Analysis of Low Level COS Using the OI Analytical SPRO 3200

Detection of Single-Digit ppbv COS using the Pulsed Flame Photometric Detector (PFPD)

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OI Analytical S-PRO 3200

- Turn-key system designed for detection and quantitation of low-level sulfur compounds in gas phase matrices
  - *E.g. natural gas, propylene, ethylene, CO_2*
- Agilent 6890N platform with Agilent GS-GasPro® column
- Integrated permeation oven for automated standards generation
- Gas sampling loop available in range of sizes
- OI Volatiles Interface, Sulfinert™ treated and capable of wide range of split ratios
- PFPD for low level sulfur detection and quantitation
  - *High selectivity and sensitivity*
  - *Low maintenance, long term stability*
  - *No coking or fouling of the detector*

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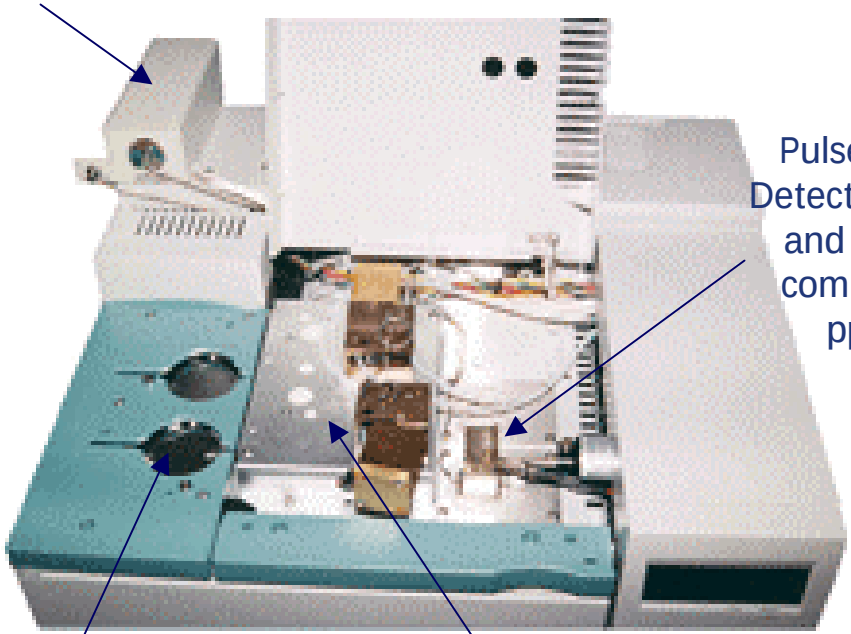
Integrated permeation oven for generation of calibration standards



Pulsed Flame Photometric Detector (PFPD) for detection and quantitation of sulfur compounds at single-digit ppbv concentrations

OI Volatiles Interface for introduction of gas phase matrices with split (Sulfinert treated)

Heated valve box with 6-port valve, gas sampling loop, and 4-port selection valve (all lines Sulfinert treated)

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Instrument Operating Conditions

- GC conditions
  - *OI Volatiles Interface at 200ºC*
  - *Agilent GS-GasPro column, 30 meter x 0.32 mm ID*
  - *Oven isothermal at 150ºC*
  - *PFPD detector configured and tuned for sulfur*

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Instrument Operating Conditions

- PFPD conditions
  - *2 mm combustor, BG-12 filter (blue/purple)*
  - *H_2/Air1 ratio tuned to optimize sulfur emission*
  - *Frequency at 3.7 Hz*
  - *Board parameters:*
    - PMT at 590v (can go as high as 700v if desired)
    - Ignitor current at 2.8
    - Trigger at 500
    - Range 1
    - Sulfur gate = 6-24 msec, square root ON
    - Attenuation = 16
    - Interpolation = spline
    - Zero < 25

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Step 1: Instrument Conditions

- COS standard generated using the integrated permeation oven
  - *COS permeation device, permeation rate of 91.5 ng/min at 30ºC*
  - *Permeation oven at 30ºC*
  - *500 mL/min dilution gas (He)*
  - *1 mL gas sample loop*
  - *1 mL/min column flow (He)*
  - *Split ratio 15:1 (18.5 mL/min split flow)*
  - *Concentration of COS (and sulfur) eluting from permeation oven = 75 ppbv*

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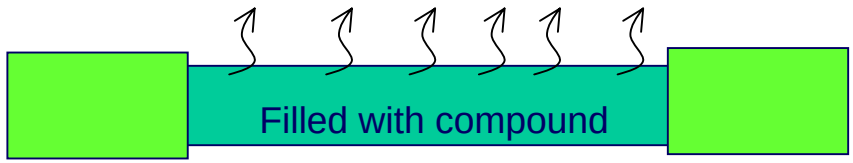
Theory of Permeation Oven

Compound diffuses out a a constant rate at a given temperature
R = ng/(min*cm)

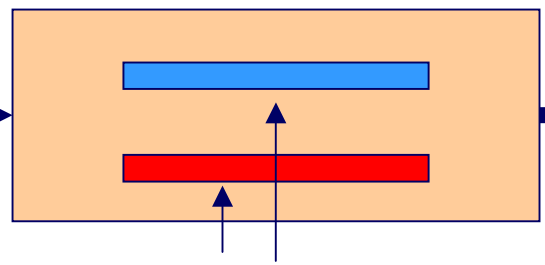


Permeation device with permeable membrane

Perm Oven
Constant Temp.
~ 30-35C

Known Gas
Flow Rate In

Aux EPC



Known Constant
Concentration Out

Permeation devices with a
known diffusion rate at
given temperature

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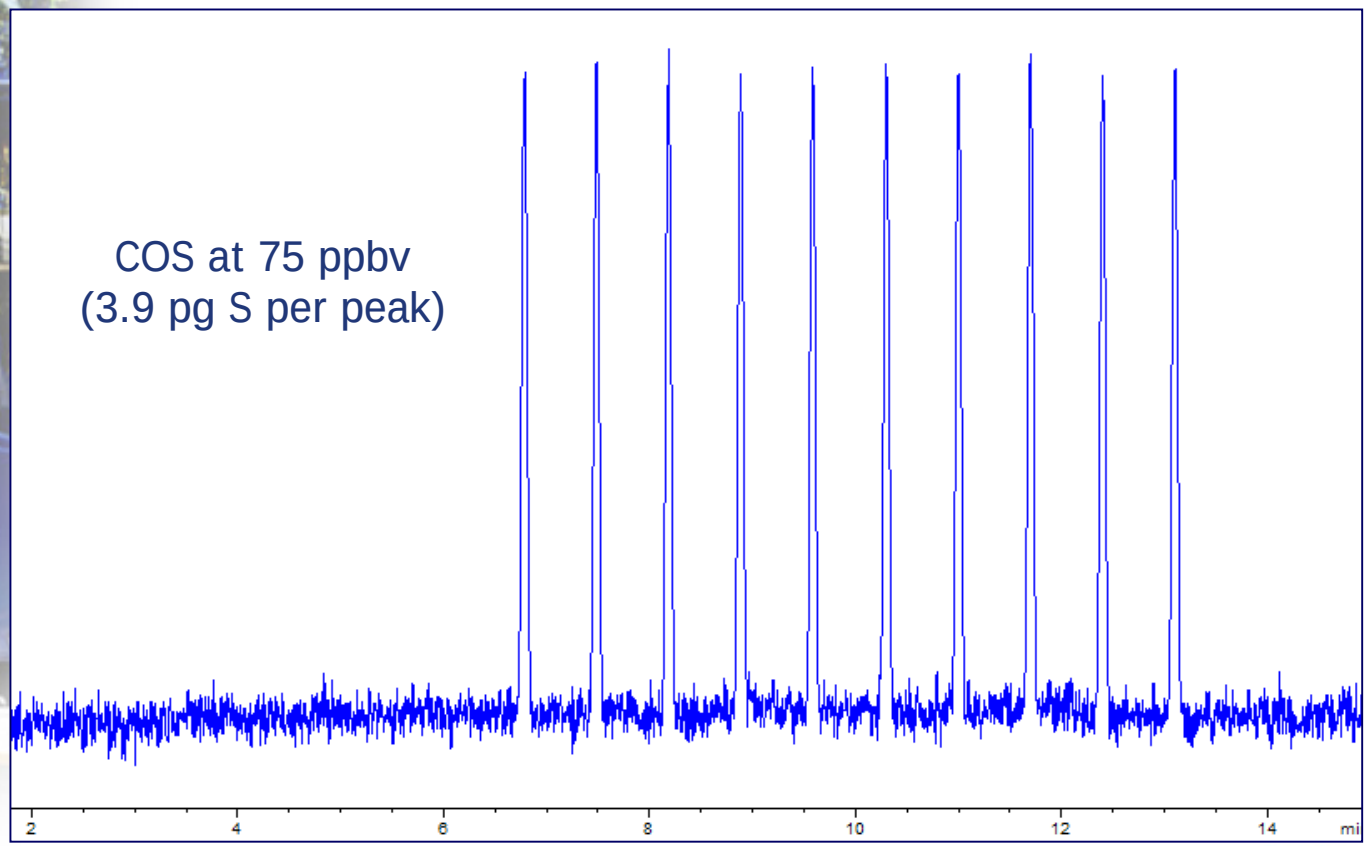
Step 1: COS at 75 ppbv

10 replicate injections of COS from the permeation oven using the 1 mL gas sample loop and 6-port valve



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Performance of COS at 75 ppbv

- S/N at 75 ppbv = 25
- Repeatability over 10 replicate peaks = 1.6%

Peak Number	Area Counts
1	1148
2	1122
3	1157
4	1154
5	1156
6	1126
7	1173
8	1122
9	1162
10	1132
Average	*1145*
%RSD	*1.6%*

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Step 2: New Instrument Conditions

- Use same conditions as shown for 75 ppbv, but increase split ratio from 15:1 to 100:1
- Generates a standard that will be equivalent to 11.2 ppbv
- Mass of sulfur on column approx 0.7 pg S

Note: The permeation rate of the COS device used for these tests was too high to generate the low level standards directly. The equivalent low level standard was generated by increasing the split ratio.

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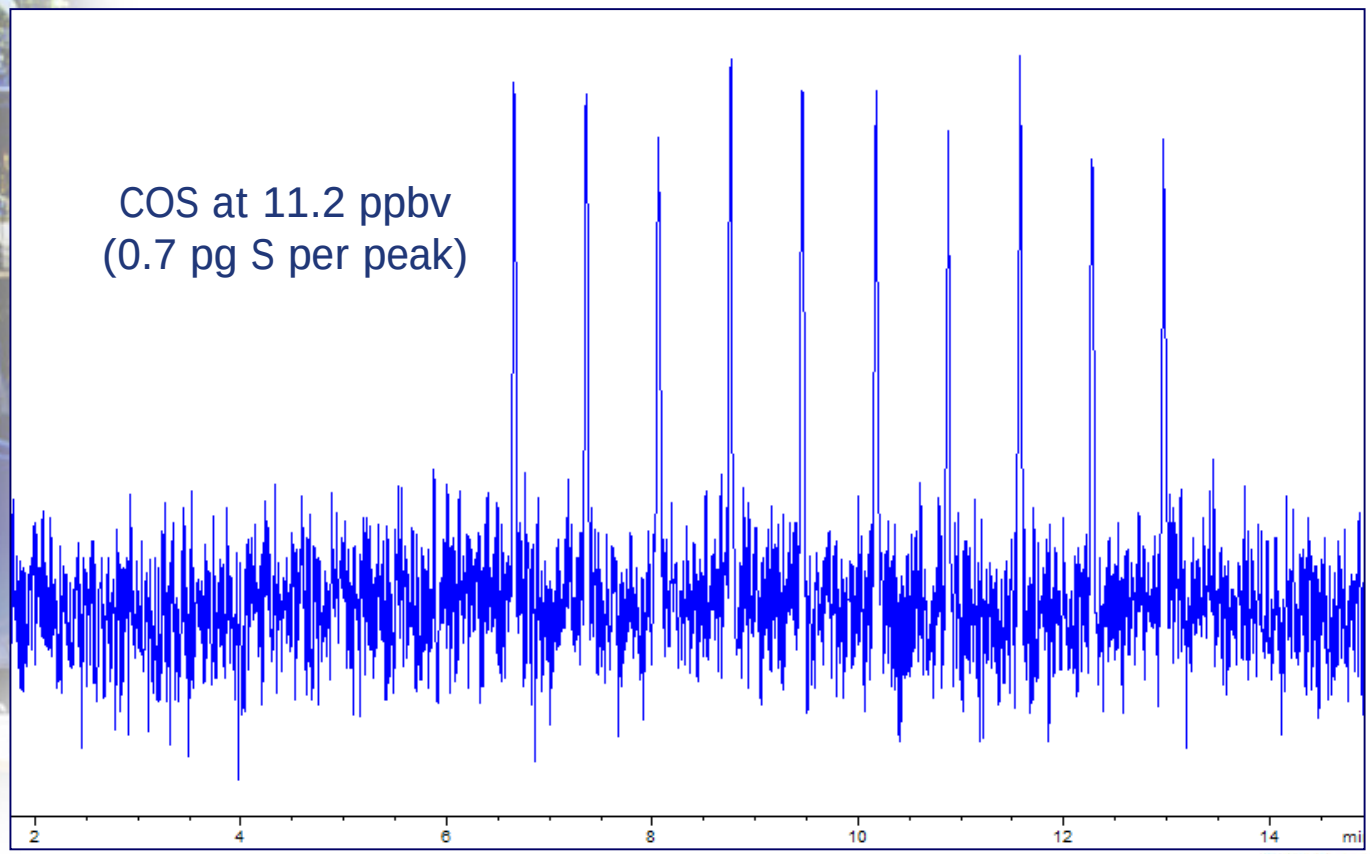
Step 2: COS at 11.2 ppbv

10 replicate injections of COS from the permeation oven using the 1 mL gas sample loop and 6-port valve



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Performance of COS at 11.2 ppbv

- S/N at 11.2 ppbv = 4
- Repeatability over 10 replicate peaks = 6.9%

Peak Number	Area Counts
1	152
2	151
3	170
4	161
5	163
6	150
7	136
8	173
9	157
10	150
Average	*156.3*
%RSD	*6.9%*

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Step 3: New Instrument Conditions

- Use same conditions as shown for 75 ppbv, but increase split ratio from 15:1 to 150:1
- Generates a standard that will be equivalent to 7.5 ppbv
- Mass of sulfur on column approx 0.5 pg S

Note: The permeation rate of the COS device used for these tests was too high to generate the low level standards directly. The equivalent low level standard was generated by increasing the split ratio.

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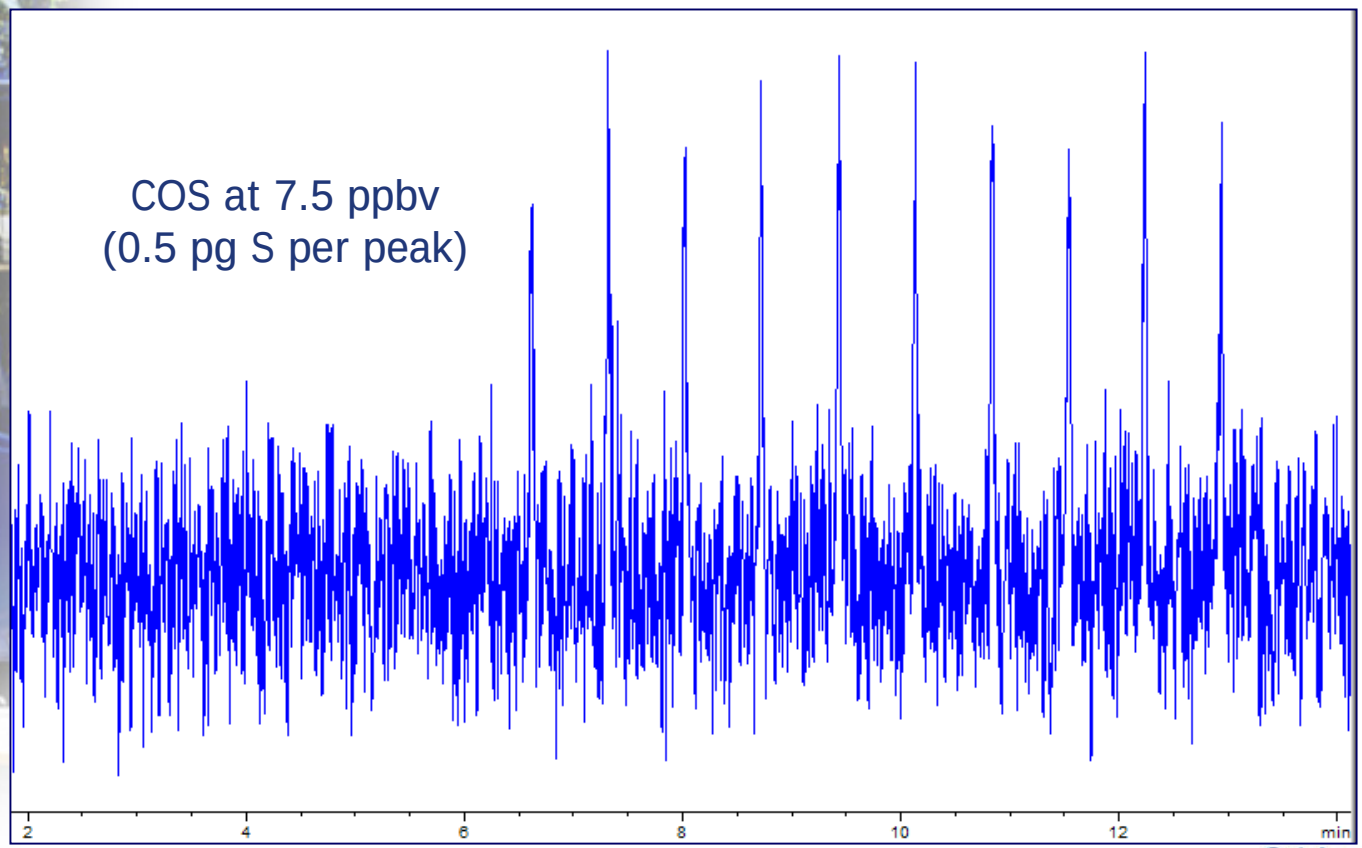
Step 3: COS at 7.5 ppbv

10 replicate injections of COS from the permeation oven using the 1 mL gas sample loop and 6-port valve



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Performance of COS at 7.5 ppbv

- S/N at 7.5 ppbv = 3
- Repeatability over 10 replicate peaks = 5.4%

Peak Number	Area Counts
1	74
2	74
3	80
4	82
5	82
6	76
7	87
8	79
9	84
10	77
Average	*79.5*
%RSD	*5.4%*

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Conclusion

- Using the conditions described here, it is possible to analyze COS at single-digit ppbv concentrations using the OI Analytical SPRO3200 system
- S/N ratio of about 3
- Repeatability of 1.6 to 6.9% (n = 10)

For more information ask for the S-PRO 3200 brochure, Publication Number 1700.