

Minutes of the joint meeting of TPWS/IRS/SCSW

Clerk of Minutes of SCSW: Olaf Hellmuth, Dresden, June 15, 2016

1. Opening remarks; adoption of agenda:

The session was opened by Alan Harvey. The agenda was corrected by addition of **item 12.3** concerning an ISO request on work properties for calibration in the oil industry (talk given by Rich Pawlowicz).

Prof. Kretzschmar informed the attendees of Prof. Phil Hill, British Columbia, who passed since the last IAPWS meeting in Stockholm. Prof. Wolfgang Wagner remembered the great contributions of Phil Hill to the work on the International Steam Table, the EoS of ordinary and heavy water, his activities in the WG TPWS and as a member of Westport Innovations Inc. Prof. Wagner characterized Phil Hill as a "gentleman through and through".

2. Clerk of minutes:

Jan Hruby for TPWS, Ingo Weber for IRS, Olaf Hellmuth for SCSW.

3. International collaborative projects:

The working groups recommend the EC to enhance the financial support for M. Duzka, Czech Republic, to continue the work on the EoS of heavy water in U.S. at the University of Maryland (group of Prof. M. Anisimov and J. Sengers). The planned regular budget was negatively affected by sudden currency exchange disturbances in the context of the Brexit decision. The EC is asked for compensation of the effective loss in the value of available Dollars required to continue with the work.

In the following, the minutes of the SCSW related issues of the joint TPWS/SCSW sessions are listed. The numbering corresponds to those in the **"Preliminary Agenda for the IAPWS Working Group Thermophysical Properties of Water and Steam (TPWS), Dresden, Germany, September 12-15, 2016"**. Items 1 to 8 belong to TPWS and IRS issues. Highlighted details are for the report to the EC.

9. Working group report on humid air fugacity and enhancement factor (by O. Hellmuth)

A new virial approximation of the enhancement factor of water in humid air and the water vapour mole fraction in saturated humid air, respectively, has been proposed. The difference between the approximative and numerical solutions of the underlying thermodynamic model was found to be statistically not significant and by an order of magnitude lower than the difference between the previous fitted Greenspan expansion (analytical form) of the enhancement factor and the underlying thermodynamic model of Hyland and Wexler. From an uncertainty analysis based on Monte-Carlo simulations it was found that the difference between relative fugacity and relative humidity is statistically significant already at atmospheric pressure. It was shown that the consideration of real-gas effects in the humidity determination at atmospheric pressure leads to an increment in the latent heat flux which is by a factor of 500 larger than the energy flux increment required to cause a global warming of 0.5 K per 30 years. Proper resolution of global-warming effects in the oceanic evaporation rates will definitively require real-gas effects in the marine atmosphere to be allowed for.

A task group (members: O. Hellmuth, R. Feistel, A. Harvey, J. Hruby, J. Cooper) was established to formulate the requirements and content of a possible IAPWS guideline as a contribution to realise the roadmap fixed at the ICPWS 2013 workshop on humidity and to support the further cooperation of IAPWS with BIPM.

11. Report of the task group on the extension of range of formulation for thermodynamic properties of seawater (by R. Feistel)

The works aim at extension the TEOS-10 standard to higher temperatures (up to 313 K), to higher pressures (up to 60 MPa) and to higher salinities (up to 45 k/kg). New speed-of-sound data are provided by Lago et al. (2015), and new vapor pressure data by J. Safarov). New measurement data are also expectable from PTB Braunschweig. **The task group is ordered to continue its work.**

12.1. IAPWS/IAPSO/SCOR activities (by Rich Pawlowicz)

An open point on the agenda is the finalization of an "best practise guide" for high-precision density measurements by pooling collective experience. This task has high priority.

The next BIPM-CCT meeting is postponed to spring 2017. SCSW recommends to EC that IAPWS support sending a representative to this meeting (as was approved at the 2015 IAPWS-EC meeting).

12.2 IAPWS/BIPM cooperation (by R. Feistel)

The speaker presented a time series on the citation number of the joint IAPWS/BIPM Metrologia position paper on metrological needs for SI-compatible definition of salinity, pH value, and relative humidity. By 10 September 2016, the following citation numbers has been reached:

(a) Part 1: overview: 2887; Part 2: salinity: 1763; Part 3: pH value: 1821; Part 4: RH: 3714; This makes these papers the most downloaded in Metrologia at present.

At TEMPMEKO 2016 Lovell-Smith, Feistel and Hellmuth gave a presentation on the topic "Toward a general definition of RH" (including the so-called extended range defined by the constraint $p < e_{w,sat}(T)$).

12.3 ISO requests for IAPWS assistance on use of water in petroleum industry (by Rich Pawlowicz)

They have a list of requirements for density correction factors as function of T aiming at the use of TEOS-10 also for natural waters like rivers and lakes which are of interest for oil exploration. Among the requirements the extension of the range of validity of TEOS-10 (temperature up to 95°C, salinity up to 140 g/kg; need for extended range isothermal compressibility) is listed as well as the availability of user friendly equations etc. The proposed list also includes possible research projects the oil industry is interested in. In order to specify the questions of common interest, especially the applicability of TEOS-10 to lakes and rivers, a task group is established to give detailed and hopefully positive answers to the ISO TG28 SC 2 WG4 chairman of the oil industry.

The task group (members: Rich Pawlowicz, Rainer Feistel, Andrey Anderko, Allan Harvey, Olaf Hellmuth) shall give a detailed reply, formulate items of common interests and to ask for the possibilities to provide some financial support. A representative of that ISO TG28 SC 2 WG4 working group should be invited to the next IAPWS meeting for further discussion of specific research targets.

13. Reports on seawater related topics

13.1 Seawater sampling handling (by G. Budeus)

The speaker gave an overview of his measurement program in seawater salinity and density and highlighted a number of sample handling problems that he has noticed though the use of his high-resolution instruments. His suggestions are worthy of attention. Several members of the audience noted that they also experienced the problem of outgassing and bubble formation from the sampling probes in particular.

13.2 Thermophysical properties of natural seawater (by J. Safarov)

The speaker gave an overview of his labs capabilities to measure a variety of thermophysical properties in natural waters from oceans and lakes.

13.3 CO₂ solubility in seawater at wide range range of salinities (by J. Safarov)

The speaker discussed the solubility of CO₂ in natural waters.

13.4 Updates of the EMPIR project (by S. Seitz)

This talk has been withdrawn. However, S. Seitz has requested a letter of support from IAPWS for his upcoming EMPIR project proposal. SCSW will propose that the EC supports this with a letter signed by the IAPWS president.

13.5. Absolute salinity and density using a hydrostatic weighing apparatus and using in situ sound velocity sensors (by H. Uchida).

Although Uchida was not present his colleague Y. Kayukawa presented preliminary results of his hydrostatic weighing measurements of the absolute density of standard seawater and many relative measurements (using the Anton Paar equipment) of standard seawater. Several audience members noted that they also found Anton Paar measurements of standard seawater resulted in a negative salinity anomaly.

13.6 Chinese Seawater Standard (by Y. Li)

The speaker presented the NCOSM institute and its certification process. NCOSM is a government-run marine measurements institute in China. They recently carried out a JCOMM salinity intercomparison project. NCOSM also creates Chinese Standard Seawater. Y. Li gave an overview of its comparison with IAPSO Standard Seawater.

13.7 Salinity anomalies in arctic rivers and hydrothermal vents (by Rich Pawlowicz)

The speaker presented salinity measurements employing both density-based and conductivity-based measurement techniques. The differences between the two approaches were found to depend on the chemical composition of the sampled water (open ocean, near rivers, near sea-ice, near hydrothermal vents). Studies on arctic rivers were carried out in summer 2015 as a part of the GEOTRACES program. Many rivers were reported to be "unconductive". The modeling of the salinity anomaly was found to perform quite well with a slight tendency for overprediction. The speaker strongly suggested that issues with Anton Paar measurements be resolved. Also, the North Pacific was reported to be a region of the largest salinity anomalies ("Line P" region). An intercomparison between TEOS-10, a semi-empirical model of R. Pawlowicz and measurements of salinity anomalies in this region revealed systematic differences between TEOS-10 and the semi-empirical model on one side and the measurements on the other side. Similar analysis has been performed in the Southern Pacific ("P18" region). The next steps are the repeat of line P measurements (done in June 2016) and P18 measurements (November 2016). A question of interest is to figure out, whether there is a sample handling problem or the observed effects are of physical origin. The speaker required to replicate measurements in another lab. There are interesting effects but artifacts must be safely excluded by further analyses (ongoing).

13.8 Salinity anomalies in the Baltic (by S. Weinreben)

The speaker reported on a decade worth of measurements of salinity anomalies in the Baltic Sea. No trend was found over time. He also noted a possible offset in measurements with the Anton Paar device. Comments by R. Pawlowicz noted that his model predictions of anomalies in the Baltic might compare well with the speakers measurements.

14. Chair: Rich Pawlowicz

14.1 Task group report on a guideline for the electrical conductivity of seawater (by Rich Pawlowicz)

The question of interest is how to link electrical conductivity $C/(S/m)$ to salinity $SA/(g/kg)$. It is known how to do it, but there is no reference document. The speaker stated the need for a guideline on conductivity of seawater with a comprehensive uncertainty analysis. The definition is given in the form of the conductivity formula with independent variables SA , t_{90} , p , and salinity anomaly. The final solution is presented in the form $SA = f(C, t_{90}, p, \text{salinity anomaly})$. There is a complicated calculational procedure with a number of intermediate variables (taking into account the structure of available primary data). An

estimation of the total uncertainty has been performed. Next steps include the finalization of the publication, the development of an IAPWS document, and the establishment of a task group. Items of cooperation with CCQM/BIPM have to be specified. R. Feistel noted that a new guideline plus a best practise measurements document are required! An IAPWS subgroup (members: Rich Pawlowicz, Rainer Feistel, Steffan Seitz, Trevor McDougall) is ordered to continue.

14.2 Task report on a supplementary release for a simplified density equation (by Rich Pawlowicz)

The report was about a supplementary release for a simplified density equation ($\rho=f(SA,CT,0)$, not yet documented). The problem is the use of CT as independent variable (CT=Conservative Temperature for oceanography, defined in TEOS-10, $CT=f(T,p,SA)$), which might not be used by non-oceanographers. Hence, we should not follow this path further, because an additional equation for CT is required. Recommendation that the task group should be disbanded.

14.3 Advisory note on IAPWS documents contributing to TEOS-10 (by Rainer Feistel)

The speaker presented an advisory note on IAPWS documents contributing to TEOS-10, draft version from 02 September 2016. Dan Friend: After editorial comments it should be adopted.

Recommendation to include an overview picture on the fundamental thermodynamic potentials. For the editorial committee:

Hyperlinks to IAPWS documents. Re-numbering according to new IAPWS annotation standard.

The cited nine IAPWS documents should be maintained at the IAPWS website.

Formal numbering of items should be revised.

Editorial committee: Allan Harvey, Jeff Cooper, A. Cook(?)

14.4 Recommendation for adoption (by vote)

15.1 Report of the task group on the use of covariances in IAPWS work (by Rainer Feistel).

The speaker identified several problems in the widely employed uncertainty analysis of empirical correlation equations. The IAPWS uncertainty analysis is also insufficient so far! A list of deficiencies has been presented (e.g. not providing covariances of the regression coefficients, ignoring statistical and cross-relation effects, analysis only partially relying on GUM recommendations.)

Basis: Feistel et al. (2016), discussion paper on uncertainty analysis.

Step 1: covariance propagation; Step 2: covariance of prediction.

Conclusions from a simple example IAPWS-95 Parameter correlation-coefficient matrix; application of the calculus to the IAPWS 2015 Eqs. for the second and third virial coefficients $B_{ww}(T)$, $C_{www}(T)$. The GLS uncertainty propagation method underestimates the uncertainty. The basis information of the new method is the covariance matrix. It should be mandatorily reported by experimentators (e.g. in a digital supplement) !!!

Items of the discussion: mathematics o.k., but provision of the covariance matrix is the problem; How to incorporate systematic errors in the calculus (very important)? Practical problems to fulfil/provide the covariance matrix from the experiments. Dan Friend: What can be recommended?

There are still several unanswered questions. The task group should continue to work over the years! Application to the next revision of virial coefficients. Continue and check this within framework of internal use (TPWS working group). Recommendation within this working group to provide parameter covariance for new correlation equations to continue with this interesting task.

19.1 For EC: proposal for funding increase for cooperation with Maryland university

D. Friend = Gibbs award representative for TPWS

Rich Pawlowicz = Gibbs award representative for SCWS

Ingo Weber = Gibbs award representative for IRS

20. Membership

Withdrawn from SCSW: P. Spitzer (retired).

21. Contribution to press release

22. Preparation of the formal motion to the EC

It was approved that the chairman should do this.