

# Sub-/Supercritical fluid chromatography with propane

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## Introduction

The recovery of pure substances from natural materials is of increasing interest. Therefore the application of adsorptive separation processes is feasible and often necessary. For the operation and development of adsorption processes, especially for multi-component systems with supercritical solvents like CO<sub>2</sub> and propane, the knowledge of adsorption and desorption equilibrium data is of fundamental importance. Adsorption equilibria of  $\beta$ -carotene have been determined with supercritical CO<sub>2</sub> and subcritical propane. Solubility of  $\beta$ -carotene in propane was also determined.

Table 1: Properties of supercritical CO<sub>2</sub> and subcritical propane

|   | Supercritical CO <sub>2</sub> | Subcritical propane |
|---|-------------------------------|---------------------|
| P <sub>c</sub> , T <sub>c</sub>                     | 7.38 MPa, 304 K               | 4.25 MPa, 370 K     |
| Operating pressure                                  | 15.0 – 25.0 MPa               | 1.0–10.0 MPa        |
| Operating temperature                               | 313 – 353 K                   | 293 – 353 K         |
| Density at operating condition [kg/m <sup>3</sup> ] | 400–900                       | 370–500             |
| Viscosity at operating condition [mPas]             | 0.03–0.08                     | 0.04–0.12           |

## Experimental Setup

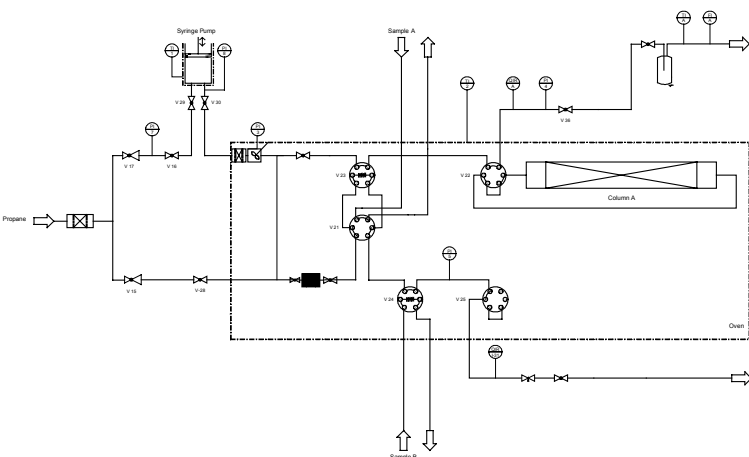


Fig. 1: Apparatus for adsorption analysis

### System components:

- Carbon dioxide and propane supply
- Syringe pump for continuous feed
- Modifier pumps
- DAD/ UV detection
- Pressure reducing and control units

### Operating conditions:

- Temperature 293 - 363 K
- Pressure P = 2 - 30 MPa
- Volume flow up to 5 ml/min

### Operating modes:

- Peak analysis
- Frontal chromatography
- Perturbation chromatography
- Solubility measurement

## Solubility measurement

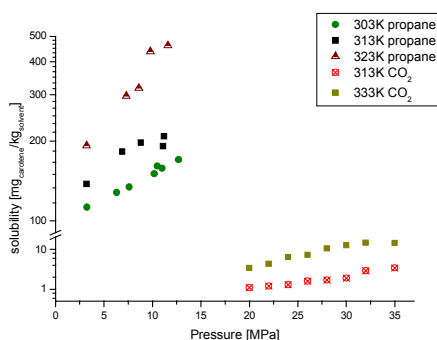


Fig. 2: Solubility of  $\beta$ -carotene in propane and in CO<sub>2</sub> [1]

The solubility of  $\beta$ -carotene in propane is shown in Figure 2. With increasing temperature and pressure, solubility of  $\beta$ -carotene increases. The solubility of  $\beta$ -carotene over the measured condition ranges from 100 to 450 mg <sub>$\beta$ -carotene</sub>/kg<sub>propane</sub>. These value are two orders of magnitudes higher than the solubility of  $\beta$ -carotene in supercritical CO<sub>2</sub> or in SC- CO<sub>2</sub> with modifier.

## Single Component Adsorption

Adsorption isotherms of  $\beta$ -carotene were determined with the peak maxima method.  $\beta$ -carotene on Nucleosil RP18 were investigated with CO<sub>2</sub>/ 2-propanol. For  $\beta$ -carotene in propane, the adsorption on Kromasil RP18 were studied. Single component adsorption for  $\beta$ -carotene is described using linear isotherm. For the adsorption equilibria of  $\beta$ -carotene on Nucleosil RP18 in CO<sub>2</sub> with 2-propanol as modifier, the loading decreases with increasing modifier content and increasing pressure. For the adsorption equilibria of  $\beta$ -carotene on Kromasil RP18 in propane, the loading achieved is much lower. A trend of decreasing loading with increasing solubility in the desorbent can be observed.

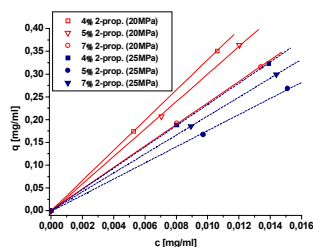


Fig. 3:  $\beta$ -carotene isotherms at 313K

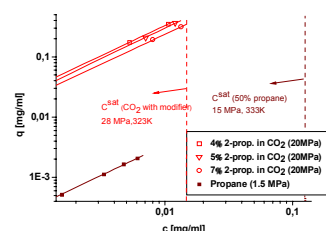


Fig. 4: Comparison of  $\beta$ -carotene isotherms

## Chromatography with propane

The identification of individual carotenes can be carried out based on wavelength where they absorb maximum UV. But  $\lambda_{max}$  values changes with different polarity of the dissolving solvents. It was observed that all individual carotenes show greater  $\lambda_{max}$  value in hexane than in SC-CO<sub>2</sub> or its mixture with entrainer [2]. A comparison of the UV-spectrum of  $\beta$ -carotene in propane and CO<sub>2</sub> with 2-propanol as modifier is shown in Figure 5. For carotenes in supercritical carbon dioxide in the presence of modifier, a shift of  $\lambda_{max}$  to a shorter wavelength can be observed. Figure 6 depicted the chromatogram of  $\beta$ -carotene in propane and CO<sub>2</sub> with 7% 2-propanol as modifier. The peak of  $\beta$ -carotene in CO<sub>2</sub> with modifier is much broadened, even though the flow rate of CO<sub>2</sub> as mobile phase is twice higher than the flow rate of propane as mobile phase.

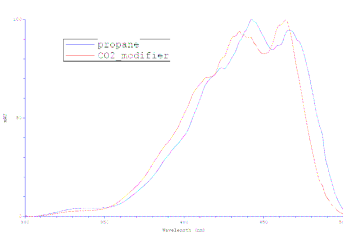


Fig. 5: UV-spectrum of  $\beta$ -carotene in propane and CO<sub>2</sub> with modifier

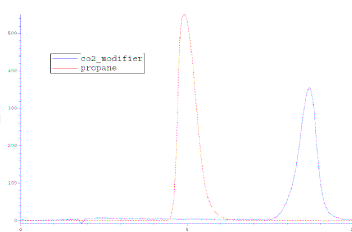


Fig. 6: Chromatogram of  $\beta$ -carotene in propane and CO<sub>2</sub> with modifier

## Conclusion

- Solubility of  $\beta$ -carotene in propane increases with increasing temperature and pressure.
- Adsorption of  $\beta$ -carotene in propane on Kromasil RP18 is lower than in CO<sub>2</sub>
- Apparatus and methods presented in this study provide a basis for further investigations.

## References

- [1] Johannsen, M.; Brunner, G: Solubilities of fat-soluble vitamins A,D,E and K in supercritical carbon dioxide, J.Chem. Eng. Data 42, 106–111, 1997.  
 [2] Ng, M.H.; Choo, Y.M.; Ma, A.N.; Chuah, C.H.; Mohd. Ali Hashim: Isolation and identification of individual palm carotenes using supercritical fluid chromatography, Malaysian Journal of Science 25, 139–145, 2006.