Single strip solid contact ion selective electrodes on pencil-drawn electrode substrate

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A simple and low-cost approach for the preparation of ion-selective electrodes (ISEs) is proposed as a favorable alternative to the traditional paper-based electrodes. This involved the application of graphite from a simple household pencil via mechanical abrasion onto a modified acetate sheet. The resulting electrodes exhibited excellent sensing properties towards all tested ions, including a wide dynamic response range, fast response time and satisfactory long-term stability. The same methodology was used to produce stable and functional reference electrodes. These electrodes were then combined with other graphite-based ISEs to yield single strip solid-contact electrodes for simultaneous detection of cations and anions in aqueous solutions. The described approach, which is simply drawing on paper, opens new avenues for the development of sensing devices using very cheap and easily accessible components.

Introduction

Over the past decade, significant effort has been placed into developing techniques and methodologies that are fully applicable to real-time sample analysis while significantly lowering per-sample and per-measurement costs. Such advancements are expected to make a great impact in many different fields ranging from environmental analysis to the health, security, and manufacturing industries.

Ion selective electrodes (ISEs) are a class of chemical sensors that, in recent years, went through a renaissance and showed excellent potential as tools for routine environmental monitoring and clinical analysis. They are easy to manufacture, show excellent selectivity and sensitivity, are readily miniaturized and can be connected to simple communication devices.

Recently, several studies have focused on the development of paper-based ISEs utilizing carbon nanotubes (CNTs) either as the underlying solid contact (electron conductor) or as ion to electron transducer separating the solid contact from ion selective membrane.1–10 This versatile character can be attributed to their excellent electrical conductivity, high tensile strength and ability to function simultaneously as recognition element and transducer (transduction via the formation of electrical double layer).11–15 Moreover, inherent hydrophobicity of CNTs prevents water layer formation between the membrane and underlying substrate.7,16 Interestingly, other reports indicate that presence of sputtered gold and conductive polymer such as poly(3-octylthiophene) is necessary to produce paper-based ISEs.2 This discrepancy between reported data could perhaps arise from differences in the thickness of CNTs layer deposited onto the paper surface, the concentration of surfactant (unwashed surfactant may reduce contact angle between water droplet and the substrate, thus increasing surface wetting)17 and purity of used materials.

However, to produce functional sensing devices, CNTs have to be typically dispersed in a liquid18–20 (often water and surfactant solution) via ultrasonication and are later deposited onto the paper/electrode by drop-casting,21,22 ink-jet printing,23–25 dip-coating26–28 or spin coating.22,29 Such processes may take several hours and are strongly limited by the low solubility of CNTs in most solvents,29,30 need of specialized instrumentation for the preparation of ISEs (ultrasonicator; sputter coater) and relatively high cost of materials required (e.g. CNTs and gold). Recently, mechanical abrasion of compressed either single or multi-walled CNTs directly onto the surface of the paper was suggested as an alternative approach to develop chemiresistive sensors for gas detection.31–35 These sensing devices exhibited sufficient conductivity (10–30 kΩ) and showed similar/improved sensing characteristics to their counterparts prepared using solvent-dispersion techniques. More recently, pencil drawn electrodes (PDEs) prepared via mechanical abrasion of graphite on solid substrate have been developed and used as voltammetric sensors for the detection of metal ions.36–38 They offered very
good performance characteristics while maintaining low cost and ease of fabrication.

Previously, weighting paper (compressed cellulose) has been identified as an excellent substrate for the fabrication of sensing devices using both solvent and solvent-free methods.\textsuperscript{6,39–44} The widespread use of paper arises from its global accessibility, low manufacturing cost and high compatibility with various printing devices.\textsuperscript{50,41,45–49} Moreover, it is a common substrate for abrasion based drawing and writing using wax or graphite pencils.\textsuperscript{31–34,50} The transport of water by capillary action in paper is identified as an important advantage in designing microfluidic devices. However, the same phenomenon may lead to potential instability in ISEs – diffused water is absorbed by the paper and transported towards the connectors. Therefore, special attention should be drawn to cheap, accessible and more hydrophobic surfaces that could be used as alternative materials to commonly employed weighting/filter paper in ISEs.

Important consequence of the above analysis is that despite of significant simplification and cost reduction, preparation of sensors is still limited to highly skilled personnel and/or access to specialized chemicals. Interestingly, we have witnessed highly exciting advances in fields that were able to open its doors to members of public. Citizen science contributed to a wide variety of fields from astronomy, to zoo science and even to art history. The growth of fields like Big Data heavily relies on the ability to collect large amounts of data, and it has been argued that the next big leap in communication will happen by integrating chemical sensors with mobile communication devices.\textsuperscript{35,51,52} Clearly, to enable such advances in chemistry, it would be important to involve members of public in collection of chemical data. This could be achieved with sensors that are so simple and cheap that citizens can prepare and use them at home using simple household items.

Herein, we demonstrate a straightforward approach to prepare ultra-simple and inexpensive ISE platforms by using commonly accessible household items. The electron conductive layer was prepared by mechanical abrasion of a very cheap graphite pencil directly onto a substrate cut from acetate sheet, while the whole setup was finished using simple adhesive tape (e.g. sellotape). All materials are readily available in ordinary bookstores. After the application of ion selective membranes, the performance of such devices was assessed for the determination of biologically and environmentally important ions. We are currently working towards replacement of traditional components of ISE membranes with common natural and household chemicals.

**Experimental**

**Reagents**

Nonactin (ammonium ionophore I), sodium ionophore X (4-tert-Butylcalix[4]arene-tetraacetic acid · tetraethylster), sodium tetrakis[3,5-bis-(trifluoromethyl)-phenyl]borate (NaTFPB), tetradeccylammonium chloride (TDACI), poly-(3-octylthiophene) (POT), high molecular weight poly(vinyl chloride) (PVC), bis(2-ethylhexyl)- sebacate (DOS), 2-nitrophenyl octyl ether (o-NPOE), and tetrahydrofuran (THF) were obtained from Sigma-Aldrich and of Selectophore grade. All aqueous solutions were prepared in ultra-pure water obtained with Purelab Ultra water purification system (resistance 18 MΩ cm).

**Preparation of pencil-drawn substrate**

Firstly, a 1.5 cm × 3.0 cm strip was cut from a parent acetate sheet and was subsequently etched with aluminium oxide (grit 240) for 30 sec to provide the surface with enhanced porosity in order to improve adhesion of graphite onto the surface of acetate. With the use of a typical graphite pencil, a line of carbon is applied/drawn by hand onto the acetate sheet. In this work we used typical pencils available in a bookstore. We used a set called Artist’s Pencils that contain 10 pencils of different hardness going from 4B to 4H which indicates that the ratio of graphite to clay decreases in order to provide increasing hardness. Interestingly, there were no differences in the concentrations of C and Si obtained using Energy Dispersive x-ray Spectroscopy (EDS) across the set of pencils (see Supplemental Info). Nevertheless we tested electrodes prepared using all pencil types from the box as well as 4B pencils from three different boxes and there were no significantly different potentiometric results originating from the pencil type or box (data not shown). Number of abrasions also did not show to be relevant - it was important only that the resistance of drawn line is < ~50 kΩ. Each sensor was partially overlain with mask of non-permeable polyester tape, as shown in Scheme 1. A hole of 0.3 cm in diameter was punched on one top end of the sellotape as an aperture to allow for the application of POT/ion selective membrane layers while an area of 0.75 cm² of its other end was exposed to provide electrical contact.

**Preparation of sodium-, nitrate- and ammonium-sensing membranes, and solid-contact reference electrode**

The NO\textsubscript{3}-selective membrane contained 5.0 mmol kg\textsuperscript{-1} of TDACI, PVC (33.2 wt %) and o-NPOE (66.4 wt %). Na\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+}-selective membrane contained 10.0 mmol kg\textsuperscript{-1} of sodium ionophore X and ammonium ionophore I respectively and 5.0 mmol kg\textsuperscript{-1} of NaTFPB, PVC (32.9 wt %) and DOS (65.8 wt %). Solid-contact reference electrode contained 12.5% tetrabutylammonium tetrabutylborate (TBA-TBB), PVC (29.2wt %) and o-NPOE (58.3 wt %). All electrodes were prepared by dissolving the above-mentioned components in 1.5 mL THF and the resulting cocktail was vortexed for 30 min for complete dissolution of components.

**Development of ISEs**

For potentiometric measurements, if needed a solution of POT (10\textsuperscript{-3} M of monomer in chloroform) was drop cast onto the aperture of the graphite-based electrodes. All electrodes were
then left at room temperature to dry. An aliquot (~20 μL) of each sensing membrane was drop cast onto the top of each electrode, and further left at room temperature to dry overnight. The following day, ISEs were conditioned in 1.0 × 10⁻³ M of respective primary ion solution while reference electrodes were conditioned in 1.0 × 10⁻² M of KCl for 18h prior to the potentiometric experiments.

Preparation of all-solid state single strip potentiometric sensing device

A 10.0 × 3.0 cm strip was cut from parent acetate sheet as was prepared as explained above. Nine lines were subsequently drawn by pencil and electrodes prepared to form a strip that contained one solid contact reference electrode, four NO₃⁻ - and four NH₄⁺ - selective electrodes as illustrated in Scheme 1.

Scheme 1. Schematic representation of proposed acetate-based electrodes fabricated via mechanical abrasion. Top) Step I: acetate sheet slightly roughened by sand paper. Step II: Line was drawn using a typical household pencil. Step III: Insulating the platform using simple sellotape leaving only a small opening at the distal end of the electrode. Step IV: Drop casting suitable cocktail. Bottom) Finished single strip potentiometric device where one electrode was used for deposition of all-solid-contact reference electrode based on TBA-TBB while the rest are used for deposition of the cocktails for required ISEs.

EMF measurements

Potentiometric responses of all electrodes were recorded using Lawson Labs Inc. 16-channel EMF-16 interface (3217 Phoenixville Pike Malvern, PA 19355, USA) in a stirred solution against a double-junction Ag/AgCl reference electrode with a 1 M LiOAc bridge electrolyte (Fluka) except in the case of single strip electrodes when all-solid-contact reference electrodes was used. All ISEs were immersed in sample solution (ultrapure water) followed by addition of aliquots of known concentration of required salt.

Selectivity measurements

Ammonium-selective electrodes were prepared and conditioned in 0.1 M NaCl. Responses towards interfering ions were recorded according to separate solution method as described by Bakker.⁵³

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance measurements were performed by using an Ivium Technologies CompactStat Impedance Analyser coupled to a Himux XR B channel electrochemical multiplexer (Ivium Technologies). The EIS measurements of ion selective membranes were performed as described previously.⁵⁴ Briefly, EIS spectra were collected using excitation amplitude of 0.01 V within the frequency range spanning from 100 kHz to 0.1 Hz for graphite electrodes only (no membrane). However, amplitude of 0.1 V was used for electrodes coated with ion selective membrane to improve signal to noise ratio. A conventional three electrodes set-up was used in this study using platinum auxiliary electrode and a silver-silver chloride electrode as the reference. Each measurement was carried out at open-circuit potential in 0.1 M solutions of metal salts at room temperature. All impedance spectra were fitted to equivalent circuits using the IviumStat software version 2.0. All measurements were done in at least triplicate. This allowed determination of resistance components.

Natural water samples and their analysis

Three different samples of natural waters were collected on and around Keele campus: A) University Lake: Surrounded by playgrounds and university estate and the concentration of nitrate is usually around 1 to 3 mg/L (1.6x10⁻⁵ – 4.8x10⁻⁵ M) and ammonium <1 mg/L (< 5.6x10⁻⁶ M); B) Mill Haft: A small stream draining farming land and forests near Newbury Junction in Staffordshire and the nitrate and ammonium concentration are relatively lower than the Coley brook and typically contain 2-10 mg/L (3.2x10⁻⁵ – 1.6x10⁻⁴ M of NO₃⁻ and 1.1x10⁻⁵ – 5.6x10⁻⁶ M) . Ammonium during flood event can be 2 mg/L (1.1x10⁻⁴ M); and C) River Coley Brook in Staffordshire: A stream draining an agricultural catchment, which is dominated by strawberry farming in southern Staffordshire. The result is usually high loading of the stream with run-off containing nitrate between 20 to 50 mg/L (3.2x10⁻⁴ – 8.1x10⁻⁴ M). Ammonium during flood event can be 2 mg/L (1.1x10⁻⁴ M). Field water samples were transported to the lab under temperature less than 4°C, and filtered immediately using 0.45 microns syringe filters (Whatman). Concentration of N-based nutrients (NH₄⁺ and NO₃⁻) were analysed using Lachat (QuickChem 8500; Hach, Colorado, USA) Flow Injection Analyser (FIA) using phenolate (Berthelot) reaction and Dionex ICS-5000 Ion Chromatography (IC) respectively.

Results and Discussion

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Impedance measurements of electrodes based on pencil-drawn substrate

The impedance spectrum recorded for graphite-based electrodes is shown in Figure 1. It is instantly apparent that the EIS spectrum is dominated by the presence of 90° line that resembles capacitive behavior thus indicating fast charge transport at the graphite/solution interface as reported previously.¹

![Figure 1](image1.png)

**Figure 1.** Impedance spectrum of randomly selected electrodes made of graphite deposited onto the acetate substrate via mechanical abrasion.

Note that the intercept of the line with the real axis (Z) is determined by the electrolyte resistance rather than by the ohmic resistance of the capacitive (graphite) coating. The small distortion in shape from the ideal 90° response may arise from chemical inhomogeneity of the deposited graphite layer as commercially available pencils can contain significant amounts of clays and other additives that can contribute towards impedance response. Moreover, physical irregularities at the electrode’s surface caused by mechanical abrasion (drawing) of graphite on acetate sheet may produce distortions from the expected theoretical response. Such response characteristics resemble those obtained for electrodes based on the presence of CNTs demonstrating that graphite can be used as effective signal transducer.¹⁻⁷,⁸ However, further studies have to be carried out to understand the above-mentioned transduction mechanism.

Characterization of ISEs based on graphite-substrate using EIS

The presence of one semicircle at high frequency region in Figure 2 demonstrates than only one relaxation process takes place during impedance measurement. The frequency dispersion in the recorded EIS spectrum resembles a compressed semicircle that is equivalent to membrane resistance in parallel with a geometric capacitance of the membrane. Roughened surface of the electrodes and membrane inhomogeneity have been previously indicated to cause deformations in the impedance spectrum of analyzed polymeric membranes.⁵⁵ However, in the context of this work, the frequency distortion can be attributed to the local differences in the thickness of the casted membrane (roughened outer surface due to solvent evaporation).⁵⁶ The bulk resistances of membranes deposited directly onto the graphite contact and those prepared with underlying POT layer were found 15.4 ± 0.01 and 16.7 ± 0.01 MΩ, respectively. The discrepancy in measured resistance values may be due to differences in the thickness of ion selective membranes (110 μm for POT based ISEs and 95 μm for graphite electrodes). The lack of second ‘kinetic’ semicircle in the low frequency part of the spectrum indicates that both the phase-transfer of ions through the solution/membrane interface and transduction from ionic into electronic signal at the membrane/solid contact interface are fast. Similar behavior as to membranes directly coated with polymeric membrane was observed for ISEs prepared with conductive polymer that was separating membrane from underlying solid contact (data not shown). Since POT based electrodes have a well-defined signal transduction mechanism (via electrical double layer) and their impedance characteristics have been extensively studied, one can assume that lack of second semicircle in the impedance spectrum of graphite-based electrodes strengthens the hypothesis that graphite can be used as signal transducer in ISEs.

![Figure 2](image2.png)

**Figure 2.** Impedance spectra of the ion selective membrane deposited directly onto graphite-substrate and the corresponding fitting results (straight line) with the simple equivalent circuits – \( R_s(R_mC_g) \) where \( R_s \) corresponds to the
electrolyte resistance, $R_m$ is membrane resistance and $C_g$ is geometric capacitance.

**Water layer test**

It has been previously reported that the presence of a thin aqueous layer between the solid contact and a membrane in ISEs can lead to potential instability and thus limit long term application of the electrodes. To study the formation of water layer, both graphite/ISM and graphite/POT/ISM electrodes were initially conditioned in 0.1 M solution of primary ions for 24 h. Subsequently, all electrodes were placed in the solution of discriminated ions for 4 h and then transferred back into the primary ion solution. No potential drift was observed for graphite and graphite/POT electrodes during the initial exposure to primary ions, as demonstrated in Figure 3. The same response characteristics were observed for all electrodes placed in 0.1 M NaCl solution and then exposed to 0.1 M NH$_4$Cl solution. The lack of potential drift during the measurement indicates that no aqueous layer is formed between the ion selective membrane and underlying solid contact. These findings could be attributed to the inherent hydrophobicity of both POT and graphite components. Moreover, it indicates that graphite is a suitable alternative to CNTs, which, up to this date, have been extensively used for the preparation of paper-based ISEs. Herein, mechanically deposited graphite demonstrates a stable redox potential and an ability to exhibit ion-to-electron transduction mechanism when used as conductive substrate in ISEs. Therefore, it would be beneficial to use graphite instead of CNTs to manufacture very cheap and simple electrodes without the need of using solvent chemistry, as is often required for the preparation of electrodes based on CNTs. Furthermore, graphite pencils are very inexpensive and widely accessible which opens more avenues for the application of ISEs worldwide, such as in developing countries. It should be noted that improved signal stability of these proposed electrodes may also be attributed to the use of a water-repelling solid substrate such as acetate sheet rather than ordinary paper (e.g. filter paper). Inherent hydrophobicity of acetate sheet reduces the risk of water diffusion through capillary action (as observed in paper), which minimizes signal instability that could be caused by water contacting the electrical conductor. Therefore, the possibility for application of graphite on acetate sheet (via mechanical abrasion) creates endless possibilities to develop a new wave of simplified and accessible ISEs.

**Figure 3. Water film tests of solid-contact NH$_4^+$-ISE based on graphite/NH$_4^+$ ISM and of the graphite/POT/NH$_4^+$ ISM. At t = 1 h, the solution of the primary ion (0.1 M NH$_4$Cl) was exchanged to 0.1 M NaCl, and after 5 h, the sample was replaced by the initial solution, and kept for another 12 h.**

**Potentiometric response of ISEs based on graphite substrate**

To demonstrate the applicability of graphite as a conductive substrate in the development of mechanically drawn ion selective electrodes, ammonium, sodium and nitrate electrodes were fabricated and their potentiometric behavior was evaluated. We compared ISEs for NH$_4^+$ and Na$^+$ ions with or without a layer of conductive polymer. Conductive polymers like poly-(3-octylthiophene) (POT), polypyrrole, play an important role in improving conductivity of solid contact electrodes and are also seen as an effective barrier to reduce water layer formation between interface of ion selective membrane and the substrate. Figure 4 shows potentiometric responses of NH$_4^+$ and Na$^+$ electrodes, including response for electrode configuration of both ions without a POT underlay.

Similar potentiometric responses observed for both set-ups support the findings obtained from the water layer test. Near Nernstian response slopes were observed in all case with LOD in the range of 10$^{-5}$ mol. More precisely, for non-POT-based electrodes LOD of 4.0 x 10$^{-6}$ M for NH$_4^+$-ISEs, and 5.0 x 10$^{-6}$ M for Na$^+$-ISEs was observed. Please note that we did not perform optimization of LOD since that would have been outside of the scope of this work. It is rather more important that our finding demonstrates that graphite within a household pencil is a suitable material for the preparation of ISEs due to its high hydrophobicity and also suggests acetate sheet as an optimal contact interface for the ISM. Importantly, the unbiased selectivity coefficients of NH$_4^+$ and NO$_3^-$ -selective ISEs obtained with the separate solution method closely match those reported for other electrodes based on the solid contact (see Supporting information Table S1 and S2). This indicates that graphite can be successfully employed as a conductive substrate for the preparation of ISEs without having any significant influence on their potentiometric response characteristics.
Figure 4. Comparison of the effect of conductive polymer POT on the potential stability of NH\(_4^+\) and Na\(^+\)-ISE. Close circles represent acetate sheet/graphite- while open circles denotes acetate sheet/graphite/POT – based electrodes. Linear fit of calibration points is obtained by fitting classical Nikolsky equation and experimentally available parameters for slope, selectivity coefficients, and sample composition.

Long-term stability of graphite-based ISEs

To this day, only a small number of non-disposable paper-based ISEs have been reported, as they often exhibit poor performance over time. Limited robustness of such sensing devices can be attributed to either mechanical issues related to the substrate/conductor itself (fragility of paper, washing away CNTs due to the presence of surfactant on the surface) or chemical problems caused by leaching of components from ISM into the sample. Therefore, we aim to assess whether the mechanically deposited graphite layer (onto the modified acetate sheet) could be used to fabricate ISEs for prolonged and repeated potentiometric measurements. For that purpose, the potentiometric behavior of seven graphite/NH\(_4^+\) electrodes (i.e. containing no POT as intermediate layer) was studied at different day intervals for a total number of 14 days. Prior to use, electrodes were conditioned overnight in 1.0 x 10\(^{-3}\) M NH\(_4\)Cl solution after casting. For potentiometric calibrations, the same electrodes were allowed to rehydrate one hour before commencing successive additions of ammonium standards. After each measurement, all electrodes were thoroughly rinsed with the deionized water and then stored dry until the next use. Figure 5 demonstrates exceptional reproducibility of ISEs over the given time. Average response slopes of electrode 4 shown here were 55.15 ± 0.93 mV/decade with response range being 1.0 x 10\(^{-5}\) M to 1.0 x 10\(^{-1}\) M. More importantly, the \(E^0\) identified by Lindner et al as critical parameters for evaluation of stability of ISEs was 383.59 ± 4.05 mV while the base line was 83.6 ± 6.26 mV\(^{61}\) (please find the data for other six used electrodes in Supplemental Information). Such a small deviation of \(E^0\) and base line potential after fairly simple storage and re-conditioning protocol bears a potentially significant consequence on the actual, true cost of sensor. In other words, large variations would necessitate relatively complicated calibration protocol, ultimately driving the per sample and per measurement cost.\(^{62}\)

Figure 5. Long term stability of NH\(_4^+\) - selective ISEs on acetate sheet/graphite – based substrate. Prior the first use electrodes were conditioned overnight 1.0 x 10\(^{-3}\) M NH\(_4\)Cl solution and stored in air. Electrodes were rehydrated in the same solution for 1 hour prior to subsequent calibration. It is known that the signal stability (i.e. deviations of \(E^0\) and base potential) of ISEs is consequence of minor variations in the transducer layer induced by fabrication protocols,\(^{63}\) changes in sensing layer composition due to chemical,\(^{64}\) and/or slow and spontaneous charging/discharging processes followed or caused by ion fluxes through the membrane.\(^{65-67}\) The latter two are addressed by the chemistry of a sensing layer, utilizing a variety of strategies including, for example, designing a single component sensing layer.\(^{68,69}\) Important for this research is that the former factors require careful manufacturing or/and precise design instrumental protocols\(^{70,71}\) which inevitably drive the cost of the device upward. Moreover, this work shows that a simple preparation of substrate (mechanical abrasion of pencil) can result in very reproducible and stable \(E^0\) and base potential implying minimal need for complex calibration protocols, and thus ultimately leading to true cost reduction of measurements.
All solid-state single strip potentiometric sensing device

Encouraged by the confirmation of suitable potentiometric response/stability towards several ions as well as upon confirmation of suitability of TBA-TBB-based all-solid-state reference electrode (please see Supplemental Information on experimental confirmation and discussion), we fabricated a single strip electrode consisting of a reference electrode drawn onto the modified acetate sheet together with a series of NH$_4^+$ and NO$_3^-$ electrodes. As demonstrated in Figure 6, simultaneous responses for NH$_4^+$- and NO$_3^-$-selective electrodes relative to all-solid-contact reference electrodes were obtained. The electrodes fabricated and included in the single-strip potentiometric sensing device exhibited near-Nernstian response characteristics with experimental slopes and LODs for NH$_4^+$ and NO$_3^-$ electrodes were 53.5 mV/decade and 6.0 x 10$^{-6}$ M, and 54.2 mV/decade and 2.5 x 10$^{-6}$ M, respectively. This is an important finding as it clearly demonstrates that very simple and cheap sensing devices can be fabricated using only inexpensive and readily available components such as graphite pencils and acetate sheets.

Figure 6. Simultaneous responses of NH$_4^+$ - and NO$_3^-$ - selective electrodes versus TBA-TBB-based reference electrode. All electrodes are prepared on acetate sheet/graphite substrate. Note that there was no practical difference between responses of herein prepared ISEs compared to the ones prepared on pencil-drawn substrate as alternative tool for environmental analysis of N-based nutrients.

The very good agreement between results obtained with ISEs and classical techniques indicates excellent potential of ISEs prepared on pencil-drawn substrate as alternative tool for environmental analysis of N-based nutrients.

**Conclusions**

In this work, a simple and robust approach for the fabrication of solid-contact ISEs via mechanical drawing of graphite material onto acetate substrate has been proposed. Graphite, as compared to other forms of carbon such as CNTs, can be used as both an ion-electron transducer and an electron conductive substrate. Therefore, it can be considered as a significantly cheaper alternative to traditionally employed materials. Due to its strong hydrophobicity, the use of acetate sheet eliminates the “wetting” effect that other forms of paper substrate are deemed to suffer, improving signal stability. In general, the electrodes manufactured using these simple and very cheap components have demonstrated excellent sensing properties towards all ions of interest. The resulting sensing devices demonstrated near-Nernstian response characteristics, good selectivity, and short response time, and thus create numerous opportunities for the development of ultra-simple and inexpensive potentiometric sensors.

**Notes and references**


**Table 1.** Concentrations of NH$_4^+$, and NO$_3^-$ in three natural water samples obtained by herein described ISEs and evaluated by FIA (NH$_4^+$) and IC (NO$_3^-$).

<table>
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<th></th>
<th>ISE/10$^{-5}$</th>
<th>FIA/10$^{-5}$</th>
<th>ISE/10$^{-5}$</th>
<th>IC/10$^{-5}$</th>
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