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Monitoring of technical oils in supercritical CO_2 under continuous flow conditions by NIR spectroscopy and multivariate calibration

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Abstract

Metal parts and residues from machining processes are usually polluted with cutting or grinding oil and have to be cleaned before further use. Supercritical carbon dioxide can be used for extraction processes and precision cleaning of metal parts, as developed at Forschungszentrum Karlsruhe. For optimizing and efficiently conducting the extraction process, in-line analysis of oil concentration is desirable. Therefore, a monitoring method using fiber-optic NIR spectroscopy in combination with PLS calibration has been developed. In an earlier paper we have described the instrumental set-up and a calibration model using the model compound squalane in the spectral range of the CH combination bands from 4900 to 4200 cm^{-1}. With this model only poor prediction results were obtained if applied to technical oil samples in supercritical CO_2. In this paper we describe a new calibration model, which was set up for the squalane/carbon dioxide system covering the 323–353 K temperature and the 16–35.6 MPa pressure range. Here, calibration data in the spectral range from 6100 to 5030 cm^{-1} have been used. This range includes the 5100 cm^{-1} CO_2 band of the Fermi triad as well as the hydrocarbon 1st overtone C─H stretching bands, where spectral features of oil compounds and squalane are more similar to each other.

The root mean-squared error of prediction obtained with this model is 4 $mg\,cm^{-3}$ for carbon dioxide and 0.4 $mg\,cm^{-3}$ for squalane, respectively. The utilizability of the newly developed PLS calibration model for predicting the oil concentration and CO_2 density of solutions of technical oils in supercritical carbon dioxide has been tested. Three types of “real world” cutting and grinding oil formulations were used in these experiments. The calibration proved to be suitable for determining the technical oil concentration with an error of 1.1 $mg\,cm^{-3}$ and the CO_2 density with an error of 6 $mg\,cm^{-3}$. Therefore, it seems possible to apply this in-line analytical approach on the basis of a cost-effective and time-saving model compound calibration for the surveillance of real world de-oiling and other extraction process based on supercritical carbon dioxide, and furthermore to establish an automated process termination criterion based on this technique.

Keywords: NIR; Fiber-optic spectrophotometry; Precision cleaning process; Supercritical CO_2; Cutting and grinding oils

1. Introduction

Supercritical carbon dioxide is used for extraction and separation processes since three decades because of its unique thermodynamic and transport properties. The phase behavior is tunable between the homogeneous and multiphase region by changing pressure and temperature conditions, while the solvent power is comparable to classical extraction solvents for less polar or non-polar hydrocarbon compounds [1]. The critical data of carbon dioxide are not far from standard conditions ($T_c = 304.25\,K$, $p_c = 7.38\,MPa$, $\rho_c = 0.46\,g\,cm^{-3}$) [2] making it good in handling as a chemically stable, non-flammable, and readily available solvent.

The technical use of supercritical carbon dioxide is mainly for the selective extraction of natural products, e.g., the production of decaffeinated coffee and tea, hops, flavors, essential oils and pharmaceuticals [1,3]. Furthermore, it can be

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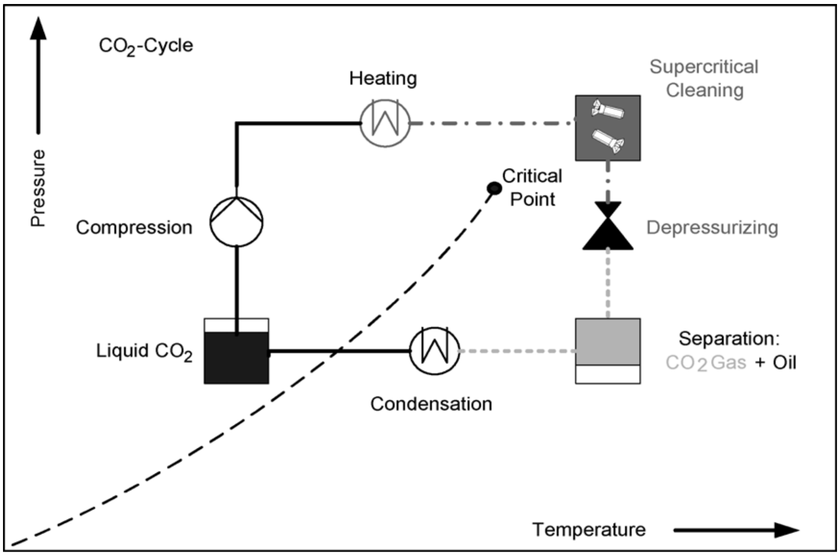

Fig. 1. Schematic diagram of the precision cleaning process using supercritical carbon dioxide (cf. Ref. [5]).

used for surface treatment in cleaning and dying processes [4], degreasing of glass and metal swarf, precision cleaning of metal parts and components [5], and the treatment of soil [6].

In this study we have focused on a cycle process for degreasing of glass and metal swarf and precision cleaning of metal parts and components from machining oils using supercritical carbon dioxide, which has been developed at Forschungszentrum Karlsruhe [5]. Fig. 1 illustrates the schematic flow diagram of this process.

The process cycle is started with liquid carbon dioxide, which is pressurized and heated up to the supercritical region. Here, the solubility for oils is high and the separation of metal parts and components from metal working oils is done by contacting them with supercritical carbon dioxide and dissolving the oils homogeneously. In the next step, the system is depressurized, the phases separate and the dissolved oil components precipitate. Finally the carbon dioxide is cooled down making a phase transition from gas to liquid and the cleaning cycle is closed.

The described supercritical cleaning process has several advantages, namely complete recovery of pure cutting and grinding oils and pure carbon dioxide, no occurrence of secondary waste and no use of environmentally problematic solvents, e.g., chlorinated hydrocarbons. Supercritical carbon dioxide dissolves cutting and grinding oils rather well [5] and the performance of the process is very good, but a prerequisite for efficiently conducting the de-oiling procedure is to find a clear criterion for terminating the cleaning process, which has not yet been available. At the beginning of the extraction process the oil concentration is close to saturation but in the next cycles it decreases drastically and finally it is approaching zero. Due to this, the main question is: At which point of time should the extraction be stopped to make the process efficient?

In this context, the goal of our work was to use NIR spectroscopy with fiber-optic adaptation for the in-line monitoring of the decrease in oil concentration during the extraction process and thus to make available a fast analytical method for defining the termination criterion of this cleaning process. Near-infrared (NIR) spectroscopy has proven to be a powerful analytical method for quantitative studies in supercritical fluids at high pressures and temperatures [7–12]. However, the classical instrumentation required installing a high-pressure cell into the spectrometer leading to a rather complicated optical set-up [7,8]. A fiber-optic adapted cell for static phase and association investigations (no flow-through conditions) of polar substances in supercritical $CClF_3$ using NIR spectroscopy has been reported by Ochel and Schneider [10,11]. Wetzel and Sweat [12] have adapted a high-pressure optical flow cell to an acousto-optic tunable filter NIR spectrometer using a lens system, where they measured semi-quantitatively lipid concentration transients in supercritical CO_2 of constant density. Recently, we have described the fiber-optic adaptation of a high-pressure cell for quantitative analytical applications in supercritical CO_2 and the application of NIR spectroscopy in combination with multivariate partial least-squares (PLS) calibration methods to supercritical carbon dioxide systems [13]. There, calibration data from CH combination bands of the model system squalane/carbon dioxide between 4900 and 4200 cm^{-1} have been used to validate the performance of the in-line monitoring set-up. The advantage of our approach for analyzing the concentration of technical oils in supercritical CO_2 is seen in

- the easy adaptation of the fiber-optic adapted high-pressure cell to the harsh process environment and simple maintenance during in-line spectrometric measurements, while the NIR spectrometer can be located remotely, e.g., in a control room;

- its utilizability for measurements in continuous flow mode;
- the use of partial least-squares (PLS) calibration modeling [14] for quantifying both, the oil concentration and CO_2 density contained in the spectral information over the whole pressure–temperature–concentration range of interest.

Focusing on the precision cleaning process with supercritical carbon dioxide, in a first step we have selected the system squalane/carbon dioxide. Squalane due to its structural similarity has been proven to be a model compound for long-chain hydrocarbons, and thus for technical cutting and grinding oils [15]. Moreover, the solubility of squalane in supercritical CO_2 is well known [7]. Thus, in a first step towards in-line monitoring of the precision cleaning process, we have determined the performance of the fast, continuous, and non-invasive NIR spectroscopic monitoring set-up with the model compound system squalane/carbon dioxide under process-like continuous flow mode using new calibration data in the spectral region from 6100 to 5030 cm^{-1}. This range includes the 5100 cm^{-1} CO_2 band of the Fermi triad as well as the HC 1st overtone C–H stretching bands, where squalane and the oil compounds have more similar spectral features than in the combination band region.

Based on this new PLS calibration model developed for squalane/carbon dioxide, in a second step technical oils have been investigated. One new aspect was to find out, to which extent the PLS method worked out for the model compound squalane dissolved in carbon dioxide would be applicable for the quantitative determination of “real world” cutting and grinding oils used in de-oiling process solutions. When transferring the squalane/supercritical carbon dioxide model for measuring real oils, even a moderately increased measuring error could be accepted because an applicability of the model system would minimize drastically the expenditure of calibration work. If on the other hand, the application of the squalane/carbon dioxide calibration model would result in unacceptable measurement errors, each technical oil would have to be calibrated individually.

A second goal of the experiments was to determine, whether the sensitivity of the developed method at low concentrations is good enough for establishing a termination criterion for the de-oiling process.

2. Experimental

2.1. High-pressure NIR spectroscopic set-up

The high-pressure NIR spectroscopic set-up has been described in detail recently [13]. 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 set-up. In this study, the device was used for measurements in the squalane/carbon dioxide system as well as for technical oils dissolved in supercritical carbon dioxide. The maximum possible path length of 11.87 mm has been set up in the high-pressure cell.

All spectra were acquired on a BRUKER VECTOR 22/N-F Fourier Transform near-infrared (FT-NIR) spectrometer equipped with a Peltier-cooled indium-gallium-arsenide (InGaAs) detector. The permanently aligned interferometer guarantees for a good wavelength stability and high light throughput. The spectrometer is equipped with four fiber-optic output ports for remote sampling applications, where a variety of fiber-optic probes or optical cells can be simultaneously attached. To obtain a good signal-to-noise ratio, 32 scans were averaged during each spectral measurement resulting in a measuring time of 30 s. Spectra were recorded with a spectral resolution of 4 cm^{-1}.

The PLS calibration model for the (squalane + supercritical CO_2) system was developed using OPUS/Quant software, which is part of the OPUS-NT 3.17 software package delivered with the VECTOR 22/N-F spectrometer (BRUKER, Ettlingen, Germany). The OPUS/Quant software contains a PLS 1 algorithm, which was applied successively to the two components of the system.

2.2. Chemicals

CO_2 (99.995 vol.%) was supplied by Messer Griesheim, Germany. Squalane (2,6,10,15,19,23-hexamethyl tetracosane) as well as the organic solvents (petroleum ether and acetone) used for cleaning the optical cell were of analytical-grade quality and used as delivered by VWR International GmbH, Darmstadt, Germany.

Three cutting and grinding oils with different compositions ranging from natural to mineral oils have been selected as typical examples for technical oils. Cutting oil A is on the basis of native oil, B is on the basis of mineral oil, while the grinding oil is composed of synthetic aliphatic hydrocarbons. They are used for machining of metals. Their composition and density is compared in Table 1. The solubility of squalane and of the technical oils in carbon dioxide is shown in Fig. 2. The densities have been measured in a pycnometer; the solubilities of squalane and the cutting and grinding oils in supercritical carbon dioxide have been adopted from Refs. [7,16].

Table 1
Comparison of squalane, cutting oil, and grinding oil properties in supercritical CO_2 for three metal working oils and the model compound squalane

Substance	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	$C_{30}H_{62}$

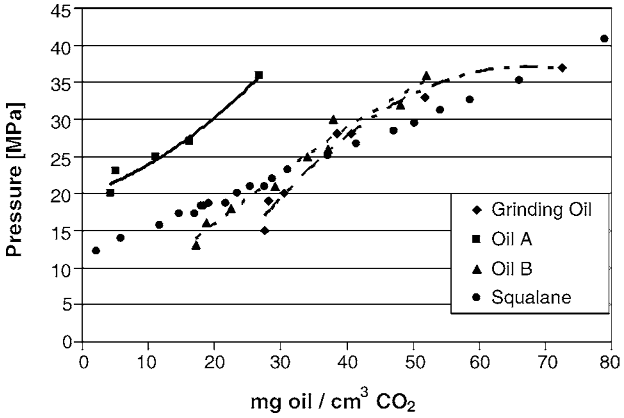

Fig. 2. Solubility of squalane [7], cutting oil A, cutting oil B and grinding oil [16] in supercritical carbon dioxide at 323 K.

2.3. *Preparation of the samples and measurement procedure*

Sample solutions of squalane and the technical oils have been prepared and measured according to the methods thoroughly described in Ref. [13].

3. Results and discussion

3.1. *NIR spectroscopy of squalane and hydrocarbon mixtures in supercritical CO_2*

Fig. 3 shows a comparison of the high-pressure NIR spectra of the long-chain hydrocarbon (HC) model compound squalane ($C_{30}H_{62}$) and the three "real world" oil formulations used normally as grinding or cutting oil in machining processes. All spectra have been acquired in the high-pressure set-up using identical experimental conditions relevant for de-oiling processes. Squalane and the oils have been dissolved in supercritical CO_2 at 16 MPa and 333 K each at a comparable concentration of approximately 7.3 mg cm^{-3}.

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 hydrocarbons (HCs). The band systems of the fluid supercritical CO_2 solvent around 5000 and 6300 cm^{-1} (both are combination bands due to Fermi resonance coupling) 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 than 4500 cm^{-1}. With the absorbance scale graduation chosen in Fig. 3, the HC combination bands around 4300 cm^{-1} still can be clearly identified. Although the bands resemble each other in general, distinct differences can be seen for the model compound squalane and the oil samples in this spectral range. In an earlier paper we had set up PLS calibration models for squalane and CO_2 using the 4900–4200 cm^{-1} spectral range of the HC combination bands [13]. When we tried to predict oil and CO_2 concentrations using the collected NIR spectra of 104 samples of the three technical oils discussed in this paper with these "older" calibration data, we got poor prediction results (data not shown). The CO_2 concentration was systematically over-estimated by the older model (root mean-squared error of prediction (RMSEP) = 0.054 g cm^{-3}, $r^2 = 0.8296$), while the technical oil concentration was systematically under-estimated (RMSEP = 3.55 mg cm^{-3}, $r^2 = 0.7932$).

The much weaker hydrocarbon 1st overtone C–H stretching bands around 5800 cm^{-1} can hardly be identified in Fig. 3. Therefore, a zoomed in view of the spectral range 6450–5400 cm^{-1} is shown in Fig. 4. Here, the various bands due to 1st overtone C–H stretching modes of CH_3, CH_2 and

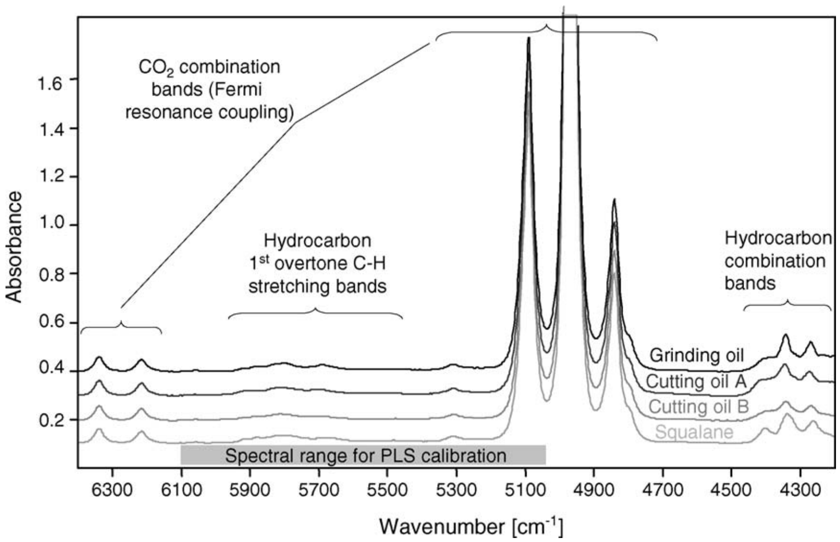

Fig. 3. Comparison of NIR absorption spectra of squalane and technical oils dissolved in $scCO_2$ ($p = 16$ MPa, $T = 333$ K, oil concentration: 7.3 mg cm^{-3}, optical path length: 11.87 mm).

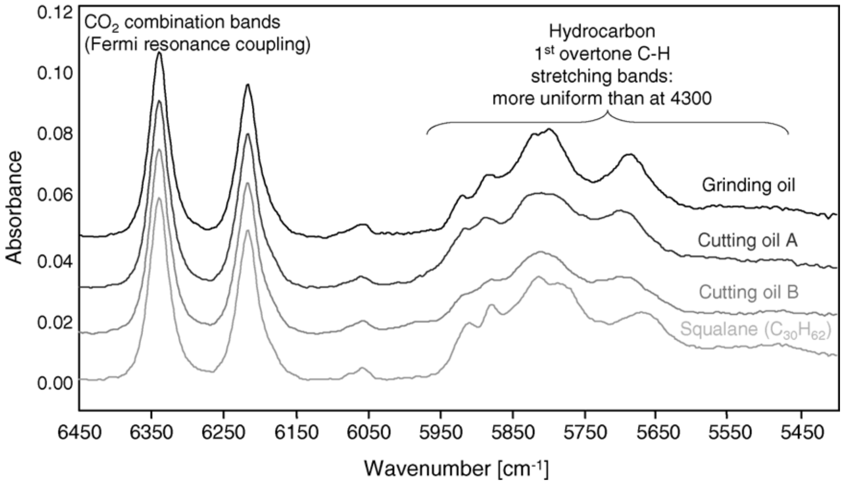

Fig. 4. Zoomed in view of the NIR 1st overtone C—H stretching band spectral range ($p = 16$ MPa, $T = 333$ K, oil concentration: 7.3 mg cm^{-3}, optical path length: 11.87 mm).

CH groups of the long-chain aliphatic HCs contribute to the band system at 6000–5450 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 variations in band shape and absorbance intensity of the 1st overtone C—H stretching band system for the different oils and squalane. The differences in band shape can be understood from the varying HC compounds and additives in the technical oils, while the differences in band intensity are mainly caused by the varying molar concentration, which depends on the density (cf. Table 1) and (mean) molecular weight of the corresponding 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, mentioned above. Therefore, the 1st overtone C—H vibrations spectral range was selected for setting up a multivariate calibration model for squalane.

3.2. 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 36 samples has been used. NIR spectra of these samples with known squalane and CO_2 concentration were measured in the high-pressure apparatus at defined temperature and pressure conditions, covering the 16–35.6 MPa pressure and 323–353 K temperature range. Absorbance data in the spectral region from 6100 to 5030 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. 3 and 4) were taken into account for setting up the calibration models. The samples span an squalane concentration range from 0 to 32 mg cm^{-3} and CO_2 densities from 0.62 to 0.86 g cm^{-3}. To account for the distinct 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 [14]) to be included into the PLS 1 models was determined by cross-validation (alternating removal of a subset of samples that are used as "internal" test set [14]) to be 6 for carbon dioxide and 8 for squalane. The performance of the calibration models was evaluated on the one hand by comparing the real concentration values with those predicted during the calibration procedure. The root mean-squared error of cross-validation (RMSECV) for squalane is 0.49 mg cm^{-3} ($r^2 = 0.9946$) and for CO_2 4.9 mg cm^{-3} ($r^2 = 0.9951$).

Additionally, the validity of the calibration models was confirmed by measuring spectra of 10 independent test set samples. Here, the squalane and CO_2 concentration was also varied within the calibrated range and the concentration of both compounds was predicted by applying the developed calibration models to these spectra. A very good agreement between true and predicted concentrations was also found for the test set samples resulting in root mean-squared errors of prediction (RMSEP) of 3.9 mg cm^{-3} for CO_2 ($r^2 = 0.9961$) and 0.42 mg cm^{-3} for squalane ($r^2 = 0.9943$). The performance of the corresponding PLS 1 calibration models for the 36 calibration and 10 test set samples is shown in Fig. 5 for CO_2 and in Fig. 6 for squalane by plotting predicted concentration data versus real concentration data. In the ideal case all data points should be in line with the diagonal of the diagram. The good performance of the calibration models is reflected in the fact that the data points of both data sets are close to the diagonal in each figure.

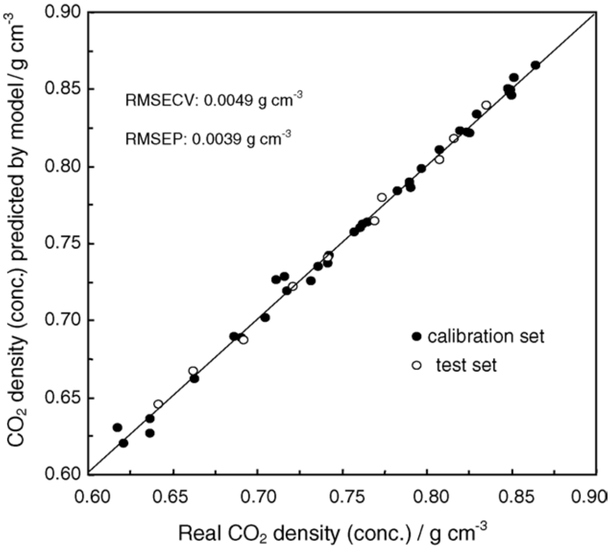

Fig. 5. Predicted vs. real CO_2 density for calibration and test set samples of the (squalane + supercritical carbon dioxide) model system.

3.3. Validation of the squalane/CO_2 PLS calibration models using technical oils

The applicability of the squalane/CO_2 PLS 1 calibration models for in-line analysis in oil extraction solutions was validated by measuring NIR spectra of “real world” technical oil samples in supercritical carbon dioxide at comparable conditions. Accordingly, spectral data of three grinding and cutting oils (see Table 1) have been acquired in-line under comparable experimental conditions in the high-pressure set-up.

From these spectral data the oil concentration and density of the supercritical CO_2 matrix were determined by applying the earlier developed squalane/CO_2 PLS 1 calibration models. The oil concentration of the 104 supercritical fluid samples has been varied in the concentration range from 1 to 15.5 mg cm^{-3} and the CO_2 density in the range from 0.63 to 0.86 g cm^{-3}, corresponding to temperatures between 323 and 343 K and pressures between 15.9 and 30.5 MPa.

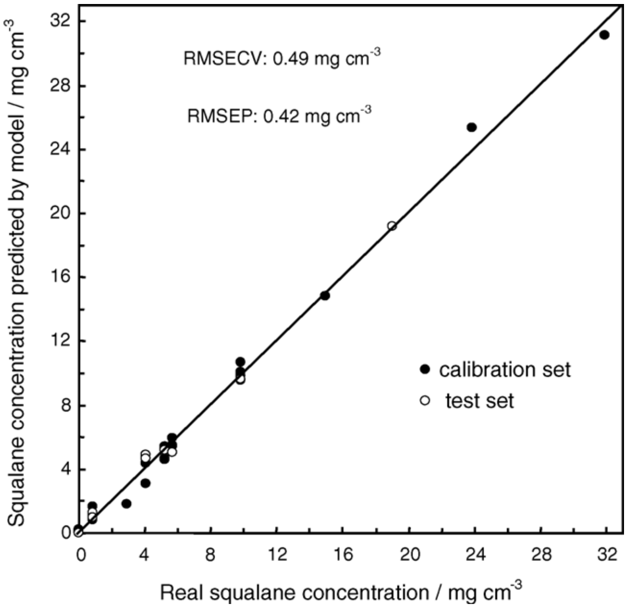

Fig. 6. Predicted vs. real squalane concentration for calibration and test set samples of the (squalane + supercritical carbon dioxide) model system.

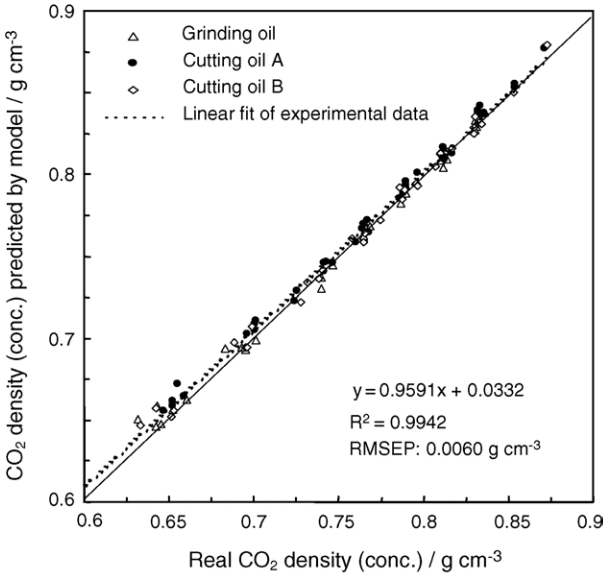

Fig. 7. Predicted vs. real CO_2 density for 104 technical grinding and cutting oil samples dissolved in supercritical carbon dioxide (prediction based on squalane/CO_2 calibration model).

Fig. 7 gives a comparison for the real CO_2 densities of the samples and the data predicted by the 6-factor PLS 1 model. A good agreement between predicted and real CO_2 densities was found, resulting in an RMSEP of 0.006 g cm^{-3} CO_2 ($r^2 = 0.9942$). This RMSEP value of CO_2 in the technical oil samples is only slightly increased compared with the RMSEP value of the test samples in the squalane/CO_2 model (which is 0.0039 g cm^{-3}, see Fig. 5). Presumably, this is caused by the fact, that we used for the validation of the squalane/CO_2 calibration model only a test set of 10 samples, while for predicting the CO_2 concentration in the technical oil samples a much higher number of test samples, namely 104 has been used. The similarity of the two RMSEP values was expected, as there is hardly any interference of the HC 1st overtone C–H stretching band system with the 5100 cm^{-1} CO_2 band (cf. Figs. 3 and 4).

Fig. 8 depicts the predicted oil concentrations obtained with the 8-factor squalane PLS 1 calibration model plotted versus the real oil concentration data.

In this case, an increased RMSEP of 1.08 mg cm^{-3} ($r^2 = 0.9499$) was found for the technical oil samples. The larger mean-squared error in predicting the oil concentration and the evident increased “scattering” of the data points around the diagonal line – compared with the squalane data – can be clearly understood from the marked differences in the shape and intensity of the hydrocarbon 1st overtone C–H stretching bands discussed above (cf. Fig. 4). Generally, at

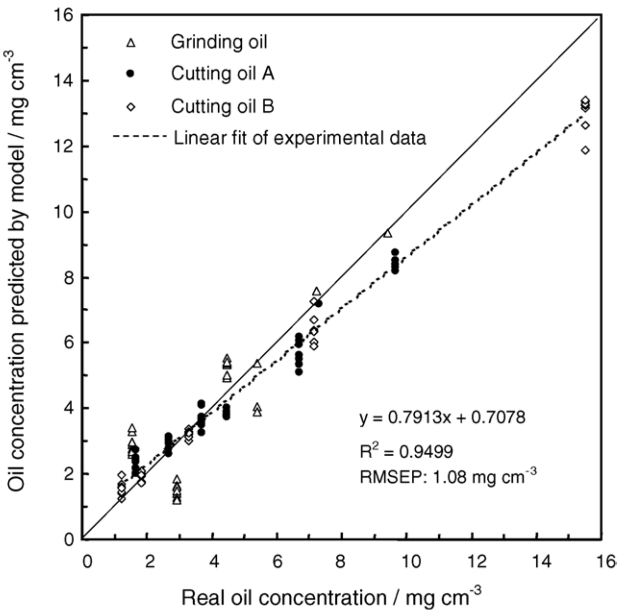

Fig. 8. Predicted vs. real oil concentration for 104 technical grinding and cutting oil samples dissolved in supercritical carbon dioxide (prediction based on squalane/CO_2 calibration model).

higher concentrations the oil concentration is underestimated by the squalane PLS 1 model. Oil B and grinding oil have similar solubilities in supercritical carbon dioxide compared with squalane, while oil A has a distinct lower solubility (see Fig. 2 and [16]). Fig. 2 shows that the spectra have been measured in a concentration range with complete solubility of the technical oils in supercritical carbon dioxide. Therefore, the underestimation of cutting oils A and B cannot be due to reaching the solubility limit. The underestimation is mainly caused by the difference in sensitivity of the spectral measurements for squalane and oils A and B due to the larger deviations in density and presumably in the difference in molecular weight. The esters and additives contained in oils A and B lead to a varying molar concentration in C–H bonds and thus in a slightly different molar extinction coefficient for the NIR measurements.

However, the important finding is that lower concentrations of the “real world” oils can be predicted with reasonable accuracy by the squalane PLS model.

Thus, at least for the three tested technical oils, it is not necessary to develop a PLS calibration model for every single “real world” oil formulation. Furthermore, it can be stated that for these oils the squalane model allows to define an effective termination criterion for the precision cleaning process. As can be seen from Fig. 8, the RMSEP for predicting the oil concentration is 1.08 mg cm^{-3}. This value roughly corresponds with the theoretical detection limit of the developed NIR spectroscopic method for oil in supercritical carbon dioxide. The stipulated industrial limit is in the range 3–4 mg cm^{-3} corresponding to a 0.5% residual oil concentration in the supercritical fluid, which is about a factor of 3 higher than the detection limit. Thus, the developed NIR spectroscopic technique allows to define an effective termination criterion and to verify whether the process is finished.

If on the other hand for other “real world” oils larger measurement errors should occur, an individual PLS calibration must be done.

4. Conclusion

In the present study the following results have been achieved:

- NIR spectral data of squalane dissolved in supercritical CO_2 can be used in combination with PLS calibration modeling to predict the oil concentration and CO_2 density of the tested technical cutting and grinding oils in de-oiling process solutions with errors of 1.08 and 6 mg cm^{-3}, respectively.
- The PLS method has the advantage that one calibration model covers the whole pressure, temperature and concentration region of interest for the two relevant compounds.
- At least for the three tested technical oils the effort of an individual calibration can be avoided using the model system calibration data from squalane/carbon dioxide in the 6100–5030 cm^{-1} spectral range (C–H 1st overtone region).
- Attempts to predict the concentrations of the technical oils and of CO_2 using model system calibration data from squalane/carbon dioxide in the C–H combination band range from 4900 to 4200 cm^{-1} (cf. Ref. [13]) resulted in poor prediction results, systematically over-estimated the CO_2 concentration and under-estimated the oil concentration.
- The developed NIR in-line monitoring method allows application of a simple, cost-effective and time-saving model compound calibration for three different types of technical cutting and grinding oils in a continuous-flow de-oiling process for metal parts based on supercritical carbon dioxide.
- It should be possible to verify the termination of the supercritical cleaning process automatically by the developed analytical technique.

The next steps to be done are the implementation in a real process and the extension to other extraction systems. The NIR set-up has also high potential for monitoring of extraction processes based on supercritical carbon dioxide, especially to perform selective extractions, and also for the monitoring of chemical reactions in supercritical carbon dioxide to obtain, e.g., kinetic data.

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