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Evaluation of the impact of replacing helium as carrier gas on a µGC-TCD analyzer for THT monitoring

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PRCI LEADING PIPELINE RESEARCH

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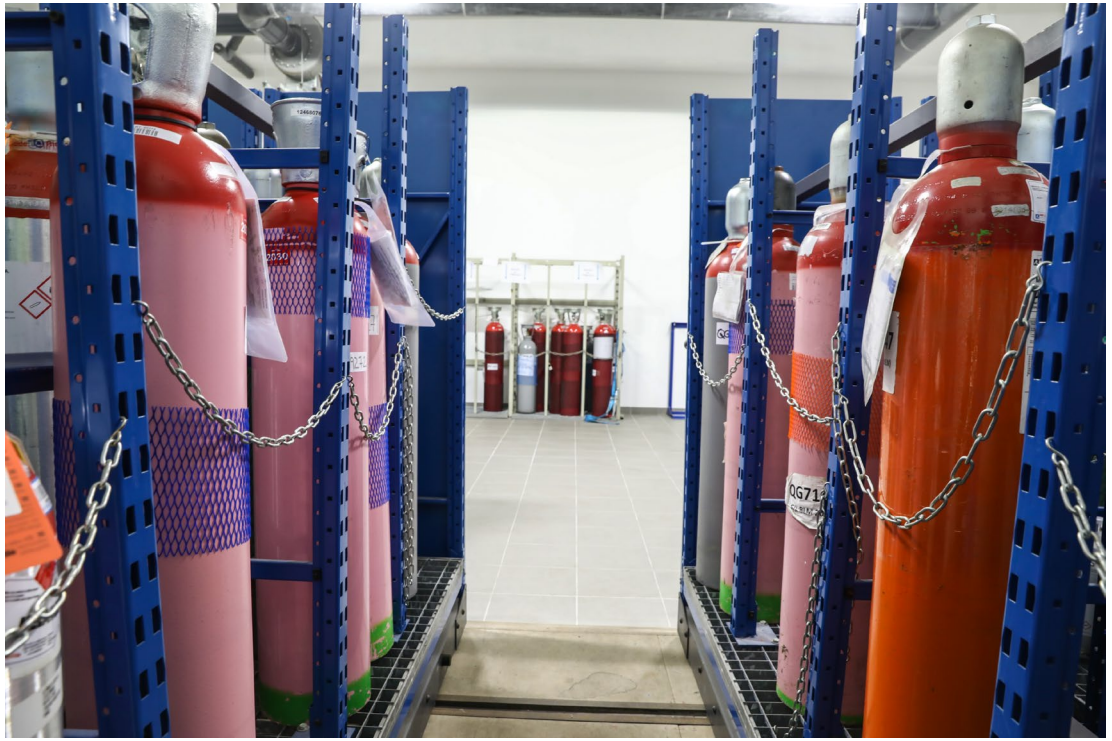
Backgrounds

- Since mid-2021, 4th wave of Helium (He) shortage
- GC use helium as carrier gas
- Possibility to switch helium for another carrier gas (N_2, argon)
- Gas odorant (THT) analysis requires measurement using a µGC



Objectives of the study

- Optimize the analytical parameters (injector temperature, column temperature, column pressure and injection time)
- Evaluate the performance of the analyzer with N_2 as carrier gas in comparison with its performance with He as carrier gas
- Study performed on CP4900 (manufactured by Varian/Agilent) [mostly used in France]

Analytical parameters

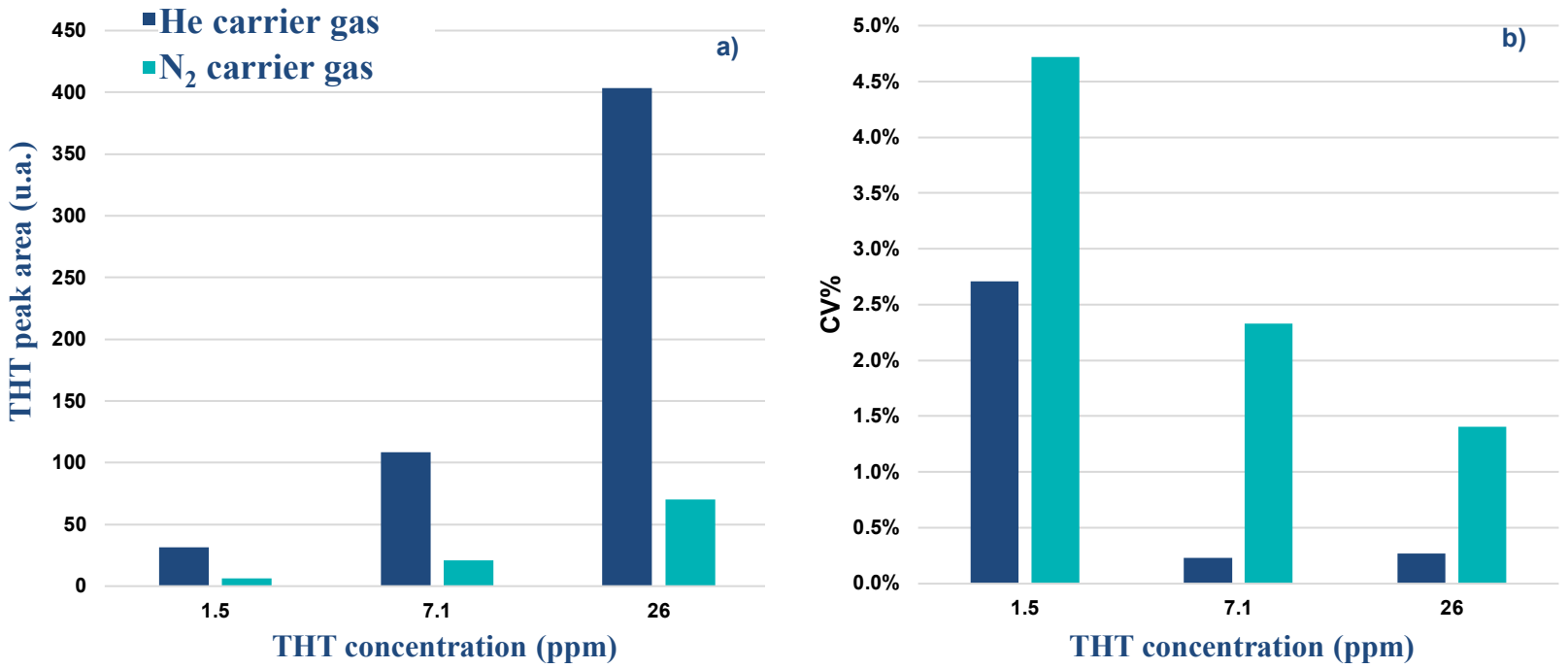
- **Current analytical method with He**

Analytical parameters	Initial values (He method)
T_{inj}: Injection temperature (°C)	85°C
T_{col}: Column temperature (°C)	85°C
P_{col}: Column pressure (kPa)	200 kPa
t_{inj}: Injection time (ms)	250 ms

Material used

Initial carrier gas	- Type: He - Purity: 5.0 - Pressure: 5.5 bar
Carrier gas tested	- Type: N_2 - Purity: 5.0 - Pressure: 5.5 bar
Calibration mixtures used	4 mixtures of THT in CH_4 (1.5, 6.1, 7.1 and 26 ppm)

Comparison with the same analysis conditions



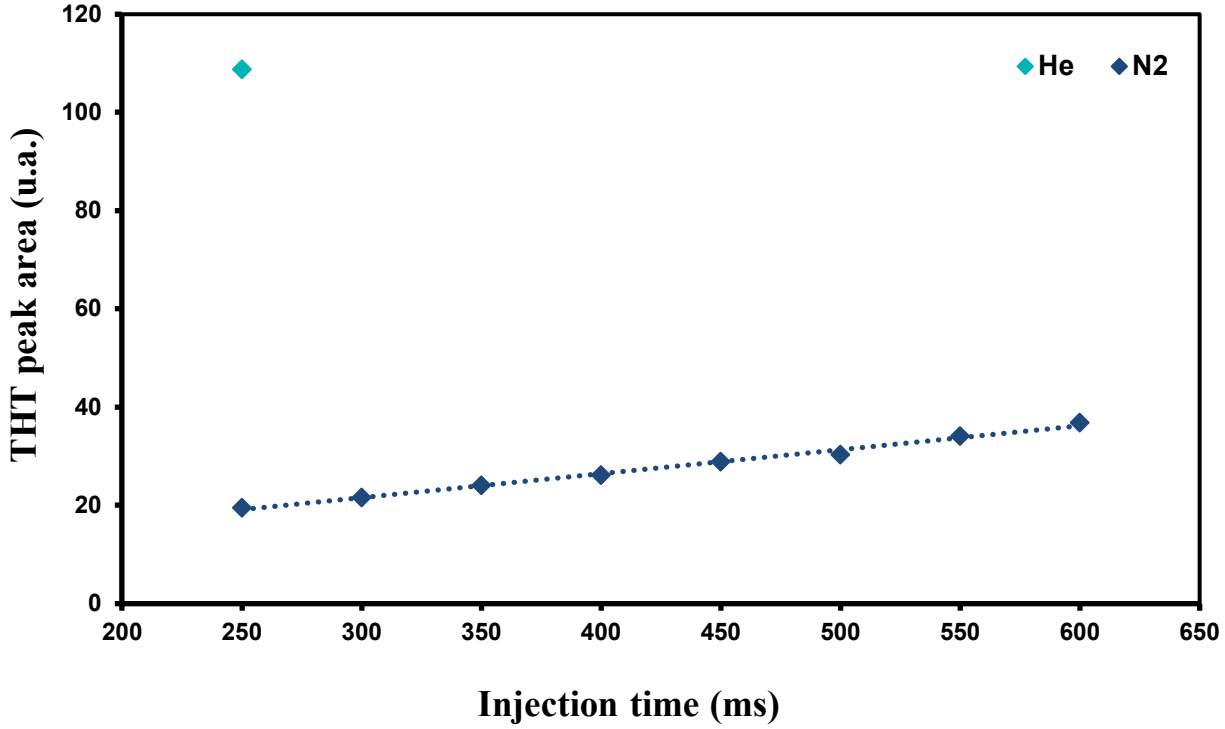
Variation (a) in peak areas and (b) in coefficients of variation (%) when switching from He carrier gas to N_2 with identical chromatographic parameters, for three different THT concentrations.

- "Light" shift for the retention time BUT still no co-elution with NG components
- Peak shape always Gaussian
- Huge decrease on the THT peak area AND increase of the coefficient of variation

→ Modification of the injection time only

(objective → Increase of the THT injected quantity→ bigger peak area)

Optimization of the injection time



To maximize the peak area

➔use of the injection time of 600 ms (89% gain in peak area by increasing the injection time with N_2 from 250 to 600 ms)

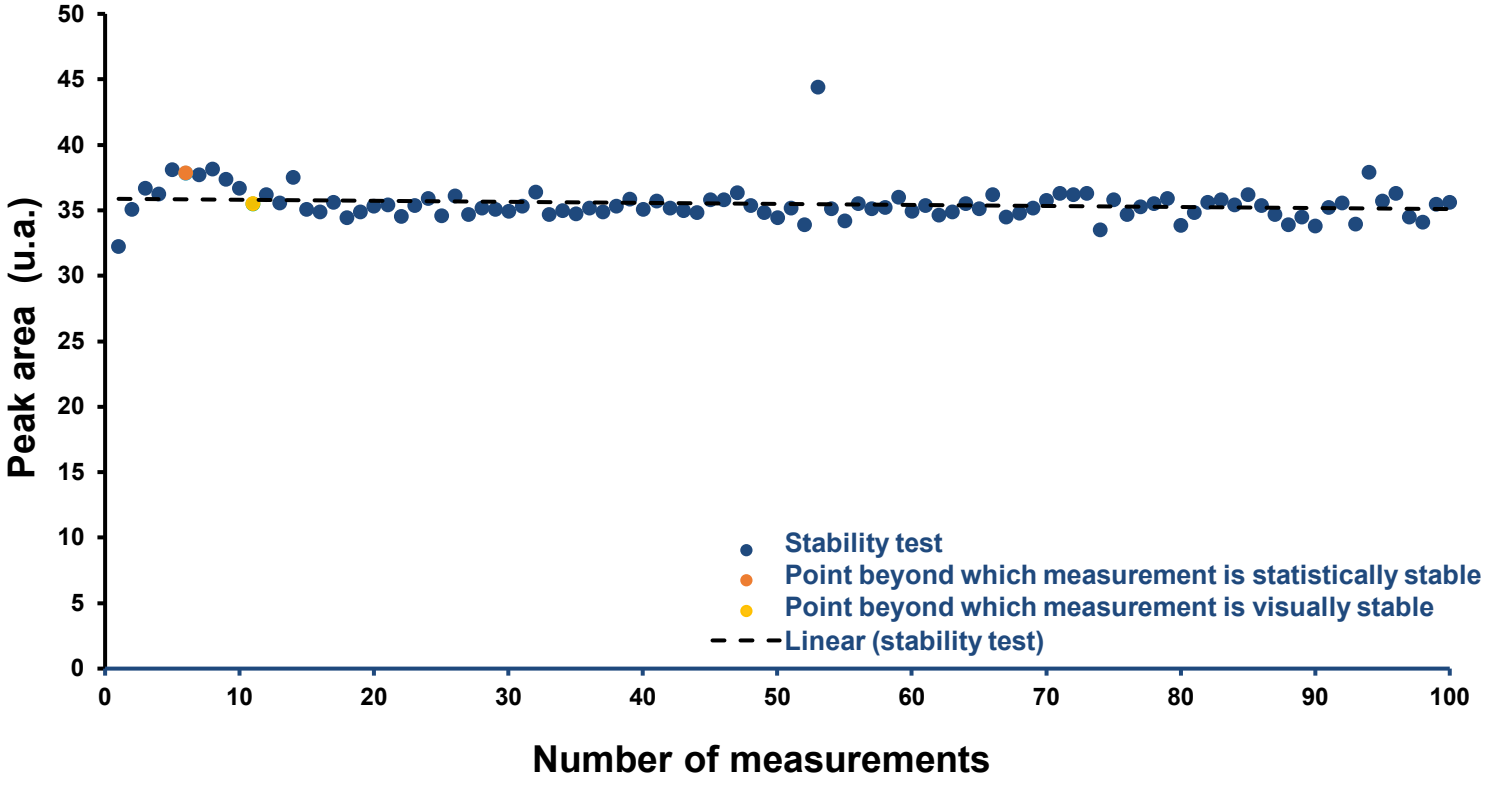
However, an important difference still exists with He as carrier gas (with an injection time of 250 ms).

Evaluation of the analytical performances with N_2

Evaluation in 4 steps:

- Stabilization time,
- Linearity of response,
- Repeatability and determination of LOQ,
- Measurement uncertainties

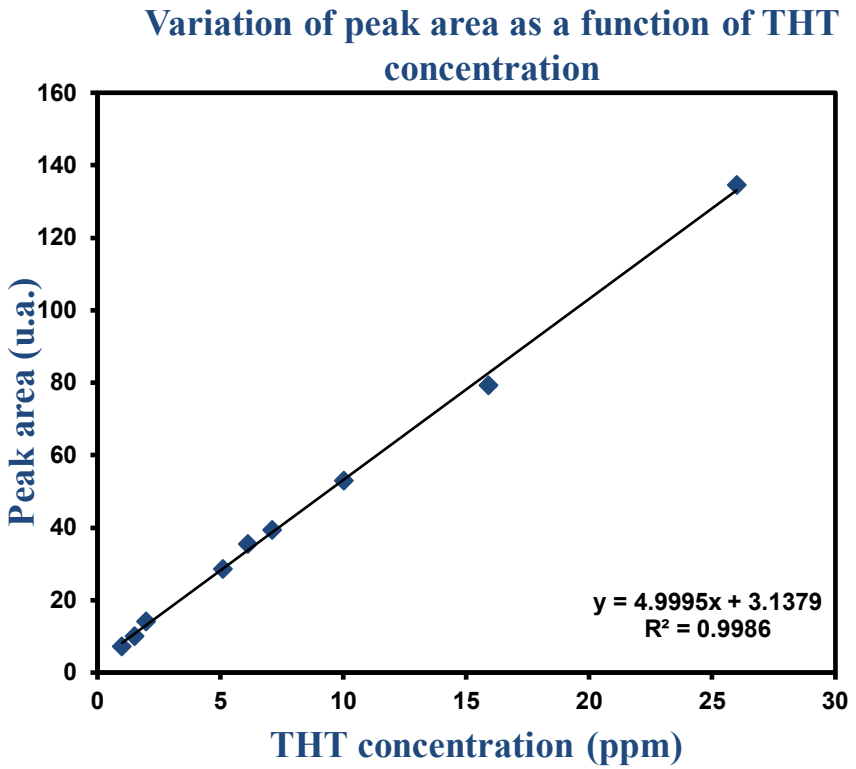
Stabilization time



Stable measurement starting measurement 11

→ Compliant with operator's requirement

Linearity of the response



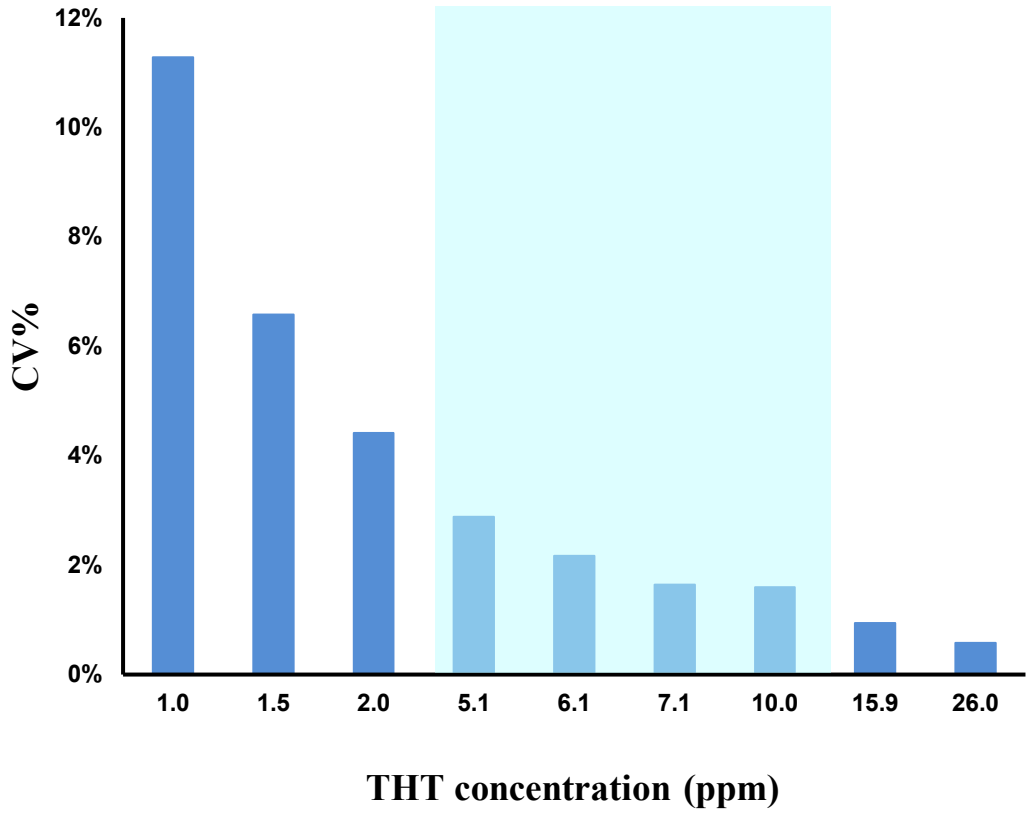
Linear regression model of THT peak area as a function of concentration.

Observation similar to that obtained with He: first order linearity (with an intercept significantly different than zero)

→ Compliant with operator's requirement

However, the calibration has to be done using at least 2 measurement points

Repeatability and LOQ



Variation of coefficient of variation (%) on peak area as a function of THT concentration. In green, the range for natural gas in France (4 to 10 ppm).

THT range: acceptable CV% (btw 2 to 3.5%)

LOQ estimated at 0.9 ppm

→ Compliant with operator's requirement

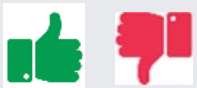
Expanded uncertainties

Cylinder THT content (ppm)	1.002	1.51	1.99	5.1	7.1	10.02	15.9	26
Expanded uncertainty (k=2) (%)	46,7%	29.2%	30.8%	10.6%	9.7%	13.4%	18.4%	14.8%
Expanded uncertainty (ppm)	0.47	0.44	0.61	0.54	0.69	1.34	2.93	3.85

Expanded uncertainties are of the same order of magnitude as those obtained using He as the carrier gas

→ Compliant with operator's requirement

Conclusion

	Gas operators' criteria (Criteria and performance levels obtained with He carrier gas)	Analyzer results
Measurement range to be tested	1-10ppm of THT range	
Sensitivity	Minimum possible loss compared to sensitivity with He as carrier gas	
Stabilization time	After the fifth consecutive test at 7 ppm and from the tenth measurement at 5.3 ppm of THT	
Coefficient of variation%	2 to 3.5% for the range (4-10 ppm)	
Influence of daytime factor	Daytime has no significant influence	
Linearity	Areas proportional to measured content. Residues randomly distributed around the measurement curve.	
Analysis time	Little or no impact (around 60 sec)	
Measurement uncertainties	Relative expanded uncertainty (k=2) in the order of 24% at 1.8 ppm of THT and 9-12% for 5.3- 7 ppm of THT	

Perspectives

- Validation of the present observations on another analyzer of the same family

- Testing N_2 as carrier gas on other analyzers used on site for THT monitoring

Acknowledgements

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thank you

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