



## Publishable Summary for 17FUN09 UnipHied Realisation of a Unified pH Scale

### Overview

To date, it is impossible to compare pH values of solutions made in different solvents. This situation is untenable, since it causes confusion and inaccuracies in many fields, extending far beyond the specific field of acid-base chemistry, to almost all spheres of life. The purpose of this project is to overcome this situation by putting the new theoretical concept of a unified  $\text{pH}_{\text{abs}}$  scale on a metrologically well-founded basis into practice. The project results will ensure that  $\text{pH}_{\text{abs}}$  measurement procedures will be developed and suitable experimental setups are available to industry and academia for accurate  $\text{pH}_{\text{abs}}$  testing in a wide variety of media.

### Need

The pH of solutions is probably the most prominent chemical concept widely utilised outside the field of chemistry. It is used in an uncountable number of areas, e.g., medicine and life sciences, biology, environmental science, agronomy, marine sciences, catalysis, materials sciences, corrosion science, energy related sciences, etc. It plays an important role in virtually all material related processes, in their production (e.g., processing metals, paper, plastics, glasses, etc.) as well as in their reprocessing (domestic and industrial wastewater, extraction of solid wastes, etc.). Accurate measurement and monitoring of pH values is therefore an extremely important task in a wide variety of technologies. This variety entails a diversity of media in which those processes occur, i.e., different solvents, solvent mixtures, and dispersions. For basic thermodynamic reasons, valid comparability of pH values in different media has been impossible for a long time, even on the theoretical level. As a result, different pH scales exist in different media, loosely correlated to each other, without the possibility of converting one scale into the other to the necessary level of accuracy. It is known that there are potentially 1.5 million pH electrodes used in industrial applications today, of which a number (10 % to 20 %) are placed in solvent mixtures that are in fact not suitable for the current offerings and lead to rapid failures.

In 2010, the unified acidity ( $\text{pH}_{\text{abs}}$ ) concept was introduced to overcome this untenable situation, enabling comparability of pH values between all phases, whether they are gaseous, liquid, or solid. Although conceptually excellent, putting this concept into practical use has proved tremendously difficult and has not yet been fully achieved. In order to be practically usable, suitable measurement and calibration procedures are required, all of which still need to be developed.

### Objectives

This project concerns the practical realisation of the theoretical concept of  $\text{pH}_{\text{abs}}$ . This includes developing the measurement systems, as well as the development and standardisation of the measurement and calibration processes of  $\text{pH}_{\text{abs}}$ . The major objectives laid out for this project are:

1. To develop and validate a reliable and universally applicable measurement procedure, that enables the measurement of  $\text{pH}_{\text{abs}}$  (expressed relative to the aqueous scale, as  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ -values) in non-aqueous and mixed solvents, colloids, etc., thereby enabling their acidities to be compared to the conventional aqueous pH scale. The target combined standard uncertainties to be 0.15  $\text{pH}_{\text{abs}}$  in "good" (mixed aqueous, alcohols, etc.) and 0.25  $\text{pH}_{\text{abs}}$  in "difficult" (colloids, aprotic, etc.) systems.
2. To create a reliable method for the experimental or computational evaluation of the liquid junction potential between aqueous and non-aqueous solutions where the bridge electrolyte is an Ionic Liquid, allowing correction of results from, for example, a glass electrode pH measurement setup calibrated with aqueous standards measuring non-aqueous samples.
3. To develop a coherent and validated suite of calibration standards (including procedure and sensor) for standardising routine measurement systems in terms of  $\text{pH}_{\text{abs}}$  values for a wide variety of media (e.g., industrial mixtures, soils/waters, food products, biomaterials).

4. Based on the outcome of the project, to contribute to the international specifications for bioethanol quality EN 15490 (e.g., by assigning values to existing certified reference materials) and other relevant standards development organisations, and to disseminate the findings to the European measurement infrastructure.

### Progress beyond the state of the art

1. To develop and validate a reliable and universally applicable measurement procedure, that enables the measurement of  $pH_{abs}$  (expressed relative to the aqueous scale, as  $pH_{abs}^{H_2O}$ -values) in non-aqueous and mixed solvents, colloids, etc., thereby enabling their acidities to be compared to the conventional aqueous pH scale. The target combined standard uncertainties to be 0.15  $pH_{abs}$  in "good" (mixed aqueous, alcohols, etc.) and 0.25  $pH_{abs}$  in "difficult" (colloids, aprotic, etc.) systems.

Depending on individual requirements and technical possibilities, several pH scales have been developed over the last century, most importantly, every solvent has its own pH scale. However, the usefulness of these scales is limited as a result of their incompatibility. *I.e.*, a certain value in one scale cannot be compared with or converted to a value on another scale with acceptable accuracy. This project established rigorous procedures enabling to measure and express acidity of any medium on an intersolvental or universal pH scale (termed here as  $pH_{abs}$ ). Most importantly, differently from the conventional pH values, the  $pH_{abs}$  values are comparable between solvents/media. The  $pH_{abs}$  values can be most conveniently expressed as  $pH_{abs}^{H_2O}$  values – aligned to the aqueous pH scale. This enables convenient comparison of  $pH_{abs}$  measured in any solvent with the conventional aqueous pH values. Two measurement methods have been implemented by the project partners and have been validated through an interlaboratory comparison carried out on three matrices: water, water-ethanol and pure ethanol. Good consistency of the results was obtained with two different  $pH_{abs}^{H_2O}$  methods pointing to the robustness of the  $pH_{abs}^{H_2O}$  measurement procedures. Additionally  $pH_{abs}^{H_2O}$  uncertainty budget shows that the target uncertainties can be reached.

2. To create a reliable method for the experimental or computational evaluation of the liquid junction potential between aqueous and non-aqueous solutions where the bridge electrolyte is an Ionic Liquid, allowing correction of results measuring non-aqueous samples.

In potentiometric pH measurement a liquid junction is formed at the interface between two solvents, typically water and the non-aqueous solvent. The liquid-junction potential (LJP) that arises has a magnitude that is generally difficult to evaluate and control, and is, therefore, considered to be the major source of bias in classical pH measurement. The issue of liquid junction potential was addressed in the present proposal by utilizing an "close to ideal" ionic liquid (IL) salt bridge composition. The ionic liquid selected for the project is the triethylammonium bis((trifluoromethyl)sulfonyl)imide also noted as  $[N_{2225}][NTf_2]$ . Experiments carried out at ALU-FR have demonstrated that if  $[N_{2225}][NTf_2]$  is used as a salt bridge electrolyte then the salt bridge formed by the mentioned IL yields negligible LJP values in a number of systems, involving solvents with very different properties, such as water, ethanol, methanol, dimethylformamide and acetonitrile. This contributes to obtain  $pH_{abs}^{H_2O}$  values that serve as a thermodynamically well-defined link between the acidity in water and the acidity in any other medium with respect to the aqueous system.

3. To develop a coherent and validated suite of calibration standards (including procedure and sensor) for standardising routine measurement systems in terms of  $pH_{abs}$  values for a wide variety of media (e.g., industrial mixtures, soils/waters, food products, biomaterials).

It is well known that in liquid chromatography, mobile phase pH is an important parameter, significantly affecting the retention of acidic and basic analytes. Yet, mobile phase pH is tricky to measure because mobile phases are usually aqueous-organic mixtures and in the case of gradient elution mobile phase composition gradually changes during elution. A number of mobile phases of interest for liquid chromatography were characterized in term of  $pH_{abs}^{H_2O}$ . The measured values were uploaded to the project website (<https://www.ppm.uni-freiburg.de/uniphied/pHabsH2O%20data>) and have become available for the analytical chemistry community.

ANB Sensors have started working on developing a sensor that can determine  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values for non-ideal solutions. An electrochemical system has been found which operates as a pH sensor and tested in laboratory conditions in the certain mixed solvent systems.

## Results

1. *To develop and validate a reliable and universally applicable measurement procedure, that enables the measurement of  $\text{pH}_{\text{abs}}$  (expressed relative to the aqueous scale, as  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ -values) in non-aqueous and mixed solvents, colloids, etc., thereby enabling their acidities to be compared to the conventional aqueous pH scale. The target combined standard uncertainties to be 0.15  $\text{pH}_{\text{abs}}$  in "good" (mixed aqueous, alcohols, etc.) and 0.25  $\text{pH}_{\text{abs}}$  in "difficult" (colloids, aprotic, etc.) systems.*

The differential potentiometry method relies on the conversion of the measured potential difference between two electrodes immersed each in a solution separated by a salt bridge, into pH difference. During the project, two  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement methods have been implemented by the partners:

- (1) reference method: based on potential measurement between two specialized (solid-contact) glass electrode half-cells connected by an ILSB. This method is not straightforward as the ladder approach necessary to assign  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values is laborious involving an important number of measurement to be carried out.
- (2) alternative method, suitable for routine laboratories: based on potential measurements using conventional measurement equipment namely glass electrode half-cell and a Ag/AgCl double junction reference electrode with two filling solutions: concentrated KCl (aq, mon 3M) inner filling solution, and ionic liquid outer filling solution, acting as an ILSB.

The traceability and method validation are central issues for ensuring that the method is robust enough for wider adoption of the concept in the field and routine applications. For this, the influencing parameters were identified with well-known and characterized solutions. The two  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  methods have been validated through interlaboratory comparisons on different aqueous standard pH buffers as well as more complex media such as ethanol and water-ethanol solvents. The validation highlights that the methods are, to a large extent, independent of the user and the used equipment. Measurement redundancy among NMIs is key to ensuring that the methods, and their quality are completely understood. Therefore, it was demonstrated that unified acidity values ( $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values) can be measured with various instruments and cell designs. An uncertainty budget for  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement values has been established based on GUM and Monte Carlo simulation approach. Target standard uncertainties of 0.15 fixed for  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement values can be reached in buffered mixed aqueous-organic solvents. Preliminary experiments in anhydrous acetonitrile (an aprotic solvent, a "difficult" system) show that standard uncertainty of an order of 0.2 can be expected. The developed procedures have been deposited to the protocols.io open access web depository and are available from the permanent links [doi.org/10.17504/protocols.io.bybxpspn](https://doi.org/10.17504/protocols.io.bybxpspn) and [doi.org/10.17504/protocols.io.byh2pt8e](https://doi.org/10.17504/protocols.io.byh2pt8e).

Objective 1 was achieved, since 9 partners developed  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  reference setups and 10 partners set up the alternative method, implemented the corresponding procedures and were able to perform measurements in different buffered mixed aqueous-organic solvents (such as liquid chromatography mobile phases, see below) with standard uncertainties of 0.15. Preliminary experiments in anhydrous acetonitrile (an aprotic solvent, a "difficult" system) show that standard uncertainty of an order of 0.2 can be expected.

2. *To create a reliable method for the experimental or computational evaluation of the liquid junction potential between aqueous and non-aqueous solutions where the bridge electrolyte is an Ionic Liquid, allowing correction of results measuring non-aqueous samples.*

It was discovered that there is a possibility of minimisation, up to elimination, of the liquid junction potential by using a salt bridge formed by a "close to ideal" ionic liquid (IL). This possibility was studied in three systems formed by water and non-aqueous solvents such as acetonitrile, ethanol and methanol. The ideal character of the IL requires, among others, identical transference numbers, or ionic mobilities, for cation and anion both in the pure IL and in solution, as well as very close solvation Gibbs energies in all used solvents, while being inert with respect to the used solvents. The IL  $[\text{N}_{2225}][\text{NTf}_2]$  selected for the project satisfies these requirements.

Although this IL enables close to ideal elimination of the LJP, there still remains a degree of uncertainty as to how complete is the elimination. Thus, the initial task of evaluating the LJP changed into evaluating the residual uncertainty due to possibly incomplete elimination of LJP. A new methodology to determine the uncertainty due to possibly incomplete elimination of LJP was proposed by ALU-FR and UT. The approach is based on the network analysis. The network is an overdetermined system, i.e. a system of equations with more equations than unknowns. Generally, the more closely meshed the network the more reliable the result. The network is used to determine the Gibbs transfer energy of the redox system  $\text{Ag}^+/\text{Ag}$  from water to various solvents  $\Delta G_{\text{tr}}^\circ(\text{Ag}^+, \text{H}_2\text{O} \rightarrow \text{S})$ . The network now comprises 145 individual measurements. Comparison of the obtained experimental values to the calculated values enabled assessment of the overall liquid junction potential.

The Gibbs transfer energy of the redox system  $\text{Ag}^+/\text{Ag}$  from water to acetonitrile (AN),  $\Delta G_{\text{tr}}^\circ(\text{Ag}^+, \text{H}_2\text{O} \rightarrow \text{AN})$ , was determined to  $-25.1 \text{ kJ mol}^{-1}$  with the accuracy level of 6 mV, see below. A widely accepted literature value is  $-23.2 \text{ kJ mol}^{-1}$  having an estimated uncertainty of 3 – 6  $\text{kJ mol}^{-1}$ . The literature value was obtained using the so-called reference electrolyte assumption that is considered to be the most reliable since it is supported by recent theoretical ab initio calculations using the cluster-pair approximation. The closeness between experimental value obtained in this project and literature value validate the setup used by ALU-FR and also the proposed network approach. Moreover, the difference of the LJPs in the given setup, i.e.  $\text{LJP}(\text{H}_2\text{O}-\text{IL}) - \text{LJP}(\text{AN}-\text{IL})$ , is stable and remains within 6,3 mV (equivalent to 0.61  $\text{kJ mol}^{-1}$  or 0.11 pH-units, respectively) in the case of low ionic strength solutions. For water-acetonitrile, LJPs are remarkably insensitive against the change of the ionic strength of the electrolyte solutions (silver salts of type  $\text{Ag}^+\text{Z}^-$ ), as long as it remains within 0.1 to 10  $\text{mmol L}^{-1}$ , and against influx of solvent into the ILSB. In addition, this indicates that the redox system  $\text{Ag}^+/\text{Ag}$  under investigation doesn't affect the LJPs either.

The Gibbs transfer energy of the redox system  $\text{Ag}^+/\text{Ag}$  from water to EtOH,  $\Delta G_{\text{tr}}^\circ(\text{Ag}^+, \text{H}_2\text{O} \rightarrow \text{EtOH})$  was determined to 1.6  $\text{kJ mol}^{-1}$  and from water to MeOH,  $\Delta G_{\text{tr}}^\circ(\text{Ag}^+, \text{H}_2\text{O} \rightarrow \text{MeOH})$  to 3.8  $\text{kJ mol}^{-1}$ . These findings can be considered reliable since are in good agreement with literature data. The consistency of the values is 0.55  $\text{kJ mol}^{-1}$ .

Objective 2 was achieved since the “close to ideal” IL studied within the project allows the experimental implementation of the  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  scale for several complex organic solvents. This contributes to obtain  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values that serve as a thermodynamically well-defined link between the acidity in water and the acidity in any other medium with respect to the aqueous system. Additionally, this specific IL provides considerable advantages against other methods, namely its non-toxicity.

3. *To develop a coherent and validated suite of calibration standards (including procedure and sensor) for standardising routine measurement systems in terms of  $\text{pH}_{\text{abs}}$  values for a wide variety of media (e.g., industrial mixtures, soils/waters, food products, biomaterials).*

ANB Sensors developed the transducers to be used in their  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  sensing device. The development of the first prototype showed the efficacy of the response of the pH sensing element in buffered/mixed solvent systems and highlighted some key issues with the reference system and when deploying the pH sensing element in low salinity media. Prototype 2 overcame these issues by developing a complete reference cell and an electrode construction to minimise the issues of low conductivity media. The results of this prototype show the effectiveness of this approach for monitoring pH in mixed solvent media with promising agreement shown between calculated and measured pH values in both aqueous and mixed solvent media.

Measurements of  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  have been performed on a number of buffered solutions used as mobile phases for liquid chromatography. The analysed solutions have been prepared in aqueous solutions with different amounts 20-80% (v/v %) of methanol or acetonitrile as organic solvent. This way, a number of mobile phases have been characterised and their  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values determined. The measured values were uploaded to the project website (<https://www.ppm.uni-freiburg.de/uniphied/pHabsH2O%20data>) and become available for the analytical chemistry community as reference values, usable for calibration of  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement systems.

$\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurements of un-buffered pure organic solvents or solvent-water mixtures remain challenging in the absence of a buffering agent. The possibility to improve the data quality by adding organic salts such as  $\text{N}_{2225}\text{NTf}_2$  or  $\text{Et}_4\text{NClO}_4$  (tetraethylammonium perchlorate) to the measured solvent has been tested for pure ethanol solvent and water-ethanol mixtures. For these unbuffered solutions, maximum standard uncertainties of 0.2 can be estimated for the measured  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values.

Objective 3 was achieved as ILSB setups for easily measuring  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  with conventional measurement equipment have been developed in the project and used to demonstrate application to field practices especially for liquid chromatography. Furthermore, a sensing concept was developed at ANB Sensors, which moved away from the traditional glass electrode to a solid state sensing system. ANB Sensors incorporated their novel reference monitoring system with an electrochemically pH active monitoring electrode. The efficacy of the approach has been demonstrated through laboratory testing. ANB Sensors will continue to pursue testing the sensor for real applications beyond the lifetime of the project.

## Impact

The project has submitted 13 open access scientific publications, more than 20 presentations (oral or by poster) at national or international conferences, 4 internal training workshops and 1 international webinar. During the lifetime of the project, regular progress updates were announced by the partners using social media and their own information channels like client meetings, newsletters, etc

### *Impact on industrial and other user communities*

The project aims to provide a reliable and practical method of measuring and expressing acidity of any medium on a universal scale (termed here as  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  values). Measurement of pH in aqueous-organic mixtures with different compositions is of high importance in science and technology, but it is, at the same time, challenging both from a conceptual and practical standpoint.

It is expected that the outputs produced during the lifetime of the project will benefit manufacturers of pH sensors and pH meters that will have a reliable means to characterise and benchmark their devices in solutions other than aqueous, since they can directly compare the results of different types of devices in various matrices using the  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  scale as a root of traceability.

The estimation of residual LJPs when salt bridge is an ionic liquid has been performed by ALU-FR using their home-made IL. The collaboration of ALU-FR with the company Iolitec, producer of IL, allowed the distribution to each partner of 50 g of ionic liquid  $[\text{N}_{2225}][\text{NTf}_2]$  produced by this company. The partners used this commercial IL to perform all the measurements for the interlaboratory comparison organized to demonstrate the robustness of the  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement procedures in solvents other than water. The exercise highlighted that the results from different setups are comparable. The IL  $[\text{N}_{2225}][\text{NTf}_2]$  used during the project is now commercially available also from other companies. Therefore, the ILSB setups developed in the project for measuring  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ , especially the one of the alternative method (see above) can be easily adopted for routine laboratory analysis. In the longer term, routine laboratories will be able to measure  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  whilst – very importantly – using their conventional measurement equipment (i.e., there will be no need to install sophisticated differential potentiometry setups). The possibility to measure  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  in a simple way is considered promising for a further uptake of  $\text{pH}_{\text{abs}}$  concept on a wider scale. Opportunities for analytical chemistry community, especially for liquid chromatography practitioners have been identified.

### *Impact on the metrology and scientific communities*

The main expected impact of this project on the metrological community is related to the transfer of knowledge related to  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurement to chemical services providers; especially those using liquid chromatography and its derivative methods, electrochemists in the field of batteries or corrosion, and those working in the food industry. The work carried out in the project was disseminated through a number of scientific publications to demonstrate the relevance and possibilities of using the  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  concept in different fields, such as liquid chromatography, chemistry of acids and bases in non-aqueous solutions and biphasic systems, design of membrane-based sensors, etc. The acidity measurements including  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  have been used to study the effects of mobile phase acidity, organic solvent, organic solvent fraction and aqueous phase properties.

The perspective of being able to compare the acid-base properties in different solvents received positive feedbacks from potential end-users community during a webinar organized in the framework of the JRP project. This event was dedicated to "Mobile Phase pH in Liquid Chromatography" and introduced the unified pH concept and its measurement methods as an advantage in interpreting retention time in relation with LC mobile phase pH. Altogether 101 people participated from 41 countries, ranging from Portugal to Philippines and from Peru to Nepal, which demonstrates the interest of  $\text{pH}_{\text{abs}}$  concept for analytical chemical applications.

It is expected that such event will continue to be organized by the University of Tartu beyond the lifetime of the project and on an annually basis. This will greatly contribute to feed scientific communities with information about the application of intersolvental pH concept.

The work undertaken in this project was also incorporated into the efforts already started by IUPAC to address pH assessment in non-aqueous and mixed solvents. The UnipHied project was promoted in the News Magazine of IUPAC as an important opportunity to secure intercomparability of pH measurement results in different media. A Technical Report presenting the state-of-the art of the meaning and assessment of pH in solvents other than water has been approved for publication by the IUPAC official journal, Pure and Applied Chemistry. A second Technical Report aiming to present the progress achieved toward practical implementation of  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  as well as the Quality of Measurement Values is currently in progress.

#### *Impact on relevant standards*

The project encouraged active participation in key European chemistry related committees such as the EURAMET TC MC, as well as knowledge transfer to international metrology in chemistry community such as BIPM CCQM. The  $\text{pH}_{\text{abs}}$  method and the results obtained on interlaboratory comparison were presented at EURAMET TC MC meetings on electrochemical analysis and the main achievements of the project were presented at BIPM EAWG (Working Group on Electrochemical Analysis) meeting.  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  is traceable to the classical standard buffer solutions which represents a good argument for a future implementation of the concept at wider scale. Therefore, the impact of the work undertaken by NMIs under the European and international metrology system i.e. EURAMET and BIPM will be expanded. Additionally, the project emphasised the key role of NMIs in increasing utility and improving meaningfulness of pH measurement results necessary for real world applications (several industrial sectors).

Within the project lifetime,  $\text{pH}_{\text{abs}}$  measurements in ethanol and water-ethanol mixtures were performed. Such solutions are of interest for biofuels sector especially for the existing standards in relation with quality assessment of bioethanol. The findings of the project suggest that  $\text{pH}_{\text{abs}}$  method is robust but the poor performances obtained in pure organic solvents like ethanol are explained by the high sensitivity of the sample itself, due to low buffering ability and conductance, possible composition instability because of solvent evaporation, quality of water and pure solvent, etc. For this reason, despite the advantage of  $\text{pH}_{\text{abs}}$  in achieving metrological comparability, its implementation will have, at least for the moment, a limited impact on existing bioethanol-related standards.

#### *Longer-term economic, social and environmental impacts*

Since pH is one of the most important chemical parameters in science, technology, environment and health, the project's broader impact is potentially enormous, yet difficult to quantify. It is clear that any uptake of the project's outcomes by any field regarding pH values or redox values in non-aqueous (but also aqueous and mixed-aqueous) solutions will lead to further development within these fields. Thus, there is a strong reason to expect beneficial effects for the European industry as a whole.

The developments in the project will enable more efficient process control in the EU chemical industry, which is a large branch of the European economy, employing 1.2 million workers and contributing €519 billion annually to the European chemical industry.

The project will be a vector of innovation for the development of the next generation of pH electrodes. Such electrodes would be useful in the biomedical field, especially for cancer chemotherapy, and could contribute towards the reduction of the cost of cancer treatment.

Europe is a key player in addressing environmental sustainability and the global climate challenge. This project therefore also contributes to a further understanding of the chemistry of water bodies (particularly sea water, a highly important ecological system). Extensive and continuing  $\text{CO}_2$  absorption by seawater causes acidification, evidenced by a reduction in pH and changes in the ocean carbonate chemistry. Serious discrepancies have been noticed in established trends in seawater acidity due to the existence of several measurands for the same quantity. The work carried out during the project lifetime by a Researcher Mobility Grant (RMG) contributed to testing the applicability of  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  to saline solutions. To this purpose, differential potentiometric measurements, with a salt bridge of ionic liquid  $[\text{N}_{2225}][\text{NTf}_2]$ , were carried out aiming at overcoming problems related to residual liquid junction potentials that affect the quality of such measurements. The ability to measure  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  with acceptable uncertainty was evaluated using standard buffer solutions prepared in a background matrix close to the characteristics of estuarine systems (salinity of 20) as well as

with NaCl solutions with ionic strength between 0.005 and 0.8 mol/kg. The study showed that for high ionic strength solutions, such as seawater, challenges remain in application of the  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  concept, first of all, because of insufficient LJP compensation ability of  $[\text{N}_{2225}][\text{NTf}_2]$  under such conditions. Improvements are envisaged from the eventual selection of a more adequate ionic liquid. Hence, the methodology developed during the project could be applied for investigated other ionic liquid for their potential to be used for seawater applications.

### List of publications

1. Sigrid Selberg, Sofja Tshepelevitsh, Ivo Leito, "Biphasic  $\text{pK}_a$  Values", Croat. Chem. Acta 2018, 91(4), <https://doi.org/10.5562/cca3405>
2. Heike Kahlert, Ivo Leito, "Generalization of Acid-Base Diagrams Based on the Unified  $\text{pH}$ -Scale", ChemPhysChem, 2019, 20, 1779 – 1785  
<https://doi.org/10.1002/cphc.201900388>
3. Valentin Radtke, Katharina Pütz, Daniel Himmel, Ingo Krossing, "The Inverted Philosopher's Stone: how to turn silver to a base metal", J Solid State Electrochem,  
<https://doi.org/10.1007/s10008-020-04633-y>
4. Ruta Veigure, Krit Lossmann, Max Hecht, Elisabeth Parman, Rasmus Born, Ivo Leito, Koit Herodes, Kari Kipper, "Retention of acidic and basic analytes in reversed phase column using fluorinated and novel eluent additives for liquid chromatography-tandem mass spectrometry", Journal of Chromatography A  
<https://doi.org/10.1016/j.chroma.2019.460667>
5. Agnes Heering, Daniela Stoica, Filomena Camões, Bárbara Anes, Dániel Nagy, Zsófia Nagyné Szilágyi, Raquel Quendera, Luís Ribeiro, Frank Bastkowski, Rasmus Born, Jaan Saame, Jaak Nerut, Silvie Lainela, Lokman Liv, Emrah Uysal, Matilda Roziková, Martina Vičarová, Alan Snedden, Lisa Deleebeeck, Valentin Radtke, Ingo Krossing, Ivo Leito, « Symmetric Potentiometric Cells for the measurement of Unified  $\text{pH}$  values », Symmetry 2020, 12(7), 1150.  
<https://doi.org/10.3390/sym12071150>
6. Ricardo J.N. Bettencourt da Silva, Jaan Saame, Bárbara Anes, Agnes Heering, Ivo Leito, Teemu Näykki, Daniela Stoica, Lisa Deleebeeck, Frank Bastkowski, Alan Snedden, M. Filomena Camões, «Evaluation and validation of detailed and simplified models of the uncertainty of unified  $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$  measurements in aqueous solutions», 182, 2021, 338923  
<https://doi.org/10.1016/j.aca.2021.338923>
7. Lainela, S.; Leito, I.; Heering, A.; Capitaine, G.; Anes, B.; Camões, F.; Stoica, D, «Toward Unified  $\text{pH}$  of Saline Solutions», Water 2021, 13(18), 252  
<https://doi.org/10.3390/w13182522>
8. Heering, Agnes; Bastkowski, Frank; Seitz, Steffen; «Glass electrode half-cells for measuring unified  $\text{pH}$  in ethanol-water mixtures», J. Sens. Sens. Syst., 9, 383–389, 2020  
<https://doi.org/10.5194/jsss-9-383-2020>
9. Deleebeeck, Lisa; Snedden, Alan; Nagy, Daniel; Szilagy Nagyne, Zsofia; Rozikova, Matilda; Vicarova, Martina; Heering, Agnes; Bastkowski, Frank; Leito, Ivo; Quendera, Raquel; Cabral, Vitor; Stoica, Daniela, «Unified  $\text{pH}$  Measurements of Ethanol, Methanol, and Acetonitrile, and Their Mixtures with Water», Sensors 2021, 21(11), 3935  
<https://doi.org/10.3390/s21113935>
10. Kutt, Agnes; Tshepelevitsh, Sofja; Saame, Jaan; Lokov, Mart; Kaljurand, Ivare; Selberg, Sigrid; Leito, Ivo, «Strengths of Acids in Acetonitrile», European Journal of Organic Chemistry, Vol 2021, Issue 9, 1407-1419, 2021

<https://doi.org/10.1002/ejoc.202001649>

11. Ruutel, Alo; Yrjana, Ville; Kadam, Sandip A.; Saar, Indrek; Ilisson, Mihkel; Darnell, Astrid; Haav, Kristjan; Haljasorg, Toiv; Toom, Lauri; Bobacka, Johan; Leito, Ivo, «*Design, synthesis and application of carbazole macrocycles in anion sensors*», J. Org. Chem. 2020, 16, 1901–1914.

<https://doi.org/10.3762/bjoc.16.157>

12. Yrjänä, V., Saar, I., Ilisson, M., Kadam, S.A., Leito, I. and Bobacka, J., «*Potentiometric Carboxylate Sensors Based on Carbazole-Derived Acyclic and Macrocyclic Ionophores*», Chemosensors 2021, 9, 4.

<https://doi.org/10.3390/chemosensors9010004>

13. Bastkowski, F., Heering, A. and Seitz, S., «*Dataset for Glass electrode half-cells for measuring unified pH in ethanol-water mixtures*»,

[10.5281/zenodo.4266452](https://zenodo.org/record/4266452)

This list is also available here: <https://www.euramet.org/repository/research-publications-repository-link/>

Project start date and duration:		1 <sup>st</sup> May 2018, 39 months
Coordinator: Daniela Stoica, LNE		Tel:+33 (0)1 40434076
Project website address: <a href="http://www.uniphied.eu">www.uniphied.eu</a>		E-mail: <a href="mailto:Daniela.stoica@lne.fr">Daniela.stoica@lne.fr</a>
Internal Funded Partners:	External Funded Partners:	Unfunded Partners:
1. LNE, France	9. ALU-FR, Germany	
2. BFKH, Hungary	10. ANB Sensor, United Kingdom	
3. CMI, Czech Republic	11. FC.ID, Portugal	
4. DFM, Denmark	12. UT, Estonia	
5. IPQ, Portugal		
6. PTB, Germany		
7. SYKE, Finland		
8. TUBITAK, Turkey		
RMG1: UT, Estonia (Employing organisation); LNE, France (Guestworking organisation)		