Vision for Development of Metrology at University of Tartu 2003-2007

05.06.2003

Ivo Leito

Testing Centre, University of Tartu

1 Introduction

In this document the vision of development of metrology at University of Tartu (UT) for the period of 2003-2007 is presented. This vision is based on the recently compiled strategy plan for the Estonian Metrology Infrastructure [1] that outlines the main directions of development of metrology in Estonia. According to the strategy plan University of Tartu is one of the three institutions of the distributed National Measurement Institute (the other two being Metrosert Ltd and Tallinn Technical University).

The fields of metrology that will be developed at UT are specified in the strategy plan and in the Fiche of the Project PHARE 2001 ES 0102.01 “Development of Conformity Assessment Infrastructure in the field of metrology” [2] as follows:

1. **Metrology in Chemistry (MiC)**
   - **1.1. Chromatography-mass-spectrometry**
   - **1.2. pH metry**
   - **1.3. Spectrophotometry**
2. **Air Humidity and Air Flow Velocity**

2 The Envisaged Activities

2.1 Overview

The envisaged activities are presented in Table 1.

Table 1. Metrology Activities Envisaged for University of Tartu.

Activity	**Beneficiary, comments**	**Financing**
1 Providing traceability in MiC (ie providing/mediating reference materials or providing reference/comparison measurements).	Beneficiaries: all institutions engaged in measurements. See chapter 2.2 for details.	Partly by the beneficiary, partly from the state budget (see chapter 2.2 for details)

2 Measurement and calibration services in the field of air humidity and air flow velocity	Beneficiaries: All institutions interested in air humidity and air flow velocity measurements	The particular services: by the beneficiary; Maintenance of the facilities: 1. Before appointment as National standard: by UT; 2. After Appointment as National Standard: from the state budget [3].
3 Developing, maintaining applying and disseminating competence in metrology, in particular MiC.		
3.1 Acting as pilot lab in implementing novel measurement and analysis methods. Carrying out applied research in MiC.	Beneficiaries: field labs	Financing of the direct costs of the activity by the beneficiaries (in special cases, e.g. critically important for the interests of the Country, by the government)
3.2 Giving guidance in applying MiC approach to chemical measurements (measurement uncertainty, traceability of measurement results, method validation, etc).	Beneficiaries: field labs	various
3.3 Providing reference measurements and comparison measurements, especially in difficult/disputable cases.	Beneficiaries: field labs also courts	Financing of the direct costs of the activity by the beneficiaries (in special cases by the government) Financing of the routine maintenance of the labs and the equipment: in part by UT, in part by the government.
4 Support to teaching and training of MiC		
4.1 Training analysts-practitioners, accreditors and end-users of measurements	Beneficiaries: all possible institutions involved in some way in measurements. Comment about the role of the equipment in training: it is impossible to develop a practice-oriented course without being involved in measurements in practical way and having good instrumentation.	Certain necessary minimum can be financed by the Government. The rest is financed by the beneficiaries
4.2 Support to teaching metrology, in particular MiC at UT	Beneficiary: The whole country	Financing from the state budget, as normal teaching activity at UT.
4.3 Training of Master and PhD students	Beneficiary: The whole country. The topic of a student is metrology-related. Whole or part of the work is carried out at the Testing Centre. The students participate in maintenance, ILCs, etc. See chapter 2.3.	Financing from the state budget as normal teaching activity at UT.
5 Maintaining an overview of the chemical measurement	Beneficiary: The whole country	Financing from the state budget

capabilities of the country and strategic planning of development of measurement capability of the country.		
6 Organising/mediating/promoting interlaboratory comparison measurements.	Beneficiaries: field labs. UT can organise ILCs that are for some reason uninteresting to commercial ILC organisers but are highly necessary to the country. See chapter 2.4.	Certain necessary minimum financed by the Government. The rest is financed by the participants.
7 Providing support in the field of metrology, (MiC in particular) to Governmental and public metrology institutions		
7.1 Support in drafting legislation	Beneficiary: The whole country	Financing from the state budget
7.2 Participation in metrology- and measurement-related National projects and programmes	Beneficiary: Various	Financing from the respective project or programme
7.3 Representatives in National Metrology council	Beneficiary: The whole country	According to the statute of the Council
7.4 Collaboration with the Estonian Centre for Standardisation (EVS) (guidance in adopting/translating international standards, guidance in drafting national standards)	Beneficiary: EVS	Financing according to the financing scheme of standardisation
8 Support to the Estonian Accreditation Centre (EAK)		
8.1 Participating in the Board of EAK	Beneficiary: EAK	According to the statute of the Board
8.2 Acting as independent external technical assessors for EAK	Beneficiary: EAK The advantage of the UT: it is neutral.	Financed according to the financial scheme applied in accreditation
9 International collaboration		
9.1 Collaborating with metrology (incl MiC) bodies in other countries and with international metrology organisations	Beneficiaries: The whole country Comments: See chapter 2.5.	Financing from the State budget [3]
9.2 Participating in international interlaboratory comparison measurements	All Beneficiaries of the measurement and calibration services	1. Before appointment as National standard: by UT; 2. After appointment as National standard: from the state budget [3].
9.3 Participating in international metrology-related projects and programmes	Beneficiaries: Various	Financing by the respective programme

Below some of the activities presented in Table 1 will be described in more detail.

2.2 Traceability of Chemical Measurements

Of all the metrological concepts the concept of traceability has been the most difficult to apply to chemical measurements and to understand in the context of MiC. There is still some confusion and only now a more or less unified understanding is starting to emerge [4, 5]. Traceability of chemical measurement results at field laboratory level is normally established using Certified Reference Materials (CRMs) [4, 5]. A large variety of CRMs are available internationally [6]. However, the need for CRMs can never be completely satisfied because there is an endless number of analyte-matrix-level combinations that can be encountered in analytical work.

Production of CRMs is a very costly endeavour and for a small country like Estonia this will come into consideration only in the case of strong need for a CRM specifically important for that country. This activity normally needs financing from the state.

Another possibility to establish traceability of chemical measurement results is to use the so-called primary measurement methods [7]. Of these the most versatile – suitable for determination of a wide range of analytes at low concentration levels – is the isotope dilution mass spectrometry. This is a very important point in favour of the LC-MS method: isotope dilution procedures can be used with this method. And on the other hand: the method can handle low concentrations of high molecular weight organic compounds – the class of analytes with which the problems with establishing traceability are the most serious. See chapter 3. The reference measurements are less costly than preparation of CRMs and the cost can normally be covered by the beneficiary of the measurement, only in certain cases financing from the state is needed.

2.3 Training of Master and Ph.D. Students and Analysts-Practitioners

One of the main features of development of metrology at UT is the synergism between the metrology-related activities on one hand and master and doctoral studies on the other hand.

The involvement of the master and doctoral students in the metrology-related activities at UT and the resulting knowledge dissemination in the country is one of the most efficient channels of benefit for the country.

All the technical activities described in the chapters 3 - 6 will be (and in several cases already are) connected to Master and Doctoral studies at the University of Tartu. This way the accumulation and dissemination of measurement competence in the country will be achieved.

Several bachelor degrees, three master degrees and one Ph. D. degree related to metrology have been defended at UT during the recent years. Several M. Sc. and Ph. D. students are currently actively working.

UT has been very active in training analysts practitioners during the last years [8]. Courses on various topics of MiC and analytical chemistry have been developed and delivered with success to practitioners from industry and field laboratories. It is planned to further intensify this activity.

2.4 Organising and Mediating Interlaboratory Comparison Measurements (ILCs)

The main beneficiaries of the ILCs and are field laboratories. ILCs in MiC are organised to some extent in Estonia but their variety is limited to wastewater, groundwater and surface water. The number of internationally offered ILCs and proficiency testing schemes (PTSs) is quite large [9]. However, the recent surveys and workshops [10, 11] have indicated that there is considerable unsatisfied demand for ILCs in Estonia, even taking into account the internationally available ILCs.

As the nearest activity in this field, on the recent Annual meeting of Lithuanian Chemists [11] it was agreed to start joint organising of Inter-Baltic interlaboratory comparison measurements in MiC. The first round is expected to be launched in Autumn 2003.

UT Testing Centre is the Estonian national co-ordinating body for the IMEP interlaboratory comparison measurements (organised by EC JRC IRMM). One round (IMEP 20 “Trace Elements in Tuna Fish”) is currently in progress. This activity will continue.

It is also envisaged to provide/mediate other interlaboratory comparison measurements meeting the unsatisfied needs of the country.

2.5 International Collaboration

Participation in the activities of EUROMET [12] (in the case of MiC the joint technical committee of EUROMET and EURACHEM: EUROMET METCHEM [13]) and in the field of MiC also participation in EURACHEM [14] is planned.

The very fruitful collaboration with the EC JRC IRMM in the field of MiC will continue and hopefully expand (teaching, training, ILCs, reference measurements, joint projects, exchange of students and staff members). The collaboration between the Baltic countries has started and will intensify (teaching, training, ILCs, reference measurements, joint projects, student mobility).

In the following chapters the planned activities are described from an equipment-technical point of view and in a more detailed way. Obvious supporting activities, mentioned in Table 1 such as maintaining and monitoring the equipment, routine participation in interlaboratory comparisons, etc will not be repeated in detail.

3 Liquid Chromatography Mass Spectrometry

3.1 Situation in the Field of LC-MS

Recent developments in LC-MS (Liquid Chromatography – Mass Spectrometry), mainly atmospheric pressure ionisation and off-axis spraying, have made the technique as reliable, versatile and easy-to-use as capillary GC-MS (Gas Chromatography – Mass Spectrometry) [15]. The situation is parallel to the situation with GC-MS in the past: what once was a clumsy and tricky technique has turned into a routine workhorse. The "turning into a workhorse" process is now nearing completion also with LC-MS [16, 17].

The very fast progress in the LC-MS field is confirmed with thousands of publications in recent years [15]. The main reason for this interest is the intrinsic advantage of LC-MS compared to GC-MS, namely: **both volatile and non-volatile compounds can be analysed with LC-MS, while the GC-MS method is restricted to volatile compounds**. Thus various polar pesticides, food constituents, doping compounds, veterinary drugs, algae toxins, etc, etc, etc can be analysed by LC-MS but not by GC-MS. LC–MS plays a key role in the development of new analytical strategies for pollutants of high priority in the European Community, namely the endocrine disrupting chemicals (EDCs) [18]. EDCs are synthetic or naturally occurring chemicals that interfere with endocrine functions. Many examples of the application of LC–MS to the analysis of EDCs can be found in the recent chromatographic and environmental literature. [18] **The LC-MS method is already now firmly established in the EU regulations** relevant to the methods of chemical analysis and measurements [19, 20].

Mass Spectrometry (MS) is rightly regarded as more than just a detection method. It is, in fact, another separation technique, and it is orthogonal to high performance liquid chromatography (HPLC), that is, it relies on a different physical property of the analyte to effect separation. Although HPLC relies on the analyte affinity for a stationary phase, MS relies on the mass-to-charge ratio (m/z) of ions derived from the compounds of interest. Liquid chromatography coupled to mass spectrometry (LC-MS) has become an indispensable tool for problem solving in virtually all analytical fields requiring "information-rich" chemical analysis. In the next decade, the LC-MS instrument market is expected to grow at more than twice the rate of the broader instrument market and **will probably surpass gas chromatography-mass spectrometry (GC-MS) as the leader of the so-called hyphenated techniques**. [21]

MS as a detector has a very important advantage from the metrological point of view: it enables to apply the isotope dilution procedures and thus establish traceability of measurement results without reference to external standard.

3.2 Planned Activities

Several of the classes of compounds mentioned above are very important also for Estonia and their determination is currently problematic in Estonia [10]. Also numerous other measurements can be carried out using the LC-MS instrumentation. Possible groups of activities with short descriptions are given below. Due to the non-routine character of most of the measurements and services it is very difficult to estimate annual volumes. They can range from few hundreds of measurements to several tens of thousands. An important point in favour of the LC-MS method is the possibility to provide primary measurements for which traceability can be demonstrated without reference to an external standard (see above). Due to the extreme versatility of the analyte-matrix-level combination it is also impossible to specify concentration ranges. The uncertainty range is expected to be from 2-3% rel (k = 2) for the most favourable conditions to 50-80% rel (k = 2) for the most difficult conditions. In some cases qualitative results can be provided only.

The fees of the services and the sums of the project contracts will be based on real expenditure taking into account all types of expenditure.

3.2.1 Services to and Joint Projects with Industry

Certain number of basic analytical services will be set up. More complicated requests from industry will be handled on project basis. The fields are for example:

- Building materials and furniture industry: elucidation of composition of paints, varnishes, lacquers, ...
- Chemical industry: wide range of analyses and investigations.
- Food industry: contaminants, minor constituents, flavour compounds, studies of food degradation, ...

3.2.2 Services to and Joint Projects with Field Laboratories

- Carrying out complicated analyses and measurements not possible at field labs.

- Development and adjustment of analytical methods, especially for newly emerging analytes.
- Providing traceability via reference measurements using the isotope dilution technique.

3.2.3 Other

- Analysis of various other objects (objects of historical value, forensics, ...).
- Establishing reference values for ILCs.

4 pH Metry

4.1 Situation

Although pH is among the most important and frequent chemical measurements, reliable measurement of pH is not straightforward [22]. This is also witnessed by the often quite wide spread of the results of pH related ILCs. Application of metrological concepts and good laboratory practices to pH measurement is essential to achieve reliable results.

Directly connected to pH measurement are other potentiometric measurements of ions using ion-selective electrodes.

4.2 Planned Activities

The activities that are already running [8] or are planned are listed below. Because in routine cases for routine laboratories the most convenient way to establish traceability is using pH CRMs, the focus is more on supporting and underpinning the laboratory community and only in more complex cases actual providing of traceability. Except the simple consultation and guidance services all of them are fee-charging. The fees are based on real expenditure.

The following services are envisaged:

- Guidance and consultation
- Calibration of a pH meters (pH range 1 .. 13 with uncertainties varying from 0.04 (k = 2) in the middle of the range to 0.15 (k = 2) at the extremes)
- Testing of pH meters and pH electrodes
- Maintenance and repairs of pH meters and pH electrodes
- Calibration, testing, maintenance and repairs of ion-selective electrodes
- Complex measurement tasks in the field of pH metry orionometry (on contract basis)

5 Spectrophotometry

5.1 The Situation

Spectrophotometry is among the most widespread analytical techniques in field laboratories. Photometers and spectrophotometers are probably the third instruments by abundance in field laboratories (after balances and pH meters). When speaking about traceability of spectrophotometric measurements then it is necessary to distinguish between the traceability of the photometric quantities (wavelength and absorbance values) and the traceability of the chemical measurement results. It is important to keep in mind that the checking and calibration of the wavelength and the absorbance scale of the photometer does not guarantee (and is in principle not necessary for) the traceability of the chemical measurement results. However, it is very advisable to have the photometric parameters of the spectrometer under close control because they are good indicators for the overall performance of the instrument. Traceability of the chemical measurement results is usually established via CRMs as in the case of the LC-MS method. Due to the extreme versatility of the analyte-matrix-level combination it is also impossible to specify concentration ranges. The uncertainty range is expected to be from 2% rel (k = 2) for the most favourable conditions to 50-60% rel (k = 2) for the most difficult conditions. In some cases qualitative results can be provided only.

5.2 Planned Activities

It will be possible to carry out the following activities. Except the simple consultation and guidance services all of them are fee-charging. The fees are based on real expenditure.

- Calibration, check and repairs on spectrophotometers
- Development of new analytical methods
- Non-routine measurements
- Consultations

6 Air Humidity and Air Flow Velocity

6.1 The Situation

Air humidity and air flow velocity are among the most frequently used parameters of microclimate. There are no national standards in Estonia on air humidity and air flow velocity and **there is currently no possibility of traceable calibration of either air humidity or air flow velocity measuring instruments in Estonia** [10]. Some low level comparison activities (not traceable calibration!) are carried out by those users of air humidity and air flow velocity measurements for whom calibration in Sweden or Finland is far too expensive.

There are eight major groups of enterprises or institutions that need traceable calibration of air humidity and air flow velocity measurement instruments:

1. Meteorology service (weather stations). There are 22 manned and 1 unmanned weather stations in Estonia and 35 agrometeorology observation points.
2. Laboratories accredited according to ISO/IEC 17025, that need to measure air humidity and air flow velocity for assessment of measurement uncertainty of their measurement results. There are 95 laboratories of that type in Estonia.
3. Companies engaged in design, construction and servicing of ventilation, heating, conditioning and other systems and installations. There are at least 15 of those in Estonia.
4. High-tech production facilities that need to maintain the microclimate parameters at constant level.
5. Laboratories that are accredited for measurements of working environment and microclimate parameters. There are 8 state laboratories in this group (the HPI and others) and at least 14 private companies.

6. Archives, museums and libraries of national importance. In this group there are currently 4 archives, 14 museums and 14 libraries.
7. Wholesale storehouses (particularly food products and delicate materials), also vehicles meant for transport of such goods.
8. Companies engaged in excavation operations.

According to the results of a recent survey [10]:

- The above mentioned 8 groups of users from various fields of activities who need traceable measurements of air humidity and air flow velocity have **total annual volume of air humidity measurements 85 000 to 120 000 and air flow velocity measurements 34 000 to 36 000**.
- **The estimated number of air humidity measurement instruments in Estonia that need traceable calibration is 200, for air flow velocity the number of instruments is 160.**
- **The estimated annual traceable calibration need in air humidity measurements is 100 calibrations, in air flow velocity 80 calibrations.**

6.2 Planned Activities

The activities in the field of air humidity and air flow velocity measurements are planned according to the Report of Jan Nielsen (NMi VSL) [23] and the recommendations of Martti Heinonen (MIKES). The main aim of the activities is to normalise the situation in Estonia with traceable calibration hygrometers and anemometers.

6.2.1 Section for Humidity

1.1. Tasks

1.1.1. Development and realisation of the National Standard for absolute and relative humidity in following content:

1) Climatic test chamber, 200 l with an optional air drier to enable dew points down to – 20 ^{0}C to be generated
2) High-precisiondewpoint-meter with operating range < –20 ^{0}C to +60 ^{0}C and expected uncertainty 0.2 K to 0.3 K

1.1.2. **Services**: Calibration of hygrometers and humidity sensors of all working principles.

1.2. Technical data of the standard

1.2.1. relative humidity, RH %	10 – 90
1.2.2. values of temperature, ^{0}C	10 – 90
1.2.3. expected uncertainty, RH %	1 – 3

1.3. Number of calibration services per year (estimated) 100

6.2.2 Section for Air Flow Velocity

2.1. Tasks

2.1.1. Development and realisation of the National Standard for air flow velocity in following content:

1) hot wire and thermistor sensors,
2) rotating calibrator of velocity,
3) wind tunnel
4) anemometers, Prandtl Pitot tubes, rotating vanes (sensors)

2.1.2. **Services**: Calibration of anemometers and air flow velocity sensors, except laser anemometers.

.

2.2. Technical data of the Standard

2.2.1. air flow velocity, m/s	0.02 – 30
2.2.2. rated values of temperature, ^{0}C	20, 23
2.2.3. best measurement capability of velocity, m/s	0.002 – 1
2.2.4. expanded temperature interval, ^{0}C	10 – 30

2.3. Calibration services per year (estimated**)**	50 – 80

7 References

1. Institution Building of Regulatory Bodies Under Supervision of the Ministry of Economic Affairs – Metrology. Strategy plan for Estonian metrology infrastructure: 2002 – 2007. NMi Van Swinden Laboratorium B.V. in co-operation with RvA. Authors: C. Oosterman and H. den Boer. Project number: PHARE ES9903.01. December **2002**.
2. Project PHARE 2001 ES 0102.01 "Development of Conformity Assessment Infrastructure in the field of metrology". Project Fiche, **2002**.
3. Metrology Act. RT I 2000, 71, 44.
4. King B *Accred. Qual. Assur. 5*, 429-436, **2000**.
5. Traceability in Chemical Measurement. A guide to achieving comparable results in chemical measurement. Voting Draft, March 2003. EURACHEM/CITAC, **2003**.
6. The COMAR database. http://www.comar.bam.de/
7. Taylor P, Kipphardt H, De Bièvre P *Accred. Qual. Assur. 6*, 103-106, **2001**.
8. UT Testing Centre. Services. http://www.ut.ee/katsekoda/services.html
9. EPTIS (European Proficiency Testing Information System). http://www.eptis.bam.de/
10. Chemical Analyses and Measurements: the Needs of Estonia. Final report. Testing Centre, University of Tartu. Tartu, **2002**.
11. Annual Meeting of Lithuanian Chemists, 26-28.05.**2003**, Palanga, Dedicated to Traceability of Chemical Measurements.
12. EUROMET, A European Collaboration in Measurement Standards. http://www.euromet.org/
13. EUROMET METCHEM. The Joint technical Committee of EUROMET and EURACHEM. http://www.npl.co.uk/environment/mic_index.html
14. EURACHEM. A Focus on Analytical Chemistry in Europe. http://www.eurachem.org/
15. LC-GC Europe. Special issue: *Guide to LC-MS* December **2001**.
16. Niessen WMA. *Journal of Chromatography A* 856 (1-2): 179-197 SEP 24 **1999**.
17. Slobodnik J, Vanbaar BLM, Brinkman UAT, *Journal of chromatography A*, 703 (1-2): 81-121 MAY 26 **1995**.
18. LC-GC Europe. Special issue: *Recent Applications in LC-MS* November **2002**.
19. Communication from the Commission to the Council and the European Parliament on the implementation of the Community strategy for Endocrine Disrupters – a range of substances suspected of interfering with the hormone systems of humans and wildlife (COM (1999) 706), Brussels, 14.06.**2001**.
20. COMMISSION DECISION of 12 August **2002** implementing Council Directive 96/23/EC concerning the performance of analytical methods and the interpretation of results (notified under document number C(2002) 3044) (Text with EEA relevance), **2002/657/EC**.
21. Simal-Gandara J, Damant AP, Castle L. *Critical Reviews in Analytical Chemistry* 32 (1): 47-78 **2002**.
22. Naumann R, Alexander-Weber Ch, Eberhardt R, Giera J,·Spitzer P *Anal. Bioanal. Chem. 374* 778–786, **2002**.
23. Institution Building of Regulatory Bodies Under Supervision of the Ministry of Economic Affairs – Metrology Centre. Report visit no. 7 Analysis of the measurement standards and

proposal for further development in the field of temperature and air humidity. Prepared by Jan Nielsen. March, **2002**.

8 Annex 1. Abbreviations

Abbreviation	**Meaning**
CRMs	Certified Reference Materials
EAK	Estonian Accreditation Centre
EC JRC IRMM	European Commission Joint Research Centre Institute for Reference Materials and Measurements
EVS	Estonian Centre for Standardisation
GC-MS	Gas Chromatography Mass Spectrometry
HPI	Health Protection Inspectorate
HPLC	High Performance Liquid Chromatography
ILCs	Interlaboratory Comparisons
IMEP	International Measurement Evaluation Programme
LC-MS	Liquid Chromatography Mass Spectrometry
MiC	Metrology in Chemistry
MS	Mass Spectrometry
NMI	National Metrology Institute
PTSs	Proficiency Testing Schemes
RH	Relative Humidity
UT	University of Tartu