Department of Energy Technology

Advances in Humidity Measurement Applications in Metrology

Hannu Sairanen

Aalto University

DOCTORAL
DISSERTATIONS

Aalto University publication series
DOCTORAL DISSERTATIONS 212/2015
VTT SCIENCE 119

Advances in Humidity Measurement Applications in Metrology

Hannu Sairanen

A doctoral dissertation completed for the degree of Doctor of Science (Technology) to be defended, with the permission of the Aalto University School of Engineering, at a public examination held at the lecture hall K216 of the school on 21 December 2015 at 12.

Aalto University
School of Engineering
Department of Energy Technology
Applied Thermodynamics

Supervising professor
Prof. Risto Lahdelma

Thesis advisor
Dr. Martti Heinonen

Preliminary examiners
Prof. Riitta Keiski, University of Oulu, Finland
Dr. Hisashi Abe, National Metrology Institute of Japan (NMIJ), AIST, Japan

Opponent
Dr. Vito Fernicola, National Institute of Metrological Research (INRiM), Italy

Aalto University publication series
DOCTORAL DISSERTATIONS 212/2015

VTT SCIENCE 119

ISBN 978-952-60-6576-2 (printed)
ISBN 978-952-60-6577-9 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)
http://urn.fi/URN:ISBN:978-952-60-6577-9

ISBN 978-951-38-8377-5 (printed)
ISBN 978-951-38-8376-8 (pdf)
ISSN-L 2242-119X
ISSN 2242-119X (printed)
ISSN 2242-1203 (pdf)
http://urn.fi/URN:ISBN:978-951-38-8376-8

Unigrafia Oy
Helsinki 2015

Finland

NORDIC ECOLABEL
441 697
Printed matter

Aalto University

Aalto University, P.O. Box 11000, FI-00076 Aalto www.aalto.fi

Abstract

Author
Hannu Sairanen

Name of the doctoral dissertation
Advances in Humidity Measurement Applications in Metrology

Publisher School of Engineering

Unit Department of Energy Technology

Series Aalto University publication series DOCTORAL DISSERTATIONS 212/2015

Field of research Applied Thermodynamics

Manuscript submitted 5 August 2015 **Date of the defence** 21 December 2015

Permission to publish granted (date) 26 October 2015 **Language** English

☐ **Monograph** ☒ **Article dissertation (summary + original articles)**

Abstract

A significant part of the development of humidity measurement applications in metrology is carried out due to the climate change. Within this thesis metrology tools for humidity measurements in energy gases were developed. In addition, a new method and apparatus for radiosonde calibrations were developed and constructed to provide traceability to the System of Units (SI) and thus improve the quality of radiosonde measured humidity data.

Metrology tools for humidity measurements of energy gases were developed by studying the water vapour enhancement factor for methane. A new hygrometer-based calibration method was developed and a set-up was assembled for calibrations of liquid microflows from syringe pumps. Metrological validation for the set-up including uncertainty analysis was carried out for flow rates from 0.1 ul min^{-1} to 10 ul min^{-1}. The set-up was applied in development and construction of a novel apparatus to measure the enhancement factor. The apparatus was metrologically validated by air and methane measurements for pressures up to 6 MPa and dew/frost-point temperatures from -50 °C to +15 °C. Utilising this apparatus, new experimental enhancement factor data was measured. Along with literature data on equilibrium states of water vapour in methane, new literature-based enhancement factors were calculated. The experimental and the calculated data were combined and an equation expressed as a function of pressure and dew-pointe temperature was fitted to the data. The equation covers dew/frost-point temperature range from -23 °C to +20 °C and pressures below 7 MPa and its expanded uncertainty ($k = 2$) is 0.23 in the whole range.

Radiosondes operate over a wide range of humidity, temperature and pressure values and thus their calibrations should also cover these conditions. However, calibrations performed with traditional methods at cold temperatures and low humidity require a lot of time and therefore a customized apparatus was developed and constructed. The new apparatus enables significantly shorter calibration times within the temperature range from -80 °C to +20 °C and the dew/frost-point temperature range between -90 °C and +10 °C. The apparatus fulfils the requirements set by Global Climate Observing System (GCOS) and its GCOS Reference Upper-Air Network (GRUAN).

Keywords Calibration, dew-point temperature, enhancement factor, humidity, methane, radiosonde, traceability, uncertainty

ISBN (printed) 978-952-60-6576-2 **ISBN (pdf)** 978-952-60-6577-9

ISSN-L 1799-4934 **ISSN (printed)** 1799-4934 **ISSN (pdf)** 1799-4942

Location of publisher Helsinki **Location of printing** Helsinki **Year** 2015

Pages 47 **urn** http://urn.fi/URN:ISBN:978-952-60-6577-9

A! Aalto-yliopisto

Tiivistelmä

Aalto-yliopisto, PL 11000, 00076 Aalto www.aalto.fi

Tekijä
Hannu Sairanen

Väitöskirjan nimi
Metrologisten kosteusmittaussovellusten kehitys

Julkaisija Insinööritieteiden korkeakoulu

Yksikkö Energiatekniikan laitos

Sarja Aalto University publication series DOCTORAL DISSERTATIONS 212/2015

Tutkimusala Sovellettu termodynamiikka

Käsikirjoituksen pvm 05.08.2015 **Väitöspäivä** 21.12.2015

Julkaisuluvan myöntämispäivä 26.10.2015 **Kieli** Englanti

☐ **Monografia** ☒ **Yhdistelmäväitöskirja (yhteenveto-osa + erillisartikkelit)**

Tiivistelmä

Merkittävä osa metrologisten kosteusmittaussovellusten kehitystyöstä on tehty ilmastonmuutoksen takia. Tässä työssä kehitettiin metrologisia keinoja energiakaasujen kosteusmittausten parantamiseksi. Lisäksi työssä kehitettiin uusi kalibrointimenetelmä, jonka pohjalta rakennettiin laitteisto radiosondien jäljitettävään kalibrointiin. Tätä kautta radiosondeilla mitattujen kosteuslukemien laatua pystytään parantamaan.

Metrologisia keinoja energiakaasujen kosteusmittausten parantamiseksi kehitettiin tutkimalla metaani-vesihöyryseoksen korjauskerrointa. Uusi kosteusmittaukseen pohjautuva nestevirtausten kalibrointimenetelmä kehitettiin, ja laitteisto ruiskumäntäpumppujen kalibrointiin rakennettiin. Valmiille kokoonpanolle tehtiin metrologinen validointi virtausalueella 0,1 ul min^{-1} - 10 ul min^{-1}. Myöhemmin tätä laitteistoa hyödynnettiin uudenlaisen korjauskertoimen mittaamiseen suunnitellun laitteiston toteutuksessa. Korjauskertoimia mittaava laitteisto kävi läpi metrologisen validoinnin ilmalla ja metaanilla kastepistelämpötilaalueella -50 °C - +15 °C painealueen yläpään ollessa 6 MPa. Tällä laitteistolla suoritettujen mittausten tulosten lisäksi korjauskertoimia laskettiin kirjallisuudesta löydettyjen vesihöyrymetaanitasapainotilojen lukuarvoista. Yhdistämällä kokeellisesti ja laskennallisesti saadut arvot pystyttiin korjauskertoimelle määrittämään yhtälö paineen ja kastepistelämpötilan funktiona. Määritetty yhtälö kattaa kastepistelämpötila-alueen -23 °C - +20 °C painealueen rajoittuessa alle 7 MPa. Yhtälön laajennettu epävarmuus ($k = 2$) on 0,23 koko alueella, jolle se on määritetty.

Radiosondeja käytetään laajalla kosteus-, lämpötila- ja painealueella, minkä vuoksi niiden kalibroinneissa tulisi huomioida nämä tekijät. Perinteisillä menetelmillä kalibrointi kylmässä ja alhaisessa kosteudessa on hidasta, minkä vuoksi erityisesti radiosondeja varten suunniteltu kalibrointimenetelmä ja –laitteisto kehitettiin. Uusi laitteisto mahdollistaa selvästi lyhyemmät kalibrointiajat lämpötila-alueella -80 °C - +20 °C ja kastepistealueella -90 °C - +10 °C. Laitteisto täyttää GCOS:n (Global Climate Observing System) perustaman GRUANin (GCOS Reference Upper-Air Network) asettamat vaatimukset.

Avainsanat Epävarmuus, jäljitettävyys, kalibrointi, kastepistelämpötila, korjauskerroin, kosteus, metaani, radiosondi

ISBN (painettu) 978-952-60-6576-2 **ISBN (pdf)** 978-952-60-6577-9

ISSN-L 1799-4934 **ISSN (painettu)** 1799-4934 **ISSN (pdf)** 1799-4942

Julkaisupaikka Helsinki **Painopaikka** Helsinki **Vuosi** 2015

Sivumäärä 47 **urn** http://urn.fi/URN:ISBN:978-952-60-6577-9

Acknowledgements

The research work presented here started in the Centre for Metrology and Accreditation (MIKES) in 2010. The work was part of the research carried out in European Metrology Research Program (EMRP) projects Characterization of the Energy Gases (2010-2013), Metrology for pressure, temperature, humidity and airspeed in the atmosphere (2011-2014) and Metrology for Essential Climate Variables (2014-2017).

I would like to express my gratitude to my student friendly supervisors Prof. Risto Lahdelma and Prof. Markku Lampinen for the opportunity to carry out my doctoral studies at Aalto University, School of Science and Engineering. Also, I would like to thank them for always finding the time for discussions.

During the work I received invaluable guidance from my instructor Dr. Martti Heinonen. I am also grateful to him for being so encouraging during each step of my studies.

I am also thankful for all of my co-authors for their efforts and colleagues at MIKES for all the support and team spirit.

Finally I would like to thank my family and friends for their inspiring support. Especially I would like to thank Emma and Venla for accepting my few a little bit longer days at work.

Espoo, 5 August 2015
Hannu Sairanen

Contents

List of Abbreviations and Symbols

CCDI	Cooled Coil Dew-point Indication
DUC	Device under calibration
EA	European co-operation for Accreditation
GCOS	Global Climate Observing System
GRUAN	GCOS Reference Upper-Air Network
GUM	Guide to the Expression of Uncertainty in Measurement
HHG	Hybrid Humidity Generator
MDFG	MIKES Dew/Frost-point Generator
MFC	Mass flow controller
MIKES	Centre for Metrology and Accreditation (until 31st December 2015); Centre for Metrology MIKES, VTT Technical Research Centre of Finland Ltd (since 1st January 2015)
MPDG	MIKES Primary Dew/Frost-point Generator
MRHG	MIKES Relative Humidity Generator
NMI	National Metrological Institute
SI	Système international d’unités, International System of Units
VIM	International Vocabulary of Metrology
VTT	VTT Technical Research Centre of Finland Ltd

a_i	Coefficient of an enhancement factor equation
A_f	Dew-point temperature dependant variable in the equation for enhancement factor
b_i	Coefficient of an enhancement factor equation
B_f	Dew-point temperature dependent variable in the equation for enhancement factor

e_{w}	Water vapour pressure
e_{ws}	Saturation water vapour pressure
f	Enhancement factor
F	Functional relationship between input quantities and measurand
G	Function to combine uncertainties
k	Coverage factor
m_{g}	Mass of gas
m_{w}	Mass of water vapour
m_{tm}	Total mass of the sample
$\dot{m}$	Mass flow rate
M_{g}	Molar mass of gas
M_{w}	Molar mass of water
n_{g}	Mole amount of gas
n_{w}	Mole amount of water vapour
N	Amount of variables
p	Pressure
r	Mixing ratio
RH	Relative humidity
T	Temperature
T_{d}	Dew-point temperature
u	Standard uncertainty
u_{c}	Combined standard uncertainty
u_{i}	Standard uncertainty of a variable
$\dot{V}_w$	Volumetric flow rate of water
x_{i}	Estimate of the input variable
x_{w}	Amount fraction of water vapour
y	Estimate of a measurement result
ρ_g	Density of gas
ρ_w	Density of water

List of Publications

This doctoral dissertation consists of a summary and of the following publications which are referred to in the text by their numerals

I Sairanen, Hannu; Heinonen, Martti. 2014. Hygrometer-based calibration method for syringe pumps providing ultra-low liquid flows. Springer. Microfluidics and Nanofluidics, volume 16, issue 1-2, pages 187-193. ISSN 1613-4982. DOI: 10.1007/s10404-013-1233-6.

II Sairanen, Hannu; Heinonen, Martti. 2014. Validation for a new apparatus measuring water vapour enhancement factors up to 6 MPa. IOP Publishing. Measurement Science and Technology, volume 25, issue 3. ISSN 0957-0233. DOI: 10.1088/0957-0233/25/3/035301.

III Sairanen, Hannu; Heinonen, Martti. 2014. Enhancement factor for water vapor–pressure correction in humid methane. Springer. International Journal of Thermophysics, volume 35, issue 6-7, pages 1280-1289. ISSN 0195-928X. DOI: 10.1007/s10765-014-1720-3.

IV Sairanen, Hannu; Heinonen, Martti; Högström, Richard; Lakka, Antti; Kajastie, Heikki. 2014. A calibration system for reference radiosondes that meets GRUAN uncertainty requirements, NCSL International. Measure, The Journal of Measurement Science, volume 9, issue 3, pages 56-60, ISSN 1931-5775.

V Sairanen, Hannu; Heinonen, Martti; Högström, Richard. 2015. Validation of a calibration set-up for radiosondes to fulfil GRUAN requirements. Accepted for publication in Measurement Science and Technology published by IOP Publishing.

Author's Contribution

Publication 1: Hygrometer-based calibration method for syringe pumps providing ultra-low liquid flows

The authors designed together the calibration principle. Additionally, the author constructed the set-up, carried out the measurements, analysed the results and prepared the manuscript.

Publication 2: Validation for a new apparatus measuring water vapour enhancement factors up to 6 MPa

The authors designed together the measurement principle. Construction of the measurement apparatus, all measurements, data analysis and manuscript preparation were carried out by the author.

Publication 3: Enhancement factor for water vapor–pressure correction in humid methane

The author carried out all the measurements and analysed the raw data together with the co-author. The new equation for humid methane enhancement factor values was derived by the author. Also uncertainty analysis and manuscript preparation were carried out by the author.

Publication 4: A calibration system for reference radiosondes that meets GRUAN uncertainty requirements

The author designed the measurement method along with the co-authors and carried out the uncertainty analysis for the apparatus. Additionally, the author prepared the manuscript.

Publication 5: Validation of a calibration set-up for radiosondes to fulfil GRUAN requirements

The author designed the apparatus along with the co-authors, constructed the measurement set-up, carried out most of the measurements, analysed the results and prepared the manuscript.

1. Introduction

1.1 Background

First humidity measurements of air were carried out in ancient China more than 2000 years ago [1]. Since that, developments of measuring humidity accelerated from 15th century leading to a gravimeter type hygrometer designed by Leonardo Da Vinci in the end of the century [2]. Advances on absolute humidity measurements continued and in the end of the 17th century a dew-point meter based on condensing water vapour by ice cooling was constructed [3]. Steps eventually leading to understanding the concept of relative humidity were taken in the end of the 18th century when the first hygrometers using hair were constructed [1], [3]. L.W. Gilbert determined in 1803 that the relative humidity is a ratio of present water vapour and maximum water vapour at the same temperature [1].

Prior to innovations leading to electronic hygrometers mechanical hygrometers based on hair stretching were used. Also psychrometers were and are still widely used [4]. The first electronic humidity sensor, and also the first radiosonde - or radio sounding device as known at the time - was developed in Finland in 1934 by Prof. Vilho Väisälä [5]. Shortly after the first radiosonde in 1938 Dr. Dunnmore invented the so called Dunmore Cell, a resistive hygrometer measuring relative humidity [1]. After the Second World War sensor technology developed rapidly and numerous new and more advanced sensors were brought into markets. Also new methods to measure humidity e.g. by chilled mirror dew-point meters and optical hygrometers were developed by the end of the 20th century.

In Finland awareness in importance of accurate humidity measurements was growing along with the growth of Vaisala Oyj. To meet the needs of industry for ensuring reliability of humidity measurements the work for developing a national humidity standard was initiated at Technical Inspection Centre at the beginning of the year 1991 and continued in the Centre for Metrology and Accreditation established 1st June 1991. The first primary standard of humidity was taken into use in customer calibrations in 1993 after completing two international comparisons [6], [7], [8]. Since the first dew-point generator was launched and traceability to International System of Units (SI) was established the research on humidity standards at MIKES has been focused on extending the operation and application ranges as well as improving methods to compare humidity standards to each other according to identified customer needs in Finland. As a result, a new dew-point generator was designed and constructed with a wider measurement range [9], uncertainty sources were studied e.g. in [10] and [11] and more challenging measurement conditions studied e.g. for calibrations of sensors sent to planet Mars [12].

Globally one of the most significant driving forces in development of humidity measurements is the climate change due to a significant contribution of water vapour to the global warming [13], [14], [15]. Studies concerning the climate change need improved quality of humidity measurements [16] and thus new humidity sensors and calibration methods for them are developed.

To slow down the climate change EU has set EU2020 goals to reduce greenhouse gas emissions and to increase usage of biofuels [17]. To underpin the goals MIKES has put effort on metrology research related to production and distribution of biofuels. In particular, metrology tools for humidity measurements in energy gases have been developed to fulfil the needs of increasing use of various gas sources. High water vapour concentration in biogas not only decreases the power output but may also cause a safety risk via increased corrosion and even plugs caused by condensation of water vapour [18].

1.2 Outline of the thesis

The natural gas grid pressure is usually significantly above atmospheric pressure e.g. in Finland the grid pressure varies between 1.6 MPa and 5.4 MPa [19]. In order to measure humidity and to enable SI traceable unit conversions, the water vapour enhancement factor with a known uncertainty is needed to correct non-ideality effects of the humid gas. The water vapour enhancement factor is well-known for air [20], [21] but for methane the available data is insufficient.

To determine experimentally the enhancement factor a new high pressure humidity generator was designed. A key unit in the generator is a gas-water mixer in which water – supplied by a syringe pump - is evaporated to a carrier gas. As there was no calibration method available for the syringe pump in the flow rate range down to 0.1 μl min^{-1} a new calibration method was needed for obtaining the SI traceability. Therefore a new calibration method and apparatus based on humidity measurement was developed, constructed and metrologically validated [Publ. I]. In the new calibration apparatus, water supplied by a syringe pump under calibration is evaporated to air flow and the dew-point temperatures before and after the water evaporation are measured. The water mass flow rate is calculated from the dew-point temperature difference and mass flow rate of air. As a part of the SI traceability a metrological uncertainty analysis was carried out in [Publ. I].

The new high pressure humidity generator was constructed based on water injection from the syringe pump for the enhancement factor studies

[Publ. II]. Three key parts of the measurement set-up are control of the dry gas, gas-water mixer and determination of dew-point temperature in a gas at pressures up to 6 MPa. The first two were developed already in [Publ. I] and the third one was designed by utilizing a cooled coil dew-point indication (CCDI) method [22]. The CCDI bases on an idea to determine the dew-point temperature by cooling the flowing gas in a coil until water vapour starts to condensate. The condensation is detected as a drop in dew-point temperature readings of a hygrometer connected to the outlet of the coil. At this momemnt the dew-point temperature equals to coil temperature. Prior to the measurements with methane the set-up was used for measuring the water vapour enhancement factor in air. The achieved results were found consistent with the values obtained from [20] and [21]. During the methane measurements the set-up was developed further by introducing a steel nozzle-like mixer for water spraying to enhance evaporation in the mixer. The new part enabled better repeatability and more stable evaporation. The new enhancement factor data is reported along with thorough uncertainty analysis in [Publ. II].

New data on the water vapour enhancement factor in pure methane was obtained by experiments with the developed setup and by calculating from the literature data available for methane–water equilibrium. Suitable sources enabling to calculate the enhancement factor were found, but they lack uncertainty analysis [23], [24], [25], [26], [27], [28]. Combining the experimental data and the calculated data from the literature it was possible to derive a new equation for humid methane enhancement factor values as a function of pressure and dew-point temperature. Also the uncertainty of the equation was estimated on the basis of uncertainty estimations for the experimental data and data analysis for the literature data [29]. [Publ. III]

Radiosondes used for high altitude humidity measurements operate at rapidly varying conditions covering a wide humidity, temperature and pressure range. Thus their traceable calibration is a challenging task. Additionally, a radiosonde is a disposable device, and thus the calibration must be as inexpensive as possibly, i.e. the duration of the calibration should be minimized to enable greater volume of calibrations. In this work a customized method for radiosonde calibration was developed [Publ. IV] and a new apparatus was designed and constructed [Publ. V]. With the new apparatus a calibration of a radisonde takes a significantly shorter time than achievable with humidity generators developed so far. The new calibration set-up enables calibrations within uncertainty requirements set by Global Climate Observing System (GCOS) and its GCOS Reference upper-air network (GRUAN) [30], [31], [Publ. IV]. Additionally, humidity generator of the apparatus has been applied in similar measurements as reported in [12] – i.e. the new apparatus enables testing sensors response times, behaviour in freezing environments and dynamic measurements in changing measurement conditions – providing more purposes of use to the apparatus [Publ. V].

1.3 Objectives of the thesis

Main objectives of the thesis are

1. to develop a new calibration method to syringe pumps and to achieve SI traceability on micro scale water flows
2. to develop an apparatus for traceable measurements of water vapour enhancement factor leading eventually to new enhancement factor data for different humid gases
3. to derive an equation along with uncertainty for water vapour enhancement factor in methane as a function of pressure and temperature
4. to develop a new calibration method for radiosondes enabling feasible calibrations of radiosondes within the uncertainty requirements set by GRUAN.

1.4 Scientific contribution

This thesis contains the following new scientific results:

1. Applying a new porous cloth water evaporator a novel hygrometer-based calibration method was developed and realised in a set-up constructed for syringe pump calibrations.
2. A new apparatus was developed for humid gases enhancement factor studies. The apparatus is capable to operate at pressures up to 6 MPa and thus applicable e.g. natural gas in the complete range of typical grid pressure.
3. New experimental data on the water vapour enhancement factor in methane were obtained and a new equation for the enhancement factor was derived. This equation is the first one published with appropriate uncertainty information enabling SI traceable two-pressure humidity measurements and unit conversions in methane.
4. A new method for calibrating radionsondes in the full temperature range of operation in a feasible time was developed. Applying this method, an apparatus was constructed to provide traceable calibrations for radiosondes within the uncertainty requirements set by GRUAN. The apparatus enables significantly shorter calibration durations than achievable with traditional humidity generators in the temperature range down to -80 °C.

2. Metrology in humidity measurements

2.1 Humidity

Humidity is a qualitative concept referring to the presence of water vapour in a gas. It is quantified with various physical quantities such as mixing ratio r, amount fraction x_w, water vapour pressure e_w, dew-point temperature T_d and relative humidity. The mixing ratio is the ratio between masses of water vapour m_w and dry gas m_g in a sample as shown in Equation (1):

$$r = \frac{m_w}{m_g} \tag{1}$$

The amount fraction of water vapour in humid air is the amount (in moles) of water vapour n_w divided by the total amount of gas components n_w+n_g in a gas sample. It can be expressed using r in Equation (1) with the molar masses of dry gas (M_g) and water vapour (M_w) in the following way:

$$x_w = \frac{n_w}{n_w+n_g} = \frac{r}{\frac{M_w}{M_g}+r}. \tag{2}$$

The molar masses can be obtained from the literature e.g. from [32]. According to the Dalton's law partial pressure of water vapour in a gas mixture equals to the amount fraction of water vapour multiplyed by the total pressure p of a gas mixture. However, Dalton's law is valid only for ideal gases and thus a water vapour enhancement factor f is introduced:

$$fe_w = x_w p \tag{3}$$

For humid air the enhancement factor can be calculated e.g. according to Hardy [20].

In order to convert water vapour pressure to dew-point temperature or to relative humidity an equation for saturation water vapour pressure e_{ws} is needed. The metrological community often uses equations by Hyland and Wexler [33] or Sonntag [34] due to their applicability to a wide temperature range. Other equations often used are e.g. Magnus', World Meteorological Organization's (WMO) and IAPWS' equations [34], [4], [35]. With the knowledge of saturation water vapour pressure the relative humidity can be calculated as

$$RH = \frac{f(p,T_d)e_{ws}(T_d)}{f(p,T)e_{ws}(T)} \cdot 100\ \%rh = \frac{x_w p}{f(p,T)e_{ws}(T)} \cdot 100\ \%\text{rh}. \quad (4)$$

When carrying out humidity calculations it is important to be aware of whether the saturation water vapour pressure is with respect to water or ice. Typically within metrological community at temperatures below 0 °C the saturation pressure is expressed with respect to ice as they are expressed throughout this thesis. However, for example in meteorology relative humidity is defined with respect to water at all temperatures [4].

2.2 Traceability in humidity measurements

Most of the work presented in this thesis aims at SI traceable measurements. Metrological traceability is defined as

> *property of a measurement result whereby the result can be related to a reference through a documented unbroken chain of calibrations, each contributing to the measurement uncertainty [36].*

Traceability is disseminated to a hygrometer by an unbroken chain of calibrations. Usually a measurement unit is realized according to definition of the quantity at a National Metrological Institute (NMI), such as VTT - MIKES Metrology. With a primary standard used in the realization the NMI carries out calibrations for the most accurate hygrometers, typically chilled mirror hygrometers. These are then used as reference standards in calibrations for other humidity sensors. Each step in the traceability chain increases the calibration uncertainty and thus humidity generators with smaller uncertainty compared to the refence hygrometers are also used in calibrations of less accurate humidity sensors.

Typically the primary realisations of humidity at NMIs are carried out in terms of dew-point temperature. The dew-point temperature is relatively easy to realize, because a single apparatus can be used for a wide measurement range at small uncertainty. Dew-point temperature means humidity at a temperature where a carrier gas, typically air or nitrogen, is in equilibrium with liquid water. The first humidity standard at MIKES is known as the MIKES Primary Dew-point generator (MPDG). The MPDG as well as its follower the MIKES Dew/Frost-point Generator (MDFG) operate at one-pressure principle meaning that the generated dew-point temperature is controlled by saturator temperature alone. As for any primary unit realisation, the traceability to SI of these generators was ensured by careful design and metrological validation of the generator, by SI traceable calibrations of measurement instruments attached to it and by international comparison [6]. [9], [37], [38].

2.3 Measurement uncertainty

According to the definition by the International Vocabulary of Metrology (VIM) the measurement uncertainty is [36]

> *a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used.*

A complete measurement result includes an estimate and an uncertainty of the estimate. A widely used method to estimate the uncertainty is to follow the Guide to the Expression of Uncertainty in Measurement (GUM) [39]. A number of guides derived from it have been published by various associations, e.g. EA-4/02 by European co-operation for Accreditation (EA) [40] or corresponding guide in America published by American Associaton for Laboratory Accreditation [41]. Throughout this thesis uncertainties are estimated according to the GUM.

An estimate of the result y is expressed as a function of input estimates x_1, x_2, ..., x_N

$$y = F(x_1, x_2, \dots, x_N) \ . \tag{5}$$

Because every input estimate has an uncertainty u_1, u_2, ..., u_N, the uncertainty of the result $u(y)$ can be expressed

$$u_c(y) = G(u_1, u_2, \dots, u_N). \tag{6}$$

How the Equation (6) is actually applied depends on uncertainty sources. In the uncertainty calculations presented in this thesis the sources are assumed to be independent. Thus, the combined standard uncertainty u_c is calculated

$$u_c^2(y) = \sum_{i=1}^{N} \left[\frac{\partial F}{\partial x_i} u(x_i) \right]^2 . \tag{7}$$

The standard uncertainty covers in the case of normally distributed results about 68 %. The coverage is often extended with an expanded uncertainty, which is calculated by multiplying the standard uncertainty with a coverage factor k. Most often the expanded uncertainty is given with k = 2 providing approximately 95 % level of confidence. More rarely k = 3 is used to achieve about 99 % level of confidence.

3. New data on the water vapour enhancement factor

3.1 Determination of the enhancement factor

Formulae for the water vapour enhancement factor are often semi-empirical, i.e. it has not been directly measured but derived by a theoretical approach from experimental thermodynamic data e.g. by Luijten et al. [21], Greenspan [42] and Hyland [43]. There are also measured data on water vapour enhancement factors e.g. by Wylie and Fisher [44], and Meyer and Harvey [45]. However, such data is lacking for methane.

Within this thesis a new approach is presented to determine the enhancement factor. The water vapour enhancement factor can be expressed as a function of pressure and dew-point temperature derived from Equation (3):

$$f(p, T_d) = \frac{x_w p}{e_w(T_d)}. \tag{8}$$

In order to use Equation (8) the water vapour amount fraction in a gas need to be generated and the dew-point temperature determined. At the time of measurements there was no commercially available high accuracy hygrometer for 6 MPa methane. Hence, the CCDI method was applied in determination of the dew-point temperature. The SI traceable water vapour amount fraction was generated by evaporating water from a calibrated syringe pump to dry gas.

3.2 Traceable water vapour generation

By applying Equations (1) and (2) the water vapour amount fraction for a known gas mixture can be calculated from the mass flow rates of water vapour and the main gas (air or methane in this thesis). Traceability to the gas flow rate is established by a calibrated mass flow controller but controlling and determining the mass flow rate of pure water vapour at the required level and with the required accuracy is not straight forward. Therefore, water was injected in liquid form into the system and evaporated to dry main gas enabling to establish the traceability by calibrating the syringe pump. For the purpose, a new calibration method and setup was needed to be developed for liquid flows in the range from 0.1 µl min^{-1} to 10 µl min^{-1} because there were no institutes carrying out calibrations for such a small flow rates at the time. A calibration facility providing the best match with the needed range had been developed by the Danish Technological Institute; its range covered flow rates down to 20 µl min^{-1} [46]. The new metrologically validated apparatus provided the needed traceability to the water flow [Publ. I].

Most of the studies and standardised procedures about liquid flow calibrations are based on weighing or volumetric dispersion e.g. [46], [47], [48], [49], [50]. The ones based on weighing have to deal with uncontrolled evaporation – i.e. water vapour diffusion out from the set-up - resulting a mass loss between the water supply and the balance used for measuring the mass of the supplied water. The evaporation can be compensated by measuring the evaporation rate separately and applying appropriate correction to the result and minimised by introducing an evaporation trap – e.g. oil on the surface of water [46] - or by sealing the set-up and controlling surrounding humidity [49]. By introducing a hygrometer-based calibration method, in which the measured water flow is completely evaporated this kind of problems were avoided.

The principle of the hygrometer-based method is described in Figure 1. A known amount of dry air is mixed with a known amount of water from a syringe pump. Thus the water content at the outlet is provided by the syringe pump. The dew-point temperature at the outlet is measured by a chilled mirror hygrometer. By applying Equations (1), (2) and (3) the volumetric flow rate of water from the pump can be calculated as

$$\dot{V}_w = \frac{\dot{V}_g \rho_g M_w}{\rho_w M_g} \frac{f(p,T_d) e_w(T_d)}{p - f(p,T_d) e_w(T_d)}, \tag{10}$$

where $\dot{V}$ and ρ are volumetric flow rate and density, respectively. Sub indexes g and w refer to air and water, respectively. The water density can be calculated using the formulae in [51].

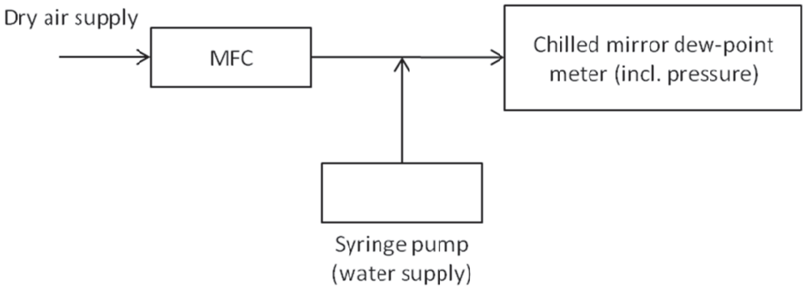

Figure 1. Process scheme of the calibration set-up for microflows. MFC means a mass flow controller.

In practise even dried air always contains water molecules, which needs to be taken into account when the hygrometer-based method is used.

Therefore, the inlet humidity content has to be determined and included in the analysis of results. Usually, the level of this background is low enough for contributing only to the measurement uncertainty.

Initial tests of the set-up pointed out that water evaporation and mixing is a vital part of the set-up. Uncontrolled evaporation would lead to a droplet by droplet evaporation and unacceptably unstable dew-point readings. As a solution a porous cloth method was introduced. The method forces air flow through a porous cloth which in one end is in the water as drawn in Figure 2. The cloth humidifies the air with a stable evaporation rate which improves significantly the stability of the outlet dew-point temperature as shown in Figure 3. More details of the method are presented in [Publ. I].

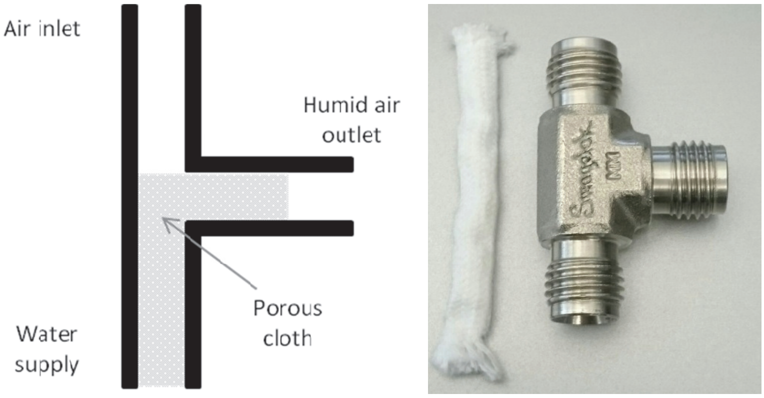

Figure 2. Assembly of a porous cloth in a 6 mm t-joint on the left and on the right a photo of the t-joint and the cloth used in the set-up.

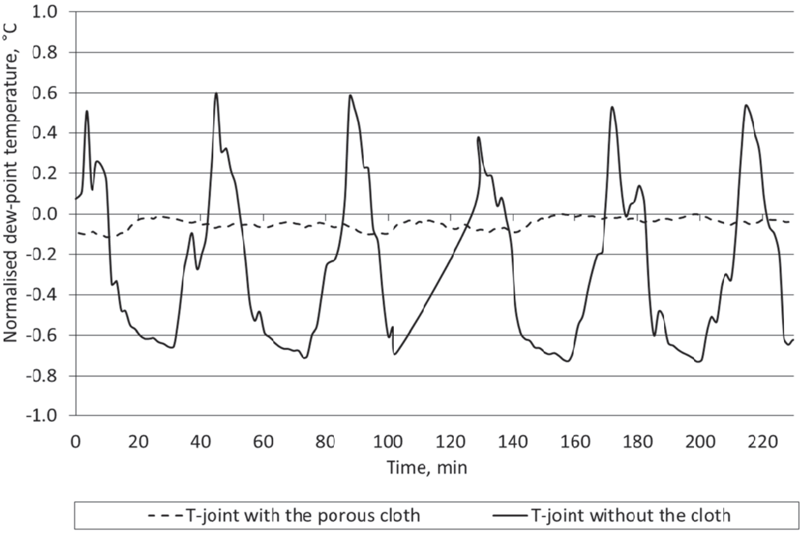

Figure 3. Outlet dew-point temperature in comparison with and without the porous cloth in a T-joint to evaporate the water flow, respectively.

The results reported in [Publ. I] show that the method is suitable to be applied in calibrations. To study uncertainty components further a gravimetric calibration set-up was developed and compared with the hygrometric method. Mean differences between the methods agree within uncertainties. The gravimetric set-up was also used in an international comparison where the results agreed with the results of other partners within estimated uncertainties [52].

3.3 Novel alapparatus for enhancement factor measurements

The final set-up for measuring the water vapour enhancement factor was constructed based on the principle shown in Figure 4. The system is capable to operate at pressures up to 6 MPa and dew/frost-point temperatures in the range from -50 °C to +15 °C. All measurement devices were calibrated prior to assembly. Detailed description about the apparatus is presented in [Publ. II]. A photoraph of the appartatus is in Figure 5.

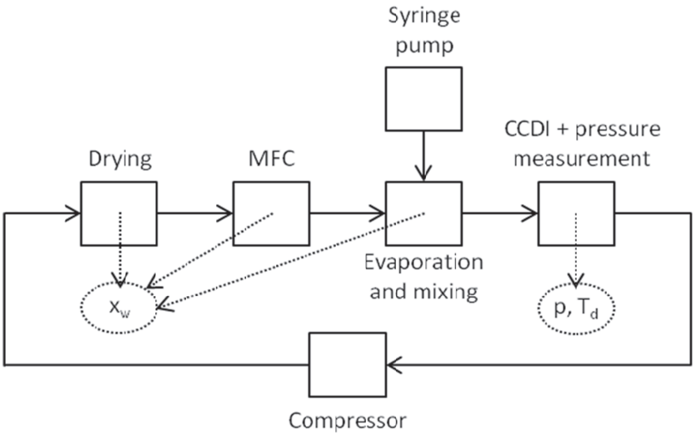

Figure 4. Key parts of the apparatus for measuring the water vapour enhancement factor. Dashed arrows and circles describe how the parameters needed in the calculation of the enhancement factor are obtained.

Figure 5. Complete apparatus for the enhancement factor studies.

The apparatus was characterized by carrying out measurements with air and by comparing the measured enhancement factor values with the literature values [20], [21]. The agreement with the literature data was well within the estimated uncertainties. Thus, it was concluded that the apparatus provides metrologically sound data for the water vapour enhancement factor.

After air measurements the porous cloth in the water vapour-gas mixer was replaced by a nozzle-like steel mixer. This was done to reduce instabilities in water evaporation due to imperfect assembly of the porous cloth. Additionally, the porous cloth could easily be contaminated leading to a random evaporation rate [53].

In case of methane the metrological validation of the system was more complicated due to lacking data on the water vapour enhancement factor for methane. There are, however, data in the literature on the equilibrium pressure of water vapour in methane [23], [24], [25], [26], [27], [54]. Using these data, i.e. equilibrium temperatures, pressures and corresponding water vapour amount fractions, it was possible to calculate the enhancement factor values. Measured experimental results were compared with the data calculated from the literature data and found consistent as reported in [Publ. II].

An appropriate uncertainty analysis is vital for obtaining metrologically sound results. To provide enhancement factor data with well characterised uncertainty information an uncertainty analysis was carried out as presented in [Publ. II]. The expanded uncertainty (k=2) for the validation data and the apparatus is in the case of air 3.6 % and in the case of methane 9.0 %.

3.4 Equation for the water vapour enhancement factor of methane

Practical usage of the enhancement factor requires an equation simple enough as a function of pressure and temperature. Additionally, it should cover typical grid pressures and humidity levels in methane and natural gas. Experimental data was obtained up to 6 MPa and the literature data up to 7 MPa, while the dew-point temperature ranges were from the hydrate forming temperature (approximately -20 °C) to 20 °C and from -25 °C to 35 °C, respectively. Most of the literature values are for pressures and humidity levels that are typically beyond the conditions of the European natural gas grid, which decreased the amount of usable data for the equation. In order to have a balanced amount of experimental and literature-based data the new equation was limited to pressures below 7 MPa and the dew-point temperatures between -23 °C and 20 °C.

The objective in developing the new equation was to find a simple model to be fitted to the experimental and the calculated data. However, the equation needs to take into account the intermolecular interaction of water vapor and methane, the Poynting effect (change of the water vapor pressure) and the Raoult effect (dissolving of water and methane) [55]. By taking these into account a suitable form of the equation was considered to include two virial coefficients. Therefore, a form presented by Heinonen for air enhancement factor was chosen [56]. By applying this form to the data of water vapour enhancement factor for methane, a two-variable equation could be expressed as

$$f(p, T_d) = A_f(T_d) + B_f(T_d)p. \tag{10}$$

Variables A_f and B_f in equation (10) are

$$\mathrm{A}_f(T_d) = \sum_{i=0}^{3} a_i T_d^i, \tag{11}$$

$$\mathrm{B}_f(T_d) = \sum_{i=0}^{2} b_i T_d^i. \tag{12}$$

Coefficients a_i and b_i for Equations (11) and (12) are listed in Table 1. The numerical values of the coefficients were calculated with the DataFit software. Prior to calculating the coefficients all the data points were analysed in order to exclude possible outliers predicted by Reshadi et al. [24]. The final data excluded six out of 155 data point because of too large deviation. The excluded data points included both experimental and literature data and they are all shown in [Publ. III].

Table 1. Coefficients for equations 12 and 13.

$a_0 = -40.90425$	$b_0 = 4.38544 \times 10^{-6}$ Pa^{-1}
$a_1 = 0.42372$ K^{-1}	$b_1 = -3.19109 \times 10^{-8}$ K^{-1} Pa^{-1}
$a_2 = -1.39620 \times 10^{-3}$ K^{-2}	$b_2 = 5.84952 \times 10^{-11}$ K^{-2} Pa^{-1}
$a_3 = 1.49431 \times 10^{-6}$ K^{-3}	

Fitting of the equation to the data and evaluation of its uncertainty are presented in details in [Publ. III]. The quality of fitting is illustrated by Figure 6.

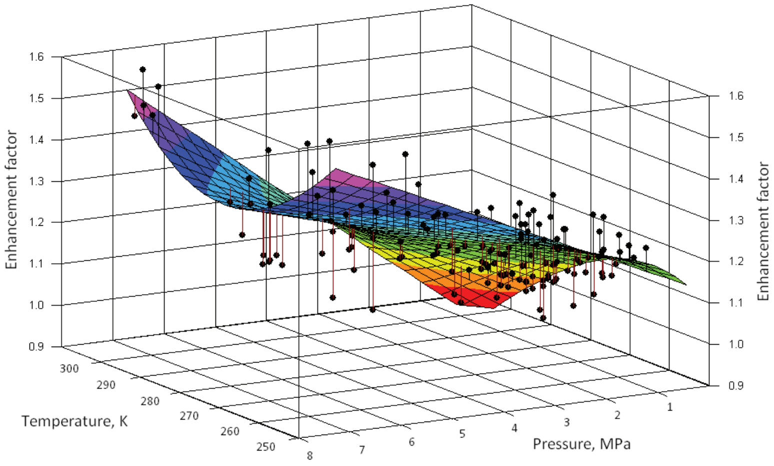

Figure 6. Methane enhancement factor according to the derived equation. Points in the figure are values of input data used in deriving the equation.

Estimated expanded uncertainty (k = 2) of the derived equation is 0.23 covering the whole ranges of pressure and temperature. The uncertainty corresponds with relative expanded uncertainty from 15 % to 25 %.

The new measurement apparatus and water vapour enhancement factor data for methane are a significant step towards more precise humidity measurements in energy gases. In areas and applications where the methane content of energy gas is high, e.g. natural gas grid in Finland, the new equation can be applied to improve the humidity measurement data. The research is continuing with different gas compositions that are more close to biogases [57]. By the future steps it will be possible to derive an equation for the water vapour enhancement factor as a function of temperature, pressure and gas composition along with reduced uncertainty. Hence, the applicability of the equation is possible to spread from natural gas to all methane-based energy gases. This enables deeper optimization of processes, e.g. to minimize unnecessary gas drying, which in turn improves the energy efficiency. It is also of interest for commerce to obtain more precise humidity measurements as water vapour content correlates with heating value of an energy gas.

4. Novel humidity calibration apparatus for radiosondes

4.1 Humidity calibration of a radiosonde

Carrying out a humidity calibration for a radiosonde in upper-air conditions, i.e. at frost-point temperatures approximately below -60 °C, is a challenging task. There are different kinds of humidity standards applicable to these conditions e.g. low temperature dew-point generators and diffusion tube generators [9], [58], [59], [60]. A common weakness to all of these is slowness in operation. The slowness is often due to the time needed to stabilize the calibration system after changing a set-point to another. The more tubing is used between the standard and a device under calibration (DUC) the longer is the stabilization time. Additionally, a measurement chamber, required in radiosonde calibration, causes even longer stabilization time. These effects are due to adsorption/desorption on internal surfaces of the calibration set-up.

Along with growing awareness of climate change, requirements for the high quality upper-air measurements increase. As a response GCOS launched GRUAN to provide SI traceable data with a minimum uncertainty. Water vapour was chosen as one of the key measurands by the GRUAN. The humidity sensors used in GRUAN should be calibrated for dew-point temperatures down to -90 °C at temperatures down to -80 °C. The calibration uncertainty should be less than 2 % in terms of mixing ratio. [31]

The work presented in [Publ. IV] describes a novel calibration method designed for radiosonde calibrations within the uncertainty requirements of GRUAN. In [Publ. V], a new calibration apparatus constructed based on the method is reported along with its characterization. This apparatus is the first one in the metrology institutes throughout the world designed for disseminating SI traceability to radiosondes. It provides for the first time a reference for radiosonde measurements with an uncertainty fulfilling the GRUAN requirements. The calibration times achieved with the system are significantly shorter than achievable with a traditional dew-point generator and a measurement chamber. The new apparatus can also be applied as a primary dew-point generator. By improved temperature control and measurements the uncertainty of the generated dew-point temperature is less compared to the MDFG, although the operation principle is the same.

4.2 Design principles for the calibration apparatus

A calibration of a device establishes traceability to the device at specific calibration conditions. However, if the device is used in varying ambient conditions, the calibration should be carried out at conditions covering the whole range of the measurement conditions. In the case of radiosondes between a launching location and upper-air, pressure, temperature and humidity varies significantly. These effects can be taken only into account by carrying out the humidity calibration at real conditions.

In order to minimize the duration of a single calibration and to obtain fast changes in the set-point it is vital to reduce adsorption/desorption effects to minimum. The net effect of water vapour adsroption and desorption is directly propotional to the internal surface area and the gas volume of the system. With careful mechanical design of the apparatus these were minimised. Additionally, to minimise the duration of a set-point change the new calibration apparatus was designed to operate in Hybrid Humidity Generator (HHG) principle presented by Meyer et al. in [61]: two controlled flows through two independently operated dew-point generators are mixed and humidity content of the outlet gas mixture is calculated with the following equation:

$$x_w = \frac{\dot{m}_{G1}}{\dot{m}_{G1}+\dot{m}_{G2}} \frac{e_{wG1} f_{G1}}{p_{G1}} + \frac{\dot{m}_{G2}}{\dot{m}_{G1}+\dot{m}_{G2}} \frac{e_{wG2} f_{G2}}{p_{G2}} \tag{13}$$

Variable $\dot{m}$ stands for the mass flow rate and subscripts G1 and G2 indentify the independent generators of the apparatus [Publ. IV]. A Block diagram of the constructed calibration apparatus is shown in Figure 7 [Publ. V]. In this version, however, a getter dryer is used for generating the low humidity level instead of a low temperature dew-point generator.

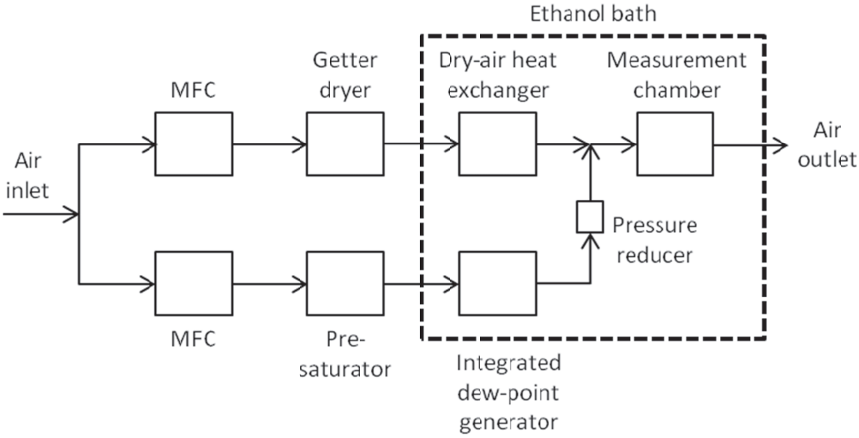

Figure 7. Block diagram of the constructed radiosonde calibration apparatus.

To minimize the adsorption/desorption effects a dew-point generator is located in the same liquid bath with the measurement chamber. Hence, the flow path prior to the measurement chamber is only about 5 cm instead of at least one meter tubing out from the bath comparing to traditional set-ups. Another significant feature in the apparatus is the careful design of the measurement chamber to obtain a short time of stabilization. A detailed description of the measurement chamber is presented with the results of its characterization by simulations and experiments by Lakka et al. in [62].

The close assembly of the generator and the chamber made easier and faster to control calibration humidity and temperature enabling smooth usage of the apparatus even at above 90 %rh without condensation problems. However, with the integrated dew-point generator and measurement chamber a pressure reducer is required to prevent condension between the generator and the measurement chamber.

4.3 Metrological validation of the new calibration apparatus

In this work the first version of the calibration apparatus for radiosondes was constructed applying the principle of operation described above and introduced in details in [Publ. IV]. The constructed apparatus is presented in details in [Publ. V]. The main parts of the system– i.e. flow control and pre-saturator, getter dryer, dry air heat exchanger, saturator of the dew-point generator and measurement chamber - are shown in Figures 8, 9 and 10.

The apparatus operates at atmospheric pressure and generates calibration conditions for a radiosonde within the temperature range from -80 °C to +20 °C and the dew/frost-point temperature range between -90 °C and +10 °C.

The calibration set-up was thoroughly characterized by investigating the performance of the dew-point generator, the dry air supply, the flow control along with the stabilization times, the measurement chamber and the pressure measurements. Eventually, the operation of the complete apparatus was investigated by carrying out test calibrations for radiosondes. The obtained results are presented and analysed in details in [Publ. V].

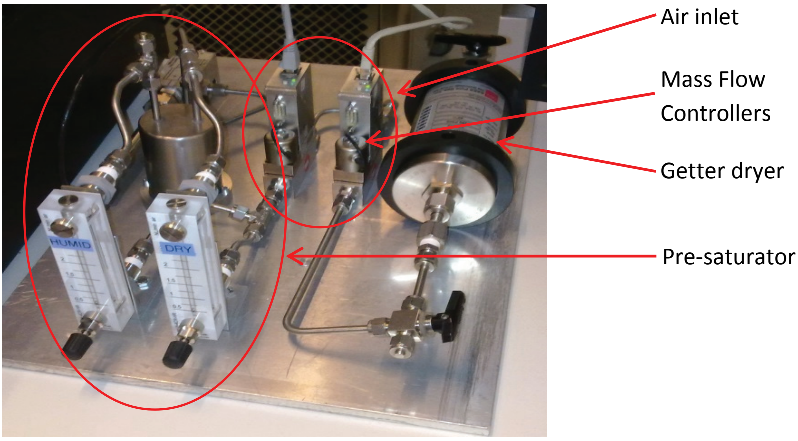

Figure 8. The flow control, the pre-saturator and the getter dryer. The MFCs controlling the air flows are located in the middle, the getter on the right and the pre-saturator on the left.

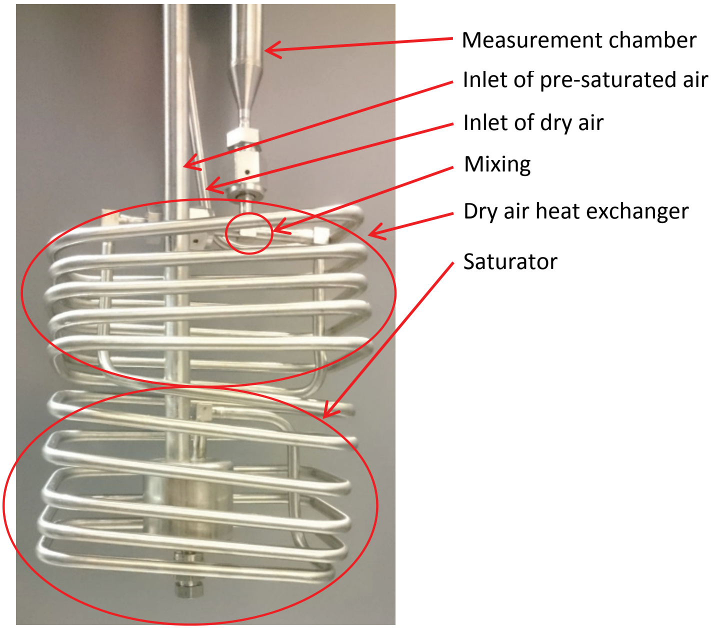

Figure 9. Pre-saturated air reaches full saturation with respect to ice or water in the saturator (bottom part) prior to mixing with dry air (supplied through the upper heat exchanger coil) and flowing to the measurement chamber (bottom part on the top of the picture).

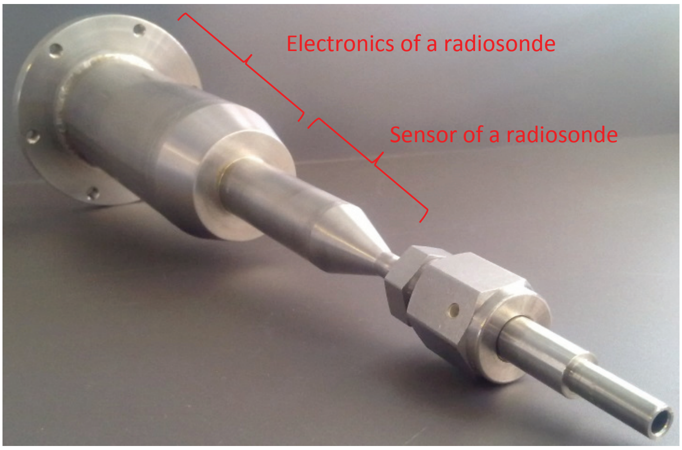

Figure 10. Measurement chamber. The sensor of a radiosonde under calibration is located in the thinner part (external diameter about 15 mm) of the chamber while the larger part is for the radiosonde electronics.

As shown in [Publ. IV] the combined standard uncertainty of the water vapour mixing ratio in the measurement chamber is about 1 % depending on the flow rates and the temperature. At best the the standard uncertainty of 0.7 % is achieved when all air flows through the generator [Publ. V]. When all air flows through the getter, however, the standard uncertainty increases to almost 5 %. This represents the worst case for the constructed apparatus.

According to the metrological validation the standard uncertainty of the dew-point generator being a part of the apparatus is 0.015 °C [Publ. V]. When connecting the generator to an external dew-point hygrometer or measurement chamber, the achievable uncertainty is somewhat larger due to the pressure drop and adsorption/desorption effects in the connection line. However, the uncertainty is in any case significantly smaller than the uncertainty assigned to the MDFG (0.1 °C at -80 °C) because of the smaller temperature deviation in the saturator bath and more stable temperature sensors.

Calibration with the new apparatus is significantly faster in operation compared to e.g. similar calibration with the MIKES Relative Humidity Generator (MRHG) consisting of the MDFG and a measurement chamber located in a climatic chamber. With the MRHG a calibration at a single temperature would last at least a week while the new apparatus is capable to carry out the calibration within few days. The performance of the apparatus has well been demonstrated in automated radiosonde calibration measurements.

When connecting the dew-point generator of the developed apparatus to an appropriate test chamber, freezing tests for humidity sensors are possible in order to characterize the behaviour of a sensor rapidly covered by ice. Also, tests with continuously changing conditions can be carried out with this set-up. These tests have already been applied in Mars sensor tests (similar with [12]). In the future, the applicability of the set-up to calibrations of various types of humidity sensors will be improved by developing the measurement chamber geometry further. Also, the development of the apparatus will continue to cover air pressures down to 7 hPa (abs.) and to improve the achievable uncertainty with the lowest dew-point temperature by introducing a low-temperature dew/frost-point generator [63]. This generator will provide significantly more stable dew-point temperature than the getter at the low end of the operation range.

5. Conclusion

The research carried out in this thesis provides new methods for humidity measurements and calibrations. It also provides internationally valuable input to microflow measurements.

A new method and an apparatus to carry out SI traceable calibrations for syringe pumps were developed and constructed [Publ. I]. This new hygrometer-based calibration method has no evaporation related systematic errors that are problematic in gravimetric approaches. Introducing a different measurement principle, the method provides important input to international microflow comparisons.

A novel method for measuring water vapour enhancement factor was developed and constructed by combining gas-water vapour mixing based on the same method as applied in the syringe pump calibration with the CCDI dew-point temperature determination in a closed gas circulation set-up. The constructed apparatus operates in the pressure range up to 6 MPa and at dew-point temperatures from -50 °C to 15 °C [Publ. II].

Using the new experimental data obtained with the apparatus and the results of calculations on the basis of thermodynamic literature data an equation for the enhancement factor of water vapour in methane was derived [Publ. III]. The equation is valid for pressures up to 7 MPa and in the temperature range from -20 °C to 20 °C.

A new method and apparatus for radiosonde calibration were developed [Publ. IV] and constructed [Publ. V]. The apparatus operates at dew-point temperatures from -90 °C to 10 °C and temperatures from -80 °C to 20 °C. It was shown that the requirements set by GRUAN can be fulfilled by applying the developed method. With the constructed apparatus the calibration uncertainty was in agreement with the target uncertainty of 2 % (in terms of mixing ratio) in most of the operating range. At the lowest temperatures, however, the achievable uncertainty is larger and therefore a new low frost-point temperature generator is being developed to replace the getter dryer in the system. It was demonstrated that the calibration time with the new apparatus is significantly shorter than achievable with existing primary humidity generators.

References

[1] P. R. Wiederhold, Water Vapor Measurement, New York: Marcel Dekker, Inc, 1997.

[2] M. Anderson, Amazing Leonardo da Vinci Inventions: You Can Build Yourself, White River Junction: Nomad Press, 2006.

[3] D. Camuffo, C. Bertolin, A. Bergonzini, C. Amore and C. Cocheo, "Early hygrometric observations in Padua, Italy, from 1794 to 1826: the Chiminello goose quill hygrometer versus the de Saussure hair hygrometer - Online Resource1: Short History of Hygrometers," *Climatic Change,* vol. 122, no. 1-2, pp. 217-227, 2014.

[4] WMO, Guide to Meteorological Instruments and Methods of Observations, Geneva: World Meteorological Organization, 2008.

[5] K.-E. Michelsen, Global Innovator - The Story of Vaisala, Helsinki: Vaisala Oyj, 2006.

[6] M. Heinonen, National basis for traceability in humidity measurements, Helsinki, 1999.

[7] M. Heinonen, "Intercomparison of humidity generators at PTB and CMA, MIKES Publication J11/1993," Centre for Metrology and Accreditation, Helsinki, 1993.

[8] M. Heinonen, "Comparison of the dew-point temperature measurement results of CETIAT and CMA, MIKES Publication J12/1993," Centre for Metrology and Accreditation, Helsinki, 1993.

[9] M. Heinonen, "Methods to investigate a dew-point temperature standard in an extended range," in *5th International Symposium on Humidity and Moisture (ISHM)*, Rio de Janeiro, 2006.

[10] M. Heinonen and M. Vilbaste, "Frost-Point Measurement Error Due to a Leak in a Sampling Line," *International Journal of Thermophysics,* vol. 29, no. 5, pp. 1589-1597, 2008.

[11] M. Vilbaste, M. Heinonen, O. Saks and I. Leito, "The effect of water contamination on the dew-point temperature scale realization with humidity generators," *Metrologia,* vol. 50, no. 4, 2013.

[12] J. Gómez-Elvira, C. Armiens, L. Castañer, M. Domínguez, M. Genzer, F. Gómez, R. Haberle, A.-M. Harri, V. Jiménez, H. Kahanpää, L. Kowalski, A. Lepinette, J. Martín, J. Martínez-Frías, I. McEwan, L. Mora, J. Moreno, S. Navarro, M. A. de Pablo and V. Peinado, "REMS: The Environmental Sensor Suite for the Mars Science Laboratory Rover," *Space Science Reviews,* vol. 170, no. 1-4, pp. 583-640, 2012.

[13] Intergovernmental Panel on Climate Change (IPCC), Climate Change 2013: The Physical Science Basis, Cambridge (UK) and New York (USA): Cambridge University Press, 2013.

[14] J. Kiehl and K. Trenberth, “Earth’s Annual Global Mean Energy Budget,” *Bulletin of the American Meteorological Society,* vol. 78, no. 2, pp. 197-208, 1997.

[15] V. Ramanathan and J. Coakley, “Climate Modelling Through Radiative-Convective Models,” *Reviews of Geophysics and Space Physics,* vol. 16, no. 4, pp. 465-489, 1978.

[16] K. Rosenlof, “How Water Enters the Stratosphere,” *Science,* vol. 302, no. 5651, pp. 1691-1692, 2003.

[17] European Comission, ”Directive 2009/28/EC of the European Parliament and of the Council on the promotion of the use of energy from renewable sources and amending and subsequently repealing Directives 2001/77/EC and 2003/30/EC,” 2009.

[18] A. Jamaluddin, N. Kalogerakis and P. Bishnoi, “Hydrate plugging problems in undersea natural gas pipelines under shutdown conditions,” *Journal of Petroleum Science and engineering,* vol. 5, no. 4, pp. 323-335, 1991.

[19] A. Riikonen, Kaasun käyttökohteiden putkistot sekä käyttölaitteiden sijoittaminen ja varustelu, Helsinki: Gasum Oy, 1998.

[20] B. Hardy, “ITS-90 formulations for water vapour pressure, frostpoint temperature, dewpoint temperature, and enhancement factor in the range -100°C to 100°C,” in *The third International Symposium on Humidity and Moisture*, Teddington, 1998.

[21] C. Lujiten, K. Bosschart and M. van Dongen, “High pressure nucleation in water/nitrogen systems,” *The Journal of Chemical Physics,* vol. 106, no. 19, pp. 8116-8123, 1997.

[22] M. Heinonen, “Investigation of the dew-point temperature scale maintained at the MIKES,” *Measurement Science and Technology,* vol. 10, pp. 36-40, 1999.

[23] A. Mohammadi, A. Chapoy, D. Richon and B. Tohidi, “Experimental Measurement and Thermodynamic Modeling of Water,” *Industrial & Engineering Chemistry Research,* vol. 43, no. 22, pp. 7148-7162, 2004.

[24] P. Reshadi, K. Nasrifar and M. Moshfeghian, “Evaluating the phase equilibria of liquid water + natural gas mixtures using cubic,” *Fluid Phase Equilibria,* vol. 302, pp. 179-189, 2011.

[25] G. Folas, E. Froyna, J. Lovland, G. Kontogeorgis and E. Solbraa, “Data and prediction of water content of high pressure nitrogen, methane and natural gas,” *Fluid Phase Equilibria,* vol. 252, pp. 162-174, 2007.

[26] A. Chapoy, A. Mohammadi, B. Tohidi and D. Richon, “Estimation of Water Content for Methane + Water and Methane + Ethane + n-Butane + Water Systems Using a New Sampling Device,” *Journal of Chemical & Engineering Data,* vol. 50, pp. 1157-1161, 2005.

[27] A. Chapoy, C. Coquelet and D. Richon, “Revised solubility data and modeling of water in the gas phase of the methane/water binary system at

temperatures from 283.08 to 318.12K and pressures up to 34.5MPa,” *Fluid Phase Equilibria,* vol. 230, pp. 210-214, 2005.

[28] E. Sloan, F. Khoury and R. Kobayashi, “Water Content of Methane Gas in Equilibrium with Hydrates,” *Industrial & Engineering Chemistry Fundamentals,* vol. 15, no. 4, pp. 318-323, 1976.

[29] J. Kondori, J. Javanmardi, A. Eslamimanes and A. Mohammadi, “Thermodynamic consistency test for isobaric experimental data of water content of methane,” *Fluid Phase Equilibria,* vol. 347, pp. 54-61, 2013.

[30] GCOS, “The GCOS Reference Upper-Air Network (GRUAN) GUIDE,” World Meteorological Organization, Geneva, 2013.

[31] GCOS, “GCOS Reference Upper-Air Network (GRUAN): Justification, requirements, siting and instrumentation options,” World Meteorological Organization, Geneva, 2007.

[32] M. Wieser, N. Holden, T. Coplen, J. Böhlke, M. Berglund, W. Brand, P. De Bièvre, M. Gröning, R. Loss, J. Meija, T. Hirata, T. Prohaska, R. Schoenberg, G. O'Connor, T. Walczyk, S. Yoneda and X.-K. Zhu, “Atomic Weights of the Elements 2011 (IUPAC Technical Report),” *Pure and Applied Chemistry,* vol. 85, no. 5, pp. 1047-1078, 2013.

[33] R. Hyland and A. Wexler, “Formulations for the Thermodynamic Properties of the Saturated Phases of H2O from 173.15K to 473.15K,” *ASHRAE Transactions,* vol. 89, no. 2A, pp. 500-519, 1983.

[34] D. Sonntag, “The History of Formulations and Measurements of Saturation Water Vapour Pressure,” in *Third International Symposium on Humidity & Moisture*, Teddington, 1998.

[35] W. Wagner and A. Pruß, “The IAPWS Formulation 1995 for the Thermodynamic Properties of Ordinary Water Substance for General and Scientific Use,” *Journal of Physical and Chemical Reference Data,* vol. 31, no. 2, pp. 387-535, 2002.

[36] JCGM, ”International vocabulary of metrology - Basic and general consepts and associated terms (VIM),” Joint Committee for Guides in Metrology 200:2012.

[37] M. Heinonen, D. Zvizdic and D. Sestan, “Intercomparison of the Dew-Point Temperature Realizations at LPM and MIKES in the Range from −70 °C to + 20 ° C,” *International Journal of Thermophysics,* vol. 33, no. 8-9, pp. 1451-1457, 2012.

[38] M. Heinonen, M. Anagnostou, S. Bell, M. Stevens, R. Benyon, R. Bergerud, J. Bojkovski, R. Bosma, J. Nielsen, N. Böse, P. Cromwell and e. al., “Investigation of the Equivalence of National Dew-Point Temperature Realizations in the −50 °C to + 20 °C Range,” *International Journal of Thermophysics,* vol. 33, no. 8-9, pp. 1422-1437, 2012.

[39] JCGM, “Evaluation of measurement data - Guide to the expression of uncertainty in measurement,” Joint Committee for Guides in Metrology 1000:2008.

[40] EA, “EA-4/02 Evaluation of the Uncertainty of Measurement in Calibration,”

European co-operation for Accreditation, 2013.

[41] A2LA, “G104 - Guide for Estimation of Measurement Uncertainty in Testing,” American Association for Laboratory Accreditation, 2014.

[42] L. Greenspan, “Functional equations for the enhancement factors for CO2 - free moist air,” *Journal of Research of National Bureau of Standards,* vol. 80A, no. 1, pp. 41-44, 1975.

[43] R. Hyland, “A Correlation for the Second Interaction Virial Coefficients and Enhancement Factors for Moist Air,” *Journal of Research of National Bureau of Standards,* vol. 79A, no. 4, pp. 551-560, 1975.

[44] R. Wylie and R. Fisher, “Molecular Interaction of Water Vapor and Air,” *Journal of Chemical&Engineering Data,* vol. 41, no. 1, pp. 133-142, 1996.

[45] C. Meyer and A. Harvey, “The Water-Vapor Enhancement Factor in Compressed Carbon Dioxide,” in *TEMPMEKO 2013 as a presentation*, Funchal, 2013.

[46] C. Melvad, U. Krühne and J. Frederiksen, “Design considerations and initial validation of a liquid microflow calibration setup using parallel operated syringe pumps,” *Measurement Science and Technology,* vol. 21, no. 7, 2010.

[47] F. Marinozzi, F. Bini and P. Cappa, “Calibrator for microflow delivery systems,” *Review of Scientific instruments,* vol. 76, no. 1, 2005.

[48] ISO 6145-4, ”Gas analysis - preparation of calibration gas mixtures using dynamic volumetric methods - part 4: continuous syringe injection method,” International Organization for Standardization, 2004.

[49] H. Bissig, M. Tschannen and M. de Huu, “Micro-flow facility for traceability in steady and pulsating flow,” *Flow Measurement and Instrumentation,* http://dx.doi.org/10.1016/j.flowmeasinst.2014.11.008, 2014.

[50] ASTM E542-01, ”Standard Practice for Calibration of Laboratory Volumetric Apparatus,” ASTM International, 2012.

[51] M. Tanaka, G. Girard, R. Davis, A. Peuto and N. Bignell, “Recommended table for the density of water between 0 °C and 40 °C based on recent experimental reports,” *Metrologia,* vol. 38, no. 4, pp. 301-309, 2001.

[52] EURAMET, “Project 1291 - Comparison of primary standards for liquid micro flow rates,” The European Association of National Metrology Institutes, http://www.euramet.org, 2015.

[53] A. Kentved, M. Heinonen and D. Hudoklin, “Practical Study of Psychrometer Calibrations,” *International Journal of Thermophysics,* vol. 33, no. 8-9, pp. 1408-1421, 2012.

[54] ASTM D1142, “Standard Test Method for Water Vapor Content of Gaseous Fuels by Measurement of Dew-Point Temperature,” ASTM International, 2012.

[55] R. Wylie and R. Fisher, “Molecular Interaction of Water Vapor and Air,” *Journal of Chemical & Engineering Data,* vol. 41, no. 1, pp. 133-142, 1996.

[56] M. Heinonen, “Simplified methods to calculate the dew-point temperature change due to a pressure drop,” in *Proceedings of TEMPMEKO 2001*, Berlin, 2002.

[57] EURAMET, “Publishable JRP Summary Report for ENG54 Biogas Metrology for biogas,” The European Association of National Metrology Institutes, http://www.euramet.org, 2014.

[58] B. Choi, J. Kim and S. Woo, “Uncertainty of the Kriss Low Frost-Point Humidity Generator,” *International Journal of Thermophysics ,* vol. 33, no. 8-9, pp. 1559-1567, 2012.

[59] G. Mamontov, “Application of the phase equilibrium method for generation of -100 °C of humid gas frost-point temperature,” *Measurement Science and Technology,* vol. 11, no. 6, 2000.

[60] H. Abe and H. Kitano, “Development of humidity standard in trace-moisture region: Characteristics of humidity generation of diffusion tube humidity generator,” *Sensors and Actuators A: Physical,* vol. 128, no. 1, pp. 202-208, 2006.

[61] C. Meyer, W. Miller, D. Ripple and G. Scace, “Performance and Validation Tests on the NIST Hybrid Humidity Generator,” *International Journal of Thermophysics,* vol. 29, no. 5, pp. 1606-1614, 2008.

[62] A. Lakka, H. Sairanen, M. Heinonen and R. Högström, “Comsol Simulations as a tool in Validating a Measurement Chamber,” in *TEMPMEKO 2013 as a presentation*, Funchal, 2013.

[63] EURAMET, “Publishable JRP Summary Report for ENV58 MeteoMet2 Metrology for Essential Climate Variables,” The European Association of National Metrology Institutes, http://www.euramet.org, 2014.

Publication errata

Publication I:

Page 188: equation 2 should be:

$$\dot{V}_w = \frac{\dot{V}_g \rho_g M_w}{\rho_w M_g} \frac{f(p,T_d) e_w(T_d)}{p - f(p,T_d) e_w(T_d)}$$

Publication 1

Sairanen, Hannu; Heinonen, Martti. 2014. Hygrometer-based calibration method for syringe pumps providing ultra-low liquid flows. Springer. Microfluidics and Nanofluidics, volume 16, issue 1-2, pages 187-193. ISSN 1613-4982. DOI: 10.1007/s10404-013-1233-6.

Publication 2

Sairanen, Hannu; Heinonen, Martti. 2014. Validation for a new apparatus measuring water vapour enhancement factors up to 6 MPa. IOP Publishing. Measurement Science and Technology, volume 25, issue 3. ISSN 0957-0233 . DOI: 10.1088/0957-0233/25/3/035301.

Publication 3

Sairanen, Hannu; Heinonen, Martti. 2014. Enhancement Factor for Water Vapor–Pressure Correction in Humid Methane. Springer. International Journal of Thermophysics, volume 35, issue 6-7, pages 1280-1289. ISSN 0195-928X. DOI: 10.1007/s10765-014-1720-3

Publication 4

Sairanen, Hannu; Heinonen, Martti; Högström, Richard; Lakka, Antti; Kajastie, Heikki. 2014. A Calibration System for Reference Radiosondes that Meets GRUAN Uncertainty Requirements, NCSL International. Measure, The Journal of Measurement Science, volume 9, issue 3, pages 56-60, ISSN 1931-5775

Publication 5

Sairanen, Hannu; Heinonen, Martti; Högström Richard. 2015. Validation of a calibration set-up for radiosondes to fulfil GRUAN requirements. IOP Publishing. Measurement Science and Technology, volume 26, issue 10. ISSN 0957-0233. DOI: 10.1088/0957-0233/26/10/105901.

Aalto-DD 212/2015
VTT SCIENCE 119

ISBN 978-952-60-6576-2 (printed)
ISBN 978-952-60-6577-9 (pdf)
ISSN-L 1799-4934
ISSN 1799-4934 (printed)
ISSN 1799-4942 (pdf)

978-951-38-8377-5 (printed)
978-951-38-8376-8 (pdf)
2242-119X
2242-119X (printed)
2242-1203 (pdf)

Aalto University
School of Engineering
Department of Energy Technology
www.aalto.fi

BUSINESS +
ECONOMY

ART +
DESIGN +
ARCHITECTURE

SCIENCE +
TECHNOLOGY

CROSSOVER

DOCTORAL
DISSERTATIONS