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3   **Polyaniline Coated Micro-capillaries for Continuous Flow Analysis**

4   **of Aqueous Solutions**

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13

14   **Abstract:** The inner walls of fused silica micro-capillaries were successfully coated

15   with polyaniline nanofibres using the "grafting" approach. The optical response of

16   polyaniline coatings was evaluated during the subsequent redoping–dedoping

17   processes with hydrochloric acid and ammonia solutions, respectively, that were

18   passed inside the micro-capillary in continuous flow. The optical absorbance of the

19   polyaniline coatings was measured and analysed in the wavelength interval of [300–

20   850 nm] to determine its optical sensitivity to different concentrations of ammonia. It

21   was found that the optical properties of polyaniline coatings change in response to

22   ammonia solutions in a wide concentration range from 0.2 ppm to 2000 ppm. The

23 polyaniline coatings employed as a sensing material for the optical detection of

24 aqueous ammonia have a fast response time and a fast regeneration time of less than 5

25 seconds at room temperature. The coating was fully characterised by Scanning

26 Electron Microscopy, Raman Spectroscopy, absorbance measurements and kinetic

27 studies. The response of the coatings showed very good reproducibility,

28 demonstrating that this platform can be used for the development of micro-capillary

29 integrated sensors based on the inherited sensing properties of polyaniline.

30 **Keywords:** polyaniline, continuous flow, sensor, ammonia, micro-capillary;

31 **1. Introduction**

32 Sensors providing continuous, direct and immediate analytical information are of

33 great interest for many areas of research as such environmental monitoring [1-6]. In

34 particular, some sectors of the water industry dealing with the detection and

35 characterisation of chemical contaminants in surface water, predominantly rely on the

36 batch sampling technique, where water samples are collected and analysed in the

37 laboratory. This is mainly due to costs or legal constrains around certified methods[7].

38 Although this technique often offers accurate detection and possesses good sensitivity

39 and limits of detection, it is time consuming, requires manpower and, most

40 importantly, it fails to provide immediate or continuous information, which is of

41 enormous interest when picking a sporadic, but fatal, event in the network. In this

42 context, flow-through sensors have attracted a lot of attention for real time monitoring

43 of water samples [8-12]. Flow-through sensors posses many advantages compared

44 with classical probe-type sensors as such facile sample transport, sensor conditioning,

45 maintenance and regeneration among others [13]. A subclass of flow-through sensors,

46 accomplished through miniaturisation of the "flow-through" unit are micro-capillary

2

47 integrated optical sensors, in which glass or plastic micro-capillaries are coated on

48 their inner surface with a chemically sensitive layer that changes its optical properties

49 (absorbance [14-17], reflectance [14], fluorescence [15, 16], swelling [16] and

50 refractive index [15, 16]) in response to a particular analyte as it passes through the

51 micro-capillary. Hence, in this type of systems, it is no longer the intrinsic optical

52 properties of the sample as it passes through the detector that are being studied, but

53 rather those of the inner micro-capillary coating, as they are modulated by the sample.

54 Because the optical properties of the coating, instead of the sample itself, are being

55 monitored, micro-capillary integrated optical sensors are virtually independent of the

56 colour and turbidity of the sample, which may interfere with the chemical sensing

57 process in a conventional optical sensor. Moreover, micro-capillary integrated optical

58 sensors offer advantages in terms of size, electrical safety, costs and have no the need

59 for a separate reference electrode, as is the case in electrochemical measurements [18].

60 In particular, several micro-capillary integrated optical sensors have been developed

61 for the optical sensing of metal ions [14], solvent polarity [19], or carbon dioxide [18].

62 Exploring new means of developing micro-capillary integrated optical sensors

63 capable of continuous flow analysis of water contaminants; we explored the optical

64 properties of the semiconductive polymer polyaniline (PAni), [20-23] for the

65 detection and quantification of aqueous ammonia. In fact, many recent articles

66 describe electrical and optical sensors for ammonia detection with PAni as the

67 sensitive layer, [24-28] or PAni composites [29, 30]. For the detection of aqueous

68 ammonia, however, to our knowledge, only one recent study presents an optical

69 sensor based on PAni. Castrellon-Uribe *et al.* [31] used a glass substrate covered with

70 a film of polyaniline produced by the chemical bath method, for which transmittance

71 is measured after immersing the glass slide in aqueous ammonia solutions and

3

72 subsequently drying the slide. Although the sensor is reported to have good signal

73 linearity over the concentration range 3–100 ppm of ammonia, the sensing method is

74 disruptive, cannot provide immediate or continuous information, and it is not suitable

75 for real-time measurements. Bearing these constraints in mind, we adopted a different

76 approach to produce polyaniline modified sensing micro-capillaries that showed fast

77 response and regeneration times providing with the possibility of working with a wide

78 range of aqueous ammonia concentrations in a continuous flow mode.

79 **2. Experimental**

80 *2.1. Materials and Methods*

81 Aniline (BDH), hydrochloric acid (Fisher Scientific), ammonium persulfate (APS)

82 (Aldrich), *N*-[3-(Trimethoxylsilyl)propyl]aniline (Aldrich), ammonium hydroxide

83 solution (28.0-30.0 % NH_3 basis) (Aldrich) were used. The aniline monomer was

84 purified by vacuum distillation before use. Other chemicals were used as received.

85 Fused-silica micro-capillaries (100 μm ID, 375 μm OD) were purchased from

86 Polymicro Technologies (Phoenix, AZ, USA).

87 Raman Spectroscopy was employed to study the chemical features of the polyaniline

88 coatings inside the micro-capillary. Raman spectra were taken with a Perkin Elmer

89 RamanStation at 2 cm^{-1} resolution, 3s per scan and 20 collections. A 785 nm laser line

90 was used as it can detect both doped and dedoped features in polyaniline.

91 UV-Vis Spectroscopy was used to study the pH dependence of the polyaniline

92 coatings. The absorbance spectra were recorded using 2 fiber-optic light guides

93 connected to a Miniature Fiber Optic Spectrometer (USB4000 - Ocean Optics) and

94 aligned using cross shaped cell (see Figure 4B). The light source used was DH-2000-

95   BAL UV-NIR deuterium tungsten halogen source (Ocean Optics). Data from the

96   spectrometer was processed using Spectrasuite software provided by Ocean Optics

97   Inc. For clarity, the absorbance spectra recorded were smoothed using Origin software

98   using Savitzky-Golay algorithm.

99   *2.2. Fused silica micro-capillaries coating protocol*

100   The functionalisation of the inner walls of the micro-capillary with PAni nanofibres

101   was achieved using chemical polymerisation. The protocol used to coat micro-

102   capillaries with polyaniline nanofibres is described in Figure 1. Prior to

103   functionalisation the inner micro-capillary surface was quickly washed with acetone

104   and water, then flushed with a solution of NaOH 0.2 M for 30 min at a flow rate of

105   0.25 μL min^{-1} using a syringe pump and then, rinsed with deionised water. Next, the

106   micro-capillary was flushed with a solution of HCl 0.2 M for 30 min at a flow rate of

107   0.25 μL min^{-1}, rinsed with water, and with ethanol. A 20 % wt solution of *N*-[3-

108   (trimethoxysilyl)propyl]aniline in ethanol was then pumped through the micro-

109   capillaries for 90 min at a flow rate of 0.25 μL min^{-1} (Fig. 1 – A). Later, the micro-

110   capillaries were washed with ethanol, dried under nitrogen stream, and left at room

111   temperature for 24h.

112   Fresh solutions of aniline and the oxidant (ammonium persulfate) in 1M HCl were

113   prepared as follow: 82 μL aniline was added to 4 mL 1 M HCl solution; 0.050 g

114   ammonium peroxydisulfate was dissolved in 4 mL 1M HCl solution. Equal volumes

115   of the two solutions were rapidly mixed together in a micro-syringe and immediately

116   used to fill the micro-capillary (Fig. 4 – B), which was after closed at both ends using

117   rubber septa. After about 10 min the solution inside the micro-capillary turns slightly

118   green which means that the polymerisation has started. The micro-capillary was left

119   on the bench over night. The next day the micro-capillaries were thoroughly washed

120   with water to remove any polyaniline nanofibres that were not attached to the inner

121   walls and any physisorbed materials.

122

123   **Figure 1.** Coating protocol of the fused silica micro-capillaries with polyaniline.

124

125   *2.3. Polyaniline coatings imaging protocol*

126   The polyaniline coatings inside the micro-capillary were imaged using scanning

127   electron microscopy (SEM) performed on a Carl Zeiss EVOLS 15 system at an

128   accelerating voltage of 3.87 kV. The micro-capillaries were cut using a SGT capillary

129   column cutter with rotating diamond blade (SHORTIX, Nederland) to create a smooth

130   cut of the micro-capillary wall. Then they were placed in vertical position in a custom

131   made metallic capillary holder that has holes of internal diameters equal to the

132   external diameter of the micro-capillary (375 μm). This set-up allows the micro-

133   capillaries to be kept in vertical position. During the imaging process, the stage was

134   tilted of an angle between 0 – 15° for better imaging of the inner wall of the micro-

135   capillary (Figure 2A).

136   For imaging purposes, a flat silicon wafer was coated with polyaniline nanofibres

137   using the same procedure as the one employed for the coating of micro-capillaries.

138   For this, a polydimethylsiloxane (PDMS) layer containing a micro-fluidic channel

139   (100 μm x 50 μm x 2 cm) incorporating one inlet and one outlet was placed on top of

140   a silicon wafer. The obtained micro-channel (PDMS/silicon wafer) was coated with

141   polyaniline following the procedure described above. Prior imaging, the PDMS layer

142   was removed and the silicon wafer containing the polyaniline film was coated with 10

143   nm Au layer. The imaging was performed on a Carl Zeiss EVOLS 15 system at an

144   accelerating voltage of 5.75 kV (Figure 2B).

145   **3. Results and Discussion**

146   *3.1. Polyaniline coatings*

147   3.1.1. Morphological Analysis

148   Fused silica micro-capillaries were covalently functionalised with polyaniline as

149   described in the experimental section. Scanning electron microscope (SEM) images

150   showed that using the described polymerisation technique, a 3D arrangement of

151   polyaniline isles, homogeneously distributed along the micro-capillary walls were

152   obtained, in which polyaniline is covalently attached to the inner walls of the micro-

153   capillary (Figure 2A). For a better visualisation of the morphology of polyaniline

154   coatings, a flat silicon wafer surface was coated (Figure 2B and C) using the same

155   procedure (see Experimental Section 3.3). Figure 2C shows that the method employed

156   produces nanofibres that are around 200 nm in diameter and up to several microns in

157   length. The great advantage of nanofiber structured films (*versus* bulk polyaniline) is

158   the high surface area that is exposed to the target molecules and the very short

159   diffusional path lengths[1, 22] which, coupled with rather thick films, produces

160   enhanced sensitivity and fast response times[32-34]. The covalent attachment of the

161   nanofibres ensures good mechanical stability of the coating, moreover no leaching has

162   been observed over a period of three months of use for lab experiments.

163   **Figure 2.** SEM images of the polyaniline coated micro-capillary (A) and silicon wafer

164   (B and C).

165   3.1.2. Structural Analysis

166   Raman spectroscopy was used to characterise the chemical structure of the

167   polyaniline since this technique allows non-invasive, *in situ* analysis of the

168   polyaniline coating inside the micro-capillary. Raman spectroscopy showed that the

169   polyaniline coating is obtained in its half-oxidised emeraldine state[35]. In addition,

170   Raman spectroscopy was also employed to study the changes in the bonding structure

171   of the coatings upon doping-dedoping, as very distinct signature bands appear for the

172   quinoid and benzenoid rings, respectively [36, 37]. Figure 3A presents the Raman

173   spectra of the polyaniline coatings in the region of interest (1000-1800 cm^{-1}) after a

174   solution of hydrochloric acid (HCl) 10^{-2} M and aqueous solution of ammonia (200

175   ppm), respectively, are passed inside the micro-capillary.

176   When a solution of 10^{-2} M HCl is passed through the micro-capillary, polyaniline

177   exists in the doped state, emeraldine salt (ES). Passing a solution of 200 ppm aqueous

178   ammonia inside the micro-capillary causes changes in the bonding structure of the

179   material (Figure 3B) reflecting the adoption of the dedoped– emeraldine base (EB)

180   state. Signature bands between 1300 and 1400 cm^{-1} appear for the doped material

181   (Fig. 3A – in green). After dedoping of the polymer with ammonia, these bands are

182   less significant, and strong bands between 1400 and 1500 cm^{-1} reflect the dedoped

183   state (Fig. 3A – in blue). Complete characterisation and assignments are listed in

184   Table 1.

185

186   **Figure 3.** (**A**) Raman Spectra of PAni functionalised micro-capillary after being filled

187   with a HCl solution 10^{-2} M (green) and with NH_3 aqueous solution 200 ppm (blue).

8

188 (**B**) Scheme showing the differences in the chemical structure of polyaniline (two

189 different states: Emeraldine Salt (ES) and Emeraldine Base (EB).

190

191 In particular, in the case of EB, an important peak can be observed at 1456 cm^{-1} and

192 is characteristic to C=N stretching vibration of the quinoid units[35, 37-40]. Other

193 bands at 1592 cm^{-1} and 1162 cm^{-1}, are assigned to C-C stretching[35, 39] and C-H

194 bending modes[35, 38], respectively, centered on the quinoid ring. Another new peak

195 at 1220 cm^{-1} appears in the spectra of polyaniline upon dedoping and is assigned to

196 C–N stretching vibrations of the benzenoid units [35, 39] (the EB form consists of

197 both C=N and C-N bonds). In the case of ES, the most important band appears at

198 1346 cm^{-1} and can be assigned to a C-N• + polaron stretch [35, 39, 41, 42] while the

199 band at 1170 cm^{-1} is characteristic to the C–H in-plane bending of the benzenoid ring

200 [35, 40]. These studies have been repeated on the same micro-capillary in similar

201 conditions after a period of two months. Raman spectroscopy indicated no noticeable

202 changes in the chemical structure of polyaniline (ES and EB).

203

204 **Table 1.** Assignment of the vibrational bands (cm^{-1}) observed between 1800 and

205 1000 cm^{-1} in the Raman spectra (λ_{ex} = 785 nm) of PAni functionalised micro-

206 capillary after being filled with a HCl solution 10^{-2} M (doped) and PAni

207 functionalised micro-capillary after being filled with NH$_3$ aqua solution 200 ppm

208 (dedoped).

209

210

211   3.1.3. Optical properties of the coating

212   To evaluate the optical response of the PAni coatings, hydrochloric acid (10^{-2} M) and

213   aqueous ammonia solution (200 ppm) were alternatively pumped through the micro-

214   capillary at a flow rate of 5 μL min^{-1} and the absorbance of the coating was monitored

215   transversally across the micro-capillary over the wavelength interval [350–1100nm]

216   (Figure 4A) using the configuration described in Figure 3B. When hydrochloric acid

217   is passed through the micro-capillary, the polyaniline coating presents a green colour

218   (ES) as depicted in Figure 4A. When the ammonia solution reaches the surface of the

219   coating, the micro-capillary rapidly changes its colour – from green to blue (Figure

220   4A - photos). This is due to the fact that when the emeraldine salt form of polyaniline

221   is exposed to a basic solution, such as ammonia, it undergoes deprotonation and it is

222   converted to the emeraldine base (EB) state which presents a blue color. The process

223   occurs on the imine nitrogen atoms as shown in Figure 3B. More specifically, the

224   doped state – emeraldine salt – has a characteristic absorption band at around 360 nm

225   associated to π-π* transition of the conjugated ring system [23] and an absorption

226   band at ~420 nm together with an extended tail at 850 nm assigned to polaron band

227   transition [23]. Dedoping the polymer with ammonia leads to a shift in the absorption

228   lambda maxima of PAni from ~360 nm (ES) to ~320 nm (EB). The band at 610 nm is

229   ascribed to the exciton formation in the quinonoid rings and this absorption gives rise

230   to the blue colour of the PAni coatings [23]. The UV-Vis spectra of the polyaniline

231   coatings obtained using the setup shown in Figure 4B is similar to the absorbance

232   spectra of polyaniline presented in the literature, in the case when polyaniline can be

233   found in the form of dispersions in aqueous solutions [20, 23, 43, 44]. Moreover, the

234   UV-Vis spectra can also provide useful information about the electronic structure of

235   the polymer and its geometric structure such as polymer chain conformation [23]. A

236   number of theoretical studies have examined the influence of PAni chain

237   conformation, in particular the effect of the phenyl and phenyl/quinoid torsional

238   angles along the chain on the electronic structure of polyaniline (and consequently

239   their absorbance spectra) [23, 45, 46]. It was found that the position of the absorption

240   bands of PAni is sensitive to the conformation adopted by the polymer chains as well

241   as the conjugation length. In the case of polyaniline coatings, having the polaron band

242   centered at around 827 nm, suggests that the PAni chains are adopting a "compact

243   coil" conformation compared with an "extended coil" conformation that is

244   characterised by a red shift in the λ_{max} to 1500-2500 nm [23].

245

246   **Figure 4.** (A) Absorbance spectra and photos of PAni functionalised micro-capillary

247   after being filled with a HCl solution 10^{-2} M (green) and PAni functionalised micro-

248   capillary after being filled with ammonia aqueous solution (blue). (B) Picture of the

249   UV-Vis flow cell set-up used for UV-Vis characterisation.

250

251   The change in colour and absorbance spectra of the coating in response to

252   hydrochloric acid and ammonia solution, respectively, shows the potential of this type

253   of coatings for building micro-capillary integrated micro-sensors capable of working

254   in continuous flow.

255   To further investigate the reversibility of color change of the micro-capillary sensor

256   during the protonation/deprotonation processes, the absorbance at fixed wavelengths

257   was monitored while pumping HCl 10^{-2} M and aqueous ammonia 200 ppm solutions

258   respectively, through the micro-capillary at a flow rate of 5 μL min^{-1}. The two

259   wavelengths monitored correspond to typical absorbance of emeraldine salt (827nm –

260   polaron strech) and emeraldine base (600nm – exciton formation in the quinoid ring).

261   An absorbance reading was taken every 100 ms and no smoothing algorithms were

262   applied for the acquired data (Figure 5).

263   Firstly, a solution of hydrochloric acid is passed through the micro-capillary and the

264   absorbance at 827 nm (Figure 5 - in green) and 600 nm (Figure 5 – in blue) is

265   recorded in real time. After approximately three to four minutes, aqueous ammonia

266   solution is injected inside the micro-capillary, replacing the previous solution and

267   causing a change in colour of the micro-capillary. The absorbance is continuously

268   monitored, recording the moment when the micro-capillary changes from green to

269   blue (decrease in the absorbance at 827 and increase in the absorbance at 600 nm).

270   The absorbance value stabilises rapidly and after another 3 to 4 minutes the 10^{-2} M

271   hydrochloric acid is injected inside the micro-capillary. The sequence of

272   doping/dedoping/ followed by dedoping/doping process is repeated seven times in

273   total. The results showed excellent reproducibility, with no visible loss in the coating

274   sensitivity. The response time and the recovery time of the PAni coating exposed to

275   aqueous ammonia and hydrochloric acid solutions, respectively, were less than 5 s at

276   room temperature when the solutions are pumped through the micro-capillary at 5 μL

277   min^{-1} flow rate (Figure 5 – Inset A and B). The response of the PAni coatings, when

278   exposed to aqueous ammonia, is depicted in Figure 5 by a decrease in the absorbance

279   at 827 nm and an increase in the absorbance at 600nm. The absorbance values

280   become stable after less than 5 seconds (4.43 ± 0.13, n = 4) and remain stable as long

281   as the solution and the flow passing through the micro-capillary is not modified. In

282   order to ensure a good coating regeneration (doped state), a solution of HCl 10^{-2} M is

283   pumped through the modified micro-capillary. The regeneration of the coating occurs

284 in less than 4 seconds (3.34 ± 0.16, n = 3) and it is characterised by an increase in the

285 absorbance at 827 nm and a simultaneous decrease of the absorbance at 600 nm to

286 their original values (doped state). These results showed that the modified micro-

287 capillary sensor exhibits very rapid response times towards ammonia and HCl

288 solutions with excellent reproducibility.

289

290 **Figure 5.** Continuous monitoring of the absorbance at 827 nm and 600 nm of the

291 PAni coatings while HCl 10^{-2} M and ammonia (200 ppm) solutions are passed

292 through the PAni coated micro-capillary in continuous flow (5 μL min^{-1}). The inset A

293 and B show the response and recovery times of the PAni coatings.

294

295 *3.2. Ammonia Sensing*

296 Different concentrations of aqueous ammonia (from 0.2 ppm - 2000 ppm) were

297 passed through the modified micro-capillary in continuous flow (5 μL min^{-1}). The

298 absorbance of the coating was recorded in the interval 300 – 850 nm, using the same

299 methodology presented above, to determine the sensitivity of the PAni coatings to

300 ammonia. Before conducting the experiments, 10^{-2} M hydrochloric acid was passed

301 through the PAni modified micro-capillary to assure the complete doping of the

302 coating. As observed in Figure 6, the absorbance intensity of the two absorption

303 bands (350 nm, 600 nm) increases with ammonia concentration. Complete dedoping

304 of the polymeric coating is achieved at 20 ppm ammonia solution, and can be

305 depicted from Figure 6 by the disappearance of the absorbance band centered at 420

306 nm. Moreover, the λ_{max} of the absorbance band, due to the exciton formation in the

13

307 quinoid rings, shows a gradual shift towards lower wavelength with increasing

308 ammonia concentrations. To further characterise the performance of the polyaniline

309 based micro-capillary sensor towards aqueous ammonia, three sets of aqueous

310 ammonia solutions (from 0 ppm - 2000 ppm) were passed through the modified

311 micro-capillary in continuous flow (5 μL min^{-1}) and this time the absorbance at 600

312 nm was recorded continuously. The integration time in the Ocean Optics software was

313 set to 1 second and an absorbance reading was recorded every five seconds for three

314 minutes for each of the solutions (see Table S1 – Supplementary data). A plot of the

315 absorbance at 600 nm versus concentration of aqueous ammonia is shown in Figure 6

316 - Inset B showing the logarithmic calibration curve. This type of logarithmic response

317 is commonly depicted in the case of ammonia sensors based on polyaniline [28, 31].

318 However, to further simplify the calibration curve, often in cases of ammonia

319 concentration over a wide range, logarithm of concentration is plotted [28]. In the

320 case of the micro-platform presented here, this approach offers a linear calibration

321 curve ($R^2 = 0.991$) between absorbance at 600 nm and log[conc] (Figure 6 – Inset B)

322 making the sensor more practical. The limit of detection and limit of quantification

323 were found to be 0.0067 ppm and 0.041 ppm, respectively. The relative standard

324 deviation of the sensor's response lies typically in the range 1-3% over the calibration

325 range. The results indicate that the PAni modified micro-capillary integrated optical

326 sensors could be used for sensing aqueous ammonia over wide concentration range

327 (0.2 – 2000 ppm).

328

329 **Figure 6.** Absorbance spectra of the polyaniline coatings exposed to different

330 concentrations of aqueous ammonia. Inset A shows the logarithmic dependency of the

331 absorbance at 600 nm *versus* ammonia concentration. Inset B shows the linear

332 dependency of the absorbance at 600 nm *versus* logarithm of ammonia concentration.

333

334 **4. Conclusions**

335   A micro-capillary integrated optical sensor suitable for the detection of

336 aqueous ammonia has been realised by coating the inner walls of a fused-silica micro-

337 capillary with polyaniline nanofibres. In this approach, the ammonia solution does not

338 need to be pretreated prior entering the micro-capillary, for the incoming optical

339 analysis, as the polymer coating itself acts as the indicator dye. The ability to form

340 nanostructures together with its intrinsically pH-sensitive property makes polyaniline

341 an excellent candidate for the fabrication of optical sensors in the visible-near IR

342 regions, capable for real time continuous-flow measurements of aqueous ammonia.

343 The performance of the PAni modified optical sensor when aqueous ammonia

344 solutions are passed through the micro-capillary in continuous flow, showed that the

345 polyaniline modified micro-capillary optical sensors can operate in a wide range (0.2

346 – 2000 ppm) of ammonia concentrations. The high surface area of the polymer offers

347 good permeability for the analyte. Very fast response times of less than 5 seconds are

348 achieved. Another distinguishing feature of the PAni-modified micro-capillary optical

349 sensor is the possibility of a fast regeneration process of less than 4 seconds by just

350 pumping hydrochloric acid solutions through the modified micro-capillary. Good

351 reproducibility of the signal was obtained when cycling ammonia and hydrochloric

352 acid solutions, respectively, showing the stability of the polyaniline coating through at

353 least 7 cycles. It was determined that by monitoring the absorbance at 600 nm, the

354 concentration of ammonia can be determined with good linearity. Therefore, we have

355 shown the feasibility of employing polyaniline to develop micro-capillary integrated

356 optical sensors capable of operating in continuous flow mode for the optical detection

357 of aqueous ammonia.

358

364 **Appendix A. Supplementary data**

365 Supplementary data associated with this article can be found, in the online version, at

366 http://dx.doi.org/

367 **References**

368 [1]   C.K. Ho, A. Robinson, D.R. Miller, M.J. Davis, Sensors, 5 (2005) 4.
369 [2]   M. Sequeira, M. Bowden, E. Minogue, D. Diamond, Talanta, 56 (2002) 355.
370 [3]   G.M.P. O'Hare, D. Diamond, K.T. Lau, J. Hayes, C. Muldoon, M.J. O'Grady, R.
371 Tynan, G. Rancourt, H.R. Kolar, R.J. McCarthy, Ibm Journal of Research and
372 Development, 53 (2009).
373 [4]   C. Fay, A.R. Doherty, S. Beirne, F. Collins, C. Foley, J. Healy, B.M. Kiernan, H.
374 Lee, D. Maher, D. Orpen, T. Phelan, Z.W. Qiu, K. Zhang, C. Gurrin, B. Corcoran, N.E.
375 O'Connor, A.F. Smeaton, D. Diamond, Sensors, 11 (2011) 6603.
376 [5]   L.M. Lechuga, F. Prieto, A. Calle, A. Llobera, C. Dominguez, Quim. Anal., 18
377 (1999) 144.
378 [6]   A. Lapresta-Fernandez, L.F. Capitan-Vallvey, Anal. Chim. Acta, 706 (2011)
379 328.
380 [7]   J. Berna, D.A. Leigh, M. Lubomska, S.M. Mendoza, E.M. Perez, P. Rudolf, G.
381 Teobaldi, F. Zerbetto, Nat. Mater., 4 (2005) 704.
382 [8]   I.P.A. Morais, M. Miro, M. Manera, J.M. Estela, V. Cerda, M.R.S. Souto, A.
383 Rangel, Anal. Chim. Acta, 506 (2004) 17.
384 [9]   P. Pulido-Tofino, J.M. Barrero-Moreno, M.C. Perez-Conde, Talanta, 51
385 (2000) 537.

386   [10]   J.S. Taurozzi, V.V. Tarabara, Environmental Engineering Science, 24
387   (2007) 122.
388   [11]   D. Perez-Palacios, S. Armenta, B. Lendl, Appl. Spectrosc., 63 (2009) 1015.
389   [12]   A. Mehta, H. Shekhar, S.H. Hyun, S. Hong, H.J. Cho, Water Sci. Technol., 53
390   (2006) 403.
391   [13]   M. Valcarcel, M.D.L. Decastro, Analyst, 118 (1993) 593.
392   [14]   B. Kuswandi, R. Narayanaswamy, Anal. Lett., 32 (1999) 649.
393   [15]   M. Borecki, M.L. Korwin-Pawlowski, M. Beblowska, J. Szmidt, A.
394   Jakubowski, Sensors, 10 (2010) 3771.
395   [16]   M.F. McCurley, Biosensors & Bioelectronics, 9 (1994) 527.
396   [17]   L. Florea, A. Hennart, D. Diamond, F. Benito--Lopez, Sens. Actuators B:
397   Chem. (2011).
398   [18]   B.H. Weigl, O.S. Wolfbeis, Anal. Chem., 66 (1994) 3323.
399   [19]   L. Florea, F. Benito--Lopez, A. Hennart, D. Diamond, Procedia Engineering,
400   25 (2011) 1545
401   [20]   A.J. Epstein, J.M. Ginder, F. Zuo, R.W. Bigelow, H.S. Woo, D.B. Tanner, A.F.
402   Richter, W.S. Huang, A.G. Macdiarmid, Synth. Met., 18 (1987) 303.
403   [21]   E.M. Genies, A. Boyle, M. Lapkowski, C. Tsintavis, Synth. Met., 36 (1990)
404   139.
405   [22]   J.X. Huang, Pure and Applied Chemistry, 78 (2006) 15.
406   [23]   G.G. Wallace, G.M. Spinks, L.A.P. Kane-Maguire, P.R. Teasdale, Conductive
407   electroactive polymers, CRC Press LLC, 2003.
408   [24]   E.K. Asijati, B.; Arifah, N.F.; Kurniawati, Y.I.; Gani, A.A.; , Sensors and
409   the International Conference on new Techniques in Pharmaceutical and
410   Biomedical Research, 2005 Asian Conference on (2005) 111
411   [25]   K. Crowley, E. O'Malley, A. Morrin, M.R. Smyth, A.J. Killard, Analyst, 133
412   (2008) 391.
413   [26]   S. Manigandan, A. Jain, S. Majumder, S. Ganguly, K. Kargupta, Sens.
414   Actuators, B, 133 (2008) 187.
415   [27]   P. Stamenov, R. Madathil, J.M.D. Coey, Sens. Actuators, B, 161 (2012) 989.
416   [28]   H. Kebiche, D. Debarnot, A. Merzouki, F. Poncin-Epaillard, N. Haddaoui,
417   Anal. Chim. Acta, 737 (2012) 64.
418   [29]   L. He, Y. Jia, F. Meng, M. Li, J. Liu, Materials Science and Engineering: B,
419   163 (2009) 76.
420   [30]   F.M. Blighe, D. Diamond, J.N. Coleman, E. Lahiff, Carbon, 50 (2012) 1447.
421   [31]   J. Castrellon-Uribe, M.E. Nicho, G. Reyes-Merino, Sens. Actuators, B, 141
422   (2009) 40.
423   [32]   J. Huang, S. Virji, B.H. Weiller, R.B. Kaner, Chemistry-a European Journal,
424   10 (2004) 1315.
425   [33]   S. Virji, J.D. Fowler, C.O. Baker, J.X. Huang, R.B. Kaner, B.H. Weiller, Small, 1
426   (2005) 624.
427   [34]   J.X. Huang, S. Virji, B.H. Weiller, R.B. Kaner, J. Am. Chem. Soc., 125 (2003)
428   314.
429   [35]   K. Berrada, S. Quillard, G. Louarn, S. Lefrant, Synth. Met., 69 (1995) 201.
430   [36]   M. Bartonek, N.S. Sariciftci, H. Kuzmany, Synth. Met., 36 (1990) 83.
431   [37]   A. Hugotlegoff, M.C. Bernard, Synth. Met., 60 (1993) 115.
432   [38]   Y. Furukawa, T. Hara, Y. Hyodo, I. Harada, Synth. Met., 16 (1986) 189.
433   [39]   J. Laska, R. Girault, S. Quillard, G. Louarn, A. Pron, S. Lefrant, Synth. Met.,
434   75 (1995) 69.

435   [40]   T. Lindfors, A. Ivaska, J. Electroanal. Chem., 580 (2005) 320.
436   [41]   C. Liu, J.X. Zhang, G.Q. Shi, F.E. Chen, J. Appl. Polym. Sci., 92 (2004) 171.
437   [42]   R. Mazeikiene, A. Statino, Z. Kuodis, G. Niaura, A. Malinauskas,
438   Electrochem. Commun., 8 (2006) 1082.
439   [43]   S.A. Chen, G.W. Hwang, J. Am. Chem. Soc., 117 (1995) 10055.
440   [44]   J.C. Chiang, A.G. Macdiarmid, Synth. Met., 13 (1986) 193.
441   [45]   P. Barta, T. Kugler, W.R. Salaneck, A.P. Monkman, J. Libert, R. Lazzaroni, J.L.
442   Bredas, Synth. Met., 93 (1998) 83.
443   [46]   Z.T. de Oliveira, M.C. dos Santos, Chem. Phys., 260 (2000) 95.