Determination of single droplet sizes, velocities and concentrations with image analysis for reactive extraction of copper

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HIGHLIGHTS

• Single organic droplet copper extraction was measured using funnel and imaging.
• Droplet inner concentrations were determined from analysis of video frames.
• Results include concentration profiles and average concentrations in droplet.
• Funnel measurement leads to higher mass transfer due to indirect measurement.
• Dynamic droplet analysis is enabled using velocity, shape and concentration.

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ABSTRACT

The proposed image analysis method allows the measurement of organic phase droplet sizes, velocities, and copper concentrations in single droplet column copper extraction using hydroxyoxime complexation. The method uses image acquisition sequences from video, detection of moving droplets, binarization of background subtracted images, and noise reduction from images. The image analysis method enabled characterizing the shape of droplets, by determining the droplet minor and major axis lengths. The method can detect droplet concentration directly inside the column wherever the droplet is visible. Image based method was validated against reference samples which were analyzed using spectrophotometry. The traditional concentration measurement using the spectrophotometric analysis of column outlet sample collection was performed for comparison purposes. The direct image analysis showed smaller variation in mass transfer results because of longer and non-uniform residence times when using sample collection. However, separately collected sample analysis together with the image analysis enables determination of the copper mass transfer during all the three steps of column experiment. Image analysis can also be used to reveal concentration profiles inside the droplet. This method is not limited to extractants, but it can be applied to systems where a suitable color change is present depending on camera sensor technology.

1. Introduction

Mass transfer is an important phenomenon affecting the design of liquid-liquid contactor units utilizing reactive extraction. To properly design the units, it is important to understand and quantitatively evaluate the effect of different mass-transfer phenomena in the whole process. These phenomena are solute transfer from bulk to the interface, interfacial reaction, and transport from interface to bulk. The mass transfer in solvent extraction depends on, among other variables, droplet sizes, velocities, and concentrations.

When the size, velocity, and inner concentration of a single droplet are determined, mass transfer into the droplet is defined. The presence of suitable reagents enhances mass transfer between the continuous and droplet phases in the reactive extraction. Especially in industrial hydrometallurgical processes, metal extraction with complex forming extractants is in common use. Also substantial application areas of reactive extraction can be found among environmental, petrochemical, chemical, and biochemical applications (Bart and Stevens, 2004). To experimentally investigate combined interfacial kinetics and mass transfer, different experimental methods are available (Hanna and Noble, 1985). Among these methods, single droplet measurements are widely applied in mass transfer experiments.
of liquid-liquid systems to determine the mass transfer coefficients, interfacial kinetics and extraction efficiencies (for example, Whewell et al., 1975; Henschke and Pfennig, 1999; Kumar and Hartland, 1999; Biswas et al., 1996, 1997; Wegener et al., 2009).

In single droplet systems, a droplet is rising or settling in an ambient continuous liquid. Droplets are collected from a funnel at the column outlet and concentrations are analyzed. Reaction kinetics and mass transfer rates can be determined from this data.

Already in the 1950s, Licht and Conway (1950) and Licht and Pansing (1953) verified that the mass transfer in single droplet extraction is divided into three stages: mass transfer during droplet formation, mass transfer in free rising/settling, and mass transfer during droplet coalescence. Experimental arrangements should be made so that contribution of each phenomena to the extraction process can be determined. It is commonly agreed that the contribution of droplet formation time to the mass transfer can be substantial, and the related error should be taken into account in the formation of mass transfer correlations (Wegener et al., 2014; Liang and Slater, 1990; Licht and Conway, 1950; Licht and Pansing, 1953). By contrast, the effect of droplet coalescence in the column outlet collector is assumed to be negligible, which has not been clearly shown.

Traditional single droplet experiments do not provide any information on the conditions inside the droplet during its rise. For example, mass transfer leads to concentration changes inside the droplet and at the interface. These changes can generate interfacial tension gradients which in turn lead to the Marangoni convection (Wegener et al., 2009, 2014). The effect of Marangoni convection cannot be directly observed in pure concentration measurements. Because of this, it would be beneficial also to be able to follow droplet velocities and concentration profiles within the droplet, at the interface and in the near vicinity of the droplet in the ambient phase. Flow pattern and concentration front visualization inside a droplet using decolorization with pH indicator have been made by Schulze (2007) and Pawelski et al. (2005) but the concentration profiles have not been measured. Decolorization, however, has been used to reveal Marangoni convection. Mörters and Bart (2000) and Baumann and Mühlfriedel (2002) have determined indirectly concentration profiles near the phase boundary using a laser induced fluorescence to track tracer concentrations. Baumann and Mühlfriedel measured time-dependent average tracer concentration profiles on the flat interface between two immiscible liquids. Mörters and Bart (2000), using D2EHPA system, determined time-dependent tracer concentration profiles inside a droplet to investigate diffusion inside and outside droplets in reactive extraction. Measured tracer concentration profiles were used as a basis to determine organic complex diffusion coefficient. The determination the effect of continuous phase flow on the droplet internal circulation was not successful due to experimental arrangements. In further studies by Mörters and Bart (2003), the measured concentration profiles were a basis for a Stefan-Maxwell based diffusion model for the mass transfer. Diffusion model was applied to zinc-D2EHPA single droplet experiments but the model was not able to describe experimental results satisfactorily and this is probably due to convective effect not included in the model.

In this work, the problems in single droplet extraction experiments are approached with a direct nonintrusive measurement system where the droplet velocity, droplet diameter, and concentration inside the droplet are determined by using digital imaging and subsequent image analysis. In this research, copper extraction from the aqueous solution to the organic solvent using Acorga M5640 extractant is analyzed. The interfacial reaction,

\[ \text{Cu}^{2+}(aq) + 2\text{HA}(org) \rightarrow \text{CuA}_2\text{org} + \text{H}^+(aq), \]

where the reactant HA (Acorga M5640) exchanges Cu-ions from the aqueous phase and the Cu-complex CuA2 can be followed directly and visually due to color change.

In experiments, concentrations, droplet velocities, and diameters are determined as averages from several droplets to minimize the effect of experimental variability. This direct droplet concentration analysis allows exact determination of mass transfer rates during the three stages in the single droplet experiment. In tradi-

**Nomenclature**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>absorbance, [-]</td>
</tr>
<tr>
<td>A, B, C, D, E, F</td>
<td>parameters of quadratic formula</td>
</tr>
<tr>
<td>c</td>
<td>concentration, [mol/L, mmol/L]</td>
</tr>
<tr>
<td>d</td>
<td>diameter [mm]</td>
</tr>
<tr>
<td>E</td>
<td>droplet aspect ratio [-]</td>
</tr>
<tr>
<td>g</td>
<td>earth gravitational acceleration [9.81 ms⁻²]</td>
</tr>
<tr>
<td>I</td>
<td>light intensity, [-]</td>
</tr>
<tr>
<td>L</td>
<td>optical path length, [mm]</td>
</tr>
<tr>
<td>l</td>
<td>length or distance, [mm]</td>
</tr>
<tr>
<td>n</td>
<td>amount of copper, [mol, mmol]</td>
</tr>
<tr>
<td>p</td>
<td>pixel value, [-]</td>
</tr>
<tr>
<td>u</td>
<td>droplet velocity, [mm/s]</td>
</tr>
<tr>
<td>V</td>
<td>volume, [mL]</td>
</tr>
<tr>
<td>V</td>
<td>droplet phase feed flow rate, [mL/min]</td>
</tr>
<tr>
<td>X</td>
<td>conversion (X = 1 - c/cₐ₀), [-]</td>
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**Greek alphabet**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
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<tbody>
<tr>
<td>Δρ</td>
<td>density difference (ρ_c - ρ_d), [kg/m³]</td>
</tr>
<tr>
<td>Δc</td>
<td>concentration difference, [mmol/L]</td>
</tr>
<tr>
<td>ρ</td>
<td>density, [kg/m³]</td>
</tr>
<tr>
<td>γ</td>
<td>interfacial tension, [mN/m]</td>
</tr>
<tr>
<td>ε</td>
<td>molar absorptivity, [L/(mmol mm)]</td>
</tr>
<tr>
<td>μ</td>
<td>dynamic viscosity [Pa s]</td>
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**Subscripts, indices**

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<th>Definition</th>
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<tbody>
<tr>
<td>0</td>
<td>initial value</td>
</tr>
<tr>
<td>aq</td>
<td>aqueous phase</td>
</tr>
<tr>
<td>bg</td>
<td>background</td>
</tr>
<tr>
<td>BOT</td>
<td>column bottom part</td>
</tr>
<tr>
<td>c</td>
<td>continuous phase</td>
</tr>
<tr>
<td>ch</td>
<td>chord length</td>
</tr>
<tr>
<td>cr</td>
<td>critical value</td>
</tr>
<tr>
<td>d</td>
<td>droplet or droplet phase</td>
</tr>
<tr>
<td>e</td>
<td>equivalent</td>
</tr>
<tr>
<td>i, j</td>
<td>pixel location indices</td>
</tr>
<tr>
<td>major, minor</td>
<td>major and minor axis of a droplet image</td>
</tr>
<tr>
<td>org</td>
<td>organic phase</td>
</tr>
<tr>
<td>p</td>
<td>value for pixel</td>
</tr>
<tr>
<td>Rise</td>
<td>rise</td>
</tr>
<tr>
<td>Sample analysis from sample</td>
<td></td>
</tr>
<tr>
<td>t</td>
<td>terminal velocity</td>
</tr>
<tr>
<td>TOP</td>
<td>column top part</td>
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**Dimensionless numbers**

<table>
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<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eo</td>
<td>Eötvös number, Eo = gΔρd²/γ</td>
</tr>
<tr>
<td>Mo</td>
<td>Morton number, Mo = gρ_c²Δρ/(ρ_d²γ³)</td>
</tr>
</tbody>
</table>
tional single droplet experiments, droplet rise time have to be controlled by adjusting the difference between the droplet feed and collection locations in order to determine, for example, the mass transfer during the droplet formation period by extrapolation. Also the assumption of the negligible effect of a coalesced droplet phase residence time in the funnel on the total mass transfer can be tested. The method provides also droplets inner concentration profiles and this reveals the inside circulation. The direct concentration analysis can be combined with numerical models and this leads to deeper understanding of mass transfer in reactive extraction and provides a basis of better equipment design. Other geometries than droplets, such as planar interfaces, can be measured if optical path length is determined. Other applications than extraction where suitable color changes exist, can be tracked with this method. The details of experimental procedure are presented in Section 2, where the experimental set-up, experiments in the column, and the analysis methods are shown in Sections 2.1–2.5. Results from experiments and discussion are combined as Section 3. The calibration, droplet size, concentration and velocity determination is discussed in Sections 3.1–3.3. To our knowledge the direct spatial quantitative concentration measurement from droplets has not been published previously.

2. Experiments

2.1. Preparation of feed solutions

The extractant (Acorga M5640 by Cytec Solvay Group, Lot n:o P3GBA524A) was contacted twice with 0.1 mol/L sulfuric acid and once with 0.1 mol/L ammonium sulfate solution prior its use. Equal volumes of organic and aqueous solutions were used. This was made in order to pre-equilibrate extractant and remove remaining soluble impurities from extractant. Finally, extractant was diluted with Exxsol D80 (by Exxon) to 10 vol% and 20 vol% solutions. The extractant active component concentration was measured by titration (Mettler Toledo T50 automatic titrator).

The equilibrated organic copper complex standard solutions were prepared by mixing 30 min the feed solutions with different copper concentrations, and 10 or 20 vol% Acorga solutions \( \left( \frac{V_{aq}}{V_{org}} = 1 : 1 \right) \). The copper content of the aqueous phase was analyzed with a spectrophotometer (Agilent 8543), and organic copper concentrations were calculated from mass balance. Organic solutions were used as standards for both the spectrophotometric analysis and the image analysis.

The copper sulfate solutions were prepared by dissolving copper sulfate \( \text{(CuSO}_4\cdot5\text{H}_2\text{O}, \text{Merck, Pro analysis) into water. The pH of solution was adjusted to 3.1 with concentrated sulfuric acid.} \}

2.2. Experimental set-up

The single organic droplet extraction experiments were made in a glass column (45 mm × 45 mm × 375 mm) filled with continuous aqueous phase. The droplets were formed at the flat tip of a 0.8 mm steel needle (nominal inner diameter 0.51 mm) at the bottom of the column using a high precision syringe pump. The droplet and column were back-illuminated with a led panel (300 mm × 300 mm, 35 W, color temperature 3000 K). The measured droplet sizes are introduced in Fig. 10. The droplets were collected at the other end of the column using a small funnel as shown in Fig. 1.

Two milliliter samples from the rising droplets were collected. Copper concentrations of the organic phase samples were directly analyzed with the spectrophotometer (Agilent 8543). The analysis was made using the absorption at 600 nm for the organic solution and at 811 nm for the aqueous solution samples. The wavelengths were selected based on the sample measurements with a spectrophotometer.

The droplet velocities and sizes were determined by analyzing the videos recorded with a Canon Legria HF R47 camera using a framerate of 50 frames per second. The concentrations inside the droplets and droplet sizes were determined from videos recorded with an AVT Oscar F-510C camera using a framerate of 7.5 frames per second. This second camera with a smaller field-of-view was used to capture more detailed images of the droplets and for more accurate representation of color information.

2.3. Column experiments

The column was filled with the continuous phase. The droplet phase was continuously pumped through the needle into the column. Flow rates of 0.1–1.0 mL/min were used in experiments. The average droplet detachment rate increased from about 4 droplet/min, to 35 droplet/min as a function of the feed flow rate. At first, the droplet phase flow rate was set to be at the minimum (0.1 mL/min) so that the droplet formation was slow enough for having a single droplet in the column. Droplets were formed until enough droplets were collected for the analysis (approximately 2 mL). Samples were collected manually using syringe in two or three batches in order to minimize sample residence time in the funnel. The average sample residence times decreased from 420 s to 60 s when flow rate increased from 0.1 to 1.0 mL/min. The funnel samples contained both phases and the phases were separated just after sampling. The samples were later analyzed with the spectrophotometer. Experiments were then repeated using higher feed rates. It is acknowledged here, that it is possible to optimize sampling procedure. However, sample residence time in the funnel cannot be removed completely as droplet coalescence is not an instantaneous process. Samples include also mass transfer over the phase interface at column outlet.

The concentrations of droplets were separately recorded at the bottom of the column (just after the droplet was detached from the tip of the needle), and at the top of column (just before the droplet entered the column outlet funnel). The results from the bottom of the column revealed the mass transfer into the droplet during its formation, whereas the results from the top of the column included the mass transfer into the droplet during its formation and rise.
The effect of rise on the mass transfer into the droplet could be determined by comparing the measured concentrations in the column bottom and top.

2.4. Image analysis

The first step in the image-based droplet analysis was to acquire image sequences using the setup described in Section 2.2. The AVT Oscar F-510C FireWire camera was used to obtain the image sequences (stored as uncompressed image files) for the concentration analysis and droplet size measurements. The Canon Legria HF R47 camera was used to obtain videos for the droplet size, velocity, and acceleration measurements. The second step was to detect moving droplets in the videos. Since the background (the column with the continuous phase) was static except for the moving droplets, the detection problem was solved using a background subtraction method. The background subtraction was performed by subtracting the previous frame in the image sequence from the input frame. This way the regions, where the subsequent frames differ due to the movement of droplets, were separated from the background (Cheung and Kamath, 2005).

The background subtracted image was then binarized by selecting an appropriate threshold value for the red color channel. The red channel was selected based on preliminary experiments where it was found to provide the most robust information for the task. The threshold value was automatically selected by using Otsu’s method (Otsu, 1979) that assumes that the image contains foreground (object) and background pixels, and calculates an optimal threshold so that the intra-class variance is minimal.

The resulting binary image typically contains noise. To eliminate the noise, connected components (connected regions of the foreground pixels) were determined and the components smaller than 10% of the predefined minimum droplet area were removed. The resulting binary images were further processed with morphological erosion using a small structuring element to remove small irregularities in the droplet edge regions. The structuring element is a binary area where black pixels (0 pixels) are excluded, and white pixels (1 pixels) are included in the morphological computation. After this step, the binary images contained at least fragments of the droplet edges.

Depending on the concentration, some of the detected regions contained holes. Moreover, with some concentrations the droplet edges were only partly visible.

To obtain full contours of the droplets, fitting an ellipse to the binary image data was used. The ellipse fitting was selected based on an assumption that the shape of droplets is oblate spheroid which causes the droplets to have an elliptical shape in the images. The ellipse fitting provides a good estimate for the true contours of the droplets and produces more reliable droplet shape parameters than using only binary descriptors of the droplet region (Szpak et al., 2012). The limits for the ellipse parameters were used to control the droplets, which were processed further and the ones which were discarded if they did not meet the limits. The full image analysis pipeline is presented in Fig. 2. The image at the top left corner shows the region of interest (ROI) (the blue rectangle) used for processing. ROI was manually selected after visual inspection of the videos to contain all the droplets moving with minimum processing area.

The basic image processing pipeline from the beginning to the ellipse fitting step was the same for the both imaging sources. After this, different feature extraction operations were performed for the Canon Legria HF R47 videos (size, velocity, and acceleration measurements) and the AVT Oscar videos (size and concentration analysis). Velocity and acceleration of the droplets were not determined from AVT Oscar videos since the lower frame rate, only 3 or 4 captured images from one moving droplet, did not allow accurate measurements. Features extracted from the Canon Legria HF R47 videos included the minor and major axis lengths, orientation, velocity, and acceleration of the droplet. The ellipse minor and major axis lengths are

$$d_{\text{minor}}(d_{\text{major}}) = \left[ \frac{2\left(\text{AE}^2 - \text{BDE} + \text{CD}^2 - 4\text{ACF} + \text{FB}^2\right)}{(4\text{AC} - \text{B}^2)(\text{A} + \text{C}) + \sqrt{(\text{A} - \text{C})^2 + \text{B}^2}} \right]^{\frac{1}{2}}. \quad (2)$$

where | denotes the logical or (disjunction) operator (the greater of the two values given by the equation is the major axis) and A, B, C, D, E, and F are the parameters of the general quadratic curve,

$$Ax^2 + Bxy + Cy^2 + Dx + Ey + F = 0. \quad (3)$$

(Weisstein, 2016). These parameters were obtained using the ellipse fitting. The velocity was calculated from the movement of the droplet center point between the consecutive frames and the acceleration as the difference in velocities between the consecutive frames.

In order to convert the pixel values of the features into the real world values (millimeters), the cameras were geometrically calibrated. To calibrate the camera, a sequence of images with a 5 mm grid was captured to provide the points of reference. The calibration was performed using the methods presented in (Heikkila and Silvén, 1997; Zhang, 2000). The process included detecting the grid from the image sequence and calculating the pairwise distances of grid lines. The collected information was used to form corrected, distortion free images. The pixel size in mm was obtained by dividing the real world grid size (5 mm) by the average distance for adjacent grid lines in images.

The concentration calculations were performed using the absorbance in the red color channel as explained in Section 2.5. The droplet geometry was taken into account by making chord length calculations assuming that the shape of droplets was oblate spheroid. This geometry was calculated from the parameters of the fitted ellipse. 15% of the droplet image area, the outer edge region of the droplet, was excluded from the concentration analysis since the light scattering at the droplet phase boundary caused problems when calculating the concentrations. Simplified process flow of the concentration analysis is shown in Fig. 3. Image analysis steps were implemented using MATLAB (2016a). The concentration analysis is described in more detail in Section 2.5.

2.5. Concentration analysis

The concentration analysis inside a droplet is based on the observation of image intensity change inside the sample. The concentration analysis is possible with imaging because of color change, which takes place when copper is complexed with hydroxyoxime. This color change is observed from the video recording of moving droplets by a digital camera.

The spectra recorded with the spectrophotometer revealed that free hydroxyoxime and its copper complex absorb light at different wavelengths (Fig. 4). The highest wavelength at which the free extractant absorbs light is approximately 400 nm whereas the copper complex absorbs also at longer wavelengths. The complex has a wide absorption peak with the absorption maximum at approximately 680 nm. The concentration analysis of organic phase samples with the UV/VIS-spectrophotometer (Agilent 8543) was made at the wavelength of 600 nm. The wavelength of 811 nm was used for the aqueous copper sulfate solution concentration analysis.

The concentration analysis with both the spectrophotometer and the cameras are based on the Lambert-Beer law. The Lambert-Beer or Bouguer-Beer law describes how, in a transmission measurement, the light intensity decreases as a function of the sample concentration and light path length. Each recorded
Fig. 2. Image analysis steps for determining the droplet movement, size and concentration. Contrast of the color images on the top row and the difference image has been enhanced for visualization purposes.

Fig. 3. Simplified process flow of the concentration analysis. The ‘logical and’-symbol is used to represent the major contributing factors (absorbance and volume) to the concentration determination in simplified form.

Fig. 4. The basis for detecting the copper complex. The red channel of camera is most sensitive for wavelengths from 550 nm to 700 nm. The visible-range spectra of organic Acorga M5640 solutions dissolved into Exxsol D80 and aqueous copper sulfate solution.
pixel of the droplet image represents a part of droplet. These droplet parts have a volume, here called as the pixel volume. The concentration in the pixel volume may not be uniform along the droplet chord (perpendicular to the image plane) as droplets were imaged only from a single direction. Uniform concentration was assumed for each pixel volume. The Lambert-Beer law and its derivation are presented and discussed by Berberan-Santos (1990), Goldstein and Day (1954) and Liebhafsky and Pfeiffer (1953) and Denney and Sinclair (1987). The Lambert-Beer equation is presented as

\[ A = \varepsilon L c \]  

(4)

where \( \varepsilon \) is molar absorbivity, \( L \) the optical path length, \( c \) is concentration and \( A \) is the absorbance:

\[ A = \log_{10}(I_0/I) \]  

(5)

that is, the logarithmic ratio of light intensity transmitted through the sample \( I \) and incoming light intensity \( I_0 \).

The camera used for the concentration analysis (AVT Oscar F-510C) is a RGB camera with 8-bit channels. The approximate range, where red channel of the camera detects light, is 550–700 nm (Fig. 4). The red channel was found to be specific only for the copper complex of extractant, and not for the uncomplexed extractant. It is also noted that copper sulfate absorbs light at the wavelength range of the red channel. The red channel background is assumed to be constant, as the continuous phase volume is much higher compared to the droplet volume and thus the amount of copper and the copper concentration in the continuous phase remains practically constant during an experiment.

The camera records incoming light intensity and encodes the intensities as pixel values in the range of 0–255 (8 bits). The pixel values are assumed to be linearly dependent on the incoming light intensity within the usable dynamic range of the camera. Analogous to Eq. (5), absorbance is determined by:

\[ A = \log_{10}(p_0/p), \]  

(6)

where the incoming light intensity is represented by the pixel value \( p_0 \) and the light transmitted through the sample with the pixel value \( p \) (compare to Eq. (5)).

The camera records a droplet as it moves through the column. The spatial uniformity of the light source is even, and the pixels of the camera are assumed to be identical. Both droplet and background are visible simultaneously in recorded images, and thus the situation is similar to the double-beam spectrophotometer where the light beam is divided into two beams, and one travels through the sample and another through the solvent (i.e., background) (Mann et al., 1974). As the background of the image, i.e., the continuous phase, absorbs light also in the red channel used for the concentration analysis, the background is corrected by subtracting the background absorbance \( A_{bg} \) from the absorbance of the droplet image \( A_d \):

\[ A = A_d - A_{bg} \]  

(7)

The droplet concentration can be calculated from absorbances, when droplet geometry is taken into account. The optical path length, i.e., the distance which light travels in a sample effects absorbance as it can be seen from the Lambert-Beer law (Eq. (4)). The chord lengths of the droplet at each pixel position were calculated by assuming that the droplet was oblate spheroid and that the axis normal to the image plane is equal to the measured major axis length.

The effect of light scattering was determined by calculating molar absorbivities \( \varepsilon \) for each pixel of single droplet image using the Lambert-Beer law (Eq. (4)). The absorbivities are shown as a function of calculated chord lengths in Fig. 5b. The edge of a droplet is darker than the rest of the droplet, which is due to light refraction and scattering. The apparent absorbivity increases towards the droplet edge and it includes both the effect of light absorption due to the copper complex and the effect of scattering. While there are correlations for the light intensity changes due to scattering (Gumprecht and Sliepecevich, 1953), the use of apparent absorbivity was chosen for this work, as the present camera detects a wide range of wavelengths. The applied interpolation function for the apparent absorbivity was

\[ e = 3.786 \times 10^{-3}/\ln(l_{ch} + 1) + 0.8977 \times 10^{-3}, \]  

(8)

where \( l_{ch} \) is the chord length. The function parameters were fitted to the droplet data and the function was used in the calculation of concentration profiles and the average concentrations of the droplets.

When the optical path length of the Lambert-Beer law \( L \) in Eq. (4) is set equal to the calculated chord length and the absorbivities are calculated with Eq. (8), the concentrations at the positions of the pixels \( (c_p) \) can be calculated from the image data based absorbances and the Lambert-Beer law (Eq. (4)):

\[ c_p = A/\varepsilon l_{ch} \]  

(9)

The calculated chord lengths \( l_{ch} \) together with the image scale, i.e., the distance per pixel \( (l_p) \), are used when the representative volume of each pixel is calculated:

\[ V_p = l_p^3 l_{ch}. \]  

(10)

where \( l_p \) is the distance per pixel. The amount of copper \( (n_p) \) at the position of each pixel can be calculated from the volume and the measured concentration of the pixel:

\[ n_p = c_p V_p \]  

(11)

When the sum of the values of \( n_p \) of the whole droplet image is determined, the amount of copper transferred into the droplet can be calculated with

\[ n = \sum_{i=0}^{d_{max}} \sum_{j=0}^{d_{max}} n_p(i,j) \]  

(12)

where \( i \) and \( j \) are indices of pixel location along the droplet image axes.

The average concentration of copper transferred into the droplet is

\[ c = n/V_d, \]  

(13)

where \( V_d \) is the droplet volume. The organic phase copper concentration is presented as a conversion of extractant, as organic feed solution includes the extractant and no copper.

The conversion \( (X) \) of extractant (HA) is calculated (Levenspiel, 1999) by:

\[ X_{HA} = 1 - C_{HA}/C_{HA,0} \]  

(14)

The extractant concentration is calculated using the extractant mass balance:

\[ C_{HA} = C_{HA,0} - 2c \]  

(15)

Copper reacts with two extractant molecules to form the complex, as also it can be seen from the reaction (Eq. (1)).

The calibration standards (see Fig. 5a) for the single droplet experiments were imaged as droplets in the column. The apparent molar absorbivity was calculated for each pixel of a droplet image \((cCu_{org} = 25.4 \text{ mmol/L})\). The interpolation function (continuous line) and \( e \) obtained from droplet center data (dotted line) in Fig. 5b are also shown. The continuous line represents the interpolation function of apparent molar absorbivity and the dotted line denotes the value of \( e \) obtained from the fit. The scattering is at minimum at droplet center, as can be seen from Fig. 5b.
The calibration standard solutions of 20 vol% Acorga M5640 containing different copper concentrations were measured from the 0.8 mm needle tip using the aqueous copper sulfate solution (0.16 mol/L) as the continuous phase. The calibration line (Fig. 5a) was computed based on the center region of the droplets where the effect of light scattering is minimized. The copper complex standard solutions of 10 vol% Acorga M5640 in 0.06 M CuSO₄ continuous phase were measured for the comparison and verification purposes. The organic standard solutions were pumped through the needle into the column filled with the copper sulfate solution. The copper concentration in organic standard solution was varied between 0 and 30 mmol/L. The standard solution analysis with the spectrophotometer revealed that calibration lines of the both extractant concentrations were essentially the same.

The similar observations can be seen in Fig. 6, where samples with known copper concentrations were analyzed. The concentration in the droplets was analyzed using the same method and the calibration line as in the actual column experiments. The results at two different extractant concentrations are overlapping, indicating that also in the image analysis the calibration lines are practically the same.

Each droplet was detected several times from the subsequent video frames. The median value of these separate detections was used as the representative value for the droplet. The subsequent droplets are here considered as repetitive measurements. The $\chi^2$ goodness of fit test for the normality was performed. The $\chi^2$ test was passed in the case of elliptical droplet major and minor axis lengths, velocity, and concentration, that is, the data is normally distributed. Standard deviation of each dataset was chosen as the basis for quantifying variation in the measurement data. The measure for the error in this work is three times dataset standard deviation. The theoretical detection limit for the proposed method is estimated by assuming that copper complex concentration in the droplet is uniform. The smallest possible detectable concentration change corresponds to pixel value $p$ change from 255 to 254. Then the absorbance is $1.7 \times 10^{-3}$. The concentration can be calculated from this using the calibration line (Fig. 5). Thus, the smallest detectable concentration is approximately 0.15 mmol/L. The method accuracy and reproducibility are presented in Fig. 6. The method reproducibility (i.e., the distribution width of the measured data at each standard solution concentration) is approximately 2 mmol/L. The accuracy of method is defined as the difference between the average of the measured data and the nominal standard solution value. The accuracy of method may be possible to improve since there are some differences between the measured and nominal concentrations (the line in Fig. 6). The method standard line is linear in the concentration range 0–30 mmol/L (Fig. 5a).

The instrument bandwidth affects recorded absorbance values (Denney and Sinclair, 1987). In case of the spectrophotometer, the spectra was recorded with interval of 1 nm. The absorbance peak of complex is at least 150 nm wide (see Fig. 4) and the ratio of instrument and sample spectral bandwidths are below 0.01 in case of the spectrophotometer. The bandwidth of the red channel of the camera is close to 150 nm. The ratio of the instrument and sample spectral bandwidths is thus approximately 1.

**3. Results and discussion**

3.1. Analysis method

The camera calibration line forms a straight line (see Fig. 5a). Thus the Lambert-Beer law is obeyed also in determining the concentration from the droplet image data. The molar absorptivity coefficients obtained for the 10 vol% and 20 vol% Acorga standard
solutions using the spectrophotometer at the wavelength of 677 nm, are $9.62 \times 10^{-3}$ and $9.43 \times 10^{-3} \text{ L/(mmol mm)}$, respectively ($L = 10 \text{ mm}$). The coefficients are nearly identical. For that reason, the only species present, which absorbs light at 677 nm, is the copper complex. The corresponding estimated absorptivities at the droplet center for the camera (AVT Oscar F-510C) were $3.4 \times 10^{-3} \pm 0.2 \times 10^{-3} \text{ L/(mmol mm)}$ for the 10 vol% Acorga solutions and $3.2 \times 10^{-3} \pm 0.2 \times 10^{-3} \text{ L/(mmol mm)}$ for the 20 vol% Acorga solutions. The optical path length ($L$) was taken to be equal to the droplet major axis length in the calculations. The measured

![Image](image_url)

**Fig. 6.** Comparison of known standard solution concentrations and concentrations from image analysis. Mean of measured data (symbols) and variation of data (error bars) are shown. Nominal values (line) are shown for comparison purposes.

![Image](image_url)

**Fig. 7.** The example distributions of measured droplet sizes, velocities, and concentrations. The histograms represent the measured data distributions and the lines denote normal distributions whose parameters are estimated from the data. The width of normal distribution is ±3 standard deviations. The average and standard deviation were estimated from data.
major axis lengths were 4.2 ± 0.1 mm in the case of 10 vol% Acorga standards and 4.1 ± 0.2 mm in the case of 20 vol% Acorga standard solutions (see also Fig. 10).

The observed absorptivities of the 10 and 20 vol% standard solutions are almost identical also in the case of droplet image analysis. The complex absorbs light at the wavelength range of the red channel. The background was constant in each case and was subtracted from the images. The observed absorptivities were lower for the camera due to the wider spectral bandwidth. The similarity of absorptivities implies that the mass transfer during droplet formation was indeed minimal.

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The effect of scattering due to droplet interface curvature was taken into account by calculating molar absorptivities for each pixel of standard solution droplet (Fig. 5b). The apparent molar absorptivity includes both the effect of copper complex light absorption and the effect of light scattering. The apparent absorptivity was assumed to depend only on the chord length, but the variation in the droplet data is notable. The interpolation function was fitted to the droplet data and it was used in the calculation of droplet copper concentrations. The interpolation function gives apparent absorptivity of 3.2 × 10⁻³ L/(mmol mm) at the droplet center (L = 4.1 mm), which is identical to the absorptivity obtained by fitting to all different concentrations. The difference between the continuous and dotted line in Fig. 5b indicates the effect of scattering. Scattering is minimal at the droplet center and increases towards the droplet edge.

It is acknowledged that copper can be transferred into the standard solution during droplet formation in the calibration experiment. The average formation time of droplets was estimated to be approximately 1.3 s. Due to the short formation time, the effect of mass transfer during the droplet formation with the standard solution is estimated to be approximately 0.3 mmol/L. This is within the variation in the analyzed concentrations of standard solutions. The estimation was made by extrapolating measured data from column bottom experiments, which contain mass transfer from droplet formation (see Fig. 8 and Table 1). The fitted extrapolation power function was used to calculate concentration at flow rate of 1.5 mL/min.

3.2. Concentration analysis

The present method determines organic phase copper complex concentration in the droplet. The results are presented as an extractant conversion and they are shown in Fig. 8. The conversion based on sample analysis (C_{Sample}) taken from the column outlet funnel are clearly higher than based on the droplets imaged at the top (C_{TOP}) and bottom of the column (C_{BOT}) (see Table 1). Results from bottom of column show mass transfer during droplet formation, while results from column top include also mass transfer during droplet rise. The difference between column top and bottom analyses, reveal mass transfer during droplet rise (see also Fig. 8b). Samples include mass transfer during droplet formation, rise and column outlet funnel.

The high concentrations in the analyzed samples are due to long residence times at the column outlet. The average sample residence times at column outlet varied from 60 s to 420 s. It is acknowledged, that the sample concentrations are high and that sampling can be optimized. However, the purpose of this work is to present direct method for determining droplet inner concentrations and sample concentrations were determined for comparison purposes. Also noteworthy is the variation between the samples at high feed flow rates (over 0.3 mL/min) compared to the variation from direct droplet analysis.

The imaging of a droplet at the column top was made just prior it enters the column outlet funnel and imaging at the column bot-

Table 1

<table>
<thead>
<tr>
<th>V (mL/min)</th>
<th>C_{TOP} (mmol/L)</th>
<th>C_{BOT} (mmol/L)</th>
<th>ΔC_{Rise} (mmol/L)</th>
<th>C_{Sample} (mmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>5.3</td>
<td>5.3</td>
<td>0.0</td>
<td>29.9</td>
</tr>
<tr>
<td>0.3</td>
<td>2.4</td>
<td>1.7</td>
<td>0.6</td>
<td>21.5</td>
</tr>
<tr>
<td>0.5</td>
<td>2.1</td>
<td>1.0</td>
<td>1.1</td>
<td>24.5</td>
</tr>
<tr>
<td>0.7</td>
<td>2.1</td>
<td>0.7</td>
<td>1.4</td>
<td>28.5</td>
</tr>
<tr>
<td>1</td>
<td>2.3</td>
<td>n.d.</td>
<td>2.3</td>
<td>24.9</td>
</tr>
</tbody>
</table>

![Fig. 8](image-url) Copper complex concentration change in column experiments. (a) Conversion of extractant to copper complex. (b) Copper complex concentration change during droplet rise.
Tom was made just after a droplet detached from the needle tip. These two positions were measured in separate experiments. Comparison of the column bottom and column top measurements reveals that the majority of copper is transferred during the droplet formation. When the flow rate increases, copper transfer during the droplet formation decreases rapidly as the droplet formation time decreases. The droplet formation time is approximately 17 s at 0.1 mL/min and it decreases below 2 s when the flow rate is 1.0 mL/min.

The copper mass transfer during the rise increases as the droplet feed flow rate increases (see Fig. 8b). The droplet sizes and the measured velocities of droplets are approximately constant (see Figs. 9 and 10) and the rise time does not vary significantly and cannot explain the difference because the rise length remains constant. Possible explanation is that, the concentration difference between droplet and continuous phase increases as a function of flow rate, due to decreasing mass transfer during droplet formation (see Fig. 8 and Table 1). This leads to observed increased mass transfer during droplet rise.

For determining droplet concentration profiles, droplets were imaged at the bottom and the top of the column, and the concentrations were calculated from the recorded video images (see Fig. 9). The shown droplet images represent examples of droplets at the top and bottom positions of the camera. The highest copper concentrations are found near the droplet interface, which is due to interfacial complexation of copper and limited interaction time for
mass transfer. The concentrations at the droplet bottom tend to be higher than at the top. The explanation for this is not clear, but a possible reason is the density difference between the extractant and copper complex because the loaded extractant is heavier. Another possible reason is the circulatory flows at both sides of the droplet phase boundary. One possible explanation for the observed concentration distribution inside the droplets is the uneven distribution of surfactants. According to Slater (1995), surfactants have a tendency to concentrate in the droplet lower part and to stop internal circulation. In this stagnant cap model the droplet upper part, having lower surfactant concentration, has a mobile interface leading to circulation and reducing concentration differences.

The effect of decreasing the formation time can be observed in Fig. 9 as the concentrations decrease from left to right. The effect is especially clear in the case of observations from the column bottom. The effect of mass transfer during the droplet rise can be seen by comparing images taken at the top and the bottom of the column with the same flow rate. The images recorded at the top of the column show higher concentrations. Comparison of the images is straightforward, as the droplet sizes are approximately equal.

3.3. Droplet sizes and velocities

Fig. 10 shows measured droplet sizes and measured and estimated droplet velocities. Terminal velocities were calculated by using Eq. (16). Data was obtained by image analysis of videos recorded by Canon Legria HF R47.

The droplet sizes are similar in all experiments (Figs. 9 and 10), which is due to identical solution properties and the same needle gauge used in the droplet formation. The increase in feed flow rate of the droplet phase from 0.1 to 1.0 mL/min had no significant effect in the droplet sizes.

Droplet velocities were determined at the top of the column and like droplet sizes, velocities are also close to each other. They varied between 112 and 115 mm/s (Fig. 10b). To validate the velocity measurement, correlation by Grace et al. (1976) was used. This correlation is for systems where, for example, surfactants are present as contaminants and correlations for pure systems are not usable. Their correlation for droplet terminal velocity is

\[
u_t = \frac{\mu_s}{(\rho_L d_s) M_0^{-0.149}} \left(J - 0.857 \right)\]

with

\[
J = 0.94 H^{0.757}, \quad 2 < H < 59.3
\]

and

\[
J = 3.42 H^{0.411}, \quad H > 59.3
\]

and \(H\) defined as

\[
H = 4/3 Eo M_0^{-0.149} (\mu_s/\mu_w)^{-0.14}, \quad \mu_w = 0.9 \text{ mPa s}
\]

where \(\mu_s\) and \(\rho_L\) are continuous phase viscosity and density, \(d_s\) volume equivalent sphere diameter, \(M_0\) is Morton number and \(Eo\) is Eötvös number. The property values for the 20 vol% Acorga and 0.16 mol/L CuSO₄-solution pair at room temperature were \(\rho_L = 1025 \text{ kg/m}^3\), \(\mu_s = 834 \text{ kg/m}^2\text{s}\) and \(\gamma = 22 \text{ mN/m}\). Copper sulfate solution density was interpolated from literature values (Lobo, 1981) and interfacial tension was measured using the drop weight method (Adamson, 1990). Using average droplet major and minor axis lengths \(d_{\text{major}} = 4.0 \text{ mm}\) or \(4.1 \text{ mm}\) and \(d_{\text{minor}} = 3.3 \text{ mm}\) (see Fig 10a), volume equivalent sphere diameters \(d_s\) are 3.76 and 3.81 mm. With given physical property values \(M_0\) and \(Eo\) numbers are 0.242 - 10⁻⁶ and 1.36 and terminal velocities \(v_t\) using Eqs. (16)-(19) are 117 and 118 mm/s, which agree well with the measured droplet velocities.

Based on the measurements, the droplet aspect ratio \(E = d_{\text{minor}}/d_{\text{major}}\) is between 0.80 and 0.83. Grace et al. (1976) have presented a correlation for the droplet aspect ratio

\[
E = 1/(1 + 0.163 Eo^{0.757}), \quad M_0 < 10^{-6}, \quad Eo < 40
\]

Using \(Eo = 1.36\), the estimated aspect ratio is 0.83 which corresponds well with the observed aspect ratios. To determine the droplet shape region, diagram presented by Grace et al. (1976) is used. With droplet Eötvös number 1.34 and Morton number 0.242 - 10⁻⁶ the shape region is ellipsoidal which is confirmed from droplet observations.

In addition to surfactants, the droplet size and form have an effect on the terminal velocities. The droplet size defines the mass transfer area, and the droplet velocity affects internal circulation in the droplet and the diffusion layer thickness. The changes in velocity lead to differences in the diffusion layer thickness and wake outside the droplet. The properties of the diffusion layer and circulation both inside and outside the droplet, have an effect on the mass transfer during extraction. The velocity of the droplet affects the rise time of the droplet. Both the droplet size and velocity are measured in order to differentiate between the mass transfer during droplet formation and rise.

4. Conclusions

The presented method was developed for direct monitoring of single organic phase droplets and their reactive copper extraction in a glass column. The developed method is based on the observation of droplet color change, which is due to the formation of strongly light absorbing copper–hydroxyoxime complex. It was verified against reference samples which were analyzed using spectrophotometry. The method can be used to detect droplet concentration directly inside the column from any position where the droplet is visible. This enables monitoring of mass transfer into a single rising droplet in the column, which can be done in separate experiments or in a single one using several cameras.

In this paper the problematic concentration analysis using the traditional sample collection has been performed for comparison purposes, and the advantages of the direct image analysis based method has been presented. The method enabled the determination of individual effect of droplet formation, droplet rise and sample collection on copper mass transfer. The effect of sample collection is most notable due to the long residence time of the droplet phase at the column outlet. The droplet formation has a notable effect on copper mass transfer at low feed flow rates, due to long droplet formation times. The image analysis method also enabled characterizing the shape of droplets, by determining the droplet minor and major axis lengths. There was a good agreement with measured and estimated droplet velocities.

The developed method can be improved in several ways. For example, when a more sensitive camera with a wide dynamic range and improved conversion to digital intensity values is used, a wider range of concentrations can be measured and with better signal-to-noise ratio. Calculation of optical paths and modeling the light scattering at the outer edge region of the droplet would possibly allow inclusion of the edge region into the concentration analysis. One possible way could be to add additional camera(s) at different angle(s) to determine the light scattering and optical properties of the edge region. Different light sources could also be considered, when determining the effects of the light scattering at the outer edge region of the droplet. While the present work is designed for copper solvent extraction, the same method can be used in any metal-extractant pair, where the color change in extraction is large enough for the imaging. This method is by no means limited to metal extraction substances, but it can be applied...
also to other systems, where a suitable color change is present. It is also possible to limit the observation bandwidth by installing special filters onto the camera optics. The camera red channel was used here, but present method is not limited to specific color channel. Depending on application, it may be possible to use different channels in detection of different reactive species. On the other hand, it is also possible to change the spectral characteristics of the illumination used and even use laser illumination. The method is not limited to the visible light, assuming that the camera sensor is sensitive to and the optics is suitable for other wavelengths, such as ultraviolet light or infra-red.

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References