UnipHied

EURAMET

FINAL PUBLISHABLE REPORT

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Project short name	UnipHied
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Coordinator: Daniela Stoica, LNE Tel:+33 (0)1 40434076 E-mail: Daniela.stoica@lne.fr Project website address: www.uniphied.eu	

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1. LNE, France 2. BFKH, Hungary 3. CMI, Czech Republic 4. DFM, Denmark 5. IPQ, Portugal 6. PTB, Germany 7. SYKE, Finland 8. TUBITAK, Turkey	9. ALU-FR, Germany 10. ANB Sensor, United Kingdom 11. FC.ID, Portugal 12. UT, Estonia	
RMG1: UT, Estonia (Employing organisation); LNE, France (Guestworking organisation)		

Final Publishable Report

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1   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 pH_{abs} scale on a metrologically well-founded basis into practice. The project results will ensure that pH_{abs} measurement procedures will be developed and suitable experimental setups are available to industry and academia for accurate pH_{abs} testing in a wide variety of media.

2   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, agrology, 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 (pH_{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.

3   Objectives

This project concerns the practical realisation of the theoretical concept of pH_{abs}. This includes developing the measurement systems, as well as the development and standardisation of the measurement and calibration processes of pH_{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 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.
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 pH_{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.

4 Results

This project offers a unique opportunity for the 12 partners (7 NMIs, 1 Designated Institute, 1 SME, and 3 universities) to pool their collective strengths, capabilities, and facilities to make a genuine impact in the field of measurement and understanding of pH in non-traditional media, especially in mixed or pure organic solvent systems. JRP partners produced during the project lifetime 12 open-access scientific publications, more than 20 presentations (oral and poster) at national or international conferences and exchanged with several stakeholders. All these efforts contribute to spreading the benefits of the unified acidity scale.

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. 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. Most importantly, every solvent has its own pH scale, with its own standard state, which makes the pH scales of different solvents mutually incomparable. The recent introduction of a unified universal acidity concept, pH_{abs}, represents an interesting approach to measure acidities and achieve direct comparability of pH in any kind of solvent. The pH_{abs} is a direct measure of the hydrogen ion chemical potential in any given medium and relies on a universal independent standard state: ideal proton gas at 1 bar and 298.15 K. As the universal standard state is experimentally not realizable, the obvious approach for pH_{abs} measurements is relative measurement, i.e. comparing pH_{abs} in different systems and anchoring the obtained values to some agreed standards. The technique for such relative measurements is differential potentiometry. This method relies on the conversion of the measured potential difference between two hydrogen ion, H^+ selective electrodes, each of them immersed in one solution, separated by a salt bridge, into pH difference. In the present project, an ionic liquid (IL) $[N_{2225}][NTf_2]$ has been chosen to form the salt bridge, in order to eliminate the effect of liquid unction potential (LJP).

The differential potentiometric measurement setups have been built up at BFKH, CMI, DFM, IPQ, LNE, PTB, TUBITAK-UME, FC-ID (Figure 1) and used to develop the pH_{abs} measurement procedure, which can be used as reference procedure.
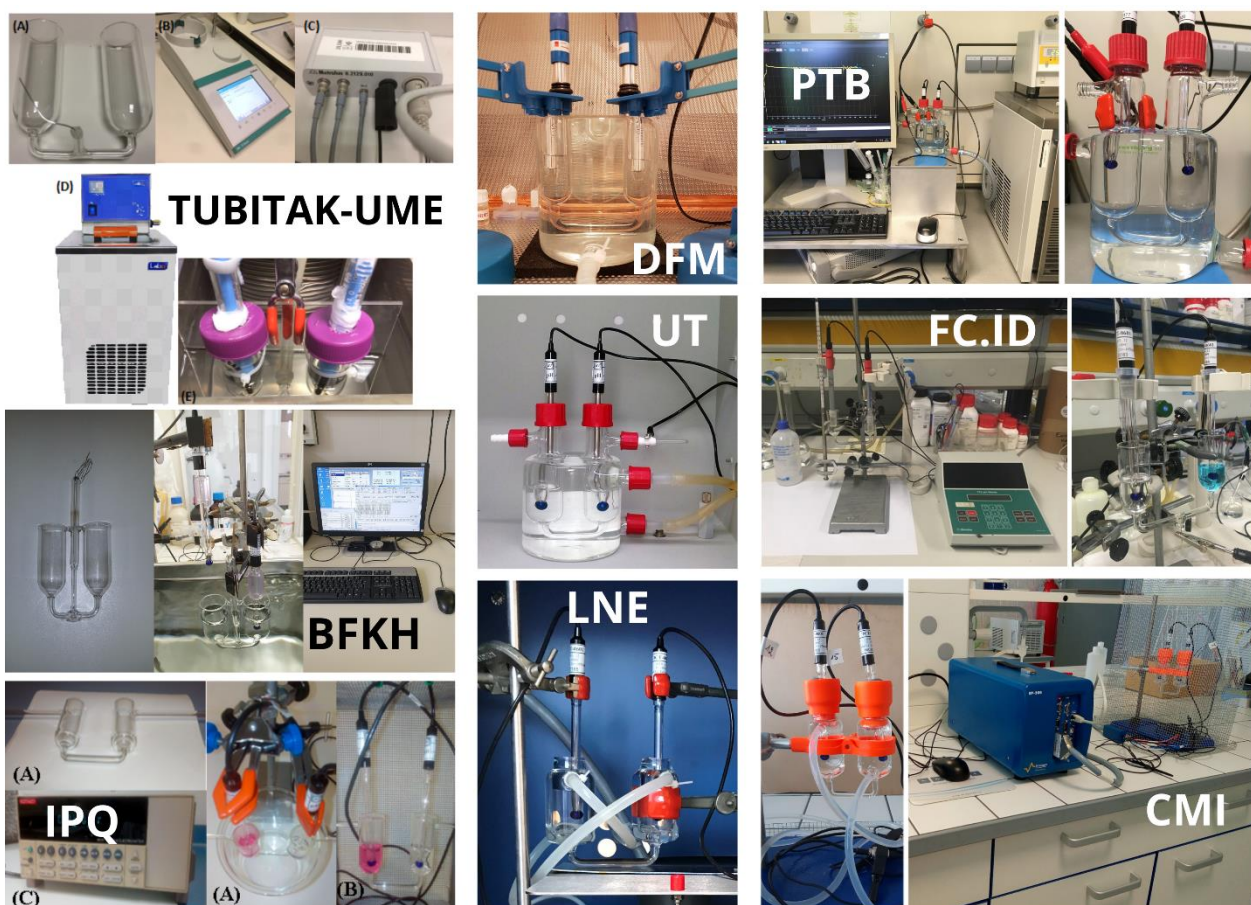
Figure 1: Differential potentiometry measurement setups (reference method) implemented at partnering institutes of JRP project

Because the conventional aqueous pH scale is the most prominent, it is favourable to define the $pH_{abs}^{H_2O}$ value to align the values of the pH_{abs} and the conventional aqueous pH scale. This means that the $pH_{abs}^{H_2O}$ of any aqueous solution is equal to its conventional pH value and in any other solvent, the $pH_{abs}^{H_2O}$ value corresponds the proton's chemical potential equal to that in the aqueous solution with the same pH value. A measurement procedure for $pH_{abs}^{H_2O}$ measurement has been developed by 9 project partners on the basis of a differential potentiometric method; IL [N$_{2225}$][NTf$_2$] was supplied by one of the partners (ALU-FR) and is now also available commercially. The $pH_{abs}^{H_2O}$ values are assigned by a so-called ladder approach outlined in Figure 2. The determination of $pH_{abs}^{H_2O}$ of a solution from a ladder of differential potentiometry measurements involves selecting the analysed unknown solutions and reference pH buffers and determining the potentials, ΔE_m, from cells built from several possible combinations of these solutions. It is essential to take care that the pH difference between any two solutions in the ladder is obtainable by at least two independent pathways of measurements – two "steps" on the measurement "ladder".
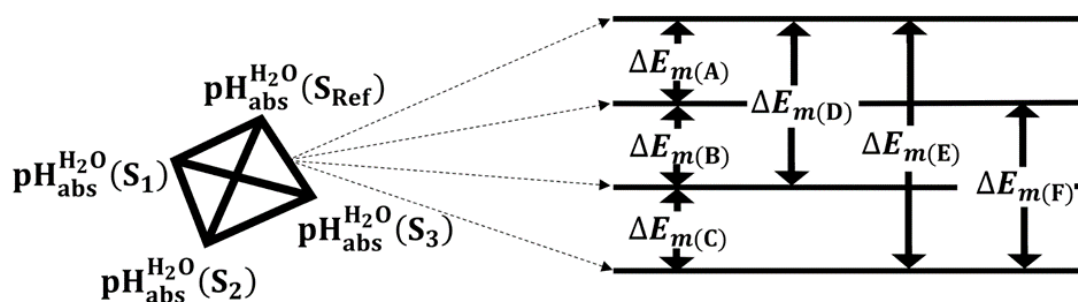
Figure 2. Ladder of differential potentiometry for determining the $pH_{abs}^{H_2O}$ of three unknown solutions (S1, S2 and S3) referenced to one reference solution (S_{Ref}). The $\Delta E_{m(x)}$ represent the potential of cells built from all solutions combination (S_i vs S_j; where $i \neq j$ =1, 2, 3 or Ref).

As to assess the general fitness for purpose and comparability of the measurement reference procedure, different aqueous standard pH buffers have been measured by BFKH, CMI, DFM, IPQ, LNE, PTB, TUBITAK-UME, FC-ID and UT and the deviations of the measured $pH_{abs}^{H_2O}$ from the expected $pH_{abs}^{H_2O}$ values among the institutes have been compared.

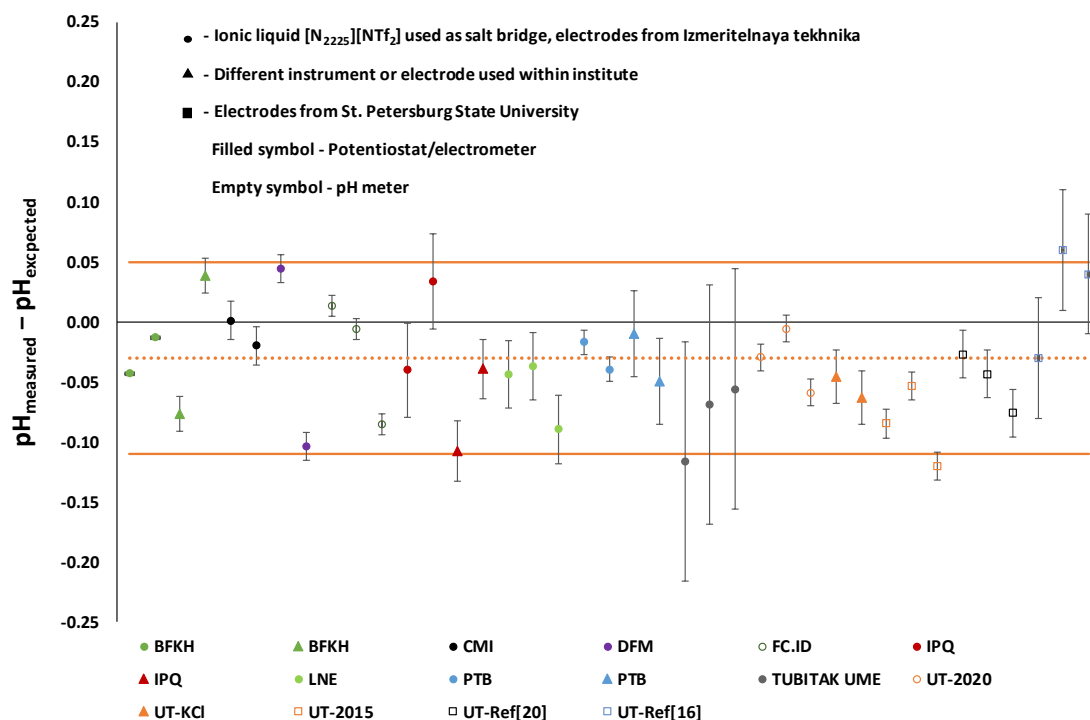**Figure 3**: $pH_{abs}^{H_2O}$ differences (measured vs. expected) obtained with differential potentiometry measurement setups implemented by partners of JRP UnipHied project. Orange lines represent the target standard uncertainty.

The application of the reference pH_{abs} method is considered to be not straightforward since the ladder approach necessary to assign $pH_{abs}^{H_2O}$ values is laborious involving a considerable number of measurements to be carried out. Therefore, an alternative, easier, method was proposed based on potential measurements using conventional measurement equipment (see Figure 4), namely glass electrode half-cell and a Ag/AgCl double junction reference electrode with two filling solutions: concentrated KCl (aq, min. 3 M) as inner filling solution, and the $[N_{2225}][NTf_2]$ ionic liquid outer filling solution, acting as an ionic liquid salt bridge (ILSB).
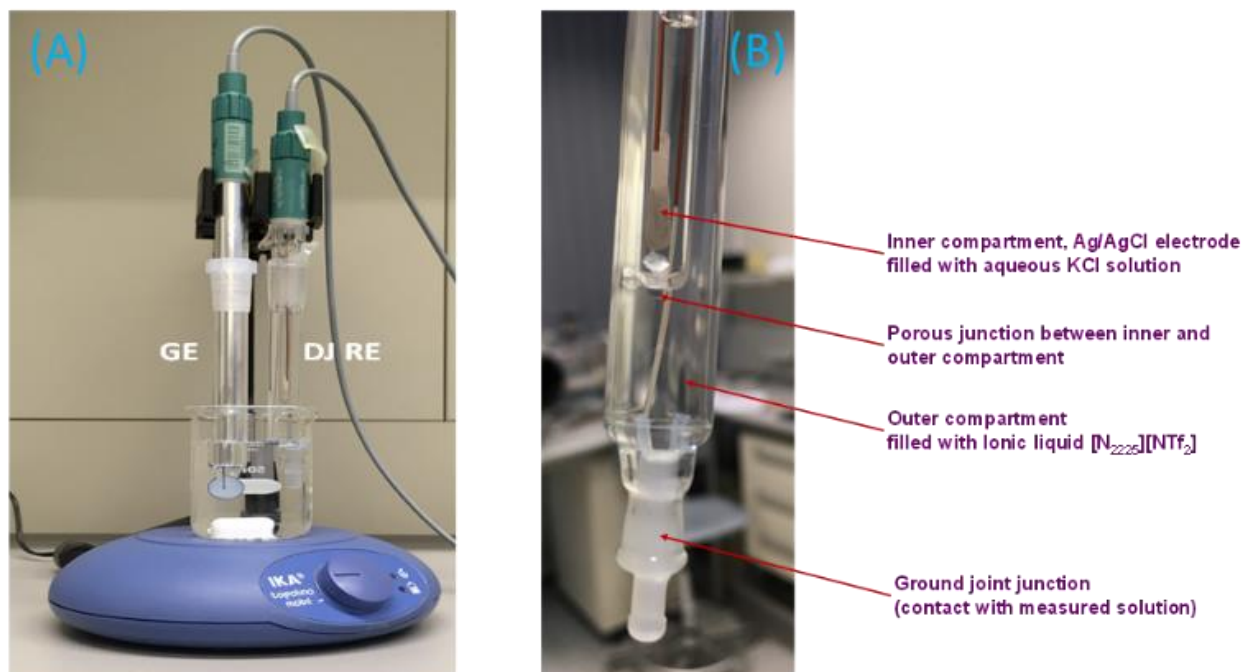
Figure 4: (A) An example of $pH_{abs}^{H_2O}$ measurement setup composed of a glass electrode half-cell (GE) and a double junction reference electrode (DJ RE) and (B) An example of double junction reference electrode with ionic liquid (IL) in the outer compartment.

An uncertainty budget for $pH_{abs}^{H_2O}$ measurement values has been established based on GUM and Monte Carlo simulation approach. To this purpose, input variables influencing $pH_{abs}^{H_2O}$ measurement values have been identified and quantified. The uncertainty due to possibly incomplete elimination of the residual liquid junction potential across the two junctions (solvent 1│IL and IL│solvent 2) represents the main factor (up to 90 %) affecting the overall uncertainty budget. As such, uncertainty calculations show that for the buffered mixed aqueous-organic solvents, the target standard uncertainties of 0.15 fixed for $pH_{abs}^{H_2O}$ measurement values can be reached. Reducing the uncertainty due to possibly incomplete elimination of the residual liquid junction potential may be achievable in the future with more targeted (i.e. involving a narrower selection of systems) studies of the LJP.

Measurement redundancy among partners is key to ensuring that a method, and the quality of its results are completely understood. An interlaboratory comparison has been organized between the project partners (BFKH, CMI, DFM, IPQ, LNE, PTB, TUBITAK-UME, FC-ID, UT and ALU-FR) on samples with different complexities. To simulate possible routine laboratory analysis, the comparison focussed on the alternative $pH_{abs}^{H_2O}$ method (see Figure 5). This method has been applied on three buffer solutions prepared in water, pure ethanol, and a water-ethanol mixture (50 wt %). LNE prepared, characterized and distributed to each participant the buffer solution prepared in the matrix simulating seawater, whereas the two other buffer solutions have been prepared by each participant to the comparison based on a common agreed excel template. For all three samples, the obtained results were found to be consistent between the participants. Additional results obtained from the reference method by LNE (saline buffer), UT (water-ethanol matrix) and PTB (pure ethanol matrix) were found to be consistent with results from the alternative method, independent from the used electrode. The findings prove the robustness of the $pH_{abs}^{H_2O}$ measurement procedure.
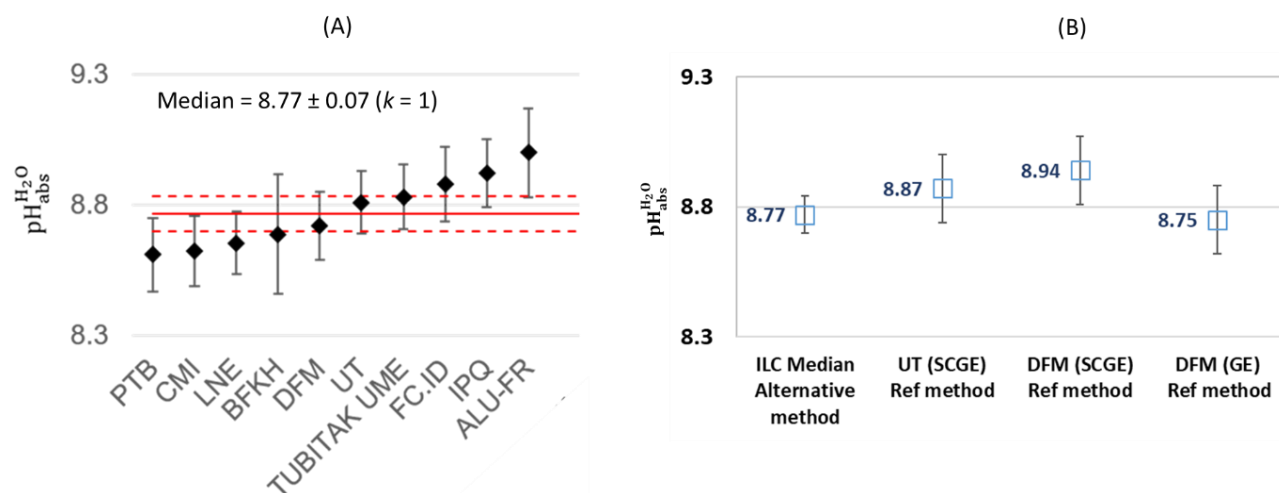
Figure 5: (A) Measurement results with corresponding standard uncertainties for the formate buffer (10 mM) in pure ethanol in increasing order of value reported for the interlaboratory comparison performed with setup shown in Figure 4. Solid contact glass electrodes (SCGE) were used to perform measurements. The proposed interlaboratory comparison reference value (Median) is displayed as the solid red line together with its standard measurement uncertainty (dashed red line); (B) Additional information values obtained from the reference method with different electrodes.

The electrodes used by the partners during the project lifetime were solid contact glass electrodes (SCGE), known for their good performance in non-aqueous solvents. These electrodes are not common and therefore are difficult to obtain. Currently they can be bought from only one company. From a metrological perspective, it is desirable that the measurand is independent on the instrument used to measure it. Consequently, during the project lifetime, the possibility of using other glass electrodes from different manufacturers i.e. Horiba Scientific (PTB), Radiometer (DFM), Mettler Toledo (PTB), Metrohm (BFKH, IPQ, LNE, PTB), Sentek (CMI), Hamilton (DFM), etc., was explored. The performed $pH_{abs}^{H_2O}$ measurements showed that all electrodes give acceptable results in standard aqueous buffers (Fig. 3). In more complex media such as unbuffered mixtures of ethanol, methanol and acetonitrile with water, limited systematic effects were noticed between half-cell glass electrodes and SCGE. However, single-junction combination pH electrodes are not recommended for $pH_{abs}^{H_2O}$ measurements as they are suffering of a leakage of KCl into the analysed water-organic mixture. At the same time, double-junction combined glass electrodes can be used. In summary, it was found that $pH_{abs}^{H_2O}$ is to a large extend, independent of the user, cell design and instrument used to measure the potential difference between the two electrodes i.e. potentiostats, electrometers and pH meters.

The IL used during the project is also commercially available. Therefore, ILSB setups developed in the project for measuring $pH_{abs}^{H_2O}$ are easily manageable for adoption by routine laboratory analysis.

Objective 1 was achieved, since 9 partners developed $pH_{abs}^{H_2O}$ reference setups and 10 partners set up the alternative method, implemented the corresponding procedures and are 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. 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 and doi.org/10.17504/protocols.io.byh2pt8e.

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 the 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. Salt bridges (SB) are commonly used to minimize LJP contributions to the electric

cell potential by creating two liquid-liquid junctions whose LJPs tend to cancel each other out. The underlying idea is that a highly concentrated electrolyte, whose cations and anions have the same transference numbers, takes over the charge transport between both half-cells of an electrochemical cell. In case of identical solvents in both half-cells the LJP can be calculated moderately well with e.g. the Henderson-equation. For all-aqueous cells (i.e. the solvent in both half-cells is water) the KCl-SB (potassium chloride is the electrolyte) is most common, and the LJPs nearly cancel out, depending on the particular case. However, in case of different solvents, the Henderson-equation and similar approaches are not suitable. The reason is the direct contact of two different solvents at least at one of the junctions, from which solvent-solvent interactions (not accounted for by the Henderson equation) arise contributing to the LJP.

Ionic liquids (IL) are electrolytes in liquid state of aggregation without being solvated, i.e. no solvent is present. Thus, solvent-solvent interactions are excluded if a SB is filled with an IL (ILSB). Further, due to their high concentration almost only the IL-ions cross the S│IL-junction between the solvent S and the IL undertaking the charge transport in the cell.

The minimisation of the liquid junction potential by using a salt bridge formed by an "ideal" ionic liquid (IL) was studied in a number of systems formed by water and non-aqueous solvents such as acetonitrile, ethanol and methanol. The ideal character of the IL requires, among others, close to identical transference numbers, or ionic mobilities, for cation and anion both in the pure IL and in solution, close to identical solvation Gibbs energies of the ions, while being inert by respect to the solvents. The IL $[N_{2225}][NTf_2]$ 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. To this purpose, a new methodology aiming 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 and was implemented by ALU-FR. 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 approximate solution can be found by statistical analysis using the method of least squares.

The network is used to determine the Gibbs transfer energy of the redox system Ag^+/Ag from water to various solvents $\Delta G_{tr}°(Ag+, H_2O \rightarrow S)$. Combinations with the solvents S_i and S_k being water (H_2O), acetonitrile (AN), propylene carbonate (PC), dimethylformamide (DMF), ethanol (EtOH) and methanol (MeOH) have been studied. The cell used for measurements (identified as A in Figure 6) is:

$$Ag│AgZ_m\,(c,\,S_i)\;│\;[N_{2225}][NTf_2]\;│\;AgZ_n\,(yc,\,S_j)│Ag$$

$$\qquad\qquad\text{LJPS}\qquad\qquad\qquad\text{LJPS}_j$$
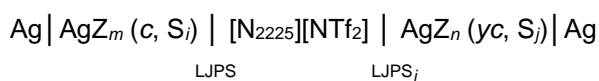
The network includes variations of concentrations c of the redox active salt AgZ (and the concentration ratio expressed by y) as well as the nature of counterion Z^- of the Ag^+ ion which is the electroactive species, expressed by n and m, resp. (whereby m may or may not be identical with n), and the solvents with $i = j = 1 - 6$, i.e. the above defined six solvents.

As such, the network analyzed during the project comprises 145 individual measurements. Comparison of the obtained experimental values to the calculated values enabled assessment of the overall liquid junction potential hence establishing whether contributions arising from solvent-solvent interactions equals to zero.
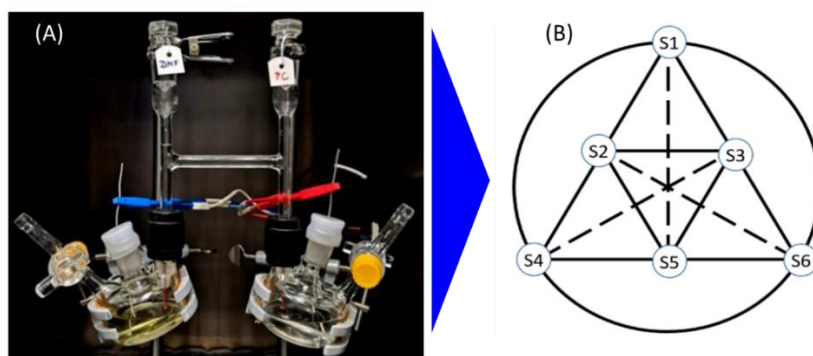
Figure 6: Experimental setup (A) and sketch of the Network (B) used to evaluate the LJPs. The nodes in (B) are the half-cells and the measurements are the connection lines in-between them.

The Gibbs transfer energy of the redox system Ag^+/Ag from water to acetonitrile (AN), $\Delta G_{tr}°(Ag^+, H_2O \rightarrow AN)$, was determined to -25.1 kJ mol^{-1} with the accuracy level of 6 mV, see below. A widely accepted literature value is -23.2 kJ mol^{-1} having an estimated uncertainty of $3 - 6$ 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 the 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. LJP(H_2O-IL) – LJP(AN-IL), is stable and remains within 6.3 mV, equivalent to 0.61 kJ mol^{-1} or 0.11 pH-units, respectively, in the case of low ionic strength solutions. This 0.11 in pH is used as the standard uncertainty contribution due to possibly incomplete LJP elimination in other tasks of this project. For water-acetonitrile, LJPs are remarkably insensitive against the change of the ionic strength of the electrolyte solutions (silver salts of type Ag^+Z^-) as long as it remains within 0.1 to 10 mmol L^{-1} and against influx of solvent into the ILSB.

In addition, this indicates that the redox system Ag^+/Ag under investigation doesn't affect the LJPs either.

The Gibbs transfer energy of the redox system Ag^+/Ag from water to EtOH, $\Delta G_{tr}°(Ag^+, H_2O \rightarrow EtOH)$ was determined to 1.6 kJ mol^{-1} and from water to MeOH, $\Delta G_{tr}°(Ag^+, H_2O \rightarrow MeOH)$ to 3.8 kJ mol^{-1}.

These findings can be considered reliable since they are in good agreement with literature data. The consistency of the values is 0.55 kJ mol^{-1}.

If the ionic liquid [N_{2225}][NTf$_2$]) forms the salt bridge, the LJP contributions are strictly valid for the studied solvents i.e. water, acetonitrile, ethanol, methanol, dimethylformamide and propylene carbonate. However, it is reasonably expected that they are equally valid for a variety of other solvents with not too low dielectric constant.

Objective 2 was achieved since the "close to ideal" IL studied within the project allows the experimental implementation of the $pH_{abs}^{H_2O}$ scale for several complex organic solvents. 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. 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 pH$_{abs}$ values for a wide variety of media (e.g., industrial mixtures, soils/waters, food products, biomaterials).

Although pH measurements are primarily performed in aqueous (water-based) samples, they are also conducted in a vast variety of industries and therefore in a diverse set of media i.e., different solvents, solvent mixtures, mixed aqueous and non-aqueous dispersions. Within JRP UnipHied, several solvents and their mixtures with water, are chosen as examples for laboratory analysis. Ethanol is selected due to its use as bioethanol in fuel applications. Methanol and acetonitrile are selected due to their extensive use in liquid chromatography separation.

The quality of $pH_{abs}^{H_2O}$ measurements carried out by DFM, IPQ, PTB, UT and LNE in pure ethanol and its mixtures with water greatly depends on the presence of the buffering agents. In water-ethanol mixtures without

a buffer system, the measured signal and consequently the $pH_{abs}^{H_2O}$ values have poor quality. Figure 7 shows $pH_{abs}^{H_2O}$ values measured by DFM, IPQ, PTB, UT and LNE for different water-ethanol mixtures with different types of electrodes.
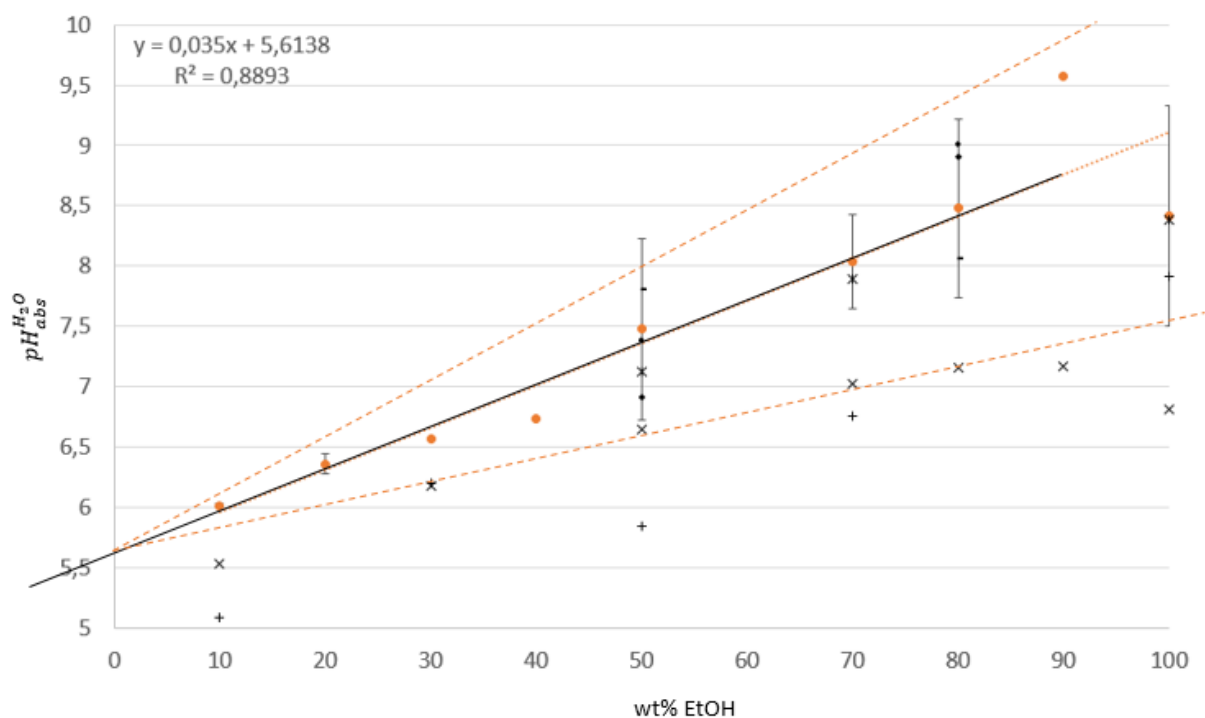

Figure 7: $pH_{abs}^{H_2O}$ values measured for unbuffered water-ethanol mixtures. Ethanol content (wt%) was varied between 10 % to 100 %. Error bars represent the distribution of values measured at different institutes, partners of JRP UnipHied. Measurements have been done with several types of electrodes summarized in Table 1.

Table 1: Glass electrodes employed for measuring $\mathbf{pH_{abs}^{H_2O}}$ of water-ethanol mixtures

Symbol	Electrode type	Electrode
●	SCGE	Izmeritelnaya Tekhnika EST-0601
x	Combination	Metrohm 6.0269.100
*		E11M001 Radiometer
+ and -	Half cell	Metrohm 6.0150.100
●		Mettler-Toledo DG300-SC
◊		Horiba Scientific/Laqua Model 1076A-10C

For unbuffered ethanol and water-ethanol solutions, $pH_{abs}^{H_2O}$ is likely to exhibit a value range, rather than a singular value. For example, for pure ethanol solutions, standard uncertainties up to 0.6 have been calculated. The obtained results enabled to understand sensitivities and challenges of measuring $pH_{abs}^{H_2O}$ in such systems. The quality of $pH_{abs}^{H_2O}$ obtained for pure ethanol is 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 pH_{abs} in achieving metrological

comparability, its implementation will have, at least for the moment, a limited impact on existing bioethanol-related standards.

A possible solution enabling to affect the quality of the data obtained for pure ethanol and water-ethanol mixtures, especially by improving the stability of the signal, was proposed by UT during the project lifetime. The solution consists in adding organic salts such as $N_{2225}NTf_2$ or Et_4NClO_4 (tetraethylammonium perchlorate) to the measured solvent. The salt concentration in the analysed solutions should be between 0.01 and 0.05 M. The influence of the nature and concentration of adding organic salts has been tested on water-ethanol mixture (50 wt %). The obtained data are shown in Table 2. Maximum standard uncertainties of 0.2 can be estimated for the measured $pH_{abs}^{H_2O}$ values.

Table 2: Influence on additive concentration on $pH_{abs}^{H_2O}$ values for water-ethanol mixture (50wt%)

Concentration (mol L^{-1})	$[N_{2225}]^+[NTf_2]^-$	Et_4NClO_4
0.01	7.93	7.89
0.02	8.00	–
0.03	7.95	7.94
0.05	7.63	7.84

Buffered water-ethanol solutions prepared in hydroethanol mixture (50 wt%) and containing potassium hydrogen phthalate (0.05 mol/kg) or equimolal (0.15 mol/kg) disodium hydrogen orthophosphate and potassium hydrogen orthophosphate or sodium tetraborate decahydrate (0.1 mol/kg), show a stable signal and good reproducibility but a limited stability in time. Preliminary findings obtained by DFM and LNE during UnipHied project, suggest against the pursuit of certifying buffered water-ethanol mixtures as certified reference materials. Instead, precise recipes, including instructions for quality and treatment of salt(s), water, and ethanol, mixing, storage, and recommended bottle material (e.g., glass, plastic), could be made available. Buffered water-ethanol mixtures, with assigned $pH_{abs}^{H_2O}$ values (and associated uncertainty), could then be reproducibly created for in-situ use (i.e., at a routine measurement laboratory).

Measurements of $pH_{abs}^{H_2O}$ have been performed by UT on a number of 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 $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ measurement systems.

ANB Sensors assessed the feasibility of developing a novel and ultimately calibration-less commercial sensor that can determine $pH_{abs}^{H_2O}$ values for non-ideal solutions. These activities initially focused solely on developing the sensor transducer and sensor interface to operate reliably in the mixed solvent environment. To this end, the first set of electronics boards were also built during the course of the project to understand the feasibility of commercialising a full sensor post project. The sensor transducer incorporated redox couples whose potential can be linked to pH$_{abs}$ and redox couples that are essentially insensitive to the solvent. 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 complex media. Prototype 2, schematically represented in Figure 8, overcame these issues by developing a complete reference cell and an electrode construction to minimise the issues specific to organic solvents which are typically low conductivity media.
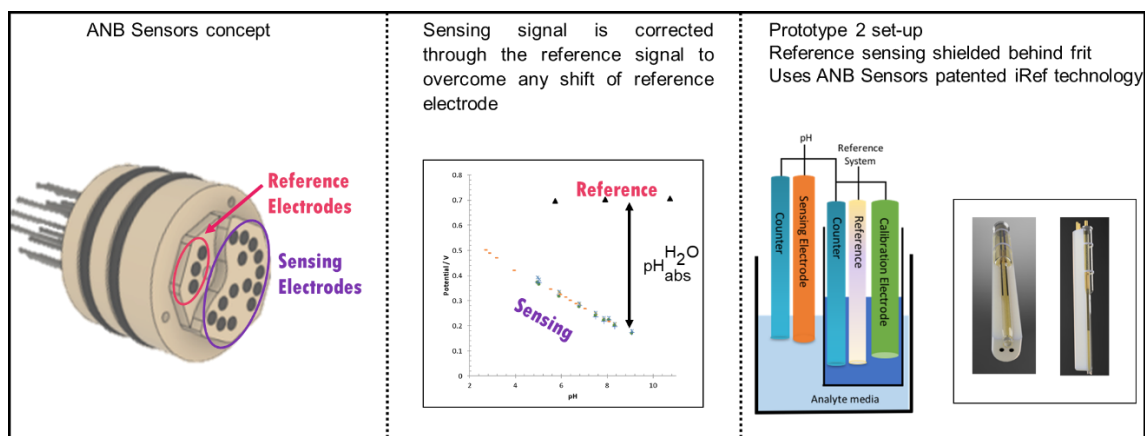
Figure 8: Principle of $pH_{abs}^{H_2O}$. measurements with second prototype of ANB Sensor. The $pH_{abs}^{H_2O}$ of the solution is derived from measuring the difference in the voltametric peak potential of each electrode. The sensor used redox couples so that its calibration is "anchored in nature", i.e., this sensor needs some verification, but not regular calibration. Square wave voltammetry provides the peak potential of the sensing system and reference system.

Specifically, for the second prototype, the external reference and counter electrodes were placed in a proximity to the sensing element so that solution conductivity would not dominate the signal in the cases of low solution resistance. Moreover, to overcome the issue of the reference electrode potential shift when directly immersed in solutions of high buffer capacity, the reference sensing system was placed behind electrically conducting frit in a solution of 1 M LiCl. The Ag/AgCl reference wire was housed in the same solution and a counter electrode was also placed within the chamber. Some of the $pH_{abs}^{H_2O}$ results obtained with Prototype 2 developed by ANB Sensors together with quality of Measurement values are provided in Table 3. The measurements were taken across a period of three repeats across 5 days without maintenance between measurements using two different sensing chemistries.

Table 3: $pH_{abs}^{H_2O}$ values determined with Prototype 2 developed by ANB Sensors

$pH_{abs}^{H_2O}$ assigned with reference method		Electrode 1	Electrode 2
4.1 ± 0.1	Standard buffer solutions	3.25 ± 0.45	3.89 ±0.04
6.9 ± 0.1		6.41 ± 0.23	6.69 ± 0.03
9.2 ± 0.1	Water matrix	8.82 ± 0.08	8.93 ± 0.07
5.9 ± 0.1	Buffer solutions	5.62 ±0.02	5.33 ± 0.36
8.8 ± 0.1		8.67 ± 0.06	8.04 ± 0.14
11.4 ± 0.1	Water – ethanol (50 wt%) matrix	11.25 ± 0.06	11.51 ± 0.17

The next steps for this are to send the prototype sensor out for external testing with potential end users. To achieve this ANB Sensors are developing the control electronics for the sensor such that a single package can be delivered to third parties incorporating both the sensing element and the electronics.

In addition to the objective of studying organic solvents and their mixtures with water, the applicability of $pH_{abs}^{H_2O}$ to saline solutions was studied by LNE and UT through a Research Mobility Grant (RMG). An RMG researcher from UT has been hosted by LNE for 6 months. To this purpose, differential potentiometric measurements, with a salt bridge of ionic liquid $[N_{2225}][NTf_2]$, were carried out aiming at overcoming problems related to residual liquid junction potentials that affect the quality of such measurements. The ability to measure $pH_{abs}^{H_2O}$ with acceptable uncertainty was evaluated at LNE 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 $pH_{abs}^{H_2O}$ concept, first of all, because of insufficient LJP compensation ability of [N$_{2225}$][NTf$_2$] under such high ionic strength 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.

Objective 3 was achieved as ILSB setups for easily measuring $pH_{abs}^{H_2O}$ 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.

5 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 $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ 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 [N$_{2225}$][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 $pH_{abs}^{H_2O}$ measurement procedures in solvents other than water. The exercise highlighted that the results from different setups are comparable. The IL [N$_{2225}$][NTf$_2$] used during the project is now commercially available also from other companies. Therefore, the ILSB setups developed in the project for measuring $pH_{abs}^{H_2O}$, 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 $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ in a simple way is considered promising for a further uptake of pH$_{abs}$ 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 $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ 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 pH_{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 $pH_{abs}^{H_2O}$ 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 pH_{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. $pH_{abs}^{H_2O}$ 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, pH_{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 pH_{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 pH_{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 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 $pH_{abs}^{H_2O}$ to saline solutions. To this purpose, differential potentiometric measurements, with a salt bridge of ionic liquid $[N_{2225}][NTf_2]$, were carried out aiming at overcoming problems related to residual liquid junction potentials that affect the quality of such measurements. The ability to measure $pH_{abs}^{H_2O}$ 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 $pH_{abs}^{H_2O}$ concept, first of all, because of insufficient LJP compensation ability of $[N_{2225}][NTf_2]$ 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.

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7   Contact details

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