

XENON GC/MS Analysis

Neutrino Platform

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EP-DT

Detector Technologies

STATUS

- detector > 700'000 kg **liquid Argon**
- Xenon bottle from Linde, purity 5.0 >> **max impurities 10 ppm**
- *Linde* declares a set of impurities, each lower than 1-2 ppm
- Ar, Kr should not affect the detector; CO₂, O₂, H₂O should be adsorbed by dedicated filters (on liquid phase, 700'000 kg recirculated every week)

BOTTLE IMPURITIES

- Impurities declared by Linde for Xenon 5.0



→ Produktdatenblatt

Xenon 5.0



Reinheit in %: $\geq 99,999$

Nebenbestandteile, ppm:

N ₂	≤ 1
O ₂	$\leq 0,5$
H ₂ O	≤ 2
KW	$\leq 0,5$
H ₂	≤ 1
Ar	≤ 1
CF ₄	≤ 1
Kr	≤ 1
CO + CO ₂	≤ 1
C ₂ F ₆	≤ 1

Angaben sind als ideale Volumenanteile (= Molanteile) zu verstehen

GC/MS ANALYSIS

- Xenon is sent to Gas Chromatograph, three columns are available: PPU, OV, MolSiev
- OV1 and PPU column can be coupled with Mass Spectrometer
- Different temperatures were tried for OV1 and PPU but with similar results, best method is standard RPCMethod (95°C)
- First analysis are done with plastic pipe as connection, then moved to inox pipe to limit possible Air/O₂/N₂/H₂O adsorption

Method: C:\Soprane\Method\LAB256_Xenon

Module	<input checked="" type="checkbox"/> Module A	<input checked="" type="checkbox"/> Module B	<input checked="" type="checkbox"/> Module C
	OV1	PPU	MS5A
Inlet temp. (°C)	<input type="text" value=""/>		
Inject temp. (°C)	<input checked="" type="checkbox"/> 70.00	<input checked="" type="checkbox"/> 80.00	<input checked="" type="checkbox"/> 85.00
Column temp. (°C)	<input checked="" type="checkbox"/> 95.00	<input checked="" type="checkbox"/> 95.00	<input checked="" type="checkbox"/> 105.00
Pump (sampling time) (s)	Pump1: <input type="text" value="60.00"/>		
Sampling time (s)	<input type="text" value="60.00"/>	<input type="text" value="60.00"/>	<input type="text" value="60.00"/>
Inject time (ms)	<input type="text" value="25.00"/>	<input type="text" value="25.00"/>	<input type="text" value="100.00"/>
Backflush time (s)	<input type="text" value=""/>	<input type="text" value=""/>	<input type="text" value=""/>
Run time (s)	<input type="text" value="240.00"/>		
Column pressure (psi)	<input checked="" type="checkbox"/> 28.00	<input checked="" type="checkbox"/> 28.00	<input checked="" type="checkbox"/> 33.00
Detector	<input checked="" type="checkbox"/> ON	<input checked="" type="checkbox"/> ON	<input checked="" type="checkbox"/> ON

GC/MS ANALYSIS

- Chromatograms can be used to quantify elements with peak area, but a calibration is needed > rough estimation with “fraction method”
- Proportionality between area and concentration is linear up to 20%
- Retention time of a peak in the GC is the same as in the MS
> we can check peak correspondence

GC/MS ANALYSIS

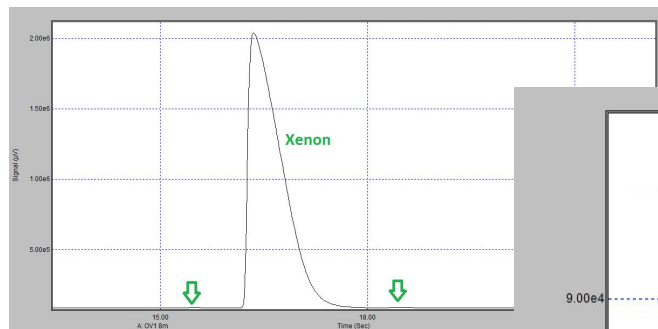
- Both coupling are tested, still the most relevant is with PPU as it can separate possible impurities we are looking for > **CF₄**, **C₂F₆**
- Mass spectrometer analysis are repeated for different mass ranges, as reducing the mass range can help improving instrument sensitivity to low concentrations (expected ~ fraction of PPM)
- NIST library available in MS software for identification
> only possible if all mass lines are identified, i.e. not in small range

BOTTLE ANALYSED

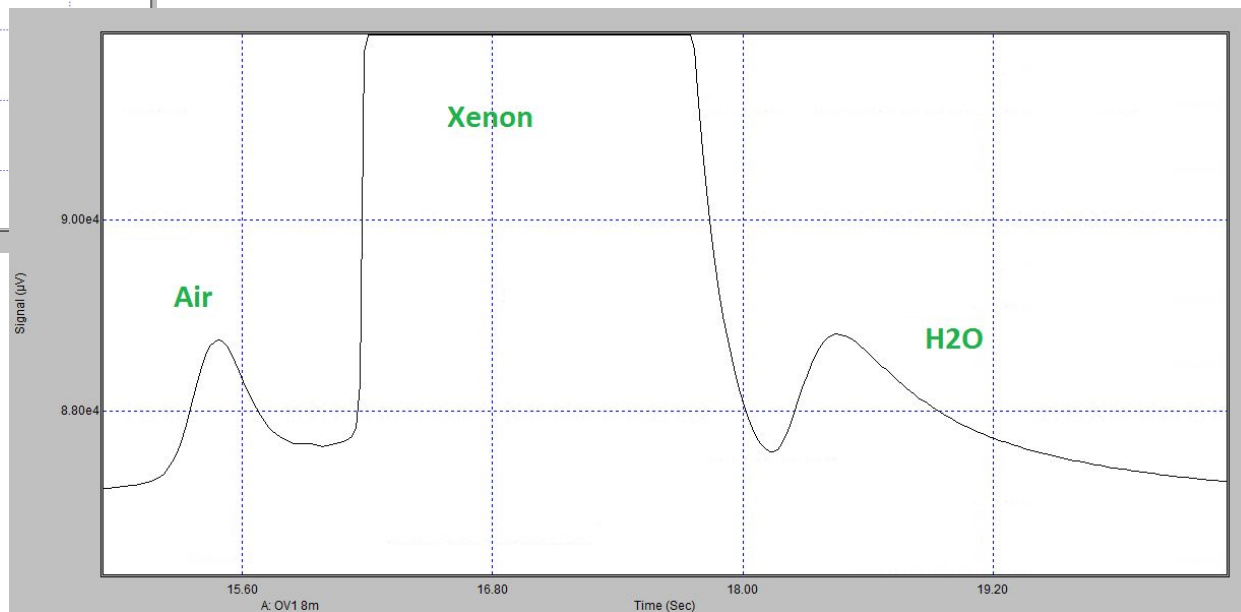
- First bottle Linde 5.0, injected in protoDUNE
- Second bottle quality 5.0, used previously at 182
- Third bottle from ATLAS quality 5.0

FIRST BOTTLE LINDE 5.0 INJECTED IN protoDUNE

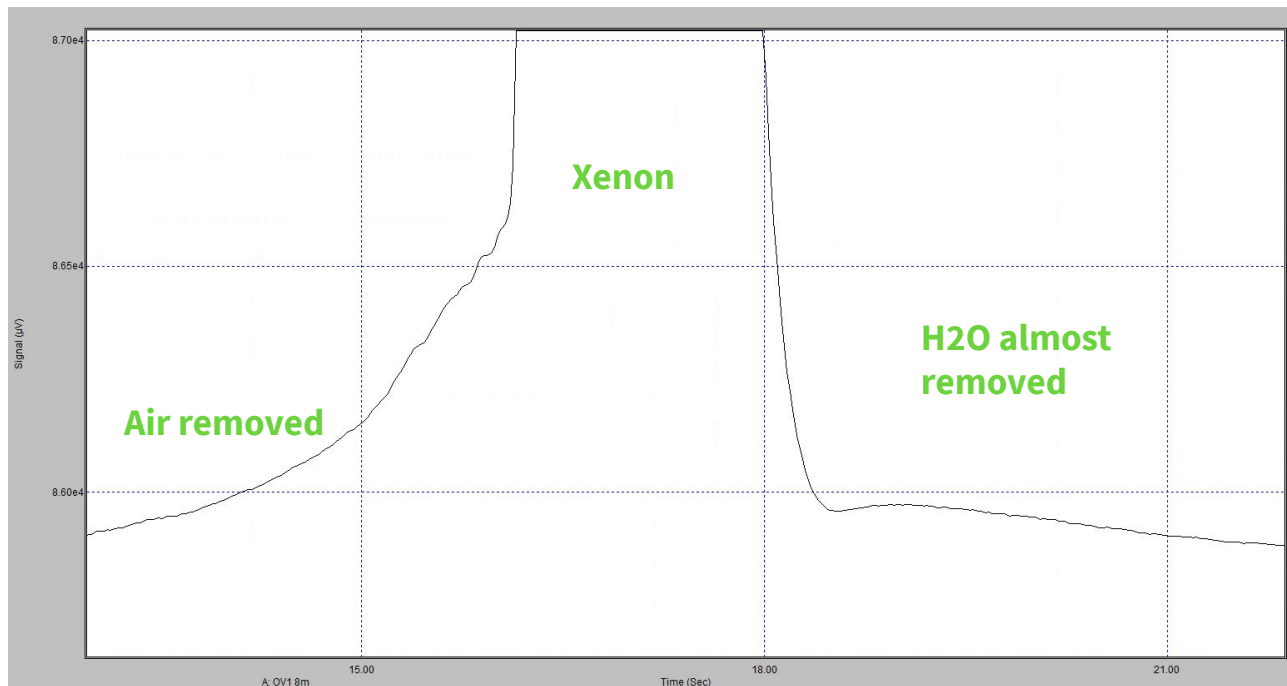
GC ANALYSIS : OV1 COLUMN plastic



RT 15.5s > Air
RT 16.5s > Xe
RT 18.5s > H2O

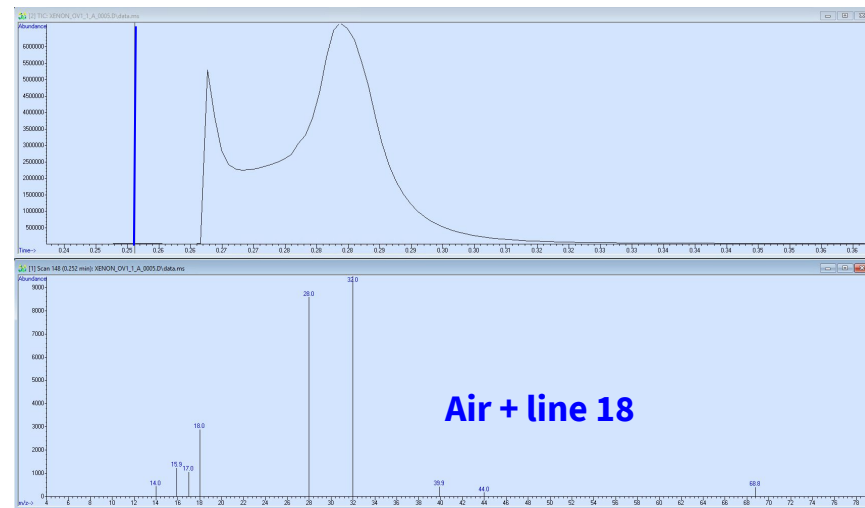
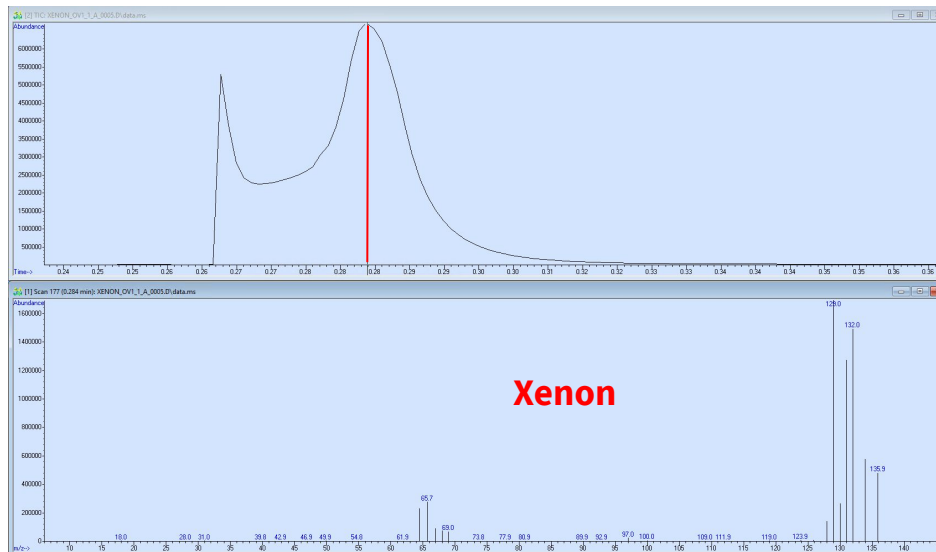


GC ANALYSIS : OV1 COLUMN inox



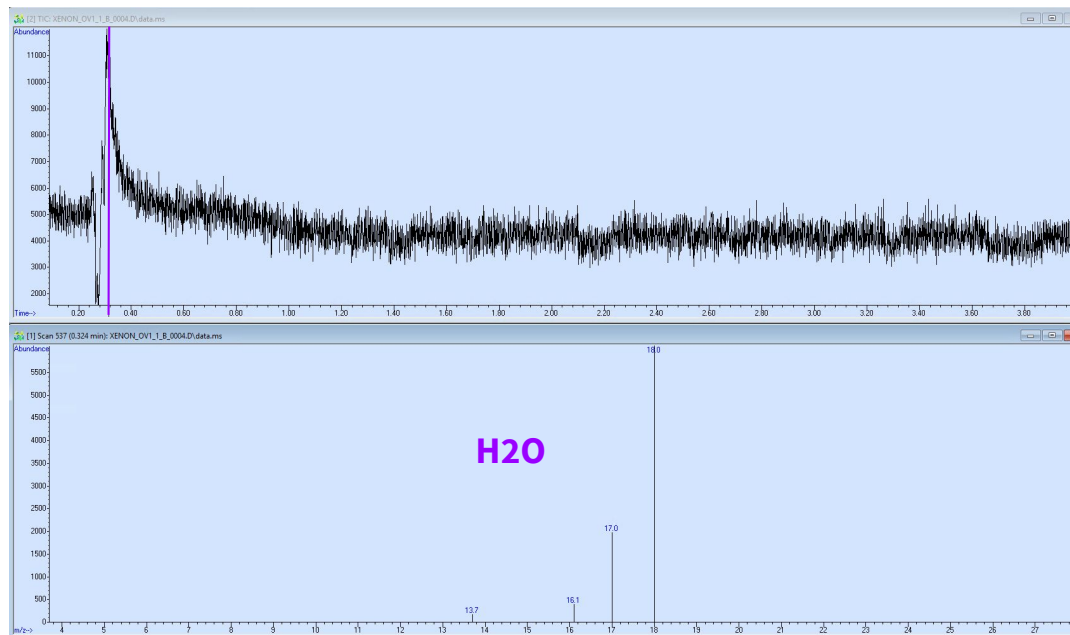
MS ANALYSIS : OV₁ COUPLING

full mass range > identified Xenon, found lines 28/32 (Air) and 18(H₂O)

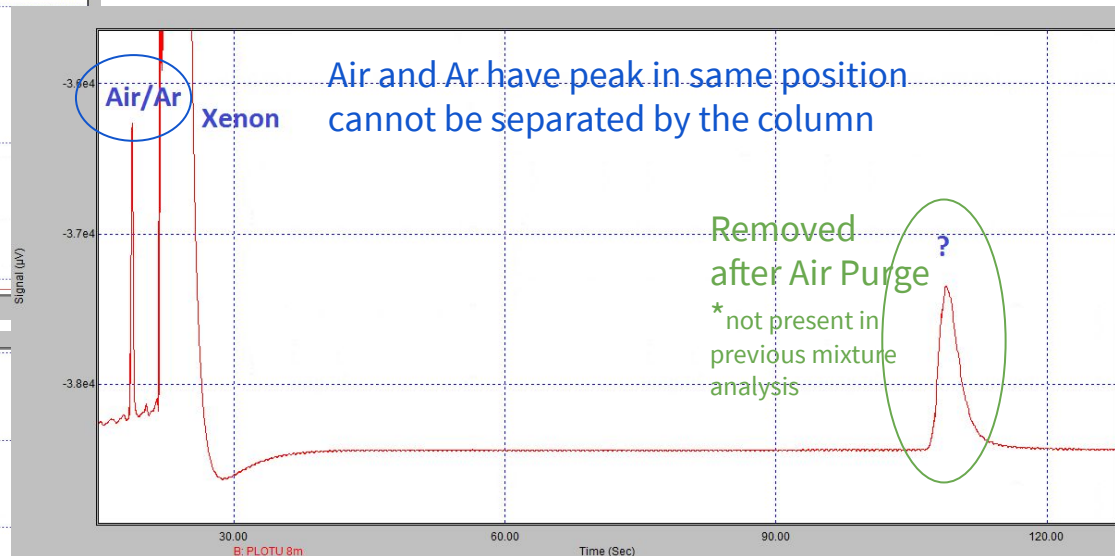
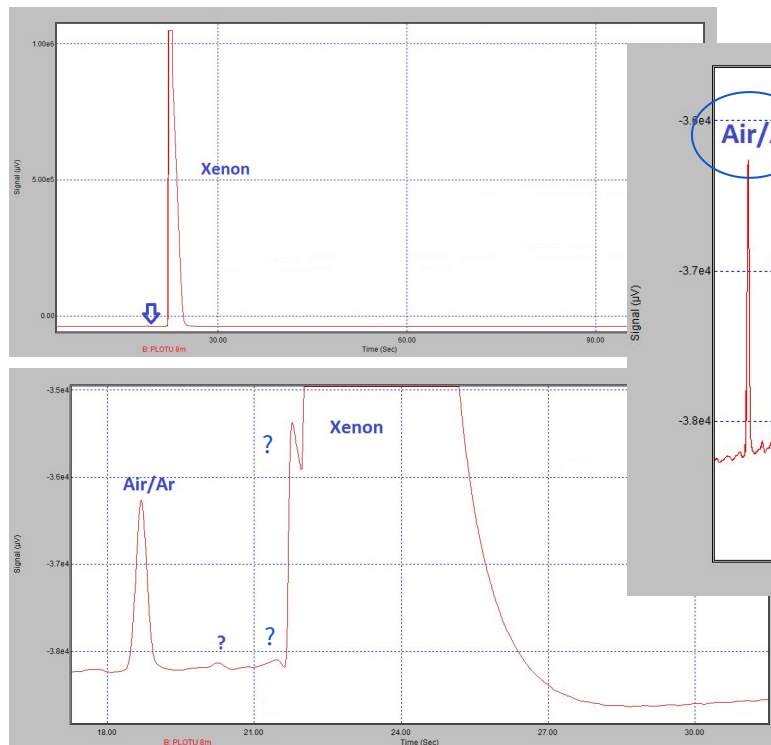


MS ANALYSIS : OV₁ COUPLING

mass range 10-15 > identified H₂O (RT same as GC)



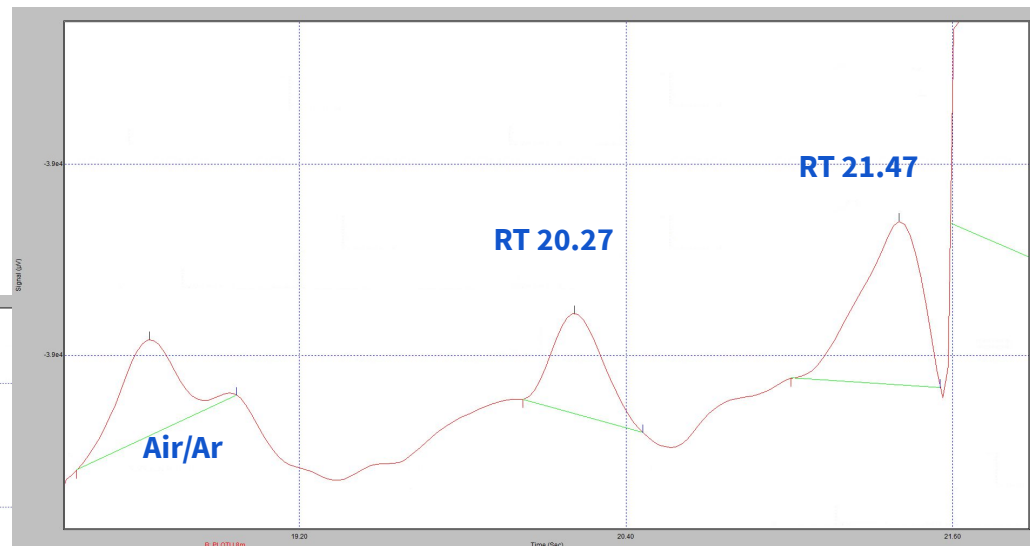
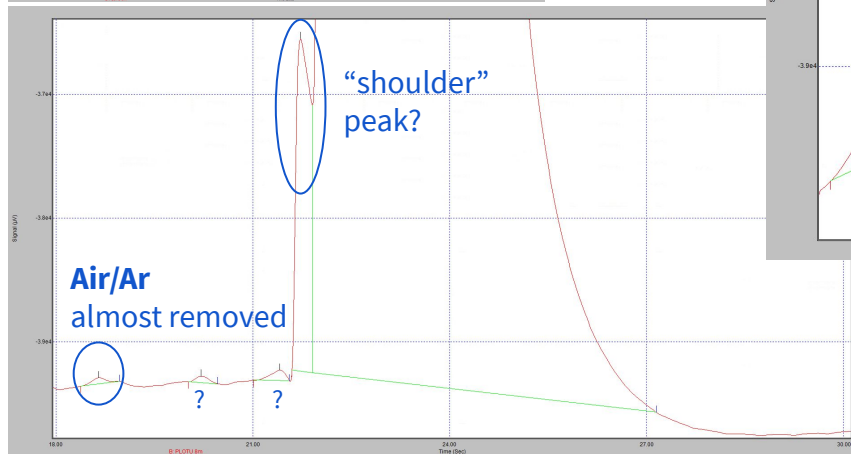
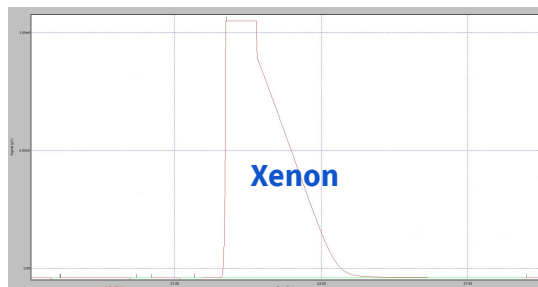
GC ANALYSIS : PPU COLUMN plastic



RT 18.7s > Air
RT 22.4s > Xe
RT 108.9s > Ion69?

RT 20.27s > unidentified
RT 21.47s > unidentified
RT 21.78s > unidentified

GC ANALYSIS : PPU COLUMN inox



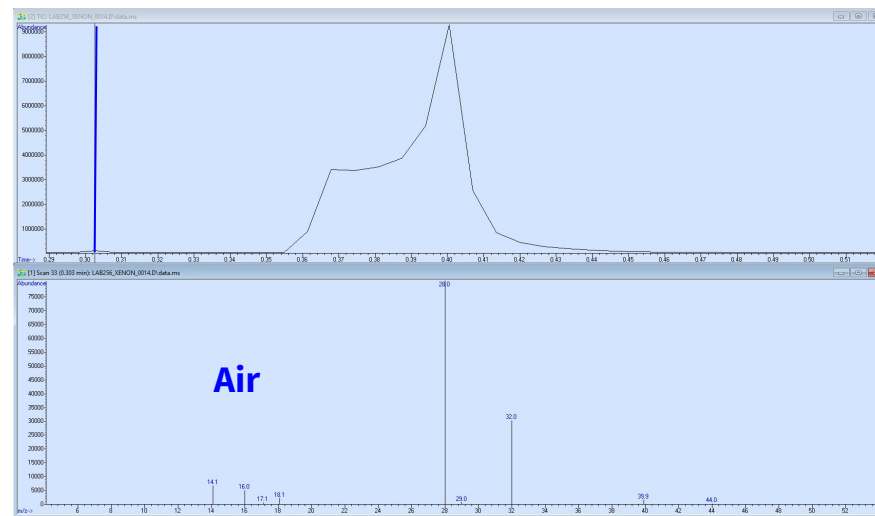
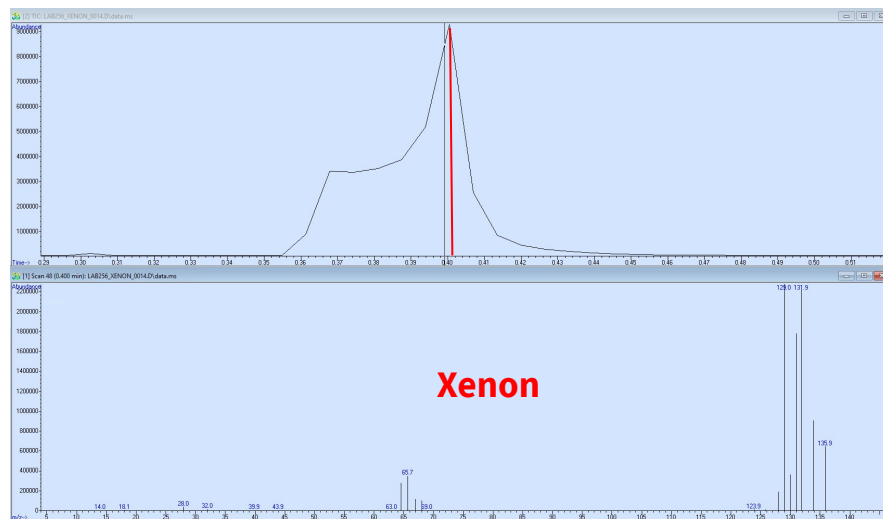
RT 18.7s > Air
RT 22.4s > Xe

RT 20.27s > unidentified
RT 21.47s > unidentified
RT 21.78s > unidentified

look at same RT in MS

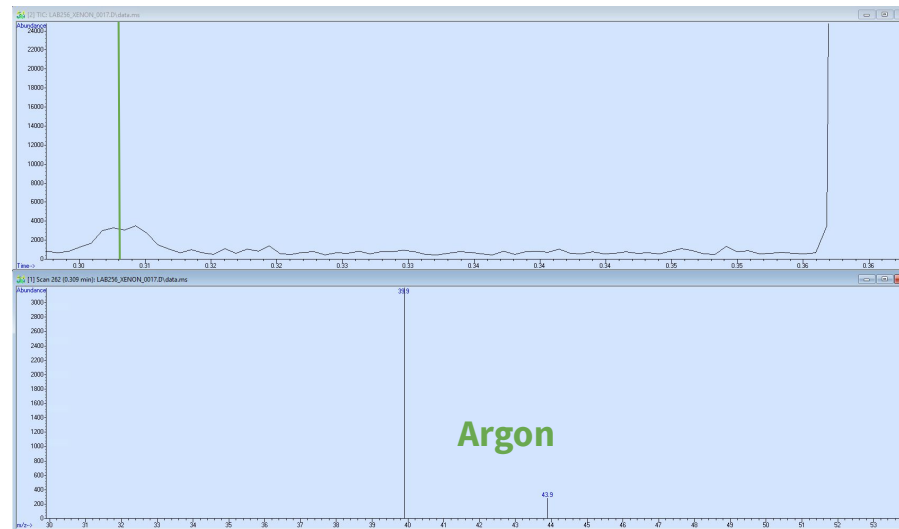
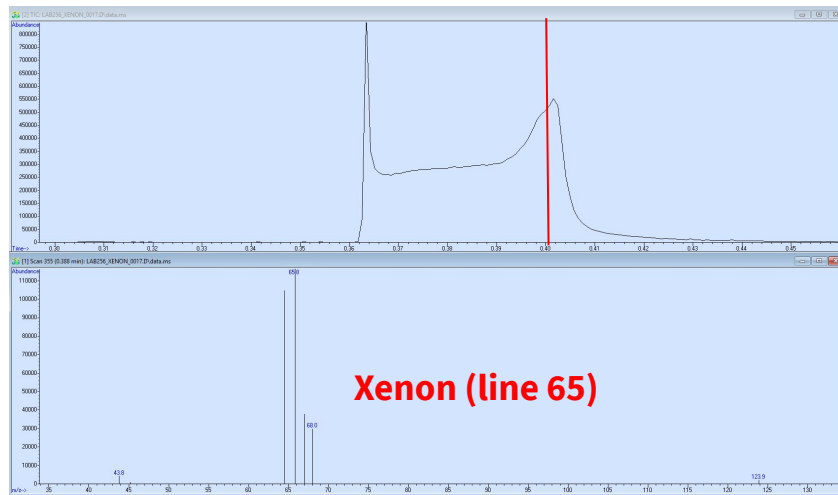
MS ANALYSIS : PPU COUPLING

full mass range > identified Air and Xenon



MS ANALYSIS : PPU COUPLING

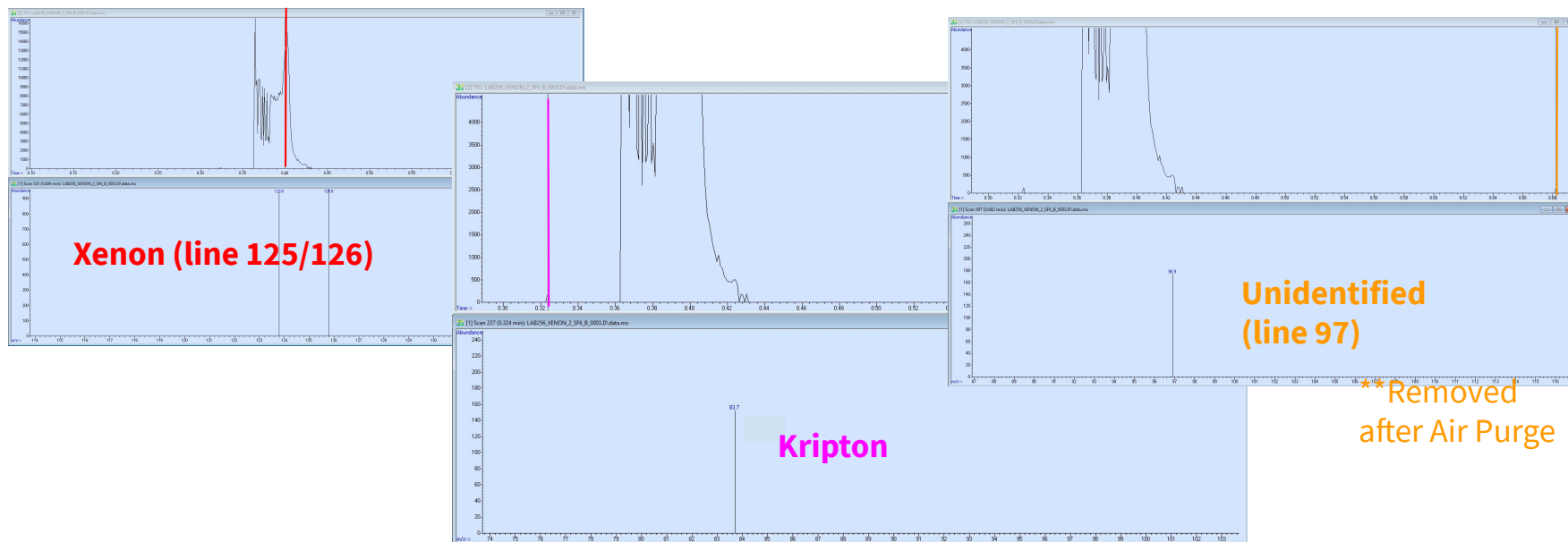
mass range 33-125 (out Air and Xe)
> identified lower line of Xe and Argon



MS ANALYSIS : PPU COUPLING

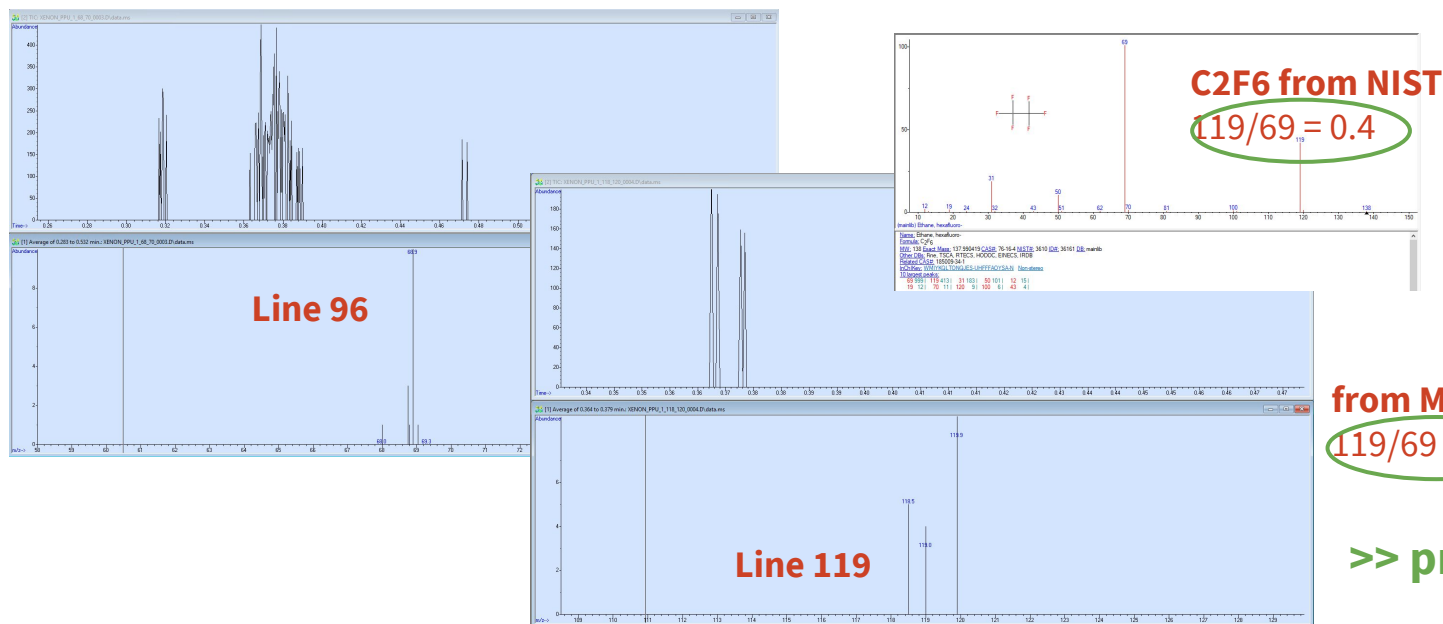
mass range 70-128 (out Air, Ar and Xe, possibly in SF6 (127))

> identified lower line of Xe, Krypton



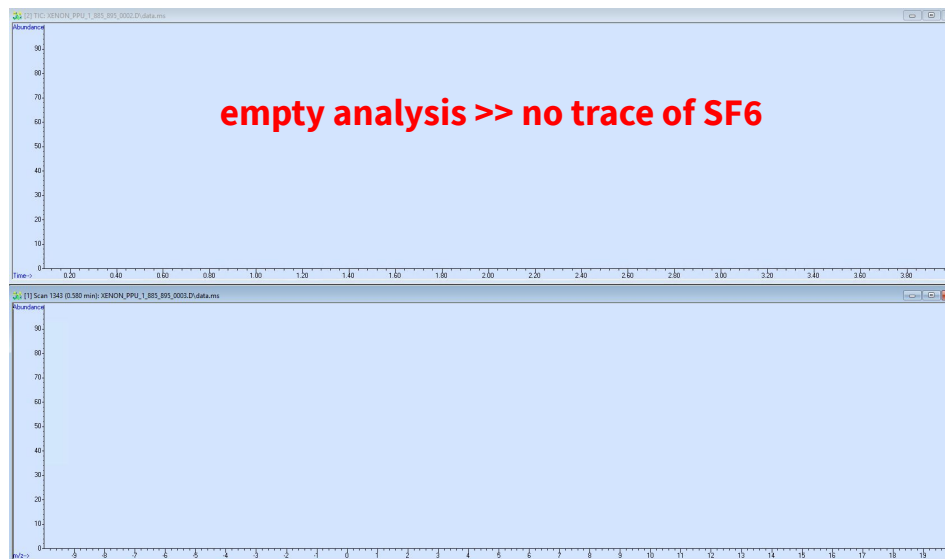
MS ANALYSIS : PPU COUPLING

specific search for $\text{CF}_4/\text{C}_2\text{F}_6$ > range around mass 69 (CF_4 , C_2F_6) and 119 (C_2F_6)

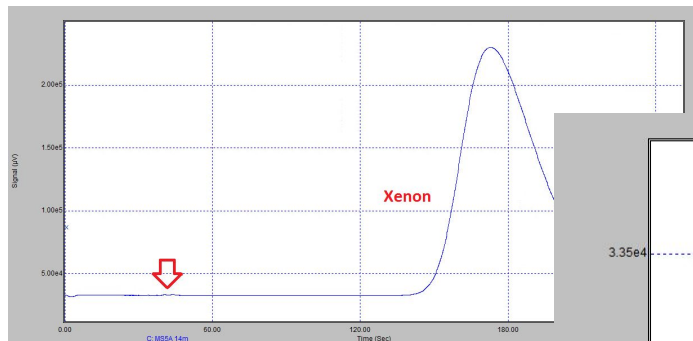


MS ANALYSIS : PPU COUPLING

specific search for SF6 > range around mass 89, 108

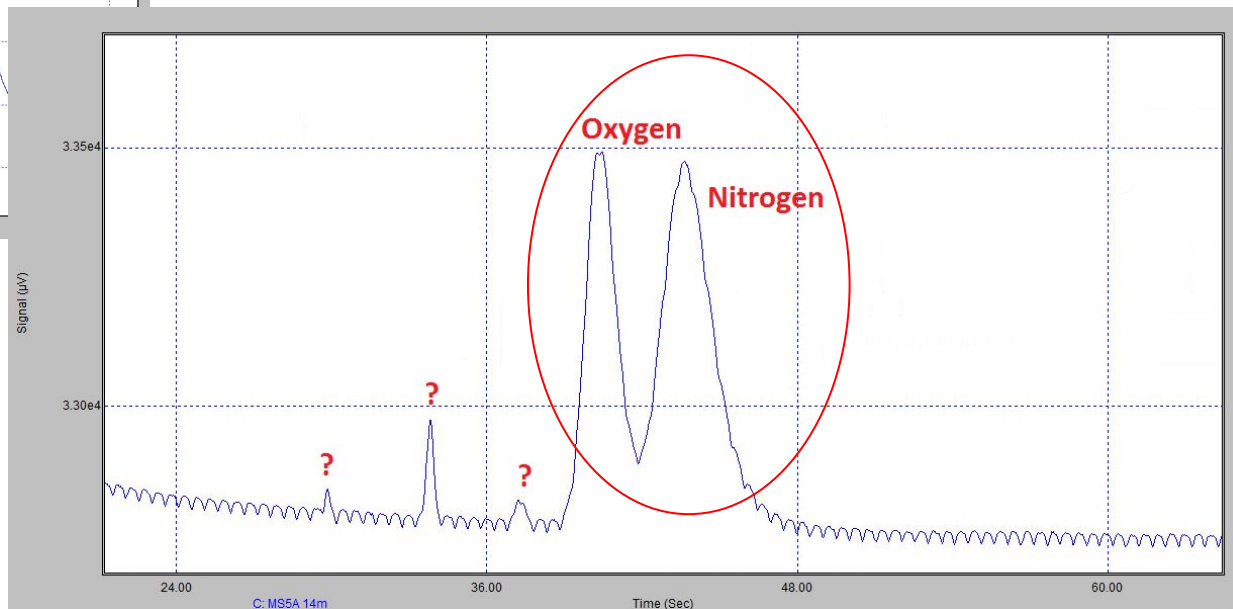


GC ANALYSIS : MS COLUMN plastic

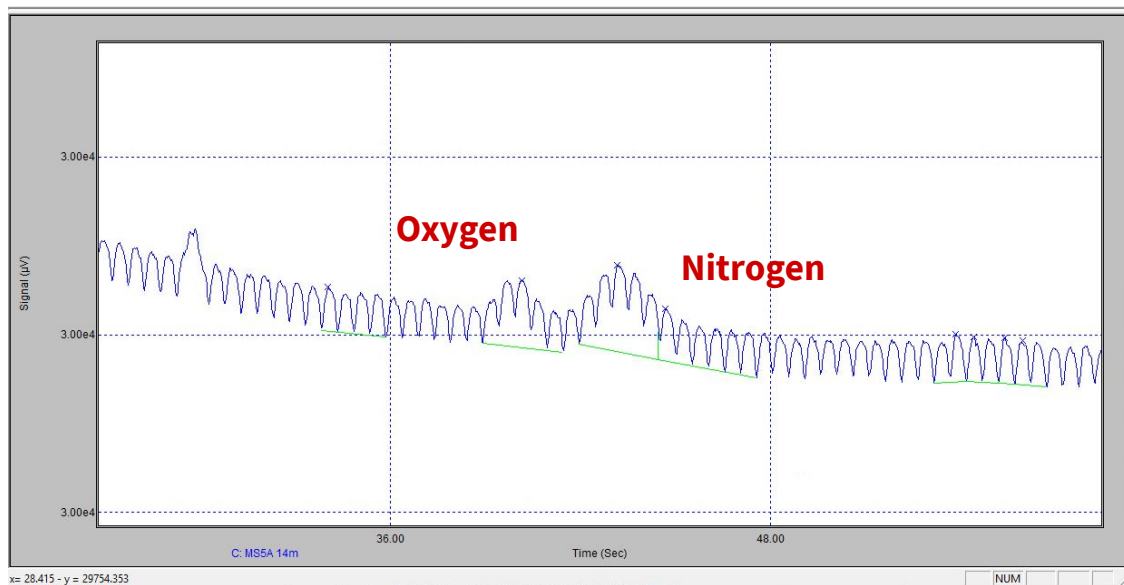


O2 and N2 peaks identified
not Air ratio (1:4)
> surely extra O2
> could be also extra N2
calibration needed to quantify

> 1k ppm > plastic pipe!



GC ANALYSIS : MS COLUMN inox



inox = almost no Air intake
O₂ and N₂ peaks identified
still not Air ratio (1:4)
>> extra O₂ is present

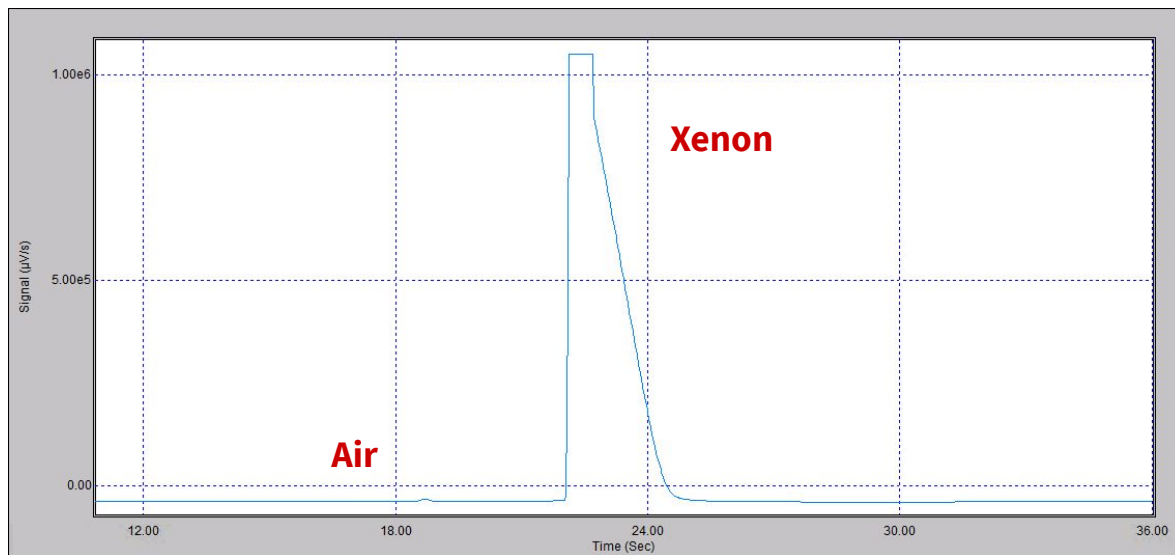
quantification done from
calibration
O₂ ~ 100 ppm

no coupling available with MS column...

OLD BOTTLE quality 5.0 USED AT BLD 182

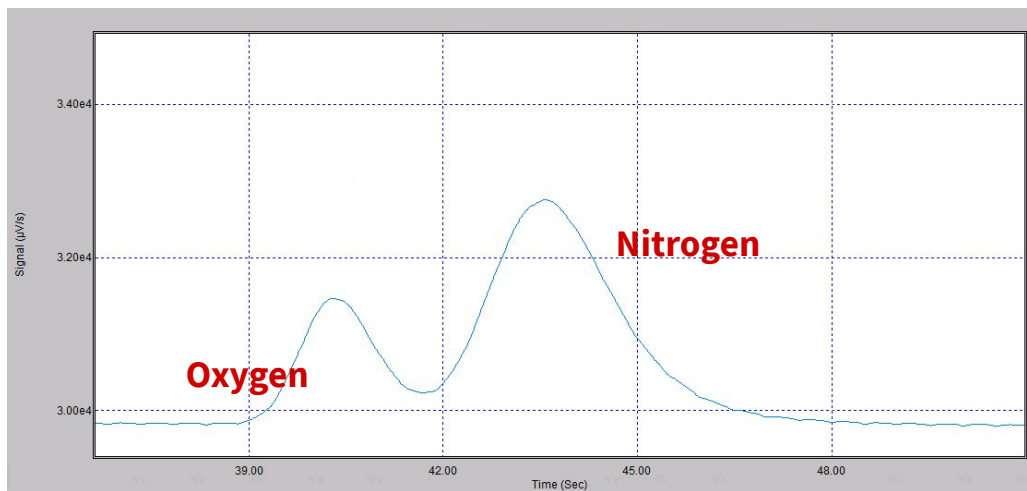
GC ANALYSIS : PPU COLUMN inox

only Xenon and air are visible in the GC PPU column



GC ANALYSIS : MS COLUMN inox

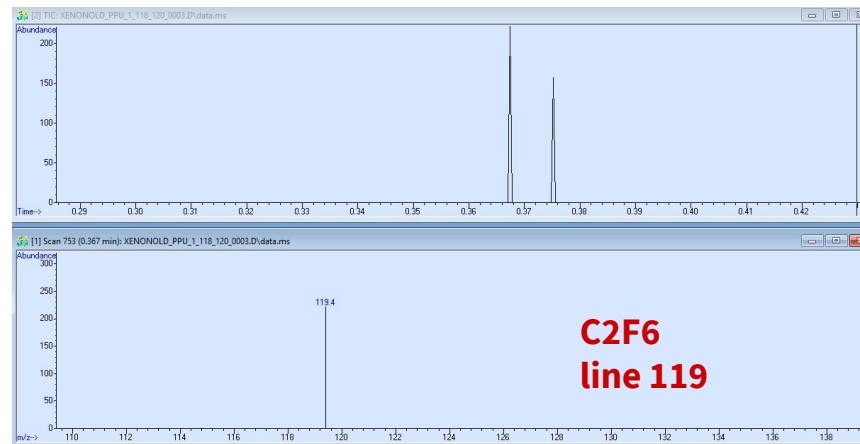
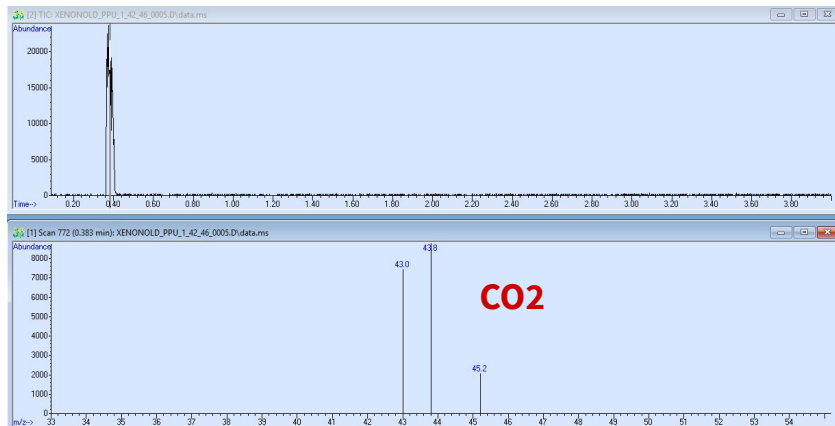
Air form PPU column is confirmed to be just Air (~1k ppm, from pipes?), no extra O₂
> concentration ratio is 1:4 as expected (*not area ratio)



MS ANALYSIS : PPU coupling

mass range 30-40 > CO₂ found

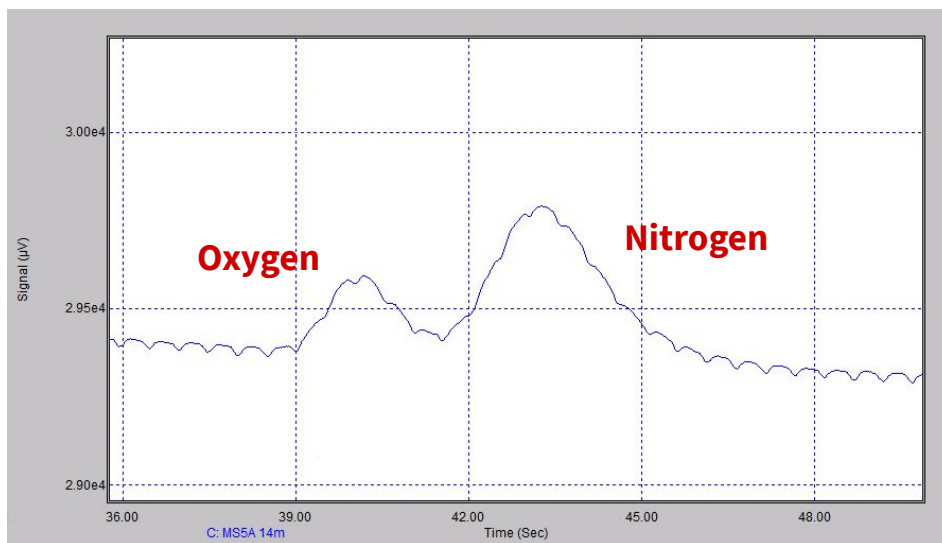
mass range 118-120 > line 119 found, characteristic of C₂F₆



NEW BOTTLE quality 5.0 FROM ATLAS

GC ANALYSIS : MS COLUMN inox

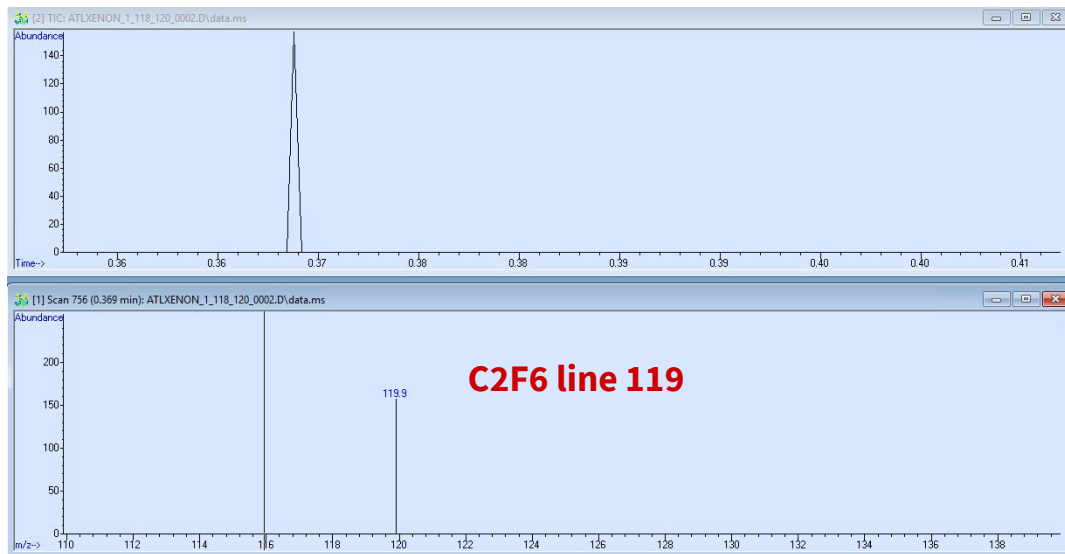
Oxygen + Nitrogen in MS column of GC, about 100ppm of Air > no extra O₂



MS ANALYSIS : PPU coupling

mass range 118-120 > line 119 found, characteristic of C₂F₆

* the peak is visible only in a fraction of the analysis done > limit of detectability



CONCLUSION - quantification

- To obtain precise quantification of the molecules found in the GC/MS
it is necessary to use suitable calibration bottles
- O₂ > calibrated with 50ppm bottle
- Bottles not available for other molecules
>> quantification is based on rough conversion of peak area
- Quantification of C₂F₆ and CO₂ are not precise,
but order of magnitude is correct

CONCLUSION - quantification

bottle	quality	O ₂	O ₂ conc.	C ₂ F ₆	C ₂ F ₆ conc.	CO ₂	CO ₂ conc.
pDUNE	5.0	GC/MS	100 ppm	MS	500 ppb	//	//
182	5.0	//	//	MS	200 ppb	MS	200 ppm
ATLAS	5.0	//	//	MS	100 ppb	//	//

↑
*assuming linear
conversion

CONCLUSION - quantification

- **C₂F₆ is definitely present** in all bottles
 - > The bottle used at protoDUNE contains a higher quantity
 - > **Minimum 500 ppb** (linear conversion), could be higher
- **O₂ is present in concentration around 100 ppm in the protoDUNE bottle**, while it is not found in the other bottles
- *182 bottle contains about 200 ppm of CO₂*, probably not affecting operation as it is filtered before injection