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Scientific and professional journal in the area
of environmental engineering

GEOTEHNIČKI
FAKULTET,
SVEUČILIŠTE U
ZAGREBU

VARAŽDIN
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FACULTY OF
GEOTECHNICAL
ENGINEERING,
UNIVERSITY OF
ZAGREB

VARAŽDIN
CROATIA

SPECIAL ISSUE
**Portable, affordable and
simple analytical
platforms**



PortASAP

COST Action CA16215 - European Network for the Promotion
of Portable, Affordable and Simple Analytical Platforms

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Editor-In-Chief opening remarks

Dear readers,

It is a great honor to introduce myself as the new Editor-in-Chief of the journal *Environmental Engineering-Inženjerstvo okoliša* published by Faculty of Geotechnical Engineering, University of Zagreb, Croatia. I would like to present you some novelties in the journal. From 2019 the journal was renamed from *Inženjerstvo okoliša* to *Environmental Engineering-Inženjerstvo okoliša*, it was entitled with the new abbreviation *EnvEng-IO*, the journal was redesigned, it was awarded by HRČAK certificate (The central portal of Croatian scientific journals) and all accepted papers were published in English language.

I am delighted to introduce You the new volume of the journal, the Special Issue number entitled **Portable, affordable and simple analytical platforms**. For this occasion, prof. Emir Karamehmedović joined us as a Guest Editor. After a fruitful cooperation the results are in front of you – the six published papers within the scope of portable, affordable and simple analytical platforms for environmental analysis. The papers were ranging from original scientific papers to a professional paper and a review paper. The papers covered different fields; from electrochemical analytical determinations, Arduino-based platforms and sensor implementation, innovative separation techniques based on magnetic materials and capillary electrophoresis, up to new concepts in optical detection and microfluidics. I am also proud to note that co-authors from six countries worldwide participated.

The topic and the scope of this Special issue was directly linked to the European Cooperation in Science and Technology (COST) Action PortASAP - European network for the promotion of portable, affordable and simple analytical platform (CA 16215) supported by COST Association under the EU Framework Programme Horizon 2020. The project Action Chair is prof. Gullaume Erny, who gave us a full support on the topic, networking and logistics.

I hope this issue is a small step in promotion of wider use of analytic platforms and open source hardware, to achieve faster and more efficient analysis employing low-cost devices and innovative principles, not limited only to environmental analysis.

At the end, I would like to give my gratitude to all team members and to our sponsors.

I hope you will enjoy it.

With best regards,



Assoc. Prof. Dr. Nikola Sakač
Editor-in-Chief

Unit for Chemical Sensors
Department of Environmental Engineering
Faculty of Geotechnical Engineering
University of Zagreb

Guest Editor introduction

Dear readers,

I was honored and pleased when Dr. Sakač invited me to be the first Guest Editor of the journal *Environmental Engineering-Inženjerstvo okoliša*, addressing issues of increasing relevance in our era. I hope that the visibility of the journal will grow as much as its contribution to the truly multidisciplinary scientific community to which it speaks.

The world-wide availability of low-cost microcontroller platforms and a wide range of sensors, as well as other components, makes it possible to build amateur analytical apparatus with performance seriously approaching that of professional equipment. We witnessed a small revolution in low-cost spectrometers and monitoring devices based on those. One project encompassed a database of geo-tagged pollution measurements using the spectrometers, yielding a better overall picture of the pollution distribution than the mapping generated by high-end equipment. When combined with the philosophy of open source hardware, sharing simple constructions can engage a large community in an effort to develop, build and validate designs applicable in environmental engineering.

In this number of *Environmental Engineering-Inženjerstvo okoliša*, contributions focus on low-cost platforms for monitoring of environmental data, which can be implemented as open source hardware. We hope that the issue will inspire individuals and groups to take on projects, even with limited funding, and envisage devices collecting data that will increase the awareness of environmental problems. At the same time, the process of building the analytical devices is extremely educational and forces one to step outside the comfort zone of one's expertise. The topics covered in this issue are far from all-encompassing, but the paradigm is clear – you are encouraged to propose an inexpensive device that measures relevant data, or offer an upgrade of an existing OSH device. Ultimately, big data analysis, deep learning or machine learning data processing may lead to accurate and scientifically useful data that serve the community.

The collection of contributions is made largely as a result of collaboration within the COST action **CA16215 European network for the promotion of portable, affordable and simple analytical platforms**, and I hereby use the opportunity to acknowledge this action. Last but not least, I thank the reviewers for their evaluation of the papers. I truly hope the readers will recognize the tremendous effort and time that were invested in setting up this journal.

With best regards,



Assoc. Prof. Dr. Emir Karamehmedović
Guest Editor

Electrical and Electronics Engineering
Faculty of Engineering and Natural Sciences
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PortASAP – supporting and encouraging an open source labs



Who we are

European network for the promotion of portable, affordable and simple analytical platform (PortASAP) is a European Cooperation in Science and Technology (COST) supported and sponsored action (CA16215; <https://www.cost.eu/actions/CA16215/#tabs|Name:overview>). It was funded in October 2017 with the main aim to promote, develop and validate low-cost scientific instrumentations for chemical analysis. Currently, PortASAP comprises of more than 200 scientists and industrials from 30 different European countries facilitating their interaction and encouraging networking via workshops, Short-Term Scientific Missions (STSM), meetings and training schools.

The action is composed of six working groups (WG) closely related one to other, namely WG1 - Validation and dissemination of open-source hardware, WG2 - Information and communication technology and software development, WG3 - Field tests and applications; WG4 Sample treatment and microfluidic; WG5 - New instrumentation; WG6 - Exploitation of results. All together they aim to fulfil the main challenge of the action - develop and promote low-cost instruments and open-source hardware capable of sensitive chemical analysis in specific areas and applications where the use of complex laboratory-based instrumentation is not the desired option. Working groups are led by experts in the field guaranteeing an adequate running of the action. All the participants are encouraged to participate in at least two WG to increase diversity among each group leading to the generation of new original ideas.

Reasons for this network

Analytical chemistry as we know it today results from three main revolutions that took places since the 1900s.¹ The first revolution, at the beginning of the twenty centuries, was the adoption of many scientific principles making analytical chemistry a scientific discipline on its own. The second revolution, around World War II, was characterised by a shift from wet chemical methods to instrumental methods. Many instruments that are used nowadays were developed during this period, including spectrometers, instrumental separation techniques, NMR, atomic absorption spectroscopy and mass spectrometry, to name a few. The third revolution started 20 years ago and is seen as the accomplishment of the two first revolutions. Analytical Chemistry is now a mature field that shifts from serving chemical science to serving society. Analytical Chemistry tools and concepts have been adopted in many areas.

However, analytical instrumentation shifted from simple wet techniques to increasingly expensive and complicated instruments that need to be used in dedicated facilities by highly trained operators. While the potential benefit of modern instrumentation to society is tremendous, in many cases, ad-hoc analysis cannot be done due to a lack of resources or expertise. The next revolution should be the democratisation of analytical techniques where many will have the mean and knowledge to perform

local analyses and share globally his results. 3D printing, low-cost electronic boards and computer and the development of Open Source Hardware philosophy and Citizen Science Project will contribute to the success of this revolution. In the past ten years, academic or private citizen designed, openly shared and promote scientific instruments at a fraction of its commercial alternative. Chemical instruments already include spectrometer, scientific microscopes, quartz crystal microbalance or fluidic platform. All this freely available information can benefit anyone and contribute to the advance since the latest developments made by one can be improved by the next also being openly available for others to use. Finally resulting not only in the easier availability of the instruments but to the progress of their improvement in the collaboration and cooperation way.

PortASAP Commitment

- * Promote low-cost alternatives and Open Source Hardware.
- * Review and validate existing Open Source instruments.
- * Create synergies for the development of new Open Source tools.

Contacts and additional information can be found here:

Action Web: <http://portasap.eu/index.html>

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Research gate: <https://www.researchgate.net/project/COST-Action-CA16215-European-network-for-the-promotion-of-portable-affordable-and-simple-analytical-platforms>

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Field study @ AQUAE IASAE (Varaždinske Toplice) during 2nd PortASAP Meeting (STSM)
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ELECTROCHEMICAL SENSORS AS SIMPLE AND CHEAP DEVICES FOR RAPID DETERMINATION OF VARIOUS SPECIES IN ENVIRONMENTAL SAMPLES

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Abstract: The electrochemical methods are very good tool for determination of trace concentrations of various species in water samples. The analysis carried out using these methods are usually simple, fast and also the cost of the required equipment is much lower comparing to other instrumental methods. Furthermore, the electroanalytical methods are easy to automate and computerize. Among five major groups of these methods (potentiometry, voltammetry, coulometry, conductometry and dielectrometry), potentiometry and voltammetry attract the greatest attention of researchers. In this paper, experimental results of research related to development of procedures (voltammetric and potentiometric) for the determination of elements in environmental water samples were presented. Due to their common occurrence in environment and possible toxic effects on living organisms, vanadium and nitrate ions were selected for investigation. Optimization of voltammetric procedure for $V(V)$ determination were carried out in matrix containing different surfactants and humic acids, using lead film electrode as a working electrode. Results showed that only nonionic surfactant Brij-35 did not interfere with the voltammetric signal. Other surfactants as well as humic acids reduced the signal, and possibility of their elimination with suitable resins were also investigated. Potentiometric measurements were consisted of preparation and determination of analytical properties of nitrate ion-selective electrodes with solid contact. The results showed that among three different membrane composition, the best response was achieved by membrane containing: Ni(Phen)₂, THTDPCL, PVC and NPOE in the ratio of 1:2:33:64 wt. %, respectively. With the detection limit of 2.8×10^{-6} mol L⁻¹, the working concentration range from 5×10^{-5} to 1×10^{-1} mol L⁻¹ and a slope of -55.1 mV per decade, this electrode showed good selectivity to sulfate, acetate, carbonate, dihydrogen phosphate, fluoride and chloride ions, and also good potential reversibility.

Keywords: voltammetry, lead film electrode, vanadium, potentiometry, nitrate ion-selective electrode

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Original scientific paper

1. INTRODUCTION

For determination of trace level of elements in environmental samples, electrochemical methods are very good tool. Simple and fast procedures, as well as the lower prices of required instruments, make these methods more attractive comparing to others. Among five different types of electrochemical methods (potentiometry, voltammetry, coulometry, conductometry and dielectrometry), potentiometry and voltammetry attract the greatest attention of researchers.

Stripping voltammetry and its use for the determination of V(V)

Stripping voltammetry (SV) is a very sensitive and rapid method for the analysis of trace concentrations of different ions in the solution. Extremely low limits of detection (10^{-10} to 10^{-12} mol L⁻¹) can be obtained using this method. High sensitivity of SV is a result of the fact that the single measurement consists of two steps. During the first step, analyzed ions are deposited onto an electrode surface. This is followed by the stripping step and the peak registered on the voltammogram is directly proportional to the concentration of analyte in the solution. Depending on the nature of preconcentration and stripping steps, stripping voltammetry can be divided into: anodic stripping voltammetry (ASV), cathodic stripping voltammetry (CSV) and adsorptive stripping voltammetry (AdSV). Besides the excellent sensitivity, these techniques also offer: multielement and speciation capabilities, possibility for automated online and in situ measurements and utilize low-cost instrumentations. These techniques are widely used for testing drinking water quality (tap water), sewage and environmental water (Zosky 2007; Settle 1997). During the development of voltammetric procedures, the key element is the selection of the working electrode on which the accumulation of the determined ions takes place. Some of the first and also the most popular electrodes used in voltammetric procedures were mercury electrodes. Now with the growing awareness of the mercury's toxicity, there is a need for new less-toxic sensors. One of such sensors that has been introduced in the replacement

of mercury electrodes is a lead film electrode (PbFE) (Grabarczyk & Wasąg 2016; Grabarczyk & Wasąg 2015; Wasąg & Grabarczyk 2016).

This paper describes the voltammetric procedure for determination of V(V) in natural water samples with organic substances in matrix, such as surface active substances and humic substances. The procedure is based on adsorptive stripping voltammetry, the essence of which is the adsorptive accumulation of V(V)-cupferron complexes on the in situ obtained lead film electrode used as a working electrode. Vanadium was selected for this investigation due to its common occurrence in environment and possible toxic effects on living organisms. Vanadium is a heavy metal whose occurrence is usually associated with natural processes in the environment (weathering of rocks, soil erosion and volcanic emissions). Anthropogenic release of vanadium into the environment is mainly related to industrial sources, especially oil refineries and power plants using heating oil and vanadium-rich coal. Vanadium occurs in three oxidation states in the environment (+III, +IV, +V), but V(V) is of greater toxicity and in higher concentrations negatively affects plants, animals and humans. Therefore, determination of V(V) in environmental samples is necessary from the point of view of environmental protection (Mampuru et al. 2015; Xiao et al. 2015). Considering the fact that the proposed voltammetric procedure is intended for the determination of V(V) in environmental samples, the influence of surface active substances and humic substances on the vanadium signal was examined. The choice of these substances was favored by the fact that they are the main components in the matrix of real samples. Since these compounds caused suppression of the vanadium voltammetric signal, it was proposed to reduce these interferences by pre-mixing the sample with an Amberlite type resin. During this mixing, surfactants and humic substances were adsorbed on the resin while vanadium ions remained in the solution which is introduced into the volumetric measuring cell.

Potentiometry and its use for the determination of nitrates

Potentiometry with ion-selective electrodes (ISEs) is known as an excellent low-cost analytical technique for selective, sensitive and rapid determination of vast variety of analytes in clinical, environmental and industrial samples (Wardak 2014; Plaza et al. 2005). Among different types of ISEs, special attention was focused on ion-selective electrodes with polymer membrane without the internal electrolyte, called Solid Contact Ion-selective Electrodes (SCISEs). These electrodes have many advantages over their classical equivalents containing an internal solution (Wardak 2012). The lack of the internal solution enables construction of electrodes which can have any shape and much smaller sizes, so consequently their production costs can be reduced. The solid contact electrodes are especially useful in measurements performed in outdoor conditions, outside the laboratory, because they are highly resistant to damage and also simple in use and transport. Besides, the SCISEs are often characterized by a lower limits of detection, due to the elimination of primary ion leaching from the internal solution via the membrane to the near-membrane layer of a sample solution (Sutter et al. 2004). The solid contact ion-selective electrodes can be considered to be the first step to constructing microelectrodes, because, in order to miniaturize ion-selective electrodes it is necessary to eliminate the internal electrolyte solution. In the case of small-sized electrodes, the electrode resistance usually increases, which leads to increased noise and potential instability. The prototype of SCISEs was a “coated wire” type construction in which the ion-selective polymer membrane covered the platinum wire (Cattrall & Freiser 1971). The problem in construction of ion-selective electrodes with solid contact is instability and weak reproducibility of potential due to thermodynamically nondefined phase boundary between the membrane of ionic conductance and the internal electrode of electron conductance (Hulanicki & Trojanowicz 1976; Hauser et al. 1995). Another reason for a drift of potential in solid contact electrodes is a very thin aqueous layer which is often formed between the polymer membrane and the internal electrode. The composition of this layer undergoes a transformation due to the changes in sample composition and pH, which results in instability of the electrode potential (Fibbioli et al. 2000).

In this paper, preparation and properties of nitrate ion-selective electrodes with solid contact are described. As active membrane component, nickel complex with 1,10-phenanthroline (Ni(Phen)₂) was used. The electrodes were constructed on the basis of Ag/AgCl electrode and phosphonium chloride was used as ionic additive and as transducer media. This compound lowers the membrane resistance and maintains constant concentration of chloride ions in the membrane phase surrounding internal Ag/AgCl electrode. This paper describes development of potentiometric solid contact sensor for nitrate determination. Nitrates are present in ground and surface waters as a results of their widespread application in the industry and agriculture. The determination of nitrates is very important because of their toxic and carcinogenic effect on humans and animals, connected with reduction of nitrate to nitrite which can take place even in the mouth under the influence of saliva (McKnight et al. 1999).

2. EXPERIMENTAL PART

2.1. Reagents

For voltammetric procedure, a stock solution of 1 g L⁻¹ V(V), cupferron, suprapur CH₃COOH and NaOH were obtained from Merck (Darmstadt, Germany). The working solutions of V(V) of lower concentrations were prepared by dilution of the stock solution by 5 × 10⁻³ mol L⁻¹ of HNO₃ as required. A solution of 1 × 10⁻² mol L⁻¹ of cupferron was prepared daily by dissolving 0.0155 g of the reagent in water in a 10 mL volumetric flask. A standard solution of 1 g L⁻¹ Pb(II), Triton X-100, Brij-35, sodium dodecyl sulfate (SDS) and

cetyltrimethylammonium bromide (CTAB) were purchased from Fluka (Buchs, Switzerland). Humic acids (HA) and fulvic acids (FA) were obtained from Aldrich. All solutions were prepared using triply distilled water. Amberlite XAD-2 resin and Amberlite XAD-16 resin were obtained from Sigma (St. Louis, MO, USA). The resins were washed four times with triply distilled water and dried up at the temperature of 50 °C.

Potentiometric procedures required chemicals: 2-Nitrophenyl octyl ether (NPOE) (Fluka), Poly(vinyl chloride) low molecular weight (PVC) (Aldrich), Trihexyltetradecylphosphonium chloride (THTDPCI) (Aldrich), 4,7-diphenyl-1,10-phenanthroline (Aldrich). Complex of Ni(II) with 1,10-phenanthroline was obtained in the reaction of 20 mL of 5×10^{-2} mol L⁻¹ aqueous solution of nickel(II) chloride and 20 mL of 0.15 mol L⁻¹ 4,7-diphenyl-1,10-phenanthroline solution in ethyl alcohol. The obtained pink solid was filtered, gently washed with distilled water. All aqueous solutions were prepared with salts of the highest purity available (pure pro analysis) using freshly deionized water.

2.2. Instrumentation

Voltammetric measurements were carried out using an Autolab analyzer (Utrecht, The Netherlands). A three electrode system consisting of a glassy carbon (GC) working electrode, a platinum auxiliary electrode and an Ag/AgCl reference electrode (filled with NaCl), was employed. Before each series of measurements, the glassy carbon electrode of 1 mm diameter was polished daily on 2000 grit sandpaper using 0.3 µm alumina slurry on the Buehler polishing pad.

The measurement of the electromotive force (EMF) of the cell composed of ion-selective electrode and reference electrode Orion 90-02, was carried out at room temperature in a solution stirred with a magnetic stirrer by means of potentiometric system (Lawson Labs. Inc., USA) and IBM PC computer.

2.3. Procedure

2.3.1. Standard voltammetric procedure for vanadium determination

All voltammetric measurements were carried out in 0.1 mol L⁻¹ acetate buffer (pH = 6.0), 3×10^{-4} mol L⁻¹ Pb(II) and 7×10^{-4} mol L⁻¹ cupferron. The experiments were carried out from undeaerated solutions with a volume of 15 mL. The voltammetric procedure consisted of the following main steps:

- -1.1 V for 20 s (lead film electrode (PbFE) was formed on the glassy carbon electrode by the reduction of Pb(II) to lead metallic state),
- -0.6 V for 30 s (accumulation of V(V)–cupferron complexes on PbFE),
- the potential was scanned from -0.6 V to -0.9 V (differential pulse stripping voltammogram was recorded corresponding to the reduction of the accumulated complex; the vanadium peak appeared at about -0.7 V and was directly proportional to the concentration of V(V) in the sample).

After each measurement, the electrochemical cleaning of GC electrode was carried out in the following way: -1.3 V for 15 s and +0.2 V for 15 s under stirring. At the potential of -1.3 V the remains from previous measurement were reduced to the metallic state and then at the second potential they were stripped from the electrode to the solution.

2.3.2. Procedure of organic interferences elimination for vanadium determination

For effective elimination of interferences caused by organic substances commonly found in environmental water samples, 10 mL of analyzed real sample or a synthetic sample (including V(V) and optionally organic interferences) was mixed during 5 min. with 0.5 g XAD-2 (or XAD-16 resin optionally) in the presence of 0.1 mol L⁻¹ acetate buffer pH = 6.0. After this step, the solution from above the resin was introduced into the voltammetric cell and the voltammetric measurement was performed as described above.

2.3.3. Preparation of ion-selective electrodes for nitrate determination

An internal Ag/AgCl electrode was prepared from a silver wire which was anodized electrochemically in HCl solution using voltage source of 5 V (KABiD-PRESS, Poland). Then the electrode was rinsed with water, dried with tissue-paper, mounted in the Teflon holder and covered by the membrane phase.

The electrode membrane phase was prepared as follows: the membrane components were weighed and thoroughly mixed. The mixture was deaerated by means of a vacuum oil pump. The Teflon holder was filled with the mixture and the mixture was gelled at 80-90 °C for 15 min. During the gelation, plasticization of PVC takes place and as a result membrane phase is in homogeneous polymer state. After cooling to room temperature the sensor was mounted in the electrode body and conditioned for at least 12 hours in 1×10^{-3} mol L⁻¹ NaNO₃ solution to saturate PVC membrane in nitrate ions. For each membrane composition (presented in Table 2.), three identical electrodes were prepared and subjected to the same studies.

3. RESULTS AND DISCUSSION

3.1. Influence of surfactants and humic compounds on vanadium determination

Organic substances occurring in natural samples can interfere with stripping voltammetry analysis mainly by adsorption onto the electrode surface causing a decrease of the peak of the analyzed substance or its total decay. The influence of different types of surface-active substances such as: cationic (CTAB), non-ionic (Triton X-100 and Brij-35), anionic (SDS) and humic compounds such as humic and fulvic acids was studied.

The influence of interferences was tested using a fixed concentration of 5×10^{-8} mol L⁻¹ V(V) and different amounts of organic substances using standard procedure of measurement (as described in subsection 2.3.1.). A tolerable limit was defined as the amount of organic substances that produced an error not exceeding 5% in the peak current of vanadium. Detailed results of the influence of different types of surface active substances and humic substances using a standard procedure are presented in **Table 1**. As shown in the table, only nonionic surfactant Brij-35 did not show any interfering effect, while others partially decreased the signal (anionic SDS to 75%) or totally reduced the signal (nonionic Triton X-100 and cationic CTAB at the amount of 2 ppm). Humic and fulvic acids showed also total interfering effect.

Table 1. The influence of different organic substances on 5×10^{-8} mol L⁻¹ V(V) analytical signal using the standard procedure

INTERFERING ORGANIC SUBSTANCE	CONCENTRATION OF INTERFERENCES [mg L ⁻¹]	RELATIVE SIGNAL OF V(V) IN %
CTAB	1	85
	2	No signal
Triton X-100	1	65
	2	No signal
Brij-35	1	100
	2	100
SDS	1	75
	2	35
	5	20
HA	1	No signal
FA	1	50
	2	No signal

3.2. Elimination of organic interferences for vanadium determination

Considering the significant interfering effects of some investigated compounds, the experiments of the elimination of those interferences with appropriate resins were carried out. The measurements were performed as described in subsection 2.4. In the ideal case, interfering compound adsorbs on the resin surface, whereas V(V) remains quantitatively in the solution. The main challenge here is to choose such measurement conditions that would provide the highest sensitivity of determinations and at the same time the greatest effectiveness in removing the interferences. The results showed that:

- resin Amberlite XAD-16 eliminates CTAB interfering effect to certain point: the signal decreased to 25% at 2 ppm (not the total reduction of signal which happened without resin);
- resin Amberlite XAD-2 eliminate Triton-X100 interfering effect to certain point: the signal decreased to 85% at 2 ppm (not the total reduction of signal which happened without resin);
- 5 ppm of SDS does not affect at all the vanadium signal in the presence of Amberlite XAD-2 nor XAD-16 for humic and fulvic acids, application of resins did not yield a sufficient elimination effect.

3.3. Potentiometric response of prepared nitrate-selective electrodes

For different composition of each electrode membrane phase, the analytical parameters such as the limit of detection, the linear concentration range and characteristic slope were determined and listed in **Table 2**. The potential response of prepared electrodes was measured in sodium nitrate solutions in concentration range from 1×10^{-6} to 1×10^{-1} mol L⁻¹. The obtained calibration curves are presented in **Figure 1**.

Electrode response obviously depends on the membrane composition. The sensor no. 1 with blank membrane without active substance and ionic additive did not respond to nitrate ions and exhibited poor cationic response, while electrode no. 2 containing in the membrane 1% wt. Ni(Phen)₂ showed anionic response with sensitivity of -44.0 mV/decade. In the case of electrode with membrane composition no. 3 incorporating Ni(Phen)₂, THTDPCl, PVC and NPOE in the ratio of 1:2:33:64 wt. %, respectively, the best anionic response was achieved. The detection

limit of electrode no. 3 was $2.8 \times 10^{-6} \text{ mol L}^{-1}$ and the working concentration range was from 5×10^{-5} to $1 \times 10^{-1} \text{ mol L}^{-1}$ with a slope of $-55.1 \text{ mV per decade}$. As a result, electrode no. 3 was chosen for selectivity and reversibility studies.

Table 2. Membrane composition and electrodes performances

No ELECTRODE	MEMBRANE COMPOSITION				LIMIT OF DETECTION [mol L^{-1}]	SLOPE [mV/decade]	MEASURING RANGE [mol L^{-1}]
	Ni(Phen) ₂ Cl [mg]	THTDPCI [mg]	PVC [mg]	NPOE [mg]			
1	-	-	330	670	poor anionic response		
2	10	-	330	660	3.3×10^{-5}	-44.0	$1.0 \times 10^{-4} - 1.0 \times 10^{-1}$
3	10	20	330	640	1.0×10^{-6}	-55.1	$5.0 \times 10^{-5} - 1.0 \times 10^{-1}$

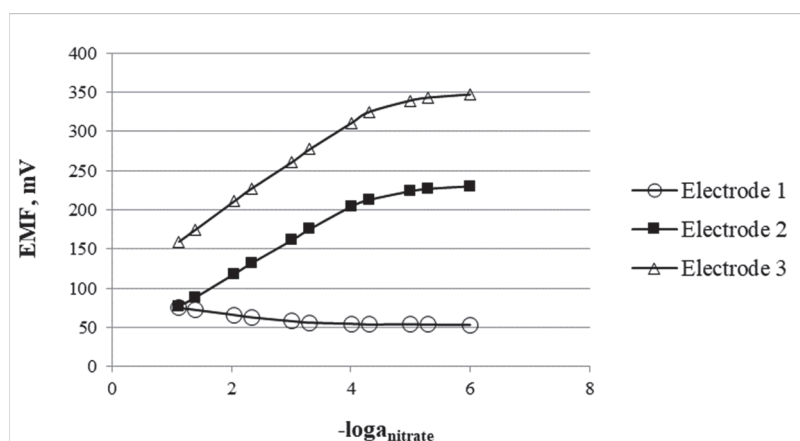


Figure 1. Potentiometric responses of studied electrodes determined in NaNO_3 solution

3.4. Selectivity study for prepared electrode

The selectivity behavior is very important characteristic of any ion-selective electrode. It determines feasibility of a reliable measurement in the real sample. The selectivity of the studied sensors was evaluated by establishing their selectivity coefficients in reference to interfering ions. The selectivity coefficients were determined by the separate solution method (SSM) (by extrapolating the response functions to $a_i = a_j = 1 \text{ mol L}^{-1}$) (Fibbioli et al. 2000). The obtained values are listed in Table 3 where it can be seen that proposed electrode exhibits good selectivity to sulfate, acetate, carbonate, dihydrogen phosphate, fluoride and chloride ions. For nitrite and bromide ions, $\log K^{\text{pot}}_{X/\text{nitrate}} > -2$. These ions can interfere the nitrate measurement if their concentration is high. In the case of samples such as natural water samples, in which they are present in trace levels, such interferences are negligible.

Table 3. Values of selectivity coefficients for electrode no.3

ION	$\log K^{\text{pot}}_{\text{NO}_3^-/X^{n-}}$
H_2PO_4^-	-4.2
SO_4^{2-}	-4.1
CO_3^{2-}	-3.9
CH_3COO^-	-3.5
F^-	-3.3
Cl^-	-2.1
NO_2^-	-1.4
Br^-	-0.6

3.5. Reversibility of the electrode potential for prepared electrode

The reversibility of the electrode response is one of the most important parameter in analytical application point of view. In order to test the reversibility of the potential, the studied electrode was immersed in $1 \times 10^{-3} \text{ mol L}^{-1} \text{ NaNO}_3$ solution for 5 minutes and next in $1 \times 10^{-4} \text{ mol L}^{-1} \text{ NaNO}_3$ solution for the same period.

This operation was repeated four times. The mean values of potential obtained from four measurements were 311.6 ± 2.3 and 260.1 ± 1.5 mV for 1×10^{-4} and 1×10^{-3} mol L⁻¹ of NO₃⁻ ions solutions, respectively. The relative standard deviation in the potential measurement was 0.7 and 0.6%. Such values proved that electrode is characterized by good potential reversibility.

4. CONCLUSIONS

Under given experimental conditions for V(V) voltammetric determination, the measurements can be performed in the presence of Brij-35 at given concentrations, without any interfering effects. However, other tested compounds which showed certain or total interfering effects need to be eliminated for successful V(V) quantitative determination. The results showed that used resins can decrease or eliminate interfering effect of surface active substances, but they are not appropriate for humic and fulvic acids under these experimental conditions.

Nitrate potentiometric sensor with solid contact was successfully developed. Proposed sensor exhibits good analytical parameters which are sufficient for nitrate determination in natural waters. Moreover it is simple to construct and easy to operate. Its significant advantage is the possibility to use directly in field measurements, in continuous mode measurements and in small laboratories that have no expensive equipment and highly qualified staff.

5. ACKNOWLEDGMENTS

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REAL-TIME WATER QUALITY MONITORING OF AN ARTIFICIAL LAKE USING A PORTABLE, AFFORDABLE, SIMPLE, ARDUINO-BASED OPEN SOURCE SENSOR

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Abstract: Water quality assessment is vital to identify existing problems and any changes that emerge in water sources over a period of time. Conventional water quality monitoring systems remain to be limited to on-site sample collection and further analysis in environmental laboratories. The progress in Arduino-based low-cost and open-source hardware has paved the way for the development of low-cost, portable, and on-site measuring platforms. In this work, we have assembled an Arduino-based open-source water testing platform out of commercially available sensors and controllers. The water testing system was powered by a 9 V battery and had the capability of measuring water turbidity, acidity, and temperature on-site in real-time. The calibration and validation studies were carried out to assess the measurement capabilities of turbidity and pH sensors in the lab using calibration samples and UV-Vis-NIR absorption spectroscopy. The water quality platform was tested in an artificial lake that is located at Sabanci University Campus (Istanbul, Turkey), which serves as a reservoir for treated wastewaters and rainwater. Untreated wastewater samples were collected from the wastewater treatment station of the university for comparison. The measurements performed on several locations along the coast of the artificial lake were also validated in the laboratory. The water testing platform showed significant potential for miniaturization and portability of such analytical platforms for on-site environmental monitoring.

Keywords: Open source, water quality, turbidity, Arduino, water treatment

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1. INTRODUCTION

Industrialization and urbanization resulted in changes on surface and groundwater quality. 844 million people do not have access to even a primary drinking water service (World Health Organization-WHO and The United Nations Children's Fund-UNICEF 2017). The term wastewater is used for any water that has been influenced by human use. In other words, wastewater can be defined as a by-product of domestic, agricultural, commercial, as well as industrial activities (Tilley et al. 2014). Thus, the composition and properties of wastewater differ widely depending on the source. It mostly consists of chemical or physical pollutants ranging from heavy metals, organic and inorganic particles to toxins. Furthermore, biological contaminants of wastewater are bacteria, viruses, and protozoa (Andersson et al. 2016). About 1.5 million children under the age of five die due to diarrhea each year (UNICEF). The fresh water, which is only 3% of the Earth's natural water resources has been contaminated gradually with increased human activity (Kumari 2018). As a result, the assessment of the water quality for drinking or agricultural purposes is imperative (Carpenter et al. 1998). However, the advanced analytical methods to measure the water quality, e.g., atomic absorption spectrophotometry, gas chromatography or flame photometry, are either expensive (United Nations Environmental Programme-UNEP and WHO 1996; Kirchner et al. 2004) or time-consuming that requires sending water samples to a laboratory for analysis (Oelen et al. 2018). Furthermore, fast-decaying pollutants such as 1,4-dioxane make the on-site measurements more credible and valuable.

Turbidity, temperature, and pH are essential parameters to evaluate water quality. Turbidity is a measure of fluid clarity or cloudiness which is caused by the microscopic plants, animals, or solids suspended in that fluid. High turbidity levels may be an indicator of the existence of pathogens such as viruses, parasites, bacteria, or chemical contamination (Mann et al. 2007). Water turbidity can be measured by using turbidity sensors that quantify the light transmittance and scattering caused by the suspended particles in the water when an incident light beam is sent. The unit for turbidity is NTU (nephelometric turbidity unit).

Temperature affects the metabolism, reproduction, and emergence of most of the organisms that live in water since they are adapted to live in a narrow temperature range. The temperature of the water may also play a

significant role in an increased toxic activity, which is caused by pollutants (Cairns et al.1975). Furthermore, less oxygen can be dissolved in warmer water. The temperature can be measured by using temperature sensors composed of thermocouples with waterproof housing.

The acidity is expressed in terms of the number of hydrogen ions, and the pH is a measure of free hydrogen ion concentration in the logarithmic scale. The pH of water decreases as it becomes more acidic ($\text{pH}<7$). Pure water has a pH of around 7, which means it is neutral. The existence of chemicals in the water affect the pH, which makes the pH of water an essential indicator of water quality. There are three different ways to measure pH (UNEP and WHO 1996). The first two are using pH indicator paper or indicator liquid, which both involve subjective assessment of the color by the human eye. The third method is to use an electrometric pH measurement, which consists in measuring the electrical potential difference between the H^+ sensitive glass electrode and the reference electrode. This technique is accurate, fast, and can be performed *in situ*.

In the past, these types of measurements were done by dated equipment in the lab. However, free and open-source software (FOSS) is an available device, nowadays, that can pave the way for important measurements. FOSS is defined as computer software available in an open-source form, and that can be utilized, modified, and redistributed without any restriction (Milanovic et al. 2018). These days, FOSS is becoming the norm in software evolution, with a variety of applications, including science and education (Pearce J. 2013), medicine (Lang 2011), engineering and nanotechnology (Pearce 2013). Creating both software and hardware is feasible by a transparent system represented by FOSS and improving open-source hardware results in a significant cost reduction, enabling the state of the art scientific tools available all over the world (Pearce et al. 2010). According to the literature, there are various open-source “do-it-yourself” devices, including: a potentiostat (Arevalo-Ramirez et al. 2017), syringe pump (Wijnen et al. 2014), a colorimeter (Anzalone et al. 2013), pH-meter (Milanovic et al. 2018) which can be provided by scientists with low costs. However, to our knowledge, the open-source device for measuring Turbidity, pH, and Temperature values has been provided in a notably smaller range (Garbacz et al. 2013). Considering that the average cost of commercially accessible measuring units and software comes at huge costs, the cost can be considered as a limiting factor for providing the abovementioned device in the developing world. To improve the assays in which these measurements are needed, the affordable open-source “Open Turbidity-pH-Temperature Control” software has been designed by using low-priced laboratory equipment.

Using open-source hardware and software is one way to decrease the cost while still acquiring reliable assessment data. As a result, alternative methods which involve practical and cheaper testing platforms with multiple sensors were reported (Rao et al. 2013; Kelley et al. 2014; Wijnen et al. 2014; Jin et al. 2018; Milanovic et al. 2018; Oelen et al. 2018; Parra et al. 2018). Rao et al. (2013) designed a continuous low-cost water quality monitoring system using an Arduino Mega 2560 to control six different sensors: temperature, light, pH, conductivity, dissolved oxygen, and oxidation-reduction potential. Kelley et al. (2014) used a 20 MHz, 8-bit microprocessor, which was programmed in the C-based Arduino language to measure turbidity. They 3D-printed the housing and produced their turbidity sensor in-house. Wijnen et al. (2014) built an open source, mobile water quality testing platform to measure the turbidity that utilizes both colorimetry and nephelometry. The data processing was performed by an Arduino Fio board. Lopez-Ruiz et al. (2014) determined the nitrite concentration and pH of water samples by using a low-cost, paper-based microfluidic device and used a smartphone as the light source and an image processing computer. Milanovic et al. (2018) constructed a pH-stat device by using free and open source software and inexpensive hardware such as Arduino Nano and 3D-printed parts. Oelen et al. (2018) controlled four different sensors with an Arduino board: a TDS (total dissolved solids), pH, turbidity, and temperature sensors. The resulting device can be used for monitoring the water quality continuously and autonomously. Moreover, Jin et al. (2018) built the inexpensive hardware for pH determination on a breadboard. They used an Arduino Nano to evaluate the pH and communicate the data over Bluetooth, utilizing a smartphone as a monitor. In this work, we have assembled an Arduino-based open-source water testing platform out of commercially available sensors and controllers.

2. METHODOLOGY

2.1. Design

All the components were assembled on a breadboard. An Arduino Nano microprocessor was used to control and monitor the sensors. The turbidity sensor (Stock Keeping Unit (SKU): SEN0189 from dfrobot.com) was composed of a light transmitter and a receiver, which comes with an amplifier. The signal pin was connected to the analog A0 input of the Arduino board. The DS18B20 temperature sensor (SKU: DFR0198 from dfrobot.com) was a 1-wire digital temperature sensor which has a unique 64-bit ID burned at the factory that allows connecting multiple temperature sensors to the same pin.

The pH sensor (SKU: SEN0161 from dfrobot.com) included a glass bulb with H^+ sensitive coating covering the electrode. The pH sensor was connected to a circuit board via a BNC (Bayonet Neill-Concelman) cable and the connection to the analog A1 input of the Arduino board was through this circuit board.

The HC-05 Bluetooth SPP (serial port protocol) module transmitted and received the serial data through its digital pins called as Transmit (TX, digital pin 1) and Receive (RX, digital pin 0) respectively. The RX pin was

connected to the digital D11 input of the Arduino. The RX line was connected to the digital D10 input after a voltage divider employing a 2.2 k and a 1 k resistor coming from the 5 V line of the Arduino.

The Arduino was powered by a 9 V battery. All the components are fed from the 5 V line of the Arduino. An illustration of the components used in the device and the real photograph of the device are shown in **Figure 1**.

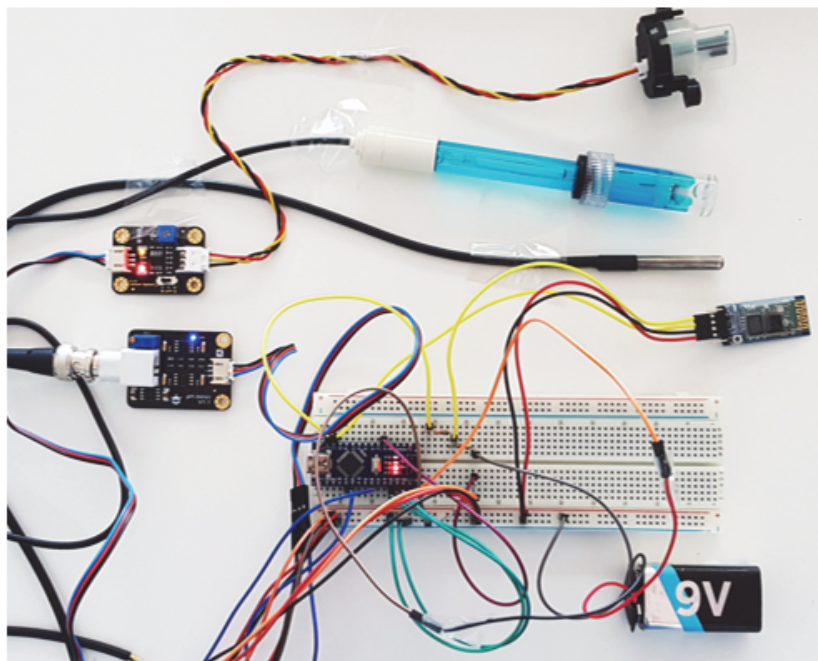
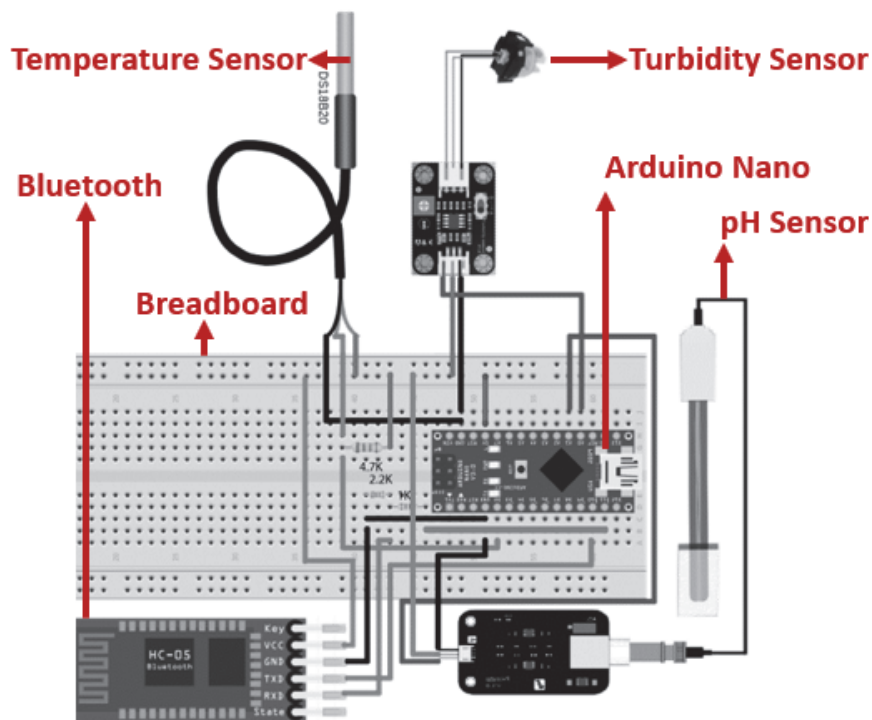


Figure 1. An illustration of the components used in the device (Top) and the actual open source hardware (Bottom)

2.2. Calibration and Validation

The turbidity sensor consists of and near-infrared light emitting diode (LED) and photodiode sensor. Depending on the turbidity of the solution, the amount of light reaching from the LED to photodiode decreases leading to decrease in the photodiode voltage with respect to the unobstructed transmission of emitted light. The turbidity sensor was calibrated using pure water as 0 NTU, calibration standarts of 400 and 1000 NTU (**Figure 2**).

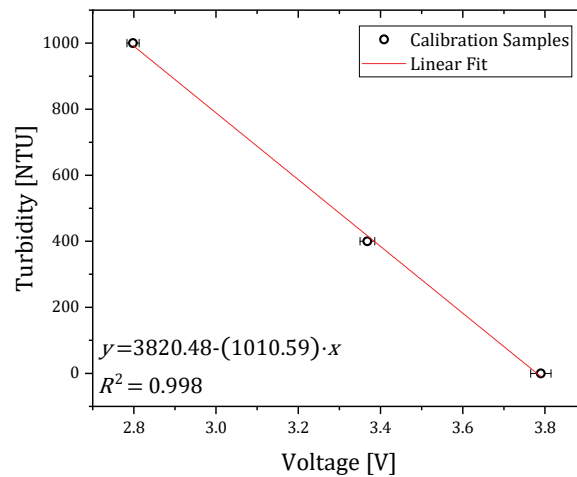


Figure 2. Turbidity calibration samples vs turbidity sensor voltage

The linear fit performed on the NTU values vs voltage readings yielded the following calibration equation:

$$\text{Turbidity value (in NTU)} = -1010.59 \times V + 3820.487 \quad (1)$$

where V is the voltage reading from the liquid whose turbidity is to be measured.

For the validation of turbidity measurements, the samples from four designated sites and treatment center as well as turbidity calibration samples of 400 NTU and 1000 NTU were also analyzed using UV-Vis-NIR spectroscopy. The absorbance of samples was recorded using Cary 5000 UV-Vis-NIR spectrophotometer. The wavelength of 750 nm was selected to bypass visible absorbance of particles in the samples. Thus, the absorbance values are highly depended on the scattering of the particles in the samples. The correlation of turbidity levels and absorbance at wavelength a of 750 nm were shown in **Figure 3**. In line with measured turbidity levels, absorbance at wavelength a of 750 nm stayed below 0.16 for Site 1 and Site 2 and rose to 0.24 - 0.28 for Sites 3, 4 and treated samples. Meanwhile, the untreated sample showed a high level of absorbance of 2.918 as expected.

The pH sensor was calibrated using three different buffer solutions with pH values of 4.01, 7.00, and 10.01. After operating the pH sensor over the Arduino Nano through the circuit board that came with the pH sensor, the potentiometer on the circuit board was adjusted to match the serial monitor reading to the correct pH value of that buffer solution. This calibration was performed for three times for an optimized setting. For validation of the pH sensor, all collected samples and calibration standards were also measured using Hanna HI2210-01 benchtop pH meter. The validation of the pH sensor readings were correlated with the benchtop readings in laboratory.

The temperature sensor does not have to be calibrated when the proper Arduino library (Dallas Temperature) was pre-calibrated. The source codes that control each of the sensors can be found online.

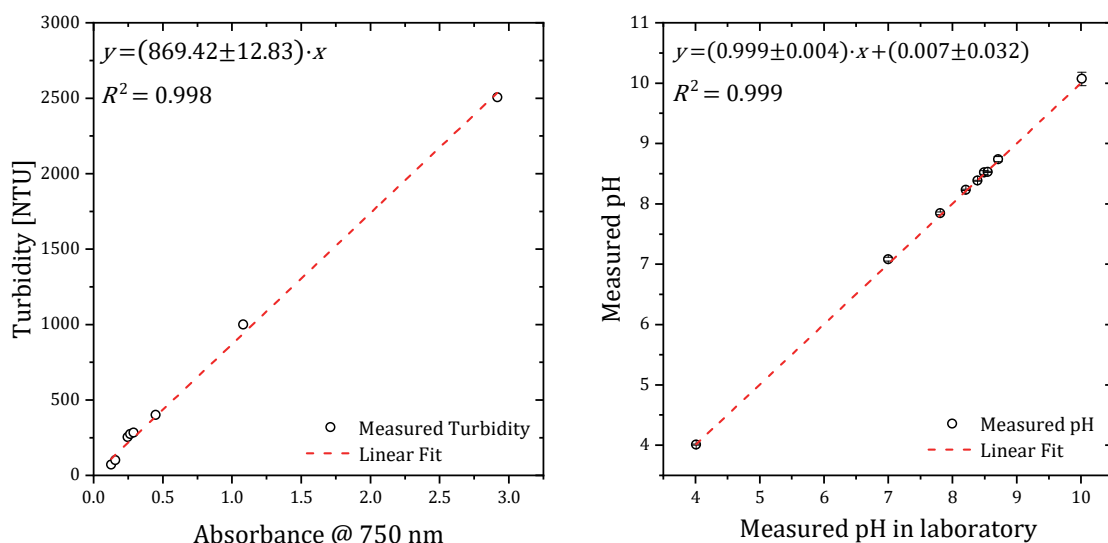


Figure 3. Validation of turbidity readings with absorbance measurements at a wavelength of 750 nm (left) for samples from 4 designated sites, untreated water waste, treated water, and 400 & 1000 NTU calibration standards and pH measurements of samples from 4 designated sites, untreated water waste, treated water and standard pH calibration solutions (pH 4.01, pH 7 and pH 10) (right).

3. RESULTS AND DISCUSSION

The Sabanci University has an artificial lake which was transformed from a 7-8 meters deep amorphous pit in the foundation of the university. While transforming the pit into an artificial lake, the bottom of the pit was levelled and deposited with clay and gravel. The artificial lake was filled with rain, stormwater drains of the campus buildings, and treated sewage. The lake remains to be used for irrigation reservoir for plants in the campus. Upon the arrival of fish eggs by seagulls, the artificial lake formed a natural fauna.

We utilized an open-source, cost-effective and portable water quality testing platform that can measure the turbidity, temperature, and pH of the water in real time, and transfer the results to smartphones over a Bluetooth module, eliminating the need for a dedicated monitoring device and expert. The samples were collected from the artificial lake inside Sabanci University campus as well as untreated and treated water from Sabanci University Wastewater Treatment Plant. In this center, treated water is provided through some operations where the first step is pre-treatment, which consists of screening, equalization, and pumping station (Sabanci University 1999). This is followed by biological treatment, including sequencing batch reactor with blower-diffuser aeration. Next step is advanced treatment such as filtration. Following this, chlorine disinfection of the effluent is applied to the sample. Finally, sludge treatment is utilized by using a sludge dewatering system. In order to provide precise results, calibration is required. By performing this step, the device offers an accurate indication or output signal when it is installed.

The samples of the artificial lake were collected from 4 different sites along the coast of the lake, as shown in **Figure 4**. Site 1 was the small artificial waterfall which feeds the artificial lake. Site 4 was close to the waterways of water treatment station feeding into the artificial lake. We also collected samples from a water treatment center to assess the quality of untreated and treated water. The collected samples were also analyzed in the lab, as shown in **Figure 5**. Initial visual assessment, the treated and samples along the coast are highly transparent with a low level of large particles inside.



Figure 4. Sites where the samples are collected on the campus of Sabanci University

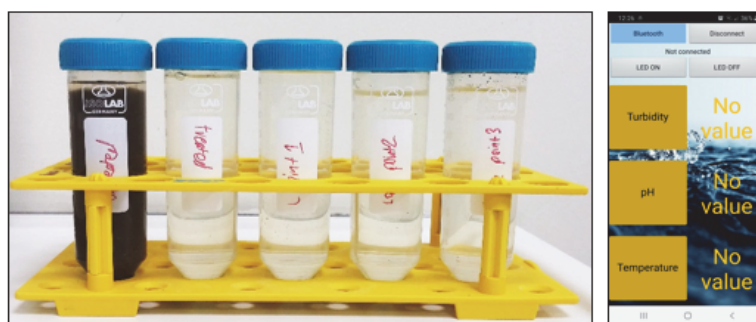


Figure 5. The samples collected from the designated sites for absorbance, and turbidity measurements (left), Android-based smartphone application interface (right).

The on-site measurements showed that the turbidity levels were below 300 NTU along the coast of the artificial lake and the treated water sample collected from the water treatment center, as shown in **Figure 6**. The untreated water sample was highly turbid, reaching around 2506 NTU, and the collected samples tended to sediment within minutes. Site 1 had an artificial waterfall, and Site 2 was placed close to the waterfall. The accelerated surface waves tend to push the large particulates to the north end of the shallow coast of the lake. Turbidity levels of Site 1 and 2 remained around 71 and 101 NTU, respectively. However, the shallow and considerable calmer Sites 3 and 4 had 253 and 273 NTU, respectively, and were close to the treated water turbidity level of 283 NTU. The samples mentioned above were also collected in falcon tubes for absorbance analysis.

The acidity of the artificial lake was measured as higher than a pH of 8. The pH levels were increased as the collection site were further away from the artificial lake and closer to the treatment channel connected to the lake. The pH level of 8.38 was measured on Site 1. Site 2 and 3 showed a slightly higher pH of 8.5. Site 4 showed highly elevated levels of pH around 8.74. Meanwhile, the collected samples from untreated and treated water showed a pH level of 7.84 and 8.23, respectively.

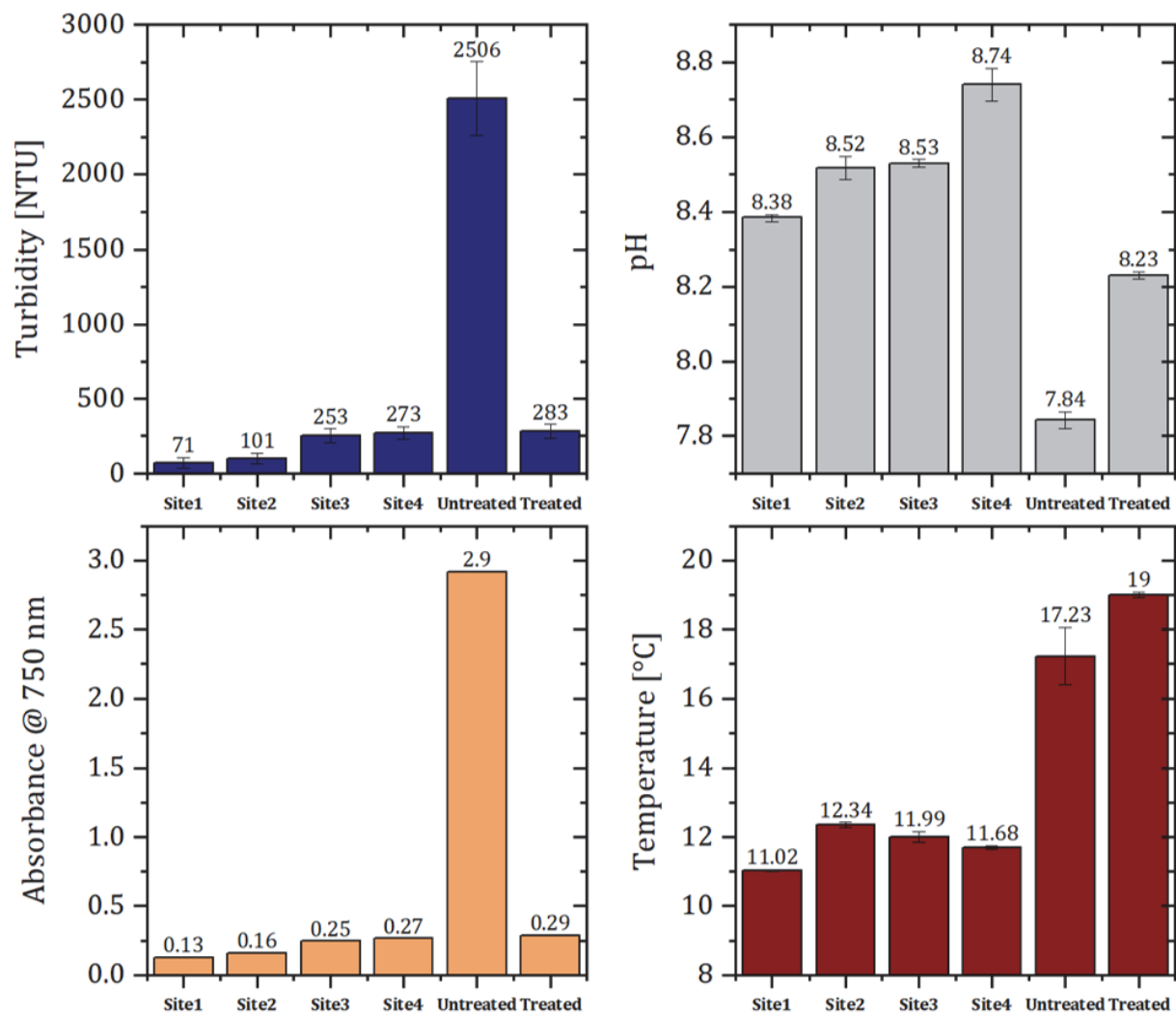


Figure 6. Graph of turbidity, pH, absorbance and temperature measurements from various sites on shores of the artificial lake, untreated, and treated samples from the water treatment center.

4. CONCLUSIONS

The low cost and widespread availability of open-source hardware enabled environmental scientists to exclude the use of high-cost analytical equipment and perform analyses on site. The presented on-site water pollution testing platform was used to monitor the water quality of an artificial lake that is feed with the treated wastewater. Noteworthy is the fact that instrument error is probable to occur due to various factors including environmental issues, electrical supply, the addition of excessive components to the output loop and process alteration. However, these errors can be minimized if not eliminated by applying a calibration procedure. An error can be defined as

the dissimilarity between the indication and the actual amount of the measured parameter. To determine and rectify device errors, periodic calibrations were applied. The most stable probe is the temperature sensor due to the standard thermometer that has been used in our assay. Also, we obtained balanced and stable data for pH measurements. Unlike temperature and pH sensors, a significant deviation was observed in the turbidity sensor. This defect is related to the structure of the turbidity sensor suffering from waterproofing, although it was weak. On the other hand, the device is cost-effective and portable, promoting the development of robust software equipment which we are growingly reliant on.

This initial work and results act as stimuli for further studies on open-source on-site measurements systems. Future work may lead researchers to construct a remote-controlled model ship, which probes the water quality continuously along the artificial lake with integrated navigation. The growing repertoire of water quality monitoring with commercially available open-source sensors such as ammonia and dissolved oxygen would further improve the applicability of the proposed open-source sensing platform.

5. ACKNOWLEDGMENTS

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MAGNETICALLY RESPONSIVE MATERIALS FOR SOLID PHASE EXTRACTION

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Abstract: Magnetically responsive materials have found many important applications in analytical chemistry. In this short review the basic information about Magnetic solid phase extraction and Magnetic textile solid phase extraction is given. These analytical techniques enable to preconcentrate target biologically active compounds or pollutants from water samples. Both procedures enable to lower the limit of detection using conventional analytical procedures.

Keywords: Magnetic solid phase extraction, Magnetic textile solid phase extraction, preconcentration, elution, image analysis

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Review paper

1. INTRODUCTION

Sensitive analytical techniques have to be used to monitor the concentration of target biologically active compounds, organic and inorganic pollutants or radionuclides present in water, other environmental media and biological materials. Sample preparation techniques such as preconcentration have to be often used to concentrate the target analytes. This treatment can significantly lower the limit of detection using conventional analytical procedures such as chromatography or spectrophotometry.

Several sample preparation procedures can be used in analytical chemistry. One of them is a well-known liquid-liquid extraction, which is based on the analyte partitioning between water and an immiscible organic solvent. However, currently alternative extraction methods known as solid phase extraction (SPE) are preferentially employed. During the extraction process, an aqueous sample passes through a solid phase (adsorbent) and afterwards is extracted by a suitable eluant (often organic solvent). In the most often applied SPE design the adsorbent is placed in a polypropylene cartridge (Buszewski & Szultka 2012).

New forms of solid phase extraction have been developed in recent years. Very important ones are based on the use of magnetically responsive materials. The following text will be focused on the description of Magnetic solid phase extraction and Magnetic textile solid phase extraction.

2. MAGNETIC SOLID PHASE EXTRACTION

In order to extract target analytes from large sample volumes or difficult-to-handle samples, magnetic solid phase extraction (MSPE) employing magnetically responsive adsorbents was developed by Safarikova and Safarik in 1999. This approach has several advantages over traditional solid phase extraction performed in cartridges, namely: (a) it provides a rapid and simple analyte separation that avoids the need for centrifugation or filtration steps, (b) it avoids time-consuming and tedious on-column SPE procedures, (c) MSPE can also be used for samples containing suspended solids, (d) the magnetically responsive adsorbents may have high selectivity, even when complex biological and environmental samples are analyzed, (e) minimal amount of organic solvents for elution is necessary, (f) since the majority of sample impurities are diamagnetic, they do not interfere with magnetic particles during the magnetic separation step, and (g) automation of the whole process is possible, which leads to rapid, selective, sensitive, and repeatable methods for routine analyte determinations (Safarik & Safarikova 2012; Azzouz et al. 2018). The scheme of MSPE is shown in **Figure 1**.

MSPE is based on the use of various magnetically responsive nano- and micromaterials, including iron oxides magnetite (Fe₃O₄) and maghemite (γ-Fe₂O₃), various types of ferrites (MFe₂O₄) where M can be copper, nickel, manganese, magnesium, etc., pure ferromagnetic metals (iron, cobalt and nickel), and various metal alloys (FePt, CoPt). Both magnetite, maghemite and magnetic mixed iron oxides exhibit sufficient magnetic moment, good stability, and low toxicity and that's why they are predominantly used. They can be prepared using several simple precipitation or alternative procedures. Magnetic materials can serve as supports for the immobilization of an

appropriate affinity ligand, or as magnetic labels for conversion of originally diamagnetic materials into magnetically modified ones.

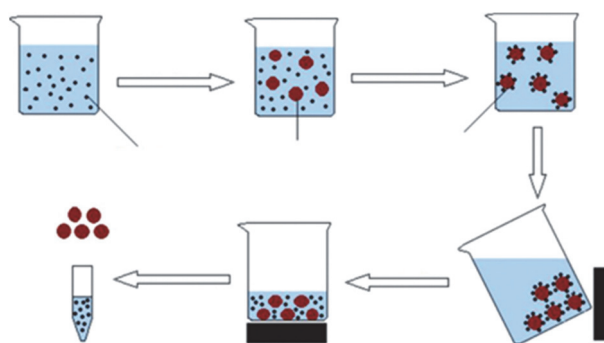


Figure 1. Magnetic solid phase extraction (reproduced from *Chen et al. 2011*)

Different types of materials have been coated onto the surfaces of magnetic particles. For example, graphene and graphene oxide, single wall and multi wall carbon nanotubes, metal-organic framework, molecularly imprinted polymers, ionic liquids, specific polymers or low molecular weight affinity ligands have been bound to magnetic particles and subsequently used as sorbents to extract and preconcentrate polyaromatic hydrocarbons, chlorophenols, phthalate esters, pesticides, fluoroquinolones, organochlorine pesticides, fungicides, hormones, monocyclic aromatic amines, bisphenol A, organophosphorus pesticides and other analytes from water solutions. The adsorption efficiency and selectivity of magnetic particles can be tuned by surface modifications with various composites and ligands, allowing the mechanisms for extracting trace-level analytes to match the nature of the target molecules. This technique greatly simplifies the extraction procedure and enhances the extraction efficiency. Magnetic adsorbents can be prepared in different shape, size and configuration. Magnetic separation is not influenced by the change of pH, ionic strength or the presence of contaminating diamagnetic materials (*Andrade-Eiroa et al. 2016; Hemmati et al. 2018; Azzouz et al. 2018*).

MSPE is now a very useful and widely used preconcentration procedure for both organic and inorganic species. Currently, there are more than one thousand records in Web of Science and ca 1100 records in Scopus. Detailed information about the recent applications of MSPE in various disciplines can be found in variety of review papers (*Ibarra et al. 2015; Ibrahim et al. 2015; Speltini et al. 2016; Vasconcelos & Fernande 2017; Hemmati et al. 2018*).

Specific problems during MSPE can appear when the sample volume is too big and very small magnetic particles are used. In this case, magnetic separation can take a long time and some loss of magnetic adsorbent can be observed. Due to these facts a complementary procedure has been developed recently, which is based on the use of magnetically responsive pieces of textile.

3. MAGNETIC TEXTILE SOLID PHASE EXTRACTION

A new type of low-cost preconcentration method, based on the use of magnetically modified textile (Magnetic textile solid phase extraction; MTSPE) has been developed recently (*Safarik et al. 2018*). In this procedure, a piece of an appropriate textile (fabric) is used as a carrier for the immobilization of a specific affinity, ion exchange or hydrophobic ligand. In order to prepare magnetically responsive adsorbent, an iron-based standard staple was inserted in the textile material using an office stapler (see **Figure 2**). Magnetically modified pieces of textile can be moved using appropriate laboratory magnetic stirrers in a similar way as magnetic stirring bars. At the end of the extraction process, the piece of textile can be easily and rapidly separated magnetically, as shown in **Figure 3**. The whole process of magnetic textile solid phase extraction is shown in **Figure 4**.

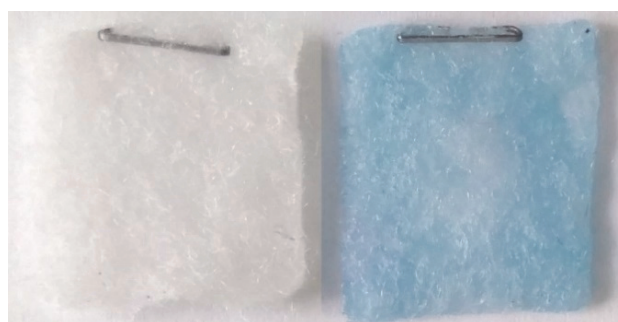


Figure 2. Magnetically responsive chitosan modified textile square and magnetically responsive chitosan modified textile square with adsorbed indigo carmine (reproduced from *Safarik et al. 2019a*)

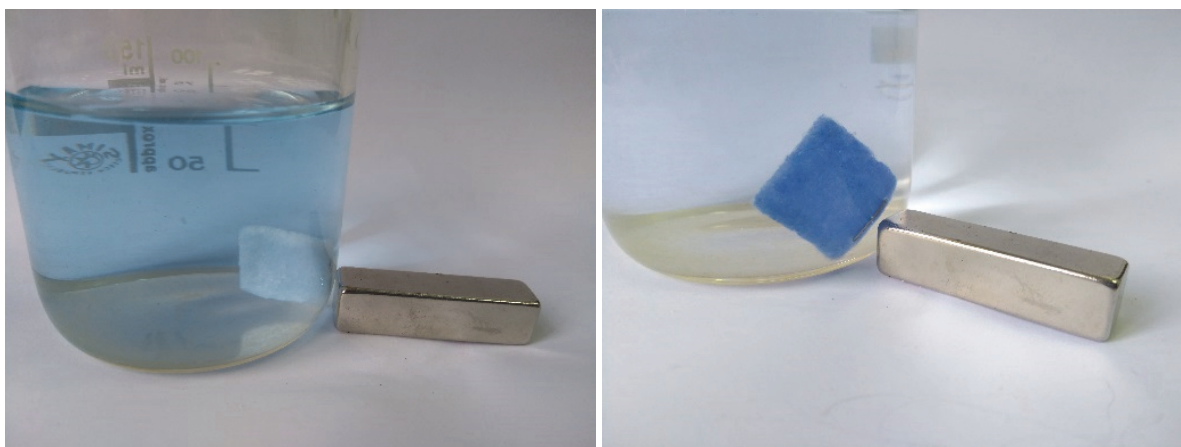


Figure 3. Magnetic separation of magnetically responsive textile squares

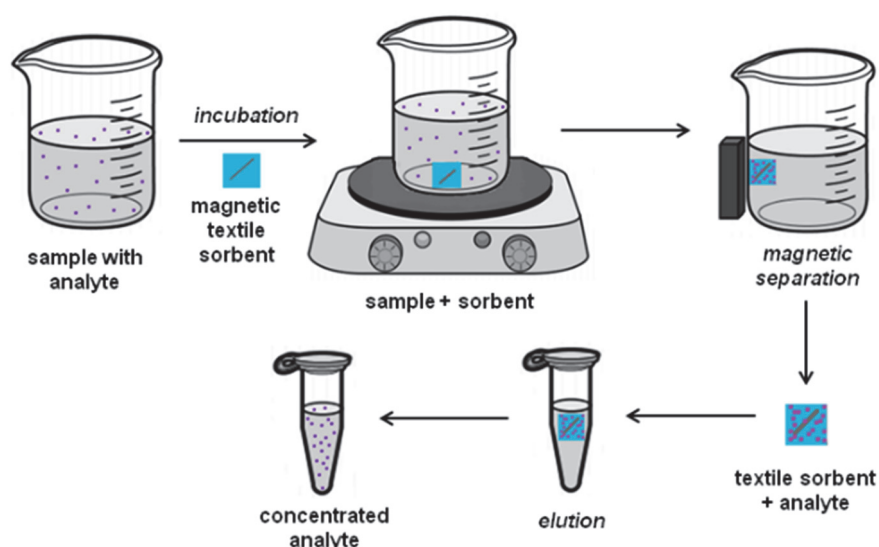


Figure 4. Magnetic solid phase extraction (reproduced from Safarik et al. 2018)

Various types of textile can be used for MTSPE. In the recent experiments, nonwoven acrylic felt was employed. The fibres have to be usually modified by an appropriate ligand. Reactive copper phthalocyanine dye covalently immobilized on the textile was used for the preconcentration of crystal violet and safranin O from diluted solutions (Safarik et al. 2018). Alternatively, textile fibres were modified with a positively charged polysaccharide chitosan (see **Figure 5**). Chitosan modified textile was applied for the preconcentration of food acid dyes tartrazine, azorubine and indigo carmine (Safarik et al. 2019; Safarik et al. 2019a) or blue fountain ink dye Acid blue 93 (Safarik & Pospiskova 2018).

Similarly to standard solid phase separation procedures, analyte bound to magnetically responsive textile is usually eluted with a small amount of an appropriate eluant. After elution, standard analytical procedures including chromatography and spectrophotometry are used for analyte determination (Safarik et al. 2018; Safarik & Pospiskova 2018; Safarik et al. 2019a).

A simple method enabling analysis of dyes adsorbed on magnetically modified textile, without the need of their elution, has been developed recently. After the dye preconcentration, photos of textile squares with the adsorbed dye were taken using a mobile phone or a digital camera (see **Figure 6**). Using an appropriate software, the square or rectangle covering maximum of homogeneously colored textile (without the staple) was cropped from the original image for the subsequent evaluation using ImageJ. Every image was analyzed using Color Inspector 3D plugin which is an integral part of ImageJ software. In this plugin, Median Cut option was used to reduce original range of colors into a single one “median” color. After that the HSB color space (Cheng et al. 2001) was applied to obtain three image parameters, namely hue (H), saturation (S) and brightness (B) (see **Figure 7**). The values of saturation were measured, which were proportional to the dye concentration in the analyzed samples (see **Figure 8**). Using this inexpensive, elution free assay it is possible to analyze dyes concentration in various solutions.

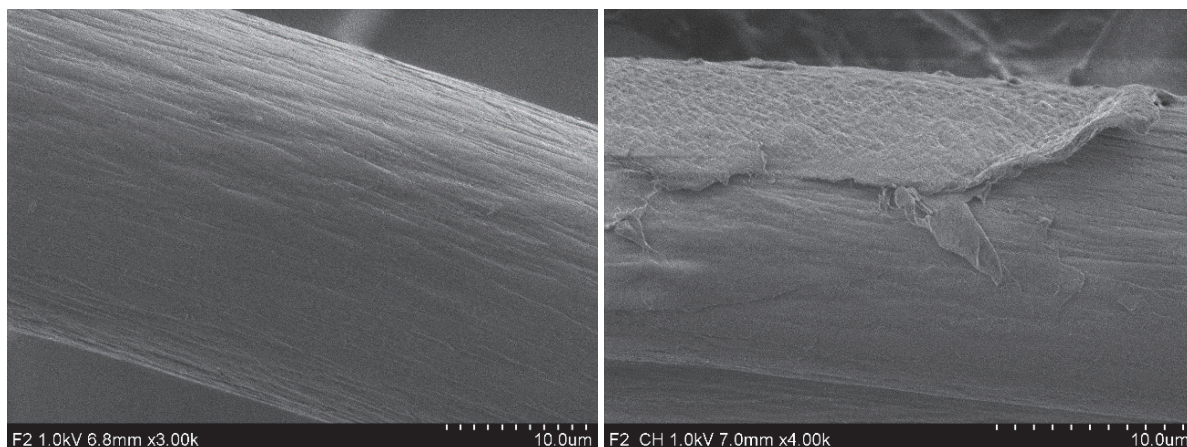


Figure 5. SEM image of native (left) and chitosan modified (right) acrylic fibers present in the non-woven textile used for MTSPE (reproduced from Safarik et al. 2019)



Figure 6. Examples of magnetically responsive, chitosan modified textile squares after azorubine extraction from water solution (100 mL; concentrations of the original solutions are shown) (reproduced from Safarik et al. 2019)

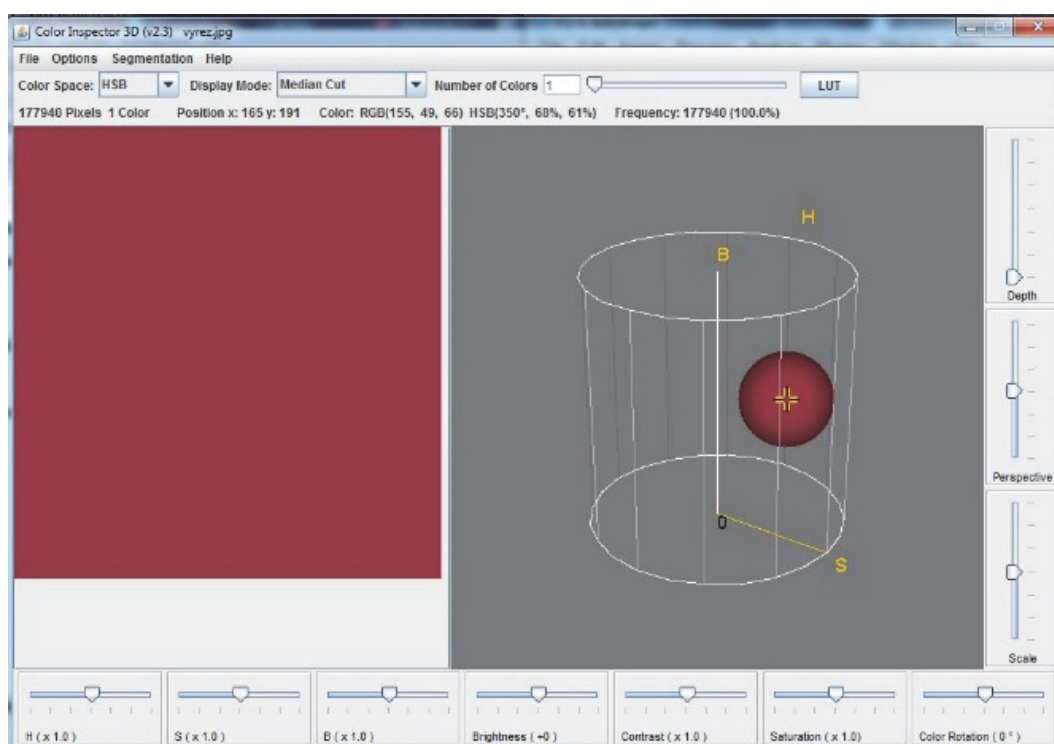


Figure 7. Appearance of the computer screen showing ImageJ software analyzing image of a textile square after MTSPE of azorubine. Reproduced from Safarik et al. 2019.

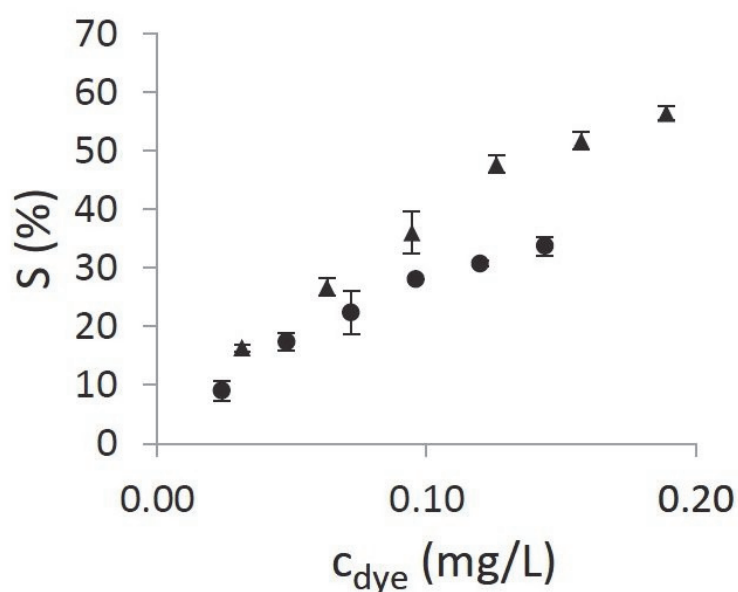


Figure 8. Dependence of values of saturation (S) on the concentration of tartrazine (▲) and azorubine (●). Reproduced from Safarik et al. 2019.

4. CONCLUSIONS

Magnetically responsive materials have already shown their great potential in analytical chemistry. In addition to already well established Magnetic solid phase extraction, a complementary procedure called Magnetic textile solid phase extraction has been developed recently. Both techniques can significantly lower the limit of detection of target analytes using conventional analytical procedures such as chromatography or spectrophotometry. Using MTSPE both elution and elution free assays can be performed. It has been proved that elution free assay enables inexpensive assay requiring only a digital camera or a mobile phone and a computer, in addition to freely available software.

5. ACKNOWLEDGMENTS

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AMMONIA CONCENTRATION MONITORING USING ARDUINO PLATFORM

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Abstract: In order to evaluate the efficacy of ammonia photocatalysis, it is necessary to continuously monitor its concentration during the process. This paper presents ammonia concentration monitoring using a low cost (non-professional) electronic device. The device is based on an open source electronic platform, and it is composed of the MQ-137 ammonia detection sensor, connected to the Croduino Basic 2 board. Sensitive material of the sensor is a metal oxide (SnO₂). The change in the ammonia concentration causes a change in the electrical resistance, which is measured and used for the ammonia concentration estimation. Four measurements, with ammonia concentration ranging from 0-500 ppm were performed in the controlled environment. With the purpose of the device calibration and repeatability test, along with a low-cost device, the monitoring was carried out also with a professional device, Geotech GA5000 gas analyser. Using the information provided in the sensor datasheet, together with the measured data, the measurement error of the low-cost device was assessed. After calibration, ammonia concentrations measured using a low-cost device, are consistent with those obtained from the professional device.

Keywords: MQ-137 sensor, Arduino, ammonia concentration, photocatalyst

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1. INTRODUCTION

Over the past several years, open hardware concepts and portable sensors have undergone a period of rapid development. During the time, open hardware concepts, i.e. Arduino platform, are becoming gradually accepted within scientific and educational community. Availability, low price, steep learning curve and abundance of available examples makes this concept very convenient for a non-professional to enter the world of hardware and software development. The focus of this paper is put on ammonia concentration monitoring during the photocatalysis process, using a low-cost MQ-137 sensor. Different examples of MQ-137 sensor application in various scientific areas are available, such as, spoiled meat classification (Kartika et al. 2018), construction of electronic nose for characterization of saffron aroma (Kiani et al. 2017) or in detection of seasonal allergic rhinitis in exhaled breath (Saidi et al. 2015). The MQ-137 sensor is also used for monitoring organic abundance in soil to advocate food security and sustaining the farming system (Dorji et al. 2017).

Increasing awareness of harmful consequences of persistent organic pollutants in water and air makes development of photocatalysis for their degradation one of significant goals in environmental engineering. A specific problem of air pollution over agricultural land is ammonia (NH₃) and other nitrogen gases. Increasing the use of pesticides and fertilizers increases the concentration of VOCs and NH₃ in the air as agricultural areas are recognized as collective emission sources. In accordance with the applicable IPPC Directive (Brinkmann et al. 2016), photocatalytic oxidation is cited as an alternative best available technique (NRT), effective for the removal of gases from the air. With this type of technology, it is possible to remove the following pollutants: VOC, unpleasant smells, H₂S, NH₃, amines and mercaptans, NO_x, SO_x, CO and O₃. (Gaya and Abdullah 2008). It is a process that uses the synergistic interaction of light radiation, catalysts - semiconductors and oxidative species to oxidize ammonia to N₂ and to break down organic pollutants in fluids to H₂O and CO₂ other inert products depending on the chemical composition of the pollutant. The basic advantage of this method is the necessary conditions that are easy to satisfy, which are the presence of UV or VIS electromagnetic radiation, atmospheric oxygen and water. All of these conditions already exist in the environment, it is only necessary to provide photocatalytically active material and photocatalytic oxidation can begin. It is applied for the purification of water and air in the industry sector, i.e. in waste treatment plants, fermentation processes, coating applications and the food industry (Boyjoo et al. 2016).

The application of this indoor air purification technology has a much higher potential for commercialization, especially for the removal of VOCs. and several recent patents can be found to confirm the applicability (Wang et al. 2007; Pingjian 2019) For the purification of polluted air, photocatalytic reactors with the immobilized photocatalyst applied to the carrier (surface) must be properly designed and placed

directly on the source of emission. Due to variations in emissions, concentration of pollutants in air should be continuously monitored before and after the photocatalytic purification to control the process efficiency and to estimate the positive impact on the air quality; hence the necessity for the development of simple analytical platform based on portable sensors and open hardware concepts.

2. EXPERIMENTAL SECTION

2.1. Experimental setup for measurement concentration of the NH_3

Low-cost sensor was calibrated in a controlled environment that is made of a plastic container connected to the ammonia supply, **Figure 1**. Calibration was conducted using a professional device Geotech GA5000, with the declared ammonia concentration measurement accuracy of 10 % ([Geotech manual](#)). For this purpose, the MQ-137 sensor was placed inside the container, and professional device was connected to it. Along with concentration measurements, temperature and relative humidity inside container was monitored by DHT-22 sensor. The MQ-137 sensor, which was used in these experiments is fabricated by Zhengzhou Winsen Electronics Technology Co., Ltd. Measurable ammonia concentration is within a range between 5 and 500 ppm. The load resistance is adjustable, and heating resistor is approx. $29 \pm 3 \Omega$. Measurement read outs were conducted using Arduino based system, Croduino Basic 2 electronic board (<https://e-radionica.com/>). The output voltage from the sensor module MQ-137 is converted to digital signal using a 10-bit analog to digital converter (ADC) which is a part of the board.

Ammonia solution, 110 μL of ammonia (25 %, Kemika) diluted in 250 mL distilled water, is inside of erlenmeyer flask that is directly connected to bottle. With help of air pump (Fluval Q2, HAGEN, 240 L/min) ammonia solution is pumped to the bottle. Some time is needed to achieve balanced atmosphere inside of a system. After achieving balance, readings are taken with both Geotech and Arduino system. Next, 110 μL of ammonia is added to flask and same process repeats until desired number of data is taken. The measured data were fitted by means of least squares fitting program using Python 3.6 program language and limfit package ([Newville et al 2014](#)).

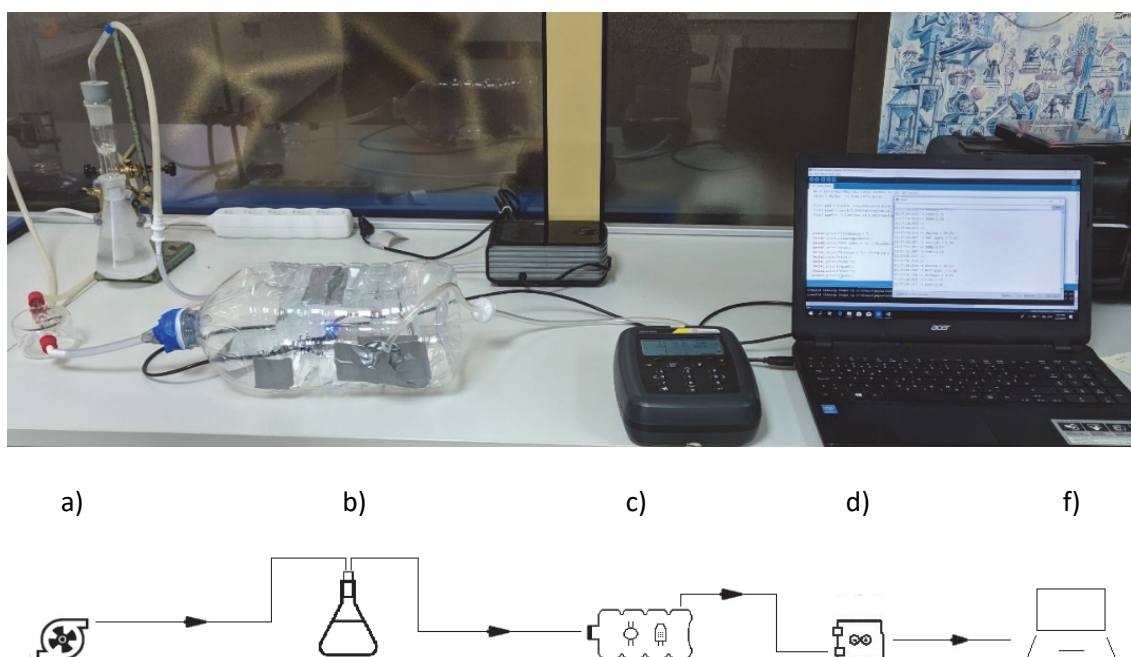


Figure 1. The photo of the setup and schematic picture of the calibration setup showing a) fan b) erlenmeyer flask c) controlled environment made of plastic container with sensors d) Croduino board f) computer.

2.2. Working principles of the MQ-137

MQ-137 is a semiconductor gas sensor which use the sensitivity of the metal oxide SnO_2 to the concentration of ammonia in the air. A detailed description principle of the work sensitive material of the sensor can be found in the paper ([Barsan & Weimar 2003](#)). In this work, focus was on the complete board with the sensor, which can be purchase on the market, the sensor module used in this work is presented in **Figure 2**. We found the examples of using MQ sensor board in determining ammonia ([Aswinth 2018](#)) and butane (<https://jayconsystems.com>)

concentration in air. The starting point in understanding MQ sensors is the schematic circuit, **Figure 2**. The variable resistor that changes its value according to the concentration of gas, in this case ammonia, it is built between A and B pin and it is connected in serial with load resistor (R_L). Between H and H pins it is built-in another resistor used for the heater of the sensitive material. This is necessary for proper work of the sensor.

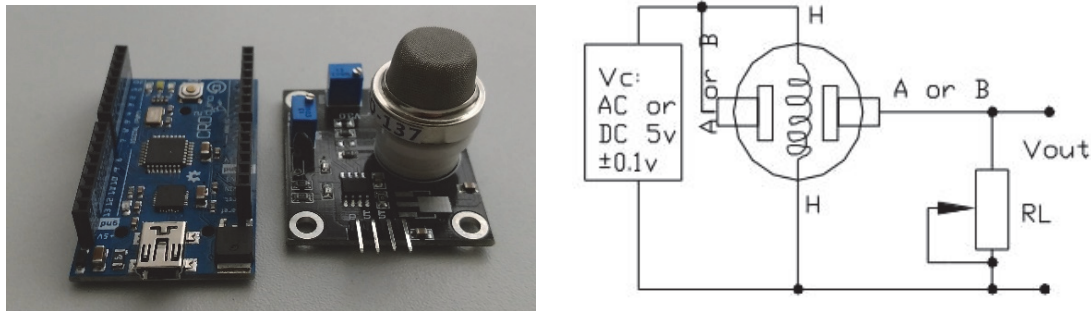


Figure 2. (left) The picture of Croduino Basic 2 board and MQ-137 sensor module. (right) The schematic representation of the sensor circuit. Download from <https://jayconsystems.com>.

The voltage (V_{out}) is measured on the R_L resistor, but it was needed to derive a formula for variable resistor (R_v) between A and B pins. Using Ohm's Law, the current I is written through R_L and R_v resistors as:

$$I = \frac{V_c}{R_L + R_v}, \tag{1}$$

where V_c is the supply voltage. Again, using Ohm's Law the voltage on R_L resistor is written as $V_{out} = IR_L$ and by inclusion of an expression for the current from **Equation 1**, the formula for R_v is gotten as:

$$R_v = \left(\frac{V_c}{V_{out}} - 1 \right) R_L. \tag{2}$$

The sensitivity characteristic of the gas concentration in parts per million (ppm) according to the resistance of the sensor is provided by the producer, **Figure 3**. The graph is on the log-log scale, where on the y-axis is shown the ratio of the resistors R_v/R_0 . The R_0 is the resistance of the variable resistor in the fresh air and according to **Equation 2** it can be rewritten as:

$$R_0 = \left(\frac{V_c}{V_{out}^{fresh\ air}} - 1 \right) R_L = konst_1 R_L. \tag{3}$$

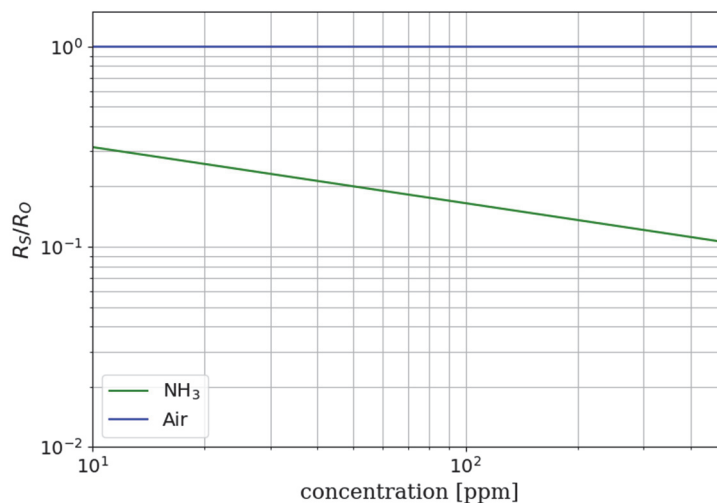


Figure 3. The sensitivity characteristics of the MQ-137 sensor provided by producer.

In the **Figure 3**, the ratio and the concentration are linearly related in the log-log graph. Therefore, by using the equation for the line and changing variable x and y with log functions, the following equation is gotten:

$$\log_{10} \frac{R_v}{R_0} = a \log_{10} ppm + b, \quad (4)$$

where constant a and b are slope of the line and y-axis intercept, respectively. The constant a and b can be calculated from the **Figure 3**. In general, the idea is to measure voltage V_{out} and calculate R_v by using **Equation 2**, after **Equation 4** is rewritten to get results in ppm . In this work, the concentration is independently measured with Geotech, therefore V_{out} dependence on change of the concentration is studied. For this reason, V_{out} can be derived from Equation 2 and 4 as follow

$$V_{out} = \frac{konst_2}{ppm^a + konst_3} \quad (5)$$

where $konst_2$ and $konst_3$ are combination of the constant V_c , $konst_1$, and b .

3. RESULTS AND DISCUSSION

In order to estimate standard error of the read out voltage from the sensor module few measurements was taken of the voltage on the fresh air and $V_{out}^{fresh\ air} = 0.4203 \pm 0.0006 V$ is gotten. In the next step, focus was on the estimation of the error in the calibration measurements.

The measured concentration of ammonia from 10 to 500 ppm and corresponding sensor voltage are presented in **Figure 4 (left)**. The data are fitted with obtained function by **Equation 5** and such fitting model reproduces almost perfectly the measured data with the coefficient of determination $R^2 = 0.999$. The extracted constants form fits are listed in **Table 1**. In photocatalysis experiment the concentration of ammonia goes until 200 ppm, for this reason measurements and analysis were repeated three times in this concentration range, **Figure 4 (right)**. The coefficient of determination in all three fitting procedure was higher than $R^2 = 0.99$. From the **Figure 4 (right)** the small deviations between calibration curve are noticed for ammonia concentration below 50 ppm and excellent repeatability for the concentration above 100 ppm.

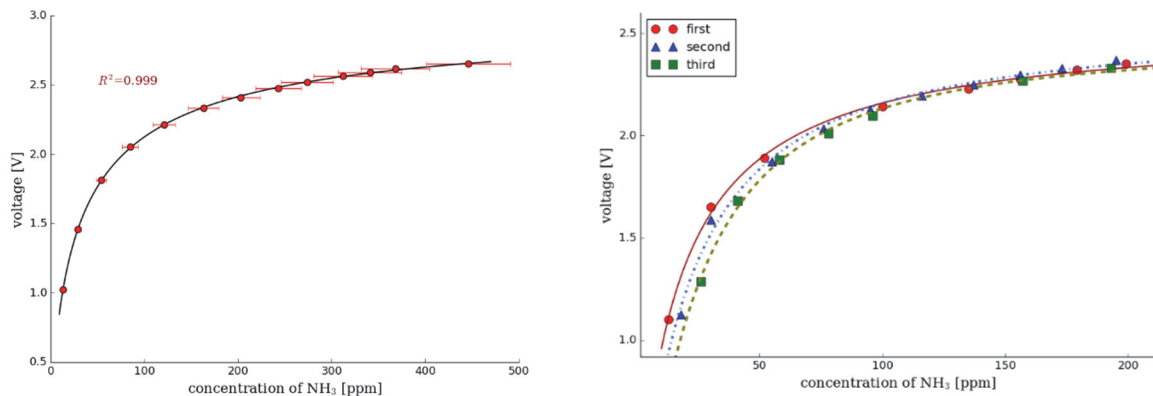


Figure 4. The voltage read from low cost sensor as a function of the concentration of ammonia measured by Geotech. (left) The concentration of ammonia in range 0 -500 ppm. (right) Three measurements in range 0-200 ppm of ammonia concentration. The insert figure represents the residual from the fitting line.

Table 1. The data extracted from the fitting procedure

MEASUREMENT	$konst_2$	$konst_3$	a
zero	0.225 ± 0.006	0.074 ± 0.002	-0.752 ± 0.009
first	0.17 ± 0.03	0.06 ± 0.01	-0.96 ± 0.06
second	0.09 ± 0.03	0.03 ± 0.01	-1.1 ± 0.1
third	0.04 ± 0.01	0.017 ± 0.006	-1.3 ± 0.1
all	0.23 ± 0.03	0.080 ± 0.009	-0.76 ± 0.05

If all measurements are treated together and analysis of the model function repeated, **Equation 5** still reproduces very good measurement data, with the coefficient of determination $R^2 = 0.987$. The experimental data are represented in **Figure 5**. The error of the calibration measurements can be calculated using partial derivative of **Equation 5** and multiplied by the error of the Geotech concentration measurements as:

$$\delta V_{out} = \left(\delta ppm \cdot \frac{-konst_2 \cdot a \cdot ppm^a}{ppm \cdot (ppm^a + konst_3)^2} \right) \quad (6)$$

The **Equation 6** can be evaluated for certain concentration; for example, in case of 100 ppm the error is $\delta V_{out} = 0.04 V$. This is two order of magnitude higher than the read-out error, but it is still relatively low.

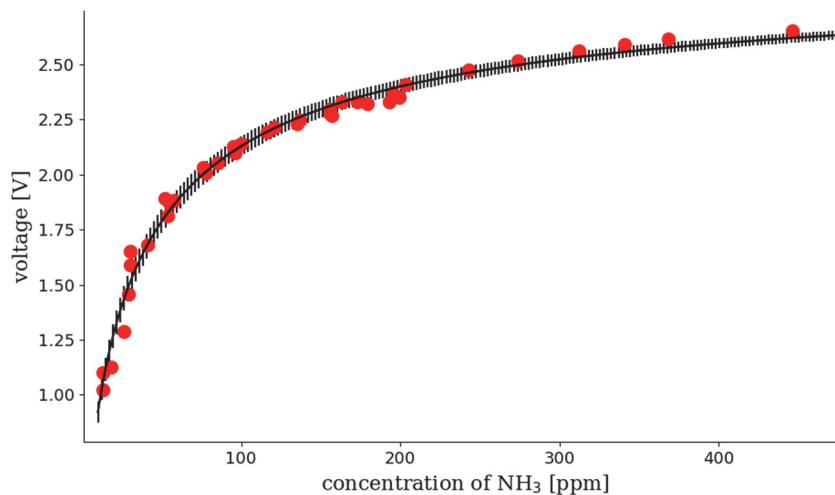


Figure 5. The voltage read from low cost sensor as a function of the concentration of ammonia measured by Geotech. The error bars of the calibration procedure are added on the fitting model.

When experimental data are compared with the data given from producer (**Figure 2**), certain deviation is noticeable as it is shown on **Figure 6**. The average absolute deviation is $\Delta \frac{R_v}{R_0} = 0.04$. The resistor values around 100 ppm is $\frac{R_v}{R_0} = 0.12$, which is 33 %. Therefore, without calibration procedure at ammonia concentration of 100 ppm the deviation can be estimated to the 33 ppm, which can be the main error in experiments with MQ-137 sensors. The cause of the deviation is difficult to locate, but some explanation can be proposed. The producer reported data for the sensor not for the module which include few additional components (resistors, diode, potentiometer) and this components produced systematic deviation.

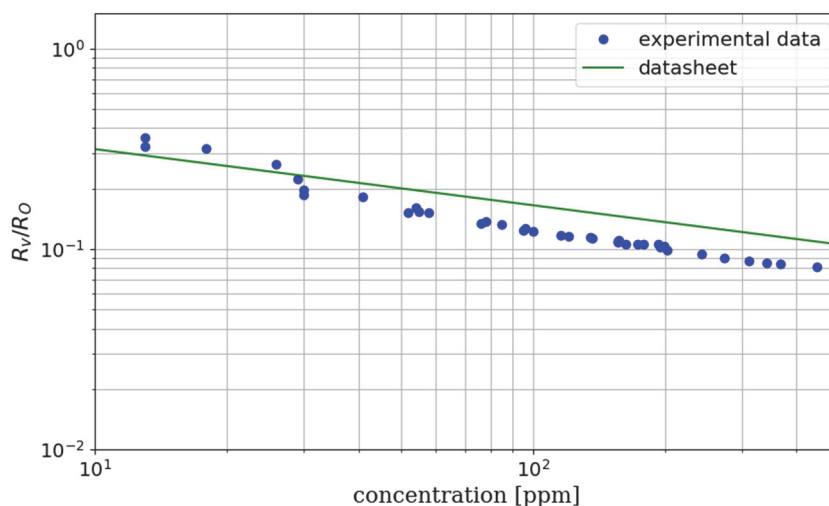


Figure 6. Comparison of the experimental data obtained in this work and calibration curve given by the producer

4. CONCLUSION

As shown in this paper, results reproducibility in measuring ammonia concentration in air can be achieved using a low-cost MQ-137 sensor. The sensor was calibrated by a professional device Geotech GA5000, with declared full scale accuracy of 10% for ammonia concentration measurement. Using measured values, along with professional device accuracy, a measurement error analysis was performed. Calculated error of 0.04 V at voltage corresponding to the concentration of 100 ppm was obtained. Considering requirements of ammonia photocatalysis process efficiency evaluation, calculated error is acceptable. It was also shown that sensor calibration parameters declared by the producer should be verified prior measurement and calibrated if necessary. Despite the low price, the MQ-137 sensor showed good overall performance during ammonia concentration measurements and with Arduino system can be used to monitor photocatalysis of ammonia.

5. ACKNOWLEDGMENTS

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LOW-COST CAPILLARY ELECTROPHORESIS INSTRUMENTATION FOR ASSESSMENT OF RAIN WATER IONIC COMPOSITION

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Abstract: The objective of this Short Term Scientific Mission was to test the suitability of capillary electrophoresis for determination of rain water chemical composition. The fully functional, open-hardware, low-cost instrument was assembled and tested. An original protocol for determination of the chemical content of rain water was established and validated in the pilot test. Capillary electrophoresis proved its highest suitability for the detection and quantification of ions in different samples, indicating substantial differences between clean and dirty snow waters. The hydrostatic sample injection method has been found very efficient and straightforward in manual and laboratory routines. An important deliverable of the Short Term Scientific Mission was a set of multimedia materials for the promotion of CE technique and especially low-cost CE instrumentation.

Keywords: capillary electrophoresis, rain water, ionic composition, COST Action CA16215

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1. INTRODUCTION

Capillary electrophoresis (CE) is an analytical chemistry method with a high potential for implementation in different real-life applications. It is capable of separation, quantification and characterization of polar and charged molecules in complex mixtures. The application field of CE includes both scientific research and industry (Seiman et al. 2009; Kobrin et al. 2014; Renzi et al. 2005; Lim et al. 2014; Gregu et al. 2016; Koenka et al. 2016). In general, the technology is well developed, including several commercial instruments available on the market, for example 7100 CE System from Agilent (2019) and Capel-205 from Lumex (2019). However, the constraint is the rather high cost of such instruments and the very limited possibility for these in-field applications, especially when compact size and portability are essential.

CE has been identified by COST Action CA16215 as one of the “model” techniques for promotion of the open hardware concept. For that reason, the Action supported a Short-Term Scientific Mission where feasibility of a CE prototype instrument was tested toward its implementation as part of the multisensory system for monitoring the environment in cities. The objective of the mission was to learn theoretical and practical knowledge necessary for properly implementing capillary electrophoresis in diverse application fields, with a special emphasis on the determination of rain water chemical composition. The paper presents some of the experiences gained, summarizing key technical aspects of the sensor and basic methodology for the proper CE implementation. It is therefore dedicated for those who are not familiar with CE, to demonstrate the advantages of the method and to convince them the usefulness of it.

2. MATERIAL AND METHODS

2.1. Low-cost and open-hardware capillary electrophoresis instrument

A prototype CE instrument used in this research was originally developed by the analytical chemistry research group at Tallinn University of Technology as the result of a multi-annual research programme. The instrument (**Figure 1**) is custom-made and contains low-cost components easily accessible on the market. Part of the sensor is custom 3D printed to minimize costs but also to allow easy adaptation of the system for specific requirements. The general schematic of the CE instrument and the configuration used in this research are presented in **Figure 1**. Dimensions of this prototype are 120 mm x 70 mm x 130 mm (width x length x height, respectively) and its mass (without batteries) is 550 g.

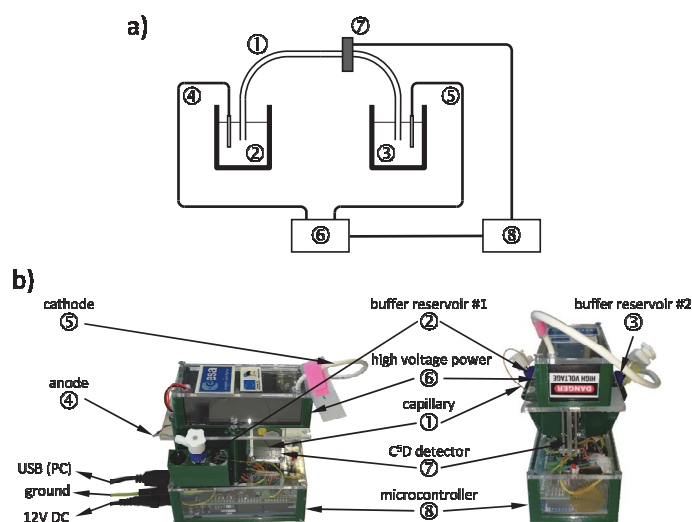


Figure 1. (a) Schematic of capillary electrophoresis instrument and (b) hardware configuration of the prototype used for measurement of the rain water chemical composition

Both ends of capillary ① are immersed during measurement in background electrolyte (BGE) reservoirs ② and ③ connected with electrodes to the high voltage power supply with negative polarity ⑥ (cathode) and ground ④ (anode). Separation by CE is based on two electro-kinetic phenomena: electrophoresis and electroosmosis. The electrically charged ions of the rain water migrate in the BGE under the presence of an electric field. Under steady-state conditions, the two opposite forces (electrical force and frictional force on a spherical ion) balance each other and a final electrophoretic velocity (v_{ep}) is reached, which remains constant at a constant electric field strength (**Equation 1**). As the velocity of different ions vary in various buffers and in function of the electrical current, it is possible to separate these ions from complex mixtures (Landers 2007).

$$v_{ep} = \frac{q * E}{6\pi r * \eta} = \mu_{ep} * E \quad (1)$$

where q is the charge, E is electric field strength, calculated as the voltage applied divided by the total length of the capillary, $6\pi r$ corresponds to the Stokes' radius of the particle, η is the viscosity of the surrounding medium. By simplifying the equation, μ_{ep} becomes the electrophoretic mobility of the charged solute in the separation medium considered.

The presence of separated ions can be detected with a Capacitively Coupled Contactless Conductivity Compensated Detector (C⁵D) that measures capacitance changes of the liquid passing through the capillary. It is an advanced variant of C⁴D detector invented by Da Silva & Do Lago (1998) and Zeeman et al. (1998). The whole system can be controlled with a real-time low-cost Arduino microcontroller ⑧, equipped with a custom electronic board interfacing all system components (Jaanus et al. 2016). The operation software controls the CE electrical voltage and C⁵D frequency (300 kHz – 2 MHz), acquires signals from the detector and detects current within the capillary. The result of measurement is an electropherogram corresponding to the time-resolved capacitance changes correlating to the quantity of ions separated from the mixture and passing by the detector.

2.2. System adjustment

Analyte standard solutions have been prepared from the previously dried (6 hours at 100°C) salts of NaCl (Honeywell), MgSO₄ (Fisher Chemical), Ba(OH)₂*8H₂O (LachNer), HCO₂Li*H₂O, CuCl₂*H₂O, C₂H₈N₂O₄*H₂O, CaCl₂ (Sigma-Aldrich). All solutions were prepared with ultra-pure water for ion chromatography (Sigma-Aldrich). Background electrolytes were prepared from the following chemicals: 2-(N-Morpholino)ethanesulfonic acid hydrate (MES), L-Histidine (His) (Fisher Chemical) and acetic acid (AA) (Honeywell). 1M NaOH solution and acetonitrile (ACN) (Sigma-Aldrich) were used for the capillary conditioning.

Polymicro (Optronics) fused silica capillary with 50 μm inner and 350 μm outer diameter, and total 40cm and effective 20 cm lengths, was prepared for the CE analysis. The capillary was cleaned before the first run following the procedure as described in the following chapter. Capillary conditioning was also performed between runs by flushing capillary with BGE.

The reference 100 μM salt mixture was used for optimization of the BGE choice. In this case, a clear separation of all peaks (without overlapping and with baseline resolution) as well as no saturated C⁵D detector readings were desired.

As a result of the CE instrument adjustments, the optimal configuration most suitable for assessment of rain water was:

- CE conditions: 8.6 kV, -16.0 μ A
- C⁵D detector: excitation frequency of 2.0 MHz
- Buffer: 6 M acetic acid
- Sample introduction: hydrodynamic, gravimetric, 10cm of diss-level and 15 s

2.3. Sample collection and preparation

Samples of the rain water were collected from the city of Tallinn (Estonia) on February 8, 2019. The fresh snow was gathered from the snowdrift interior (5 cm below the outer surface) and then melted in the laboratory at room conditions (20 °C). Similarly, a dirty sample of the snow deposited along the transportation road was collected as a not-pure water trial. Finally, the tap water was sampled directly from the waterpipe as a drinking water example. All the samples were stored in closed containers as shown in **Figure 2**.

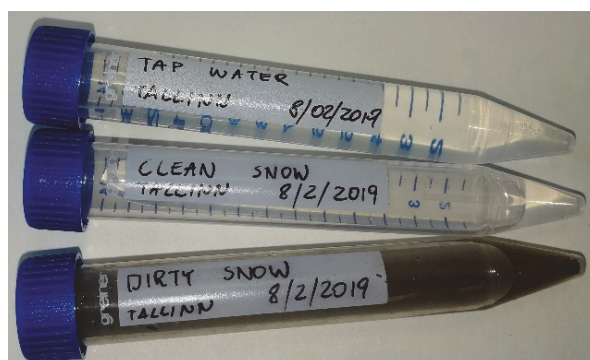


Figure 2. Water samples used for determination of chemical composition

All the water samples were filtered before measurement with a mechanical filter (type SF-NYL25-45) in order to remove any solid-state contaminations and particles. An ordinary syringe-based solution was identified as the most efficient filtering technique, performing well with water samples.

2.4. Measurement protocol

Such pre-processed (filtered) samples were ready for a direct measurement on the CE instrument. The sequence of actions related to the system preparation, together with installation of a brand-new capillary, include:

1. refresh instrument by dusting with ethanol or isopropanol
2. inspect electrodes (electrical connections, tightness, broken wires)
3. clean electrodes with ethanol or isopropanol
4. inspect detector cell (plug, hole for pass of capillary, cleanse)
5. prepare and/or inspect capillary:
 - a. cut to the length or cut-out broken edges
 - b. search for microcracks
 - c. inspect capillary edges
 - d. measure capillary total length
 - e. mark position of the detector (effective length)
6. clean capillary outside surface with ethanol or isopropanol
7. install capillary in the detector cell
8. clean and regenerate inside capillary by forcing flow of following liquids in a specific order and duration:
 - a. 1M sodium hydroxide (NaOH) for 10 minutes
 - b. 0.1M sodium hydroxide (NaOH) for 5 minutes
 - c. distillate water (H₂O) for 2 minutes
 - d. acetonitrile (ACN) for 5 minutes
 - e. distillate water (H₂O) for 2 minutes
 - f. (BGE), same as used in subsequent analysis, for 5 minutes
9. install capillary in the buffer reservoirs #1 and #2 and connect anode and cathode electrodes
10. apply high voltage and check the current (low value indicates improper capillary preparation, air bubble in the capillary, problem with electrical wiring or power supply)

The use of standard plastic syringes is a recommended solution to implement low-cost cleaning of capillary. It allows both application of vacuum or over-pressure on one side of the capillary, while perceiving the microflow of liquid that confirm openness of the tube. The air tightness can be assured by using a laboratory gum gasket and syringe needles as capillary guides when setting up the cleaning procedure.

The proper CE measurement requires a precise injection of the sample to capillary. There are several techniques usable, even if the simplest is a hydrostatic “syphon effect” approach. The sequence of actions to properly implement sample injection is presented in **Figure 3**. The sample injection initiates when a single end of the cleaned capillary filled with the buffer (a) is immersed in the investigated sample solution (b). It is important to assure that the initial level of the sample liquid is below the reference level of both buffer reservoirs. The proper sample injection is occurring when the sample liquid container rises over the reference level at an appropriately selected and consistent (over the series of measurements) height. Both the height and time of lifting affect the quantity if the sample liquid injected. It was found that for the needs of the rain water ionic composition diss-level of 10 cm and lifting time of 15 seconds were optimal conditions. The injection process ends when the sample container with capillary immersed is moved back below the reference level (d) and the capillary containing trace sample liquid is finally re-installed in the buffer reservoir (e) lifted to the reference level.

It has to be mentioned that no electrical field should be applied to the system when implementing hydrostatic samples injection in contrast to the electro-kinetic approach. In the second case, the sample liquid solution is mixed with the buffer in a separate container (f). The capillary is gently moved to that container, together with the electrode, assuring minimal diss-levelling and avoiding air bubble creation (g). The electrical current is applied between temporary and #2 reservoirs, promoting the certain quantity of the tested liquid injection (h). The procedure is finalized when capillary with the sample injected is re-installed in the buffer reservoir #1 (i) lifted to the reference level. The proper measurement and liquid separation starts afterward, and the measurement procedure is identical for both sample injection methodologies.

The quantity of the sample injected with the electro-kinetic solution depends primarily on analytes charge and electroosmotic flow, secondly on the sample concentration, capillary diameter, electrical voltage applied and time of injection. Those conditions illustrate the biggest limitation of the electro-kinetic injection resulting in “electrokinetic bias”. It can be used effectively and reliably with diverse background electrolytes that produce electroosmotic flow (EOF) with the same or higher than analytes velocity. Electrokinetic injection cannot be used reliably in the case of 6 M acetic acid, as the EOF velocity is lower than of the analyte. Although, electro-kinetic injection of rain water can be implemented with His and MES background electrolytes, where pH of the separation liquid varied from 4 to 8.

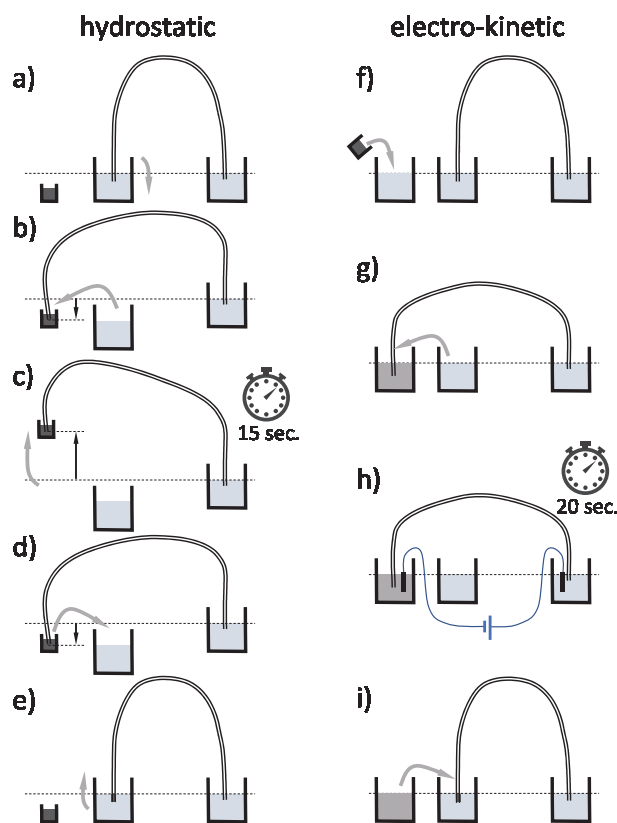


Figure 3. Procedure of the tested liquid injection to the capillary by means of hydrostatic “syphon effect” (left) and electro-kinetic (right) methods.

As for more, this first approach study shows good potential for the implementation of hydrostatic injection in the automatic system by changing from siphoning effect to pressurised or vacuum injection modes (Pham et al. 2014; Xu et al. 2009).

The liquid separation and acquisition of electropherograms starts immediately after sample injection, when the high voltage electricity passes from anode, through capillary, to cathode. At the same time, conductivity changes as measured by a C^5D sensor are recorded and stored for further post-processing. The duration of experiment depends on many factors, such as BGE type, electrical voltage, ions mobility, temperature, capillary length and diameter, among others.

2.5. Analysis of electropherograms

The electropherogram contains time resolved changes of the conductivity as recorded by C^5D when the electrical current flows from BGE reservoir #1 to #2. The deviation of conductivity values from the baseline is correlated with the kind and amount of separated ions. The simple approach for analysis of electropherograms is visual identification of peaks and manual marking of the baseline. The area and shape of the peak, along with the identified retention time, are then used for qualitative and quantitative analysis. Even if manual evaluation of experimental results is acceptable as a laboratory routine, it is not a suitable approach for automatic analysis of data. For that reason, an original software was developed in LabView 2018 (National Instruments Corp., USA) and implemented for detection and quantification of peaks. Wavelets were used here as an algorithm for the baseline detection, subtracted from the original electropherogram (Perrin et al. 2001). Peak detection was implemented as a derivative computation, and area under the peak was an integration of C^5D signal.

3. RESULTS

Typical electropherograms of the rain water acquired during the mission are presented in **Figure 4**. The reference liquid data are also provided to simplify data interpretation. A great advantage of using the reference solution is a possibility to introduce chemical markers, simplifying the peak identification and, especially, determination of the time when first separated ions reach the detector location. It is noticeable that a low-cost, open-hardware CE instrument was capable to accurately detect several ions, both in the reference liquid as well as in the characterized water samples.

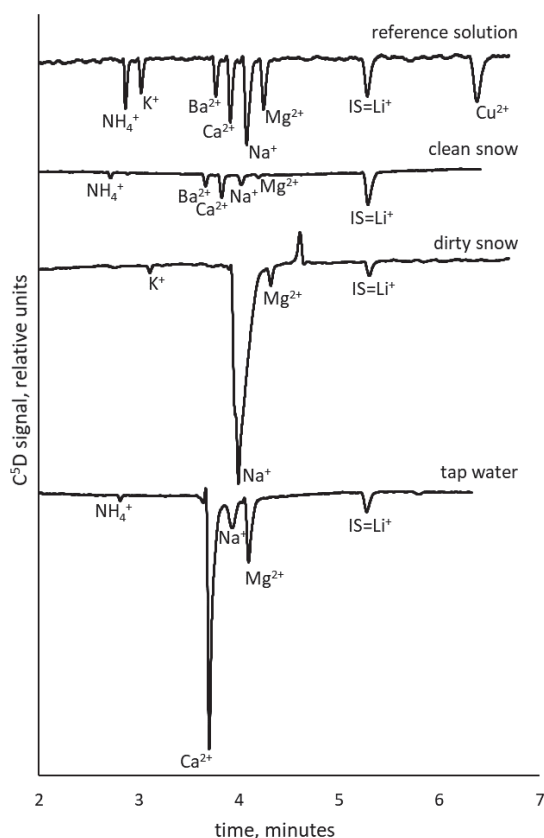


Figure 4. Capillary electropherograms of the investigated water samples: reference solution of model ions $100 \mu M$ (a), clean snow (b), dirty snow (c) and tap water (d). CE conditions: $6 M$ acetic acid, $2 MHz$, $8.5 V$. Capillary: $50/350 \mu m$, $20/40 cm$, BGE changed after each experiment. Injection is hydrodynamic: lifting above diss-level $10 cm$ and 15 seconds.

Table 1. Inorganic cations composition detected in the water samples.

ANALYTE	PURE SNOW (μM)	DIRTY SNOW (μM)	TAP WATER (μM)
NH_4^+	12	<i>n.d.</i>	13
K^+	<i>n.d.</i>	49	<i>n.d.</i>
Ba^{2+}	29	<i>n.d.</i>	<i>n.d.</i>
Ca^{2+}	36	<i>n.d.</i>	1031
Na^+	13	2546	128
Mg^{2+}	2	708	357
Cu^{2+}	<i>n.d.</i>	<i>n.d.</i>	<i>n.d.</i>

Relative standard deviation of the presented results did not exceed 20% of the mean value, *n.d.* – not detected

Results of quantitative analysis of electropherograms are summarized in **Table 1**, separately for clear, dirty snow and tap waters. Ammonium, sodium and magnesium cations were quantified in all water samples. On the contrary, copper was found only in the reference solution (**Figure 4**). The presence of barium ions in the clean samples and potassium in the dirty snow samples can be explained by residual contamination remaining as an effect of the student's fireworks festival taking place around the sample collection place (Steinhauser et al. 2008). The relatively high amount of sodium identified in the dirty snow was interpreted as an effect of street maintenance with sea salt used in winter to dissolve the snow from the roads of Tallinn. Similarly, a fairly high concentration of magnesium present in the dirty snow water sample was explained by seasonal road care activities.

It was found that the tap water composition differs from that declared by the Tallinna vesi - Tallinn's tap water supplier (Veepuhastusjaam 2017). Mean difference was noticed in ammonium ion, exceeding 20 times nominal concentration. The presence of a high amount of calcium was also observed. No potassium, barium or copper ion traces were detected. Sodium content correlated well with the data provided by Tallinna vesi. Even so, the sodium ion concentration in Tallinn's tap water was 67 times lower than the level recommended by the World Health Organization. It has to be stated however, that discrepancy between Tallinna Vesi and results obtained in this pilot test might be due to some unidentified problems in instrument calibration, as related to a very short time of the STSM visit.

4. CONCLUSION

Capillary electrophoresis proofed its highest suitability for detection and quantification of ions in different samples of water including that collected as snow. The fully functional, open-hardware, low-cost CE instrument was assembled and tested. An original protocol for determination of the chemical content of rain water was established and validated in the pilot test. Hydrostatic sample injection method has been found very efficient and straightforward in manual and laboratory routines.

The pilot research results indicated substantial differences between clean and dirty snow water. While detected ions concentration in the clean snow water varied from 2 μM (Mg^{2+}) to 36 μM (Ca^{2+}), the dirty snow contained higher ions concentration ranging from 49 μM (K^+) to 2.54 mM (Na^+). Tallinna tap water sodium ions concentration was 67 times lower than WHO limitations, with no barium nor copper ions identified.

An important deliverable of the Short-Term Scientific Mission was a set of multimedia materials for promotion of CE technique and, especially, low-cost CE instrumentation. It includes series of movies presenting:

- procedure of water samples collecting
- presentation of capillaries and preparation (inspection, cutting, measurement)
- cleaning of capillaries sequence, including handling and adopting of standard syringes for optimal and minimal cost operation
- installation of the capillary in the instrument and filling with the background electrolytes
- presentation of the CE instrument, its components and functionalities
- common trouble corrections (hints and tips)
- routine operation (measuring water samples) with CE
- sample injection procedure
- basic operation of the software

All movies are available on the COST Action CA16215 website (<http://portasap.eu/>).

5. ACKNOWLEDGMENTS

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A MULTI-PARAMETER MINIATURE PHOTOMETRIC ANALYSER FOR FULLY AUTOMATED ENVIRONMENTAL WATER MONITORING

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Abstract: Nowadays, the increasing demand for constant in-situ monitoring of clean water, wastewater and sea water requires the deployment of automated platforms capable of on-line autonomous sampling, extended unattended operation and of multi-analyte detection. The Micro Loop Injection Analyser (μ LIA) system hereby presented relies on integrated additively manufactured opto-fluidic components which allow for increased performance solutions to be implemented cost-effectively and in miniaturised footprints, targeting a wide spectrum of applications which ranges from in-situ environmental monitoring and field water testing to industrial process analysis. Preliminary tests of the μ LIA unit have shown good reproducibility and stability of the system and a good performance of its self-calibration routines.

Keywords: automated analyser, microfluidic, photometer, water analysis

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Professional paper

1. INTRODUCTION

The development of in-situ, capillary, fully automated environmental water monitoring networks is thwarted by the high cost and large footprints of currently available analysers and laboratory instrumentation (Mellander et al. 2015; Perks et al. 2015). The aim of the environmental water pollution monitoring is to gather a data through sampling, in situ, to make a rapid action at some hazardous events (Howden et al. 2010). Recent advances in flow injection analysis (Trojanowicz & Kołacińska 2016) have shown, during a time frame of approximately four decades, a rapid and dynamic evolution of these technologies and their respective detections methods, increasingly focused on nanotechnology and miniaturization (Mills & Fones 2012). Furthermore, a current trend has lowered the gap between research and commercial instrumentation: increasingly often, instruments are no longer purchased, but self-designed and self-fabricated ad hoc, directly in the lab. This empowers scientists with a high degree of customisation which well suits today's increasingly specific experiments and applications (Heinz et al. 2012). The hereby presented system relies on integrated additively manufactured opto-fluidic components which allow for increased performance solutions to be implemented cost-effectively and in miniaturised footprints, targeting a wide spectrum of applications which ranges from in-situ environmental monitoring and field water testing to industrial process analysis.

2. SYSTEM DESCRIPTION

The Micro Loop Injection Analyser (μ LIA) hereby presented is a versatile stand-alone microprocessor (ARM CORTEX M4F) based system which integrates a modular design and is capable of multi-parameter (up to 4 simultaneously) colorimetric and fluorometric detection in a compact footprint (16x11x10 cm), with small reaction volumes (typ. 400 to 1200 μ l), low reagent consumption (5 to 200 μ l per analysis) and extended unattended operation (Figure 1). It also features auto-dilution, calibration and self-diagnosis routines.

The operation principle of colorimetric analysis is based on the Beer-Lambert optical law, which relates the attenuation of light to the properties of the material through which the light is travelling. Suitable reagents will target specific analytes and react with them to produce coloured compounds. By relying on a monochromatic beam - with a wavelength suitable for the reagent's absorbance spectrum - the light transmission through the sample - and thus the colour of the solution - can be assessed before and after the addition of the reagent. In particular, the Beer-Lambert law establishes a linear relationship between the absorbance of the medium and the concentration of the light-absorbing species in the medium. By comparing these measurements against factory calibration curves, the concentration of the target analyte can be determined.

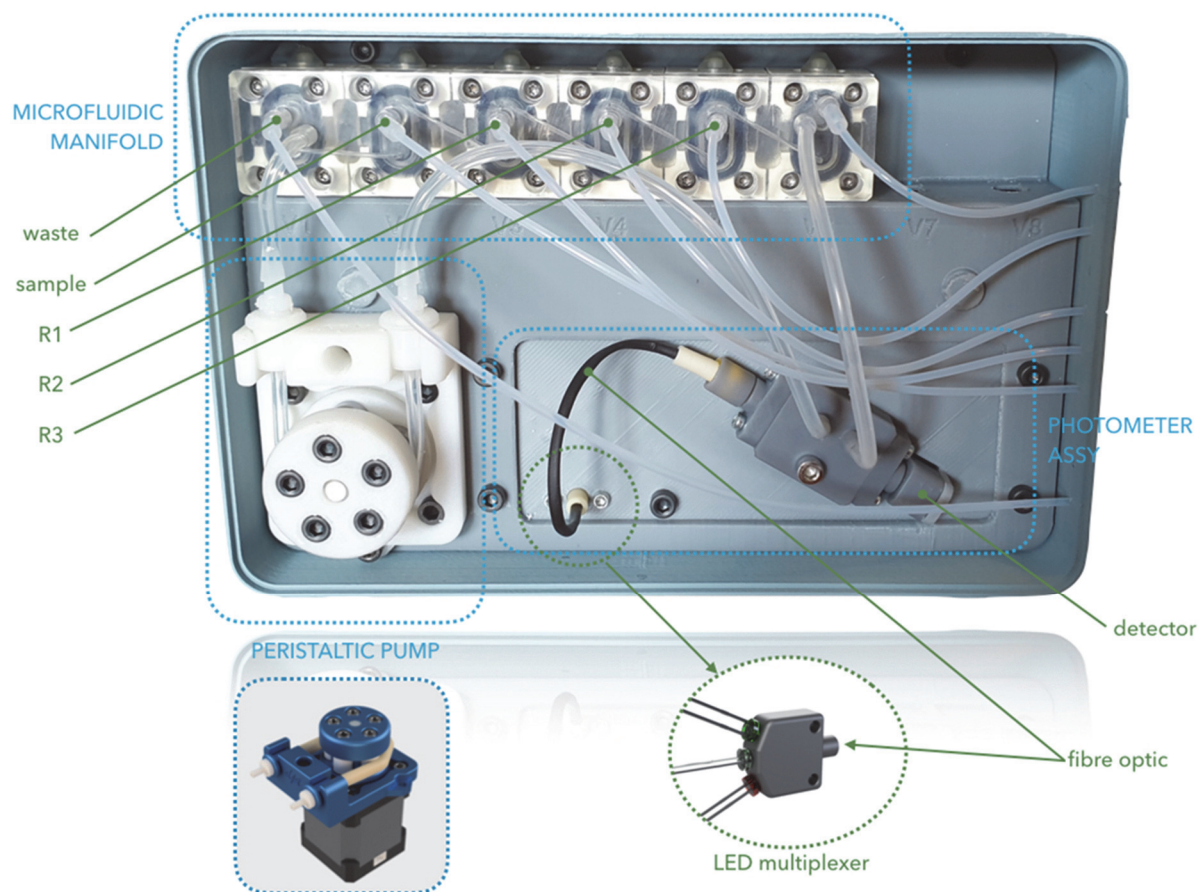


Figure 1. General layout of the instrument Micro Loop Injection Analyser (μ LIA)

The system design revolves around an integrated, additively manufactured fluidic block, which handles the injection of sample(s) and reagents into the fluidic circuit. It allows the continuous circulation and monitoring of the reaction mixture through the detector(s). The combination of a versatile analysis setup with the modular and multi-wavelength optical detection system allows a wide range of methods to be implemented with minimal effort, such as phosphate (ascorbic acid/molybdate), nutrients, chlorine (DPD), silica, trace metals and more. Standard solutions are programmatically drawn into the analyser at fixed time intervals to perform the automated calibration routines. Similarly, cleaning buffers are regularly used to wash the fluidics and prevent solid precipitates and/or biofilms from fouling the channels. The mechanical construction allows a complete separation of the electronics from the fluidic sections, for greater reliability and safety in case of leakages.

3. MANIFOLD AND FABRICATION

The manifold is fabricated by stereolithography in methacrylate photosensitive transparent resin (Formlabs Clear) using a Formlabs Form 2 printer. It houses 6 solenoid direct-actuation isolation rocker membrane valves (ASCO 260) used for fluid selection, which can be easily replaced in case of obsolescence and/or malfunctioning. The monolithic design integrates embedded custom designed valve seats and fluidic interfaces with a minimised total volume of 400 to 1200 μ l and optimised flow paths which enhance washing and mixing. The wetted materials are methacrylate resin in the manifold body, while the valve membranes are either in EPDM (ethylene-propylene diene monomer, ASCO, **Figure 2**), FKM (fluoroelastomer) or FFKM (perfluoroelastomer). After the printing and post-curing steps, the resin block surface was hydrolysed in order to ease de-bubbling and achieve a small degree of surface passivation and hydrophilicity.

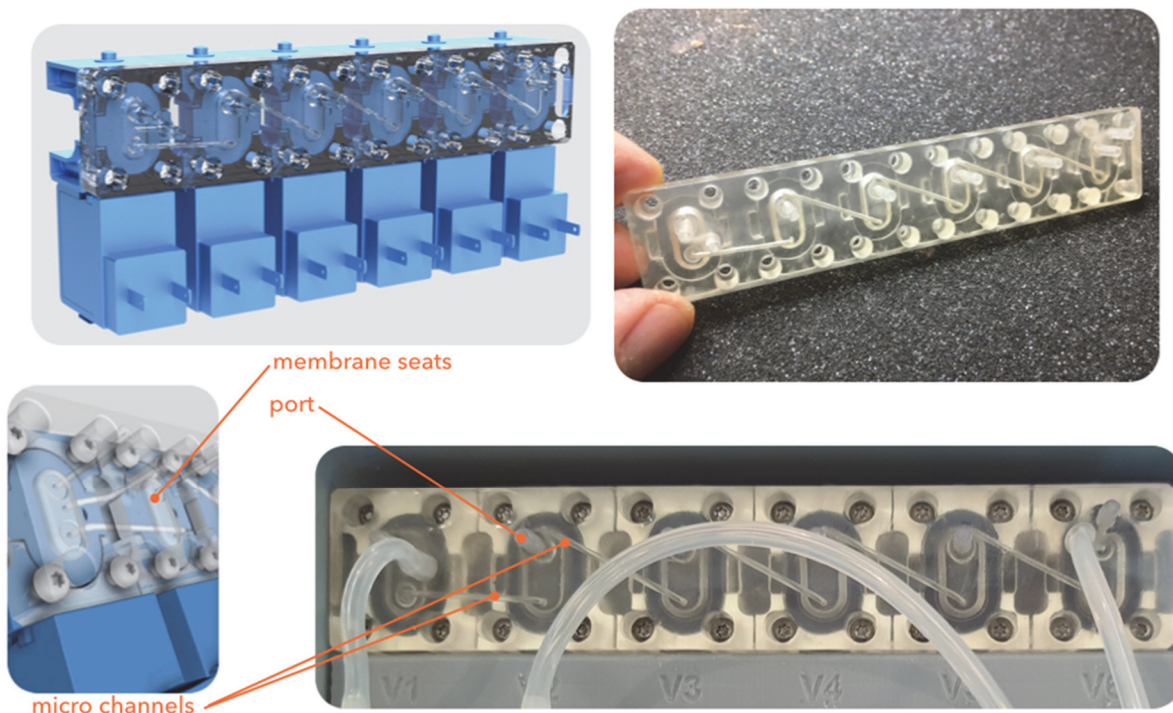


Figure 2. Fluidic block. Top left: CAD model rendering; top right: the block right after printing (supports removed); bottom: channels and valve seat detail. The fluidic channels connecting valve chambers and the inlet/outlet nipples for tubing interconnection are visible.

4. FLOW-CELL AND OPTICAL DESIGN

At the heart of any photometric system lies the design of the detection module. The one currently presented is based on a colorimetric transmission measurement mode, realized with a custom SLA printed micro volume flow-cell. Some of the most common challenges in photometric systems design are both of a geometrical (optical alignment, source aperture control, intrinsic stray light), environmental (background stray light), electronic (non-linearity and ageing of the optoelectronic components) and chemical nature (micro-bubbles and fouling).

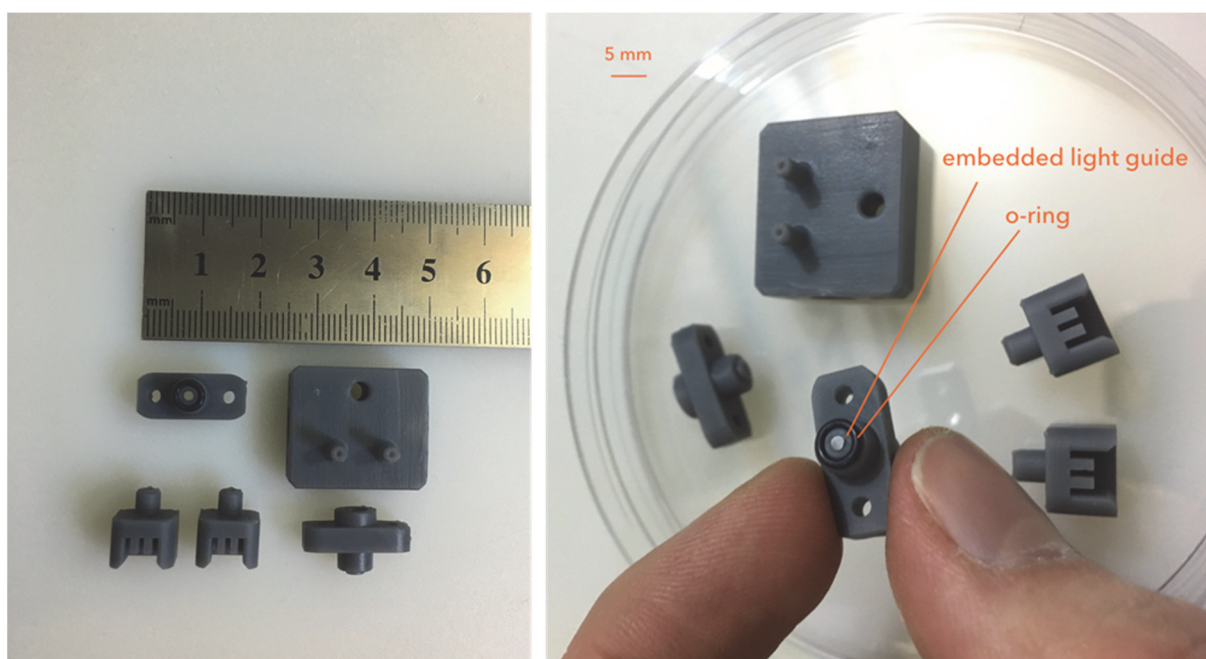


Figure 3. Flow cell components. Left: components right out of the printer (cell caps, cell body and detector holders). Right: ELG detail.

The flow-through transmission cell was realized by SLA fabrication in tinted methacrylate resin (Formlabs Grey Standard). The monolithic body houses the 15 mm optical path, the fluidic ports, for a total volume inferior to 35 μ l (included connections). Path-lengths, detectors and sources are customizable and easily interchangeable, thanks to push-in optical connections (**Figure 3**). The optical windows feature an embedded light guide (ELG), a light-pipe integrated in the finished assembly, yielding a seamless joint at the fluid interface. The resulting finished components were pressurised and tested up to 3 bar and exhibited no sign of leakage. The ELG represents the core of cost savings and of increased performance, as it suppresses the need to purchase expensive off-the-shelf optical glass or fused quartz flow-cells or optical windows. Additionally, the ELG guarantees a precise and reproducible beam alignment, as the caps are registered directly into their respective recesses on the cell body. Any misalignment in the coupling of the sources and detector is cancelled, as light is homogenized and aligned right before and after passing through the optical path (**Figure 4**).

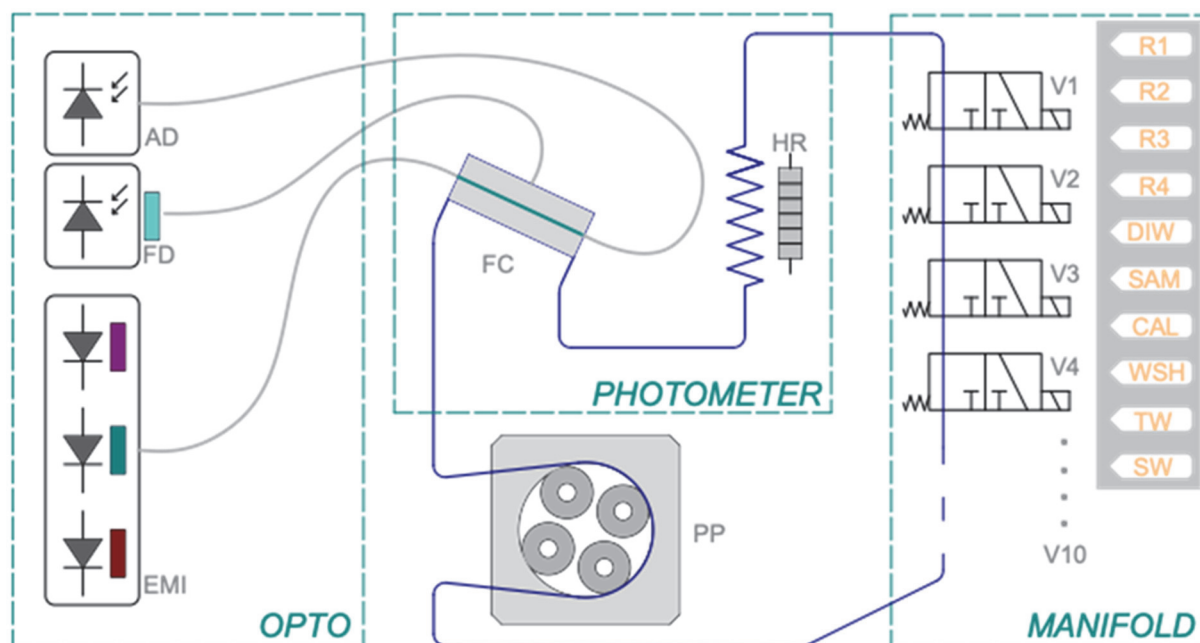


Figure 4. Opto-fluidic schematic. HR: heating resistor; FC: flow-cell; PP: peristaltic pump; V1- V10: solenoid valves 1 to 10; EMI: LED emitter section with BP filters; FD: fluorimetric mode detector; AD: absorbance mode detector; R1-R4: reagents 1 to 4; DIW: de-ionised water; SAM: sample port; CAL: calibration buffer; WSH: cleaning solution; TW-SW: toxic waste and safe waste discharge ports.

The emitter side features three LED sources with optional 10 nm FWHM bandpass filters (Knight Optical), which are multiplexed using a 3-to-1 custom multimode fibre optic combiner and then fibre-optic coupled to the cell. The detector is a light-to-frequency converter (TAOS-AMS) with spectral sensitivity ranging from 300 to 1100 nm, peaking at around 690 nm, which shows excellent linearity and great thermal stability.

Electronics and control

LEDs generally exhibit significant intensity drifts and minor wavelength shifts associated with environmental changes in temperature and/or self-heating, resulting in one of the most common causes of instability in photometric detection. Each LED emitter is current regulated using the microprocessor on-board 12-bit DAC and a current pump, in steps of 0.1 mA from 0 to 25 mA (**Figure 5**). This allows the microprocessor to automatically adjust sources intensity during each analysis cycle, independently of sample turbidity and temperature, thus eliminating any non-linearity of the electronics and specifically of the detector, which is always kept in the same and reproducible operating point. Continuous dark correction is performed during each measurement many times per second (20 to 50 times per second), allowing the system to operate in noisy and changing environments, without the need for light shields. The measurements are then validated by detecting light instability between mixing steps, which is commonly associated with the presence of gas bubbles in the optical path. The development of the reaction is monitored continuously, and the measurement is performed once an established absorbance plateau is detected. This setup also allows for fixed time, kinetics, endpoint, and differential techniques to be performed. The resulting CV for 10 consecutive optical readings was generally found to be in the order of 0.1 % for sample blank, and slightly higher after color development.

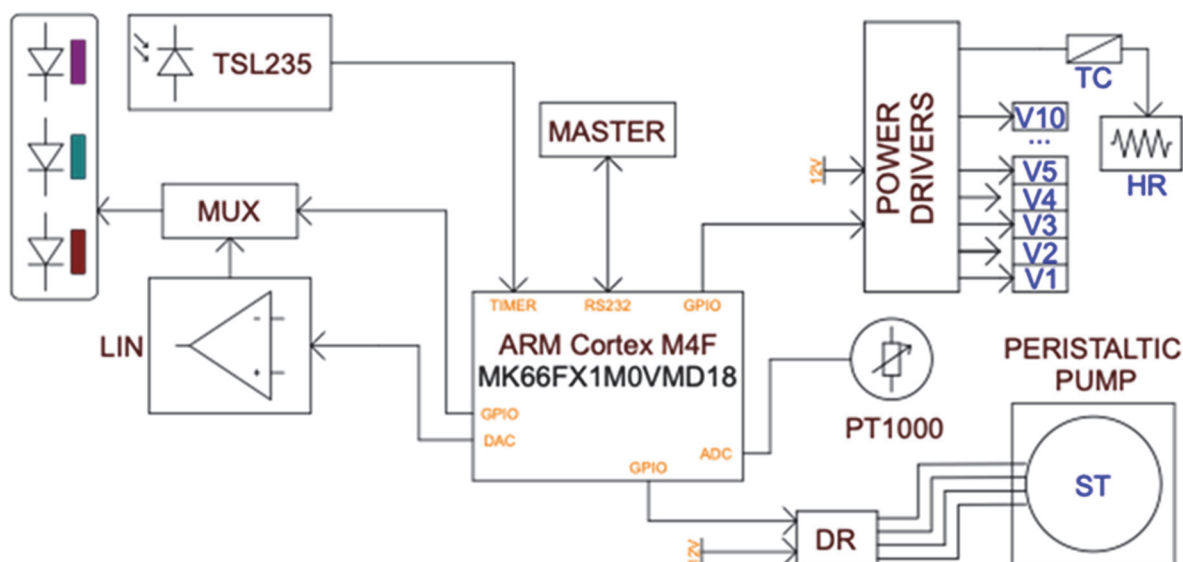


Figure 5. Electronics block diagram

5. CALIBRATION

The one or two-point auto-calibration is performed automatically by injecting into the loop one or more standard solutions. A sample calibration curve, instead, is shown in **Figure 6**, composed of 6 calibration points of 7 repetitions each, and generated autonomously by the analyser. It is relative to the vanadate/ascorbic acid method for phosphate measurement according to APHA Standard Method 4500-P-E: ammonium molybdate and potassium antimonyl tartrate (R1) will produce, in presence of orthophosphate and an acidic medium, phosphomolybdic acid, which, by means of ascorbic acid (R2), is in turn reduced to molybdenum blue, which is finally read at 880 nm.

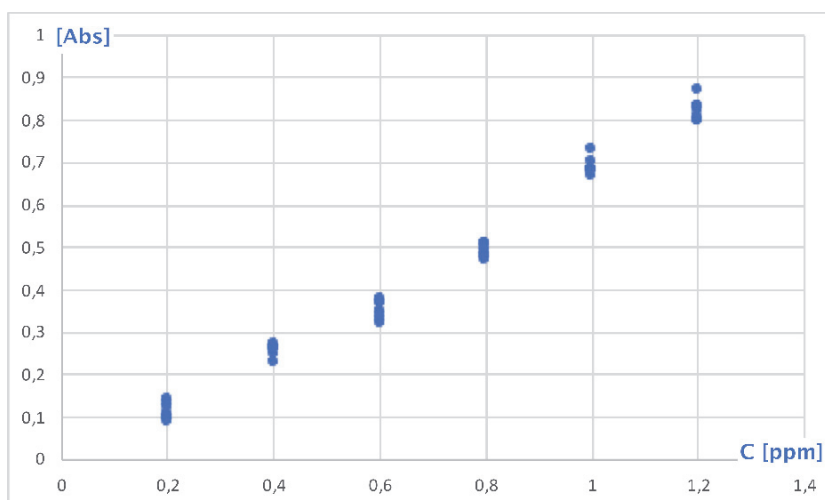


Figure 6. Phosphate APHA 4500-P E calibration at 6 different concentrations.

4. CONCLUSION

This short analysis of the uLIA analyser will hopefully serve as a proof of concept with regards to how additive manufacturing can ease and enhance the design of fluidic systems. By balancing the selection between commercial and custom-made components, the cost and performance of these systems can be tailored to a diverse range of environmental monitoring needs. Also, the progressive tendency towards the integration of diverse technologies and sub-systems into single monolithic and multi-functional components will further reduce both the cost and the physical footprint of these platforms, while increasing their reliability. Again, the use of additive manufacturing proves itself as a smart tool for easing and combining such a specialised integration level with a highly modular and scalable design.

5. ACKNOWLEDGEMENTS

More information about the uLIA analyser is available at dptechnology.jimdo.com.

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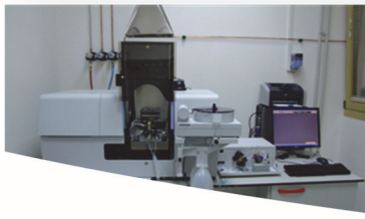
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LABORATORIJ ZA GEOKEMIJU OKOLIŠA

- osnovan je 2006. godine sa znanstvenom, stručnom i obrazovnom svrhom
- opremljen instrumentima i pratećom opremom za prikupljanje uzoraka tala, sedimenata, prirodnih i otpadnih voda
- vrši terenske i laboratorijske analize prikupljenih uzoraka
- obavlja usluge agrokemijskih analiza tla za poljoprivrednike na temelju kojih se daje preporuka za gnojidbu

Zavod za hidrotehniku



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LABORATORIJ ZA GEOKEMIJU OKOLIŠA

Laboratorij za geokemiju okoliša osnovan je u sklopu Zavoda za hidrotehniku Geotehničkog fakulteta u Varaždinu. Laboratorij sudjeluje u izvođenju praktične nastave iz kolegija preddiplomskog i diplomskog studija te Zdrženog međunarodnog doktorskog studija kao i u znanstvenim te stručnim projektima. Na taj način ispunjava svoju obrazovnu, znanstvenu i stručnu svrhu. Smješten je na 100 m² prostora i opremljen modernom opremom za provedbu geokemijskih terenskih i laboratorijskih ispitivanja, što uključuje prikupljanje uzoraka tla, sedimenata i vode. U laboratoriju se obavljaju i usluge agrokemijskih analiza tla.

Pokazatelji koje mjerimo u uzorcima voda, eluata tala i sedimenata:

- ~ atomskom apsorpcijskom spektrometrijom: Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Li, Mg, Mn, Mo, Na, Ni, Pb, Se, Si, Sr, Ti, V, Zn
- ~ amonijak, nitriti, nitrati, ukupni dušik
- ~ bromidi, fenoli, fluorida, fosfati, jodidi, kloridi
- ~ silikati, sulfidi, sulfati, sulfiti
- ~ suspendirana tvar, mutnoća, KPK
- ~ alkalitet, ukupna tvrdoća, karbonatna tvrdoća, nekarbonatna tvrdoća, kalcijeva tvrdoća, magnezijeva tvrdoća
- ~ slobodni CO₂, koncentracija otopljenog kisika i zasićenost kisikom
- ~ pH, električna vodljivost, ukupna otopljena tvar - TDS
- ~ trasiranje podzemnih tokova (koncentracija natrijevog fluoresceina)
- ~ ukupni organski ugljik i ukupni dušik - TOC/DOC/TN
- ~ razaranje tla zlatotopkom
- ~ ekstrakcija izmjenjivih kationa iz tla amonijevim acetatom i kalijevim kloridom



Ispitivanje fizikalnih i kemijskih svojstava prirodnih i otpadnih voda.



Provođenje agrokemijskih analiza tla u svrhu modernizacije poljoprivredne proizvodnje, racionalizacije gnojidbe, povećanja prinosa i zaštite prirodnih resursa.



Ispitivanje sastava eluata otpada.



Određivanje pH, pKCl, ukupnog CaCO₃, NO₃⁻, NO₂⁻, NH₄⁺, fosfora i kalija, humusa, teških metala i drugih kemijskih svojstava tla.

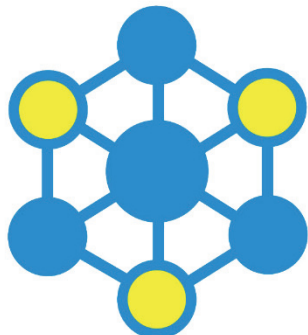
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U svom proizvodnom programu ima proizvodnju kamenih agregata, betona, stočne krede i materijala za kalcizaciju. Sjedište s proizvodnim pogonima je u općini Ljubešćica, u Varaždinskoj županiji, geografski smješteno na sjevernim obroncima Kalničkog gorja.

Dugogodišnjom tradicijom u proizvodnji agregata proizvodimo najkvalitetnije agregate za autoceste, hidroelektrane, betone i betonsku galanteriju. Djelatnost poduzeća se temelji na eksploataciji mineralnih sirovina dijabaza i vapnenca tradicijom duljom od četrdeset godina na lokalitetima Hruškovec, Špica i Jazvine.

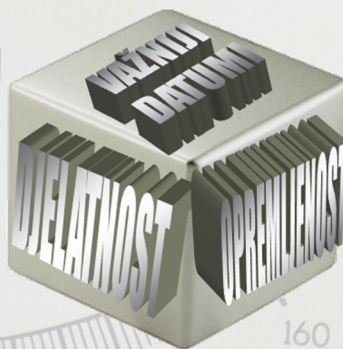
Tradicija rudarenja poznata tijekom ovog stoljeća prerasla je u eksploataciju i preradu kamena. Visoko kvalitetna tehnologija prerade, pomno praćena školovanim kadrovima, daje tržištu proizvode ugrađene u vrijedne graditeljske objekte: autoceste, mostove, aerodrome...



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- Godine 2006. potpuno obnovljen, moderniziran i proširen
- Član udruge Hrvatski laboratoriji CROLAB
- Akreditiran od HAA prema normi HRN EN ISO/IEC 17025

Sudjeluje u

- Znanstvenim projektima čiji su nositelji djelatnici Geotehničkog fakulteta
- Stručnim i gospodarskim projektima iz područja geoinženjerstva, inženjerstva okoliša i graditeljstva



- Opremljen za provođenje svih standardnih geomehaničkih ispitivanja tla prema zahtjevima nacionalnih i svjetskih normi
- Raspolože s modernom opremom za znanstvena istraživanja iz područja mehanike tla
- Razvija vlastite uređaje za specijalna ispitivanja

Opća fizikalna svojstva tla

- vlažnost
- gustoća ; vlažna, suha, najmanja, najveća, čvrstih čestica tla
- relativna zbijenost nekoherentnog tla
- poroznost
- zasićenost vodom

2. Klasifikacijski testovi

- Atterberg-ove granice koherentnog tla: tečenja, plastičnosti, stezanja
- granulometrijski sastav: metoda sijanja, metoda areometrijanja

3. Čvrstoća tla

- aksijalna čvrstoća sa slobodnim bočnim širenjem
- posmična čvrstoća; izravni posmik: UU, CD, reversni, po metodi Krey-Tiedemann
- troosni posmik: UU, CIU, CID
- nedrenirana čvrstoća: krilnom sondom, konusnim penetrometrom

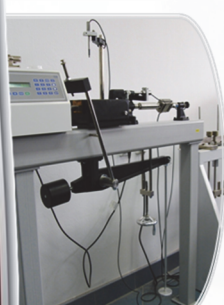
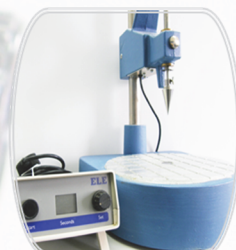
4. Deformabilnost tla

ispitivanja u:

- standardnom edometarskom uređaju
- hidrauličkom edometarskom uređaju s mjerenjem pornog tlaka
- hidrauličkom edometarskom uređaju s ćelijom promjera 50 cm
- troosnom uređaju s dirigiranim odnosima vertikalnih i horizontalnih deformacija ili opterećenja

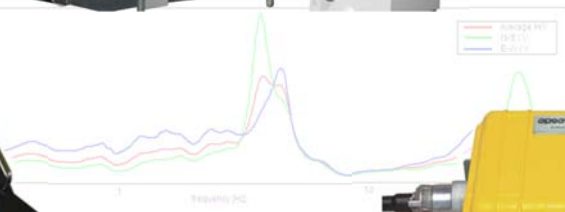
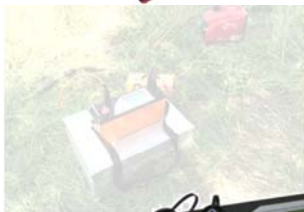
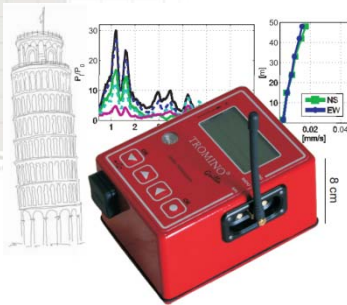
5. Posebna svojstva tla

- koeficijent hidrauličke vodljivosti (vodopropusnost) u ćelijama tipa FH i CH
- optimalna vlažnost prema standardnoj ili modificiranoj energiji zbijanja
- sadržaj organskih i gorivih tvari
- sadržaj kalcij-karbonata
- kut trenja suhog, rahlo nasipanog tla
- pH vrijednost





ZAVOD ZA GEOTEHNIKU GEOFIZIČKO-GEOTEHNIČKI ISTRAŽNI RADovi



GEOFIZIČKI ISTRAŽNI RADovi

- Geoelektrična istraživanja (sondiranje, profiliranje, tomografija)
- Seizmička refrakcija (P i S valovi)
- Višekanalna analiza površinskih valova (MASW)
- Seizmička karotaža
- Seizmički efekti miniranja
- Mikrotremor
- Georadar



GEOTEHNIČKI ISTRAŽNI RADovi

- Istražno bušenje u svim vrstama tla i stijena
- Statički penetracijski test (CPT, CPTU, SCPT)
- Standardni penetracijski test (SPT)
- Bušenje, ugradnja i pokusno crpljenje zdenaca i piezometara
- Izrada geotehničke dokumentacije (izvješća, elaborati, projekti)
- Geotehnički nadzor i savjetovanje

**BESTSDI Project Objectives**

The wider objectives of the BESTSDI project is to improve the quality of higher education in Geographical Science and Technology field, SDI and geodesy, enhance its relevance for the labour market and society and to improve the level of competences and skills in HEI's by developing new and innovative education programmes within the field of SDI. These wider objectives are fully compliant with the priorities of the Capacity Building projects within the Erasmus+ program. The specific project objectives are to develop, test and adapt new curricula, courses, learning

BESTSDI Expected Results

To develop appropriate curricula, courses and their content for both target groups (SDI providers and SDI users) of academic institutions. This includes the development of:

- SDI compulsory course for undergraduate study programs in geodesy
- SDI modules for graduate study programs in geodesy and geoinformatics
- SDI user course components for undergraduate study programs of partner faculties
- SDI elective courses for graduate study program of partner faculties (SDI users)
- Development of sustainable training courses (life-long education) of broad scope of professionals.

Additional benefits:

- New level of communication and cooperation among the partner universities with the emphasis on SDI but expanding it on institutional and project cooperation.
- Exchange of students and staff will be fostered through the project activities and information about activities conducted by the partners communicated among the partner universities.

BESTSDI Partners

Coordinator: **University of Zagreb, Faculty of Geodesy, Croatia**

Partner: **University of Zagreb, Faculty of Geotechnical Engineering, Croatia**

Other Partners:

Katholieke Universiteit Leuven (Catholic University of Leuven), Belgium

Sveučilište u Splitu (University of Split), Croatia

Univerzitet "Sv. Kiril i Metodij" Skopje (Ss. Cyril and Methodius University in Skopje), Macedonia

Hochschule Bochum (Bochum University of Applied Sciences), Germany

Universiteti Politekniki i Tiranës (Polytechnic University of Tirana), Albania

Universiteti Bujqësor i Tiranës (Agricultural University of Tirana), Albania

Univerzitet u Banjoj Luci (University of Banja Luka), Bosnia and Herzegovina

Sveučilište u Mostaru (University of Mostar), Bosnia and Herzegovina

Univerzitet u Sarajevu (University of Sarajevo), Bosnia and Herzegovina

Javna Ustanova Univerzitet u Tuzli Universitas Studiorum Tuzla (University of Tuzla), Bosnia and Herzegovina

Universiteti Nderkombetar per Biznes dhe Tehnologji UBT (University for Business and Technology), Kosovo

Javna ustanova Univerzitet Crne Gore Podgorica (University of Montenegro), Montenegro

Unvierzitet u Beogradu (University of Belgrade), Serbia

Univerzitet u Novom Sadu (University of Novi Sad), Serbia

Universiteti "Ukshin Hoti" ne Prizren (University of "Ukshin Hoti" in Prizren), Kosovo

Associated Partners:

Republic Administration for Geodetic and Property Affairs of Republika Srpska, BiH

Federal Administration for Geodetic and Property Affairs of Federation of Bosnia and Herzegovina, BiH

Agency for Real Estate Cadastre, Macedonia

Subcontractors:

Lantmäteriet (Swedish National Mapping and Cadastre Authority), Sweden

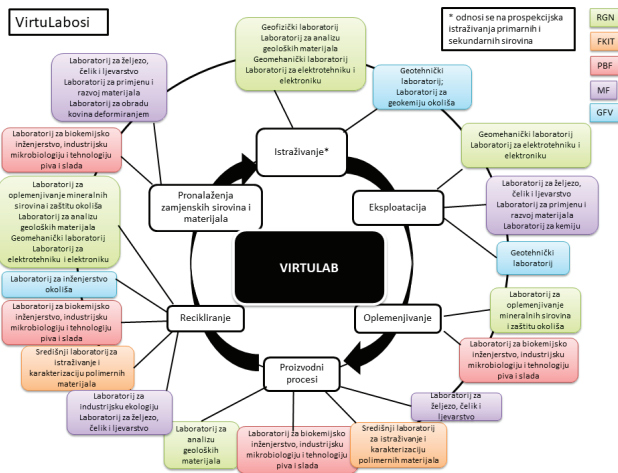
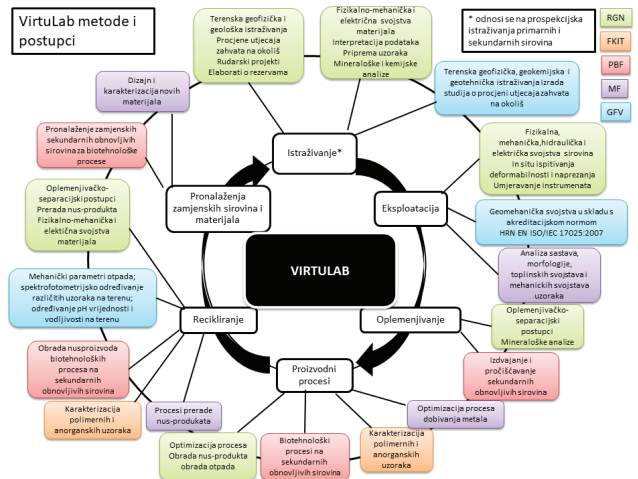
Novogit AB, Sweden

PROJEKT VIRTULAB - INTEGRIRANI LABORATORIJ ZA PRIMARNE I SEKUNDARNE SIROVINE

A great step forward was made in the preparation for the realization of the VIRTULAB project, whose goal is to strengthen the scientific and exploratory capacity of fifteen labs of the five Faculties at the University of Zagreb. The Ministry of Science, Education and Sports recognized this project as strategic for the Republic of Croatia and thus it was placed on the Ministry's indicative list. The intention is to begin the setting up of the University exploratory center for primary and secondary raw materials in the next period.

Projektom će se ulagati u opremanje laboratorija na pet fakulteta Sveučilišta u Zagrebu (Rudarsko-geološko-naftni fakultet - RGN, Fakultet kemijskog inženjerstva i tehnologije - FKIT, Metalurški fakultet - MF, Prehrambeno-biotehnoški fakultet - PBF i Geotehnički fakultet - GFV), s ciljem jačanja njihovih znanstveno-istraživačkih kapaciteta i uspostave virtualnog istraživačkog centra za primarne i sekundarne sirovine koji će omogućiti višu kvalitetu izvođenja nastave, ojačat će znanstvenoistraživački rad na fakultetima, omogućit će im ravnopravno sudjelovanje u KIC inicijativi, a istovremeno će stvoriti prostor za komercijalizaciju rezultata znanstvenih istraživanja i praktičnu primjenu inovacija u gospodarstvu. Projektni partneri nastavit će rad s korisnicima usluga u gospodarstvu, a istovremeno će nastojati proširiti postojeću suradnju.

Grafički prikaz VIRTULAB-a nakon integracije pet fakulteta – metode i postupci



Grafički prikaz VIRTULAB-a nakon integracije pet fakulteta – VirtuLabosi

KIC za mineralne sirovine (eng. raw materials) jest dugoročno integrirano partnerstvo više od 100 europskih organizacija iz znanstvenog i gospodarskog sektora koje s ciljem implementacije rezultata klasičnih R&D projekata prema tržištu. „Raw materials“, odnosno mineralne sirovine su ne-energetske sirovine: metali, nemetali, kamen, drvo, biomasa i sekundarne sirovine (eng. reused).

Sveučilište u Zagrebu se priključilo konzorciju koji čine Austrija, Belgija, Danska, Estonija, Finska, Francuska, Grčka, Irska, Italija, Mađarska, Nizozemska, Njemačka, Poljska, Portugal, Rumunjska, Slovačka, Slovenija, Španjolska, Švedska i Velika Britanija. Glavni koordinatorski za područje istočne i jugoistočne Europe je Sveučilište u Leobenu (Montanuniversität Leoben), a koordinatorski za Sveučilište Zagrebu je Rudarsko-geološko-naftni fakultet.

Koordinator projekta na Geotehničkom fakultetu: izv. prof. dr. sc. Igor PETROVIĆ

Suradnici na projektu s Geotehničkog fakulteta:

- Izv.prof.dr.sc. Nikola SAKAĆ
- Izv.prof.dr.sc. Anita PTIČEK SIROČIĆ
- Doc.dr.sc. Ivana GRČIĆ
- Dr.sc. Vitomir PREMUR
- Damir ŠTUHEC, dipl.ing.geot.
- Nikola KANIŠKI, mag.ing.amb.
- Nikola HRNČIĆ, mag.ing.geoinž.

Trajanje projekta: 18 mjeseci

Ukupna vrijednost projekta: 14.186.222,23 kuna

Ukupni prihvatljivi troškovi: 12.300.603,45 kuna

Iznos financiranja za Geotehnički fakultet: 1.035.042,83 kuna



SVEUČILIŠTE U ZAGREBU
GEOTEHNIČKI FAKULTET



RawMaterials
Connecting matters

USPOSTAVNI ISTRAŽIVAČKI PROJEKT

ISPITIVANJE I MODELIRANJE MEHANIČKOG PONAŠANJA BIOOSUŠENOG OTPADA KAO PREDUVJET ENERGETSKE OPORABE – **WtE**

TESTING AND MODELLING OF MECHANICAL BEHAVIOUR OF BIODRYED WASTE AS A WASTE-TO-ENERGY PREREQUISITE

Projekt je primarno orijentiran na detaljno eksperimentalno ispitivanje i numeričko modeliranje mehaničkog ponašanja bioosušenog otpada.

Biosušenje je varijacija aerobne razgradnje koja se primjenjuje za parcijalnu stabilizaciju komunalnog otpada.

Nakon biosušenja, otpad se upućuje u daljnju mehaničku rafinaciju gdje se izdvaja organski bogata sitnozrnata frakcija koja je pogodna za odlaganje na bioreaktorsko odlagalište.

Jednom odložena, ova se frakcija ponovno podvrgava postupku vlaženja, s ciljem intenziviranja procesa razgradnje i proizvodnje bioplina.

Proizvedeni bioplin potom se može iskoristiti za energetske oporabu kroz proizvodnju toplinske i/ili električne energije.

Trenutno u Republici Hrvatskoj postoje dva funkcionalna MBO postrojenja s tehnološkim procesom obrade čiji je izlazni proizvod pogodan za odlaganje na bioreaktorsko odlagalište.

Pravilnik o načinima i uvjetima odlaganja otpada, kategorijama i uvjetima rada za odlagališta otpada (NN 114/15) prepoznaje bioreaktorsko odlagalište kao odlagalište otpada za neopasni otpad - podkategorija 1.

Unatoč tome što su u RH bioreaktorska odlagališta dozvoljena i već postoje postrojenja čiji je izlazni produkt pogodan za energetske oporabu, u RH trenutno ne postoji niti jedno bioreaktorsko odlagalište.

Voditelj projekta: izv. prof. dr. sc. Igor PETROVIĆ, Geotehnički fakultet

Suradnici:

- Erich BAUER, Dipl.-Ing. Dr.techn., habil., ao.Univ.-Prof., Institute of Applied Mechanics, Graz University of Technology, Austria
- Doc.dr.sc. Ivan HIP, Geotehnički fakultet
- Doc.dr.sc. Anita PTIČEK SIROČIĆ, Geotehnički fakultet
- Doc.dr.sc. Boris KAVUR, Geotehnički fakultet
- Dr.sc. Marko PETRIC, Geotehnički fakultet
- Linke LI, Graz University of Technology, Austria

Doktorandi zaposleni na projektu:

- Nikola Kaniški, mag.ing.amb., Geotehnički fakultet
- Nikola Hrnčić, mag.ing.geoing., Geotehnički fakultet

Visit us on web page: http://wte.gfv.hr/index_en.html



Trajanje projekta: 01.01.2018. – 31.12.2022.

Iznos financiranja: 920.000,00 kuna

Web stranica projekta: wte.gfv.hr

Kao jedan od razloga ovakvoj situaciji svakako se može istaknuti nedovoljan broj eksperimentalnih podataka o geotehničkim parametrima sitnozrnate frakcije bioosušenog MBO otpada.

Drugi razlog je nedostatak prikladnog numeričkog modela za ovu vrstu otpada.

Usljed ovih nedostataka projektiranje bioreaktorskog odlagališta nije moguće.

Stoga je glavni cilj novog istraživanja, na temelju utvrđenih eksperimentalnih podataka, razviti prikladan konstitutivni model za opisivanje 3-D stanja naprežanja i deformacija sitnozrnate frakcije bioosušenog otpada.

Razvijeni model tada bi se mogao koristiti za potrebe projektiranja bioreaktorskih odlagališta ne samo u RH već i u drugim zemljama regije kod kojih MBO tehnologija tek treba biti implementirana.

HRZZ
Hrvatska zaklada
za znanost



Stjecanjem ekspertize u provođenju pokusa i numeričkom modeliranju bioosušenog otpada na Geotehničkom fakultetu Sveučilišta u Zagrebu omogućit će se otvaranje specifičnog područja istraživanja, visoko komplementarnog s postojećim istraživačkim iskustvom u Hrvatskoj.

Rezultati ovog projekta dozvolit će racionalniji pristup u projektiranju odlagališta otpada.

Osim toga, rezultati pokusa će pružiti sveobuhvatan skup dobro kontroliranih, novih generičkih mjerila za računalnu validaciju različitih aspekata modeliranja MBO otpada te doprinijeti unaprjeđenju njegove prediktivne snage za potrebe projektiranja odlagališta otpada.

Cilj projekta je stvoriti specifičnu i dugoročnu istraživačku nišu za Eksperimentalni i numerički laboratorij na Geotehničkom fakultetu Sveučilišta u Zagrebu, u suradnji s centrom izvrsnosti u Austriji.

Spomenuta suradnja temelji se na višegodišnjoj ekspertizi u području numeričkog modeliranja profesora Ericha Bauera s Tehničkog sveučilišta u Graz-u.



Sveučilište u Zagrebu
GEOTEHNIČKI FAKULTET



Sveučilište u Zagrebu • University of Zagreb
STUDENTSKI CENTAR VARAŽDIN
 Student Centre Varaždin



- A** Dom |A| Dormitory
- B** Dom |B| Dormitory
- #** Studentski klub / Student Club
- +** Studentska ambulanta / Student Infirmary
- Gym**
- Sportsko igralište** / Sports Playground
- Fitness park** / Fitness Park
- Student servis** / Student Service
- Gym**
- Solarni park** / Solar Park
- Studentski restoran** / Student Restaurant
- 60°C** Praonica rublja / Student Laundry Room
- Učionica** / Classroom
- Spremište za bicikle** / Bicycle Storage
- Ulaz u podzemnu garazu** / Underground Garage Entrance



www.scvz.unizg.hr



f scvarazdin





Student Council

Faculty of Geotechnical Engineering

- Makes sure that all legal decisions regarding the student rights, obligations and initiatives are taken in consideration at the meetings of the Faculty Council.
- Establishing the international merit of the Faculty and participation in international projects and student exchange based on the Bologna principles.
- Increasing the quality of student life and promoting student activity in the City of Varaždin as well as youth involvement in the wider community.
- Development of students positive attitudes, participation and affirmation of creative ideas as well as of constructive, well-grounded and positive critical thinking.
- Establishing the Faculty brand in correspondence with the development of the image of the City of Varaždin and the University of Zagreb as recognizable brands.



STUDIJSKI
INŽENJERSTVA
OKOLIŠA



FAKULTET S KOJIM ĆEŠ MIJENJATI SVIJET NA BOLJE



STUDIJ
INŽENJERSTVA
OKOLIŠA

SVEUČILIŠTE U ZAGREBU
Geotehnički fakultet
Hallerova aleja 7, Varaždin

Akademski nazivi

Prema Nastavnom planu I programu izvode se:

- Preddiplomski studij Inženjerstvo okoliša koji traje tri godine i čijim se završetkom stječe 180 ECTS bodova te akademski naziv sveučilišni prvostupnik/prvostupnica (baccalaureus/baccalaurea) Inženjer/Inženjerka Inženjerstva okoliša
- Diplomski studij Inženjerstvo okoliša koji traje 2 godine i čijim se završetkom stječe 120 ECTS bodova te akademski naziv magistar/magistra Inženjer/Inženjerka Inženjerstva okoliša.

Kriteriji za bodovanje za upis na studijski program Inženjerstvo okoliša

Lista poretka prijavljenih kandidata za upis sastavlja se prema sljedećem sustavu bodovanja:

- Na temelju uspjeha u srednjoj školi - do 400 bodova
- Na temelju položenih ispita na državnoj maturi
 - Matematika (osnovna razina riješenosti): do 400 bodova
 - Izborni predmet*(najbolje ocijenjeni jedan od predložena tri predmeta - Fizika, Kemija ili Biologija): do 200 bodova
 - *Nije uvjet za upis na studij, ali donosi bodove ako su predmeti položeni na državnoj maturi.
- Na temelju dodatnih postignuća učenika - osvojeno jedno od prvih tri mjesta na državnim natjecanjima u RH iz matematike, fizike, kemije, biologije, Informatike, astronomije ili tehničkih znanosti za vrijeme srednjoškolskog obrazovanja - IZRAVAN UPIS - 1000 bodova

Dodatne informacije

TAJNISTVO: pon-pet: 07:00 - 15:00
tel: 042/408-901
ured.tajnika@gfv.hr

REFERADA: pon-pet: 09:00 - 12:00
tel: 042/408-904
studentska.referada@gfv.hr

Točne datume upisa i ostale relevantne informacije možete potražiti na web stranicama fakulteta :

www.gfv.unizg.hr

Facebook: Studij Inženjerstva okoliša – Geotehnički fakultet

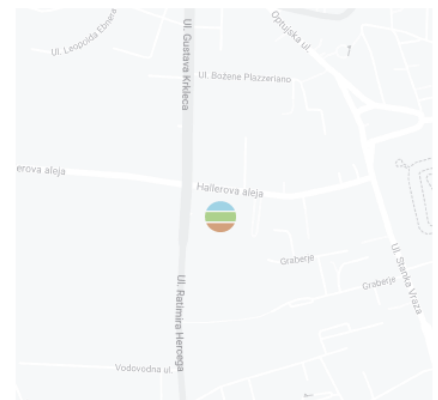
ADRESA: Hallerova aleja 7, 42000 Varaždin



Sveučilište u Zagrebu



Geotehnički fakultet



Zašto studirati Inženjerstvo okoliša na Geotehničkom fakultetu?

S našeg fakulteta izlaze Inženjeri zaštite okoliša. Kroz preddiplomski i diplomski studij Inženjerstva okoliša studenti stječu kompetencije iz područja gospodarenja otpada, zaštite okoliša, zaštite voda, geotehnike, zelene energije i cirkularne ekonomije te otvaraju vrata u područje tzv. zelenih poslova.

Sama nastava koncipirana je na bazičnim znanjima iz temeljnih prirodnih, tehničkih i informatičkih znanosti koja su preduvjet za razumijevanje osnovnih načela Inženjerstva okoliša; inovativnim rješenjima i završava obaveznom stručnom praksom u trajanju od 160 sati, čime studenti rano dolaze u priliku primijeniti naučeno.

Novi doktorski studij Inženjerstvo okoliša (prvi takav u Hrvatskoj) nastoji interdisciplinarno povezati teme zaštite voda, tla, zraka, gospodarenje otpadom i energetike.

Preddiplomski studijski program Inženjerstvo okoliša

Preddiplomski sveučilišni studij Inženjerstva okoliša traje tri godine, tijekom kojih se stječu znanja iz temeljnih prirodnih, tehničkih i informatičkih znanosti kao preduvjet za razumijevanje osnovnih principa Inženjerstva okoliša, koji uključuju znanja iz zaštite okoliša, gospodarenja otpadom te ostalih mjera i postupaka u zaštiti okoliša.

Na taj način student tijekom studija razvija sposobnost prepoznavanja i opisivanja različitih problema u Inženjerstvu okoliša, sposobnost usvajanja najkvalitetnijih rješenja u struci, sposobnost korištenja laboratorijske i terenske opreme, promatranja, bilježenja i analize podataka dobivenih laboratorijskim i terenskim ispitivanjima.

Diplomski studijski program Inženjerstvo okoliša

Kroz diplomski studijski program studenti detaljnije ulaze u problematiku Inženjerstva okoliša kroz tri studijska usmjerenja:

- Geoinženjerstvo okoliša omogućava sudjelovanje u planiranju, projektiranju, organiziranju i izvođenju poslova na projektima i studijama: očuvanja, nadzora, zaštite i remedijacije okoliša, procjene utjecaja planiranih zahvata na okoliš, istraživanja terena u okolišne i geotehničke svrhe kao i stručnih poslova u niskogradnji i rudarstvu.
- Upravljanje vodama obrađuje problematiku vodnih resursa, gdje se podjednaka težina daje količini i kakvoći vode, problematiki otpadnih voda, njihovoj dispoziciji i remedijaciji, složenom području energetskog iskorištavanja vodnih potencijala, zaštiti vode za piće, te melioracijskim sustavima i regulaciji vodotoka.
- Upravljanje okolišem interdisciplinarno je smjer koji obuhvaća inženjerski pristup u identificiranju, sprječavanju i ublažavanju nepovoljnih utjecaja na okoliš. Širok spektar znanja omogućava rješavanje niza okolišnih izazova poput gospodarenja otpadom, energetske tranzicije, remedijacije tla, procjene životnog vijeka proizvoda, procjene utjecaja na okoliš, inspekcijskog nadzora u zaštiti okoliša i sl.



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INSTRUCTIONS FOR AUTHORS

The journal „ENVIRONMENTAL ENGINEERING-INŽENJERSTVO OKOLIŠA“ publishes scientific and technical papers and other articles in the interdisciplinary area of environmental engineering. The scientific topics covered by the Journal include geo-engineering, water resources management, technical aspects of environmental protection and similar areas. The journal publishes papers in English. Papers are accepted for publication after they have received a positive review and are categorized as an original scientific paper, preliminary communications, review paper or technical paper.

The journal is published biannually. There are no charges for printing the paper. As a rule, the length of the paper is not limited. However, it is recommended that it should not be longer than 15 single-spaced A4 pages, all figures included.

Figures are printed in greyscale, and authors should take it into account when preparing their manuscript. However, authors may, in agreement with the editorial board, prepare figures in colour when they deem it necessary for the understanding of what the figure shows. The figures in colour approved by the editorial board will not be additionally charged.

When a paper is submitted for review, this implies that the paper has not been previously published or that it is not being reviewed by another journal. The author is responsible for the content of the paper and for obtaining consent, where applicable, to publish particular data.

The first page should contain the title of the paper, the authors' names, the institution of employment, the authors' email addresses, the abstract and keywords. It is recommended that the title of the paper should be illustrative and clearly reflect the content of the paper. If the title contains local names, then a generally recognizable name in a wider region should be included. The abstract should not exceed 300 words, and there should be 4 to 6 keywords. If none of the authors has been specified as lead author, the editors will exclusively contact the first mentioned author.

Authors should submit their paper by e-mail to: casopis@gfv.hr. The paper should be prepared in Microsoft Word in A4 page format, with 25 mm margins and 1.5 line spacing, in one column aligned to both sides. The text should be written in 10 pt Times New Roman, and the pages should have automatic numbering in the bottom right corner. Depending on the content, the text should be divided into several sections whose headings are in 11 pt bold and aligned to the left. The paper should be written in the third person singular and has to be terminologically harmonized with legal regulations in force and the international system of units (SI). All equations have to be numbered; tables and figures should also be numbered with a heading and inserted in the appropriate place in the article. **For citation of equations, figures and table in text use bold font.** All figures (images, diagrams, photographs) have to be prepared for graphic reproduction at a minimum resolution of 300 dpi and submitted in a separate map.

When **citing papers in the text** with **blue colour**, only previously published papers should be mentioned. If authors consider it necessary, personal communication and unpublished papers may be cited in the paper, but in an appropriate manner, either as part of the text or in acknowledgements at the end of the paper. **References** include an alphabetical list of published papers that have been cited in the text. The **Harvard citation** and referencing style should be used.

If the paper is accepted for publication, the authors are obliged to harmonize the paper with the instructions given by the reviewers/editors. If the authors do not accept the reviewers'/editors' remarks or if they do not submit the corrected version of the paper within three months, the editorial board will deem that the authors have withdrawn their paper from the procedure and no longer wish to have it published.

Prior to its publication, the authors will receive the paper for inspection and final revision.

The paper which has been through all the phases of text preparation will first be published online, and then in the printed edition. Authors will receive a separate in pdf format as well as one copy of the journal in which the paper was published.