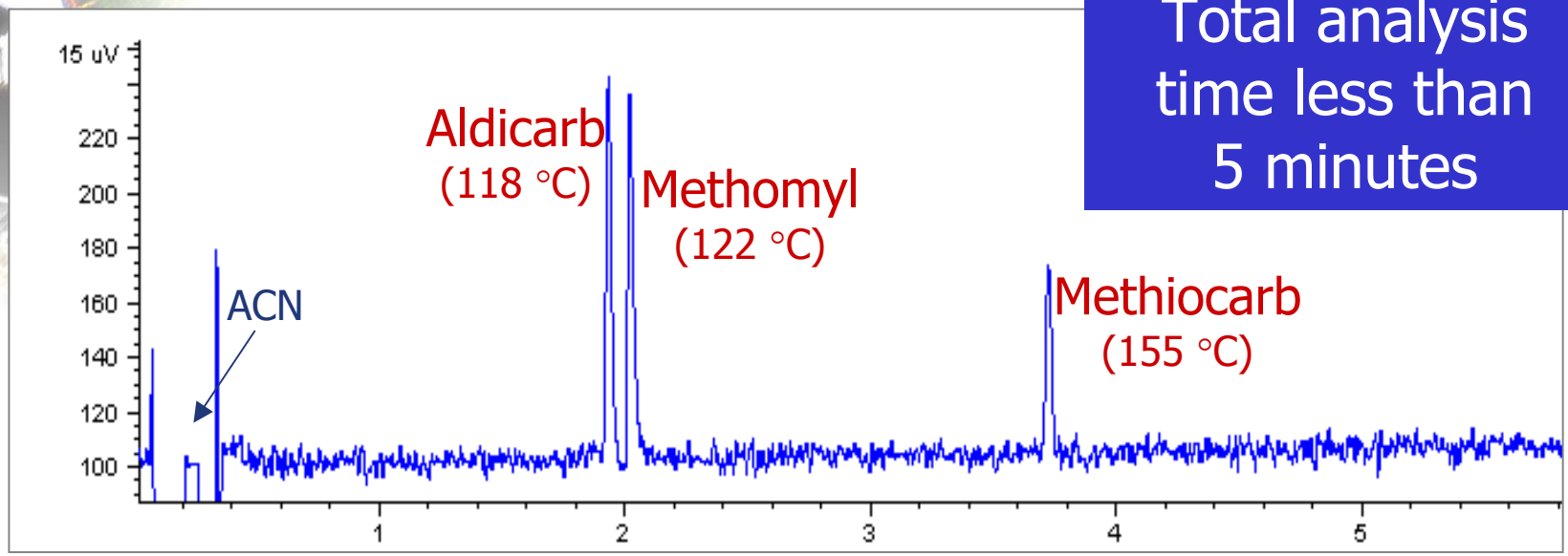
Chromatogram at 100 ppb

- 100 ppb each aldicarb, methomyl, and methiocarb
- Correlates to 20 ng/g (20 ppb) with 5 g/mL extracts
- S/N of 10 or better



Total analysis time less than 5 minutes

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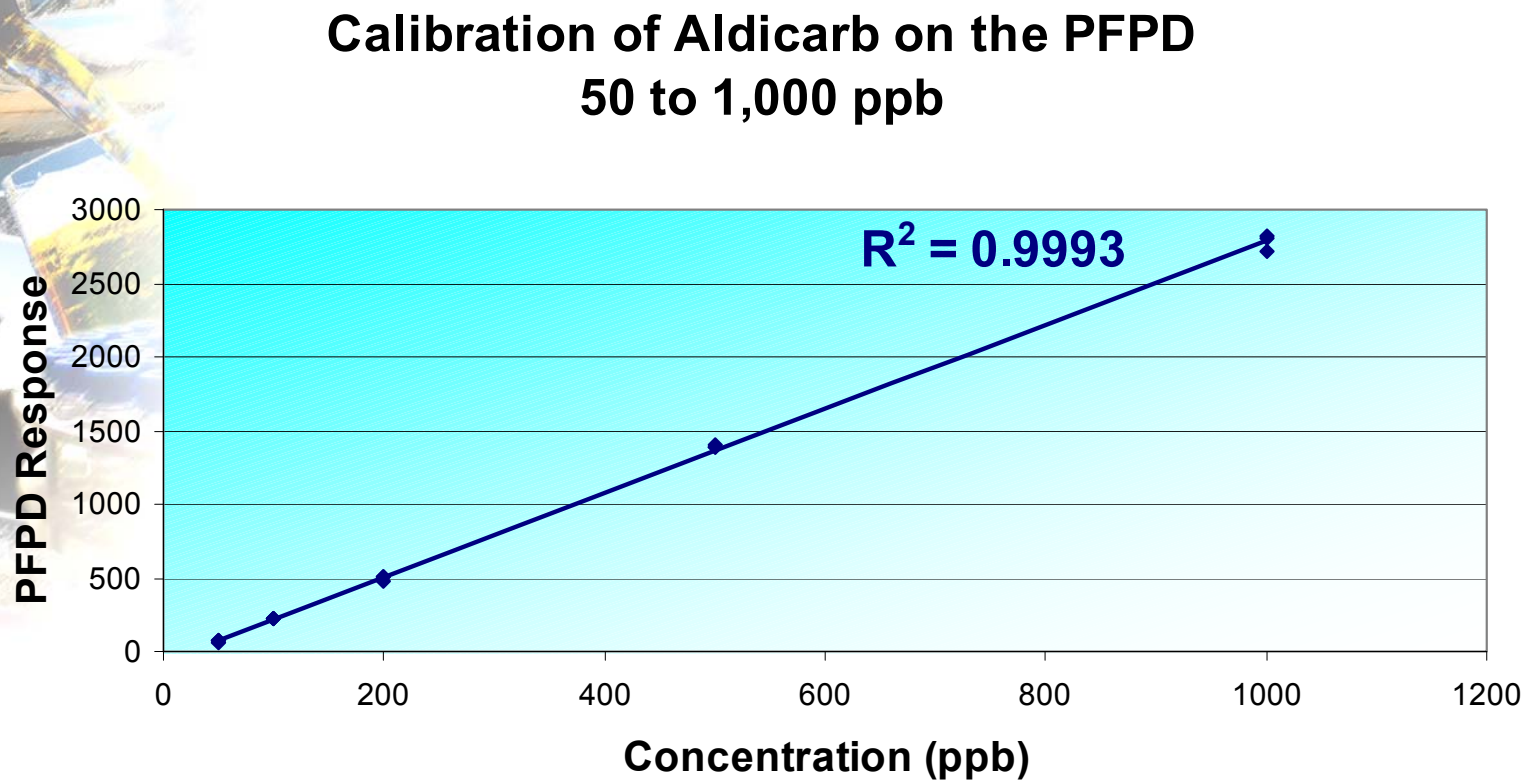
Aldicarb Calibration Curve



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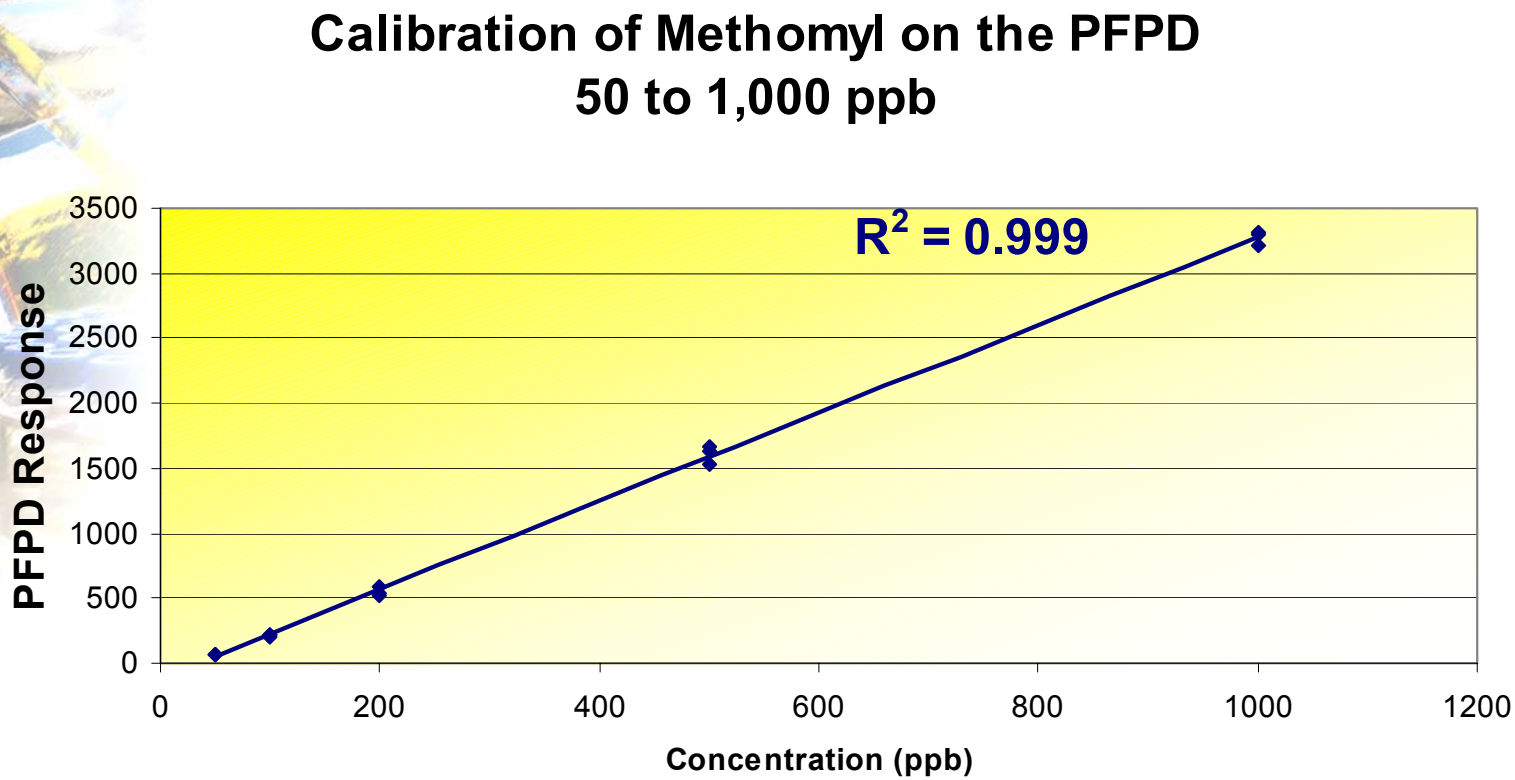
Methomyl Calibration Curve



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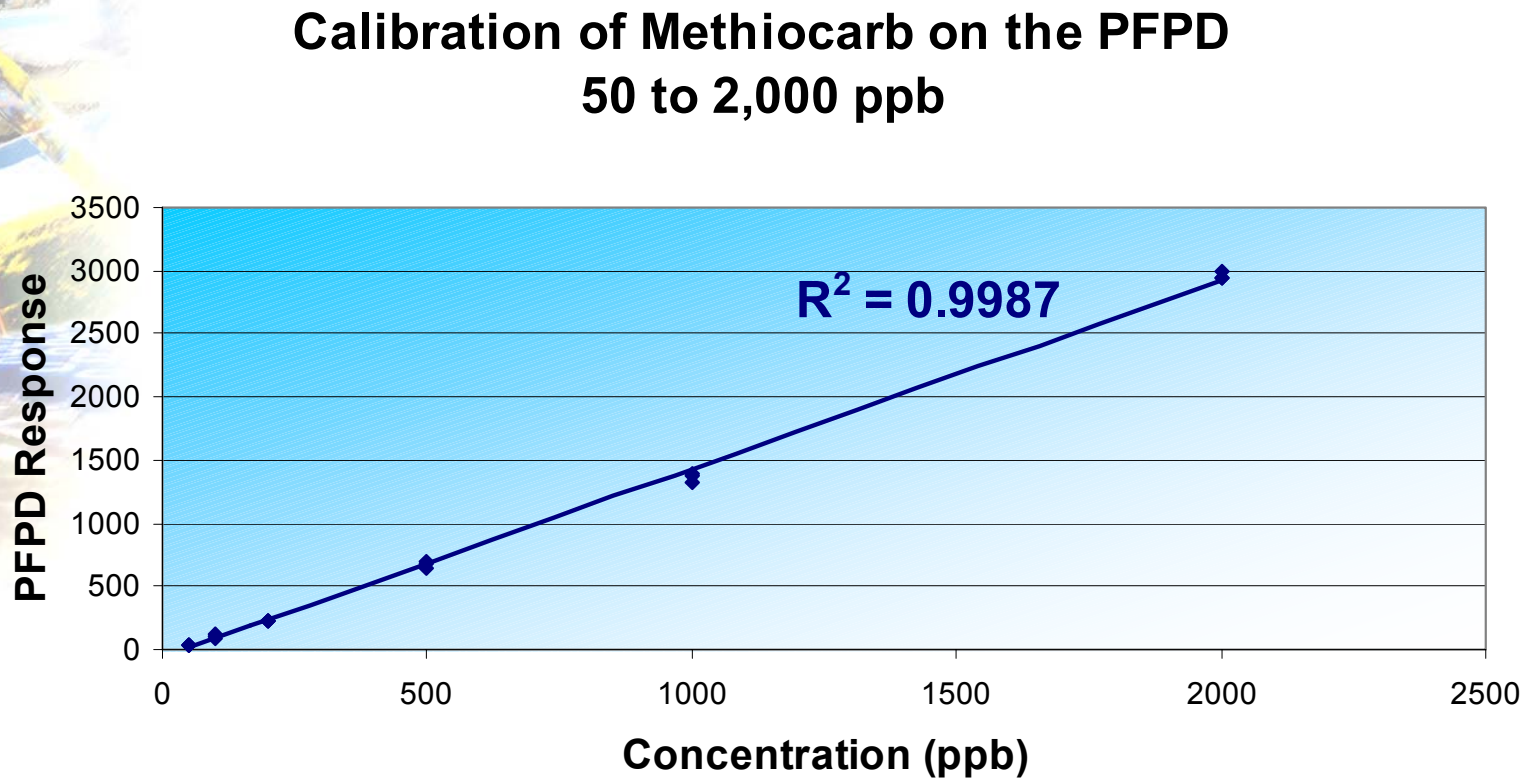
Methiocarb Calibration



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Calibration Summary

Compound	Calibration Range	R^2
Aldicarb	50–1,000 ppb	0.9993
Methomyl	50–1,000 ppb	0.9990
Methiocarb	50–2,000 ppb	0.9987

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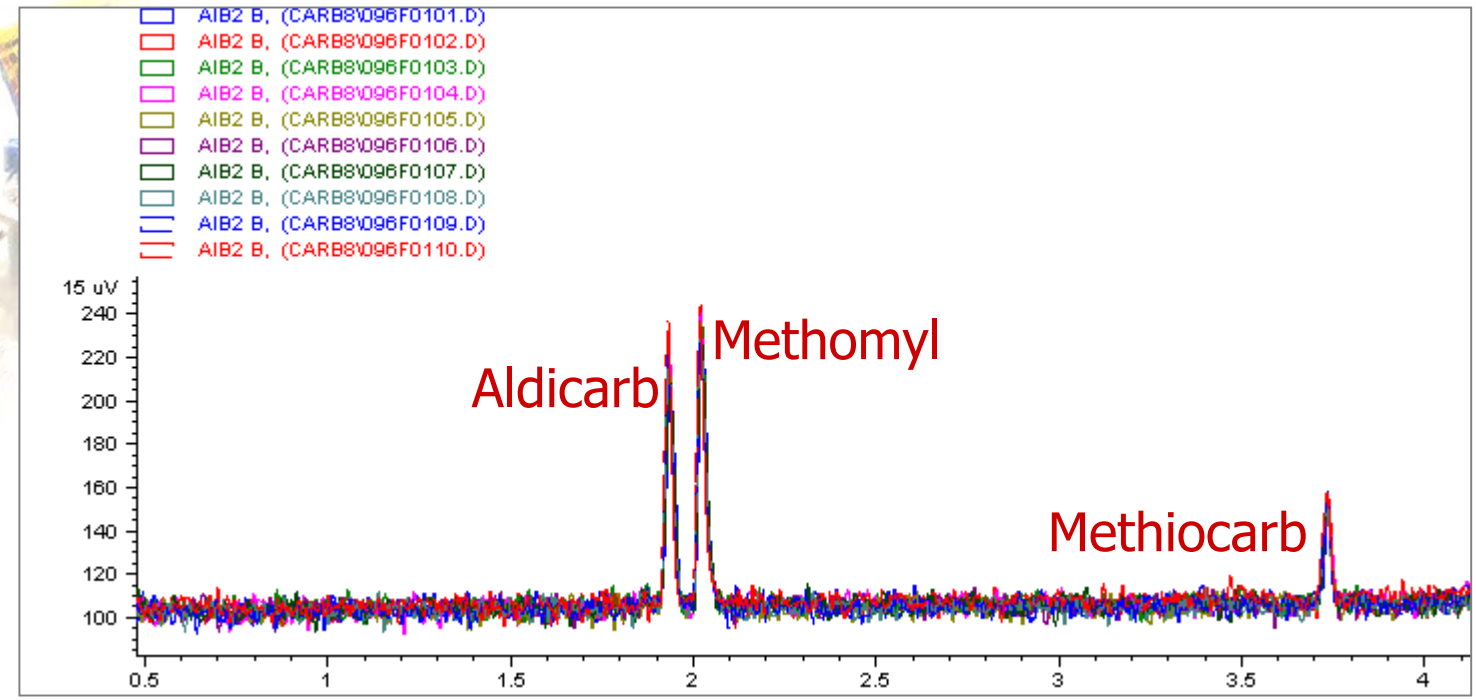
Repeatability at 100 ppb

- Overlaid chromatograms; n=10
- 100 ppb
- 1 µL splitless injections; 4-meter column



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Repeatability at 100 ppb

Run No.	Aldicarb	Methomyl	Methiocarb
1	181.3	229.2	67.9
2	175.7	232.1	83.1
3	190.5	232.3	71.2
4	196.7	221.4	71.3
5	184.8	215.3	78.5
6	173.1	216.5	70.7
7	171.2	210.2	60.7
8	201.0	214.1	69.8
9	179.5	196.7	77.4
10	177.8	195.6	81.4
Average	183.2	216.3	73.2
%RSD	***5.5***	***6.1***	***9.4***

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Repeatability Summary

%RSD for 10 replicate analyses
at different concentrations

Compound	100 ppb	500 ppb	1 ppm
Aldicarb	5.5	4.0	2.5
Methomyl	6.1	6.8	3.9
Methiocarb	9.4	6.2	3.2

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Summary

- Short column and high column flow rate resulted in lower elution temperatures by ~100 °C
- Lower elution temperatures reduced or eliminated thermal degradation of the pesticides
- Loss of GC resolution compensated for by the excellent PFPD S/C selectivity
- Resolution still better than LC method

Summary (cont.)

- Linear calibrations: $R^2 \geq 0.999$
- Excellent repeatability: RSD <10%
- The other non-sulfur carbamates are less thermally labile (carbaril, carbofuran and propoxur) and can be analyzed using standard GC/MS methods

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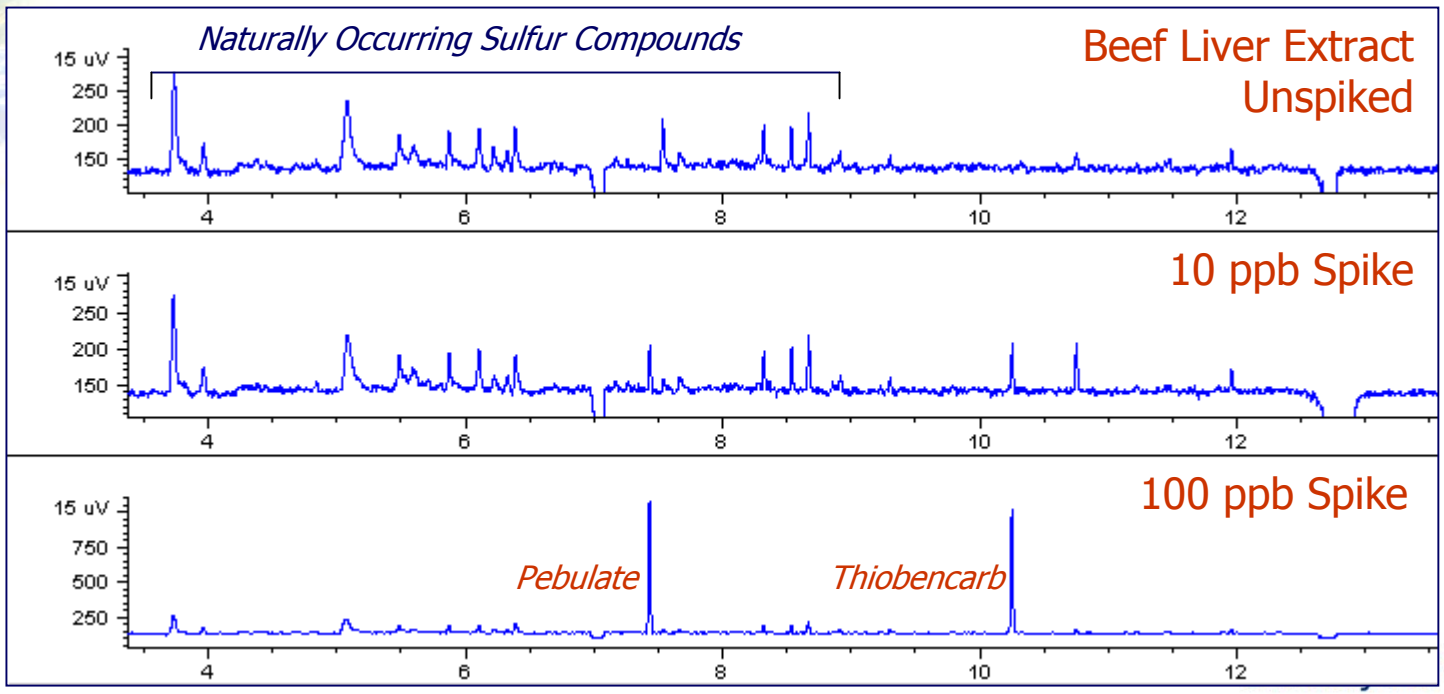
PFPD: Carbamates in Beef Liver

- Pebulate and thiobencarb at 10 ppb by a "conventional" GC/PFPD method (30-m column, ramping to 300 °C, 220 °C injection port, etc.)
- High PFPD S/C selectivity eliminates most of the usual matrix interferences



For a thorough explanation of the low temperature elution of thermally labile compounds, see the following:

"Extending the Range of Compounds Amenable for Gas Chromatography/Mass Spectrometry Analysis," A. Fialkov, A. Gordin, and A. Amirav, *J. Chromatog. A.*, **991**, 217–240, 2003.