

# Portable Capillary Electrophoresis Instrument with Automated Injector and Contactless Conductivity Detection

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**ABSTRACT:** A portable capillary electrophoresis instrument featuring an automated, robust, valve-based injection system was developed. This significantly facilitates operation in the field compared to previous injection approaches. These generally required delicate manual operations which are difficult to perform outside the laboratory environment. The novel system relies on pressurized air for solution delivery and a micromembrane pump for sample aspiration. Contactless conductivity detection was employed for its versatility and low power requirement. The instrument has a compact design,



with all components arranged in a briefcase with dimensions of  $45 \times 35 \times 15$  cm (w × d × h) and a weight of about 8 kg. It can operate continuously for 9 h in the battery-powered mode. Depending on the task at hand, the injection system allows easy optimization for high separation efficiency, for fast separations, or for low limits of detection. To illustrate these features, the separation of four anions within 16 s is demonstrated as well as the determination of nitrite below 1  $\mu$ M. The determination of phosphate at a sewage treatment plant was carried out to demonstrate a field application.

The use of portable instrumentation for field analysis is of interest due to the rapid availability of results, elimination of complications with sample storage and transport, and better cost effectiveness than conventional benchtop analytical systems. A mobile analytical instrument should satisfy requirements of compact size, lightweight, robustness, and low power consumption. Automation of operation is also desirable. Capillary electrophoresis (CE), with advantageous properties including a wide range of accessible analytes, high separation efficiency, short analysis time, low power requirements, limited consumption of chemicals, and ease of installation, operation, and maintenance, is a particularly interesting candidate for portable analytical instrumentation.

One challenge for a portable CE system is detection. Optical detection methods can only be implemented with nonstandard light sources such as light-emitting diodes (LEDs) or laser-diodes because of the high power requirement of conventional UV or visible sources, and these are not ideal for non-light-absorbing inorganic or organic ions. Electrochemical detection methods, on the other hand, are better suited for portable CE, as their fully electronic configuration can easily be miniaturized and translated into the compact, low power format. Of the variants of electrochemical detection methods, capacitively coupled contactless conductivity detection ( $C^4D$ ) is very attractive, as it can be considered universal for all ionic species, which includes the non-UV/vis-active ones, and the axial

tubular arrangement of the electrodes positioned outside the capillary offers ease in construction and operation. Publications on fundamental aspects of  $C^4D$  are available<sup>1-9</sup> and discussions of general applications of  $C^4D$  for CE can be found in recent reviews.<sup>10–14</sup>

To our knowledge, the first portable CE instrument was reported by our group in 1998 and was based on potentiometric and amperometric detection.<sup>15,16</sup> The addition of contactless conductivity detection was then reported in 2001,<sup>17</sup> and this was later followed by a version with an improved detector in 2007.<sup>18</sup> Li and co-workers introduced a portable CE instrument with potential gradient detection,<sup>19</sup> which was later also fitted with a contactless conductivity detector.<sup>20,21</sup> The instrument is commercially available, and Haddad and co-workers reported its use for the determination of residues from improvised explosive devices using an optical detector based on a light-emitting diode<sup>22</sup> as well as a contactless conductivity detector.<sup>23</sup> Kaljurand and co-workers developed a system for the on-site determination of chemical warfare agent degradation products.<sup>24</sup> Lee et al. described a system with laser-induced fluorescence (LIF) detection based on a solid-state laser.<sup>25</sup> A detailed discussion of the portable CE

Received: November 16, 2012 Accepted: January 22, 2013 Published: January 22, 2013 instruments based on conventional capillaries up to 2010 can be found in a review by Macka and co-workers.<sup>26</sup> Also reported have been portable systems based on microchip-CE devices.<sup>27–29</sup>

A weak point of the field-portable CE instruments reported thus far has been the injection systems. These have generally been very delicate, requiring careful manual operations. From our experience with previous instruments,<sup>15–18</sup> it has become clear that a robust, automated injection system is necessary to make the instruments amenable to routine use in field analysis. The difficulty arises from the fact that in capillary electrophoresis very small volumes in the nanoliter range must be injected into tiny capillaries. Because of the low volumes and the high voltages involved, it is not possible to use rotary injection valves for direct injection as ordinarily employed for column chromatography. Therefore, usually the capillary itself is placed temporarily into the sample container. Two modes of injection are then possible. For electrokinetic injection, high voltage is applied, while for hydrodynamic injection, siphoning or pressurization is used, before the capillary is moved back to a buffer container for application of the separation voltage. While electrokinetic injection is easier to implement, the hydrodynamic mode is preferred, as it avoids a sampling bias. Commercial benchtop instruments for the laboratory feature a robotic system for movement of sample and buffer vials and/or capillary end and pneumatic pressurization or application of a vacuum. Little effort has been spent to date on the development of injection systems for portable instruments. The commercially available unit<sup>19</sup> has a turntable and an automated hydrodynamic injection arrangement similar to conventional benchtop instruments. However, this is relatively complex and fairly delicate. The research instruments reported have relied on electrokinetic injection or improvised hydrodynamic injection, typically by manually elevating the injection end of the capillary for a few seconds timed with a wristwatch.<sup>15-18,25</sup> Kaljurand and co-workers have addressed this general weakness by developing different versions of split injectors and used this approach in their instrument developed for the determination of chemical warfare agents.<sup>24,30,31</sup> Injection was carried out by emptying a sample into the splitting device using a syringe. This is easier to perform than manual injection directly into capillaries and was essential for the reported field work on chemical warfare agents where the operator had to wear full body protective clothing.<sup>24</sup> However, a limitation of this system was the fact that the injection relied largely on the reproducibility of the pressure created by hand when emptying the syringe.

The aim of the project reported herein was the development of a further improved injection system for a portable instrument which is fully automated and thus eliminates the operational difficulties as well as any measurement bias of manual injections. The arrangement employed is based on a split injector which had been used in previous stationary instruments based on sequential injection (SI) manifolds employing a syringe pump and a multiposition valve.<sup>32,33</sup> It takes the approach reported by Kaljurand and co-workers<sup>31</sup> for their portable system further, in that the sample is passed through the splitter automatically. The use of fixed pressurization and computer-controlled timing precludes the variations of manual operation. The injected volume can be set readily over a large range, which allows easy optimization for different tasks. The sample is drawn into the system automatically by using a small membrane pump.

## EXPERIMENTAL SECTION

Chemicals, Sample Collection, and Preparation. All chemicals were of analytical or reagent grade and purchased from Fluka (Buchs, Switzerland) or Merck (Darmstadt, Germany). Stock solutions (10 mmol/L) of chloride, nitrate, sulfate, nitrite, fluoride, phosphate, oxalate, malonate, citrate, succinate, phthalate, acetate, lactate, benzoate, vanillate, ascorbate, and gluconate were used for the preparation of the standards of inorganic and organic anions, using their respective sodium or potassium salts. Before use, the capillary was preconditioned with 1 M NaOH for 10 min and deionized water for 10 min prior to flushing with buffer. Deionized water purified using a system from Millipore (Bedford, MA) was used for the preparation of all solutions and for sample dilution if required. The soft drinks were passed through 0.45  $\mu$ m membrane filters and diluted 10 times before analysis. The orange juice sample was first centrifuged for 10 min at 6000 rpm and filtered to remove the flesh content and then diluted 50 times due to the high concentration of citrate. For the analysis of phosphate in wastewater, samples were filtered with 0.45  $\mu$ m membrane filters and injected directly into the system for analysis. No further treatment was carried out.

Instrumentation. The injection interface accommodating the capillary and the ground electrode was machined in a plexiglass block (3 cm  $\times$  2 cm  $\times$  2 cm) according to a previously reported design.<sup>34</sup> This was fitted with a micrograduated needle valve obtained from IDEX (P-470, Oak Harbor, WA) and solenoid valves from NResearch (product nos. 116T021 and 116T031, West Caldwell, NJ). Pressurization was achieved using a steel cylinder (Swagelok 304L-HDF4-150), a regulating valve (Swagelok 1ELA2C1000BK), and a pressure gauge (Swagelok PGI-40M-BG6-LANX-0) (Arbor, Niederrohrdorf, Switzerland). The miniature membrane pump (NF-5-DCB) for sample aspiration was purchased from KNF (Balterswil, Switzerland). All fluidic connections were made with 0.02 in. inner diameter (I.D.) and 1/16 in. outer diameter (O.D.) Teflon tubing and with polyether ether ketone (PEEK) flangeless nuts and ferrules 1/4-28 UNF (IDEX). Two high voltage modules (DX250 and DX250N) capable to provide a maximum of 25 kV of either polarity were obtained from EMCO (Sutter Creek, CA). Polyimide-coated fused silica capillaries of 50 µm I.D. and 365 µm O.D., and capillaries of 25  $\mu$ m I.D. and 365  $\mu$ m O.D. (from Polymicro, Phoenix, AZ), were used for separation. The high voltage end of the capillary was isolated with a safety cage made from Perspex, which was equipped with a microswitch to interrupt the high voltage upon opening.

The purpose-made contactless conductivity detector was based on a design reported previously<sup>9</sup> and used an integrated circuit oscillator from Exar (XR-2206, Fremont, CA) to create a sine wave of 300 kHz, an OPA627 operational amplifier (Texas Instruments, Dallas, TX) to bring the amplitude to  $\pm 10$  V, an OPA602 operational amplifier (Texas Instruments) fitted with a 1.5 M $\Omega$  feedback resistor to convert the pick-up current to voltage, and a monolithic AD630 synchronous detector (Analog Devices, Norwood, MA) for rectification. The voltage signal was then amplified, low-pass filtered,<sup>9</sup> and passed to an ADC-20 from Pico Technology (St. Neots, UK) connected to a notebook class personal computer for data acquisition. Most of the parts, i.e., valves, high voltage modules, and membrane pump, were controlled from the same computer using an Arduino Nano microcontroller board (RS Components,



Figure 1. Diagram of the fluidic connections of the instrument. Pt denotes the two platinum electrodes for application of the high voltage (HV) for separation. The injector/interface is grounded, while the voltage is applied from the detector end.

Wädenswil, Switzerland) programmed using the Arduino integrated development environment and appropriate interface circuitry. The instrument features built-in rechargeable lithiumion batteries. A battery pack of 14.8 V and a capacity of 6.6 Ah with the dimensions of  $73 \times 55 \times 67$  mm (CGR 18650CG 4S3P, Contrel, Hünenberg, Switzerland), which was fitted with a voltage regulator to produce a 12 V output, was used to provide power to the valves, membrane pump, and the high voltage modules. A separate pair of smaller Li-ion batteries with a capacity of 2.8 Ah each (CGR 18659CG 4S1P, Contrel), which was fitted with positive and negative 12 V regulators, provided the split  $\pm 12$  V supply for the detector circuitry. Alternatively, mains power can be utilized when available via appropriate external adaptors.

# RESULTS AND DISCUSSION

System Design. A schematic drawing of the system is shown in Figure 1. Precise propulsion of fluids through the system is made possible by pressurizing a reservoir of background electrolyte with compressed air. This is provided from a small metal cylinder which is filled with a manual pump (normally used to pressurize shock absorbers of bicycles). The pressure delivered can be set with a regulating valve and monitored with a small gauge. The sample is loaded into a sample loop which is extended between two three-way valves as described previously by Sweileh and Dasgupta.<sup>35</sup> Note that it would also be possible to use a rotary valve as is customary for flow-injection analysis or column chromatography, but the use of the solenoid valves is simple and less expensive. The loop is filled by using a small membrane pump to aspirate a sample directly through a thin tube. If preferred, manual filling of the loop with a syringe is also possible. Subsequently, the sample is moved to the injector block by switching the three-way valves 1 and 2 (V1 and V2) to allow background electrolyte to flow from the pressurized reservoir. A fraction of the sample is pushed into the capillary for hydrodynamic injection as the plug is located at its front end while applying a back-pressure for a determined period of time. The back-pressure is set by adjustment of the needle valve (a bleeding type which splits the flow into two paths) and applied for the desired duration by closure of gate valve V3 (while V4 stays open). Flushing of the interface and the manifold ahead of the interface, as well as of the capillary, is possible by either opening or closing V3 and V4

at the same time. All components were integrated into an aluminum briefcase with the dimensions of 35 cm (w)  $\times$  45 cm (d)  $\times$  15 cm (h), and the system had a weight of 8 kg. A photograph of the assembly is shown in Figure 2. The fluidic



Figure 2. Photograph of the instrument. (1) Membrane pump, (2) valves, (3) splitter, (4) detector, (5) safety cage for application of high voltage, (6) pressurized air.

parts are seen on the left. The plexiglass cage to the right contains the high voltage electrode, and the small metal box sitting on top is the C<sup>4</sup>D-cell. The pneumatic parts for pressurization of the buffer reservoir are seen to the far right. The control and detector electronics as well as the rechargeable batteries are contained in the back of the instrument, and some manual switches and connectors are mounted on the panel. The internal batteries were found to provide sufficient power for typically about 9 h of operation before recharging was necessary.

**Performance.** Standard Separation of Some Common Inorganic Cations and Anions. To demonstrate the versatility of the system in analyzing different target analytes, the separation of some common inorganic anions and cations was carried out using a background electrolyte consisting of 12 mM histidine adjusted to pH 4 with acetic acid in the presence of 2 mM 18-crown-6, which is commonly used for the separation of inorganic cations and anions by CE-C<sup>4</sup>D.<sup>32</sup> The crown ether facilitates the separation of NH<sub>4</sub><sup>+</sup> and K<sup>+</sup>. The separations of these cations and anions were carried out by switching the polarity of the system between negative and positive modes. The relatively low pH-value of the buffer leads to a limited electroosmotic flow so that the anions can be determined without surface modification of the capillary. Separations of standard solutions of these cations (NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, and Li<sup>+</sup>) and anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>2</sub><sup>-</sup>, F<sup>-</sup>, and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>) at 50  $\mu$ M for each ion are shown in Figure 3. The quantitative performance data for the conditions



**Figure 3.** Typical separation of a standard solutions containing: (A) inorganic anions; (B) inorganic cations; 50  $\mu$ M for each ion. Background electrolyte: His 12 mM adjusted to pH 4 with acetic acid in the presence of 2 mM of 18-crown-6. Capillary: 50  $\mu$ m I.D., 36 cm effective length, and 50 cm total length. Separation voltage: +15 kV for anions and -15 kV for cations. Injection: pressure, 1 bar; sample loop, 150  $\mu$ L; splitting valve set to 0.15; injection time, 4 s.

used is given in Table 1. The limits of detection were in the lower micromolar range. The linear ranges depended on the species. Baseline separation between NH<sub>4</sub><sup>+</sup> and K<sup>+</sup> as well as the peaks of Ca<sup>2+</sup> and Na<sup>+</sup> were still achieved at the concentration of 100  $\mu$ M for each cation. However, at higher concentrations, baseline separation of these peaks was lost. In the case of Mg<sup>2+</sup> and Li<sup>+</sup>, linear ranges extended to 200 and

1000  $\mu$ M, respectively. The reproducibilities of peak areas and migration times were determined over a period of 8 h. The system was programmed to autonomously carry out repeated injections and separations of the standard mixture of 50  $\mu$ M every 10 min throughout this duration, i.e., a total of 48 measurements. The standard deviations for peak areas were well acceptable, being about 1%, and the stability of migration times was also excellent. Note, that the standard deviations were calculated from the nine data points acquired after each hour. A systematic drift in these parameters over the time period is not apparent in the data. This demonstrates the inherent stability of the mechanical and electronic design of the system. However, under field conditions, due to temperature changes and other effects, larger fluctuations can be expected.

Fast Separation. The system can be optimized differently to meet different objectives. Very fast separations are possible by using a capillary with a short effective length of only a few centimeters. Note, that this is not readily possible with standard benchtop instruments, as these are not designed accordingly. A further requirement is a fast and well reproducible automated injection system for small sample plugs,<sup>36,37</sup> which has not been available for portable CE instruments. The separation of four inorganic anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) within 17 s carried out on the current system is demonstrated in Figure 4. To accelerate the migrations of anions, an elevated electric field was applied by introduction of a high voltage of +15 kV over a short capillary of only 25 cm. The detector was positioned 4.5 cm from the injection end. To inject only a short plug, the back-pressure was reduced compared to the test reported in the previous section and the injection time was shortened to 1 s only. While baseline separation was achieved in both cases, it is clear from a comparison of Figures 3 and 4 that a more complex sample would require the better separation possible in the longer capillary. Under the conditions for fast separation, the LODs for Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and NO<sub>2</sub><sup>-</sup> were 5  $\mu$ M and the LOD for  $SO_4^{2-}$  was 2.5  $\mu$ M, which is still acceptable and only approximately 2 times higher than those for normal conditions.

Enhanced Detection Limit. When separation efficiency is not a limitation, LODs can be enhanced by introducing a large sample volume. This is illustrated in Figure 5 for the analysis of a tap water sample spiked with 1  $\mu$ M NO<sub>2</sub><sup>-</sup> as a potential analyte of interest which is well separated from other species. As can be seen from electropherogram (a) of Figure 5, for a normal injection volume, for which chloride, nitrate, and sulfate are well separated, a peak for nitrite is not visible, as its concentration is below the detection limit. When the injected volume is increased, by prolonging the injection time from 4 to 10 s and increasing the backpressure, nitrite becomes detectable as the LOD is lowered to 0.7  $\mu$ M (electropherogram b). However, it is clear that the separation of the three major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) was not possible under these conditions.

High Peak Capacity. Complex samples containing a relatively large number of similar ions require conditions that give good peak capacities. This usually requires relatively long residence times with long capillaries if the sensitivity is not to be compromised. Such an application is illustrated for the current system with the simultaneous separation of 11 slowly migrating organic anions, namely oxalate, malonate, citrate, succinate, phthalate, acetate, lactate, benzoate, vanillate, ascorbate, and gluconate. These compounds are found in various beverages either as major constituents or as additives. Separation was successfully achieved using a basic background

Table 1. Linearity, Detection Limits (LODs), Correlation Coefficients  $(r^2)$ , and Reproducibilities for the Determination of Inorganic Cations and Anions

ion	linear range ( $\mu M$ )	$r^2$	$LOD^{a}$ ( $\mu M$ )	intraday reproducibility of peak area $(\% RSD)^b$	intraday reproducibility of migration time $(\% RSD)^b$
$NH_4^+$	6-100	0.9994	2	1.1	0.5
$K^+$	6-100	0.9996	2	1.7	0.4
Ca <sup>2+</sup>	6-100	0.9983	2	0.6	0.4
$Na^+$	10-100	0.9994	3	1.4	0.5
Mg <sup>2+</sup>	10-200	0.9992	3	1.0	0.3
Li <sup>+</sup>	10-1000	0.9999	5	1.8	0.3
Cl-	10-1000	0.9999	3	0.9	0.6
NO <sub>3</sub> <sup>-</sup>	10-450	0.9999	3	1.0	0.4
SO4 <sup>2-</sup>	5-450	0.9999	1.5	0.6	0.3
$NO_2^-$	10-1000	0.9999	3	0.7	0.6
F <sup>-</sup>	27-2000	0.9998	8	2.1	0.5
$H_2PO_4^-$	57-500	0.9991	17	2.4	0.3

<sup>a</sup>Peak heights corresponding to 3 × baseline noise. <sup>b</sup>Determined for 50  $\mu$ M, n = 9, over a period of 8 h.



**Figure 4.** Fast separation of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and NO<sub>2</sub><sup>-</sup> at 50  $\mu$ M. Background electrolyte: His 12 mM adjusted to pH 4 with acetic acid in the presence of 2 mM of 18-crown-6. Capillary: 25  $\mu$ m I.D.,  $l_{eff}/L_{tot}$  = 4.5/25 cm. Separation voltage: +15 kV. Injection: pressure, 1 bar; sample loop, 150  $\mu$ L; splitting valve set to 0.20; injection time, 1 s.

electrolyte of Tris/CHES at a concentration of 70 mM for each compound and in the presence of 200  $\mu$ M CTAB for reversal of the electroosmotic flow. Three different soft drinks were analyzed as illustrative samples for this demonstration. The electropherograms for a standard mixture and for soft drink samples are shown in Figure 6. Electropherogram b is for a soft drink made from a byproduct of cheese production and for this reason contains a large concentration of lactate besides other anionic species. The cola beverage (electropherogram c) was found to contain phosphate, while the orange juice (electropherogram d), as expected, contained a high concentration of citrate.

Application Example. Field Measurements of Phosphate at a Wastewater Treatment Plant. To demonstrate its suitability for field work, the instrument was taken to a local sewage treatment plant and set up for the determination of phosphate. A solution of 1 mM His/25 mM acetic acid (pH 3.5) was found to be an optimal background electrolyte for the



**Figure 5.** Sensitive determination of a tap water sample spiked with 1  $\mu$ M NO<sub>2</sub><sup>-</sup>. (a) Normal injection volume: 1 bar, 150  $\mu$ L, splitting valve set to 0.15, 4 s. (b) Large volume injection: pressure, 1 bar; sample loop, 150  $\mu$ L; splitting valve set to 0.10; injection time, 10 s. Background electrolyte: His 12 mM adjusted to pH 4 with acetic acid in the presence of 2 mM of 18-crown-6. Capillary: 50  $\mu$ m I.D., 36 cm effective length and 60 cm total length. Separation voltage: +15 kV.

determination of this species. Under this condition, the phosphate peak is very well separated from the very broad peak of the major anions (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and SO<sub>4</sub><sup>2-</sup>) which are present in the sewage water at very high concentrations (ranging from 1 to 4.5 mM). An electropherogram for separation of phosphate in a sewage water sample is shown in Figure 7. In Table 2 the phosphate concentrations (mg P/L) measured with the new instrument in several samples are given together with the results from the standard photometric molybdenum blue method for validation. The first six samples were determined in the field (single measurements), and the remainder back in the laboratory (in triplicate). As shown in Table 2, the results from the CE method are in good agreement with those obtained from the molybdenum blue reference method (errors between the two methods were less than 10% for measurement done in the lab). However, the on-site



**Figure 6.** High efficiency separations. (a) Eleven organic compounds often found in beverages and carbonate. (b) Lactate-containing softdrink. (c) Cola beverage, (d) Orange juice. Background electrolyte: Tris/CHES 70 mM and CTAB 0.2 mM (pH 8.5). Capillary: 25  $\mu$ m I.D.;  $l_{eff}/L_{tot} = 36/65$  cm. Separation voltage: +15 kV. Injection: pressure, 1 bar; sample loop, 60  $\mu$ L; splitting valve set to 0.15; injection time, 4 s. Peaks: (1) oxalate, (2) malonate, (3) citrate, (4) succinate, (5) phthalate, (6) carbonate, (7) acetate, (8) lactate, (9) benzoate, (10) vanillate, (11) ascorbate, (12) gluconate, (13) chloride, (14) nitrate, (15) sulfate, (16) phosphate, (17) unidentified compound.



**Figure 7.** Detection of phosphate (1.6 mg P/L) in a sewage sample. Background electrolyte: His 1 mM/acetic acid 25 mM (pH 3.47). Capillary: 50  $\mu$ m I.D.;  $l_{eff}/L_{tot} = 29/50$  cm. Separation voltage: +15 kV. Injection: pressure, 1 bar; sample loop, 60  $\mu$ L; splitting valve set to 0.12; injection time, 4 s.

measurement generally gave higher deviations which is ascribed to the fact that the freshly collected wastewater samples contained some bubbles of dissolved gases. As no degassing could be carried out in the field, these would have influenced

 Table 2. Concentrations of Phosphate in Sewage Samples

 Measured in the Field and in the Laboratory

sample	capillary electrophoresis (mg P/L)	molybdenum blue method (mg P/L)	% error
1	2.1	2.4	13
2	2.3	2.1	6
3	1.5	1.6	8
4	1.5	1.6	9
5	1.5	1.8	16
6	1.8	2.1	15
$7^a$	3.6	3.6	1
8 <sup>a</sup>	4.9	4.6	7
9 <sup>a</sup>	3.5	3.4	2
$10^a$	0.54	0.58	8
11 <sup>a</sup>	0.76	0.78	2
<sup>a</sup> Sampla	s massured in the laborate	2011	

"Samples measured in the laboratory.

the precision of injection. The detection limit of the method was 0.15 mg P/L (5  $\mu$ M) (based on S/N = 3), and its linear range extended from 0.5 mg P/L (16  $\mu$ M) to 10 mg P/L (320  $\mu$ M).

# CONCLUSIONS

The portable CE-C<sup>4</sup>D instrument with automated injection built in-house showed a good performance with high reproducibility. The results obtained confirm its suitability for on-site measurements. The system may be optimized for different compromise conditions with regard to detection limits, dynamic range, separation efficiency, and analysis time according to the task at hand. As demonstrated by the autonomous stability test, which extended over 8 h duration, the instrument also has the potential to be set up for unattended monitoring operations. This is facilitated by the automated aspiration of the sample.

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## Notes

The authors declare no competing financial interest.

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