

# Ion Sensing Pencil: draw your own sensor

Martin Jendrlin,<sup>†</sup> Suntisak Khumngern,<sup>†,‡,§</sup> Apon Numnuam,<sup>‡,§</sup> Panote Thavarungkul,<sup>‡,#</sup> Proespichaya Kanatharana,<sup>‡,§</sup> Dmitry Kirsanov,<sup>¥</sup> Vladimir L. Zholobenko,<sup>†</sup> Lukasz Mendecki,<sup>†</sup> and Aleksandar Radu<sup>\*,†</sup>

<sup>†</sup> Lennard-Jones Laboratories, Birchall Centre, Keele University, Keele, Staffordshire ST5 5BG, United Kingdom

<sup>‡</sup> Center of Excellence for Trace Analysis and Biosensor, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand

<sup>§</sup> Department of Chemistry, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112, Thailand

<sup>#</sup> Department of Physics, Faculty of Science, Prince of Songkla University, Hat Yai, Songkhla, 90112 Thailand

<sup>¥</sup> Applied Chemometrics Laboratory, Institute of Chemistry, St. Petersburg State University, Universitetskaya nab 7/9 St. Petersburg 199034

---

**ABSTRACT:** We demonstrate for the first time the concept of ion sensing pencil (ISP). The pencil's lead carries chemical sensing functionality and is constructed by compression of graphite and zeolite, while the clutch is prepared by 3D printing. The ISP can be used to draw a chemical sensor by simple abrasion onto a hydrophobic surface. The ISP can be stored at home, used immediately off-the-shelf without any handling prior to measurements. Its simple preparation, handling, and measuring protocols offer the possibility of integration into large scale sensor networks or to be offered to the general public for use at home using readout devices already present at many homes. We demonstrate the chemical functionality of ISP by producing 14 ISPs prepared by compression of graphite and one of 14 different zeolites individually in 60:40 wt%. These ISPs are then used to draw electrodes which were characterized in analogy to ion-selective electrodes. The ISP-drawn electrodes were utilized as a multi-sensor array for the determination of water quality in a model sample, which is a first reported case of using zeolite-based electrodes in multisystem arrays, followed by the demonstration of their potential to be used by non-trained personnel. The implementation ISPs in potentiometric detection holds promise for further development of inexpensive and accessible tools for obtaining chemical information in areas where utilization of chemical sensors is currently limited.

---

## INTRODUCTION

The development of information technology facilitated the remote monitoring and control of physical devices and everyday objects over the internet. The Internet of Things (IoT) as the previous concept is named, has penetrated into many aspects of life. Among many other applications, specialized IoT devices can monitor the health and general wellbeing of citizens,<sup>1-3</sup> provide data to optimize food production,<sup>4</sup> control air and water quality,<sup>5</sup> and to increase the quality of the services offered to the citizens, while reducing the operational costs of the public administrations<sup>6</sup>, etc. Such systems utilize a range of sensors for monitoring relevant key parameters. A keen chemist's eye will notice that IoT systems utilize very few truly chemical sensors. Chemical information (if relevant) is typically inferred from a range of physical sensors (position, vibration, temperature, humidity)<sup>4,7</sup> or image analysis etc. Despite significant recent advances,<sup>8-10</sup> chemical sensors still require relatively complex handling protocols (storage, calibration, cleaning), which drives their price beyond the possibility to be routinely used in IoT. Interestingly, the same disadvantages limit penetration of chemical sensors in Citizen Science (CS) as a field that some view as the next frontier in the expansion of research.<sup>11,12</sup> Involving citizens in large scientific projects opens up exciting opportunities in many application fields.<sup>13</sup> Unfortunately, chemical sensors are not yet at the stage of development that

would allow routine operations by non-specialists and integration into large, autonomous sensor networks which are seen as essential for applications in CS and IoT. If chemical sensors are to be applied for the acquisition of large arrays of chemically-relevant information, they have to be readily available, extremely simple to use, and versatile (able to obtain a variety of relevant chemical information). Ideally, their price would be affordable, and they could be plugged into a simple, readily available, non-specialized read-out system.

Arguably, a pencil is one of the simplest, ubiquitous, versatile (in terms of colour range), and foolproof tools. Thus, a pencil-like chemical sensor would have a great opportunity for penetration into fields where their applications are currently severely limited. A pencil-type sensor concept has very recently been investigated by utilizing carbon nanotubes (CNTs) or metal-organic frameworks (MOFs).<sup>14-17</sup> However, these approaches rely on long and laborious modifications of experimental protocols and substantial chemical changes to the bulk or surface of materials in order to achieve required selectivity for specific ions or gasses. In our view, a suitable solution for this complex challenge lays in exploiting relevant advantages of existing very low cost materials. Graphite is interesting as it has a long history of use in analytics,<sup>18-20</sup> while its price is >1000 times lower than simplest, non-modified commercially available CNTs. Zeolites attracted our attention

due to their selective ion exchange properties exploited effectively in areas such as petroleum industry, catalysis, water purification,<sup>21</sup> as well as elements in electrochemical sensors.<sup>22–24</sup> Zeolites are microporous aluminosilicate materials that can accommodate a variety of cations e.g.  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , etc). The functionality of zeolites is based on the selective exchange of these ions influenced by the topology, pore size, and Al:Si ratio within the zeolite framework.<sup>22,23,25</sup> Thus, the selectivity of a zeolite framework for a target ion offers an opportunity for utilization in chemical sensing in analogy to ISEs, while zeolite's solid structure allows mechanical compression into stable pencil lead-like shapes. Herein, we suggest that compression of a simple solid mixture of graphite and a zeolite enables preparation of chemical sensors that look and can be operated as a pencil but offer analytical characteristics analogous to ion-selective electrodes (ISEs). We used 14 zeolites to prepare 14 ISPs and recorded their responses to 9 cations. The choice of zeolites and ions was guided by the expectations of selectivity to a specific ion in environmental samples as a function of zeolite's affinity to that ion.<sup>24–26</sup>

## EXPERIMENTAL

### Materials

Graphite powder (<20 $\mu\text{m}$ , synthetic), sodium chloride (NaCl), potassium chloride (KCl), ammonium chloride ( $\text{NH}_4\text{Cl}$ ), calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), zinc chloride ( $\text{ZnCl}_2$ ), 2-nitrophenyl octyl ether (>99.0%), tetra-n-butylammonium tetrafluoroborate (TBA-TBB), tris(hydroxymethyl)aminomethane hydrochloride (Tris-HCl) were purchased from Sigma-Aldrich, UK. Hydrochloric acid (HCl), manganese chloride ( $\text{MnCl}_2$ ) and iron (III) chloride ( $\text{FeCl}_3$ ) were obtained from Fisher while nickel chloride ( $\text{NiCl}_2$ ) and copper (II) chloride ( $\text{CuCl}_2$ ) from Harris reagents. OHP universal film removable top stripe 100 (clear 4243 - 100 $\mu\text{m}$ ) from Q-connect was used as a substrate. All the chemicals were of a Selectophore grade and used without any further purification. All the standard aqueous solutions were prepared with ultrapure water obtained from Pico Pure 3 water system. Zeolites NaX, KX, NaY, KY were obtained from Riogen, USA. Zeolites, NaA and KA were from Crosfield, UK. Zeolites,  $\text{NH}_4\text{-MOR}$ ,  $\text{NH}_4\text{-FER}$ ,  $\text{NH}_4\text{-BEA12}$ ,  $\text{NH}_4\text{-BEA19}$ , and  $\text{NH}_4\text{-ZSN-5}$ , were from Zeolyst, Netherlands, Zeolite K-LTL was from Tosoh, Japan. Natural zeolite HEU-A (USA) was from Zeodex, UK, Natural zeolite HEU-B (Bulgaria) was from Zeodex, UK and natural zeolite HEU-C was generously provided by Prof A. Walcarius (Universite de Lorraine, France). The list of all zeolites used in this work with their structure type, Si/Al ratio, and origin are provided in SI Table SII.

### Ion-selective pencil preparation

A zeolite of choice and graphite powder were thoroughly mixed using a ball mill. The solid mixture was transferred into the pellet die and compressed in the hydraulic bench press by applying necessary pressure to obtain a mechanically robust pellet (a.k.a ISP lead). It was inserted into a pencil clutch prepared using a 3D printer (PLA filament, Wanhao Duplicator 4S). Obtained ISP was used to draw a line onto a hydrophobic surface to obtain electrode as illustrated in Figure 1.

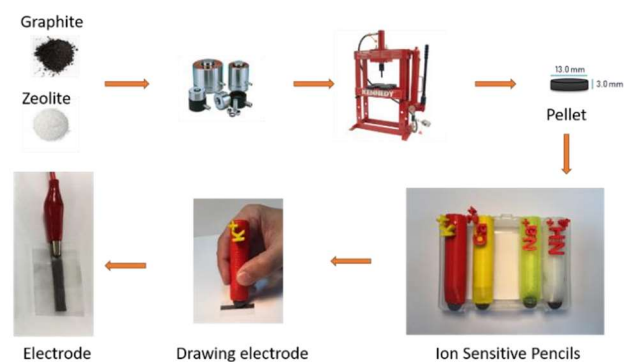


Figure 1. Process of preparation of Ion Selective Pencil and electrodes. Graphite and zeolite powders are mixed in a ball mill and compressed using hydraulic bench press to form a pellet, which is then integrated in a 3D printed clutch to form an ion sensitive pencil (ISP). The characteristics of the used zeolite define the specificity and selectivity of that ISP. An electrode is prepared using the ISP to draw onto a hydrophobic substrate.

In order to test the concept of ISP, we used a range of zeolite types including Faujasite (FAU), Linde Type A (LTA), Mordenite (MOR), Ferrierite (FER), Beta type (BEA), MFI for mobil five (also known as ZSM-V for zeolite Socony Mobil - five after the company that invented it), Linde Type L (LTL), and naturally occurring zeolites of Heulandite type (HEU) of USA, Bulgarian, and Romanian origin. The rationale for using such a wide variety of zeolite types was to scan zeolites of various factors affecting their selectivity (pore size, topology and Al:Si ratio) for potential to be utilized in ISPs. A more detailed study of the impact of these factors on ISP's functionality is forthcoming in a separate publication.

ISPs were prepared using 0%, 1%, 10%, 20%, 40%, and 60% wt of zeolite in graphite and compressions of 2, 4, and 6 tonnes. Detailed characterization of potentiometric responses is presented in SI section 1.1. titled 'Preparation of Ion Selective Pencil'. Briefly, ISPs prepared with 40% wt of zeolite compressed with 4 tonnes of pressure exhibited Nernstian slopes and these conditions were adopted as optimal. Figure 1 provides a representative calibration plot of ISP prepared by compressing 40% wt of NaX zeolite using 4 tonnes of pressure.

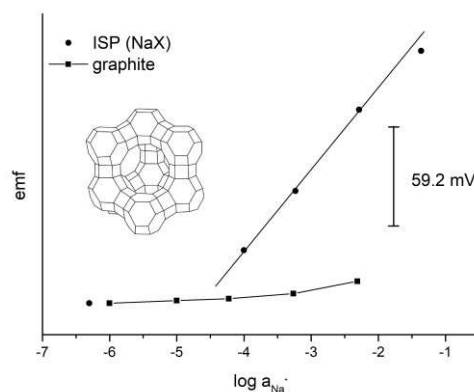


Figure 2. The potentiometric response of NaX-based ISP (circles) and pure graphite (squares) to Na<sup>+</sup>. Slope of NaX-based ISP = 55.1 mV/decade, limit of detection (LOD) = 2 × 10<sup>-5</sup> M. An inset provides the structure of faujasite (FAU).

It is noteworthy that ISPs with no zeolite (0% wt) showed slopes of >3mV/decade thus indicating that response indeed originates from zeolite. In addition, pellets prepared using 60% wt of zeolite and all pellets prepared using 2 and 6 tonnes of pressure were too brittle for drawing.

The discussion on graphite as a sensing matrix for application in ISP is provided in the SI section '1.2 Advantages and disadvantages of graphite as a sensor matrix for application in ISP'.

## Electrode substrate preparation and characterization

The hydrophobic electrode substrates were prepared by cutting a PET sheet (2.0x3.0 cm) as a single electrode from a parent PET sheet, which was then etched with the aluminium oxide (grit 240) for 30 seconds to provide the rough surface with enhanced porosity and improved adhesion of ISP lead onto the surface of the PET. The zeolite-graphite line was subsequently drawn of onto the PET sheet by abrasion until the resistance of the drawn line was lower than 3.0 k $\Omega$  as suggested previously.<sup>27</sup> The midsection of the line is insulated using a simple sticky tape. Fabrication of electrode substrate is illustrated in SI Figure SI3. The substrate is characterized using ATR-FTIR and SEM. Results and associated discussion is provided in SI section 'Substrate Characterization' and Figures SI4-SI6.

**Polymer membrane-based reference electrode:** Polymermembrane reference electrode was prepared according to the previously reported procedure.<sup>28</sup> Briefly, a 10.0 x 3.0 cm strip was cut from parent PET sheet and prepared as explained above. A line was subsequently drawn by pencil (Staedtler, HB). Each reference electrode was partially overlaid with a mask of sticky tape. A hole of 0.3 cm in diameter was punched on one top end of the sellotape. An aliquot (~20  $\mu$ L), contained 12.5 wt% tetrabutylammonium tetrabutylborate (TBA-TBB), PVC (29.2 wt%) and o-NPOE (58.3 wt%) in 1.5mL THF was drop cast onto the top of the electrode, and further left at room temperature to dry overnight. The following day, reference electrodes were conditioned in 0.01 M KCl solution for 18 h prior to the potentiometric experiments.

## Measurements

**Potentiometry:** Responses of all electrodes were recorded using the Lawson Labs Inc. 16-channel EMF-16 interface (3217 Phoenixville Pike Malvern, PA 19355, USA) in the stirred solution against a double-junction Ag/AgCl reference electrode with a 1.0 M of LiOAc bridge electrolyte (Fluka). For the measurement of analytes, all ISPs were immersed into 200.0 mL of the ultra-pure water in a beaker followed by stepwise addition of known concentration of the standard. Electrodes were rinsed with ultra-pure water and dried before immersing into the next sample to avoid carryover. Potential responses (EMF) were then measured, and activities calculated from the calibration curve using the Nikolsky-Eisenman equation. Activity coefficients (log a) were calculated according to the Debye-Hückel approach. At least three electrodes of the same type were used.

Selectivity coefficients were determined using separate solutions method utilising dry ISPs. Signal was obtained by exposure to calibration solutions of no longer than 5 min for each calibration point and no longer than 30 min overall. Following the recording of the response to a specific ion, ISPs were thoroughly dried using absorbing paper and the protocol was repeated for the next ion.

**Instrumental characterization:** Electrodes and the precursor materials were characterised by X-ray powder diffraction (XRD), Scanning electron microscopy (SEM), thermogravimetric analysis (TGA), attenuated total reflectance Fouriertransform infrared spectroscopy (ATR-FTIR), and contact angle measurements. XRD patterns were collected using a Bruker D8 Advance diffractometer with a Cu anode at 40 kV and 40 mA, the 2 $\theta$  range was set from 5 to 60°. SEM images were obtained using the Hitachi TM 3000 at 600x magnification. Prior to collecting SEM images samples were mounted on aluminium holders, fixed by carbon cement and coated with carbon. TGA analyses were carried out utilising a Rheometric Scientific STA 1500, from 20 to 800°C, at a heating rate of 10°C/min with the 40 mL/min air flow). ATR-FTIR spectra were acquired using Thermo iS10 spectrometer equipped with a DTGS detector and an ATR attachment with a diamond crystal. Spectral range was 4000-600 cm<sup>-1</sup>, 64 scans, 4 cm<sup>-1</sup> resolution. Results and associated discussion is provided in SI section '1.4. Instrumental characterization' and Figures SI7-14 and Table SI4.

The contact angle was measured on a custom setup using a camera with attached magnification lens (Carl Zeiss, Jena; GF-P

10x) and analysed using ImageJ software with "Contact angle" plugin.

**Multisensor array data processing:** In the case of analysis of model mixtures containing four different inorganic cations, the set of zeolite-based sensors was considered as a sensor array. In order to relate the response of the sensors in the mixtures with the content of metal ions, we have employed partial least squares (PLS) regression.<sup>29</sup> The derived models were validated using segmented cross-validation with a random split of samples leaving three samples out of calibration at each of the sixfolds. Root mean square error of cross-validation (RMSECV) was used to evaluate models' performance. All calculations were performed with The Unscrambler 9.7 software package (CAMO, Oslo, Norway).

**Analysis of bottled water and instant soup samples:** Three bottled drinking water and an instant-tomato soup were purchased from a local shop. Firstly, the calibration curve was obtained by using two-point calibration at 5.0x10<sup>-5</sup> and 5.0x10<sup>-3</sup> M of Na<sup>+</sup> concentrations. Signal was obtained using a digital multimeter (WhiteGold WG 023 digital multimeter) and a polymerbased solid-contact reference electrode (TBA-TBB). Three bottled drinking water were directly analysed without any sample preparation and tomato soup was diluted 1000-fold using 10  $\mu$ M Tris-HCl buffer solution (pH 7.50).

## RESULTS AND DISCUSSION

### Analytical characterization and application of ISPs

The sensing functionality of ISP-drawn electrodes was characterized using potentiometry analogous to ISEs. The response of electrodes prepared using 14 different ISPs was determined against a double-junction Ag/AgCl reference electrode. Electrodes were immersed into a beaker filled with a known volume of the ultra-pure water followed by stepwise addition of known concentration of the standard solution of the measured ion.

Figure 3 demonstrates the heat map of potentiometric sensitivities with the bar illustrating obtained slopes. It is important to note that responses were obtained from the freshly prepared, dry ISP-based electrodes without any pre-treatment. This was quite exciting as it offered desired functionality; sensors can be easily stored at home without the need for any special handling prior to the measurement while demonstrating sensitivity expressed as near-Nernstian response slopes.

Before moving to demonstrate application potential of ISP, we would like to point out an issue we observed with more hydrophilic zeolites (types X, Y). Namely, attempts to apply conditioning protocol traditional for ISEs (~12 hours of continuous exposure of the sensor to an aqueous solution of target ion) resulted in a slow and steady signal drift ending in the almost complete loss of response most likely originating from adsorption of water within the zeolite.<sup>25</sup> The return of the near-Nernstian response after drying overnight confirms this hypothesis, Figures SI15, SI16. Detailed characterization of water uptake is presented in Supplemental Information (section 2.1. ‘Signal Drift’ and Figures SI15-19 and Table SI5). Note that signal drifts were significantly smaller and/or non-existent in other, more hydrophobic zeolites. However, in the spirit of critical analysis, we present here results for NaX as the example of a zeolite showing the strongest drift.

While the water uptake may present as an issue for long-term use of ISP-drawn electrodes, it should be kept in mind that ISPs are conceived as sensors that are inexpensive and extremely simple to use. Thus, ISP-drawn electrodes can be treated as disposable. ISPs can be used to simply draw additional sets of electrodes.

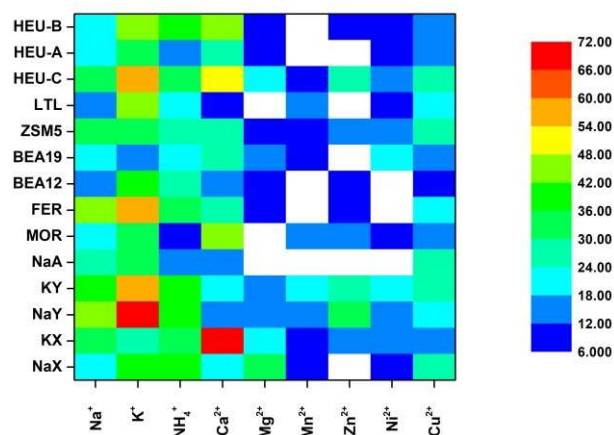


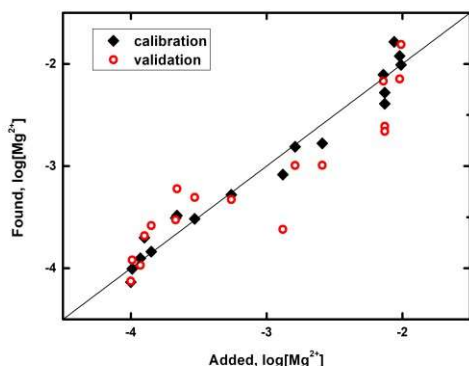
Figure 3. ISP sensitivity heatmap illustrating slope in mV/dec (bar on the right). ISPs are based on the given zeolite (Y -axes) and response slopes are obtained for each of the analysed ion (X -axes) Slopes of <6mV/dec are not shown (white). Response slopes of 59.2 mV/dec and 29.6 mV/dec are considered theoretical (Nernstian) for single and double charged ions respectively. The reproducibility of slopes determined in triplicates was within  $\pm 2$  mV.

**Multi-sensing system in complex mixtures:** Critical analysis of responses reveals that ISP-drawn electrodes exhibit responses and selectivities that are inferior to classical ionophorebased ISEs. This was expected given that the selectivity of zeolites is known to be inferior to ionophores. However, this is a compromise that should be made in order to demonstrate sensors that can be easily prepared and handled. Since arrays of nonspecific, low-selective sensors exhibiting cross-sensitivity to different species in the solution are well-established analytical tools,<sup>30</sup> we believe that the combination of easy preparation with relatively low selectivity dictated that ISP-drawn electrodes could be best utilized as a multi-sensor system in the analysis of complex mixtures.

We decided to demonstrate the functionality of the multi-sensor system based on ISPs in the evaluation of water quality. To the best of our knowledge, this is the first reported case of using zeolite-based electrodes in multi-sensing array systems. Having in mind the potential application of the multi-sensing array system in environmental analysis, we decided to prepare a model solution that contained some of the major plant nutrients ( $K^+$ ,  $NH_4^+$ ,  $Ca^{2+}$ , and  $Mg^{2+}$ ). In this mixture, we attempted to quantify  $Mg^{2+}$  as the least discriminated ion in such a mixture using an array of all 14 ISP-drawn electrodes. Concentrations of all ions in this mixture varied from  $10^{-4}$  to  $10^{-2}$  mol  $dm^{-3}$ . We prepared a total of 20 different mixtures. The concentration of each ion in the mixture was determined according to the uniform experimental design for multivariate calibration.<sup>29</sup> The composition of the mixtures is given in SI Table SI6. Relationship of the response of the array of 14 ISPs in these complex mixture to the  $[Mg^{2+}]$  was done using partial least squares (PLS) regression.<sup>31</sup> Root mean square error of cross-validation (RMSECV) was used to evaluate the model's performance.

At the first step PLS model was cross-validated using the procedure described in the Experimental section ‘Multy-sensor Array data processing’. The optimal number of latent variables in the model was found to be five. Figure 4 shows the resulted “added vs found” plot.

The  $R^2$  coefficient in cross-validation was 0.83 and RMSECV



2+

Figure 4. Found vs added plot for cross-validated PLS model predicting Mg content in the mixtures of four salts.

was 0.34  $\log[Mg^{2+}]$ . These values indicate the applicability of the ISP array for quantitative analysis of complex multi-component solutions. At the next step, six randomly chosen samples were set aside and the PLS model was constructed with the rest of the samples. This model was then applied for predicting  $[Mg^{2+}]$  in the test set. Excellent correlation between predicted and real  $[Mg^{2+}]$  was obtained (Pearson’s  $r = 0.944$ ) as shown in Table 1 and Figure 5. The value of mean relative error for six studied samples is 8.4%.

Table 1. Prediction of magnesium concentration in test set samples.

#	log added $[Mg^{2+}]$ ,	log $[Mg^{2+}]$ , predicted by PLS model	Relative error, %
1	-3.260	-3.298	1.2
2	-3.990	-3.764	5.7
3	-2.590	-3.099	19.7
4	-3.900	-3.692	5.3
5	-3.850	-3.468	9.9
6	-2.130	-2.311	8.5

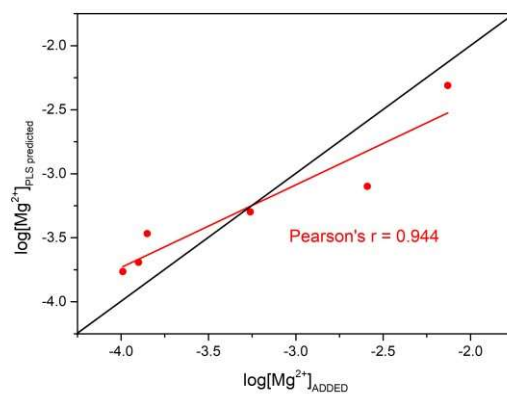


Figure 5. Correlation of  $[Mg^{2+}]$  obtained as PLS predicted vs Added with Pearson’s  $r = 0.944$

Considering an extreme simplicity of the proposed sensor architecture and ultimately inexpensive and widely available production materials, we believe these results provide proof of concept for ISP-drawn arrays.

**ISPs as a tool for use by non-trained personnel:** In the Introduction, we argued that penetration of chemical sensors in fields such as IoT and CS depends on the simplicity of preparation and handling of chemical sensors. So far, we illustrate that handling of ISPs and operation protocols for ISP-drawn electrodes have the required level of simplicity for such applications while their real power lays in multi-sensing systems combined with chemometric approach. Owing to simplicity of handling and the level of data processing automatization using chemometrics, we are optimistic about the notion of application of ISPs by nontrained personnel.

We have also argued that data collected using readout devices that are present in many homes, can open up very interesting applications. At present, we are not aware of devices suitable for use with multi-sensor systems. However, using a non-optimal, single-electrode setup is indeed possible.

In order to showcase the simplicity and the potential for ISPbased electrode to be used by non-trained personnel, we decided to demonstrate its use in the determination of total salt content in bottled water and store bought soup.

Firstly, we developed a simple experimental protocol for calibration and measurement analogous to the protocol for using pH electrode (two-point calibration followed by the determination of signal using direct potentiometry). The analysis is completed in <10min (up to ~3min per measurement for the total of three measurements including calibration). This protocol enabled us to use even NaX-based electrode despite it exhibiting the strongest signal drift as discussed earlier. In other words, relatively short measurement time enabled us to use NaX-based ISP effectively. Note that the NaX-based electrode was calibrated in the solution of  $Na^+$  ions due to perceived selectivity to  $Na^+$ . Further discussion on the selectivity of NaX is provided in the SI section ‘2.3. ISPs as a tool for use by non-trained personnel’.

Secondly, we use digital multimeter as an example of a readout device present in may homes with the caveat that it allows only single-electrode setup.



Thirdly, we use hand-made reference electrode in the spirit of showcasing simplicity of experimental setup. We envision the possibility to develop reference electrode pencil (REP) which will, in ideal case scenario, present as the optimal example of the utilization of drawn electrodes. While we work on the development of REP, we prepared a reference electrode by the deposition of a polymer membrane-based membrane utilizing lipophilic salt as first reported by Mattinen<sup>32</sup> onto the handdrawn, PET-based substrate as suggested previously.<sup>33</sup> We think that such a setup is a suitable transition from classical ISE:glass electrode to fully pencil drawn system. The suitability of ISP:polymer membrane-based reference electrode setup was confirmed through an initial characterization against a glass reference electrode and using classical high input impedance data logger.

We have also developed an MS Excel sheet for calculations of unknown concentration and its associated standard deviation according to protocols suggested by Wiora and Wiora.<sup>34</sup> This offered simplicity and automatization of data processing thus further contributing to the notion of suitability of the use of ISPs by non-trained personnel.

Figure 5 illustrates the use of digital multimeter as a readout device used to determine salt content in bottled drinking water and instant soup obtained from a local shop. Obtained data are presented in Table 2.

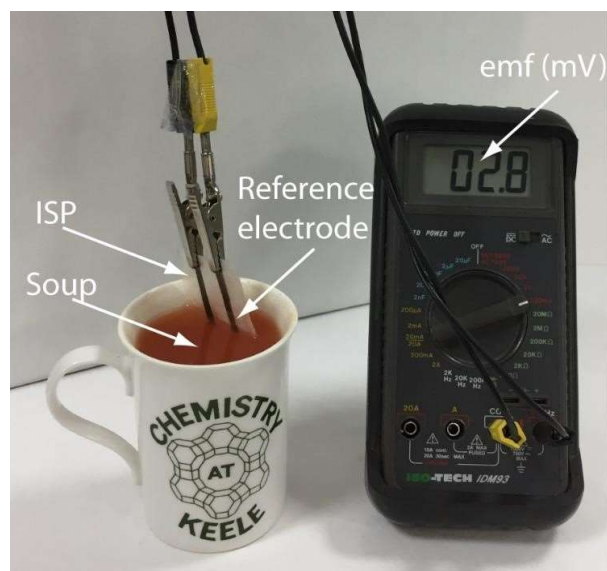


Figure 5. Illustration of experimental setup using digital multimeter and ISP in conjunction with simplified reference electrode to determine salt content in store bought soup.

Table 2. Concentrations of Na<sup>+</sup> in three bottled drinking water (sample 1-3) and instant soup samples (sample 4) obtained by herein described ISEs.

ISP (mmol L <sup>-1</sup> )	Bottle label (only Na <sup>+</sup> ) (mmol L <sup>-1</sup> )	Label (mmol L <sup>-1</sup> )
--------------------------------	--	----------------------------------

Water sample 1	1.8 ± 0.6	0.36	2.40 <sup>[a]</sup>
Water sample 2	1.2 ± 0.5	0.50	1.28 <sup>[a]</sup>
Water sample 3	1.3 ± 0.3	0.34	1.28 <sup>[a]</sup>
Soup	260 ± 50 <sup>[b]</sup>	-	120 <sup>[c]</sup>

<sup>[a]</sup>Total salt concentration including Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>; <sup>[b]</sup> after 10-fold dilution; <sup>[c]</sup> labeled as 'salt'

Table 2 illustrates that we have determined the overall salt content in both samples with the good degree of agreement with data presented on labels. Further discussion and characterization of such a system are presented in the SI section '2.3. ISPs as a tool for use by non-trained personnel' illustrated by associated Figures.

Simplifications of electrode preparation, handling, measuring protocols, and calculations allowed us to recruit persons with basic training in chemistry (1<sup>st</sup>-year chemistry students) to perform sample analysis with very limited instructions. This opens unprecedented opportunities for the generation of chemical information by non-trained personnel (i.e. general public).

## CONCLUSIONS

In this work we demonstrated the concept of an ion-sensitive pencil; it can be used to draw electrode that does not need any handling prior to application and uses a very simple readout device that can be found in an average household. The ISP is prepared by mixing ultra-low-cost materials (the materials required to make a 14-ISP-drawn array cost significantly less than £1) and compression of the solid mixture using a hydraulic press. An array of 14 ISP-drawn electrodes was tested against 9 different cations relevant for environmental water quality measurements. Most sensors exhibited near-Nernstian responses. To improve discrimination power, the array was utilised as a multisensor system enhanced by the partial least square statistical model as exemplified by the analysis of magnesium ion concentration in a complex mixture containing 3 strongly interfering ions (ammonium, potassium, and calcium). Moreover, sensor preparation, handling, and measuring protocols are so simple that persons with basic training in chemistry (1<sup>st</sup>-year undergraduate chemistry students) were able to use ISP with minimal instructions and determine salt content in store bought water and soup albeit in a non-optimal, single electrode setup.

Coupling the simplicity of operation and extremely low cost of ISPs offer an unprecedented opportunity for the application of chemical sensors in areas that require a large number of sensors and inclusion of general public such as IoTs and CS. The key limitations of ISP open further opportunities for chemists, for example, to develop zeolites and ISPs with better selectivity while unlocking potential collaboration with IT engineering and science communication experts in projects that were previously considered impossible.

## ASSOCIATED CONTENT Supporting Information

Further experimental details. This material is available free of charge via the Internet at <http://elsevier.com>.”

## AUTHOR INFORMATION

**Corresponding Author** \*[a.radu@keele.ac.uk](mailto:a.radu@keele.ac.uk)

### Author Contributions

The manuscript was written through the contributions of all authors. All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interests.

## ACKNOWLEDGEMENT

Authors are thankful for funds provided by NSF-UKRI (NE/T012331/1), The British Council, Newton Fund, (grant #261867079) and The Thailand Research Fund (grant No. PDG60W0017).

## REFERENCES

- (1) Suri, J. T.; Cordes, D. B.; Cappuccio, F. E.; Wessling, R. A.; Singaram, B. Continuous Glucose Sensing with a Fluorescent Thin-Film Hydrogel. *Angew. Chem. Int. Ed.* **2003**, *42* (47), 5857–5859. <https://doi.org/10.1002/anie.200352405>.
- (2) Zhao, J.; Lin, Y.; Wu, J.; Nyein, H. Y. Y.; Bariya, M.; Tai, L. C.; Chao, M.; Ji, W.; Zhang, G.; Fan, Z.; Javey, A. A Fully Integrated and Self-Powered Smartwatch for Continuous Sweat Glucose Monitoring. *ACS Sens.* **2019**, *4* (7), 1925–1933. <https://doi.org/10.1021/acssensors.9b00891>.
- (3) Chung, A. E.; Jensen, R. E.; Basch, E. M. Leveraging Emerging Technologies and the “Internet of Things” to Improve the Quality of Cancer Care. *J. Oncol. Pract.* **2016**, *12* (10), 863–866. <https://doi.org/10.1200/JOP.2016.015784>.
- (4) Bouzembrak, Y.; Klüche, M.; Gavai, A.; Marvin, H. J. P. Internet of Things in Food Safety: Literature Review and a Bibliometric Analysis. *Trends Food Sci. Technol.* **2019**, *94*, 54–64. <https://doi.org/10.1016/j.tifs.2019.11.002>.
- (5) Cho Zin, M.; Lenin, G.; Huo Chong, L.; Prassana, M. RealTime Water Quality System in Internet of Things. *IOP Conf. Ser. Mater. Sci. Eng.* **2019**, *495*, 012021. <https://doi.org/10.1088/1757-899X/495/1/012021>.
- (6) Zanella, A.; Bui, N.; Castellani, A.; Vangelista, L.; Zorzi, M. Internet of Things for Smart Cities. *IEEE Internet Things J.* **2014**, *1* (1), 22–32. <https://doi.org/10.1109/JIOT.2014.2306328>.
- (7) Güder, F.; Ainla, A.; Redston, J.; Mosadegh, B.; Glavan, A.; Martin, T. J.; Whitesides, G. M. Paper-Based Electrical Respiration Sensor. *Angew. Chem. Int. Ed.* **2016**, *55* (19), 5727–5732. <https://doi.org/10.1002/anie.201511805>.
- (8) Cammann, K.; Lemke, U.; Rohen, A.; Sander, J.; Wilken, H.; Winter, B. Chemical Sensors and Biosensors—Principles and Applications. *Angew. Chem. Int. Ed. Engl.* **1991**, *30* (5), 516–539. <https://doi.org/10.1002/anie.199105161>.
- (9) Swager, T. M. Sensor Technologies Empowered by Materials and Molecular Innovations. *Angew. Chem. Int. Ed.* **2018**, *57* (16), 4248–4257. <https://doi.org/10.1002/anie.201711611>.
- (10) Wang, X.; Sun, M.; Ferguson, S. A.; Hoff, J. D.; Qin, Y.; Bailey, R. C.; Meyerhoff, M. E. Ionophore-Based Biphasic Chemical Sensing in Droplet Microfluidics. *Angew. Chem. Int. Ed.* **2019**, *58* (24), 8092–8096. <https://doi.org/10.1002/anie.201902960>.
- (11) Bonney, R.; Shirk, J. L.; Phillips, T. B.; Wiggins, A.; Ballard, H. L.; Miller-Rushing, A. J.; Parrish, J. K. Next Steps for Citizen Science. *Science* **2014**, *343* (6178), 1436–1437. <https://doi.org/10.1126/science.1251554>.
- (12) Newman, G.; Wiggins, A.; Crall, A.; Graham, E.; Newman, S.; Crowston, K. The Future of Citizen Science: Emerging Technologies and Shifting Paradigms. *Front. Ecol. Environ.* **2012**, *10* (6), 298–304. <https://doi.org/10.1890/110294>.
- (13) Jollymore, A.; Haines, M. J.; Satterfield, T.; Johnson, M. S. Citizen Science for Water Quality Monitoring: Data Implications of Citizen Perspectives. *J. Environ. Manage.* **2017**, *200*, 456–467. <https://doi.org/10.1016/j.jenvman.2017.05.083>.
- (14) Ko, M.; Aykanat, A.; Smith, M. K.; Mirica, K. A. Drawing Sensors with Ball-Milled Blends of Metal-Organic Frameworks and Graphite. *Sensors* **2017**, *17* (10), 2192. <https://doi.org/10.3390/s17102192>.
- (15) Liu, Y.-Q.; Zhang, Y.-L.; Jiao, Z.-Z.; Han, D.-D.; Sun, H.-B. Directly Drawing High-Performance Capacitive Sensors on Copying Tissues. *Nanoscale* **2018**, *10* (36), 17002–17006. <https://doi.org/10.1039/C8NR05731A>.
- (16) Mirica, K. A.; Azzarelli, J. M.; Weis, J. G.; Schnorr, J. M.; Swager, T. M. Rapid Prototyping of Carbon-Based Chemiresistive Gas Sensors on Paper. *Proc. Natl. Acad. Sci.* **2013**, *110* (35), E3265–E3270. <https://doi.org/10.1073/pnas.1307251110>.
- (17) Mirica, K. A.; Weis, J. G.; Schnorr, J. M.; Esser, B.; Swager, T. M. Mechanical Drawing of Gas Sensors on Paper. *Angew. Chem. Int. Ed.* **2012**, *51* (43), 10740–10745. <https://doi.org/10.1002/anie.201206069>.
- (18) Unwin, P. R.; Güell, A. G.; Zhang, G. Nanoscale Electrochemistry of Sp<sup>2</sup> Carbon Materials: From Graphite and Graphene to Carbon Nanotubes. *Acc. Chem. Res.* **2016**, *49* (9), 2041–2048. <https://doi.org/10.1021/acs.accounts.6b00301>.
- (19) Foster, C. W.; Brownson, D. A. C.; Ruas de Souza, A. P.; Bernalte, E.; Iniesta, J.; Bertotti, M.; Banks, C. E. Pencil It in: Pencil Drawn Electrochemical Sensing Platforms. *The Analyst* **2016**, *141* (13), 4055–4064. <https://doi.org/10.1039/C6AN00402D>.
- (20) Kawahara, R.; Sahatiya, P.; Badhulika, S.; Uno, S. Paper-Based Potentiometric PH Sensor Using Carbon Electrode Drawn by Pencil. *Jpn. J. Appl. Phys.* **2018**, *57* (4S), 04FM08. <https://doi.org/10.7567/JJAP.57.04FM08>.
- (21) *Advanced Zeolite Science and Applications*; Jansen, J. C., Ed.; Studies in surface science and catalysis; Elsevier: Amsterdam; New York, 1994.
- (22) Walcarius, A. Zeolite-Modified Electrodes in Electroanalytical Chemistry. *Anal. Chim. Acta* **1999**, *384* (1), 1–16. [https://doi.org/10.1016/S0003-2670\(98\)00849-6](https://doi.org/10.1016/S0003-2670(98)00849-6).
- (23) Walcarius, A.; Rozanska, S.; Bessière, J.; Wang, J. ScreenPrinted Zeolite-Modified Carbon Electrodes. *The Analyst* **1999**, *124* (8), 1185–1190. <https://doi.org/10.1039/a904025k>.
- (24) Hamlaoui, M. L.; Kherrat, R.; Marrakchi, M.; Jaffrezic-Renault, N.; Walcarius, A. Development of an Ammonium ISFET Sensor with a Polymeric Membrane Including Zeolite. *Mater. Sci. Eng. C* **2002**, *21* (1–2), 25–28. [https://doi.org/10.1016/S09284931\(02\)00059-0](https://doi.org/10.1016/S09284931(02)00059-0).
- (25) Van Bekkum, H.; Jacobs, P. A.; Flanigen, E. M. *Introduction to Zeolite Science and Practice*; Elsevier: Burlington, 2001.
- (26) Haralambous, A.; Maliou, E.; Malamis, M. The Use of Zeolite for Ammonium Uptake. *Water Sci. Technol.* **1992**, *25* (1), 139–145. <https://doi.org/10.2166/wst.1992.0021>.
- (27) Fayose, T.; Mendecki, L.; Ullah, S.; Radu, A. Single Strip Solid Contact Ion Selective Electrodes on a Pencil-Drawn Electrode Substrate. *Anal. Methods* **2017**, *9* (7), 1213–1220.
- (28) Mattinen, U.; Bobacka, J.; Lewenstam, A. Solid-Contact Reference Electrodes Based on Lipophilic Salts.

- Electroanalysis* **2009**, *21* (17–18), 1955–1960. <https://doi.org/10.1002/elan.200904615>.
- (29) Kirsanov, D.; Panchuk, V.; Agafonova-Moroz, M.; Khaydukova, M.; Lumpov, A.; Semenov, V.; Legin, A. A Sample-Effective Calibration Design for Multiple Components. *The Analyst* **2014**, *139* (17), 4303–4309. <https://doi.org/10.1039/C4AN00227J>.
- (30) *Multisensor Systems for Chemical Analysis: Materials and Sensors*; Lvova, L., Ed.; Pan Stanford Publishing: Singapore, 2014.
- (31) Wold, S.; Sjöström, M.; Eriksson, L. PLS-Regression: A Basic Tool of Chemometrics. *Chemom. Intell. Lab. Syst.* **2001**, *58* (2), 109–130. [https://doi.org/10.1016/S0169-7439\(01\)00155-1](https://doi.org/10.1016/S0169-7439(01)00155-1).
- (32) Mattinen, U.; Bobacka, J.; Lewenstam, A. Solid-Contact Reference Electrodes Based on Lipophilic Salts. *Electroanalysis* **2009**, *21* (17–18), 1955–1960. <https://doi.org/10.1002/elan.200904615>.
- (33) Choosang, J.; Numnuam, A.; Thavarungkul, P.; Kanatharana, P.; Radu, T.; Ullah, S.; Radu, A. Simultaneous Detection of Ammonium and Nitrate in Environmental Samples Using an Ion-Selective Electrode and Comparison with Portable Colorimetric Assays. *Sensors* **2018**, *18* (10), 3555. <https://doi.org/10.3390/s18103555>.
- (34) Wiora, J.; Wiora, A. Measurement Uncertainty Calculations for PH Value Obtained by an Ion-Selective Electrode. *Sensors* **2018**, *18* (6), 1915. <https://doi.org/10.3390/s18061915>.



Supplementary Material