

DEVELOPMENT OF AN IN-LINE NIR MONITORING METHOD FOR SUPERCRITICAL CARBON DIOXIDE-BASED EXTRACTION PROCESSES

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Supercritical carbon dioxide can be used for extraction processes like deoiling of glass and metal swarfs and metal parts polluted, e.g., with cutting oil from metalworking. For efficiently conducting the extraction process in-line monitoring is desirable and therefore a method using fiber-optic NIR spectroscopy in combination with PLS calibration has been developed. A calibration model was set up for the squalane-carbon dioxide system, where squalane was used as model compound for technical oils. The root mean-squared error obtained with this model is 6 mg cm^{-3} for carbon dioxide and 0.8 mg cm^{-3} for squalane, respectively. The predictive ability of this model compound PLS method has been tested for real cutting oil formulations of different type. The calibration proved to be suitable for determination of the oil concentration with an error of 1.2 mg cm^{-3} . Therefore, it seems possible to apply this in-line analytical approach for the surveillance of real world deoiling process solutions and to establish an automated process termination criterion with this technique.

I - INTRODUCTION

Supercritical fluids offer unique properties compared with other solvents, e.g., the continuous variation of density and other thermophysical properties ranging from gas-like to liquid-like behavior without any phase transition by tuning pressure and temperature. The homogeneous phase can be used for extraction or reaction processes, the phase separation can be used for product recovery [1,2]. Supercritical carbon dioxide has critical data not far from standard conditions [3] and has several advantages in handling as it is chemically stable, non-flammable, and readily available. Because of its solvent power comparable with usual organic solvents it can dissolve less or non-polar compounds very well. Therefore, most technical applications of supercritical carbon dioxide focus on the extraction of natural products, e.g., caffeine from coffee and tea, hops, flavors, as well as on cleaning processes, e.g., degreasing of glass and metal parts and metal swarf [4]. If supercritical carbon dioxide is used in extraction processes, it can be easily removed from the extract as a gas by depressurizing and afterwards can be recompressed and used in a closed circuit. Such a closed CO₂ circuit is also used in the cleaning and deoiling processes for metal pieces from machining processes, which have been developed at Forschungszentrum Karlsruhe, ITC-CPV [4]. A prerequisite for efficiently conducting the deoiling procedure is to find a clear criterion for terminating the process. In this context, in-line process monitoring and analysis regarding the main components in the system is of fundamental importance. Among other techniques, spectroscopic methods are advantageous for in-line analysis in supercritical fluids because they do not disturb the phase equilibrium [5]. Near-infrared (NIR) spectroscopy has proven to be a powerful analytical method for quantitative studies in supercritical fluids at high pres-

tures and temperatures [6,7]. However, the classical instrumentation required installing a high-pressure cell into the spectrometer leading to a rather complicated optical set-up. Recently, we have described the fiber-optic adaptation of high-pressure cells for quantitative analytical applications in supercritical CO₂ and the application of multivariate partial least squares (PLS) calibration methods in combination with quantitative NIR spectroscopy [8]. The performance of the spectroscopic set-up has been demonstrated in the system squalane-carbon dioxide. Here, squalane has been used as a model compound for technical oils due to its structural affinity and because the solubility in supercritical CO₂ is well known [6]. Based on the developed PLS calibration model for squalane-carbon dioxide, in a second step real technical oils have been investigated with the experimental set-up. One objective was to find out, whether the PLS method worked out for the model compound squalane dissolved in carbon dioxide can also be used for "real world" oils in deoiling process solutions. If this is not the case, the technical oils have to be calibrated individually. A second aspect, was to determine whether the accuracy of this method at low concentrations is good enough for establishing a termination criterion for the deoiling process.

II - MATERIALS AND METHODS

A thorough description of the high-pressure set-up SINASCO has been given recently [8]. It consists of a high-pressure view cell with a fiber-optic adaptation for NIR spectroscopy and a pumped recirculation system providing thermodynamic equilibrium in the whole system. It has been used for fiber-optic NIR spectroscopic measurements in the squalane-carbon dioxide system as well as for technical oils dissolved in supercritical carbon dioxide. Three cutting or grinding oils with different compositions ranging from natural to mineral oils have been selected as typical examples for technical oils. Table 1 shows the relevant data, the densities have been measured in a pycnometer and the solubilities have been described in [9].

Oil	Liquid density [g/cm ³] (measured at 293.15 K)	Composition
cutting oil A	0.892	native oil with esters, additives
cutting oil B	0.927	mineral oil, synthetic and natural esters, additives
grinding oil	0.801	synthetic aliphatic hydrocarbons, additives
squalane	0.797	C ₃₀ H ₆₂

III - RESULTS AND DISCUSSION

NIR spectroscopy of squalane and hydrocarbon mixtures in supercritical CO₂

Fig. 1 shows a comparison of the high-pressure NIR spectra of the long-chain hydrocarbon (HC) model compound squalane (C₃₀H₆₂) and the three "real world" HC formulations used normally as grinding or cutting oil in machining processes. All spectra have been acquired in the SINASCO high-pressure set-up using identical experimental conditions relevant for deoiling processes. Squalane and the oils have been dissolved in supercritical CO₂ at 16 MPa and 333 K using a comparable concentration of approximately 7.3 mg/cm³, respectively.

The band systems around 5000 and 6300 cm⁻¹ (both are combination bands due to Fermi resonance coupling) can be assigned to the supercritical CO₂ matrix. The bands of the fluid solvent are well separated from the HC 1st overtone C-H stretching bands in the spectral range 6000-5450 cm⁻¹ and the more intense HC combination bands at wavenumbers smaller

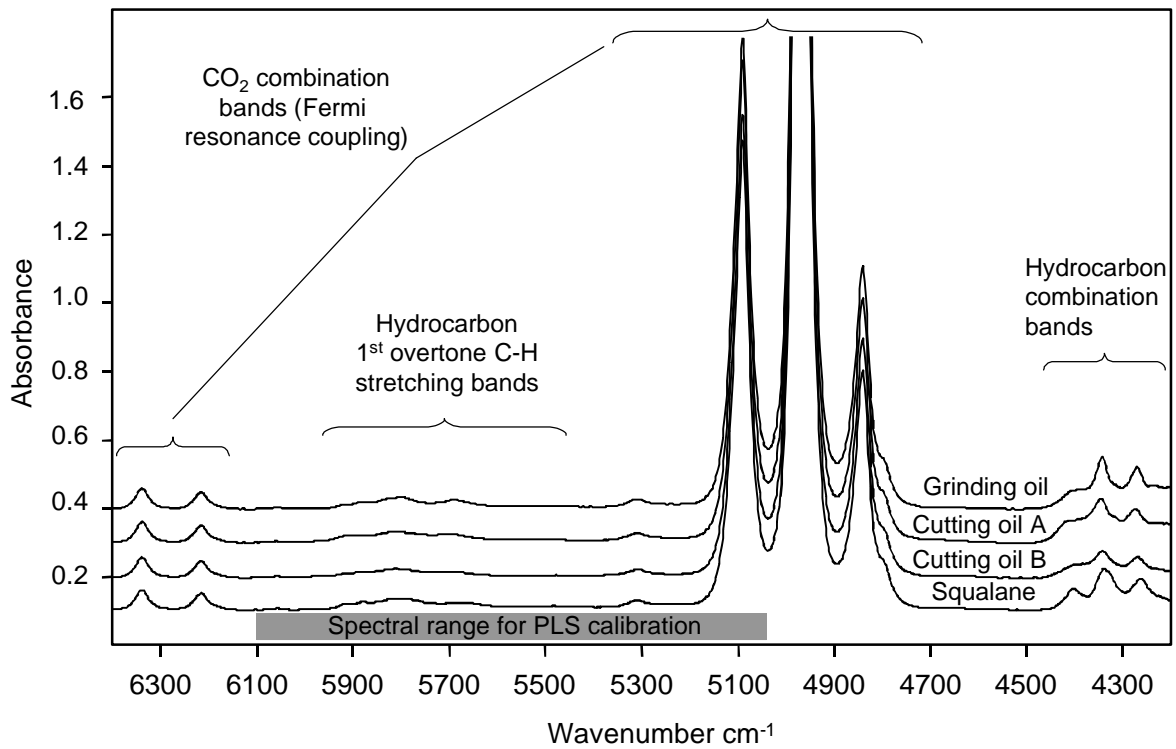


Fig. 1.: Comparison of NIR absorption spectra of squalane and technical oils dissolved in supercritical CO₂ (in-line measurement in SINASCO apparatus); p=16 MPa, T= 333 K, oil concentration: 7.3 mg cm⁻³; opt. path length: 11.87 mm.

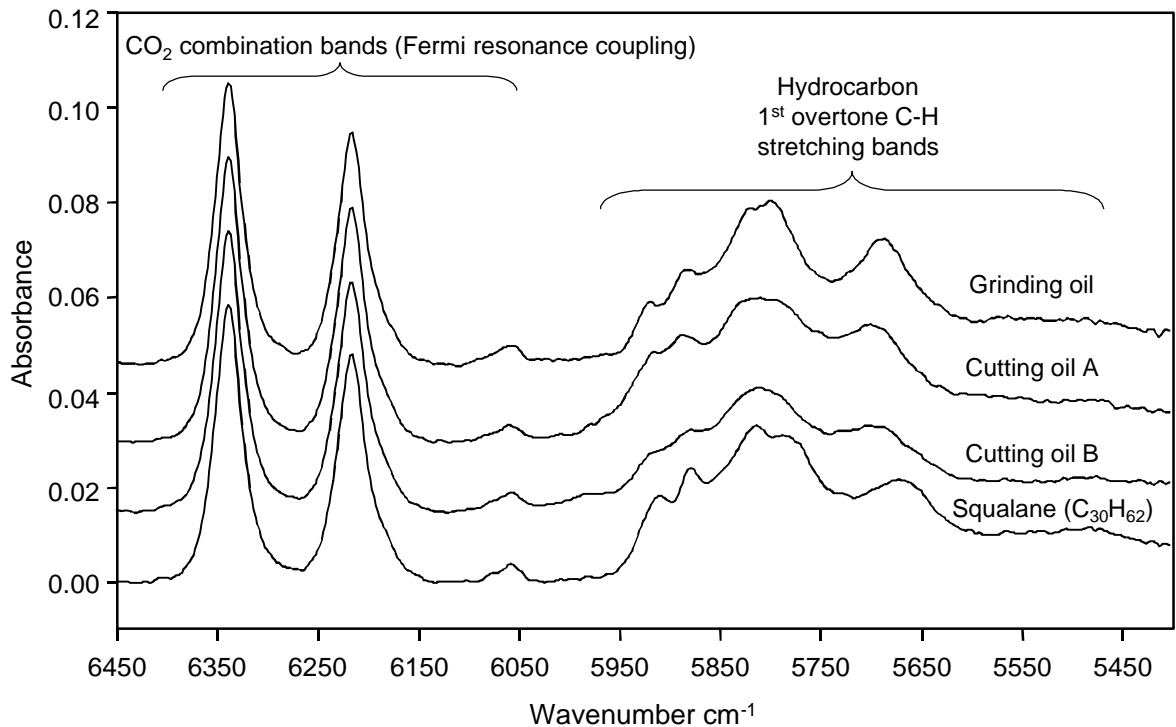


Fig. 2.: Zoomed in view of the NIR 1st overtone C-H stretching band spectral range of squalane and technical oils dissolved in supercritical CO₂ (in-line measurement in SINASCO apparatus); p=16 MPa; T=333 K; oil concentration: 7.3 mg cm⁻³; opt. path length: 11.87 mm.

than 4500 cm^{-1} . Generally, the spectra are dominated by the strong triad bands of the supercritical CO_2 around 5000 cm^{-1} , which are by 1-2 orders of magnitude more intense than the bands of the dissolved HCs. With the absorbance scale graduation chosen in Fig. 1, the 4300 cm^{-1} HC combination bands still can be clearly identified. Although the bands resemble each other in general, distinct differences can be seen for squalane and the HC mixtures in this spectral range. The much weaker HC 1st overtone C-H stretching bands around 5800 cm^{-1} can hardly be identified in this graph. Therefore, a zoomed in view of the spectral range $6450\text{--}5400\text{ cm}^{-1}$ is shown in Fig. 2. Here, the various bands due to 1st overtone C-H stretching modes of CH_3 , CH_2 and CH groups of the long-chain aliphatic HCs contribute to the band system at $6000\text{--}5450\text{ cm}^{-1}$.

Compared with the oil formulations the bands of the pure compound squalane are more pronounced. This can be explained by band broadening in the oil spectra due to slight shifts of the 1st overtone C-H stretching modes of the numerous long-chain HC compounds contributing to the spectrum. There are also perceptible differences in absorbance intensity of the 1st overtone C-H stretching band system for the different HC compounds. These differences are mainly caused by the varying molar concentration, which depends on the density (cf. Table 1) and (mean) molecular weight of the oil. However, the variations of the oil band shape and intensity compared with the model compound squalane are much smaller in this spectral area than for the combination band system at lower wavenumbers. Therefore, the 1st overtone C-H vibrations spectral range was selected for setting up a multivariate calibration model for squalane.

PLS calibration model for squalane / supercritical CO_2 using NIR spectral data

To develop PLS calibration models for squalane solutions in supercritical CO_2 a calibration set of 40 samples has been used. NIR spectra of these samples with known squalane and CO_2 concentration were measured in the SINASCO apparatus at defined temperature and pressure conditions, covering the pressure range $16\text{--}35.6\text{ MPa}$ and $323\text{--}353\text{ K}$ temperature range. Absorbance data in the spectral region from $6100\text{--}5030\text{ cm}^{-1}$ including the 5100 cm^{-1} CO_2 band of the Fermi triad as well as the HC 1st overtone C-H stretching bands (cf. Figs. 1 and 2) were taken into account for setting up the calibration models. The samples span a squalane concentration range from $0\text{--}32\text{ mg/cm}^3$ and CO_2 densities from $0.54\text{--}0.86\text{ g/cm}^3$. To account for temperature and pressure effects on the spectra [7,8] all parameters influencing the spectral response (squalane and CO_2 concentration, pressure, and temperature) have been varied independently of each other.

The optimum number of factors (latent variables[8]) to be included into the PLS models was determined by cross-validation (alternating removal of a subset of samples that are used as "internal" test set [8]) to be 8 for CO_2 as well as for squalane. The performance of the calibration models was evaluated by comparing real and predicted concentration values during the calibration procedure. The root mean-squared error of cross-validation (RMSECV) for squalane is 0.81 mg/cm^3 ($r^2 = 0.9858$) and for CO_2 0.006 g/cm^3 ($r^2 = 0.9938$).

Validation of the squalane- CO_2 PLS calibration models using technical oils

The best way to confirm the applicability of the squalane- CO_2 PLS calibration models for in-line analysis in oil extraction solutions was to validate the predictive ability of the models using NIR spectra of "real world" oil samples in supercritical carbon dioxide. Thus, the corresponding spectral data of the three grinding and cutting oils (see Table 1) have been acquired in-line in the SINASCO set-up. From these spectral data the oil concentration and density of the supercritical CO_2 matrix using the developed squalane- CO_2 PLS calibration

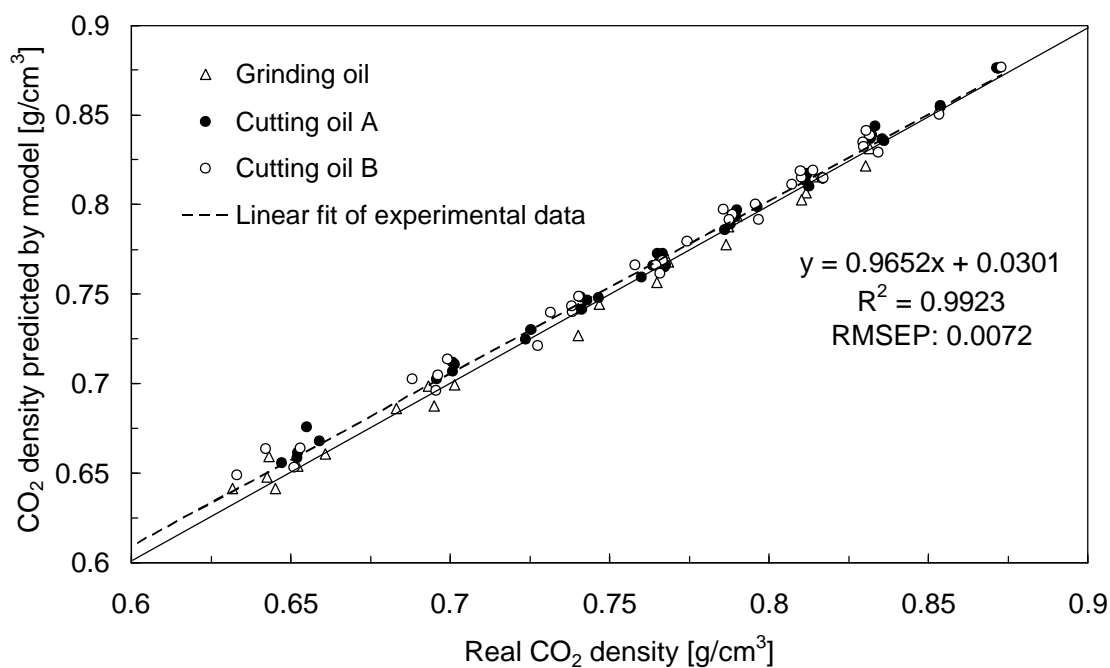


Fig. 3.: Predicted vs. real CO₂ density for 104 grinding and cutting oil test samples; data were predicted from 8-factor CO₂ PLS model.

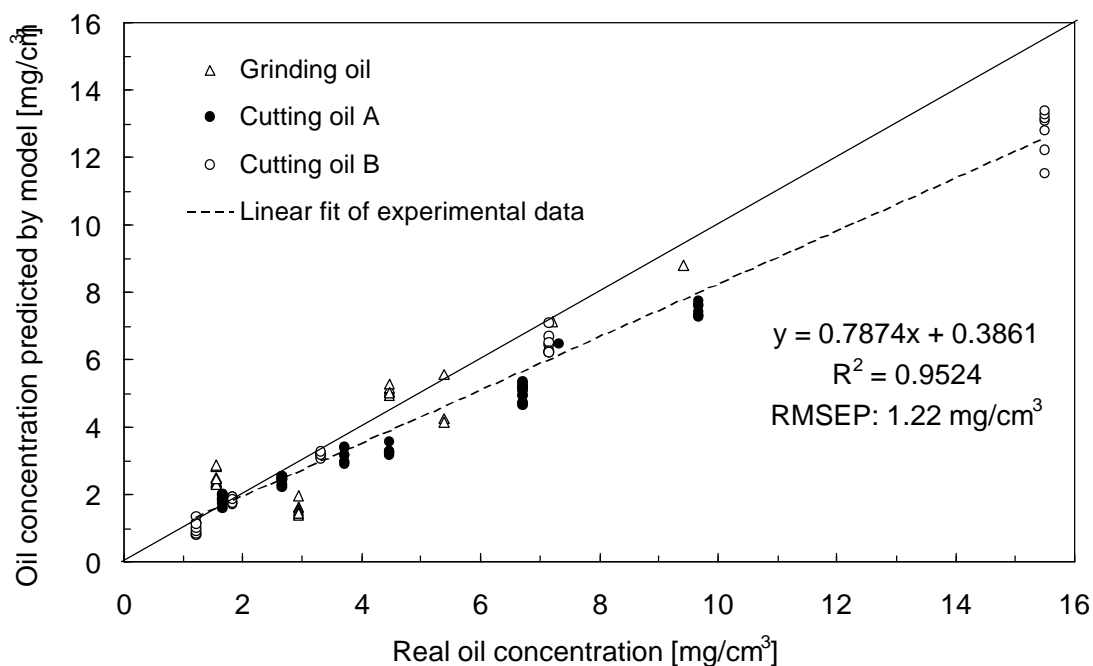


Fig. 4.: Predicted vs. real oil concentrations for 104 grinding and cutting oil test samples; data were predicted from 8-factor squalane PLS model.

models developed earlier have been determined. The oil concentration of these 104 supercritical fluid samples has been varied in the concentration range from 1-15.5 mg cm⁻³ and the CO₂ density in the range from 0.63-0.86 g cm⁻³, corresponding to temperatures between 323 and 343 K and pressures between 15.9 and 30.5 MPa.

The applicability of the squalane-CO₂ PLS calibration models to the oil samples is shown in Figs. 3 and 4 by plotting predicted versus real concentrations. Fig. 3 gives the comparison for CO₂ densities obtained from the 8-factor PLS model. A good agreement between predicted and real CO₂ densities was found for these cutting and grinding oils in supercritical CO₂ resulting in a root mean-squared error of prediction (RMSEP) of 0.007 g cm⁻³ CO₂ (r²=0.9923). This result was expected as there is hardly any interference of the HC 1st overtone C-H stretching bands with the 5100 cm⁻¹ CO₂ band.

Fig. 4 depicts the predicted oil concentrations obtained with the 8-factor squalane PLS calibration model versus the real oil concentration data. In this case an increased RMSEP of 1.22 mg cm⁻³ (r² = 0.9524) was determined for the test samples. At higher concentrations, the real oil amount is underestimated; the PLS model here gives too low results. This can be partially explained by the above mentioned differences in the shape and intensity of HC 1st overtone C-H stretching bands and also by the somewhat lower solubility of the real world oils in supercritical CO₂ compared with squalane [9]. However, the important finding is that the lower concentrations of the real world oils can be predicted with reasonable accuracy by the PLS model with the long-chain HC model compound squalane. Thus, it is not necessary to develop a PLS calibration model for every single "real world" oil formulation.

IV - CONCLUSION

Fiber-optic NIR absorption spectrophotometry in combination with PLS calibration has the potential to provide a rapid and reliable means of determining both the oil and CO₂ concentration in extraction processes based on supercritical carbon dioxide with one single spectral measurement. In this way a simple in-line monitoring of deoiling process solutions seems to be achievable in the future and the method is accurate enough to establish a termination criterion for deoiling processes.

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