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Cite this: *Environ. Sci.: Processes Impacts*, 2015, 17, 1941

In-house-made capillary electrophoresis instruments coupled with contactless conductivity detection as a simple and inexpensive solution for water analysis: a case study in Vietnam†

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A simple and inexpensive method for the determination of various ionic species in different water matrices is discussed in this study. The approach is based on the employment of in-house-made capillary electrophoresis (CE) instruments with capacitively coupled contactless conductivity detection (C⁴D), which can be realized even when only a modest financial budget and limited expertise are available. Advantageous features and considerations of these instruments are detailed following their pilot deployment in Vietnam. Different categories of ionic species, namely major inorganic cations (K⁺, Na⁺, Ca²⁺, Mg²⁺, and NH₄⁺) and major inorganic anions (Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, and phosphate), in different water matrices in Vietnam were determined using these in-house fabricated instruments. Inorganic trivalent arsenic (As(III)), which is the most abundant form of arsenic in reducing groundwater, was determined by CE-C⁴D. The effect of some interfering ions in groundwater on the analytical performance was investigated and is highlighted. The results from in-house-made CE-C⁴D-instruments were cross-checked with those obtained using the standard methods (AAS, AES, UV and IC), with correlation coefficients $r^2 \geq 0.9$ and deviations from the referenced results less than 15%.

Received 30th July 2015
Accepted 23rd September 2015

DOI: 10.1039/c5em00362h
rsc.li/process-impacts

Environmental impact

This work provides a simple and inexpensive analytical approach for water-quality monitoring which can be realized even when only a modest financial budget and limited expertise are available. This approach renders the aqueous environmental control activities more realizable even in local and decentralized areas. The case study was carried out in Vietnam where arsenic contamination in groundwater has been a serious problem. Inorganic major cations and anions, which are the primary indicators of water quality, together with abundantly present arsenite in groundwater were successfully monitored with the purpose-made instruments. Information on some water contaminants, *i.e.* ammonium and arsenic contamination, could be obtained without having recourse to expensive and sophisticated commercial instrumentation.

1. Introduction

The concentrations of major ionic species, *i.e.* K⁺, Na⁺, Ca²⁺, Mg²⁺, NH₄⁺, Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻ and phosphate, are the primary indicators for the evaluation of water quality. Whether it is rain water, surface water or groundwater, only when the concentrations of these ions are determined to be within the regulated ranges, further analyses of other compounds (heavy

metals, arsenic for instance) for confirmation of water quality are implemented. In Vietnam, groundwater has been used as an important source of drinking water, especially in rural areas.^{1,2} The quality of groundwater therefore is controlled periodically by monitoring the concentrations of different ionic species, of which those of major inorganic anions and cations are the first parameters to be determined. So far, inorganic cations usually have been determined by flame atomic absorption spectrometry (F-AAS, for earth alkali ions) or flame atomic emission spectrometry (F-AES, for alkali ions), whereas most of the inorganic anions have been determined by ion chromatography (IC).^{1,3-5} Ammonium and phosphate contents have been determined spectrophotometrically using respectively the nitroprusside and molybdenum blue methods.^{1,3-5} The need for these different instrumental methods accompanied by different sample storage strategies for subsequent in-lab analyses renders this water quality-control operation costly (with AAS, AES, and IC)

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† Electronic supplementary information (ESI) available. See DOI: [10.1039/c5em00362h](https://doi.org/10.1039/c5em00362h)



and time consuming. This monitoring operation therefore could be implemented only by central/national institutions with sufficient infrastructure support and funding. Routine analyses of the ionic species of water in local laboratories with limited financial resources have hardly been possible so far.

The aforementioned issue led to the desire for a more approachable alternative for water analysis. From our point of view, the most suitable option is the employment of a system based on capillary electrophoresis (CE) with capacitively coupled contactless conductivity detection (C⁴D). In this case, ionic species are electrophoretically separated by application of a high voltage along a narrow separation capillary and are detected based on the difference of their electrical conductivities from that of the background electrolyte (BGE). Fundamental aspects of C⁴D can be found in ref. 6–13, whereas applications of CE-C⁴D for water analyses can be found in several reviews.^{8,14–18} While commercial CE-C⁴D benchtop instruments for such operations are available, an option that is more suitable for modest infrastructures is the construction and utilization of CE-C⁴D instruments which were designed and developed in our laboratory. These systems are referred to as in-house-made CE-C⁴D throughout the text. As for CE-C⁴D both the separation and detection of ions are based on electronic principles and the method only requires low-pressure fluidic components; CE-C⁴D offers many advantageous features, including the possible translation into portable instrumentation, high configuration flexibility and ease of construction and operation. Since the launch of the first in-house-made (portable) CE instrument in 1998,¹⁹ different prototypes have been developed and introduced by Hauser and co-workers, ranging from instruments with manual injection and flushing,^{20–22} systems where this has been semi-automated²³ to fully automated single-channel versions^{24–27} and dual-channel configurations using one common buffer.^{28,29} In parallel, significant contributions have been made by other groups to in-house-built (portable) CE instrumentation. The more recent studies were communicated by Breadmore *et al.* for automated pK_a determination³⁰ and for simultaneous separation of anions and cations,³¹ Kaljurand *et al.* for fingerprinting postblast explosive residues,³² Porto *et al.* for analysis of ecstasy tablets³³ and Gaertner *et al.* for on-site food analysis.³⁴ A review on all in-house made (portable) CE instruments up to 2013 could be found in ref. 35 and 36. The C⁴D design has also been refined to match this evolution of CE setups. The most recent versions were designed for ease of construction and were miniaturized by integrating the entire circuitry in the detection cell and built for battery operation.^{28,37} An alternative compact version of C⁴D-cells has also been described by Lago and co-workers.³⁸ For good performance with CE-C⁴D, BGEs having low specific conductivities but high ionic strengths are preferable. Organic molecules with low/moderate mobilities are thus normally used to prepare the BGE solutions. More details on guidance for BGE selection for CE-C⁴D operation can be found in ref. 8, 17, and 39.

Herein, the feasibility of the employment of in-house-built CE-C⁴D-instruments for water analysis as an alternative to the standard techniques (*i.e.* AAS, AES, IC and UV) is evaluated. The

case study was implemented in Vietnam where these systems have been deployed for systematic analyses of different surface water and groundwater matrices. Some considerations on the use of in-house-made CE-C⁴D as well as the effects of some interfering ions on the analytical performance are discussed. In addition to the determination of major inorganic cations and anions, the CE-C⁴D approach was applied to the direct analysis of the widely present inorganic tri-valent arsenic As(III) in anaerobic groundwater, taking into account the adverse effect of the groundwater matrix (*i.e.* the abundant presence of ferrous and bicarbonate/carbonate ions). Arsenic contamination in groundwater is a highly critical issue for the water supply arrangements in the Red River Delta of Vietnam.^{2,40} Sensitive determination of arsenic in groundwater is normally carried out by hydride vapor generation (HVG)-AAS.⁴¹ CE has also been coupled with different detection/preconcentration techniques for arsenic determination/speciation in water.^{42–50} In our pioneering work on arsenic determination by CE-C⁴D,⁴² it was possible to detect As(III) prepared in standard solutions down to 22 µg L^{–1}. The direct determination of As(III) in groundwater samples at the time however was not successful due to the presence of interfering ferrous ions. As(III) had to be oxidized to As(V) to be analyzed under acidic conditions to eliminate the adverse effect of this ion. The groundwater matrix effect on the CE-C⁴D performance for the determination of As(III) was not considered in that work. In this study, As(III) in groundwater samples was directly quantified with the improved detection limit (LOD) of 5 µg L^{–1}. This LOD is below the regulated level of 10 µg L^{–1} for As(III) in drinking water that was set by the Environmental Protection Agency (EPA) in 2008.⁵¹

2. Experimental

2.1. Chemicals and materials

All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). Stock solutions (10 mmol L^{–1}) of chloride, nitrate, sulfate, nitrite, and phosphate were used for the preparation of the standards of inorganic anions, using their corresponding sodium or potassium salts. Those of the inorganic cations (ammonium, potassium, calcium, sodium and magnesium) were prepared from the chloride salts. Tri-valent arsenic solution was prepared from sodium (meta)arsenite (Fluka, Buchs, Switzerland). Chemicals used for preparation of CE-C⁴D buffers include: arginine (Arg), acetic acid, histidine (His), 18-crown-6, cetyltrimethylammonium bromide (CTAB), 2-(N-morpholino)ethanesulfonic acid (MES), 3-(N-morpholino)propanesulfonic acid (MOPS), N-cyclohexyl-2-aminoethanesulfonic acid (CHES), tris(hydroxymethyl)aminomethane (TRIS) and 3-(cyclohexylamino)-1-propanesulfonic acid (CAPS).

Fused silica capillaries of 50 µm ID and 365 µm OD were obtained from Polymicro Technologies (Phoenix, AZ, USA). Before use, the fused silica capillaries were pre-conditioned with 1 M NaOH for 10 min and deionized water for 10 min prior to flushing with the buffer. The capillaries were then used continuously for successive analyses. Deionized water purified using a water purification system from Millipore – model



Simplicity UV (Bedford, MA, USA) was used for the preparation of all solutions and for sample dilution if required.

2.2. Instrumentation

Both manual and automated in-house-built CE instruments were used for analytical method development and sample analyses. Details on the construction and operation of different in-house-made CE prototypes can be found in ref. 20 and 21 for the single-channel version with manual siphoning injection,²³ for the semi-automated single-channel setup,^{24–27} for the automated single-channel variants and^{28,29} for the multi-channel configurations. The automated CE instruments were controlled *via* a home-made computer program written with either LabView for Windows XP or Arduino. The controlling program has a graphical user interface that allows facile and intuitive operations.

Detection was carried out with miniaturized high voltage (HV)-C⁴D built in-house according to the design reported previously.²⁸ The resulting signals were recorded with a 12 V DC-powered E-corder 201 data acquisition system (eDAQ, Denistone East, NSW, Australia) connected to the USB-port of a personal computer. For data processing, the program Chart (version 5.1) developed by eDAQ was used. For powering the electrophoretic and fluidic parts, a lithium battery pack of 14.8 V and a capacity of 6.6 A h (CGR 18650CG 4S3P, Contrel, Hünenberg, Switzerland) fitted with a voltage regulator for production of a 12 V output was used. A separate pair of smaller Li-ion batteries with a capacity of 2.8 A h each (CGR 18659CG 4S1P, Contrel), which were fitted with positive and negative 12 V regulators, provided the split \pm 12 V supply for the C⁴D circuitry. Alternatively, main power can be utilized when available.

2.3. Field sampling

2.3.1. Groundwater. Groundwater was sampled from the boreholes using a down-hole pump (model GP 1692, Whale, Bangor, N. Ireland, UK). Five borehole volumes were flushed before taking the sample. Groundwater was immediately filtered with 0.45 μ m cellulose acetate membrane filters (Sartorius, Göttingen, Germany) which were pre-flushed with nitrogen gas to remove oxygen trapped inside the membranes, and then transferred into two 250 mL bottles for subsequent CE-C⁴D measurements. For subsequent cross-checking purposes, other separated bottles of groundwater samples were collected as well. The bottles served for analyses of Na⁺, Ca²⁺, Mg²⁺ and K⁺ were preserved with 2% of a 7 M HNO₃ solution and refrigerated until analysis in the laboratory by AAS and AES. Samples for NH₄⁺ and major inorganic anions were collected in 20 mL polypropylene vials and frozen immediately after sampling for later measurements by UV-Vis and IC, respectively.

For groundwater samples used for the As(III) determination by CE-C⁴D, 1,10-phenanthroline was added into the sample after filtration to complex with ferrous ions in order to avoid aerobically induced precipitation of ferric hydroxide that may lead to co-precipitation of inorganic arsenic species. The samples were then flushed through cartridges containing a

strong cation exchanger Wolfatit KPS 200 (VEB Farbenfabrik Wolfen, Germany) which released protons to react immediately with bicarbonate/carbonate in groundwater to form carbon dioxide. The sample was purged with nitrogen to completely remove the produced carbonic gas. Prior to each analysis, the sample was alkalized to pH 9.2 with arginine. The final sample solution contained 20 mM of Arg and 1.8 mM of 1,10-phenanthroline.

For subsequent cross-checking purpose, aqueous As(V) and As(III) ions were separated by filtering the water sample first through a 0.2 μ m membrane filter (Sartorius, Göttingen, Germany) and then a disposable anion exchange cartridge,⁵² at a flow rate of 5–6 mL min⁻¹ using a syringe. The anion exchange cartridge was mounted directly on the filter and the combination was carefully flushed with nitrogen before use. The cartridges contained 0.8 g aluminosilicate adsorbent that selectively adsorbs As(V) but not As(III).³ The sample containing only As(III) was then acidified with hydrochloric acid to pH < 2 and stored at 4 °C until subsequent in-lab analysis.

2.3.2. Surface water. 20 water samples from 5 lakes in Hanoi (Vietnam) were collected for monitoring of the concentrations of Cl⁻, NO₃⁻, NO₂⁻, SO₄²⁻, K⁺, NH₄⁺, Mg²⁺, Ca²⁺ and Na⁺ in an annual water quality control campaign. Water samples were collected at 20 cm below the surface, pre-filtered with 2 μ m paper filters (for lakes containing much algae and having a deep green color) and finally filtered with 0.45 μ m membrane filters (Sartorius, Göttingen, Germany).

2.4. Analytical methods

All CE-C⁴D operations for the determination of major inorganic anions and cations in ground and surface water samples were carried out immediately upon conclusion of the sampling campaign to avoid/minimize sample nature modification. Samples were fed into the CE-C⁴D systems manually (without an autosampler). Hydrodynamic sample injection was carried out either *via* the siphoning effect (with the manual or semi-automated version) or *via* pressurization of the sample flow at the ground end of the capillary (with the automated systems). As thermostated chambers were not included in our CE-C⁴D instruments, on-site measurements were implemented only when the external temperature was moderate (25–35 °C) and the humidity was not too high (less than 90%). Otherwise these operations were done either in an air-conditioned room or in the lab. Determinations of inorganic anions, cations and phosphate were carried out independently on three different CE-C⁴D runs with the average time for each run of about 15 min. Unless otherwise stated, a BGE composed of 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with acetic acid and one composed of 12 mM histidine adjusted to pH 4 with acetic acid were employed for the determination of major inorganic cations and anions, respectively. The buffer used for phosphate determination was composed of 1 mM histidine adjusted to pH 3.5 with acetic acid. Samples collected from 5 lakes in Hanoi were analyzed with CE-C⁴D using the aforementioned BGE compositions. Samples were diluted with deionized water if



needed to avoid peak overlaps with CE-C⁴D when the concentrations were out of the calibration ranges.

The surface water and groundwater samples were also transported to the lab and stored at 4 °C for subsequent in-lab analysis and cross-checked with the standard methods. The cations *i.e.* earth alkali and alkali metals were analyzed by F-AAS or F-AES on a Shimadzu AAS 6800 instrument. Anions were analyzed by IC using a Shimadzu LC20AD/HIC-20ASuper instrument. Ammonium was determined spectro-photometrically using nitroprusside whereas phosphate was analyzed by the molybdenum blue method using a Shimadzu UV 3101 equipment. More details on analytical procedures can be found in ref. 1 and 3.

As(III) in groundwater samples was determined by CE-C⁴D using the standard addition method (3 points) with the average analysis time for each sample of 45 min. The final sample solution contained 20 mM of Arg and 1.8 mM of 1,10-phenanthroline. The optimized BGE for As(III) analysis was 12 mM MES/21 mM Arg/30 µM CTAB (pH 8.9). Samples were electrokinetically injected at -6 kV for 60 s and separated at -20 kV in a capillary of 60 cm total length. The C⁴D detector was situated at an effective length of 52 cm. For cross-checking purpose, arsenic was determined with a Shimadzu AAS 6800 instrument using a hydride vaporization generator (HVG) according to the standard method detailed in ref. 53.

3. Results and discussion

3.1. Instrumental aspects

3.1.1. General considerations. For the in-house-built CE systems, the complex options which are often found in benchtop commercial CE instruments *i.e.* a sample tray, a robotic arm for vial lifting and a thermostated chamber were excluded in order to minimize the power consumption and the construction cost, as well as to maximize the portability. When using commercial benchtop instruments often the capillaries are reconditioned between sample runs, typically with sodium hydroxide solutions. This is a complication which is not always necessary, especially when working with non-wall-adsorbing inorganic ions. From our experience, when allowing equilibration of the capillary with the BGE for an extended period of time (hours) before analyses, good baseline stability and reproducibility of migration times are obtained when the capillaries are simply flushed with the BGE between successive runs.

A CE-C⁴D system should always be earthed because the high voltage supplies may lead to charging up of the (insulated) boxes of the instruments, which in turn can create a hazard to the user if the system is not earthed. This can however not always be done readily because in developing countries in general and in Vietnam in particular, the earth is often excluded from the main sockets of the electricity system for economical reasons. An alternative earth then has to be improvised. If available, a connection to a metallic water pipe may be made, or a metallic rod is buried in the ground.

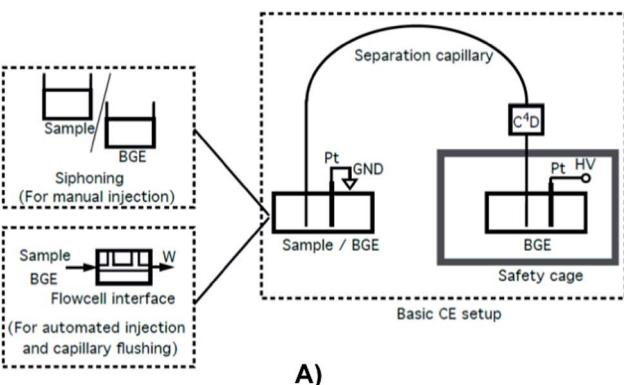
Another challenge to overcome when working with CE-C⁴D in Vietnam is the high humidity. While a CE-C⁴D system may work fine for in-lab analyses in dry weather, noisy signals were at times observed when the humidity increased. The problem

became more pronounced when the systems were set up outside the lab for mobile deployment. This is due to the discharge of the applied high voltage through humid air which renders the high voltages for separation not maintainable. The discharge could also produce pronounced noise on the C⁴D signal if the detector was not positioned far enough from the high-voltage electrode. To solve the problem, the first approach is to make the high voltage cage as large as possible and free of conducting parts inside. The vial containing the BGE, the capillary end and the electrode should be positioned in the center of this cage. Secondly, a reduction in the high voltage from 30 kV possible with conventional instruments may be necessary.

When possible the CE system should be operated in an air-conditioned room to avoid temperature variations and high humidity. This may not lead to additional expenses as the households in Vietnam are often equipped with air-conditioners for their own use. Application of the standard addition or internal standardization method may be needed for peak identification and quantification when there are significant drifts of the baseline and migration time due to ambient temperature fluctuations in the absence of an air-regulated condition.

3.1.2. Specific considerations for different in-house-made CE-C⁴D prototypes. Various in-house-made CE-C⁴D setups, including instruments with manual injection and capillary flushing,^{20,21} a semi-automated instrument with siphoning injection,²³ instruments with fully automated injection with a single-channel arrangement^{24,25} and an instrument with fully automated injection having a dual-channel configuration with the same buffer,²⁸ were deployed in Vietnam for water analysis. A block-diagram showing the basic set-up of a CE system with some automatable parts as an option and a photo demonstrating an in-house-made CE system in operation are given in Fig. 1A and B, respectively. Portable CE instruments were employed for some on-site operations. For in-lab work, *i.e.* method development and the major part of sample analyses, the manual and automated versions were used. While these systems showed no significant performance difference in terms of detection sensitivity (see Table S1 in the ESI† file), each configuration has its own positive and limited points for consideration. Manual and semi-automated CE-C⁴D setups are the least expensive and simplest versions that are most suitable for wide-spread use. Roughly estimated construction costs for these systems are 5000 and 7000 Euros, respectively. The most essential part is a high voltage module, which can normally go up to 30 kV. These are available from different suppliers and have different feature sets.⁵⁴ For a partly automated system extra cost is incurred by valves and gas pressure regulators. No controlling program is needed and all operations, *i.e.* application of a high voltage, capillary flushing, and sample injection, are carried out using simple mechanical switches. These versions however require frequent intervention of an operating person and therefore are not suitable for unattended analysis. The employment of the siphoning technique for hydrodynamic sample injection may produce some contaminant peaks in the electropherograms if air containing suspended particles is accidentally sucked into the injection end of the capillary during





A)



B)

Fig. 1 (A) A block-diagram demonstrating the basic set-up of a CE system with some optional automatable parts; (B) demonstration of an in-house-made CE system in operation. Pt: platinum electrode; W: waste; GND: ground electrode; BGE: background electrolyte; HV: high voltage; C⁴D: capacitively coupled contactless conductivity detector.

its movement. To avoid this problem, the capillary's injection end should be always immersed in a solution (either the BGE or sample) when it is lifted to a higher position for siphoning injection. Employment of gloves is recommended to prevent any contamination due to the sweat retained onto the capillary tip when it is in contact with the operator's bare fingers.

The automated versions of in-house-built CE-C⁴D^{24,25,28} on the other hand can eliminate some aforementioned inconveniences encountered in manual and semi-automated versions. No capillary back and forth movement is needed and the systems can be operated in an unattended manner. In the case of the dual-channel CE system using the same buffer,²⁸ different ionic categories, *i.e.* cationic and anionic species, can be simultaneously determined in a single run. Higher construction cost (up to 15 000–20 000 Euros) and requirement of certain knowledge about operation of computer-based controlling programs however are two considerations to be taken into account when only modest financial funding and little expertise are available. These automated versions may be more vulnerable to the noisy signal problem when good grounding is not guaranteed. Commercial C⁴D and data acquisition units with software are available for some thousands of Euros. If the

electronics expertise is available, a C⁴D can be built in-house for a few hundred Euros depending on the design. A good data acquisition system is essential and will have to be bought. The expenses for the mechanical hardware are minimal, but the workshop cost is possibly incurred.

3.2. CE-C⁴D determination of major inorganic cations and anions in different water matrices

3.2.1. Determination of major inorganic cations and anions in groundwater. The optimizations of BGE compositions were implemented for best CE-C⁴D performances with the groundwater matrices, taking into account the presence of some interfering parameters such as carbonate and ferrous ions. Baseline separations of major anions could not be achieved in our preliminary experiments with different BGE solutions composed of His/MES, MOPS/His or TRIS/MOPS (see Fig. S1 in the ESI† file). In addition, at high pH of the BGE the obtained CE-C⁴D baseline was not stable and drastic baseline drifting was observed from time to time. These may occur due to the presence of dissolved organic carbon and high alkalinity concentrations which could be up to 1000 mg HCO₃²⁻ per L in groundwater.³⁻⁵ On the other hand, when working with the acidic BGE, this baseline fluctuation problem was alleviated. Another consideration was the presence of some major ions in groundwater at very high concentrations (for example Cl⁻ up to 20 mg L⁻¹ and Ca²⁺ and Mg²⁺ up to 40 mg L⁻¹) that may overlap the adjacent peaks of some other target ions. This prediction of ion concentrations was made based on data reported in ref. 1 and 3. Accordingly, BGE optimization for CE-C⁴D separation of inorganic cations and anions in groundwater was carried out based on an acidic condition that was already successfully applied for surface water.^{24,25} It was found that a BGE containing 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with acetic acid offered good separation of inorganic cations. 18-Crown-6 was included to facilitate the separation of K⁺ and NH₄⁺ thanks to its selective complexation with K⁺ that leads to the increase in the migration time of K⁺ compared to that of NH₄⁺. In groundwater in Vietnam, ferrous cations are from time to time found at concentrations of up to 20 mg L⁻¹ (360 µM).^{1,3-5} The presence of ferrous cations at high concentrations (more than 2 mg L⁻¹ or 36 µM) may cause peak overlaps with Mg²⁺ (see Fig. S2 in the ESI† file). This problem, on the other hand, can be avoided just by allowing aqueous ferrous cations to be naturally oxidized to form ferric hydroxide precipitates when aerated for 15 min. Sample filtering was needed to remove the formed precipitates prior to CE-C⁴D determination of major inorganic cations.

For separation of anions, 18-crown-6 was not needed and was removed from the electrolyte. At this low pH the electroosmotic flow (EOF), which is the bulk movement of the liquid inside the capillary under an applied electrical field, is suppressed; therefore no EOF modification is needed. While a BGE consisting of 12 mM histidine adjusted to pH 4 with acetic acid resulted in good separations of major anions including Cl⁻, SO₄²⁻, NO₃²⁻ and NO₂⁻, it was found experimentally that this high content of histidine in the BGE hindered sensitive

detection of phosphate (see Fig. S3 in the ESI† file). To improve the sensitivity for phosphate, the concentration of histidine in the BGE was reduced and the optimized BGE for phosphate determination was composed of 1 mM histidine adjusted to pH 3.5 with acetic acid.

The effect of bicarbonate on the performance of anion separation is illustrated in Fig. 2. By increasing the added concentration of bicarbonate from 0 to 600 mg L⁻¹ (10 mM) into a standard solution containing inorganic anions of 100 μ M, it was found that the optimized BGE at pH = 4 can tolerate the presence of bicarbonate up to 300 mg L⁻¹ (5 mM). At bicarbonate concentrations higher than 5 mM, the peaks of Cl⁻, NO₃⁻, SO₄²⁻ and NO₂⁻ became distorted and were difficult to quantify. The reason for this problem however is not understood. A solution for avoiding this bicarbonate disturbance can be direct acidification of the sample with acetic acid prior to anion analysis by CE-C⁴D and the subsequent purging the samples by nitrogen stream.

An example of the analyses of standard mixtures of cations and anions with three different BGE solutions is shown in Fig. 3. The calibration data for the ions of interest are given in Table 1. The detection limits, determined from the peak heights corresponding to 3 times the baseline noise, were in the range of 2.5–10 μ M. For inorganic cations, linear calibration curves were obtained up to 2000 μ M whereas somewhat shorter linear ranges were achieved for the inorganic anions (up to 1000 μ M). The obtained correlation coefficients were better than 0.99. The repeatability of the measurements of peak areas and migration times were better than 5% and around 2%, respectively.

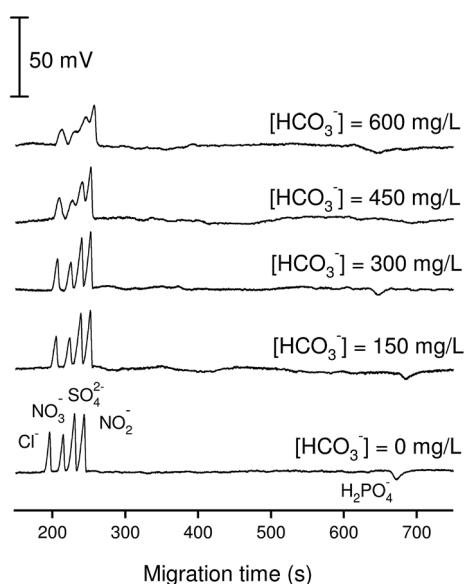


Fig. 2 Effect of bicarbonate ions on the performance of anion separation by CE-C⁴D. Bicarbonate at different concentrations from 0–600 mg L⁻¹ was spiked into the standard mixture solutions containing Cl⁻ (100 μ M), NO₃⁻ (100 μ M), SO₄²⁻ (50 μ M), NO₂⁻ (100 μ M) and phosphate (100 μ M). Electrolyte solution: 12 mM histidine adjusted to pH 4 with CH₃COOH; voltage: -15 kV; capillary: fused-silica, 25 μ m id, L_t = 52 cm (L_{eff} = 36 cm), L_{eff} = 36 cm).

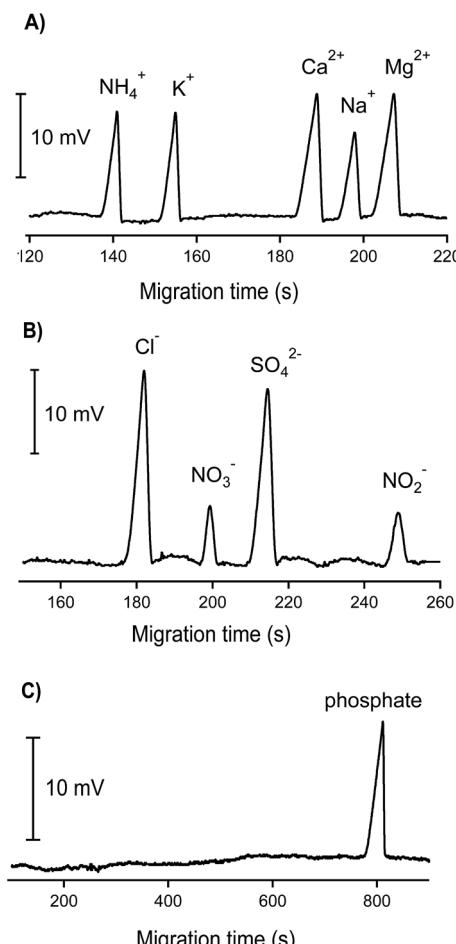


Fig. 3 CE-C⁴D separations of inorganic anions and cations. (A) Cations: NH₄⁺ (200 μ M), K⁺ (200 μ M), Ca²⁺ (200 μ M), Na⁺ (200 μ M), and Mg²⁺ (200 μ M); electrolyte solution: 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with CH₃COOH; voltage: 15 kV; capillary: fused-silica, 25 μ m id, L_t = 65 cm (L_{eff} = 49 cm); (B) anions: Cl⁻ (200 μ M), NO₃⁻ (50 μ M), SO₄²⁻ (100 μ M), and NO₂⁻ (50 μ M); electrolyte solution: 12 mM histidine adjusted to pH 4 with CH₃COOH; voltage: -15 kV; capillary: fused-silica, 25 μ m id, L_t = 52 cm (L_{eff} = 36 cm); (C) phosphate (50 μ M); electrolyte solution: 1 mM histidine adjusted to pH 3.5 with CH₃COOH; voltage: -15 kV; capillary: fused-silica, 25 μ m id, L_t = 52 cm (L_{eff} = 36 cm).

Electropherograms of one groundwater sample are demonstrated in Fig. 4. As can be seen, Ca²⁺, Na⁺, Mg²⁺, Cl⁻ and SO₄²⁻ appeared in abundant amounts, reflected by high and large peaks whereas much smaller peaks of NH₄⁺ and K⁺ were observed. No nitrogen-containing anions (NO₃⁻ and NO₂⁻) were found in this groundwater sample. The concentration of phosphate (if any) was below the quantification limit; therefore the electropherogram of the CE channel used for phosphate determination is not shown. To verify the reliability of the results obtained by CE-C⁴D, all concentrations were cross-checked using the standard reference methods, *i.e.* AAS, IC and UV spectrometry. High correlation coefficients with $r^2 \geq 0.9$ were achieved showing very good agreement between the results obtained by CE-C⁴D and those by the standard reference techniques (see Tables S2 and S3 in the ESI† file). Among the 15



Table 1 Calibration ranges, detection limits (LODs) and reproducibility for the CE-C⁴D determination of various inorganic ionic species

Ion	Range ^a (μM)	Correlation coefficient r^2	LOD ^b (μM)	RSD% MT ^c (n = 4)	RSD% PA ^d (n = 4)
Channel 1^e					
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^f					
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^g					
PO ₄ ³⁻	10–100	0.997	5.0	2.7	3.8

^a 5 concentrations. ^b Based on peak heights corresponding to 3 times the baseline noise. ^c Migration time (measurement unit: second). ^d Peak area (measurement unit: mV s). ^e Determination of major inorganic cations: electrolyte solution: 12 mM histidine and 2 mM 18-crown-6 adjusted to pH 3.7 with CH₃COOH. Voltage: +15 kV. Capillary: fused-silica, 25 μm id, L_t = 65 cm (L_{eff} = 49 cm). ^f Determination of major inorganic anions: electrolyte solution: 12 mM histidine adjusted to pH 4 with CH₃COOH. Voltage: -15 kV. Capillary: fused-silica, 25 μm id, L_t = 52 cm (L_{eff} = 36 cm). ^g Determination of phosphate: electrolyte solution: 1 mM histidine adjusted to pH 3.5 with CH₃COOH. Voltage: 15 kV. Capillary: fused-silica, 25 μm id, L_t = 52 cm (L_{eff} = 36 cm).

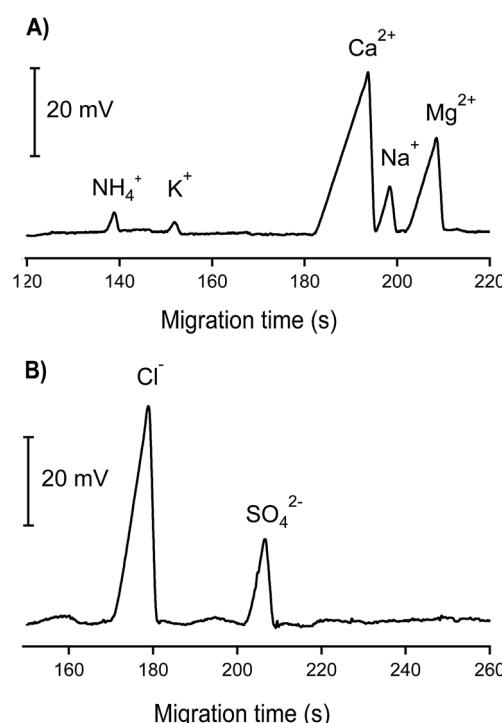


Fig. 4 CE-C⁴D electropherograms of inorganic cations and anions in one groundwater sample. CE conditions as in Fig. 3.

groundwater samples tested, NO₃⁻ and NO₂⁻ were not detected by our CE-C⁴D method whereas phosphate was found in only 1 sample. The concentration of phosphate determined by CE-C⁴D in this case fell in the range between 5 μM (LOD) and 10 μM (LOQ). Verification by IC revealed a phosphate concentration of 6 μM, which matched well with the result obtained by CE-C⁴D.

Note that the concentrations of nitrogen-containing ions and phosphate can fluctuate significantly in different seasons and are also much dependent on the nature of the groundwater. Most groundwaters in the Red River Delta are anaerobic. As a result, dissolved inorganic nitrogen occurs mostly as NH₄⁺ rather than NO₃⁻ and NO₂⁻. The phosphate concentration below the LOD in most of the collected groundwater samples can be reasonably explained that these groundwater resources are neither close to the domestic waste, agricultural activities nor natural mineral resource containing phosphate (e.g. apatite).

3.2.2. Major inorganic cations and anions in lake water samples. The BGE compositions optimized for groundwater analysis were employed for CE-C⁴D determination of ionic species in water from 5 lakes in Hanoi. Fig. 5 shows electropherograms of some surface water samples. The data obtained by CE-C⁴D can be seen in Table S4 in the ESI† file, with deviations obtained from some cross-checks by referenced methods always less than 15%. NO₂⁻ and NO₃⁻ were detected in many surface water samples, with the concentrations of NO₂⁻ in most of the cases exceeding the acceptable level in Vietnam (0.01 mg L⁻¹, or ≈ 0.2 μM). The cationic NH₄⁺ was also present at concentrations higher than the acceptable level (0.1 mg L⁻¹). The presence of these nitrogen-ionic species and the phosphate concentrations below 5 μM in these water samples are due to the biological activity of algae growing in the lakes. The growing activity of algae (or many other lemma species in aqueous media) can be connected using a nitrogen fixation mechanism, which in turn may promote the formation of ionic nitrogen species.

3.3. Determination of As(III) in groundwater

Together with Bangladesh and India, Vietnam belongs to the countries in South and South East Asia suffering from a natural



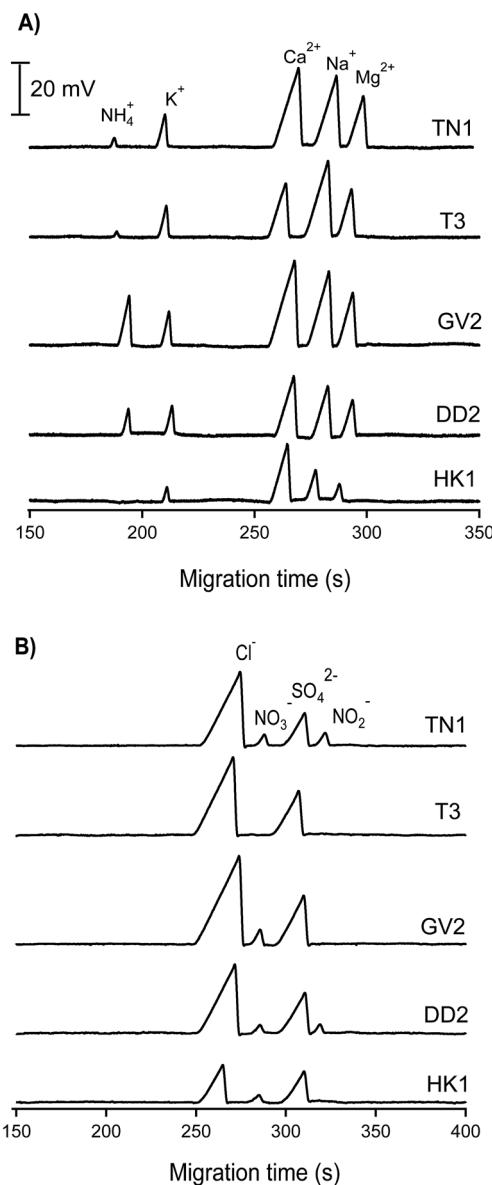


Fig. 5 CE-C⁴D electropherograms of inorganic cations and anions in water samples collected from different lakes in Hanoi. CE conditions as in Fig. 3.

contamination of groundwater by arsenic. Under the reducing conditions of the Red River Delta groundwater, together with the abundant presence of microbacteria and organic matter, ferrous and As(III) ions can be released from sediments into groundwater.^{3,40} We showed earlier that As(III) in standard solutions could be determined by CE-C⁴D with a LOD of 22 $\mu\text{g L}^{-1}$.⁴² The interfering effect of ferrous and bicarbonate/carbonate ions on CE-C⁴D determination of As(III) in groundwater samples however was not considered in this pioneering work. Herein, we propose a new CE-C⁴D method for direct quantification of As(III) species in groundwater taking into account various interfering parameters which may adversely affect its analytical performance. The detection limit for As(III) determination was improved to 5 $\mu\text{g L}^{-1}$ (determined for

standard solutions without recourse to the standard addition method), which is below the regulated level of arsenic in water (10 $\mu\text{g L}^{-1}$).

3.3.1. BGE composition optimization. As arsenous acid is dissociated only at high pH ($\text{p}K_{\text{a}1} = 9.2$), the BGE for CE separation of As(III) should be in a basic medium to ensure its negative charge. Various BGE compositions based on combinations of MES, MOPS, CHES or CAPS with either of arginine, diethylamine, triethylamine and *tert*-butylamine were tested. It was found that only Arg-based BGEs offered clear and sharp peaks of As(III). Fig. 6 shows electropherograms for the separation of As(III) using buffers composed of Arg and either of MES, MOPS, CHES or CAPS. Note that the digitized appearance of the electropherograms is due to the low data acquisition rate that was set to the ADC system by the operator. Such appearance nevertheless did not significantly affect the As(III) identification and quantification. While both CAPS/Arg and MES/Arg produced the highest signal to noise ratios, the longer distance between the peak of As(III) and that of EOF in the case of MES/Arg rendered the identification and quantification of As(III) easier. After optimization of buffer's pH from 8.3 to 9.2 by varying the concentrations of MES and Arg (see Fig. S4 in the ESI† file), the BGE composed of MES (12 mM) and Arg (21 mM) at pH 8.9 was found to provide the highest and sharpest peak of As(III). CTAB of 35 μM was added into the BGE solutions for reversal of EOF to facilitate the electrophoretic movement of the slow-migrating arsenite at high pH. In order to increase the amount of As(III) injected into the capillary for sensitivity enhancement, the groundwater samples were first alkalized with 20 mM Arg to pH 9.2 and then electrokinetically injected at

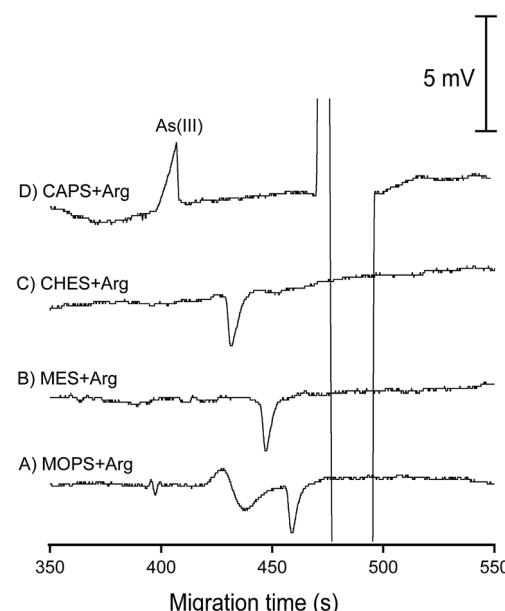


Fig. 6 Electrophoretic separation of As(III) (5 mg L^{-1}) using different BGEs. Samples were injected with the siphoning effect at a height of 20 cm for 45 seconds and separated at -20 kV over a capillary of 60 cm total length. The C⁴D detector was situated at an effective length of 52 cm.

–6 kV for 60 s to employ the stacking of negatively charged As(III) at the boundary of the buffer and the sample zones for online pre-concentration. Compared to hydrodynamic injection (siphoning at 20 cm high for 60 s), the electrokinetic injection mode offered a 4-time improved sensitivity. Electrokinetic injection was preferred in this case because (1) all groundwater samples had a relatively low conductivity compared to the BGE and (2) addition of Arg into the groundwater samples helped equalize their conductivity. These in turn minimized the sampling bias problem inherent to electrokinetic injection.

3.3.2. Effect of major inorganic anions on As(III) measurement performance. One consideration with the chosen electrokinetic injection mode is the sampling bias due to the abundant presence of major fast-migrating inorganic anions in the groundwater matrix. It was found experimentally that when their concentrations exceeded 5 mg L^{−1} the peak of As(III) was decreased by 30% compared to that obtained with a standard solution prepared in deionized water. To minimize this bias problem, the standard addition method was implemented to avoid significant measurement deviation caused by interfering ions that may exceed 5 mg L^{−1} in the sample matrix.

3.3.3. Effect of bicarbonate/carbonate on As(III) measurement performance. The abundant presence of bicarbonate/carbonate in groundwater may result in distortion of the peaks of target analytes, as already illustrated in Fig. 2. In the case of As(III) measurement, the peak of arsenite became much smaller at the alkalinity concentrations higher than 30 mg L^{−1} (0.5 mM, see Fig. S5 in the ESI† file), which in turn may affect adversely the sensitivity for As(III). Note that the peak of As(III) is well separated from that of bicarbonate and those of other faster-migrating anions (*i.e.* Cl[−], SO₄^{2−}, NO₃[−], and NO₂[−]). BGE optimization was thus carried out for sensitivity for As(III) rather than selectivity. Conventional acidification of the sample with a strong acid to convert bicarbonate/carbonate into carbonic gas was not feasible in this case due to the need for use of a high pH (pK_a of H₃AsO₃ = 9.2) and avoidance of strong anion addition that may adversely affect electrokinetic injection. To solve this problem, the groundwater samples were flushed through a strong cation exchange resin KPS 200 that released protons, leading to the formation of carbonic gas without significantly changing the pH of the groundwater sample. The sample was purged with nitrogen to remove the produced carbonic gas. Another advantage of this technique is that no additional anion was present in the sample matrix after this bicarbonate/carbonate elimination process. This technique worked well even when the bicarbonate concentration in the sample was increased up to 1000 mg L^{−1} (17 mM), as illustrated in Fig. 7.

3.3.4. Effect of ferrous cations on As(III) measurement performance. Ferrous cations are frequently detected in groundwater in Vietnam at the concentrations up to 20 mg L^{−1}.^{3–5} At high pH and under aerobic conditions, ferrous ions are easily converted to ferric oxy-hydroxide that adsorbs and co-precipitates aqueous arsenic species. Removal of ferrous ions from the groundwater samples was therefore required to guarantee accurate determination of As(III) concentrations. Four complexing reagents, namely 4-(2-pyridylazo)resorcinol (PAR), 1-(2-pyridylazo)-2-naphthol (PAN), ferroin and 1,10-phenanthroline,

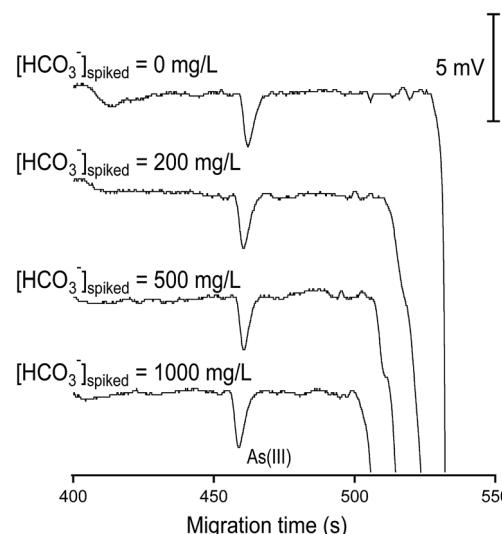


Fig. 7 Bicarbonate removal capacity of the cation exchange resin KPS 200. This evaluation was made with As(III) of 100 $\mu\text{g L}^{-1}$. Samples were electrokinetically injected at –6 kV for 60 s and separated at –20 kV over a capillary of 60 cm total length. The C⁴D detector was situated at an effective length of 52 cm.

that could produce stable complexes with ferrous and ferric cations at pH from 6 to 10 were tested. As illustrated in Fig. 8, the inclusion of 1,10-phenanthroline into the sample offered a stable baseline with the height and sharpness of the As(III) peak remaining unchanged even in the abundant presence of ferrous cations at 20 mg L^{−1}. This however was not the case with the other complexing reagents (see Fig. S6 in the ESI† file).

3.3.5. Determination of As(III) in groundwater samples. For CE-C⁴D determination of As(III) in groundwater, after filtration

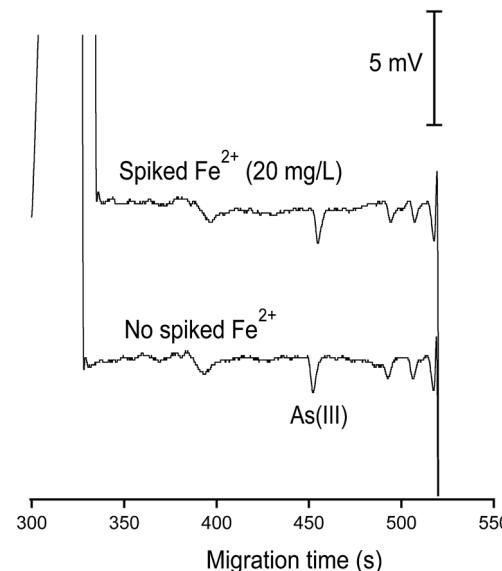


Fig. 8 Demonstration of the prevention of the loss of As(III) in the abundant presence of Fe²⁺ (20 mM) by the addition of 1,10-phenanthroline (1.8 mM). This evaluation was made with As(III) of 100 $\mu\text{g L}^{-1}$. CE conditions as in Fig. 7.



1,10-phenanthroline (18 mM) was added to the samples at the volumetric 1,10-phenanthroline/sample ratio of 1/10. The samples were then flushed through a strong cation exchange resin KPS 200, alkalinized with 20 mM Arg to pH 9.2 prior to electrokinetic injection at -6 kV for 60 s. As(III) was then electrophoretically separated from the matrix using a BGE composed of 12 mM MES, 21 mM Arg and 30 μ M CTAB. Salient performance data for As(III) measurements using this optimized procedure include a calibration curve (based on peak areas *vs.* predefined concentrations) acquired from 20 to 150 μ g L⁻¹ with a correlation coefficient r^2 of 0.998, the limit of detection of 5 μ g L⁻¹ and relative standard deviations (RSDs) for the migration time and peak area of 1% and 7%, respectively. The developed method was then applied to the determination of As(III) in 15 groundwater samples collected in Van Phuc (Hanoi) which is a typical "hot-spot" of arsenic contamination in Vietnam.¹ Electropherograms for separation of As(III) in a groundwater sample using the standard addition method are shown in Fig. 9. Note that the standard addition method alone may be adequate to minimize bias caused by the complex sample matrices. Sample dilution nevertheless is still needed to render the measured As(III) concentration fitting well for the linear (calibrated) range of 20–150 μ g L⁻¹. Good agreement between the data obtained with CE-C⁴D and those with the standard reference HVG-AAS method was achieved, with measurement deviations less than 7% and a correlation coefficient r^2 of 0.9967 (see Table S5 in the ESI† file). High concentrations of As(III) from about 50 μ g L⁻¹ to 400 μ g L⁻¹ were found in these samples, indicating serious contamination of the groundwater in Van Phuc with arsenic. Note that the

acceptable level of arsenic in groundwater that is regulated by the World Health Organization (WHO) is 10 μ g L⁻¹.

4. Conclusions

In-house-made CE-C⁴D was found to be a simple and inexpensive solution for analysis of various inorganic ionic species in different water matrices. A simple CE-C⁴D setup can be built at the construction cost of 5000–7000 Euros. This approach eliminates the requirement of costly and sophisticated commercial instrumentation, thus rendering the water-quality monitoring activities feasible even at local laboratories where only modest budget and limited expertise are available. More laborious work with manual operations may nevertheless be encountered with in-house built CE-C⁴D instruments due to (i) exclusion of some/all automated options to reduce construction cost and (ii) lack of decent controlling software. Acceptable agreement between the results obtained with CE-C⁴D for determination of major inorganic ions as well as trivalent arsenic and those with the standard reference methods, *i.e.* AAS, AES, IC and UV, was achieved (with correlation coefficients $r^2 \geq 0.9$ and cross-check deviations less than 15%), demonstrating the reliability of the analytical data provided by CE-C⁴D. Extension of the CE-C⁴D application spectrum to other ionic water-quality indicator species (heavy metals for example) is envisaged.

Acknowledgements

The authors are grateful for financial support from the National Foundation for Science and Technology Development of Vietnam (NAFOSTED, Grant No. 104.07-2010.21). Jorge Sáiz (University of Alcalá, Madrid, Spain), Israel Joel Koenka (University of Basel, Switzerland) and 3SAnalysis JSC (<http://www.3SAnalysis.vn>) are acknowledged for their instrumental support. We also would like to thank MSc. Thi Thanh Thuy Pham, MSc. Thi Mai Lan Vi, MSc. Thanh Dam Nguyen, MSc. Duy Chien Nguyen and MSc. Van Tang Nguyen (CETASD) for their help in sampling and cross-checking analysis operations.

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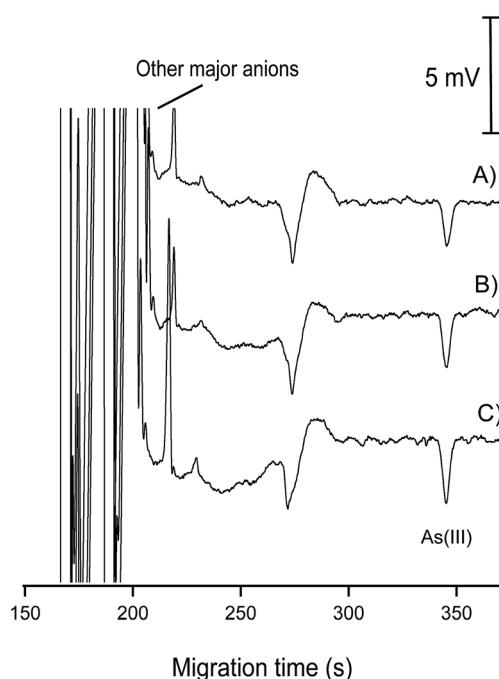


Fig. 9 Electropherograms for the determination of As(III) in 1 groundwater sample. (A) Groundwater sample without As(III) spiking; (B) groundwater sample with spiked As(III) of 30 μ g L⁻¹; (C) groundwater sample with spiked As(III) of 50 μ g L⁻¹. CE conditions as in Fig. 7.

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