

1                   **AN IMPROVED SCALABLE METHOD OF ISOLATING**  
2   **ASPHALTENES.**

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14   **KEYWORDS:** asphaltenes, bitumen, soxhlet, precipitation, sorbents, extraction

15 **ABSTRACT**

16 A new, improved and scalable procedure of asphaltene fraction isolation is presented and  
17 compared to standard test methods. The new procedure uses 1:40 feedstock to solvent (n-  
18 heptane) ratio (g/mL), filtration through a cellulosic thimble and extensive washing in a  
19 Soxhlet type extractor. The group type composition and purity of the asphaltene fractions  
20 have been examined using thin-layer chromatography with flame-ionization detection. This  
21 study revealed that the new procedure provides a higher purity of asphaltene fraction  
22 resulting in a more accurate determination of its content in bitumens when comparing to the  
23 standard test method. Moreover, an attempt of evaluation of the scale-up possibility of the  
24 proposed and standard test methods was made, revealing that new procedure is more  
25 scalable than standard test methods. It is possible to obtain large quantities of a high purity  
26 asphaltene fraction even on a process scale. This feature is crucial for technical analytics, for  
27 researchers studying asphaltenes characteristic as well as for other novel applications of  
28 asphaltenes such as its use as sorbents in separation techniques.

29

## 30 1. Introduction

31 Asphaltenes are the most aromatic group of chemical compounds present in the  
32 crude oil and the heaviest products of its processing; they quantitatively remain in a residue  
33 from vacuum distillation. Due to their complex composition, asphaltenes are a class of  
34 compounds defined on the basis of solubility (Linton, 1894; Marcusson, 1911; Parr et al.,  
35 1909) rather than molecular structure. They are insoluble in n-alkanes e.g. n-heptane, and  
36 soluble in toluene or benzene (Ferris et al., 1967; Hubbard and Stanfield, 1948;  
37 Kleinschmidt, 1955; Mitchell and Speight, 1973; O'Donnell et al., 1951; Strieter, 1941). In  
38 terms of molecular structure, asphaltenes are polycyclic aromatic compounds (PACs)  
39 comprised of 4-10 fused aromatic rings, peripherally attached alkyl chains and polar  
40 functional groups e.g. carboxylic acids, phenol, and pyridines (Groenzin and Mullins, 2000;  
41 Mullins, 2011, 2010). They consist mostly of hydrogen and carbon, with H:C ratio of about 1-  
42 1.2, and additionally heteroatoms such as oxygen, sulfur, nitrogen and trace amounts of  
43 vanadium and nickel can be found in their backbone (Leyva et al., 2013; Trejo et al., 2004).  
44 Typical asphaltene molecules have an average molecular weight of 750 g/mole (Badre et al.,  
45 2006; Groenzin and Mullins, 2000; Pomerantz et al., 2015) and are arranged into planar type  
46 structures with a tendency to form nanoaggregates (about six asphaltene molecules) and  
47 clusters (about eight nanoaggregates) (Mullins, 2010; Pomerantz et al., 2015; Schuler et al.,  
48 2015).

49 Asphaltenes exhibit wide range of interactions e.g. van der Waals, Coulombic,  
50 hydrogen bonding, and  $\pi$ - $\pi$  stacking (Murgich, 2002). Because of their physicochemical  
51 similarity to resins, asphaltenes exhibit strong sorption interactions with them. In solution,  
52 asphaltene-resin interactions can be favoured over asphaltene-asphaltene interactions  
53 (Speight, 2004). Resins can adsorb in the form of multilayers on the surface of the  
54 asphaltenes and penetrate their microporous structure (León et al., 2002; Liao et al., 2005).  
55 This is beneficial when considering stability of refinery process streams, as resins stabilize

56 asphaltenes in colloidal form (Aguilar and Mansur, 2015; Andersen and Speight, 2001; Koots  
57 and Speight, 1975), but can be a drawback if the purpose is to isolate pure asphaltenes.

58         Asphaltenes are of crucial importance in the petroleum industry, mainly due to the  
59 several technological issues created by them in crude oil processing *i.e.* formation of  
60 emulsions, fouling, well-bore and pipelines clogging, coke formation, and catalyst  
61 deactivation in conversion processes (Akbarzadeh et al., 2007; Almehaideb, 2004; Idris and  
62 Okoro, 2013; Kokal and Sayegh, 1995; Ramirez-Jaramillo et al., 2006). Currently,  
63 asphaltenes are utilized only in the production of bitumens, bitumen mixtures and mineral  
64 rubber (Rostler and Sternberg, 1949). Their content in bitumen is increased by oxidation (air  
65 blowing process) (Moschopedis and Speight, 1975) for upgrading of primary properties of  
66 vacuum residue, measured by penetration, softening point and breaking point parameters.  
67 They describe the stiffness and behavior of bitumen in high and low temperatures of its  
68 usage.

69         Recently, Boczkaj et. al. (2016) showed that asphaltenes present the possibility of  
70 being applied as a sorbent in separation techniques. Their unique selectivity, high thermal  
71 stability and low production cost makes it an interesting material for stationary phases for gas  
72 chromatography, as well as for preparative and process separations (Boczkaj et al., 2016,  
73 2015). However, current methods of isolation are not sufficient for providing large scale  
74 quantities of this material. Therefore a new method is required.

75         Traditionally, asphaltenes are isolated by means of precipitation with saturated  
76 hydrocarbons, such as *n*-pentane and *n*-heptane (ASTM D2007, 2003; ASTM D3279, 2001;  
77 ASTM D4124, 2001; ASTM D6560, 2000). Precipitation conditions *i.e.* type of solvent type,  
78 solvent to feedstock ratio, standing time and temperature have a significant impact on the  
79 yield of obtained asphaltenes and co-precipitated resins (Andersen and Birdi, 1990; H.  
80 Alboudwarej et al., 2002; Mitchell and Speight, 1973; Speight et al., 1984). Thus, asphaltene  
81 fractions isolated under different conditions are not identical and consequently have different  
82 properties. Although some groups indicate that the mechanism of precipitation is  
83 independent of the isolation method, but rather that the quantity of isolated asphaltenes is of



84 the same magnitude, their characteristic should also be the same (Andersen and Birdi,  
85 1990).

86 The type of solvent and its amount have the most evident effect on the precipitate.  
87 The yield of asphaltenes increases with increasing number of carbons in an n-alkane and  
88 reaches a plateau using n-heptane. The usage of n-heptane as a solvent is favoured when  
89 asphaltenes are the subject of research, because their properties are virtually stable for n-  
90 alkanes above n-hexane (Andersen and Birdi, 1990; H. Alboudwarej et al., 2002; Mitchell  
91 and Speight, 1973; Speight et al., 1984). Studies revealed that to provide efficient separation  
92 of asphaltenes, at least 30mL of solvent to each gram of feedstock is necessary (H.  
93 Alboudwarej et al., 2002; Speight et al., 1984). Although settling time can have a significant  
94 impact on the obtained asphaltene fraction purity, it varies considerably in standard test  
95 methods; from 30 minutes (ASTM D2007, 2003) up to 16 hours (ASTM D4124, 2001).  
96 Studies revealed that to ensure stable yields of asphaltenes, standing time of about 8-10h is  
97 needed. Extending this time above 16h may lead to the adsorption of resins from the liquid  
98 on the asphaltenes surface (Speight et al., 1984).

99 A number of studies investigated the effect of temperature on asphaltenes  
100 precipitation. However in this case, conflicting information emerges, with some report a  
101 decrease in asphaltenes yield with increasing temperature (Ali and Al-Ghannam, 1981;  
102 Mitchell and Speight, 1973) and the possibility of enhanced co-precipitation of resins  
103 (Speight et al., 1984), while others indicate increased yield in higher temperatures  
104 (Andersen, 1994; Andersen and Birdi, 1990; Hu and Guo, 2001). Andersen and Birdi (1990)  
105 observed an increased yield of precipitate followed by decrease after reaching maximum at  
106 25 °C. He ascribed it to enhanced adsorption of smaller molecules and further rupture of  
107 those interactions (desorption of molecules) as the temperature increases further. However,  
108 the most recent studies seem to confirm a decrease in yield of asphaltenes with increasing  
109 temperature (Andersen, 1995, 1994, Andersen et al., 1998, 1997; Andersen and Stenby,  
110 1996; Hu and Guo, 2001; Maqbool et al., 2011) and a lower content of resins when  
111 precipitation is carried out at higher temperatures (Pineda et al., 2007). UV fluorescence



112 studies revealed that when temperature decreases more compounds with smaller fused rings  
113 precipitate. Conversely, when the precipitation temperature increases, the isolated fraction is  
114 dominated by larger aromatic structures (Andersen and Birdi, 1990). This result is supported  
115 by molecular weight studies, as molecular mass increase when asphaltenes are precipitated  
116 at elevated temperatures. Another consequence of increased precipitation temperature is  
117 higher aromaticity (*i.e.* lower H/C ratio) and polarity of isolated fraction (Andersen, 1995,  
118 1994; Andersen et al., 1997; Pineda et al., 2007). In the scope of the definition and up-to-  
119 date structural information about asphaltenes, as well as being insoluble in n-alkanes and  
120 consisting of aromatic core of 4-10 fused rings, the variation of temperature affects the  
121 precipitate yield due to the co-precipitation of smaller molecules (e.g. resins). Although, one  
122 need to remember that there is no distinct border between asphaltenes and resins.

123 The last step of almost all precipitation procedures include washing of the isolated  
124 asphaltenes, is to remove adsorbed resins as well as other components of the primary  
125 material (ASTM D2007, 2003; ASTM D3279, 2001; ASTM D4124, 2001; ASTM D6560,  
126 2000). If asphaltenes-resins interactions are adsorptive, then it should be possible to remove  
127 resins with re-precipitations and/or intensive washing with the correct solvent. The second  
128 phenomenon that can hinder the isolation of pure asphaltenes is to block access of the  
129 solvent by occlusion, thus retaining resins (or generally other than asphaltene fractions) by  
130 asphaltenes (Derakhshesh et al., 2013; Liao et al., 2006, 2005; Strausz et al., 2006).  
131 Although, the importance of the washing step is recognised intuitively, it is the most  
132 imprecise and ambiguous step. Usually it is performed on a filter with the solvent used for the  
133 precipitation. A common criterion is to continue washing until the effluent is colourless (ASTM  
134 D4124, 2001). This implies arbitrariness and leads to different extents of washing. Another  
135 popular method of washing is to use a reflux extractor (ASTM D6560, 2000). Results  
136 presented in (H. Alboudwarej et al., 2002) revealed that using Soxhlet's extractor led to  
137 removal of 22% w/w of maltenes from filter-washed asphaltenes.

138 As we have shown, a number of methods and refinements exist to isolate  
139 asphaltenes, but none allow for large scale production of a consistently pure product.



140 Therefore, the aim of this paper was to propose simplified, reproducible, easy to scale – up  
141 procedure of asphaltenes isolation, which will give at least similar results as the standard test  
142 method. It would be of great importance, not only for studies in our research group (Boczkaj  
143 et al., 2016), but for researchers studying asphaltenes characteristic and technical analysis  
144 of petroleum products as well. Usually asphaltenes are characterized by their average  
145 properties e.g. elemental composition and molar mass. In this paper, thin-layer  
146 chromatography with flame ionization detection (TLC-FID) was used to compare group type  
147 composition of asphaltene fractions obtained by studied methods. Moreover operation  
148 effectiveness, scale-up possibility as well as economic aspects of this methods were  
149 evaluated.

## 150 **2. Experimental**

### 151 **2.1. Materials**

152 Bitumen 20/30 SDA (Lotos Group, Gdansk, Poland) and n-heptane EMPLURA®  
153 (Merck, Germany) were used to isolate the asphaltene fraction. Depending on the isolation  
154 method used, mixture was filtered through a 0.45µm PTFE membrane filter (Achrom,  
155 Belgium) or a standard single thickness 33x100mm cellulose thimble (VWR, United States).  
156 During hydrocarbon group type analysis of the isolated fractions, the following analytical  
157 grade chemicals were used: dichloromethane (POCH, Poland), methanol (POCH, Poland),  
158 toluene (POCH, Poland) and hexane (Merck, Germany). To filter samples prior to analysis,  
159 0.45µm PTFE syringe filters (Achrom, Belgium) were used.

### 160 **2.2. Apparatus**

161 To perform filtration a vacuum glass set (Glassco, India) was used. Isolated samples  
162 were washed in a Soxhlet type extractor. Weight measurements were performed with a WLC  
163 6/A2 (readability 0.1g) and WPA 180/C (readability 0.1mg) balances (RADWAG, Poland).

164 To analyze the group type composition of the isolated fractions by means of TLC-FID  
165 technique an Iatroscan Mk.V (Iatron Lab., Japan), silica gel Chromarods S5 (Iatron Lab.,

166 Japan), 3200/IS-01 semiautomatic sampler (SES, Germany), 7102KH 2 $\mu$ L syringe (Hamilton,  
167 USA), TLC TK-8 Chromarods dryer (Iatron Lab., Japan), chromatographic chambers, AD  
168 converter, and corresponding software (Chomik, Poland) were used.

## 169 **2.3. Procedures**

### 170 **2.3.1. Asphaltene fractions isolation**

#### 171 **2.3.1.1. Procedure ASTM D4124**

172 The reference samples of asphaltene fraction were isolated using the conditions  
173 described in ASTM D4124 (ASTM D4124, 2001). As a reference standard method of  
174 isolation ASTM D4124 was selected, because it exploits high solvent to feedstock ratio  
175 (100mL : 1g), long contact time (ca.16h) and extensive washing of isolated asphaltenes (till  
176 effluent is colorless). This should ensure high purity (low content of resins) of the asphaltene  
177 fraction. Bitumen was heated in an oven at 70°C for 1h and 6g (weighed to the nearest 0.1g)  
178 were placed in 1L flask, which was gently heated to disperse bitumen on the bottom and  
179 lower sides of the flask. Next, the n-heptane was added in the ratio of 100mL per 1g of  
180 bitumen. The mixture was heated to boiling and refluxed for 1h with occasionally stirring.  
181 After the mixture was allowed to cool for 16h, it was filtered through 0.45 $\mu$ m PTFE  
182 membrane filter under the vacuum. The precipitate was washed with hot n-heptane until a  
183 colorless filtrate was obtained. The filtrate was consequently washed with 80mL of fresh n-  
184 heptane, and heated for 30min with occasional stirring and filtered again through a fresh  
185 tared PTFE membrane filter. The asphaltene cake was washed with hot n-heptane till the  
186 filtrate was colorless, dried (1h at 100°C) and weighed.

#### 187 **2.3.1.2. Procedure B1 and B16**

188 The novel procedure of isolation proposed and tested in this paper is as follows:  
189 bitumen is heated in an oven at 70°C for 1h and 15g of it is placed in 1L round-bottom flask.  
190 The flask is gently heated to disperse bitumen on the bottom and lower sides of the flask.  
191 Next, the n-heptane is added in the ratio of 40mL per 1g of the bitumen. The mixture is  
192 brought to a boil and refluxed for 1h with occasional stirring. Then it is set aside for 1h



193 (procedure B1) and 16h (procedure B16) to cool and the content of the flask is filtered  
194 through a tared cellulose thimble. In procedure B1 the filtration started at temperature of the  
195 mixture being 55 °C, and in B16 procedure at 20 °C. The thimble is placed in a Soxhlet  
196 extractor and washed with n-heptane for 24h. Next, it is dried at 100°C for 1h and weighed.

197 Figure 1 and 2 present steps of standard and proposed procedures for isolation of  
198 asphaltene fraction and experimental glassware setup, respectively.

### 199 **2.3.2. Hydrocarbon group type analysis of isolated fractions.**

200 The group type composition of bitumen and the isolated fractions was investigated by  
201 TLC-FID technique which allows a relatively fast analysis. A normal phase separation  
202 mechanism is used, resulting in a so-called SARA (Saturates, Aromatics, Resins,  
203 Asphaltenes) analysis. In this conditions asphaltenes are defined as a group of compounds  
204 having the highest retention.

205 Samples were prepared by dissolving the samples in dichloromethane to yield  
206 concentration of 2 mg/mL. This prevents overloading of the stationary phase and leads to a  
207 better separation of asphaltenes and resins. To remove any undissolved particles, the  
208 samples were filtered through 0.45µm PTFE syringe filters. Before spotting the samples, the  
209 Chromarods were activated in the flame of FID detector: once in time of 35s and twice in  
210 50s. Then, they were placed in desiccator for 10min to cool down.

211 1µL of the samples were spotted in a small aliquots on the three Chromarods each, to  
212 obtain quantitative results. Next, the Chromarods with the spotted samples were placed in  
213 the dryer (set to 70°C) for 3min. A three-step elution sequence was used, with eluents in the  
214 following order:

- 215 1. dichloromethane:methanol (95:5 v/v) elution up to 45% of a stationary phase height
- 216 2. toluene elution up to 80% of a stationary phase height
- 217 3. n-hexane (95% water saturated) elution up to 100% of a stationary phase height

218 The set of solvents used in this work is a typical set used for hydrocarbons group type  
219 analysis of petroleum heavy fractions using TLC-FID technique (Sharma et al., 1998).

220 However, atypical is the sequence of the elution, which is contrary to what can be typically  
221 found in literature (Jiang et al., 2008; Sharma et al., 1998). In our work we developed the  
222 Chromarods beginning with the solvent ensuring the elution of asphaltene fraction. It follows  
223 from the high amount of asphaltene in the sample which are not solubilized and eluted by n-  
224 hexane (which is used as the first solvent in typical procedures). In our opinion fractions  
225 other than asphaltenes (i.e. saturates and aromatics) can be trapped under asphaltenes and  
226 shielded/covered by them, hence not eluted by the n-hexane used as first solvent. First  
227 solvent (dichloromethane:methanol) eluted all components of the spotted sample and  
228 increased accessibility of two other solvents to the whole amount of the sample. This  
229 approach was validated in our lab during a series of quality control analysis of bitumen,  
230 performed for a local refinery in Gdansk.

231 Each TLC chamber was lined with chromatographic paper, filled with eluent and left for  
232 saturation for 15min. The Chromarods were placed in the chamber and eluted accordingly.  
233 Before elution with toluene and n-hexane the frame with rods was held in headspace of  
234 eluent for 5 min to saturate the stationary phase with vapors of the eluent. After each elution  
235 step the rods were dried for 3min (or longer if a scent of a solvent was noticeable) and left in  
236 desiccator for 10 min to cool down.

237 Detection was carried out in a TLC-FID analyzer. Rod scanning time was set to 35s,  
238 hydrogen and air flow were 150mL/min and 1800mL/min respectively. Chromatograms were  
239 integrated with a normalization method. Obtained results were used comparatively for  
240 evaluation of purity of asphaltene fraction obtained by means of studied in this paper  
241 methods of isolation.

#### 242 **2.4. Quality assurance of data.**

243 The average results for isolation of asphaltene fraction, by each procedure, are the mean  
244 values of three separate isolations. The average yield is a mass ratio of asphaltene fraction  
245 and feedstock (bitumen). For TLC-FID analysis, each sample was spotted on three rods to  
246 provide quantitative data. The average of asphaltenes content was calculated as a mean of



247 the means for individual samples isolated with given procedure. The relative standard  
248 deviation (RSD%), which expresses the precision and repeatability was calculated as a ratio  
249 of standard deviation to the mean value of asphaltenes content, multiplied by one hundred.

250 To compare the accuracy of investigated procedures, mean results (which were obtained  
251 by the same analyst) were evaluated by means of F-Snedecor test, to confirm the  
252 homogeneity of variances and next with t-Student test. t-Student test is used for determining  
253 whether the observed difference between obtained means is statistically significant or not. F-  
254 Snedecor test is performed to check whether the variances of the two samples are equal and  
255 if t-Student test without correction can be used.

### 256 3. Results and discussion

257 Figure 3 shows exemplary TLC-FID chromatograms (SARA analysis) of analyzed  
258 sample isolated by B1 (B) procedure and feedstock bitumen (A). A baseline separation  
259 between resins and asphaltenes is obtained, allowing to control the precipitation.

260 Table 1 presents results of TLC-FID analysis of obtained asphaltene fractions. Table  
261 2 presents differences between values of parameters given in Table 1 for the tested  
262 procedures.

263 Isolated asphaltene fractions were dark brown, black mat solids. Quantitative analysis  
264 revealed some differences which are consistent with obtained yields of asphaltene fractions.  
265 It is clear from data in Table 1 that ASTM standard test method has a false positive error i.e.  
266 it reports higher content of asphaltenes in bitumen due to the presence of impurities of resins  
267 fraction co-precipitating or adsorbing on asphaltenes. The studied alternative procedures  
268 exhibit an improved purity of obtained asphaltene fraction. It is possible, that in the case of  
269 bitumens having lower content of asphaltenes and higher of resins, this error for ASTM  
270 methods would be higher.

271 The average result of asphaltene fraction yield was 10.14 % w/w from the ASTM  
272 D4124 procedure and 8.79 % w/w from the new B1 procedure. This difference is mainly the  
273 result of lower resins content when proposed B1 procedure is used. These conclusions are

274 supported by the TLC-FID data, which revealed that the asphaltenes content in isolated  
275 fraction is higher by 1.59% for B1 procedure.

276 The lowest yield of asphaltene fraction was obtained for our procedure with B1  
277 contact time. At the same time this procedure gave the highest purity of asphaltenes. This  
278 indicates that B1 procedure, involving the washing in the Soxhlet, washed out more maltenes  
279 than the ASTM D4124, in which washing of the filter cake is performed manually.  
280 Additionally, the developed procedures have improved reproducibility, as the RSD% value is  
281 lower, comparing with ASTM method.

282 The second variant of the procedure, in which contact time was the same as in ASTM  
283 D4124 method, gave the results between standard and B1 procedures. The yield of  
284 asphaltene fraction was higher and purity of asphaltenes lower than in B1 procedure.  
285 Probably, it is due to a lower temperature of a mixture at the beginning of filtration and  
286 resulting higher adsorption of resins in B16 procedure. Still, this method provided higher  
287 purity of asphaltenes than ASTM method. This result clearly indicates the problem of the  
288 presence of resins fractions in precipitated asphaltenes fraction, which is almost completely  
289 solved in the developed method for optimized conditions of settling the solution, filtration and  
290 Soxhlet extraction stages.

291 The precision and repeatability of each procedure was sufficient and comparable, as  
292 the RSD% value was below 5% (Table 1). Table 3 presents values of calculated and critical  
293 parameters for the t-Student and F-Snedecor test. The t-Student test revealed statistical  
294 difference between mean results for ASTM D4124 and proposed B1 procedure. No statistical  
295 difference was observed for B16 and ASTM D4124 method. Between B16 and B1  
296 procedures difference in purity of asphaltene fraction was insignificant, while difference in  
297 yield of asphaltene fraction was slightly significant. Comparison of standard deviations  
298 revealed that both proposed methods were slightly more precise than the standard test  
299 method.

300 As abovementioned, the goal of this research was to develop simple, cost-effective  
301 and easy to scale-up procedure of asphaltenes isolation which will give at least similar



302 results, in terms of asphaltene purity, as standard test method. This has been achieved by  
303 lowering the feedstock to solvent ratio from 1g per 100mL to 1g per 40mL (this ratio is  
304 reported in some of ASTM methods as allowable) along with modification of purification step.  
305 As shown in Table 4 solvent consumption in B1 procedure was calculated as three times  
306 lower than in ASTM D4124. For ASTM D4124 calculation has been made on the basis of the  
307 amount of the solvent used in abovementioned experiment, while for the other two standard  
308 test methods quantities of solvent and feedstock specified in standard test method were  
309 used.

310 The studies revealed, that washing step is crucial for final asphaltenes purity. Lower  
311 solvent consumption allowed the use of bigger quantities of feedstock without fall-off in  
312 asphaltene fraction purity (in fact, a higher purity was obtained). This may be not only  
313 important for process scale isolation, but also in terms of asphaltenes research. Due to the  
314 high complexity of petroleum and its subfractions, asphaltenes are still relatively unknown  
315 and poorly studied group of chemical compounds. One of the difficulties associated with the  
316 correct characterization of asphaltenes is the lack of one universal and standardized method  
317 of isolation. Different research teams isolate asphaltenes by means of different ASTM or  
318 other standard methods described in the literature or perform isolation by means of their own  
319 developed procedures. This affects strongly the purity of asphaltenes and reproducibility of  
320 results, thus making comparisons limited. Proposed simple, reproducible procedure giving  
321 high quantities of asphaltene fraction with very low resins content is an important contribution  
322 to this issue.

323 Table 4 compares selected parameters of investigated procedures and two additional  
324 standard test methods.

325

#### 326 *Time consumption*

327 B1 procedure is the most time consuming but it is caused by the most extensive  
328 washing among compared procedures. This extended purification is a must to obtain pure  
329 asphaltenes fraction and accurate results of determination.

330 In the case of standard test methods the isolation procedure time can be extended by  
331 problems with filtration rate. When isolating asphaltene fraction according to ASTM D4124-  
332 01, 0.45 $\mu$ m PTFE filters were used and especially in the case of higher amounts of  
333 asphaltene fraction, the filters have tendency to clog, thus decreasing the rate of filtration and  
334 significantly increasing the time of the filtration stage. The same issue may be observed in  
335 ASTM D3297 and D6560 procedures which utilize glass filter pads and cellulose quantitative  
336 filters, respectively. In B1 procedure filtration under vacuum with sub micrometer filter was  
337 replaced with simple filtration through cellulose thimble, in which the washing step is carried  
338 out later. No issues with filtration were observed when filtering through thimble and filtrations  
339 were completed in time under 15 minutes. To check if no asphaltenes are going through  
340 thimble during filtration, effluent was filtered through 0.45 $\mu$ m PTFE membrane filter and no  
341 solid particles were retained.

342

#### 343 *Solvent consumption, washing and purity of asphaltene fraction*

344 The B1 procedure has the lowest solvent consumption yet the most extensive  
345 washing of the isolated fraction, giving the highest purity of asphaltene fraction. ASTM D3279  
346 procedure consumes almost three times more solvent than B1 procedure and washing step  
347 is very limited. Although there is no data available about purity of asphaltene fraction isolated  
348 with ASTM D3279, because it is similar to ASTM D4124, the purity probably will not exceed  
349 the one obtained with ASTM D4124.

350 ASTM D6560 uses similar amount of n-heptane but incorporates dissolution/re-  
351 precipitation with toluene. It also involves washing in reflux extractor. However, contrary to  
352 Soxhlet extractor used in B1 procedure, it is constructed in a way that the solvent is  
353 constantly drained from sample. In Soxhlet extractor a chamber is flooded with hot solvent  
354 and periodically emptied by siphon. This ensures longer contact time and in case of bigger  
355 sample the whole asphaltene fraction should be evenly washed. ASTM D6560 procedure is  
356 somewhat alike to B1 in terms of solvent consumption and washing and can yield asphaltene  
357 fractions of similar purity.



358

359 *Arbitrariness and laboriousness*

360 Filtration in thimble and further Soxhlet washing allowed to omit a part of ASTM  
361 D4124 test method in which filter cake is transferred to beaker for extra washing and avoid  
362 manual washing of filter cake, which lowered the labor consumption and reduced  
363 arbitrariness.

364 Washing of asphaltene fraction in Soxhlet for a fixed amount of time eliminates the  
365 necessity of setting arbitrary end time of washing. Arbitrariness was evaluated on the basis  
366 of the precision of end points. In case of B1 and ASTM D3279 procedures end points are  
367 quantitative whereas in ASTM D4124 it is qualitative (color of effluent). In ASTM D6560 the  
368 washing step end point is measured in hours, however it is not fixed and only minimal time of  
369 washing is given.

370

371 *Scaling up/automation*

372 Table 5 presents the results of scaling up possibility evaluation. To estimate scaling  
373 up difficulty, the isolation process was divided into three parts: precipitation, filtration and  
374 washing. To every stage two numbers were ascribed: one representing its significance  
375 (wage) and second one describing difficulty of scaling up this stage. Difficulty was multiplied  
376 by significance of considered step and sum of those multiplications was treated as scaling up  
377 possibility parameter. Table 6 presents scale which was used to determine overall scale up  
378 possibility of the procedure.

379 Precipitation step was considered as having the lowest significance for the  
380 differentiation of the procedures because in every procedure it is conducted in the same way  
381 and only volume of a solvent differs. This difference was used to determine difficulty of  
382 scaling up. The bigger the feedstock to solvent ratio the bigger the vessel needed for  
383 precipitation step.

384 When evaluating filtration step, time and power consumption were taken under  
385 consideration. In case of ASTM D4124 significant problems with filtration resulting in



386 extended filtration time were discussed above. Additionally in ASTM D4124 and D3279  
387 procedures vacuum is used for filtration which increases power consumption. Those remarks  
388 are also true for washing step.

389 Due to the availability of wide range of Soxhlet dimensions, proposed procedure can  
390 be easily scaled up, from laboratory scale to automated. Continuous washing with hot  
391 solvent is also easier to implement on a process scale, than filtration through sub micrometer  
392 filters. Moreover, in B1 procedure after filtration asphaltenes remain in thimble in which they  
393 are washed and it should be easy to make it “one-pot” process. Additionally in B1 procedure  
394 asphaltenes are not dissolved in toluene after washing with n-heptane as in ASTM D6560  
395 and there is no need for evaporation to reprecipitate asphaltenes.

396

#### 397 *Safety*

398 Conducting purification step in Soxhlet extractor reduces risk to safety and health. In  
399 ASTM D4124 procedure washing with hot solvent is done manually and redissolving of  
400 asphaltene fraction in hot n-heptane takes place in an open beaker. The lack of proper  
401 attention can lead to overheating of the mixture, which may result in bumping, thus  
402 representing a hazard.

403

#### 404 **4. Conclusion**

405 The procedures of asphaltene fraction isolation developed and tested in this paper  
406 provided higher purity of isolated fractions (containing less resins) and are characterized by  
407 improved reproducibility and precision comparing to standard test method, which is  
408 corroborated by the RSD% values.

409 Implementation of filtration through cellulose thimble and washing off isolated fraction  
410 in Soxhlet extractor is less laborious, less arbitrariness and easy to scale-up. This simplicity  
411 makes the scale-up easier which in connection with smaller solvent consumption per 1g of  
412 feedstock can lead to obtaining higher quantities of asphaltene fraction, which may be



413 especially interesting for researchers working on characterization of asphaltenes e.g.  
414 structural analysis and further if kilograms of asphaltenes are needed for different studies. In  
415 this field particularly important are studies on bitumen properties related to asphaltene  
416 content and their physico-chemical character.

417 As abovementioned, asphaltenes are currently under investigation in terms of their  
418 sorption properties and employing them in separation techniques (Boczkaj et al., 2016,  
419 2015). Such sorbents can be used in process scale separations or as a stationary phase for  
420 gas chromatography. In this case further scaling-up will be needed and previously mentioned  
421 advantages of proposed procedures can be crucial for isolating large quantities of this  
422 material. Furthermore, in process scale isolation, washing step can be based on the same  
423 principle as in Soxhlet extractor (recirculation of the hot solvent) and in turn will result in cost  
424 reduction of this step.

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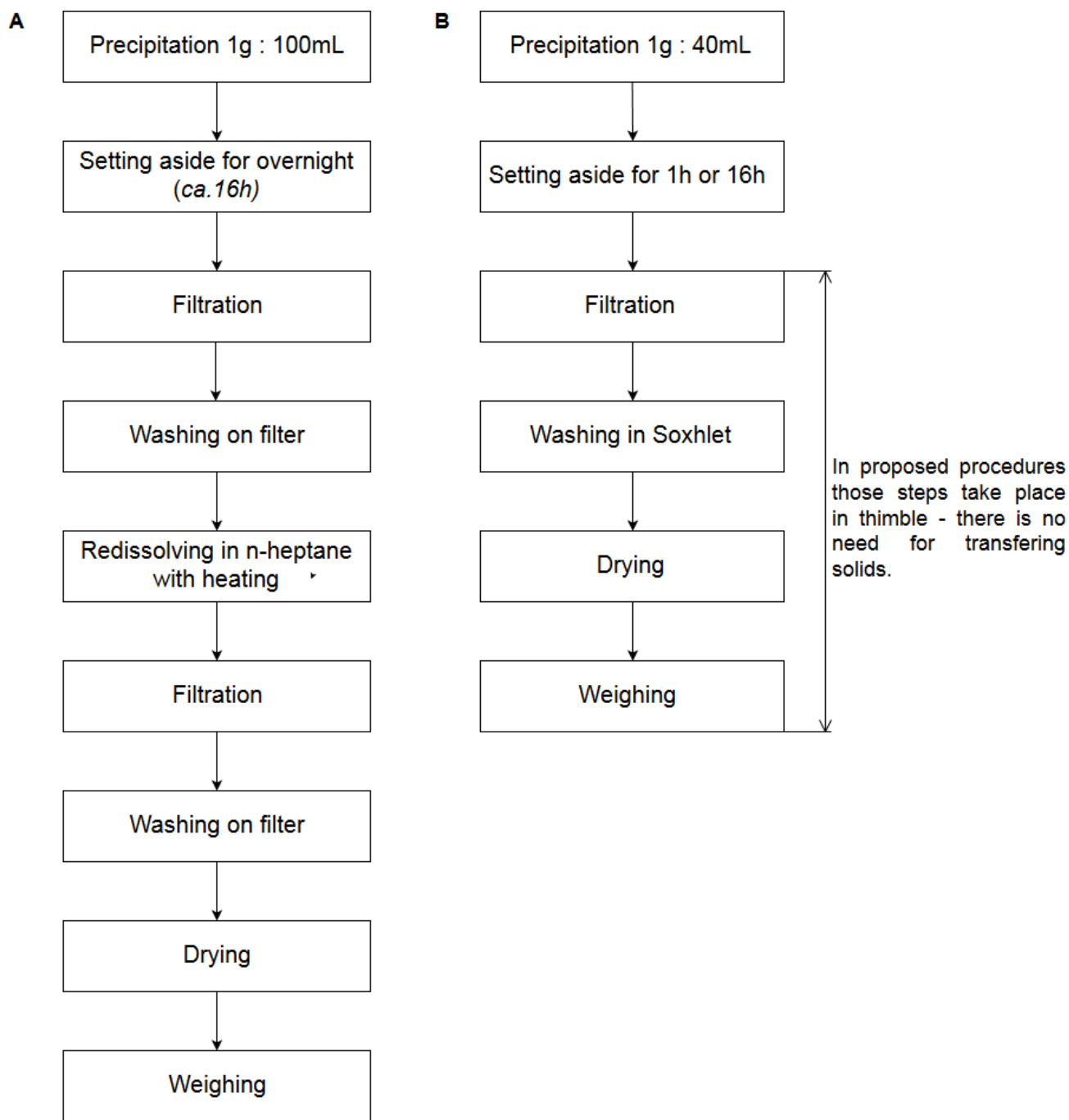
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549



550

551 *Figure 1. Scheme of studied procedures for isolation of asphaltene fraction. (SINGLE COLUMN)*

552 *A) standard test method ASTM D4124. B) Proposed procedures. For two tested variants B1 and B16 the scheme*

553 *is the same, only time of setting aside changes (1h vs 16h).*

554

555  
556

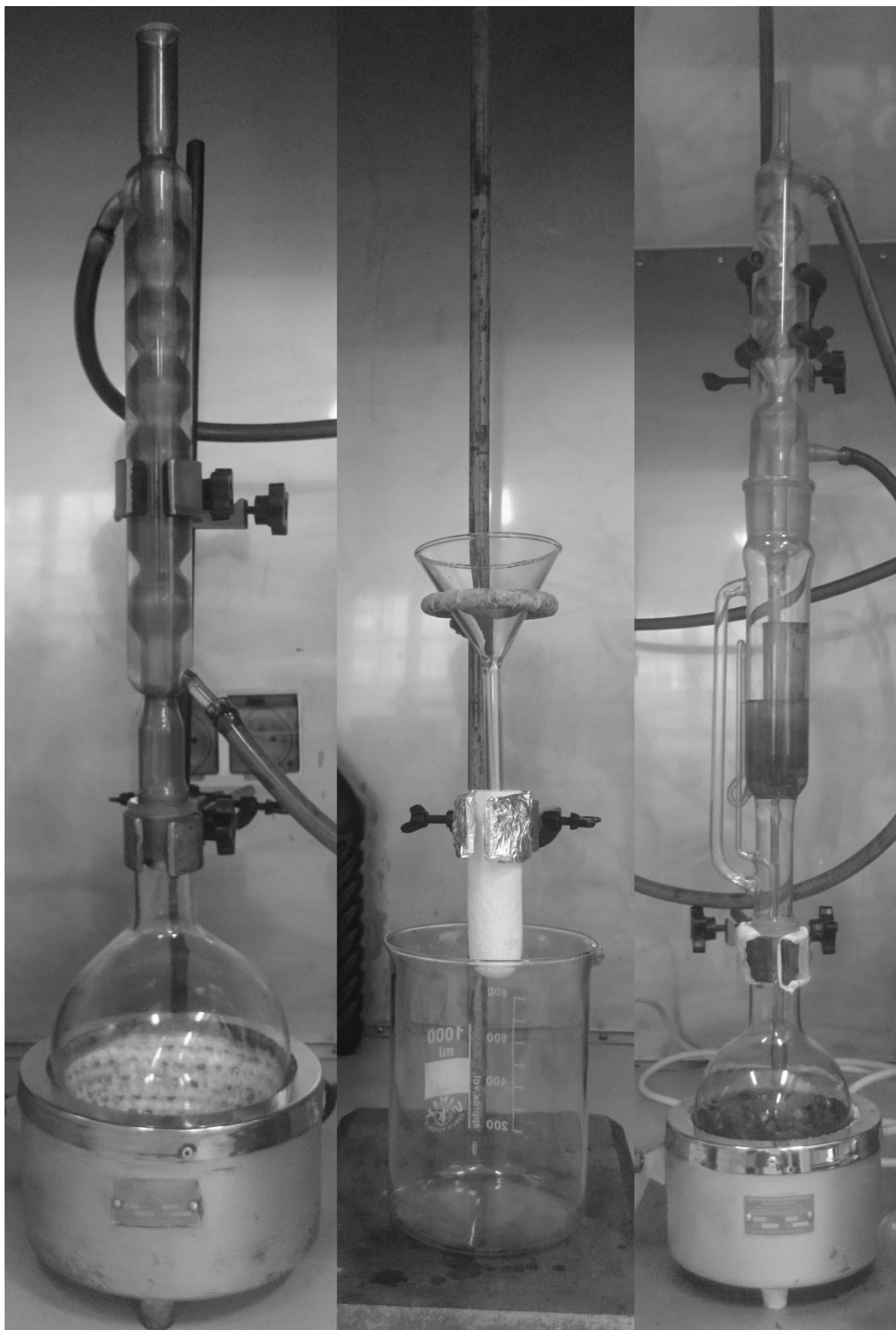
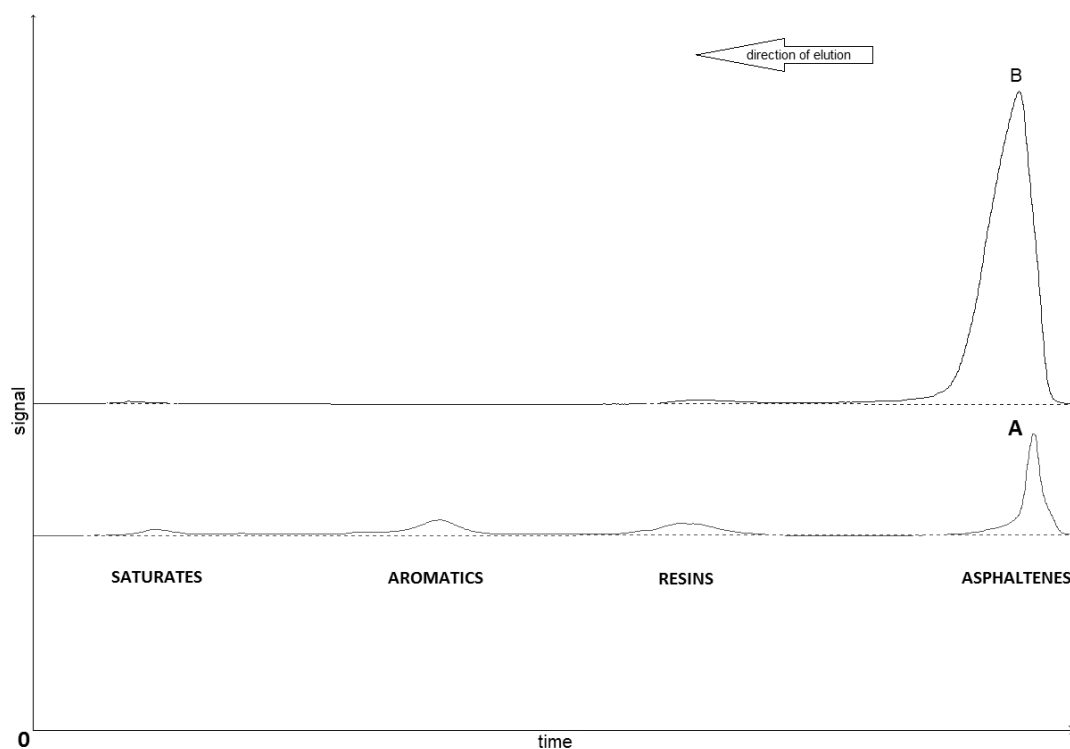


Figure 2. Experimental glassware setup. From left: precipitation set, filtration set, washing (Soxhlet) set. (**SINGLE COLUMN**)





558

559 *Figure 3. Exemplary TLC-FID chromatograms of SARA fractionation. (1.5-COLUMN)*560 *A) feedstock – bitumen 20/30 SDA and B) the asphaltene fraction isolated with tested B1 procedure.*

561

562 *Table 1. Comparison of asphaltenes isolation results obtained with tested procedures.(2-COLUMN)*

Method	ASTM D4124			B16			B1		
	Mean	STD	RSD%	Mean	STD	RSD%	Mean	STD	RSD%
Yield of asphaltene fraction [% m/m]	10.14	0.46	4.49	9.59	0.32	3.34	8.79	0.35	3.99
Asphaltene fraction purity[%]	95.80	0.30	0.31	96.49	0.47	0.49	97.39	0.76	0.78

563

564 *Table 2. Differences between results for tested procedures. (1.5-COLUMN)*

	ASTM D4124 – B16	ASTM D4124 – B1	B16 – B1
Yield of asphaltene fraction [% m/m]	0.55 ± 0.14	1.35 ± 0.11	0.80 ± 0.03

<b>Asphaltenes content [%]</b>	0.69 ± 0.17	1.59 ± 0.46	0.90 ± 0.29
--------------------------------	-------------	-------------	-------------

565

566 *Table 3. Comparison of variances and means for two sets of results. (1.5-COLUMN)*

	<b>ASTM D4124 – B16</b>	<b>ASTM D4124 – B1</b>	<b>B16 – B1</b>
	<b>F-Snedecor</b>		
	$F_{cr} (\alpha=0.05, f_1=f_2=2) = 19.00$		
	F		
<b>Yield of asphaltene fraction [% m/m]</b>	2.07	1.73	1.20
<b>Asphaltenes content [%]</b>	2.45	6.42	2.61
	<b>t-Student</b>		
	$t_{cr} (\alpha=0.05, f=n_1+n_2-2=4) = 2.776$		
	t		
<b>Yield of asphaltene fraction [% m/m]</b>	1.70	4.04	2.92
<b>Asphaltenes content [%]</b>	2.14	3.37	1.74

567

568 *Table 4. Comparison of procedures for isolation of asphaltene fraction. (2-COLUMN)*

	<b>B1</b>	<b>ASTM D4124-01</b>	<b>ASTM D3279-07</b>	<b>ASTM D6560-00 (IP 143/01)</b>
<b>Time consumption</b>	ca. 28h	ca. 20h	ca. 3h	ca. 10h
<b>Solvent consumption</b>	50 mL/g	ca. 150 mL/g	ca. 130 mL/g	heptane: ca. 50 mL/g toluene: ca. 10 mL/g
<b>Washing</b>	24h Soxhlet	on filter washing, until filtrate is colorless	on filter, 3 x 10mL	min. 1h reflux extractor
<b>Laboriousness</b>	+	-	+	--
<b>Purity of asphaltene fraction</b>	97.39 ± 0.76	95.80 ± 0.30	NA	NA

<b>Scaling up/automation</b>	easy	difficult	moderate	moderate
<b>Safety</b>	safe	hazardous steps	safe	safe
<b>Arbitrariness</b>	++	-	++	+

569

570 *Table 5. Collation of grades ascribed to isolation process stages describing its importance and difficulty of scaling*

571 *up. (2-COLUMN)*

Stage	Wage	B1		ASTM D4124-01		ASTM D3279-07		ASTM D6560-00	
		Difficulty	Mult.	Difficulty	Mult.	Difficulty	Mult.	Difficulty	Mult.
Precipitation	1	2	2	4	4	4	4	2	2
Filtration	2	2	4	5	10	3	6	3	6
Washing	3	2	6	4	12	3	9	4	12
Scaling up parameter			12		26		19		20

572

573 *Table 6. Scale used to determine the possibility of process scale up. (SINGLE COLUMN)*

Scaling up parameter	Scaling-up difficulty
≤ 15	easy
15-20	moderate
> 20	difficult

574