Accepted Manuscript

ROYAL SOCIETY
OF CHEMISTRY

rsc.li/process-impacts

-1-

Graphical abstract:

A simple and inexpensive approach for determination of various ionic species in different water matrices is reported. Major inorganic cations and anions in different water matrices in Vietnam were determined using purpose-made CE-C^{4}D instruments. Inorganic trivalent arsenic (As(III)) in reducing groundwater was determined by CE-C^{4}D with LOD of 5 µg / L.

-1-

1   **Environmental impact statement:**

2   This work provides a simple and inexpensive analytical approach for water-quality monitoring

3   which can be realized even when only a modest financial budget and limited expertise are

4   available. This approach renders the aqueous environmental control activities more realizable

5   even at local and decentralized areas. The case study was carried out in Vietnam where

6   arsenic contamination in groundwater has been a serious problem. Inorganic major cations

7   and anions, which are the primary indicators of water quality, together with abundantly

8   present arsenite in groundwater were successfully monitored with the purpose-made

9   instruments. Information on some water contaminants, *i.e.* ammonium and arsenic

10   contamination, could be obtained without having recourse to expensive and sophisticated

11   commercial instrumentation.

12

13

14

15

16

1　**In-house-made capillary electrophoresis instruments coupled with contactless**

2　**conductivity detection as a simple and inexpensive solution for water analysis: a case**

3　**study in Vietnam**

4

5　**Hong Anh Duong[1], Minh Duc Le[1], Kim Diem Mai Nguyen[1], Peter C. Hauser[2], Hung Viet**

6　**Pham[1]*, Thanh Duc Mai[1]***

7

8　*[1] Centre for Environmental Technology and Sustainable Development (CETASD), Hanoi*

9　*University of Science, Nguyen Trai Street 334, Hanoi, Viet Nam*

10　*[2] University of Basel, Department of Chemistry, Spitalstrasse 51, 4056 Basel, Switzerland*

11

12　e-mail:　　　maithanhduc83@gmail.com; Tel : ++33 651 37 79 49;

13　　　　　　　phamhungviet@hus.edu.vn ; Fax: +84 4 3858 8152

14　Website:　　http://www.ce-vietnam.com/

15

19

20

21

22

23

24

25

-2-

26 **Abstract**

27 A simple and inexpensive method for determination of various ionic species in different water

28 matrices is discussed in this study. The approach is based on the employment of in-house-

29 made capillary electrophoresis (CE) instruments with capacitively coupled contactless

30 conductivity detection (C^4D), which can be realized even when only a modest financial

31 budget and limited expertise are available. Advantageous features and considerations of these

32 instruments are detailed following their pilot deployment in Vietnam. Different categories of

33 ionic species, namely major inorganic cations (K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+) and major

34 inorganic anions (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, phosphate) in different water matrices in Vietnam

35 were determined using these in-house fabricated instruments. Inorganic trivalent arsenic

36 (As(III)), which is the most abundant form of arsenic in reducing groundwater, was

37 determined with CE-C^4D. The effect of some interfering ions in groundwater on the analytical

38 performance was investigated and is highlighted. The results from in-house-made CE-C^4D-

39 instruments were cross-checked with those obtained with the standard methods (AAS, AES,

40 UV and IC), with correlation coefficients $r^2 \geq 0.9$ and deviations from the referenced results

41 less than 15 %.

42

43

44

45

46

47

48

49

50

-3-

51　**1. Introduction**

52　The concentrations of major ionic species, *i.e.* K^+, Na^+, Ca^{2+}, Mg^{2+}, NH_4^+, Cl-, NO_3^-, NO_2^-,

53　SO_4^{2-} and phosphate are the primary indicator for evaluation of water quality. Whether it is

54　rain water, surface water or groundwater, only when the concentrations of these ions are

55　determined to be within the regulated ranges, further analyses of other compounds (heavy

56　metals, arsenic for instance) for confirmation of water quality are implemented. In Vietnam,

57　groundwater has been used as an important source of drinking water, especially in rural areas

58　[1, 2]. The quality of the groundwater therefore is controlled periodically by monitoring the

59　concentrations of different ionic species, of which those of major inorganic anions and cations

60　are the first parameters to be determined. So far, inorganic cations usually have been

61　determined with flame atomic absorption spectrometry (F-AAS, for earth alkali ions) or flame

62　atomic emission spectrometry (F-AES, for alkali ions), whereas most of the inorganic anions

63　have been determined with ion chromatography (IC) [1, 3-5]. Ammonium and phosphate content

64　have been determined spectrophotometrically using respectively the nitroprusside and

65　molybdenum blue methods [1, 3-5]. The need for these different instrumental methods

66　accompanied with different sample storage strategies for subsequent in-lab analyses renders

67　this water quality-control operation costly (with AAS, AES, IC) and time consuming. This

68　monitoring operation therefore could be implemented only by central / national institutions

69　with sufficient infrastructure support and funding. Routine analyses of the ionic species of

70　water in local laboratories with limited financial resources have hardly been possible so far.

71

72　The aforementioned issue led to the desire for a more approachable alternative for water

73　analysis. From our point of view, the most suitable option is the employment of a system

74　based on capillary electrophoresis (CE) with capacitively coupled contactless conductivity

75　detection (C^4D). In this case, ionic species are electrophoretically separated by application of

-4-

76   a high voltage along a narrow separation capillary and are detected based on the difference of

77   their electrical conductivities from that of the background electrolyte (BGE). Fundamental

78   aspects of C^4D can be found in [6-13], whereas applications of CE-C^4D for water analyses can be

79   found in several reviews [8, 14-18]. While commercial CE-C^4D benchtop instruments for such

80   operations are available, an option that is more suitable for modest infrastructures is the

81   construction and utilization of CE-C^4D instruments which were designed and developed in

82   our laboratory. These systems are referred as in-house-made CE-C^4D throughout the text. As

83   for CE-C^4D both the separation and detection of ions are based on electronic principles and

84   the method only requires low-pressure fluidic components, CE-C^4D offers many

85   advantageous features, including the possible translation into portable instrumentation, high

86   configuration flexibility and ease in construction and operation. Since the launch of the first

87   in-house-made (portable) CE instrument in 1998 [19], different prototypes have been developed

88   and introduced by Hauser and coworkers, ranging from instruments with manual injection and

89   flushing [20-22], systems where this has been semi-automated [23] to fully automated single-

90   channel versions [24, 25 26 27] and dual-channel configurations using one common buffer [28, 29]. In

91   parallel, significant contributions have been made by other groups to in-house-built (portable)

92   CE instrumentation. The more recent works were communicated by Breadmore *et al*. for

93   automated pKa determination [30] and for simultaneous separation of anions and cations [31],

94   Kaljurant *et al*. for fingerprinting postblast explosive residues [32], Porto *et al*. for analysis of

95   ecstasy tablets [33] and Gaertner *et al*. for on-site food analysis [34]. A review on all in-house

96   made (portable) CE instruments up to 2013 could be found in [35, 36]. The C^4D design has also

97   been refined to match this evolution of CE setups. The most recent versions were designed for

98   ease of construction and were miniaturized by integrating the entire circuitry in the detection

99   cell and built for battery operation [28, 37]. An alternative compact version of C^4D-cells has also

100   been described by Lago and coworkers [38]. For good performance with CE-C^4D, BGEs having

-5-

101   low specific conductivities but high ionic strengths are preferable. Organic molecules with

102   low / moderate mobilities are thus normally used to prepare the BGE solutions. More details

103   on guidance for BGE selection for CE-C^{4}D operation can be found in [8, 17, 39].

104

105   Herein, the feasibility of the employment of in-house-built CE-C^{4}D-instruments for water

106   analysis as an alternative to the standard techniques (*i.e.* AAS, AES, IC and UV) is evaluated.

107   The case study was implemented in Vietnam where these systems have been deployed for

108   systematic analyses of different surface water and groundwater matrices. Some considerations

109   on the use of in-house-made CE-C^{4}D as well as the effects of some interfering ions on the

110   analytical performance are discussed. In addition to the determination of major inorganic

111   cations and anions, the CE-C^{4}D approach was applied to the direct analysis of the widely

112   present inorganic tri-valent arsenic As(III) in anaerobic groundwater, taking into account the

113   adverse effect of the groundwater matrix (*i.e.* the abundant presence of ferrous and

114   bicarbonate / carbonate ions). Arsenic contamination in groundwater is a highly critical issue

115   for the water supply arrangements in the Red River Delta of Vietnam [2, 40]. Sensitive

116   determination of arsenic in groundwater is normally carried out with hydride vapor generation

117   (HVG) - AAS [41]. CE has also been coupled with different detection / preconcentration

118   techniques for arsenic determination / speciation in water [42-50]. In our pioneer work on arsenic

119   determination by CE-C^{4}D [42], it was possible to detect As(III) prepared in standard solutions

120   down to 22 µg / L. The direct determination of As(III) in groundwater samples at the time

121   however was not successful due to the presence of interfering ferrous ion. As(III) had to be

122   oxidized to As(V) to be analyzed under acidic conditions to eliminate the adverse effect of

123   this ion. The groundwater matrix effect on the CE-C^{4}D performance for the determination of

124   As(III) was not considered in that work. In this study, As(III) in groundwater samples was

125   directly quantified with the improved detection limit (LOD) of 5 µg / L. This LOD is below

-6-

126   the regulated level of 10 μg / L for As(III) in drinking water that was set by the Environmental

127   Protection Agency (EPA) in 2008 [51].

128

129   **2. Experimental**

130   **2.1. Chemicals and Materials**

131   All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs,

132   Switzerland) or Merck (Darmstadt, Germany). Stock solutions (10 mmol/L) of chloride,

133   nitrate, sulfate, nitrite, phosphate were used for the preparation of the standards of inorganic

134   anions, using their corresponding sodium or potassium salts. Those of the inorganic cations

135   (ammonium, potassium, calcium, sodium and magnesium) were prepared from the chloride

136   salts. Tri-valent arsenic solution was prepared from sodium (meta)arsenite (Fluka, Buchs,

137   Switzerland). Chemicals used for preparation of CE-C⁴D buffers include: arginine (Arg),

138   acetic acid, histidine (His), 18-crown-6, cetyltrimethylammonium bromide (CTAB), 2-(N-

139   morpholino)ethanesulfonic acid (MES), 3-(N-Morpholino)propanesulfonic acid (MOPS), *N*-

140   Cyclohexyl-2-aminoethanesulfonic acid (CHES), tris(hydroxymethyl)aminomethane (TRIS)

141   and 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS).

142

143   Fused silica capillaries of 50 μm ID and 365 μm OD were obtained from Polymicro

144   Technologies (Phoenix, AZ, USA). Before use, the fused silica capillaries were pre-

145   conditioned with 1 M NaOH for 10 min and deionized water for 10 min prior to flushing with

146   the buffer. The capillaries were then used continuously for successive analyses. Deionized

147   water purified using a water purification system from Millipore - model Simplicity UV

148   (Bedford, MA, USA) was used for the preparation of all solutions and for sample dilution if

149   required.

150

151   **2.2. Instrumentation**

152   Both manual and automated in-house-built CE instruments were used for analytical method

153   development and sample analyses. Details on the construction and operation of different in-

154   house-made CE prototypes can be found in [20, 21] for the single-channel version with manual

155   siphoning injection, [23] for the semi-automated single-channel setup, [24, 25 26 27] for the

156   automated single-channel variants and [28, 29] for the multi-channel configurations. The

157   automated CE instruments were controlled via a home-made computer program written with

158   either LabView for Windows XP or Arduino. The controlling program has a graphical user

159   interface that allows facile and intuitive operations.

160

161   Detection was carried out with miniaturized high voltage (HV) - C^4D built in-house according

162   to the design reported previously [28]. The resulting signals were recorded with a 12 V DC-

163   powered E-corder 201 data acquisition system (eDAQ, Denistone East, NSW, Australia)

164   connected to the USB-port of a personal computer. For data processing, the program Chart

165   (version 5.1) developed by eDAQ was used. For powering the electrophoretic and fluidic

166   parts, a lithium battery pack of 14.8 V and a capacity of 6.6 Ah (CGR 18650CG 4S3P,

167   Contrel, Hünenberg, Switzerland) fitted with a voltage regulator for production of a 12 V

168   output was used. A separate pair of smaller Li-ion batteries with a capacity of 2.8 Ah each

169   (CGR 18659CG 4S1P, Contrel), which was fitted with positive and negative 12 V regulators,

170   provided the split ±12 V supply for the C^4D circuitry. Alternatively, main power can be

171   utilized when available.

172

173   **2.3. Field sampling**

174   *Groundwater*

175   Groundwater was sampled from the boreholes using a down-hole pump (model GP 1692,

176   Whale, Bangor, N. Ireland, UK). Five borehole volumes were flushed before taking the

177   sample. Groundwater was immediately filtered with 0.45μm cellulose acetate membrane

178   filters (Sartorius, Göttingen, Germany) which were pre-flushed with nitrogen gas to remove

179   oxygen trapped inside the membranes, and then transferred into two 250 mL bottles for

180   subsequent CE-C^{4}D measurements. For subsequent cross- checking purposes, other separated

181   bottles of groundwater samples were collected as well. The bottles served for analyses of Na^+,

182   Ca^{2+}, Mg^{2+} and K^+ were preserved with 2% of a 7 M HNO_3 solution and refrigerated until

183   analysis in the laboratory with AAS and AES. Samples for NH_4^+ and major inorganic anions

184   were collected in 20-mL polypropylene vials and frozen immediately after sampling for later

185   measurement with UV-Vis and IC, respectively.

186

187   For groundwater samples used for As(III) determination with CE-C^{4}D, 1,10-Phenanthroline

188   was added into the sample after filtration to complex with ferrous ion in order to avoid

189   aerobically-induced precipitation of ferric hydroxide that may lead to co-precipitation of

190   inorganic arsenic species. The samples were then flushed through cartridges containing a

191   strong cation exchanger Wolfatit KPS 200 (VEB Farbenfabrik Wolfen, Germany) which

192   released protons to react immediately with bicarbonate / carbonate in groundwater to form

193   carbon dioxide. The sample was purged with nitrogen to completely remove the produced

194   carbonic gas. Prior to each analysis, the sample was alkalized to pH 9.2 with arginine. The

195   final sample solution contained 20 mM of Arg and 1.8 mM of 1,10-phenanthroline.

196

197   For subsequent cross-checking purpose, aqueous As (V) and As (III) ions were separated by

198   filtering the water sample first through a 0.2 μm membrane filter (Sartorius, Göttingen,

199   Germany) and then a disposable anion exchange cartridge [52], at a flow rate of 5 - 6 mL/min

-9-

200   using a syringe. The anion exchange cartridge was mounted directly on the filter and the

201   combination was carefully flushed with nitrogen before use. The cartridges contained 0.8 g

202   aluminosilicate adsorbent that selectively adsorbs As (V) but not As (III) [3]. The sample

203   containing only As (III) was then acidified with hydrochloric acid to pH < 2 and stored at 4 °C

204   until subsequent in-lab analysis.

205

206   *Surface water*

207   20 water samples from 5 lakes in Hanoi (Vietnam) were collected for monitoring of the

208   concentrations of Cl^-, NO_3^-, NO_2^-, SO_4^{2-}, K^+, NH_4^+, Mg^{2+}, Ca^{2+} and Na^+ in an annual water

209   quality control campaign. Water samples were collected at 20 cm below the surface, pre-

210   filtered with 2 μm paper filters (for lakes containing much algae and having a deep green

211   color) and finally filtered with 0.45μm membrane filters (Sartorius, Göttingen, Germany).

212

213   **2.4. Analytical methods**

214   All CE-C^{4}D operations for determination of major inorganic anions and cations in ground and

215   surface water samples were carried out immediately upon conclusion of the sampling

216   campaign to avoid / minimize sample nature modification. Samples were fed into the CE-C^{4}D

217   systems manually (without autosampler). Hydrodynamic sample injection was carried out

218   either via the siphoning effect (with the manual or semi-automated version) or via

219   pressurization of the sample flow at the ground end of the capillary (with the automated

220   systems). As thermostated chambers were not included in our CE-C^{4}D instruments, on-site

221   measurements were implemented only when the external temperature was moderate (25°C -

222   35°C) and the humidity was not too high (less than 90 %). Otherwise these operations were

223   done either in an air-conditioned room or in the lab. Determinations of inorganic anions,

224   cations and phosphate were carried out independently on three different CE-C^{4}D runs with the

-10-

225   average time for each run of about 15 min. Unless otherwise stated, a BGE composed of 12

226   mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with acetic acid and one composed of

227   12 mM histidine adjusted to pH 4 with acetic acid were employed for the determination of

228   major inorganic cations and anions, respectively. The buffer used for phosphate determination

229   was composed of 1 mM histidine adjusted to pH 3.5 with acetic acid. Samples collected from

230   5 lakes in Hanoi were analyzed with CE - C^{4}D using the aforementioned BGE compositions.

231   Samples were diluted with deionized water if needed to avoid peak overlaps with CE-C^{4}D

232   when the concentrations were out of the calibration ranges.

233

234   The surface water and groundwater samples were also transported to the lab and stored at 4 °C

235   for subsequent in-lab analysis and cross-checked with the standard methods. The cations *i.e.*

236   earth alkali and alkali metals were analyzed by F-AAS or F-AES on a Shimadzu AAS 6800

237   instrument. Anions were analyzed by IC using a Shimadzu LC20AD/HIC-20ASuper

238   instrument. Ammonium was determined spectro-photometrically using nitroprusside whereas

239   phosphate was analyzed with the molybdenum blue method using a Shimadzu UV 3101

240   equipment. More details on analytical procedures can be found in [1, 3].

241

242   As (III) in groundwater samples was determined with CE-C^{4}D using the standard addition

243   method (3 points) with the average analysis time for each sample of 45 min.. The final sample

244   solution contained 20 mM of Arg and 1.8 mM of 1,10-phenanthroline. The optimized BGE

245   for As(III) analysis was 12 mM MES / 21 mM Arg / 30 µM CTAB (pH 8.9). Samples were

246   electrokinetically injected at - 6 kV for 60 s and separated at - 20 kV in a capillary of 60 cm

247   total length. The C^{4}D detector was situated at the effective length of 52 cm. For cross check,

248   arsenic was determined with a Shimadzu AAS 6800 instrument using a hydride vaporization

249   generator (HVG) according to the standard method detailed in [53].

-11-

250

251   **3. Results and Discussion**

252   **3.1. Instrumental aspects**

253   *3.1.1. General considerations*

254   For the in-house-built CE systems, the complex options which are often found in bench-top

255   commercial CE instruments, *i.e.* a sample tray, robotic arm for vial lifting and thermostated

256   chamber were excluded in order to minimize the power consumption and the construction

257   cost, as well as to maximize the portability. When using commercial benchtop instruments

258   often the capillaries are reconditioned between sample runs, typically with sodium hydroxide

259   solutions. This is a complication which is not always necessary, especially when working with

260   non-wall-adsorbing inorganic ions. From our experience, when allowing equilibration of the

261   capillary with the BGE for an extended period of time (hours) before analyses, good baseline

262   stability and reproducibility of migration times are obtained when the capillaries are simply

263   flushed with BGE between successive runs.

264

265   A CE-C^{4}D system should always be earthed because the high voltage supplies may lead to

266   charging up of the (insulated) boxes of the instruments, which in turn can create a hazard to

267   the user if the system is not earthed. This can however not always be done readily because in

268   developing countries in general and in Vietnam in particular, the earth is often excluded from

269   the main sockets of the electricity system for economical reasons. An alternative earth then

270   has to be improvised. If available, a connection to a metallic water pipe may be made, or a

271   metallic rod is buried in the ground.

272

273   Another challenge to overcome when working with CE-C^{4}D in Vietnam is the high humidity.

274   While a CE-C^{4}D system may work fine for in-lab analyses in dry weather, noisy signals were

-12-

275   at times observed when the humidity increased. The problem became more pronounced when

276   the systems were set up outside the lab for mobile deployment. This is due to the discharge of

277   the applied high voltage through humid air which renders the high voltages for separation not

278   maintainable. The discharge could also produce pronounced noise on the C^4D signal if the

279   detector was not positioned far enough from the high-voltage electrode. To solve the problem,

280   the first approach is to make the high voltage cage as large as possible and free of conducting

281   parts inside. The vial containing the BGE, the capillary end and the electrode should be

282   positioned in the center of this cage. Secondly, a reduction in the high voltage from the 30 kV

283   possible with conventional instruments may be necessary.

284

285   When possible the CE system should be operated in an air-conditioned room to avoid

286   temperature variations and high humidity. This may not lead to additional expenses as the

287   households in Vietnam are often equipped with air-conditioners for their own use. Application

288   of standard addition or internal standardization method may be needed for peak identification

289   and quantification when there are significant drifts of baseline and migration time due to

290   ambient temperature fluctuations in the absence of an air-regulated condition.

291

292   *3.1.2. Specific considerations for different in-house-made CE-C^{4}D prototypes*

293   Various in-house-made CE-C^4D setups, including instruments with manual injection and

294   capillary flushing [20, 21], a semi-automated instrument with siphoning injection [23], instruments

295   with fully automated injection with a single-channel arrangement [24, 25] and an instrument with

296   fully automated injection having a dual-channel configuration with the same buffer [28] were

297   deployed in Vietnam for water analysis. A block-diagram showing the basic set-up of a CE

298   system with some automatable parts as an option and a photo demonstrating an in-house-made

299   CE system in operation are given in Fig. 1A and 1B, respectively. Portable CE instruments

-13-

300   were employed for some on-site operations. For in-lab work, *i.e.* method development and the

301   major part of sample analyses, the manual and automated versions were used. While these

302   systems showed no significant performance difference in terms of detection sensitivity (see

303   table S1 in the ESI file), each configuration has its own positive and limited points for

304   consideration. Manual and semi-automated CE-C^{4}D setups are the least expensive and

305   simplest versions that are most suitable for wide-spread use. Roughly estimated construction

306   costs for these systems are 5,000 and 7,000 Euros, respectively. The most essential part is a

307   high voltage module, which can normally go up to 30 kV. These are available from different

308   suppliers and have different feature sets [54]. For a partly automated system extra cost is

309   incurred by valves and gas pressure regulators. No controlling program is needed and all

310   operations, *i.e.* application of a high voltage, capillary flushing, and sample injection are

311   carried out using simple mechanical switches. These versions however require frequent

312   intervention of an operating person and therefore are not suitable for unattended analysis. The

313   employment of siphoning technique for hydrodynamic sample injection may produce some

314   contaminant peaks in the electropherograms if air containing suspended particles is accidently

315   sucked into the injection end of the capillary during its movement. To avoid this problem, the

316   capillary's injection end should be always immersed in a solution (either the BGE or sample)

317   when it is lifted to a higher position for siphoning injection. Employment of gloves is

318   recommended to prevent any contamination due to the sweat retained onto the capillary tip

319   when it is in contact with the operator's bare fingers.

320

321   The automated versions of in-house-built CE-C^{4}D [24, 25, 28] on the other hand can eliminate

322   some aforementioned inconveniences encountered in manual and semi-automated versions.

323   No capillary back and forth movement is needed and the systems can be operated in an

324   unattended manner. In the case of the dual-channel CE system using the same buffer [28],

-14-

325   different ionic categories, *i.e.* cationic and anionic species can be simultaneously determined

326   in a single run. Higher construction cost (up to 15,000 - 20,000 Euros) and requirement of

327   certain knowledge about operation of computer-based controlling programs however are two

328   considerations to be taken into account when only modest financial funding and little

329   expertise are available. These automated versions may be more vulnerable to the noisy signal

330   problem when good grounding is not guaranteed. Commercial C^4D and data acquisition unit

331   with software are available for some thousands of Euros. If the electronics expertise is

332   available, a C^4D can be built in-house for a few hundred Euros depending on the design. A

333   good data acquisition system is essential and will have to be bought. The expenses for the

334   mechanical hardware are minimal, but workshop cost is possibly incurred.

335

336

337   **3.2. CE-C^{4}D determination of major inorganic cations and anions in different water**

338   **matrices**

339   *3.2.1. Determination of major inorganic cations and anions in groundwater*

340   The optimizations of BGE compositions were implemented for best CE-C^{4}D performances

341   with the groundwater matrices, taking into account the presence of some interfering

342   parameters such as carbonate and ferrous ions. Baseline separations of major anions could not

343   be achieved in our preliminary experiments with different BGE solutions composed of His /

344   MES, MOPS / His or TRIS / MOPS (see Fig. S1 in the ESI file). In addition, at high pH of the

345   BGE the obtained CE-C^{4}D baseline was not stable and drastic baseline drifting was observed

346   from time to time. These may occur due to the presence of dissolved organic carbon and high

347   alkalinity concentrations which could be up to 1000 mg HCO_3^{2-} /L in groundwater [3-5]. On the

348   other hand, when working with acidic BGE, this baseline fluctuation problem was alleviated.

349   Another consideration was the presence of some major ions in groundwater at very high

-15-

350　concentrations (for example Cl^- upto 20 mg/L and Ca^{2+}, Mg^{2+} upto 40 mg/L) that may overlap

351　the adjacent peaks of some other target ions. This prediction of ion concentrations was made

352　based on data reported in [1, 3]. Accordingly, BGE optimization for CE-C^{4}D separation of

353　inorganic cations and anions in groundwater was carried out based on an acidic condition that

354　was already successfully applied for surface water [24, 25]. It was found that a BGE containing

355　12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with acetic acid offered good

356　separations of inorganic cations. 18-crown-6 was included to facilitate the separation of K^+

357　and NH_4^+ thanks to its selective complexation with K^+ that leads to the increase in the

358　migration time of K^+ compared to that of NH_4^+. In groundwater in Vietnam, ferrous cations

359　are from time to time found at concentrations of up to 20 mg/L (360 μM) [1, 3-5]. The presence

360　of ferrous cation at high concentrations (more than 2 mg/L or 36 μM) may cause peak overlap

361　with Mg^{2+} (see Fig. S2 in the ESI file). This problem, on the other hand, can be avoided just

362　by allowing aqueous ferrous cation to be naturally oxidized to form ferric hydroxide

363　precipitates when aerated for 15 min.Sample filtering was needed to remove the formed

364　precipitates prior to CE-C^{4}D determination of major inorganic cations.

365

366　For separation of anions, 18-crown-6 was not needed and was removed from the electrolyte.

367　At this low pH the electro-osmotic flow (EOF), which is the bulk movement of the liquid

368　inside the capillary under an applied electrical field, is suppressed; therefore no EOF

369　modification is needed. While a BGE consisting of 12 mM histidine adjusted to pH 4 with

370　acetic acid resulted in good separations of major anions including Cl^-, SO_4^{2-}, NO_3^{2-} and NO_2^-,

371　it was found experimentally that this high content of histidine in BGE hindered sensitive

372　detection of phosphate (see Fig. S3 in the ESI file). To improve the sensitivity for phosphate,

373　the concentration of histidine in BGE was reduced and the optimized BGE for phosphate

374　determination was composed of 1 mM histidine adjusted to pH 3.5 with acetic acid.

-16-

375

376   The effect of bicarbonate on the performance of anions separation is illustrated in Fig.2. By

377   increasing the added concentration of bicarbonate from 0 to 600 mg/l (10 mM) into a standard

378   solution containing inorganic anions of 100 µM, it was found that the optimized BGE at pH =

379   4 can tolerate the presence of bicarbonate up to 300 mg/L (5 mM). At bicarbonate

380   concentrations higher than 5 mM, the peaks of Cl^-, NO_3^-, SO_4^{2-} and NO_2^- became distorted

381   and were difficult to quantify. The reason for this problem however is not understood. A

382   solution for avoiding this bicarbonate disturbance can be direct acidification of the sample

383   with acetic acid prior to anions analysis with CE-C^4D and the subsequent purging the samples

384   by nitrogen stream.

385

386   An example of the analyses of standard mixtures of cations and anions with three different

387   BGE solutions is shown in Fig. 3. The calibration data for the ions of interest is given in Table

388   1. The detection limits, determined from the peak heights corresponding to 3 times the

389   baseline noise, were in the range of 2.5 - 10 µM. For inorganic cations, linear calibration

390   curves were obtained up to 2000 µM whereas somewhat shorter linear ranges were achieved

391   for the inorganic anions (up to 1000 µM). The obtained correlation coefficients were better

392   than 0.99. The repeatability of the measurements of peak areas and migration times were

393   better than 5 % and around 2 % respectively.

394

395   Electropherograms of one groundwater sample are demonstrated in Fig. 4. As can be seen,

396   Ca^{2+}, Na^+, Mg^{2+}, Cl^- and SO_4^{2-} appeared in abundant amounts, reflected by high and large

397   peaks whereas much smaller peaks of NH_4^+ and K^+ were observed. No nitrogen-containing

398   anions (NO_3^- and NO_2^-) were found in this groundwater sample. The concentration of

399   phosphate (if any) was below the quantification limit; therefore the electropherogram of the

-17-

400   CE channel used for phosphate determination is not shown. To verify the reliability of the

401   results obtained with CE-C^{4}D, all concentrations were cross-checked with the standard

402   reference methods, *i.e.* AAS, IC and UV spectrometry. High correlation coefficients with r$^2 \geq$

403   0.9 were achieved showing very good agreement of the results obtained with CE-C^{4}D and

404   those with the standard reference techniques (see Tables S2 and S3 in the ESI file). Among

405   the 15 groundwater samples tested, NO_3^- and NO_2^- were not detected with our CE-C^{4}D

406   method whereas phosphate was found in only 1 sample. The concentration of phosphate

407   determined by CE-C^{4}D in this case fell in the range between 5 µM (LOD) and 10 µM (LOQ).

408   Verification with IC revealed a phosphate concentration of 6 µM, which matched well with

409   the result obtained with CE-C^{4}D. Note that the concentrations of nitrogen-containing ions and

410   phosphate can fluctuate significantly in different seasons and are also much dependent on the

411   nature of the groundwater. Most groundwaters in the Red River Deltaare anaerobic. As a

412   result, dissolved inorganic nitrogen occurs mostly as NH_4^+ rather than NO_3^- and NO_2. The

413   phosphate concentration below the LOD in most of the collected groundwater samples can be

414   reasonably explained that these groundwater resources are neither close to the domestic waste,

415   agricultural activities nor natural mineral resource containing phosphate (*e.g.* apatite).

416

417   3.2.2. *Major inorganic cations and anions in lake water samples*

418   The BGE compositions optimized for groundwater analysis were employed for CE-C^{4}D

419   determination of ionic species in water from 5 lakes in Hanoi. Fig. 5 shows electropherograms

420   of some surface water samples.   The data obtained with CE-C^{4}D can be seen in Table S4 in

421   the ESI file, with deviations obtained from some cross-checks with referenced methods

422   always less than 15 %. NO_2^- and NO_3^- were detected in many surface water samples, with the

423   concentrations of NO_2^- in most of the cases exceeding the acceptable level in Vietnam (0.01

424   mg/L, or $\approx$ 0.2 µM). The cationic NH_4^+ was also present at concentrations higher than the

425   acceptable level (0.1 mg/L). The presence of these nitrogen-ionic species and the phosphate

426   concentrations below 5 µM in these water samples are due to the biological activity of algae

427   growing in the lakes. The growing activity of algae (or many other lemma species in aqueous

428   media) can be connected with nitrogen fixation mechanism, which in turn may promote the

429   formation of ionic nitrogen species.

430

431   **3.3. Determination of As(III) in groundwater**

432   Together with Bangladesh and India, Vietnam belongs to the countries in South and South

433   East Asia suffering from a natural contamination of groundwater by arsenic. Under the

434   reducing conditions of the Red River Delta groundwater, together with the abundant presence

435   of microbacteria and organic matter, ferrous and As (III) ions can be released from sediment

436   into groundwater [3, 40]. We showed earlier that As(III) in standard solutions could be

437   determined by CE-C^{4}D with the LOD of 22 µg/L [42]. The interfering effect of ferrous and

438   bicarbonate / carbonate ions on CE-C^{4}D determination of As(III) in groundwater samples

439   however was not considered in this pioneer work. Herein we propose a new CE-C^{4}D method

440   for direct quantification of As(III) species in groundwater taking into account various

441   interfering parameters which may adversely affect its analytical performance. The detection

442   limit for As(III) determination was improved to 5 µg / L (determined for standard solutions

443   without recourse to the standard addition method), which is below the regulated level of

444   arsenic in water (10 µg /L).

445

446   *3.3.1.BGE composition optimization*

447   As arsenous acid is dissociated only at high pH ($pK_{a1} = 9.2$), BGE for CE separation of

448   As(III) should be under a basic medium to assure its negative charge. Various BGE

449   compositions based on combinations of MES, MOPS, CHES or CAPS with either of arginine,

-19-

450 diethylamine, triethylamine and tert-butylamine were tested. It was found that only Arg -

451 based BGEs offered clear and sharp peaks of As(III). It is shown in Fig. 6 electropherograms

452 for the separation of As(III) using buffers composed of Arg and either of MES, MOPS,

453 CHES or CAPS. Note that the digitized appearance of the electropherograms is due to the

454 low data acquisition rate that was set to the ADC system by the operator. Such appearance

455 nevertheless did not significantly affect the As(III) identification and quantification. While

456 both CAPS / Arg and MES / Arg produced the highest signal to noise ratios, the longer

457 distance between the peak of As(III) and that of EOF in the case of MES / Arg rendered the

458 identification and quantification of As(III) easier. After optimization of buffer's pH from 8.3

459 to 9.2 by varying the concentrations of MES and Arg (see Fig. S4 in the ESI file), BGE

460 composed of MES (12mM) and Arg (21 mM) at pH 8.9 was found to provide the highest and

461 sharpest peak of As(III). CTAB of 35 µM was added into the BGE solutions for reversal of

462 EOF to facilitate the electrophoretic movement of the slow-migrating arsenite at high pH. In

463 order to increase the amount of As(III) injected into the capillary for sensitivity enhancement,

464 the groundwater samples were firstly alkalized with 20 mM Arg to pH 9.2 and then

465 electrokinetically injectied at -6 kV for 60 s to employ the stacking of negatively charged

466 As(III) at the boundary of the buffer and the sample zones for on-line pre-concentration.

467 Compared to hydrodynamic injection (siphoning at 20 cm high for 60 s), the electrokinetic

468 injection mode offered a 4-time improved sensitivity. Electrokinetic injection was prefered in

469 this case because 1) all groundwater samples had a relatively low conductivity compared to

470 that of the BGE and 2) addition of Arg into the groundwater samples helped equalize their

471 conductivity. These in turn minimized the sampling bias problem inherent to electrokinetic

472 injection.

473

474 *3.3.2. Effect of major inorganic anions on As (III) measurement performance*

-20-

475   One consideration with the chosen electrokinetic injection mode is the sampling bias due to

476   the abundant presence of major fast-migrating inorganic anions in the groundwater matrix. It

477   was found experimentally that when their concentrations exceeded 5 mg /L the peak of As(III)

478   was decreased by 30 % compared to that obtained with a standard solution prepared in

479   deionized water. To minimize this bias problem, the standard addition method was

480   implemented to avoid significant measurement deviation caused by interrering ions that may

481   exceed 5 mg/L in the sample matrix .

482

483   *3.3.3. Effect of bicarbonate / carbonate on As (III) measurement performance*

484   The abundant presence of bicarbonate / carbonate in groundwater may result in distortion of

485   the peaks of target analytes, as already illustrated in Fig. 2. In the case of As(III)

486   measurement, the peak of arsenite became much smaller at the alkalinity concentrations

487   higher than 30 mg/L (0.5 mM, see Fig. S5 in the ESI file), which in turn may affect adversely

488   the sensitivity for As(III). Note that the peak of As(III) is well separated from that of

489   bicarbonate and those of other faster-migrating anions (*i.e.* Cl^- ,SO_4^{2-}, NO_3^-, NO_2^-). BGE

490   optimization was thus carried out for sensitivity for As(III) rather than selectivity.

491   Conventional acidification of the sample with a strong acid to convert bicarbonate / carbonate

492   into carbonic gas was not feasible in this case due to the need for use of a high pH (pK_a of

493    $H_3AsO_3 = 9.2$) and avoidance of strong anion addition that may adversely affect electrokinetic

494   injection. To solve this problem, the groundwater samples were flushed through a strong

495   cation exchange resin KPS 200 that released protons, leading to the formation of carbonic gas

496   without significantly changing the pH of the groundwater sample. The sample was purged

497   with nitrogen to remove the produced carbonic gas. Another advantage of this technique is

498   that no additional anion was present in the sample matrix after this bicarbonate / carbonate

-21-

499   elimination process. This technique worked well even when the bicarbonate concentration in

500   the sample was increased up to 1000 mg /L (17 mM), al illustrated in Fig. 7.

501
502
503   *3.3.4. Effect of ferrous cation on As (III) measurement performance*

504   Ferrous cation isfrequently detected in groundwater in Vietnam at the concentrations up to 20

505   mg/L [3-5]. At high pH and aerobic conditions, ferrous ion is easily converted to ferric oxy-

506   hydroxide that adsorbs and co-precipitates aqueous arsenic species. Removal of ferrous ion

507   from the groundwater samples was therefore required to guarantee accurate determination of

508   As(III) concentrations. Four complexing reagents, namely 4-(2-pyridylazo)resorcinol (PAR),

509   1-(2-pyridylazo)-2-naphthol (PAN), ferroin and 1,10-phenanthroline, that could produce

510   stable complexes with ferrous and ferric cations at pH from 6 to 10 were tested. As illustrated

511   in Fig. 8, the inclusion of 1,10- phenanthroline into the sample offered a stable baseline with

512   the height and sharpness of As(III) peak remaining unchanged even at the abundant presence

513   of ferrous cation at 20 mg/L. This however was not the case with the other complexing

514   reagents (see Fig. S6 in the ESI file).

515

516   *3.3.5. Determination of As (III) in groundwater samples*

517   For CE-C[4]D determination of As(III) in groundwater, after filtration 1,10-phenanthroline (18

518   mM) was added to the samples at the volumetric 1,10-phenanthroline / sample ratio of 1/10.

519   The samples were then flushed through a strong cation exchange resin KPS 200, alkalized

520   with 20 mM Arg to pH 9.2 prior to electrokinetic injection at -6 kV for 60 s. As(III) was then

521   electrophoretically separated from the matrix using a BGE composed of 12 mM MES, 21 mM

522   Arg and 30 µM CTAB. Salient performance data for As(III) measurement with this optimized

523   procedure includes a calibration curve (based on peak areas *vs*. predefined concentrations)

524   acquired from 20 to 150 µg/L with a correlation coefficient r^2 of 0.998, the limit of detection

-22-

525   of 5 µg/L and a relative standard deviations (RSDs) for migration time and peak area of 1 %

526   and 7 %, respectively. The developed method was then applied for determination of As(III) in

527   15 groundwater samples collected in Van Phuc (Hanoi) which is a typical "hot-spot" of

528   arsenic contamination in Vietnam [1]. Electropherograms for separation of As (III) in a

529   groundwater sample with the standard addition method are shown in Fig. 9. Note that the

530   standard addition method alone may be adequate to minimize bias caused by the complex

531   sample matrices. Sample dilution nevertheless is still needed to render the measured As(III)

532   concentration fitting well for the linear (calibrated) range of 20 - 150 µg/L.. Good agreement

533   between the data obtained with CE-C^{4}D and those with the standard reference HVG-AAS

534   method was achieved, with measurement deviations less than 7 % and correlation coefficient

535   r^2 of 0.9967 (see table S5 in the ESI file). High concentrations of As (III) from about 50 µg/L

536   to 400 µg/L were found in these samples, indicating serious contamination of the groundwater

537   in Van Phuc with arsenic. Note that the acceptable level of arsenic in groundwater that is

538   regulated by World Health Organization (WHO) is 10 µg/L.

539

540   **4. Conclusions**

541   In-house-made CE-C^{4}D was found to be a simple and inexpensive solution for analysis of

542   various inorganic ionic species in different water matrices. A simple CE-C^{4}D setup can be

543   built at the construction cost of 5000 - 7000 Euros. This approach eliminates the requirement

544   of costly and sophisticated commercial instrumentation, thus rendering the water-quality

545   monitoring activities feasible even at local laboratories where only modest budget and limited

546   expertise are available. More laborious work with manual operations may nevertheless be

547   encountered with in-house built CE-C^{4}D instruments due to (i) exclusion of some / all

548   automated options to reduce construction cost and (ii) lack of decent controlling software.

549   Acceptable agreement between the results obtained with CE-C^{4}D for determination of major

-23-

550   inorganic ions as well as trivalent arsenic and those with the standard reference methods, *i.e.*

551   AAS, AES, IC and UV was achieved (with correlation coefficients $r^2 \geq 0.9$ and cross-check

552   deviations less than 15 %), demonstrating the reliability of the analytical data provided with

553   CE-C^{4}D. Extension of the CE-C^{4}D application spectrum to other ionic water-quality indicator

554   species (heavy metals for example) is envisaged.

555

556

565

-24-

566   **References**

567   1.   K. S. Nitzsche, V. M. Lan, P. T. K. Trang, P. H. Viet, M. Berg, A. Voegelin, B.

568   Planer-Friedrich, J. Zahoransky, S.-K. Muller, J. M. Byrne, C. Schroder, S. Behrens and A.

569   Kappler, *Sci. Total Environ.*, 2015, **502**, 526-536.

570   2.   A. van Geen, B. C. Bostick, P. Thi Kim Trang, V. M. Lan, N.-N. Mai, P. D. Manh, P.

571   H. Viet, K. Radloff, Z. Aziz, J. L. Mey, M. O. Stahl, C. F. Harvey, P. Oates, B. Weinman, C.

572   Stengel, F. Frei, R. Kipfer and M. Berg, *Nature*, 2013, **501**, 204-207.

573   3.   D. Postma, F. Larsen, N. T. Minh Hue, M. T. Duc, P. H. Viet, P. Q. Nhan and S.

574   Jessen, *Geochim. Cosmochim. Acta.*, 2007, **71**, 5054-5071.

575   4.   D. Postma, S. Jessen, N. T. M. Hue, M. T. Duc, C. B. Koch, P. H. Viet, P. Q. Nhan

576   and F. Larsen, *Geochim. Cosmochim. Acta.*, 2010, **74**, 3367-3381.

577   5.   S. Jessen, F. Larsen, D. Postma, P. H. Viet, N. T. Ha, P. Q. Nhan, D. D. Nhan, M. T.

578   Duc, N. T. M. Hue, T. D. Huy, T. T. Luu, D. H. Ha and R. Jakobsen, *Applied Geochemistry*,

579   2008, **23**, 3116-3126.

580   6.   T. D. Mai and P. C. Hauser, *Chem. Rec.*, 2012, **12**, 106-113.

581   7.   W. K. T. Coltro, R. S. Lima, T. P. Segato, E. Carrilho, D. P. de Jesus, C. L. do Lago

582   and J. A. F. da Silva, *Anal. Methods*, 2012, **4**, 25-33.

583   8.   P. Kubáň and P. C. Hauser, *Electrophoresis*, 2009, **30**, 176-188.

584   9.   P. Kubáň and P. C. Hauser, *Electrophoresis*, 2004, **25**, 3387-3397.

585   10.   P. Kubáň and P. C. Hauser, *Electrophoresis*, 2004, **25**, 3398-3405.

586   11.   J. G. A. Brito-Neto, J. A. F. da Silva, L. Blanes and C. L. do Lago, *Electroanalysis*,

587   2005, **17**, 1198-1206.

588   12.   J. G. A. Brito-Neto, J. A. F. da Silva, L. Blanes and C. L. do Lago, *Electroanalysis*,

589   2005, **17**, 1207-1214.

590   13.   A. J. Zemann, *Electrophoresis*, 2003, **24**, 2125-2137.

591   14.   P. Kuban and P. C. Hauser, *Electrophoresis*, 2014, **36**, 195-211.

592   15.   P. Kubáň and P. C. Hauser, *Electrophoresis*, 2011, **32**, 30-42.

593   16.   P. Kubáň and P. C. Hauser, *Electrophoresis* 2013, **34**, 55-69.

594   17.   P. Kubáň and P. C. Hauser, *Anal. Chim. Acta*, 2008, **607**, 15-29.

595   18.   P. Kubáň and P. C. Hauser, *Electroanalysis*, 2004, **16**, 2009-2021.

596   19.   T. Kappes and P. C. Hauser, *Anal. Commun.*, 1998, **35**, 325-329.

597   20.   P. Kubáň, H. T. A. Nguyen, M. Macka, P. R. Haddad and P. C. Hauser,

598   *Electroanalysis*, 2007, **19**, 2059-2065.

599   21.   N. T. Torres, P. C. Hauser, G. Furrer, H. Brandl and B. Mueller, *Environ. Sci.:*

600   *Processes Impacts*, 2013, **15**, 715-720.

601   22.   N. T. Torres, L. M. Och, P. C. Hauser, G. Furrer, H. Brandl, E. Vologina, M. Sturm,

602   H. Burgmann and B. Muller, *Environ. Sci.: Processes Impacts*, 2014, **16**, 879-889.

603   23.   T. A. H. Nguyen, T. N. M. Pham, T. T. Doan, T. T. Ta, J. Sáiz, T. Q. H. Nguyen, P. C.

604   Hauser and T. D. Mai, *J. Chromatogr. A*, 2014, **1360**, 305-311.

605   24.   T. D. Mai, S. Schmid, B. Müller and P. C. Hauser, *Anal. Chim. Acta*, 2010, **665**, 1-6.

606   25.   T. D. Mai, T. T. T. Pham, J. Sáiz and P. C. Hauser, *Anal. Chem.*, 2013, **85**, 2333-2339.

607   26.   J. Sáiz, T. D. Mai, P. C. Hauser and C. García-Ruiz, *Electrophoresis* 2013, **34**, 2078-

608   2084.

609   27.   J. Sáiz, T. D. Mai, L. María López, C. Bartolomé, P. C. Hauser and C. García-Ruiz,

610   *Sci. Justice*, 2013, **53**, 409-414.

611   28.   T. T. T. Pham, T. D. Mai, T. D. Nguyen, J. Sáiz, H. V. Pham and P. C. Hauser, *Anal.*

612   *Chim. Acta*, 2014, **841**, 77-83.

613   29.   J. Sáiz, M. T. Duc, I. J. Koenka, C. Martin-Alberca, P. C. Hauser and C. Garcia-Ruiz,

614   *J. Chromatogr. A*, 2014, **1372**, 245-252.

-26-

615   30.   J. M. Cabot, E. Fuguet, M. Rosés, P. Smejkal and M. C. Breadmore, *Anal. Chem.*,

616   2015, **87**, 6165-6172.

617   31.   A. J. Gaudry, R. M. Guijt, M. Macka, J. P. Hutchinson, C. Johns, E. F. Hilder, G. W.

618   Dicinoski, P. N. Nesterenko, P. R. Haddad and M. C. Breadmore, *Anal. Chim. Acta*, 2013,

619   **781**, 80-87.

620   32.   E.-G. Kobrin, H. Lees, M. Fomitšenko, P. Kubáň and M. Kaljurand, *Electrophoresis*

621   2014, **35**, 1165-1172.

622   33.   S. K. S. S. Porto, T. Nogueira, L. Blanes, P. Doble, B. D. Sabino, C. L. do Lago and L.

623   Angnes, *J Forensic Sci.*, 2014, **59**, 1622-1626.

624   34.   C. Gaertner, R. Sewart, R. Klemm and H. Becker, *Sensing Technologies for Global*

625   *Health, Military Medicine, and Environmental Monitoring Iv*, 2014, **9112**.

626   35.   A. P. Lewis, A. Cranny, N. R. Harris, N. G. Green, J. A. Wharton, R. J. K. Wood and

627   K. R. Stokes, *Meas. Sci. Technol.*, 2013, **24**.

628   36.   M. Ryvolová, J. Preisler, D. Brabazon and M. Macka, *Trends Anal. Chem.*, 2010, **29**,

629   339-353.

630   37.   M. Stojkovic, I. J. Koenka, W. Thormann and P. C. Hauser, *Electrophoresis*, 2014, **35**,

631   482-486.

632   38.   K. J. M. Francisco and C. L. do Lago, *Electrophoresis* 2009, **30**, 3458-3464.

633   39.   T. D. Mai and P. C. Hauser, *Electrophoresis*, 2013, **34**, 1796-1803.

634   40.   M. Berg, H. C. Tran, T. C. Nguyen, H. V. Pham, R. Schertenleib and W. Giger,

635   *Environ. Sci. Technol.*, 2001, **35**, 2621-2626.

636   41.   D. Q. Hung, O. Nekrassova and R. G. Compton, *Talanta*, 2004, **64**, 269-277.

637   42.   H. T. A. Nguyen, P. Kubáň, V. H. Pham and P. C. Hauser, *Electrophoresis* 2007, **28**,

638   3500-3506.

-27-

639   43.   N. Jia, M. Han, G. Zhao, L. Zhang, B. Liu and Y. Li, *Asian J. Chem.*, 2014, **26**, 5271-

640   5274.

641   44.   L. Liu, B. He, Z. Yun, J. Sun and G. Jiang, *J. Chromatogr. A*, 2013, **1304**, 227-233.

642   45.   B. Deng, X. Qin, Y. Xiao, Y. Wang, H. Yin, X. Xu and C. Shen, *Talanta*, 2013, **109**,

643   128-132.

644   46.   K. Cheng, K. Choi, J. Kim, I. H. Sung and D. S. Chung, *Microchem. J.*, 2013, **106**,

645   220-225.

646   47.   P. M. Flanigan, D. Ross and J. G. Shackman, *Electrophoresis*, 2010, **31**, 3466-3474.

647   48.   H. Zhang, J. Gavina and Y.-L. Feng, *J. Chromatogr. A*, 2011, **1218**, 3095-3104.

648   49.   O. S. Koshcheeva, O. V. Shuvaeva and L. I. Kuznetzova, *Electrophoresis*, 2009, **30**,

649   1088-1093.

650   50.   C. A. Suarez, G. C. L. Araujo, M. F. Gine, M. H. Kakazu and J. E. S. Sarkis,

651   *Spectrosc. Lett.*, 2009, **42**, 376-382.

652   51.   D. Melamed, *Anal. Chim. Acta*, 2005, **532**, 1-13.

653   52.   X. G. Meng and W. Wang, *Book of posters of the 3 rd Inter. Conf. on Arsenic

654   Exposure and Health Effect, Society of Envir. Geochemistry and Health, University of

655   Colorado at Oenner, USA*, 1998, University of Colorado at Oenner, USA.

656   53.   APHA, *22nd Edition of Standard Methods for the Examination of Water and

657   Wastewater*, 2012, American Public Health Association (APHA), Method 3113 B - 3114 B

658   54.   L. Blanes, W. K. Tomazelli Coltro, R. M. Saito, A. Van Gramberg, C. L. do Lago and

659   P. Doble, *Electrophoresis*, 2012, **33**, 893-898.

660

661

-28-

662 **Table 1**. Calibration ranges, detection limits (LODs) and reproducibility for the CE-C^{4}D

663 determination of various inorganic ionic species.

Ion	Range (μM)[a]	Correlation coefficient r^2	LOD[b] (μM)	RSD % MT[c] (n=4)	RSD % PA[d] (n=4)
Channel 1					
NH_4^+	20-400	0.999	5.5	0.7	4.2
K^+	20-400	0.997	6.0	1.4	2.7
Ca^{2+}	100-2000	0.998	4.5	1.6	2.8
Na^+	50-500	0.999	10.0	2.0	6.4
Mg^{2+}	50-1000	0.994	5.0	1.7	3.5
Channel 2					
Cl^-	50-1000	0.999	4.0	0.7	3.7
SO_4^{2-}	10 - 1000	0.998	2.5	0.8	4.3
NO_2^-	20 - 200	0.994	4.5	1.0	2.6
NO_3^-	20-200	0.992	4.5	1.2	3.4
Channel 3					
PO_4^{3-}	10-100	0.997	5.0	2.7	3.8

664 [a] 5 concentrations

665 [b] Based on peak heights corresponding to 3 times the baseline noise

666 [c] Migration time (measurement unit: second)

667 [d] Peak area (measurement unit: mV·s)

668

669 ***Determination of major inorganic cations***: Electrolyte solution: 12 mM histidine and 2 mM

670 18-crown-6 adjusted to pH 3.7 with CH_3COOH. Voltage: +15 kV. Capillary: fused-silica, 25

671 μm id, L_t = 65 cm (L_{eff} = 49 cm).

672 ***Determination of major inorganic anions***: Electrolyte solution: 12 mM histidine adjusted to

673 pH 4 with CH_3COOH. Voltage: -15 kV. Capillary: fused-silica, 25 μm id, L_t = 52 cm (L_{eff} =

674 36 cm).

675 ***Determination of phosphate***: Electrolyte solution: 1 mM histidine adjusted to pH 3.5 with

676 CH_3COOH. Voltage: 15 kV. Capillary: fused-silica, 25 μm id, L_t = 52 cm (L_{eff} = 36 cm).

677

-29-

678   **Figure captions:**

679

680   Fig. 1.   A) A block-diagram demonstrating the basic set-up of a CE system with some

681   optional automatable parts; B) Demonstration of an in-house-made CE system in

682   operation. Pt: Platinum electrode; W: waste; GND: ground electrode; BGE:

683   background electrolyte; HV: high voltage; C^4D: capacitively coupled contactless

684   conductivity detector.

685

686   Fig. 2.   Effect of bicarbonate ion on the performance of anions separation with CE-C^4D.

687   Bicarbonate at different concentrations from 0 - 600 mg/L was spiked into the

688   standard mixture solutions containing Cl^- (100 µM), NO_3^- (100 µM), SO_4^{2-} (50

689   µM), NO_2^- (100 µM) and phosphate (100 µM). Electrolyte solution: 12 mM

690   histidine adjusted to pH 4 with CH_3COOH; Voltage: - 15 kV; Capillary: fused-

691   silica, 25 µm id, L_t = 52 cm (L_{eff} = 36 cm).

692

693   Fig. 3.   CE-C^4D separations of inorganic anions and cations. **A)** Cations: NH_4^+ (200 µM),

694   K^+ (200 µM), Ca^{2+} (200 µM), Na^+ (200 µM), Mg^{2+} (200 µM); Electrolyte

695   solution: 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with

696   CH_3COOH; Voltage: 15 kV; Capillary: fused-silica, 25 µm id, L_t = 65 cm (L_{eff} = 49

697   cm); **B)** Anions: Cl^- (200 µM), NO_3^- (50 µM), SO_4^{2-} (100 µM), NO_2^- (50 µM);

698   Electrolyte solution: 12 mM histidine adjusted to pH 4 with CH_3COOH; Voltage:

699   - 15 kV; Capillary: fused-silica, 25 µm id, L_t = 52 cm (L_{eff} = 36 cm); **C)** phosphate

700   (50 µM); electrolyte solution: 1 mM histidine adjusted to pH 3.5 with CH_3COOH;

701   Voltage: -15 kV; Capillary: fused-silica, 25 µm id, L_t = 52 cm (L_{eff} = 36 cm).

702

-30-

703   Fig. 4.   CE-C^{4}D electropherograms of inorganic cations and anions in one groundwater

704   sample. CE conditions as for Fig. 3.

705

706   Fig. 5.   CE-C^{4}D electropherograms of inorganic cations and anions in water samples

707   collected from different lakes in Hanoi. CE conditions as for Fig. 3.

708

709   Fig. 6.   Electrophoretic separation of As(III) (5 mg/L) using different BGEs. Samples were

710   injected with the siphoning effect at a height of 20 cm for 45 seconds and separated

711   at - 20 kV over a capillary of 60 cm total length. The C^{4}D detector was situated at

712   the effective length of 52 cm.

713

714   Fig. 7.   Bicarbonate removal capacity of the cation exchange resin KPS 200. This

715   evaluation was made with As(III) of 100 µg/L. Samples were electrokinetically

716   injected at - 6 kV for 60s and separated at - 20 kV over a capillary of 60 cm total

717   length. The C^{4}D detector was situated at the effective length of 52 cm.

718

719   Fig. 8.   Demonstration of the prevention of the loss of As(III) in the abundant presence of

720   Fe^{2+} (20 mM) by addition of 1,10-phenanthroline (1.8 mM). This evaluation was

721   made with As(III) of 100 µg/L. CE conditions as for Fig. 7.

722

723   Fig. 9.   Electrophopherograms for the determination of As(III) in 1 groundwater sample. A)

724   Groundwater sample without As(III) spiking; B) Groundwater sample with spiked

725   As(III) of 30 µg/L; C) Groundwater sample with spiked As(III) of 50 µg/L. CE
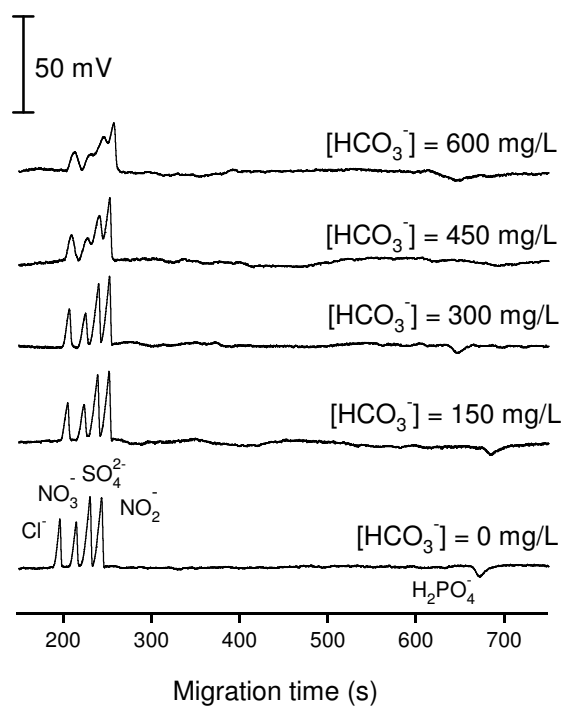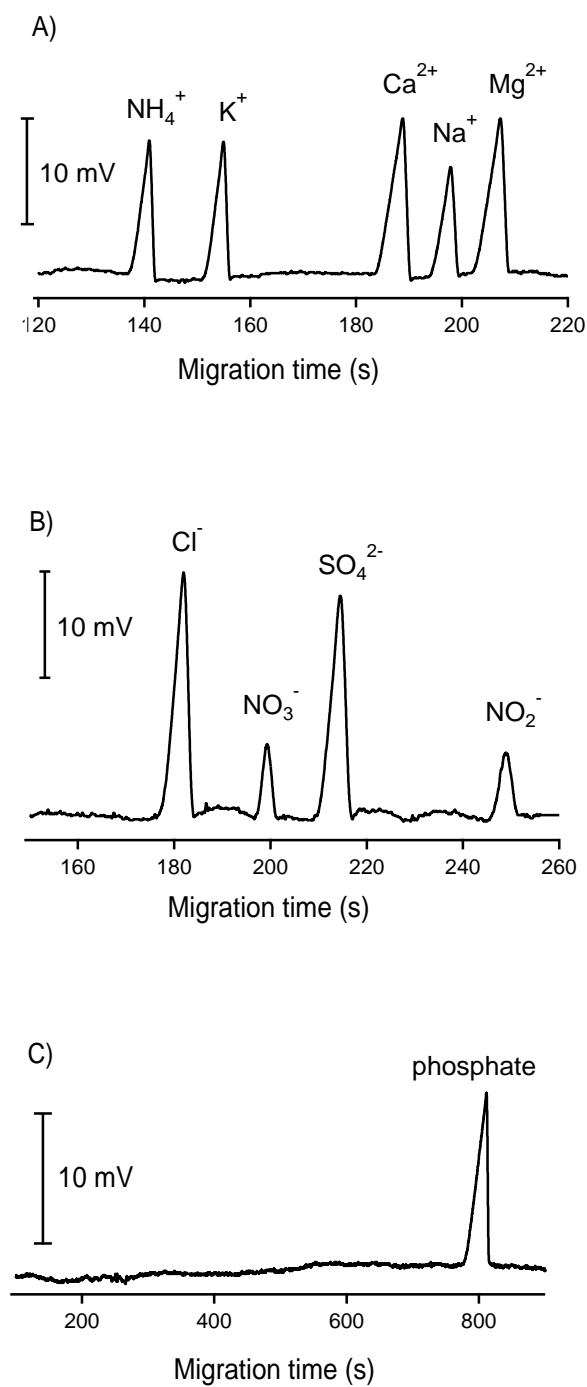
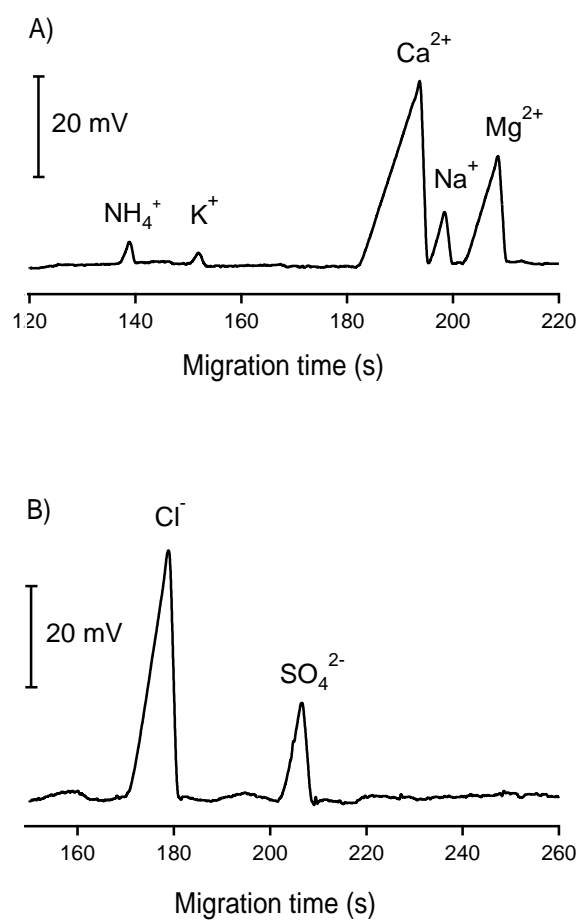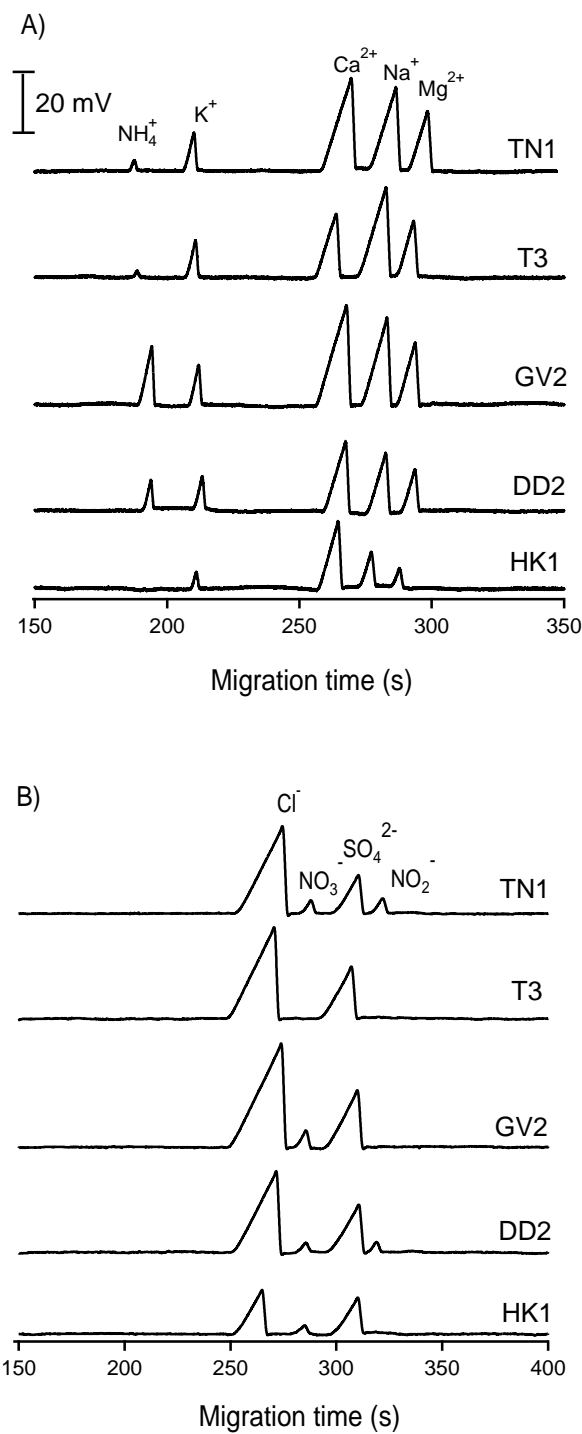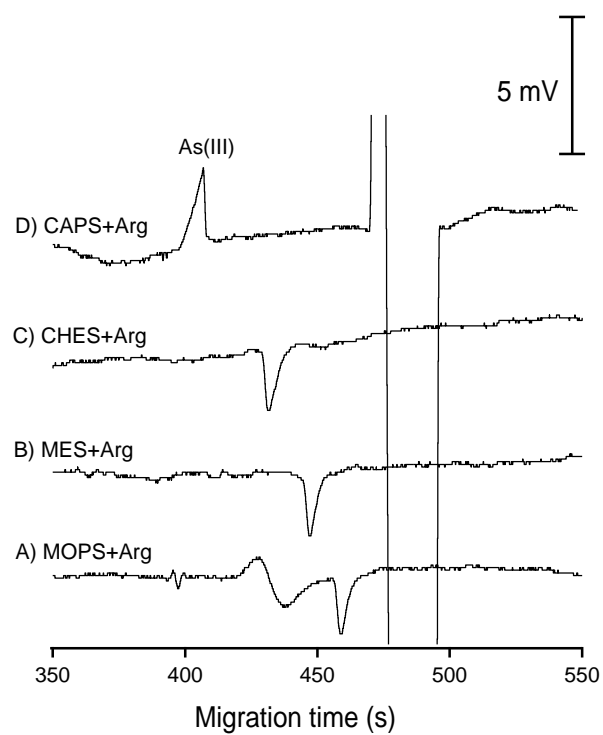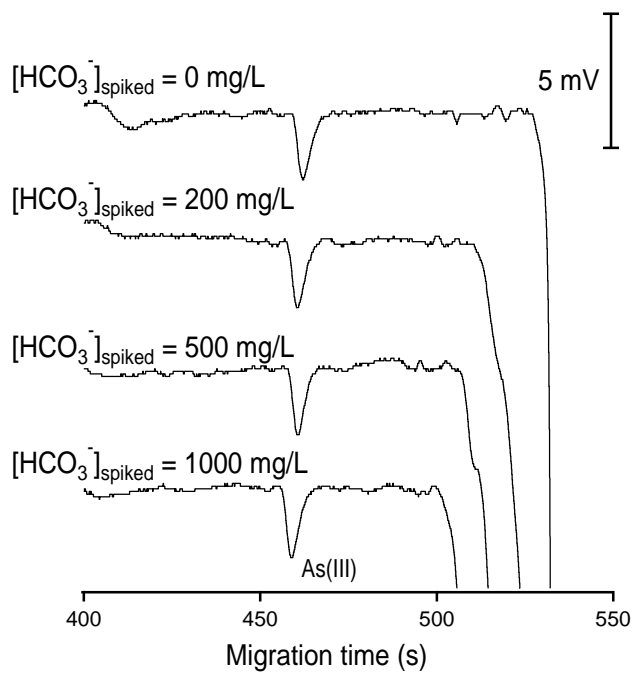726   conditions as for Fig. 7.

727
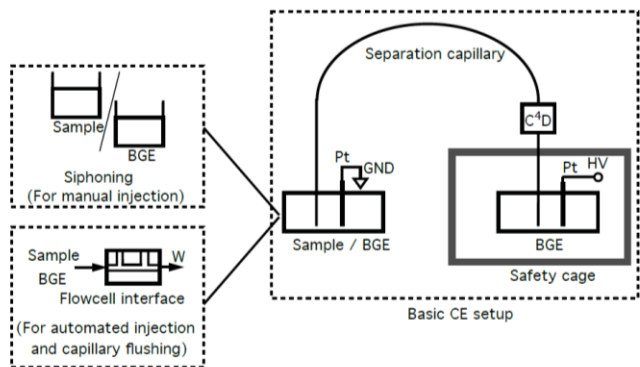
A)

B)

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Fiigure 6

Figure 7

Figure 8

Figure 9