

Online, non-intrusive composition measurements of circulating CO₂ based mixtures in an experimental heat pump by means of infra-Red spectroscopy

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Paul BOUTEILLER – PhD student

Marie-France TERRIER, Maria-Isabel BARBA-GARRANCHO,
Pascal TOBALY

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Introduction



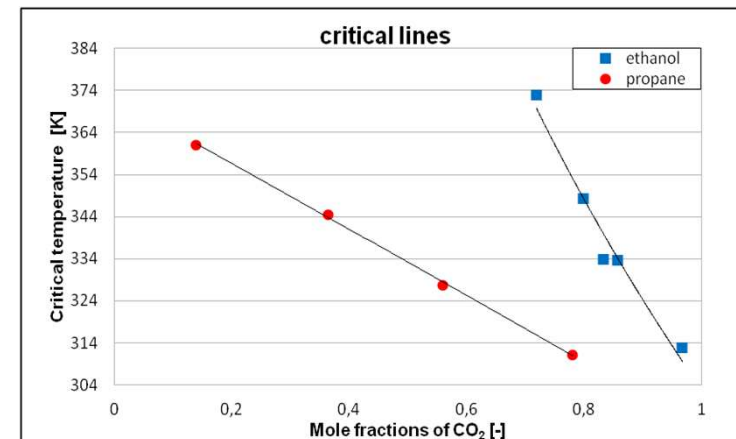
General context

| Regulations & protocols | Aims |
|----------------------------------|---------------------------|
| Montreal protocol | CFC & HCFC |
| Kyoto protocol | High GWP HFC |
| French RT2012 & EU ErP directive | Higher performances |
| F-gas revision | HFC phase-out |

High need for harmless, “green” and efficient refrigerant alternatives.

Thesis main objective

Exploratory research on natural refrigerant mixtures, suited to domestic hot water and central heating production.



Sources: Galicia-Luna & Ortega-Rodriguez (2000) et Niesen & Rainwater (1990)



Introduction



Previous works:

| Authors | Topic | Remarks |
|-----------------------------------|---------------------------------------|---|
| Meunier <i>et Al.</i> (2005) | CO ₂ + HFC mixtures for AC | REFROP predicted COP _C \searrow whereas bench tests showed COP _C \nearrow . |
| Kim <i>et Al.</i> (2007, 2008) | CO ₂ + Propane | COP _C \nearrow , circulating composition is different from that charged. |
| Onaka <i>et Al.</i> (2008) | CO ₂ + DME simulations | COP _H \nearrow and is maximal with xDME = 10% |

Simulations are not accurate enough due to the lack of accurate thermodynamic properties of such mixtures. Experimental heat pump loop along with refrigerant composition measurements are required.

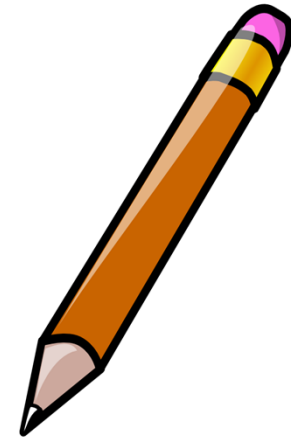
Secondary objective: implementation of a non intrusive method for fluid composition measurements.



Summary



- Experimental setup
 - Experimental heat pump loop
 - Gas chromatography setup
 - Near infra-red spectroscopy setup
- NIR spectroscopy data
- Concentration models generation using PLSr
- First results for CO₂ + Propane mixtures as refrigerant
- Conclusion





Experimental setup



- CO₂ heat pump (2 to 5kW)
 - Scroll compressor with inverter.
 - Brazed plates evaporator and gas cooler.
 - Electronic expansion valve.
 - Internal heat exchanger with suction line accumulator.
- Gas Chromatograph
 - 3 Rolsi® micro samplers.
- NIR spectrometer:
 - Fourier transform spectrometer 10000 to 4500 cm⁻¹.
 - 8 ways optical multiplexer.
 - 5 on tube optical cells.

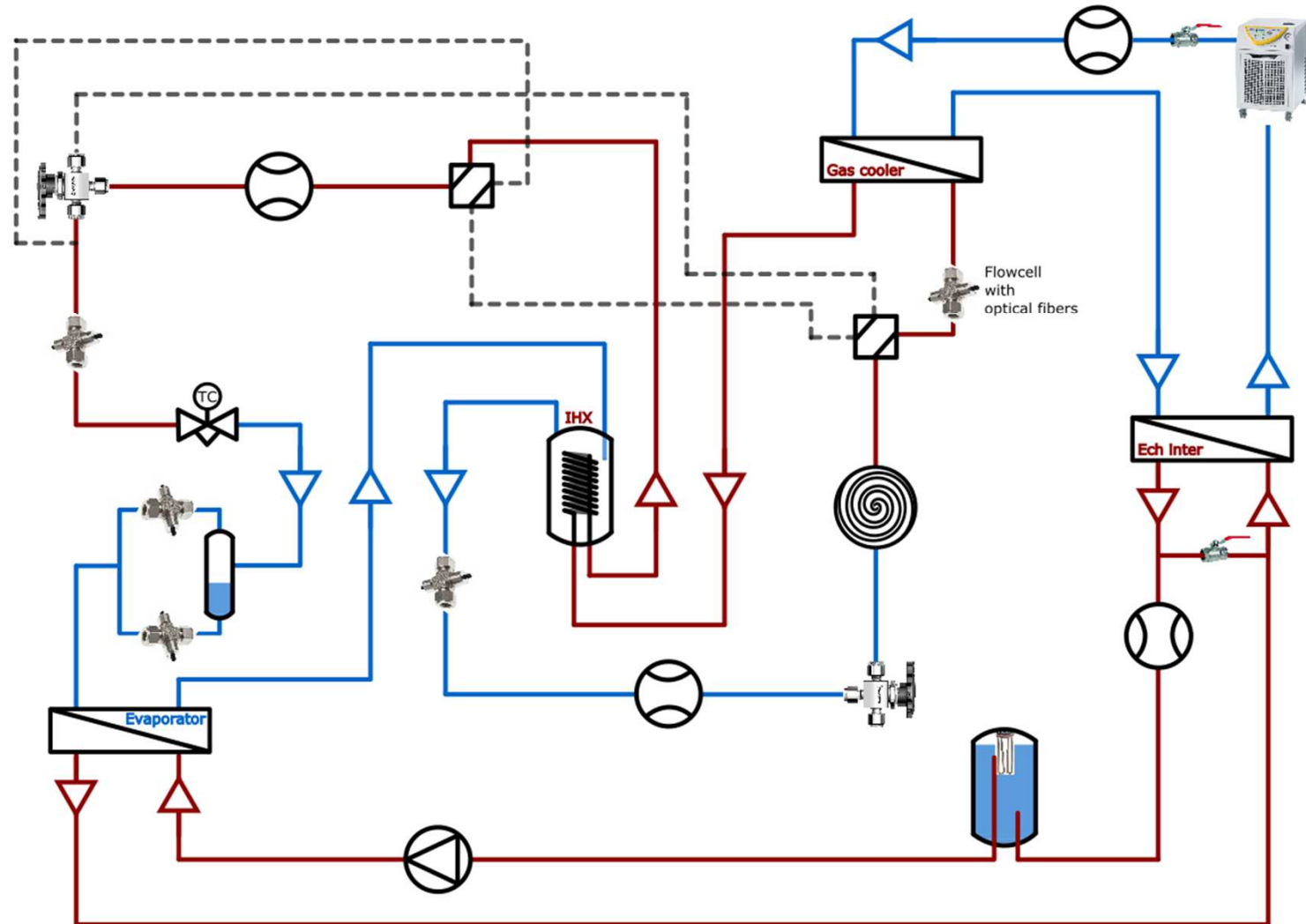




Experimental setup



- Scroll compressor with inverter.
- Brazed plates evaporator and gas cooler.
- Electronic expansion valve.
- Internal heat exchanger with suction line accumulator.
- Auxiliary water + glycol loops





Experimental setup



- CO₂ heat pump (2 to 5kW)
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Gas chromatograph HP 5890



Rolsi® micro-sampler



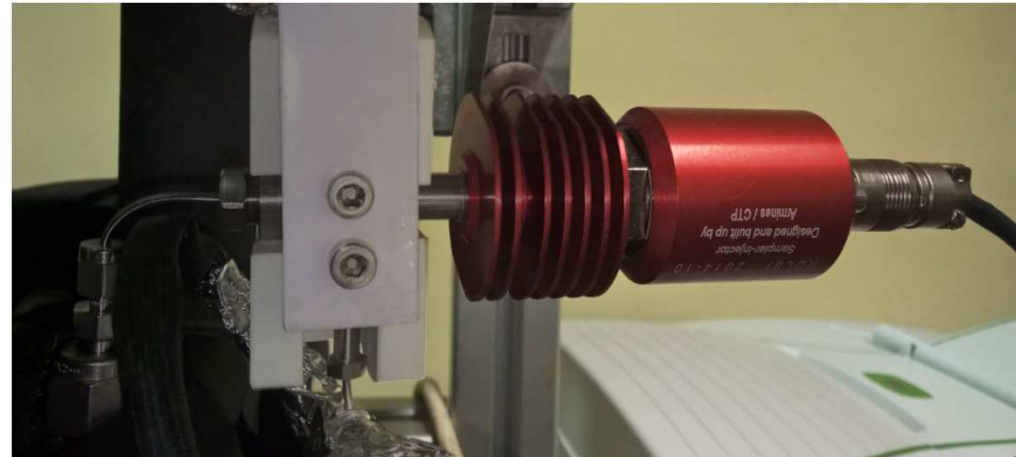
Experimental setup



- Gas Chromatograph
 - 3 Rolsi® micro samplers.
 - Helium transfer line for samples carrying



Gas chromatograph HP 5890



Rolsi® micro-sampler



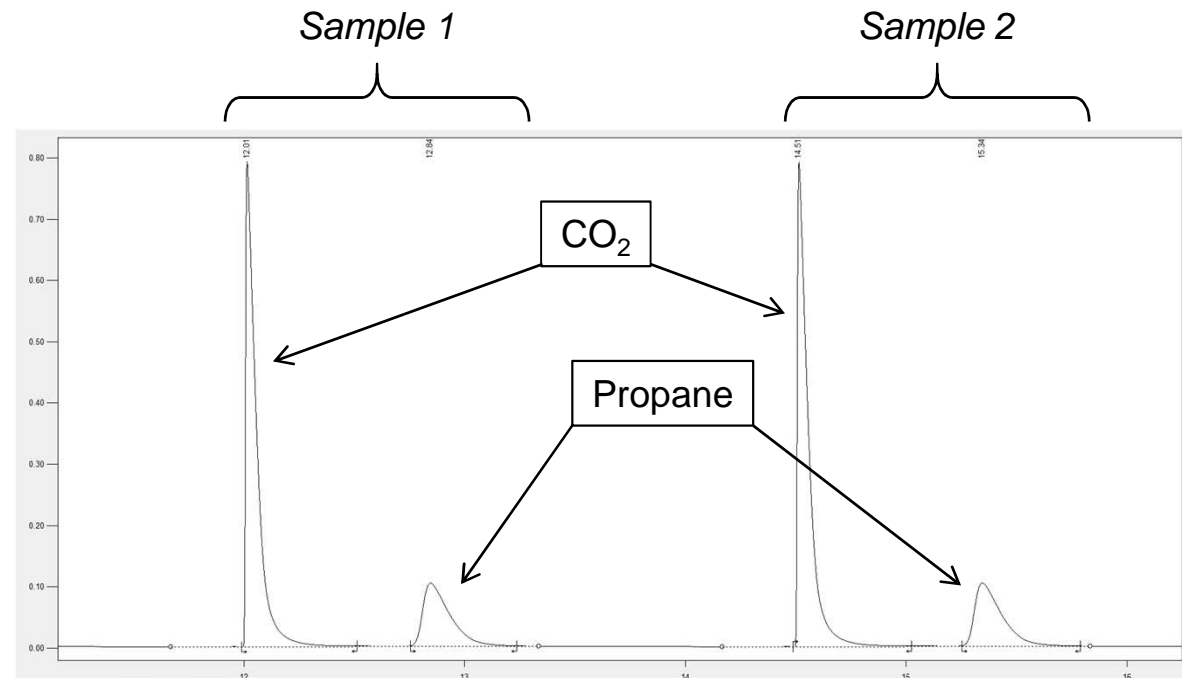
Experimental setup



- Gas Chromatograph
 - 3 Rolsi® micro samplers.
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Gas chromatograph HP 5890



$$\text{Nbr of Moles} = f(\text{peak area})$$

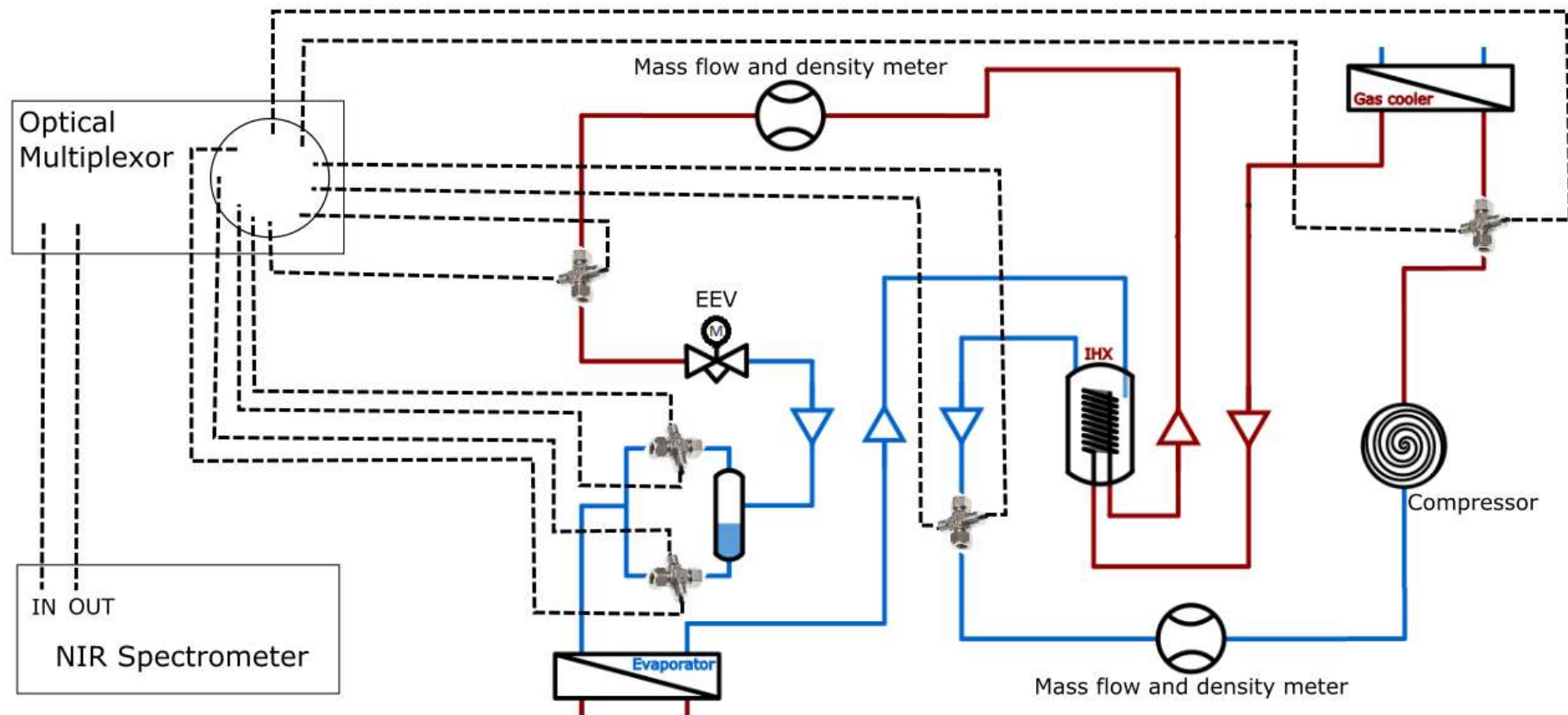
Slow & intrusive method for molar analysis of samples.



Experimental setup



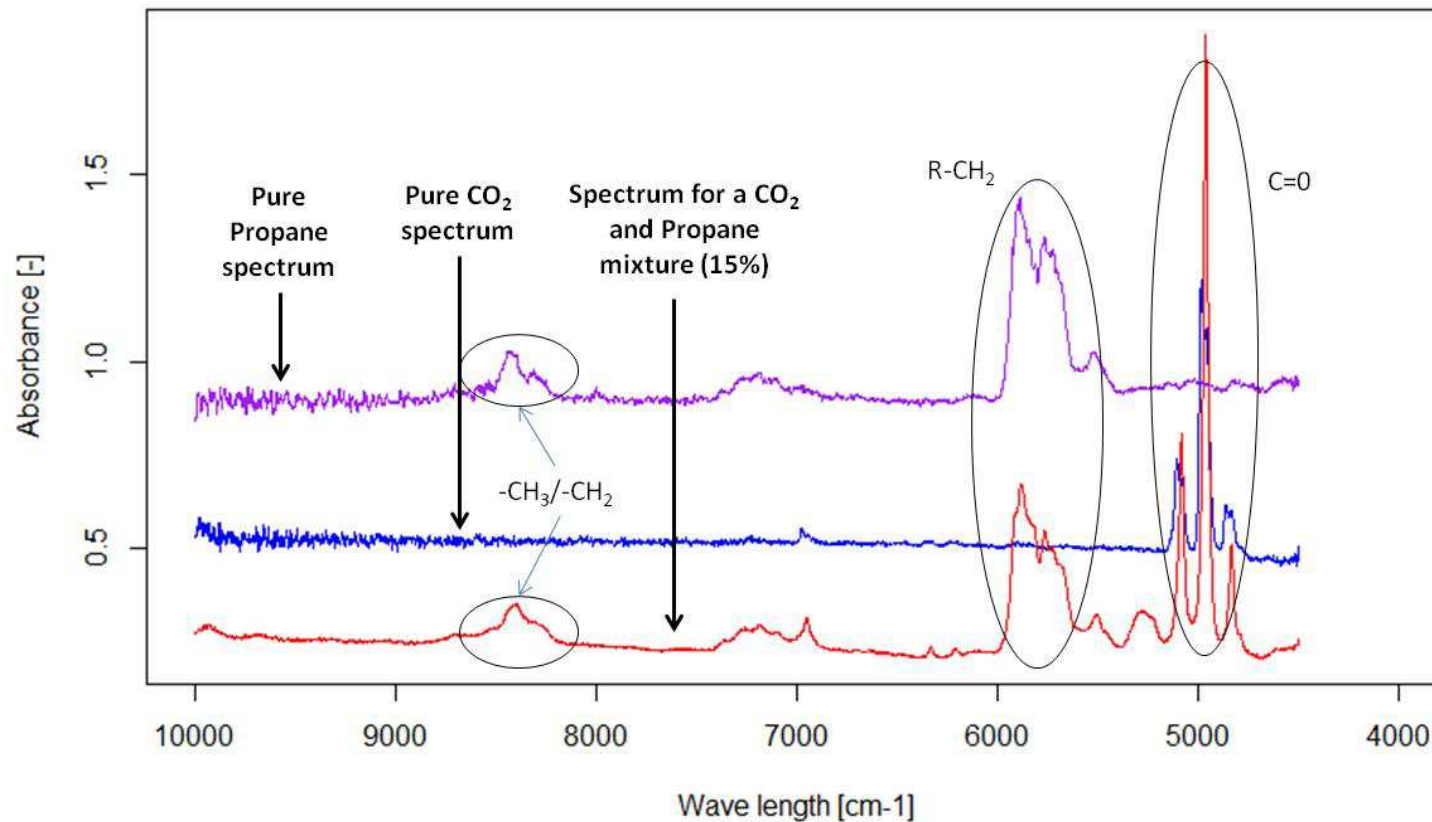
➤ NIR spectroscopy setup





NIR Spectroscopy data

Absorbance spectra for CO₂ and Propane



Fast & non-intrusive method for concentration analysis of circulating fluids.



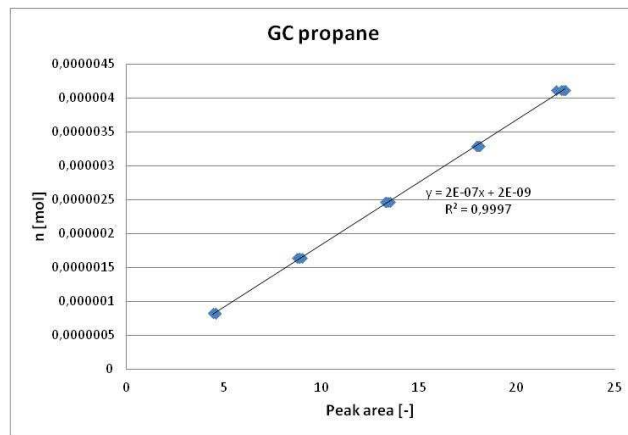
Concentration models generation using PLSr



- Overhaul process

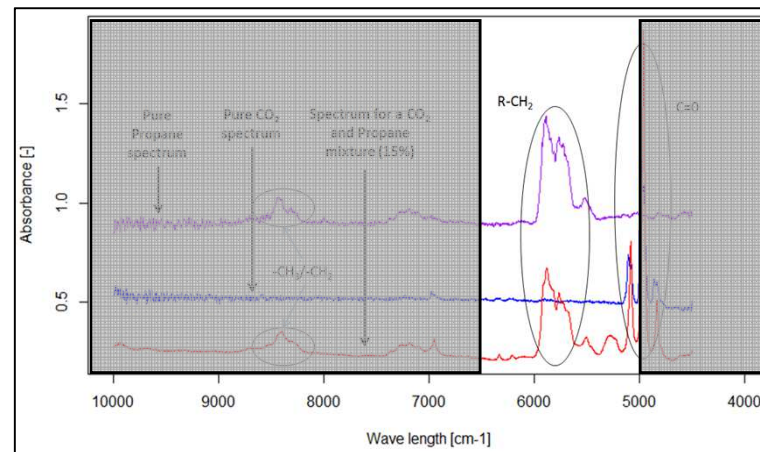
GC calibration

Successive injections of known molar quantities



$$n \text{ (mol)} = a \cdot \text{peak-area}$$

Input data for concentration models calibration



NIR spectra of mixtures with known concentrations (determined via GC).



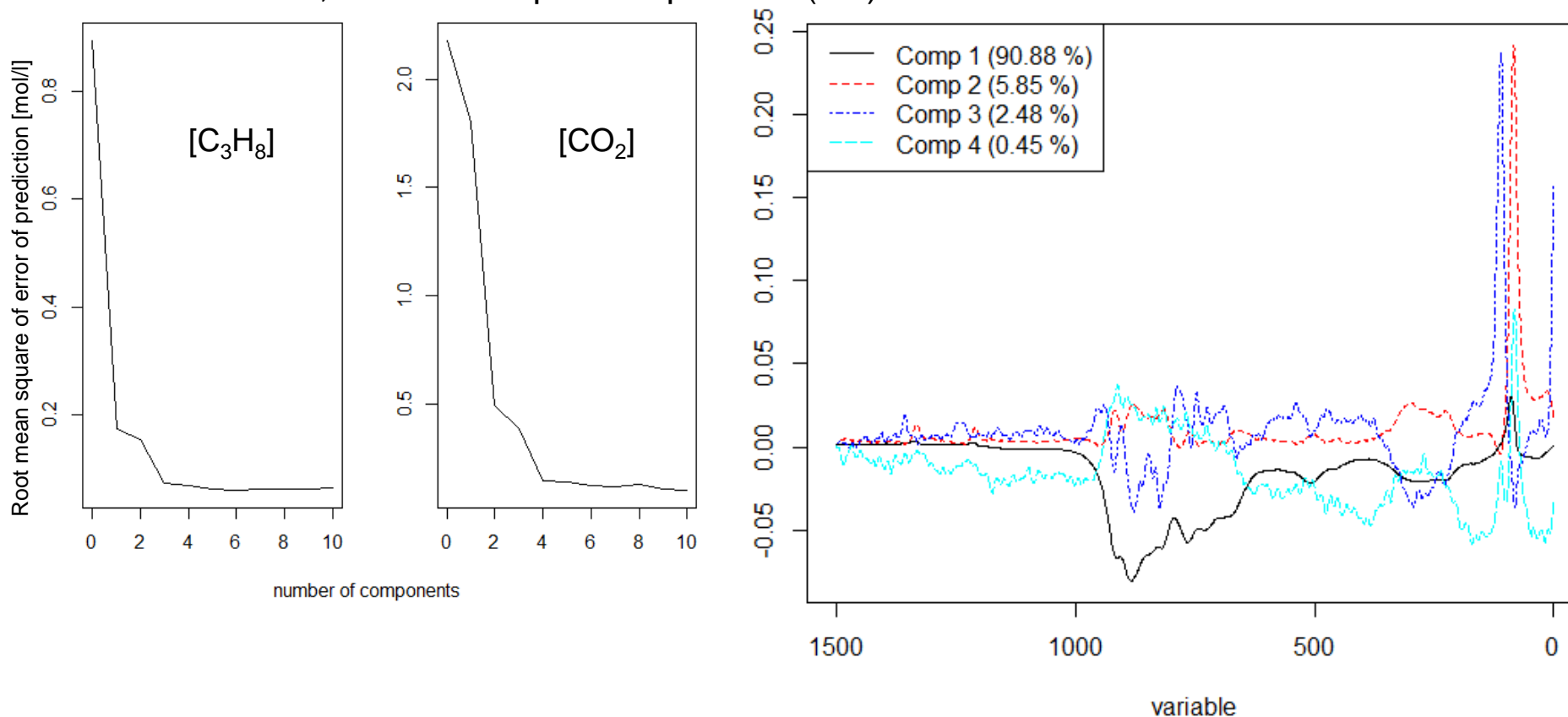
Aim: Elaborate models for [CO₂] and [C₃H₈] depending on spectral data (1500 variables)



Concentration models generation using PLSr



- The spectra database is processed through a Partial Least Square (PLS) regression algorithm (here with 10 random spectra used for cross-validation) (*Source: Chemometrics with R, by Ron Wehrens*).
- New variables, called Principal Components (PC) are determined.

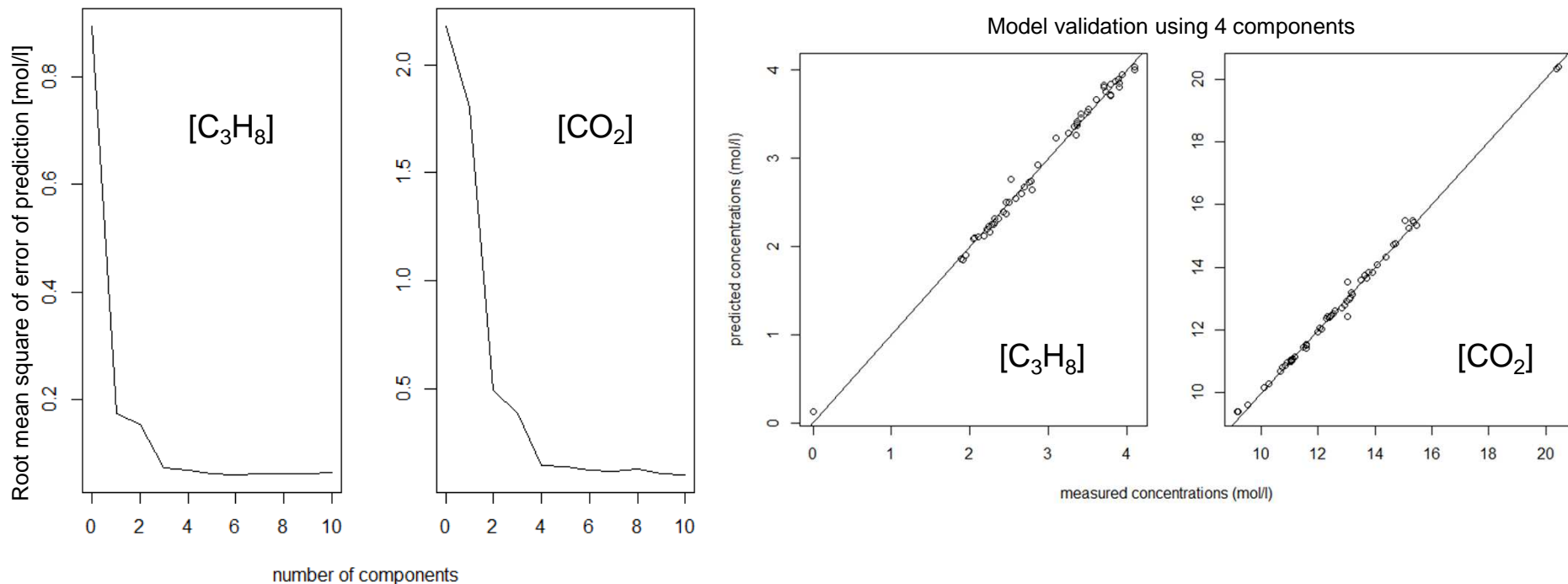




Concentration models generation using PLSr



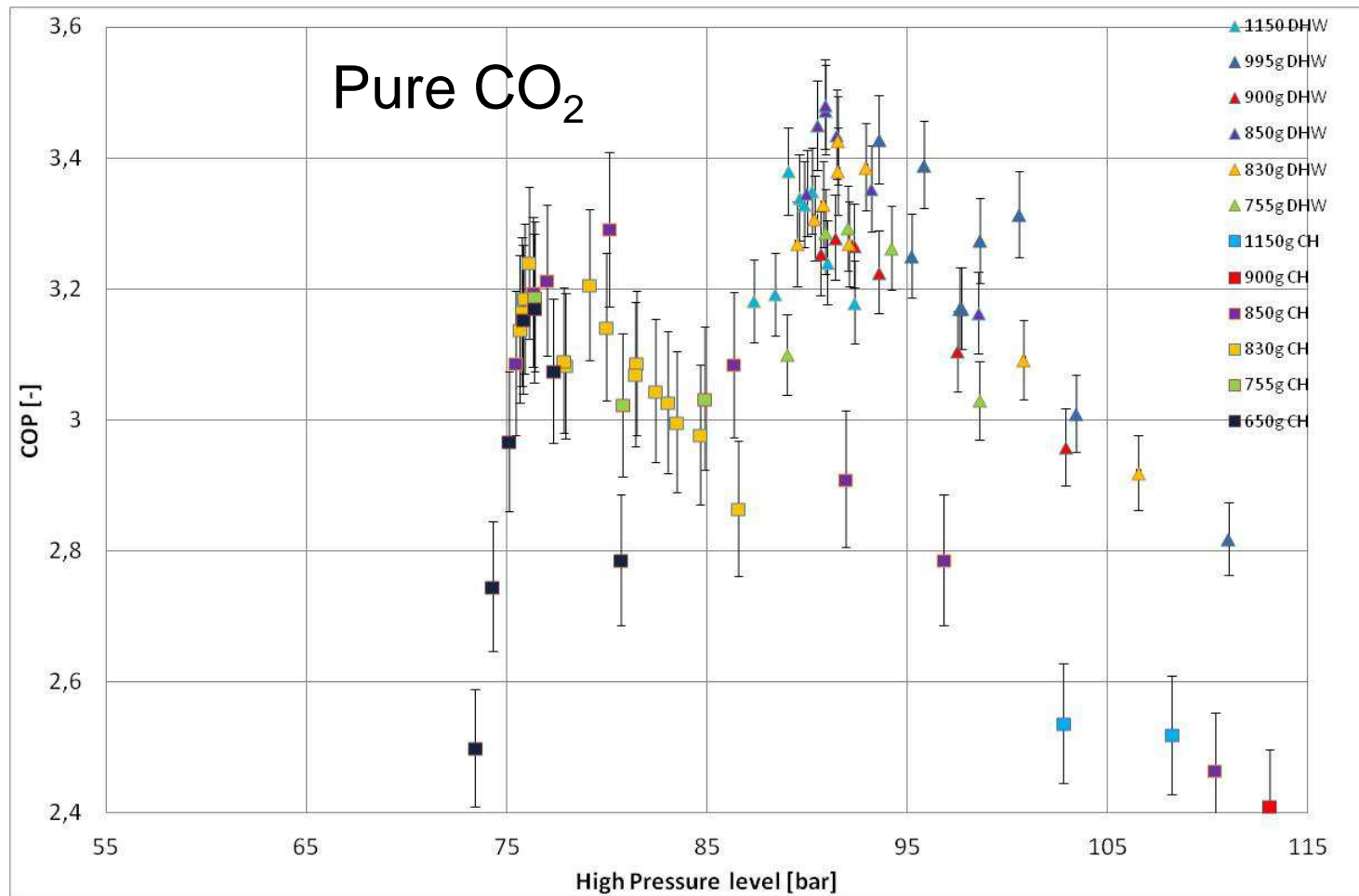
- The spectra database is processed through a Partial Least Square (PLS) regression algorithm (here with 10 random spectra used for cross-validation) (*Source: livre*).
- New variables, called Principal Components (PC) are determined.



4 principal components end up here with a mean error of 0.07 mol/l (max 3.5%) for propane and 0.14 mol/l (max 1.5%) for CO_2 .



Results for CO₂ + propane mixtures

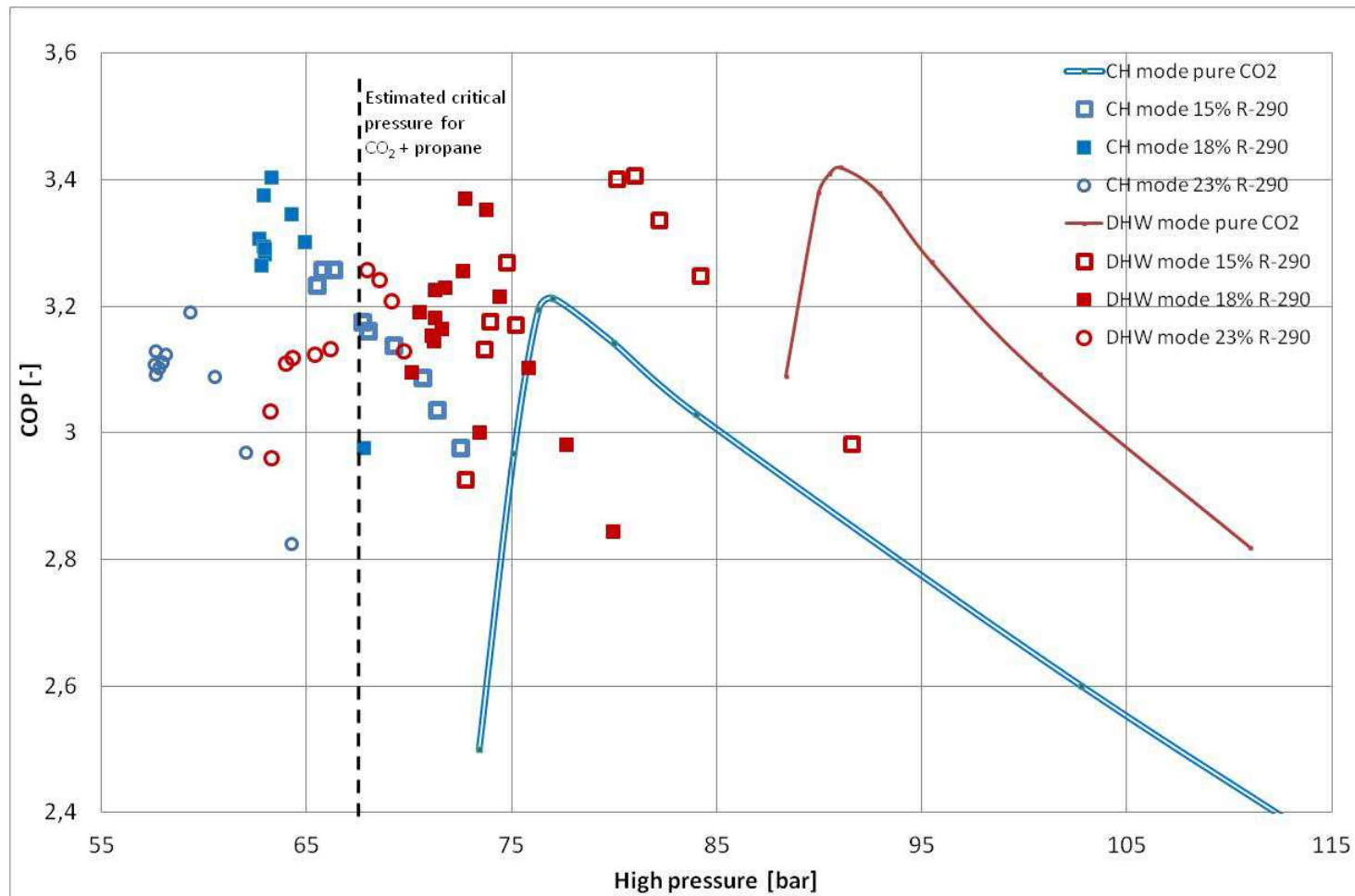


Refrigerant charge => available working points

Max COP for CH is 3.2 at 76 bar – Max COP for DHW is 3.4 at 92 bar



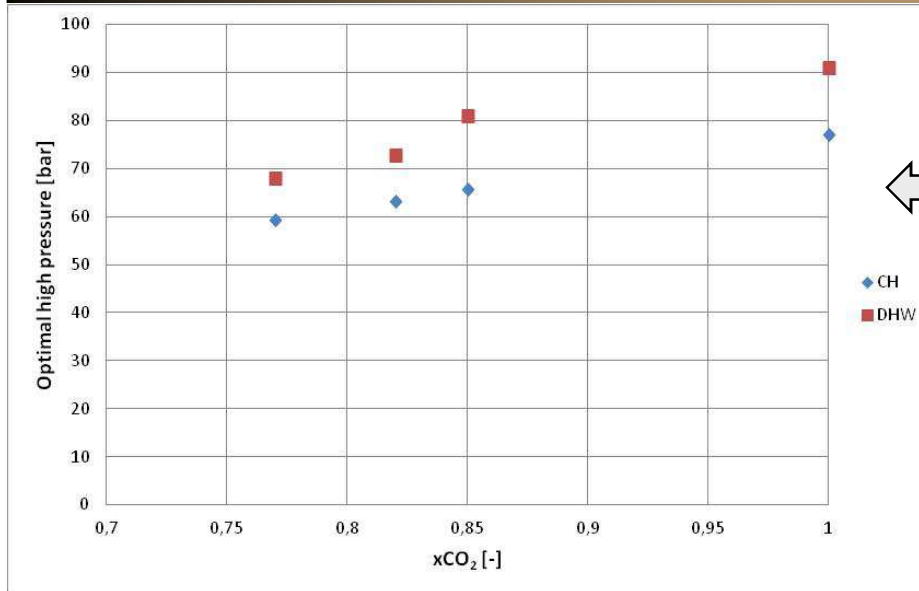
Results for CO₂ + propane mixtures



Subcritical cycles are available for central heating.

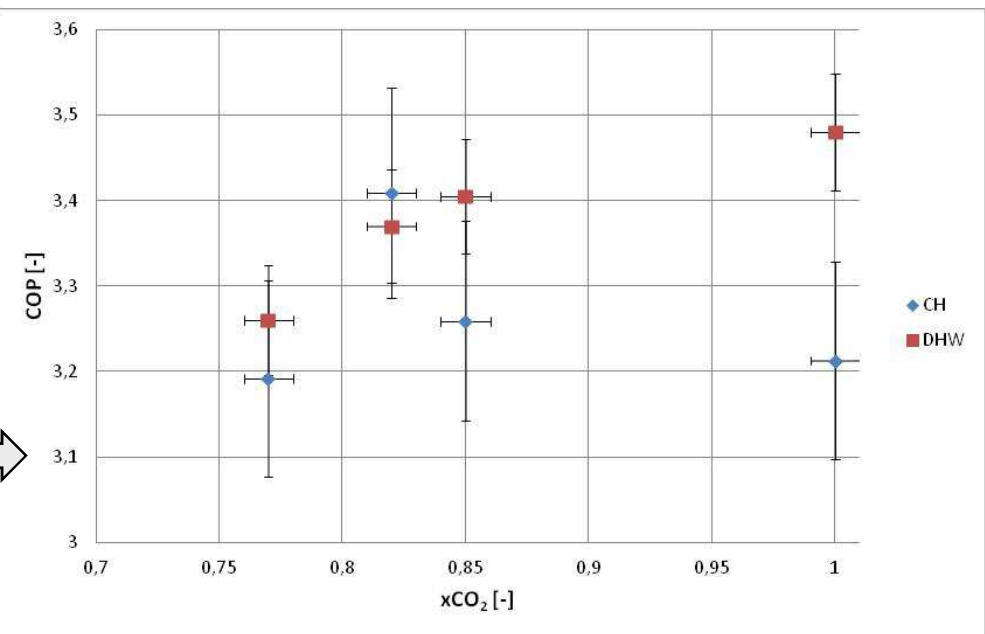


Results for CO₂ + propane mixtures



Addition of propane reduces the optimal high pressure

We observe a slight performance enhancement for central heating mode



Performance enhancements needs to be confirmed regarding the compressor efficiency.



Conclusion



- Design for a complete heat pump loop bench for mixtures studies.
- Composition of the circulating fluid can be monitored using an optical non intrusive method.
- Studies of CO₂ based mixtures are still ongoing, but a performance enhancement for central heating applications has already been observed.

