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Multi-angle near infrared spectroscopy associated with common components and specific weights 5 analysis for in line monitoring

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14 **4 Multi-angle near infrared spectroscopy associated with common components and specific weights**
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16 **5 analysis for in line monitoring**
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38
39 13 **Abstract**
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41
42 14 Near infrared (NIR) spectroscopy offers a number of important advantages for process monitoring. In
43
44 15 addition to its numerous practical advantages, an important reason to use NIR spectroscopy for process
45
46 16 monitoring is its ability to supply versatile and multivariate information. However, in heterogeneous samples
47
48 17 the interaction of light is complex and includes transmission, absorption and scattering simultaneously which
49
50 18 all affect spectra. The measurement of the signal at one point may be insufficient. A solution is to measure the
51
52 19 medium at several points and to use specific multivariate analysis.
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56 20 In our study we propose to associate multipoint measurements with a Common Components and Specific
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58 21 Weight Analysis (CCSWA). We monitored two media online by angular multipoint Near infrared (NIR)
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3 22 spectroscopy. For the first medium, in which only the scattering varies over time, the precipitation of silica
4
5 23 was chosen to illustrate such a medium. For the second medium, both scattering and absorption vary,
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7 24 whereby microemulsions implemented for enhanced oil recovery illustrate this medium. The results showed,
8
9 25 by combining multi-angle measurements to CCSWA, the interest of measuring at different angles. In the first
10
11 26 case, two scattering regimes have been identified and it was possible to access the anisotropy coefficient
12
13 27 during the silica precipitation reaction. In the second case study, on microemulsions, it was possible to
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15 28 identify the different phases, and to separate the phenomena related to absorption and those related to
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17 29 diffusion.
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22 30 These encouraging results validate the interest of coupling multi-angle measurements with multivariate
23
24 31 multiblock analysis tools.
25
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28

29 33 Keywords

30 34 Near infrared spectroscopy, multipoint, multi-angle, common components specific weights analysis, in line,
31
32 35 monitoring, silica, EOR, microemulsions
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39 41 Introduction

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41 38 Process control is a topic of increasing research in recent years ¹ in the chemical industry and, is now even
42
43 39 regulated for the pharmaceutical industry ². As mentioned by Kessler et al ³ “cost, pressure, globalization and
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45 40 quality assurance will undoubtedly stimulate significant demand for process analytical technology (PAT)”.
46
47 41 PAT, aims to give a better scientific understanding of manufacturing process, which leads to knowledge-
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49 42 based production. This implies the monitoring of operating parameters, such as pressure, temperature or flow
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51 43 rates, but also physicochemical parameters as compositions, concentrations or particle sizes.
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3 44 Spectroscopic techniques, such as near infrared (NIR) spectroscopy, have proven useful in process control for
4
5 45 several years and many uses attest of their high efficiency ⁴⁻⁷. Near infrared spectroscopy offers a number of
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7 46 important advantages for inline analysis ⁸⁻⁹. It is a nondestructive method, requiring minimal or no sample
8
9 47 preparation, it is fast, and can be carried out without contact. Its implementation online is simple, and signal
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11 48 transport using optical fibers offers the advantage of relocating the analyzer away from hazardous areas.
12
13
14 49 Besides the practical advantages, an important reason for using NIR spectroscopy for process monitoring is
15
16 50 its ability to supply versatile and multivariate information. Indeed, NIR spectroscopy is based on the principle
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18 51 of light interaction with matter allowing to obtain qualitative and quantitative physical and chemical
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20 52 information.
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23
24 53 In combination with multivariate data analysis the spectral information can be correlated to product
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26 54 properties, as it has been done for a large number of applications in various fields. For instance:

- 27
28 55 • Qualitative monitoring can be done such as on wet agglomeration of wheat flour ¹⁰, the conversion of
29
30 56 a monomer during a polymerization reaction ¹¹⁻¹², to verify that a product is in specification by
31
32 57 comparing it to reference spectra ¹³ or to follow the structural modifications of a medium and detect
33
34 58 the formation of a homogeneous gel as in the study of Mas et al. ¹⁴ for example.
35
36
37 59 • In combination with multivariate data analysis NIR spectroscopy can be used for quantitative
38
39 60 monitoring of various chemical concentrations such as glucose ^{15,16}, paracetamol ¹³, lactose ¹⁷,
40
41 61 moisture content ^{13,10}, or the quantification of heavy products in oil ¹⁸, but also for physical properties
42
43 62 like particle size^{11, 19-23}.

44
45
46 63 However, in heterogeneous samples, the interaction of light with matter is complex and spectra contain
47
48 64 combinations of the effects of transmission, absorption and diffusion ²⁴. Generally, as the chemical
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50 65 information is sought, it is usual to correct for the scattering effects by means of empirical pretreatments ²⁵.
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52
53 66 But in the case of PAT, there is an interest to exploit the full potential of the spectral information and use both
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55 67 absorbance (which describes the chemistry) and scattering (which describes physicals properties as particle
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3 68 size, agglomeration, porosity) information. However heterogeneous systems cannot be fully characterized by
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5 69 a single measurement.
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8 70 Recently, some studies focused on the use of multipoint measures for monitoring in situ heterogeneous
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10 71 systems. Scheibelhofer et al ²⁶ have combined multipoint NIR measurements with Monte Carlo simulation to
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12 72 understand the behavior of light in pharmaceutical tablets. Boiret and Chauchard ²⁷ have combined multipoint
13
14 73 measurements in reflection with chemometrics tools, such as partial least squares (PLS) regression and
15
16 74 principal component analysis (PCA), to predict sample hardness and active pharmaceutical ingredient (API)
17
18 75 distribution within tablets respectively. The association of PLS regression with multipoint reflection measures
19
20 76 has also shown good results for quantifying proteins and fat in milk ²⁸, to predict the fat and moisture content
21
22 77 of meat ²⁹, for in-line moisture content analysis during freeze-drying ³⁰, or for in-situ estimation of
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24 78 concentration and particle size in colloidal suspensions ³¹. In the study by Igne et al. ³², a traditional single-
25
26 79 point NIR measurement was compared with that of a spatially resolved spectroscopic (SRS) measurement for
27
28 80 the determination of tablet assay by applying PLS regression also. Multipoint measurements have been shown
29
30 81 to be more sensitive to tablet heterogeneity, even if the authors stated that multivariate multiblock analysis
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32 82 may further enhanced those.
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38 83 Indeed, there would be an interest in associating multipoint measurements with specific multivariate data
39
40 84 analysis methods, like common components specific weights analysis (CCSWA) ³³. CCSWA, also known as
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42 85 ComDim, is a multiblock analysis which makes it possible to analyze simultaneously several data matrices,
43
44 86 considering them as blocks, and to extract the information that is common among them. Historically, this
45
46 87 method was developed by Qannari et al. ³³⁻³⁶ in order to analyze tables as part of sensory assessments.
47
48 88 CCSWA has since been used to study samples analyzed on different instruments, to find relationships
49
50 89 between tables and to discriminate samples on the basis of the global information included in all tables. For
51
52 90 example Ammari et al. ³⁷ has studied the recognition of geological material by means of laser induced
53
54 91 spectroscopy, coupled with three different spectrometers. They used CCSWA to analyze jointly the signals
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56 92 delivered by the three devices and to retrieve the best wavelength regions. In Kulmyrzaev et al. ³⁸, CCSWA
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1
2
3 93 was used to investigate changes in cheeses mixing rheology, infrared spectroscopy and front-face
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5 94 fluorescence spectroscopy. This technique has also been successfully used to show that there is a correlation
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8 95 between particle size distribution and wheat flour NIR spectra ³⁹.

9
10 96 In the present paper, CCSWA coupled with multi-angle spectra measurements is proposed as a novel method
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12 97 to monitor in situ heterogeneous systems. Two heterogeneous systems are studied in this article. One where
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14 98 only the scattering varies, and another where the absorption and the scattering both change.

15
16
17 99 The silica precipitation reaction was chosen to illustrate the environment where only the scattering varies ⁴⁰.

18
19 100 The manufacture of silica is a high-stakes industrial application because silica is a product with added value
20
21 101 which can be used for many applications in various fields. The precipitation reaction stage is a crucial step in
22
23 102 the silica production chain as the main characteristics of the final product depend on it. From these
24
25 103 characteristics depend the uses of the silica produced. It is then essential to understand the mechanisms of this
26
27 104 reaction and to follow it online.

28
29
30 105 The monitoring of processes to improve oil extraction was chosen to illustrate a situation where the
31
32 106 absorption and the scattering both vary. The enhanced oil recovery (EOR) process involves injecting a saline
33
34 107 solution containing surfactants into the rock. With this formulation, microemulsions are formed with the oil
35
36 108 and extraction yields are improved. However, obtaining microemulsions is critical and depends on many
37
38 109 parameters such as the nature of oil, the nature of the rocks or surfactants. Depending on these parameters,
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40 110 microemulsions with different physicochemical characteristics can be obtained. It is therefore essential to
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42 111 understand what happens in microemulsions, to identify the type of system created and to monitor in real time
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44 112 to ultimately optimize the process.

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46
47 113 This paper is organized as follows. First, experimental set up are described for both studies. Then, the
48
49 114 CCSWA is presented. Results are discussed in two parts: one from the silica precipitation study, and the other
50
51 115 from the microemulsions study.

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57 117 Materials and methods

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3 118 Study 1: Silica precipitation monitoring
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6 119 Material
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9 120 A specially designed probe (Sam-Flex, from Indatech, Chauvin Arnoux, France) was used for spectral
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11 121 measurements. It was composed of 5 positions for spectral measurements at 5 different angles, 3 in
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13 122 transmission at 150° from the incoming beam, 170° and 180°, and 2 in reflection at 30° and 90°. The diagram
14
15 123 of the probe is represented in Figure 1. The air-gap of the probe was 3 mm which correspond to the optical
16
17 124 path. The probe was connected to a spectrometer (Hy-ternity, Indatech, France) composed of an NIR camera
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19 125 equipped with an InGaAs detector (340 * 256 pixels) allowing the simultaneous measurement of all spectra.
20
21 126 Spectral data were measured in the wavelength region from 950 to 1650 nm at 5 nm intervals.
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23
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25
26

27 128 (i.e. "[insert Figure 1.]")
28

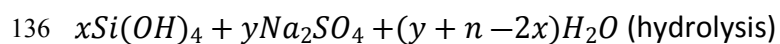
29
30 129 Figure 1: Multiangle probe diagram (Sam-Flex, Indatech)
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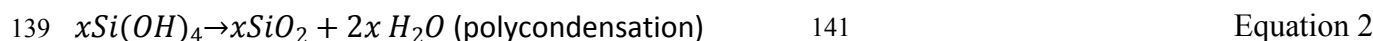
35 131 Experimental setup
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37 132 Silica was prepared by neutralization of a sodium silicate solution (water glass) with sulfuric acid according
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39 133 to Equation 1 and Equation 2.
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56 142 During the reaction Si–O–Si siloxane bonds have formed basic units of inorganic polymer. Spherical
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58 143 structures of approximately ten monomers, named nuclei, were formed and then grew to between 5 and 40
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3 144 nm to form so-called elementary particles. These particles have coalesced into aggregates that are resistant to
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5 145 grinding or dispersion in a matrix. Aggregate dimensions can range between 50 and 500 nm. At one specific
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7 146 moment in the reaction, the gel point, the entire volume has aggregated to form a continuous gel. Finally,
8
9 147 because of a shear stress created continuously in the reaction medium, new aggregates of size between 0.2
10
11 and 40 μm were formed ^{41, 42}.
12
13

14 149 The synthesis (or batch) was carried out on a laboratory pilot in a perfectly stirred 25 L reactor. An aqueous
15
16 150 solution of sodium sulfate was prepared and introduced in the reactor. Then, sulfuric acid and sodium silicate
17
18 151 (provided by Solvay) were added alternatively according to the protocol established by the manufacturer (it is
19
20 152 not possible to itemize). Their rate flows were regulated and automatized.
21
22

23 153 The probe was installed on a fast loop to monitor the precipitation reaction. The probe head was oriented so
24
25 154 that the flow circulates in the gap. The experimental setup is represented in Figure 2.
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31 156 (i.e. "[insert Figure 2.]")
32

33 157 Figure 2 : Experimental setup
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38 159 Spectral acquisition
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41 160 Spectra were acquired continuously with an integration time of 55 ms every 2 s. The spectra recording was
42
43 161 started at the first addition of reagents. It was stopped few minutes after the end of the reaction, when the
44
45 162 product was stable.
46

47
48 163 The I_0 reference was measured on air at angle 180° .
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50 164 In order to compensate for the source spectrum and the internal response of the sensors, the transmission was
51
52 165 calculated at each angle according to Equation 3:
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1
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4 167 $S_m = \frac{I_m}{I_0}$ Equation 3
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11 170 Where I_0 is the intensity measured on air at angle 180° and I_m is the intensity measured on the sample at
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13 171 angle m , with $m = 30^\circ, 90^\circ, 150^\circ, 170^\circ$ and 180° .
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19 173 Study 2: Micro emulsion monitoring

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22 174 Material

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24 175 A specially designed probe (Sam-Flex, from Indatech, Chauvin-Arnoux) was used for spectral
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26 176 measurements. It was composed of 5 positions at 5 different angles, 3 in transmission at 170° from the
27
28 177 incoming beam, 175° and 180° , and 2 in reflection at 5° and 10° . The air-gap of the probe was still 3 mm.

29
30 178 The probe was connected to the same spectrometer as before
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32

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35
36 180 Samples

37
38 181 The operating protocol applied to prepare the samples came from the work of Fukumito et al. ⁴³. In this
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40 182 publication, the different phases of the samples have been characterized, which makes it possible to know the
41
42 183 state of the system when reproducing the exact same protocol: aqueous phase W, or organic O, micro
43
44 184 emulsion water in oil W/O, or oil in water O/W, or oil and water M.

45
46 185 First, solutions of SDBS (Sigma Aldrich) at 140 g/L and NaCl (VWR chemicals) at 200 g/L were prepared
47
48 186 separately in flasks.

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51 187 Then three different samples were made in 30 ml glass bottles by successively adding:

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53 188 - 2 mL of the SDBS solution
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189 - water and NaCl solutions. The volume of water and solution were calculated so that, in all samples,
190 there was an aqueous phase volume of 13.58 ml covering a set of salinity of 4, 32 and 64 g of NaCl /
191 L of water.

192 - Also, 0.84 mL of isobutanol (Alfa Aesar) was added and carefully mixed.

193 - Finally, 13.58 mL of decane (Alfa Aesar) was added and carefully mixed.

194 Samples were mixed gently by turning the bottles upside down and left to be equilibrated for 1 month at
195 room temperature.

196 For all 3 samples, the aqueous phases are in the lower part of the bottle and the organic phases in the upper
197 part.

199 Experimental setup

200 A specific setup was developed to analyze the phase in line, in order to simulate the outflow of coreflood[‡]
201 pilots^{44, 45}. Spectra were acquired off-contact through a quartz tube. The tube, with its internal diameter of 1
202 mm and its external diameter of 3 mm, was put in the probe air-gap. Its upper end was crimped with a
203 Swagelok fitting to seal. A non-beveled syringe needle was positioned at its lower end. The Swagelok fitting
204 was connected to a 1/16th inch PTFE tubing. The other end of the tubing was connected to a 50 ml glass
205 syringe. The syringe was installed on a syringe pump to make the sample flow. The setup is shown in Figure
206 3.

[‡] A laboratory test in which a fluid or combination of fluids is injected into a sample of rock. Objectives include measurement of permeability, relative permeability, saturation change, formation damage caused by the fluid injection, or interactions between the fluid and the rock. A coreflood is typically used to determine the optimum development option for an oil reservoir and often helps evaluate the effect of injecting fluids specially designed to improve or enhance oil recovery.

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3 208 (i.e. "[insert Figure 3.]")
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6 209 Figure 3 : Photograph of the experimental setup
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9 210 Spectral acquisition
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11 211 The syringe pump flow rate was set to 1 ml/min and maintained constant until 28 ml of product was pumped.
12

13 212 Spectra were acquired continuously with an integration time of 1.65 ms every second.
14

15 213 The I_0 reference was measured on the empty quartz tube for each angle.
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17 214 In order to compensate for the light spectrum and the internal response of the sensors, the transmission was
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19 215 calculated at each angle according to
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22
23 216
24 217 Equation 4:

25
26 218 $S_a = \frac{I_a}{I_{0a}}$ 220 Equation 4
27
28

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32 221 Where I_a is the intensity measured on the sample through the tube at the angle a , and I_{0a} is the intensity
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34 222 measured on the empty tube at the angle a , with $a = 5^\circ, 10^\circ, 170^\circ, 175^\circ$ and 180° .
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39
40 224 Multivariate analysis
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43 225 Both sets of data were processed with MATLAB 2015b (The Mathworks, Natick, MA, USA).
44

45 226 Both times, the Savitzky-Golay function was performed to smooth spectra (2nd order, 13 points, no
46

47 227 derivative).
48

49
50 228 A CCSWA was applied on each data base. In both cases, the data bases were k blocks of n samples and p
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52 229 wavelengths, here $p=201$ and $k= 5$ which corresponded to the angle number.
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54
55 230 The objective of CCSWA is to describe simultaneously the k matrix \mathbf{X}_i observed for every n samples.
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231 For each block i , the matrix \mathbf{X}_i has been centered by columns and the inertia matrix has been calculated as

$$232 \mathbf{W}_i = \mathbf{X}_i \cdot \mathbf{X}_i'$$

233 The matrix \mathbf{W}_i reflects the dispersion of the samples in the data space, for the block i . Since the number of
 234 samples was the same for all blocks, all \mathbf{W}_i matrices had the same size ($n \times n$). The common dimensions of all
 235 matrix was calculated iteratively according to ^{35, 46}:

$$236 \mathbf{W}_i = \sum_{dim=1}^d \lambda_{dim}^{(i)} \cdot \mathbf{q}_{dim} \cdot \mathbf{q}'_{dim} + \mathbf{R}_i \quad 238 \text{ Equation 5}$$

237
 239 Where d is the number of dimensions which has to be fixed, $\lambda_{dim}^{(i)}$ is the specific weight (= 'saliency') of the
 240 matrix \mathbf{X}_i in the construction of the common component \mathbf{q}_{dim} in the dimension dim , and \mathbf{R}_i the residual matrix
 241 of \mathbf{X}_i . So, each common component \mathbf{q}_{dim} is weighted by a scalar $\lambda_{dim}^{(i)}$ reflecting the contribution of the matrix
 242 \mathbf{X}_i in the construction of \mathbf{q}_{dim} ^{47, 36}.

243 The method consists in determining a common space for all k blocks, with each matrix having a specific
 244 contribution ("saliency"), $\lambda_{dim}^{(i)}$, to the definition of each dimension, \mathbf{q}_{dim} , of this common space by
 245 maximizing the variance common to all blocks.

246 Global scores, individual scores and loadings, and saliences in the construction of common dimensions were
 247 obtained by CCSWA.

248

249 Results and discussions

250 Study 1: Silica precipitation monitoring

251 Spectral interpretation

252 Figure 4 shows spectra S_m acquired during the silica precipitation reaction. For all angles the same
 253 transmission profiles are observed. These are due to water absorption bands⁴⁸. The second overtone of the
 254 OH stretching band ($3\nu_{1,3}$) is at 970 nm, the combination of the first overtone of the OH stretching band and
 255 the OH bending band ($2\nu_{1,3} + \nu_2$) are at 1190 nm, and the first overtone of the OH stretching band ($2\nu_{1,3}$) is at
 256 1450 nm. The transmission profiles are stuck to the baseline when the signal is saturated in absorption. The
 257 optical path of 3 mm is too important to exploit the absorption band at 1450 nm.

258
 259 (i.e. "[insert Figure 4.]")

260 Figure 4 : Spectra I/I_0 at the five angles throughout the batch

261

262 CCSWA

263 Study of contributions

264 A CCSWA was applied on the batch. Table 1 presents the contributions of angles in the construction of
 265 common dimensions (= common components)

266

267 Table 1: Contribution of angles in the construction of common dimensions

	Dimension 1	Dimension 2	Dimension 3	Residuals
30°	83.2 %	10.8 %	6.0 %	0.1 %
90°	97.6 %	0.5 %	1.9 %	0.1 %
150°	99.3 %	0.6 %	0.1 %	0.05 %

170°	4.7 %	95.2 %	0.1 %	0.02 %
180°	90.2 %	9.2 %	0.6 %	0.1 %
Variance	69.6 %	30 %	0.4 %	

268

269 The explained variance and the residuals of the sum of the contributions of angles to each dimension show
 270 that three dimensions are sufficient to explain almost the entire variance of the dataset. Calculations for 2 and
 271 4 dimensions were carried out but was not considered as relevant.

272

273 The first two dimensions carry the major part of variance. All angles but 170° participate in the construction
 274 of the first dimension. Symmetrically, the second dimension mainly relies on the 170° angle. Dimension 3 is
 275 built mainly by the angle at 30° and to a lesser extent at 90°.

276

277 Study of common scores across all dimensions

278 CCSWA also provided overall scores, they are plotted against time for the three dimensions in Figure 5.

279

280 (i.e. "[insert Figure 5.]")

281 Figure 5 : Common scores for three common dimensions according to time. The dotted lines correspond to
 282 the modifications of the process, the star and the numbered strips correspond to product evolutions

283 Overall, two main types of events are observed at each dimension on Figure 5.

1
2
3 284 On the one hand, sharp slope changes are observed in all three dimensions. They are highlighted on the
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5 285 figure by dashed lines. Thanks to the readings of the automaton from the pilot, it was possible to link these
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8 286 slope changes to process actions: such as, adding or stopping sodium silicate or sulfuric acid.
9
10 287 On the other hand, general slopes with minima and / or maxima are observed on the dimensions. These
11
12 288 slopes modifications are not linked to instants of the reaction but to changes in the product. These are shown
13
14 289 in Figure 5 by the green star and the numbered frieze in the lower part. The number represent the main steps
15
16 290 of product evolution (although they are not fixed and probably are entangled as product is gradually
17
18 291 evolving from one stage to the next). They are determined based on the knowledge acquired by the
19
20 292 manufacturer and to the literature ⁴⁹⁻⁵³. Step 1 corresponds to elementary particles aggregation. At one
21
22 293 specific moment in the reaction, represented by the green star in Figure 5, the entire volume aggregates to
23
24 294 form a continuous gel. It is called the gel point. At this point, the physical structure of the medium instantly
25
26 295 changes. The moment the gel point occurs was validated by a turbidity monitoring retrospectively. During
27
28 296 step 2, because of the shear stress created continuously in the reaction medium, aggregates are formed. Then
29
30 297 during step 3, agglomerates rearrange and become denser, their internal structure is consolidated. During step
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32 298 4, only one of the 2 reagents is added which dilutes the medium. Finally, the medium remains constant in the
33
34 299 last section.
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301 Study of common scores

302 For all dimensions the scores profile is constant until the gel point, around 800 AU, with more or less noise.
303 This profile is linked to the fact that at the beginning of the reaction the medium is almost limpid and
304 contains few particles (this had been observed in a previous laboratory study ⁴⁰). Particles, if present had a
305 diameter smaller than tens of nanometers. For the studied wavelengths, the scattering that can be generated
306 by these particles is very small, and is not detected.

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5 308 The scores profile of the second dimension show a maximum. A very strong increase is observed
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8 309 simultaneously to the gel point up to about 1200 AU. In the rest of the batch, the scores decrease until they
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10 310 stabilize at the end of the reaction. Table 1 which gives the contribution of angles in the construction of
11
12 311 dimensions showed the specialization of the angle at 170° for the construction of the second dimension. It
13
14 312 turns out that this angle is sensitive to serpentine photons. These photons are the ones that have slightly
15
16 313 scattered while maintaining their rectilinear trajectory. It is likely that this dimension is sensitive to the
17
18 314 simple scattering in the medium. This would be in line with the scores profile at the gel point and during
19
20 315 shearing. Indeed, during the gel formation, the scores increase because the gelation makes the whole sapphire
21
22 316 window and reaction medium's refractive index more homogeneous, creating an optical continuity of the
23
24 317 medium. The gel conducts the light forward. Then, when shearing the gel, more and more particles are
25
26 318 generated. There are therefore fewer serpentine photons and therefore less simple scattering, hence the
27
28 319 decrease in scores.
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33 320 This sensitivity to the simple scattering has been observed on the loadings too. In the Figure 6 the loadings
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35 321 obtained at 170° in the second component and the average spectrum of the batch are represented.
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41 323 (i.e. "[insert Figure 6.]")
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44 324 Figure 6: Average spectrum of the batch and loadings obtained for the angle 170° in the second dimension
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49 326 Two scattering consequences can be observed. From 1350 to 1600 nm, an absorption band is observed. It
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51 327 correspond to water absorption band. This band is related to the optical path of the photon. In a previous
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53 328 study ⁴⁰, the absorption was considered as constant during the reaction. Therefore, a variation of the height of
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3 329 the band is related to the increase of the optical path and thus to the scattering of the photons ⁵⁴. A higher
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5 330 absorption makes the spectrum lower in this region. Consequently, the higher the diffusion, the longer the
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7 331 optical path and the lower the spectrum. When multiplied by the positive peak of the loading, it produces a
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10 332 lower score. Then, a slope is observed on loadings from 950 to 1350 nm. This part of the loading calculates
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12 333 the general slope of the spectrum between 950 and 1350 nm. It appears as a rotation of the average spectrum.
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14 334 This slope is connected to the scattering too ^{55, 56}. The higher the diffusion, the steeper the slope. Thus high
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16 335 diffusion leads to low scores. Consequently, the loadings are sensitive to the diffusion of light. High scores
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18 336 correspond to low diffusion, such as after the gel point, when the gel acts as a light guide.
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20 337 Finally, thanks to the scores of the second dimension represented in Figure 5, it is possible to detect the gel
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22 338 point very precisely and accurately. This aspect is very important as this gel point is critical for determining
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24 339 the products future qualities. It shows that the second dimension is very informative and necessary to ensure
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26 340 the monitoring of the reaction. The CCSWA therefore demonstrated the specific interest of the 170° angle to
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28 341 monitor this manufacturing process.
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35 343 The score profile of the first dimension increases throughout the reaction. With regard to Table 1, all angles
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37 344 except the one at 170° participate in its construction. These angles do not detect the same type of photons.
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39 345 Ballistic photons are detected at 180°, backscattered photons at 30° and 90° and forward scattered photons at
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41 346 150°. This first dimension seems to represent the general scattering of the reaction medium, that is to say the
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43 347 global propagation of photons without distinction between ballistic and scattered photons. Therefore we
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45 348 assume that the multiple scattering in the reaction medium is represented in the first dimension
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51 350 The scores of the third dimension show a minimum and a maximum. The decrease to reach the minimum
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53 351 takes place in the same period as the growth to reach the maximum of the second dimension, just after the gel
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3 352 point. At the opposite, during shearing, the scores of the third dimension increase to reach a maximum when
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5 353 those of the second dimension decrease. Lastly, the scores decrease until they stabilize at the end of the
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7 354 reaction. The third dimension probably represents the backscattered photons since the angles at 30° and 90°
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9 355 contribute mainly to its construction (see Table 1). At the gel point, it has been said previously that the
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11 356 optical continuity of the sapphire window with the reaction medium conducts to better light transmission.
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13 357 More photons propagate forward, fewer backscatter. The decrease in the amount of backscattered photons
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15 358 results in a decrease in the profile of the scores in the third dimension. CCSWA tends to consider the optical
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17 359 system as a distribution of a total amount of photons. That is why, compared to the totality of photons at the
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19 360 five angles, the number of photons detected at angles 30 ° and 90 ° decreases. Then during shearing, the
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21 361 number of particles increases while their size decreases. This induces the increase of scores in the third
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23 362 dimension and the decrease of scores in the second dimension. When the medium is sheared further, there is
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25 363 a decrease in serpentine photons and an increase in backscattered multi-scattered photons. Shear causes
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27 364 increased scattering of particles and the decrease in their size influences the direction of scattering. This is in
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29 365 agreement with the theory¹³ demonstrating that the smaller the particle size, the less photons will tend to
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31 366 scatter forward. The final decrease in the third dimension scores takes place in the last stage of the
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33 367 precipitation reaction. Parallel to the formation of new particles in the medium, aggregates fill the already
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35 368 existing agglomerates. They rearrange themselves, their internal structure is modified and more compact.
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37 369 This modifies, both the specific surface area and thus the micro porosity and the number of hydrogen bonds¹.
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39 370 These phenomena reduce the amount of light backscattered, hence the decrease in scores in the third
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41 371 dimension. Even if at the same time, the multiple scattering continues to increase as shown by the scores of
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43 372 the first dimension.
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45 373 The third dimension seems to be clearly related to the direction of the scattering of photons in the medium
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47 374 during the reaction.
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376 Study 2: Micro emulsion monitoring

377 Samples

378 Solutions which were obtained are represented in the Figure 7.

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380 (i.e. "[insert Figure 7.]")

381 Figure 7 : Photograph of the 3 samples for the micro emulsion application

382 The sample's number corresponds to the salinity of the aqueous phase (always the lower phase in the vials).

383 The different phases present in these 3 samples can be grouped into five classes, as described in Table 2.

384

385 Table 2: Phase classification

Salinity of the aqueous phase	64	32	4
Organic phases (upper)	1	2	2
Aqueous phases (lower)	4	4	3
Middle phases	NC	5	NC

386

387 Class 1 contains the organic phase where there is a micro emulsion of water in oil (W/O), as in sample 64,
388 which can be described as a Winsor II in the literature ⁴³.

389 Class 2 are the organic phases consisting only of decane (O), as in samples 32 and 4.

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3 390 Class 3 is the aqueous phase where there is a micro emulsion of oil in water (O/W), as in sample 4, which
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5 391 can be described as a Winsor I.

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8 392 Class 4 are the aqueous phases consisting only of salt water with different concentrations of salt, as in
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10 393 samples 64 and 32.

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12 394 Class 5 is the middle phase (M) where there is a micro emulsion of water and oil which are only present in
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14 395 Winsor III samples.

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19 397 The visual inspection of the phases (Figure 7) shows that Class 2 phases are transparent and colorless. The
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21 398 Class 1 and 3 phases seem slightly cloudy. For Class 4, sample 64 phase is transparent and colorless, but
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23 399 sample 32 is whitish in its upper part and tends to be transparent in the lower part. Finally, the Class 5 phase
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25 400 is whitish and cloudy throughout.

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28 401 The cloudiness is probably due to the presence of micro emulsions. The medium appears whiter the more oil
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30 402 is dispersed in the water. Therefore, micro emulsions probably generate scattering. The aqueous phase of
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32 403 sample 32, should belong to a Class 4 and therefore not contain oil. This sample's whitish gradient is
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34 404 probably due to a transition between the O/W micro emulsion and the pure aqueous phase.

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40 406 Spectral interpretation

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42 407 For a spectral interpretation of classes, only the mean absorption spectrum of each class for the 180° angle is
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44 408 represented in Figure 8.

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49 410 (i.e. "[insert Figure 8.]")

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51
52 411 Figure 8 : Mean absorption spectra of classes

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3 412 Two groups can be observed, separated by an important absorption difference at 1450 nm and their baseline.
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5 413 A first group contains Classes 1 and 2 and a second group the Classes 3, 4 and 5.
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8 414 The first group contains organic phases. The absorption bands of decane are found at 1208 nm and 1408 nm.
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10 415 The second overtone of symmetrical and asymmetric elongations of CH₂ and CH₃ groups is observed at 1208
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12 416 nm, while the absorption band at 1408 nm corresponds to the first overtone of the combination between the
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14 417 symmetric and asymmetric elongations of the CH bonds in the CH₂ and CH₃ groups and the deformations of
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16 418 the C-H bonds. Between the mean spectrum of Class 1 and the mean spectrum of Class 2, an absorption
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18 419 difference is observed at the band at 1408 nm. This is the absorption of water present in the Class 1.
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20 420 By observing the absorption bands of the mean spectra of the second group, the water absorption bands at
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22 421 970 nm, 1190 nm and 1450 nm are found. Their identification was made for the previous application. Within
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24 422 this group, the mean spectrum of Class 5 differs from the other two classes. At 1208 nm an absorption band
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26 423 is observed, which is assigned as the absorption band of decane. The absorption at 1408 nm is not
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28 424 observable, as it is hidden under the large water band at 1450 nm. In this wavelength range, the absorption of
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30 425 water is much stronger than the absorption of decane. Between the mean spectra of Class 3 and 4, a slight
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32 426 difference is observed on the 1450 nm band. The band seems slightly shifted to the left for the Class 4
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34 427 spectrum. This may be due to the presence of salt in the Class 4 phases which could create a slight band
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36 428 shift^{14, 48}. In addition, the baseline of the mean spectrum of Class 4 is higher than that of the mean spectrum
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38 429 of Class 3. The presence of a baseline is one of the consequences of photon scattering⁴⁰. This is in line with
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40 430 the visual observation of the samples in Figure 7, where a whitish appearance of Class 4 was observed,
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42 431 probably related to scattering effects.
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3 433 The observation of mean spectra shows that it is possible to identify almost all classes by NIR spectroscopy.
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6 434 For each class, differences are observable at water and decane absorption bands. The goal for the next part of
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8 435 this study is to determine if there is a gain to associate multi-angle analysis with CCSWA.
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437 CCSWA

438 Study of contributions

439 A CCSWA was applied on all five classes of all 5 angles spectra.

440 Table 3 presents the contribution of angles in the construction of common dimensions.

441

442 Table 3: Contribution of angles in the construction of common dimensions

	Dimension 1	Dimension 2	Dimension 3	Residuals
5°	68.2 %	26.4 %	5.4 %	0 %
10°	69.0 %	25.5 %	5.5 %	0 %
170°	91.3 %	8.2 %	0.5 %	0 %
175°	85.7 %	10.9 %	3.4 %	0 %
180°	86.5 %	12.4 %	1.1 %	0 %
Variance	87.1 %	12.4 %	0.5 %	

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3 444 The explained variance shows that three dimensions are sufficient to explain almost the entire variance of the
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5 445 dataset. (With regard to residuals, we see that the contributions of each angle are distributed in the three
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7 446 dimensions.)
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10 447 All angles participate in the construction of the first dimension and predominantly those in transmission.
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12 448 Contrary to the second dimension where the contributions of reflection angles are predominant. The third
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14 449 dimension, is also built mainly by angles 5° and 10° with a contribution of the angle at 175° to a lesser
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16 450 extent. The third dimension represents very little variance in comparison with the first two.
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21 452 Study of common scores across all dimensions

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23 453 CCSWA provided common scores. The scores obtained for each class were put end to end, to be able to
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25 454 compare them. The 2 phases of Classes 2 and 4 being identical, only the scores of the binary samples were
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27 455 represented. They are plotted according to the class for the three dimensions in Figure 9.
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33 457 (i.e. "[insert Figure 9.]")
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36 458 Figure 9 : Common scores for three common dimensions according to the class
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39 459 Overall, common scores for the three dimensions show that each class has a different profile. It is already
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41 460 possible to say that the CCSWA makes it possible to separate the different classes.
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45 462 The common scores of the first dimension (shown in blue) separate three groups of classes. Classes 1 and 2,
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47 463 then Classes 3 and 4 and finally Class 5. Classes 1 and 2 have negative scores, while Classes 3 and 4 have
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49 464 positive scores. Those in Class 5 are positive but almost null. This dimension seems related to the presence
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51 465 of water in the samples. Indeed Classes 1 and 2, having negative scores, are organic phases and contain little
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53 466 or no water, while Classes 3 and 4, which have positive scores, are aqueous phases. Finally, Class 5 contains
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3 467 water and oil in almost equal proportions. This observation of the scores relate to the observations made in
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5 468 Figure 8 representing the mean spectra of Classes at 180 °. Moreover, this is in line with the individual
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7 469 loadings of the transmission angles, shown in Figure 10, which strongly resemble the absorption spectrum of
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9 470 water.

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14 472 (i.e. "[insert Figure 10.]")

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17 473 Figure 10: Individual loadings of transmission angles to the first dimension

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22 475 The common scores of the second dimension allow to separate the classes within the groups identified in the
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24 476 first dimension. Thanks to the second dimension, Class 1 differs from Class 2, and Class 3 differs from Class
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26 477 4. Class 5 remains separate in this dimension as well. Class 5 scores are the most important, followed by
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28 478 Class 4, Class 3 and Class 1, and Class 2 scores, which are the lowest. This order is very close to the order of
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30 479 the baseline of the mean absorption spectra of the phases shown in Figure 8. The second dimension probably
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32 480 is a general indication of the scattering in general of photons ²⁴.

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39 482 The common scores of the third dimension bring together two groups of classes that had never been grouped
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41 483 before. A first group consists of Classes 2, 3 and 5, and a second group consists of Classes 1 and 4.

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43 484 In the first group, the commonality between classes is the presence of decane. For Classes 3 and 5, decane is
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45 485 dispersed in water. In Class 2, only decane is present.

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47 486 In the second group, the commonality between classes is the presence of water. In Class 1, water is dispersed
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49 487 in decane and in Class 4, only water is present.

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52 488 The third dimension is mainly constructed by the angles at 5 ° and 10 ° according to the Table 3.

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3 489 To try to interpret the profile of the scores, the individual loadings of the angles 5° and 10° were represented
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5 490 in the Figure 11.

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8 491 (i.e. "[insert Figure 11.]")
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10 492 Figure 11: Individual loadings of angles at 5° and 10° of the third dimension
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13 493 Although these loadings are very noisy, information can still be exploited. Around 1660 nm, the beginning of
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15 494 a hollow is observed. This hollow is the beginning of the absorption band of the first harmonic symmetrical
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17 and asymmetrical elongations of the CH₂ and CH₃ groups of decane. This decane absorption band is much
18 495 larger than those at 1208 nm and 1408 nm and is even greater than the water absorption. It is probably the
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20 496 presence of this band, which makes it possible to differentiate the groups in the profile of the common scores
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22 497 in the third dimension. It may be that the third dimension is related to the presence of decane as a scattering
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24 498 product.
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34 501 Conclusions and perspectives
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37 502 This study, implemented on two industrial applications, shows the interest of multi-angle spectral
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39 503 measurements and their coupling to a Common Component and Specific Weight Analysis for monitoring
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41 504 processes.
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46 506 In the case of monitoring the precipitation of silica, where only light diffusion effect varies, CCWAS
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48 507 associated with multi-angle NIR measurements has demonstrated the complementarity of the angles and its
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50 508 interest for process monitoring. Thanks to the scores obtained by the CCSWA, the actions inherent to the
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52 509 progress of the process could be identified by the different slopes breaks in the dimensions scores plot. Each
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54 510 physicochemical modification of the reaction medium induced scattering phenomena⁵⁷ which resulted in
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3 511 curvatures, maxima and minima depending on the dimensions observed. It has been possible to identify a
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5 512 multiple scattering regime, a simple scattering regime, and the preferred direction of light propagation in the
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8 513 medium during the advancement of the precipitation reaction. CCSWA also confirmed the complementarity
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10 514 of the angles for monitoring this reaction and the interest of multi-angle measurements. This first study
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12 515 shows the interest of using this type of multivariate analysis on multi-angle spectral data.
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15 516 Regarding the preliminary study about micro emulsion measurements, where both absorption and
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17 517 scattering vary, CCSWA has allowed unequivocal identification of the different phases. At each dimension,
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19 518 different phenomena have been observed. This is a gain for users because through this identification, it will
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21 519 be possible to know in real time the type of medium obtained (aqueous phase W, or organic O, micro
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23 520 emulsion water in oil W/O, or oil in water O/W, or oil and water M) without sampling and with only one
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25 521 analytical technique. This monitoring is a real asset in the optimization of operational parameters on R & D
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28 522 pilots.
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33 524 Overall, the tests implemented have shown that it is very interesting to couple multi-angle measurements
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35 525 with common component and specific weight analysis. Initially, this CCSWA tool was developed to analyze
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37 526 data from sensory analyzes of different dimensions⁴⁷. But, the results obtained allowed reversion to the
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39 527 physicochemical information of the mediums, starting from multi-angle spectral measurements having the
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41 528 same dimension. Nevertheless, it would be interesting to explore the results of other existing tools for multi-
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43 529 array multivariate analysis, and even to develop a specific tool for the analysis of multi-angle spectral data.
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46 530 This study also shows the gain of monitoring in line processes, even when complex medium are involved.
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52 532 Conflict of interest
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3 533 The authors declare that they have no conflict of interest
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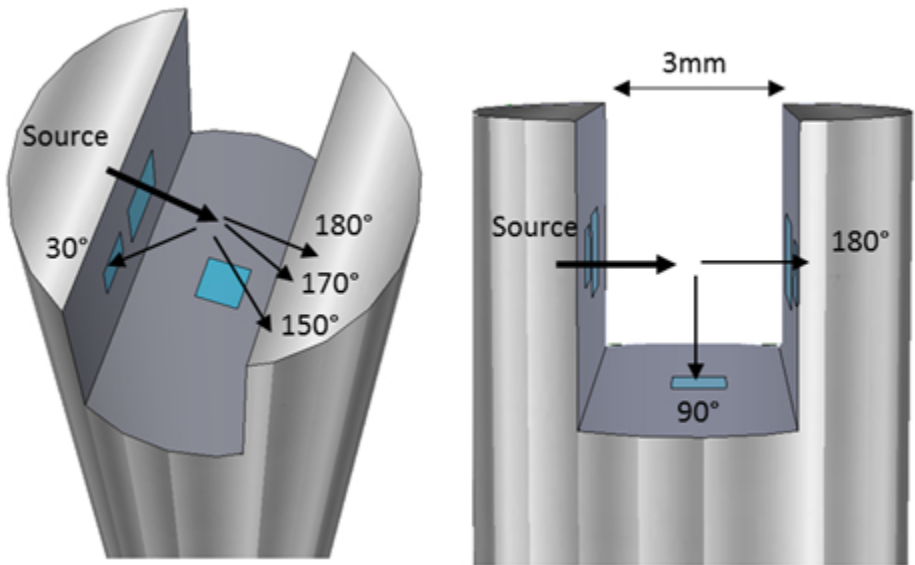
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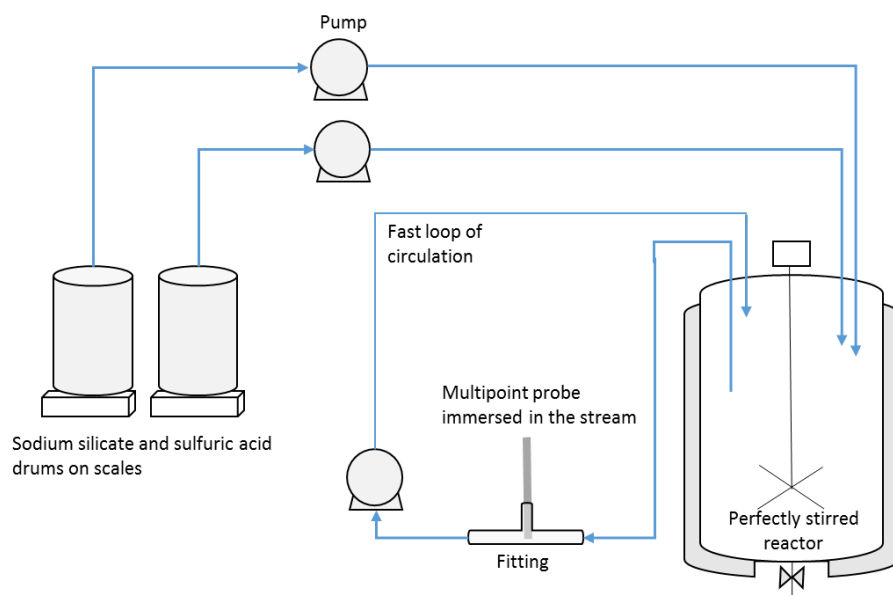
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Multi-angle probe diagram (Sam-Flex, Indatech)

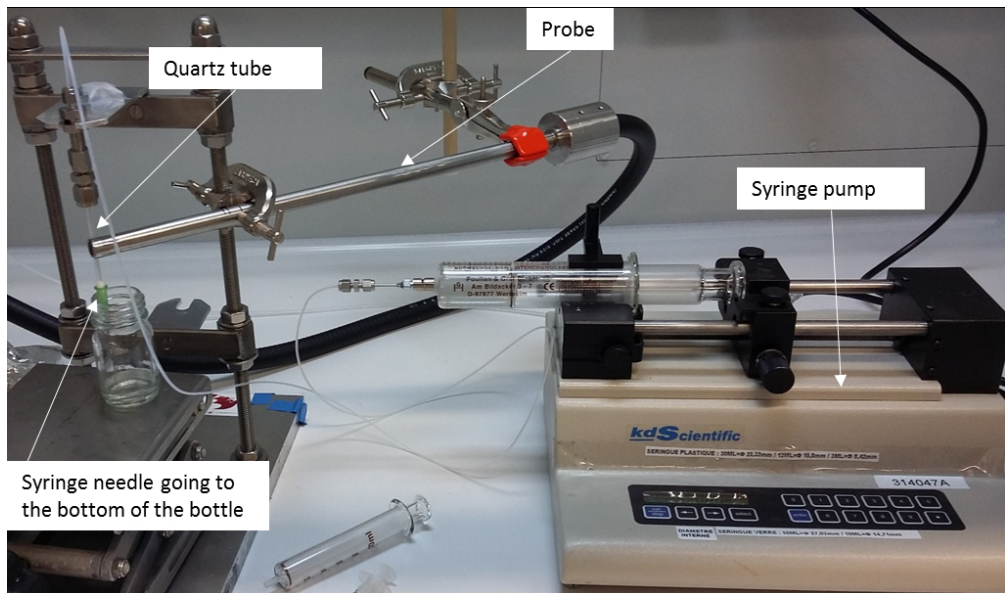
81x51mm (150 x 150 DPI)



Experimental set up

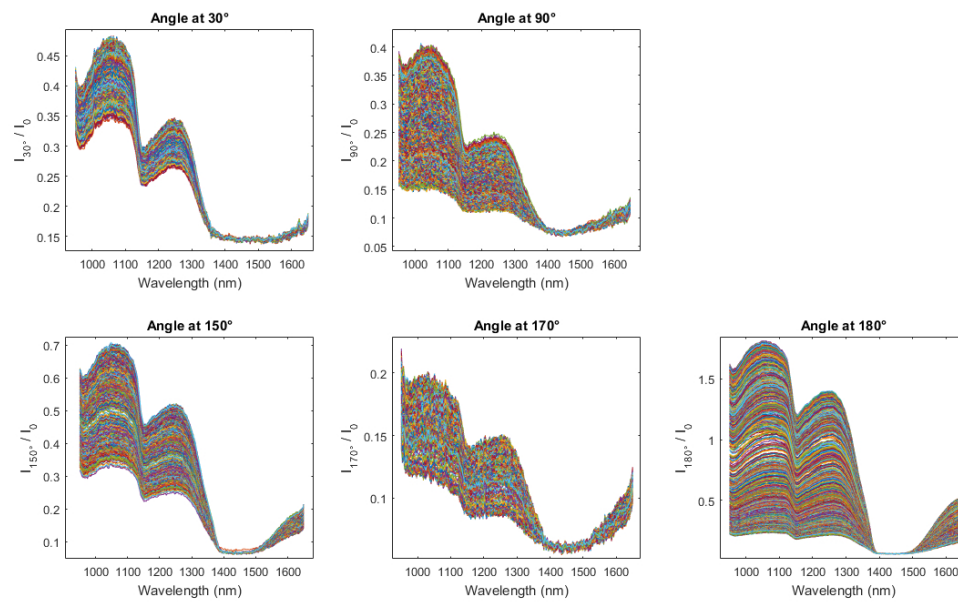
192x122mm (150 x 150 DPI)

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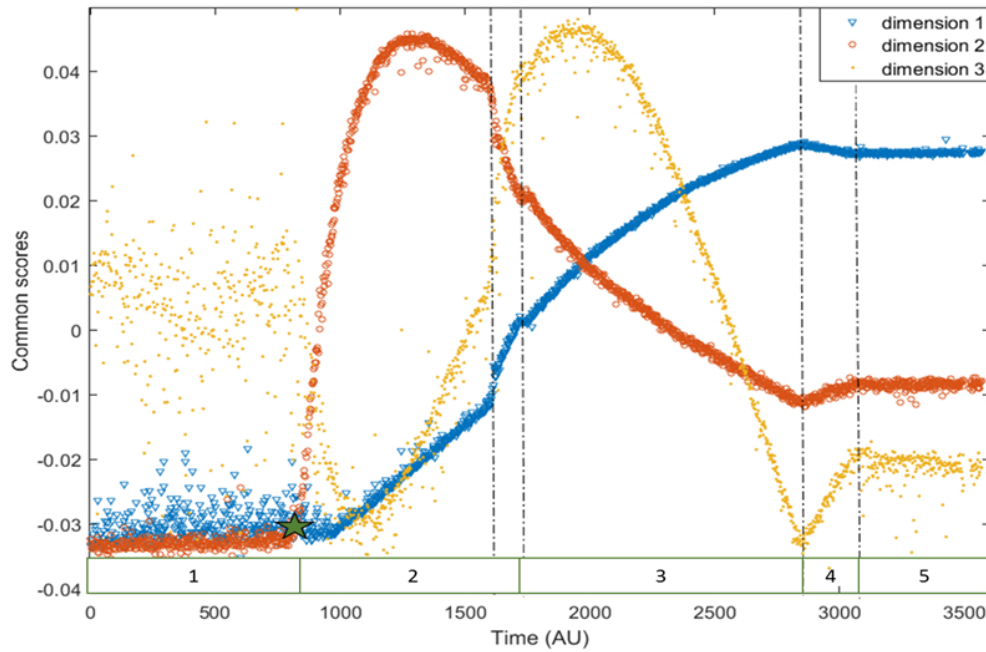
Photograph of the experimental set up

173x101mm (150 x 150 DPI)



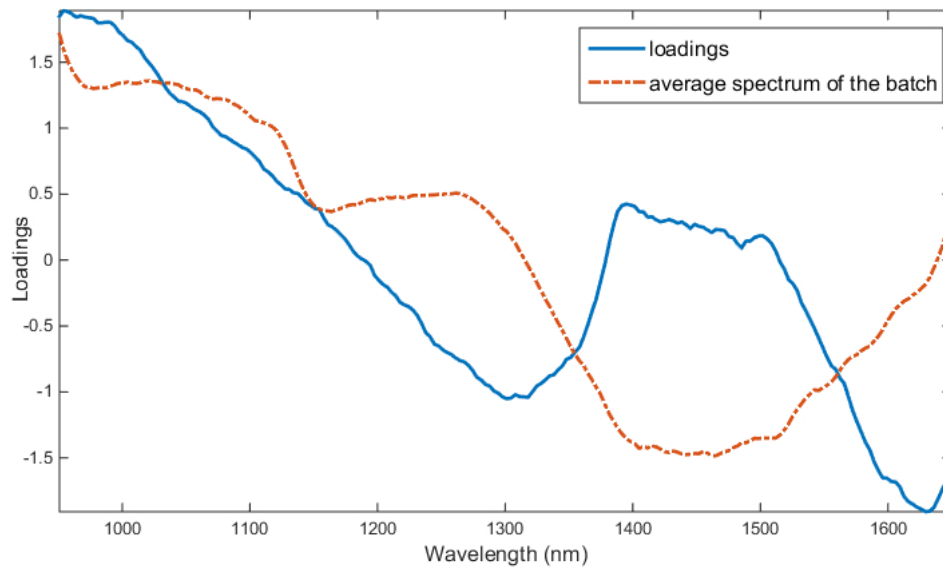
Spectra I/I_0 at the five angles throughout the batch

290x182mm (96 x 96 DPI)



Common scores for three common dimensions according to time. The dotted lines correspond to the modifications of the process, the star and the numbered strips correspond to product evolutions

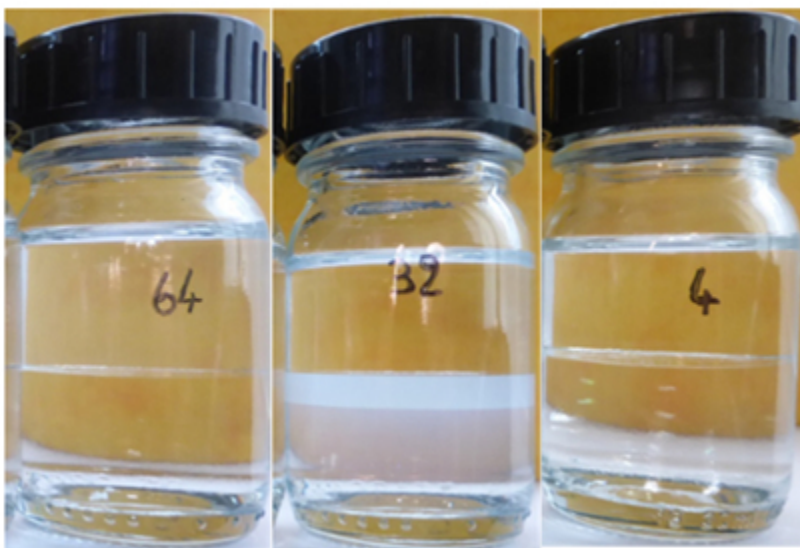
135x89mm (150 x 150 DPI)



Average spectrum of the batch and loadings obtained for the angle 170° in the second dimension

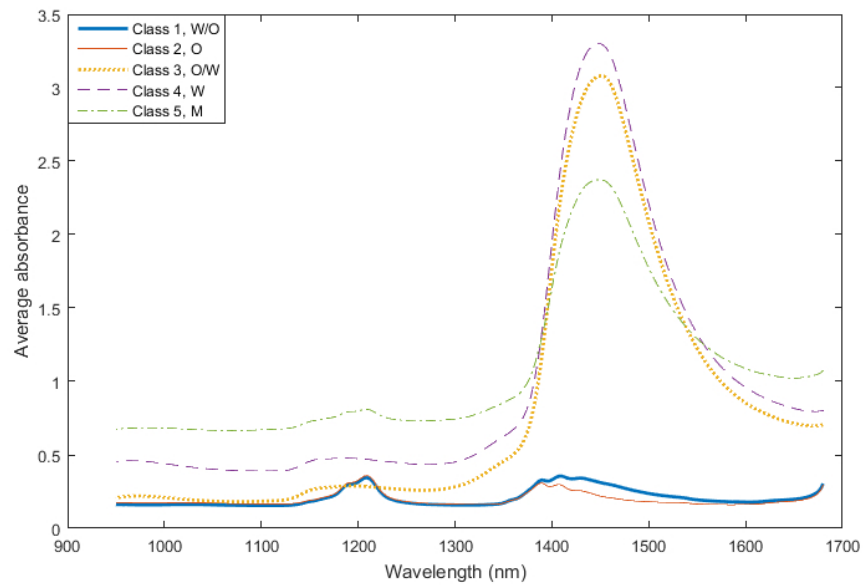
197x143mm (96 x 96 DPI)

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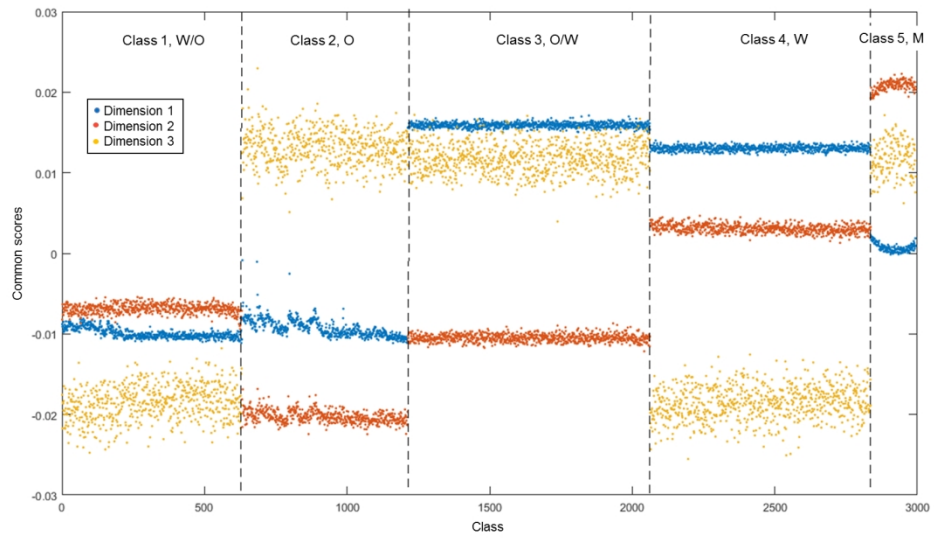
Photograph of the 3 samples for the micro-emulsion application

74x50mm (150 x 150 DPI)



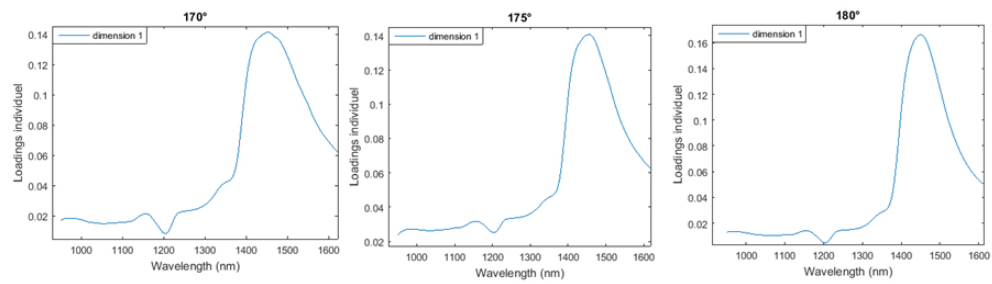
Mean absorption spectra of classes

212x134mm (96 x 96 DPI)



Common scores for three common dimensions according to the classes

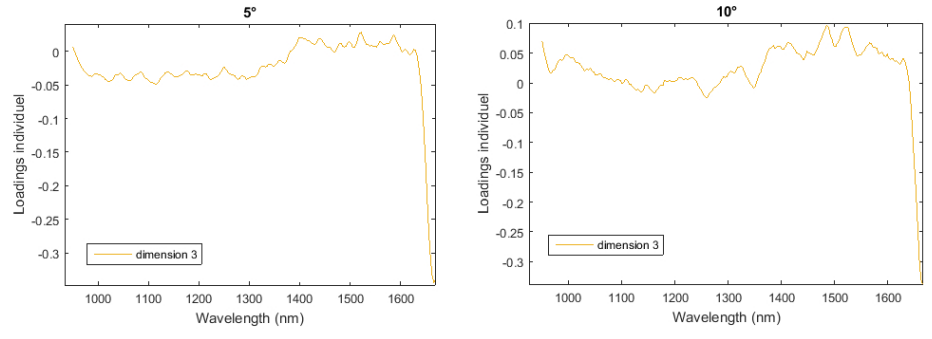
306x177mm (150 x 150 DPI)



Individual loadings of transmission angles to the first dimension

240x70mm (96 x 96 DPI)

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Individual loadings of angles at 5° and 10° of the third dimension
278x130mm (96 x 96 DPI)