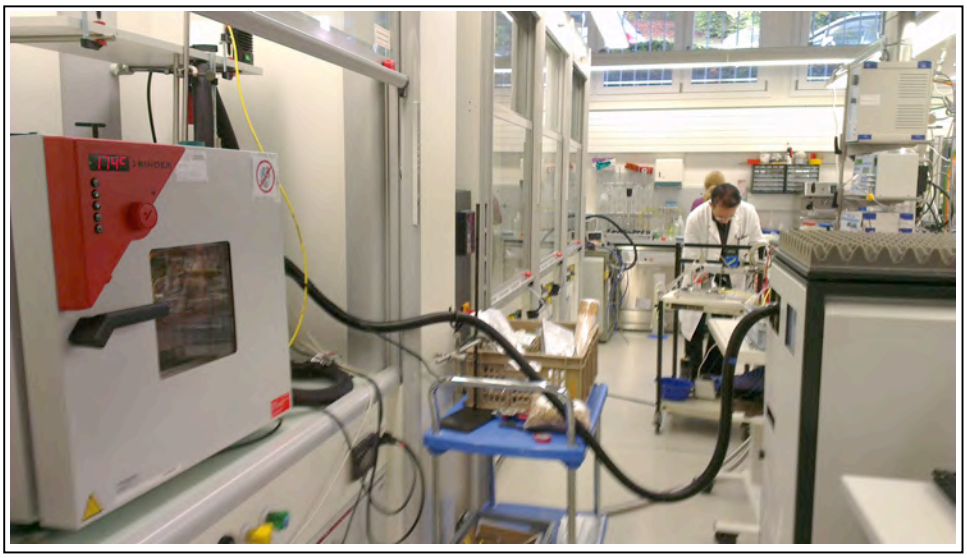
Improving quality of wine maturation products through real-time analysis of oak wood volatiles using Proton-Transfer-Reaction Mass Spectrometry



FINAL REPORT to
GRAPE AND WINE RESEARCH & DEVELOPMENT CORPORATION

Project Number: **GWT 1308**

Principal Investigator: **Ross Farrell**

Principal Supervisor: **Assoc. Prof. Robert Shellie**

Research Organisation: **Australian Centre for Research On Separation Science, University of Tasmania.**

Date: **10/01/2014**

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Executive Summary

The author (Ross Farrell) travelled to Switzerland to undertake a research placement at Zurich University of Applied Science (ZHAW), from September-December 2013. A GWRDC travel grant was used to part fund the flight costs to Zurich. The balance of funding (accommodation and living expenses) was provided by ZHAW and UTAS. The research placement was conducted under the supervision of Professor Chahan Yeretzian (Head of Analytical and Physical Chemistry). Prof. Yeretzian is an expert in the application of real-time mass spectrometry, (primarily) in the coffee industry.

The placement was focused on gaining experience in Proton Transfer Reaction Mass Spectrometry (PTR-MS) as a real-time technology for monitoring and analysing volatile organic compounds (VOC's). The specific objective was to evaluate the potential PTR-MS for real-time analysis of oak aroma compounds of oenological importance. This report also summarises (in brief) previous applications of PTR-MS relevant to the grape and wine industry. The majority of time at ZHAW was spent on the development and set-up of an experimental system to monitor aroma development during the oak toasting process in real-time. Sample staves were provided by Canton Cooperage (Kentucky, USA) part of the Chene & Cie group of cooperages. Once the instrument parameters and experimental set-up were refined, a number of toasting experiments were conducted. The aims of the experiments were to elucidate aromatic development during oak toasting and demonstrate "proof-of-principle" for the application of PTR-MS for real-time analysis of oak aroma compounds. A manuscript is currently being prepared for publication in a suitable Analytical Chemistry journal, detailing the experimental methodology and results.

The 1st International Mass Spectrometry Summer School, Siena, Italy (15-20th September) was also attended through a Fellowship from the International Mass Spectrometry Foundation (IMSF). This provided a remarkable opportunity to network and engage with world leaders and visionaries in the field of mass spectrometry (MS). Informal discussions were had with distinguished Professors and MS peers regarding the application of MS techniques for real-time analysis of oak wood volatiles. Such discussion has helped identify and refine analytical approaches highly relevant to my PhD research.

A leading manufacturer of field deployable mass spectrometry instruments (Tofwerk, Thun Switzerland) was also visited (12th December 2013). A tour of the facility was conducted including a hands-on demonstration of the instruments relevant to my particular application and compounds of interest. Discussions were had with key R&D personnel and ideas explored regarding the analytical platforms available and a strategy for future collaboration. Immediate work at ACROSS will focus on the development of a prototype sampling system that can be interfaced with a suitable Tofwerk analytical platform. Several possibilities exist here and the most promising methods will be short-listed following discussion and review with the project supervisors and ACROSS peers (February 2014).

Overall, the research placement at ZHAW provided a great learning opportunity through development of networks with a range of academic and industry members. The experience has helped refine and focus my future PhD activities and GWRDC, ZHAW and UTAS are gratefully acknowledged for enabling this opportunity.

Background

This travel award supported an international research placement undertaken as part of my PhD research currently underway at the Australian Centre for Research on Separation Science, UTAS. The project (Optimising oak expression in wine through real-time flavour profiling of maturation products) seeks to develop a tool for real-time flavour profiling of oak wood to objectively classify wine maturation products according to their chemical composition and thus better predict and control wine flavour impact.

The research placement (September to December 2013) was undertaken at Zurich University of Applied Sciences (ZHAW) with Professor Yeretzian's research group who specialise in analytics applied in the coffee industry. Their expertise includes a wealth of experience regarding on-site, real-time analysis of volatile organic compounds (VOC's) from industrial coffee roasters. Prof. Yeretzian was a pioneer in the application of Proton Transfer Reaction Mass Spectrometry (PTR-MS) in the coffee industry during his early work at Nestle. The primary objective of this research placement was to gain practical experience in the application of a real-time mass spectrometry technique and to evaluate the potential to apply PTR-MS to the quality control of wine maturation products (i.e. oak barrels and barrel alternatives).

Project Objectives and Outputs

Objectives

1. Work with leading researchers with expertise in the application of real-time mass spectrometry and chemometrics at Zurich University of Applied Sciences (ZHAW).

2. Gain practical experience of proton-transfer-reaction mass spectrometry (PTR-MS).

3. Conduct preliminary assessment of the potential of this technology for real-time analysis of oak wood volatiles.

4. Meet with R&D personnel of an innovative and highly regarded manufacturer of mass spectrometry instruments to discuss instrument developments, alternative analytical approaches and potential collaboration (Tofwerk, Thun, Switzerland).

5. Attend the 3rd MS Food Day conference in Trento Italy to learn about state-of-the-art applications of mass spectrometry in food chemistry.

Activities associated with all objectives were carried out with the exception of attendance of the 3rd MS Food Day Conference due to a timing conflict with experimental work at ZHAW. However, I was fortunate to attend the 1st International Mass Spectrometry Summer School (15^{th}-20^{th} September – Siena, Italy) whilst based in Switzerland.

Planned Project Outputs

Output	Performance Targets	Date
Assessment of oak wood volatiles using PTR-MS	Develop model to predict toasted aroma profile from untoasted wood. Assess model quality using error of prediction. Potential for real time control of toasting process to be discussed.	15/12/13
Dissemination of knowledge gained via GWRDC travel report and an industry article.	Preparation of GWRDC final report. Preparation of short article suitable for publication in R&D@Work, reviewing state-of-the-art mass spectrometry and how these techniques can be applied to quality control of cooperage products and implications for winemakers (if deemed of interest).	31/12/13
Determine analytical strategy and methodology for detailed investigation (focus of PhD).	Present findings to peers at ACROSS. Obtain feedback regarding analytical techniques and best solution strategy.	13/02/14
Publication discussing application of PTR-MS for real-time analysis of oak wood volatiles.	Prepare and submit manuscript to a suitable peer reviewed Analytical Chemistry journal TBD	30/04/14

Key Activities

Research Placement - Zurich University of Applied Science

Introduction To PTR-MS

Proton transfer reaction mass spectrometry (PTR-MS) is a commercial technology (via IONICON Analytic, Austria or Kore Technolgy, UK) used for on-line monitoring and analysis of VOC's. The primary requirements for an instrument to perform real-time VOC analysis are a high sensitivity for detection of compounds, a fast response time and no or minimal sample pre-treatment or preparation[1]. PTR-MS fulfils these criteria, offering low limits of detection (linear range from 10 pptv to ~10 ppmv) and provides "soft ionization" of target compounds resulting in low fragmentation rates compared to other ionisation methods (e.g. electron ionisation). The soft ionisation retains the "molecular ion" in the mass spectrum providing a valuable tool in the identification of unknown compounds.

PTR-MS has been applied for real-time measurement in a wide variety of fields[1–10] including medical diagnostics (e.g. detection of disease markers in human breath), security (e.g. detection of explosives and contraband), food and flavour (e.g. direct analysis of volatiles from fruit, olive oils and coffee) and environmental research (e.g. atmospheric research and air quality analysis). Proton transfer mass spectrometry holds promise for real-time online monitoring and industrial process control as demonstrated in the reported applications[11–14]. This potential is supported by previous research conducted at ZHAW applying the method for on-site, real-time analysis of industrial coffee roasting and tobacco toasting processes.

The PTR-MS instruments at ZHAW include a PTR quadrupole (PTR-QMS) and a PTR Time-Of-Flight (PTR-TOFMS) instrument, both from Ionicon Analytik. The latter instrument was utilized in the research summarized in this report. The advantage of the TOFMS instrument (**Figure 1**) is primarily related to the higher mass resolution allowing discrimination of nominally isobaric compounds and determination of exact formulae i.e. elemental composition.

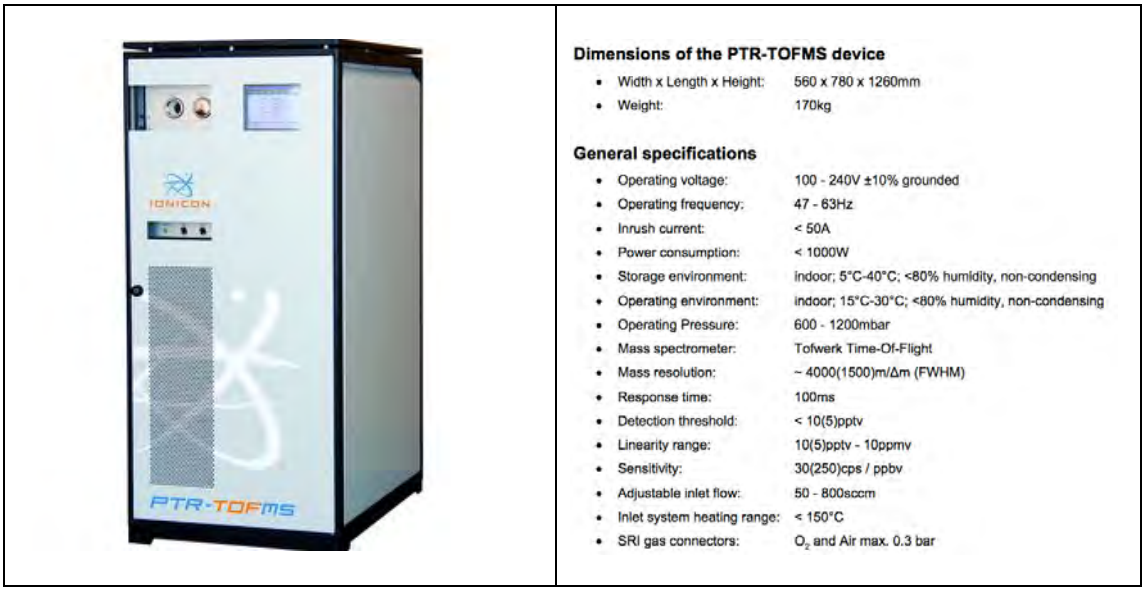


Figure 1: PTR-TOFMS From Ionicon Analytik

These factors permit greater certainty in the identification of the detected VOC's compared to the unit resolution (1 Da) of a QMS instrument. The second advantage of the TOFMS is the speed of data acquisition. A QMS instrument must continuously switch (scan) between

compounds of interest limiting sensitivity and accuracy with small time resolutions, whilst the TOFMS instrument can attain all detected compound spectra within a fraction of a second[15]. The disadvantage of TOFMS versus QMS is the higher instrument cost. However, future application of PTR-MS to oak volatiles could utilize the lower cost instrument once compound identification has been confirmed using a high-resolution instrument. A similar strategy has been employed in related research by other authors[3,16]

In a PTR-MS analysis trace quantities of VOC's can be measured directly by introducing a sample gas stream via the heated instrument inlet. Prior to analysis in the mass analyser the VOC's must first be charged (ionised). The sample VOC's enter the drift tube (**Figure 2**) where compounds with a proton affinity (PA) greater than that of water (PA = 691 kJ mol−1) undergo ion−molecule reactions by receiving a proton from hydronium cations (H_3O^+). As the PA of water lies well above the PA of all common air constituents (N_2, O_2, Ar, CO_2, etc.) air itself can be used as a carrier gas, and no additional gas supply is needed. As most VOC's have a higher PA than water a wide variety can be analysed via PTR-MS. Hydronium ions are generated in the ion source from water vapour. The protonated (positively charged) compounds can then be transferred to the analysing system (mass spectrometer) that separates the ions according to their mass to charge ratio (m/z).

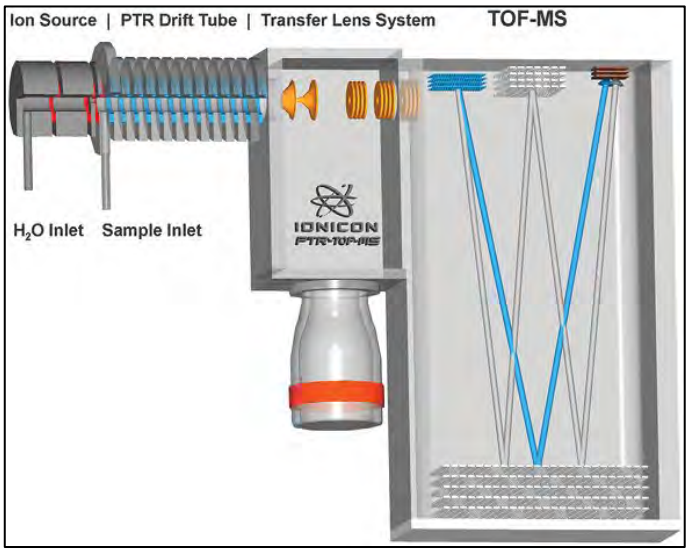


Figure 2: PTR-TOFMS Schematic (Ionicon Analytik)

A switchable reagent ion (SRI) source is now available that uses NO^+ and O_2^+ as reagent ions extending the range of VOC's that can be analysed to include those with a PA lower than water.

Application of PTR-MS to real-time assessment of oak volatiles

To best utilize and learn from the expertise at ZHAW (i.e. online analysis of thermal flavour development processes) we decided to investigate the utilisation of PTR-MS as a tool for real-time dynamic monitoring of the oak toasting process. This provided useful experience in the set-up / development of a suitable system for sampling the exhaust gas from a toasting process and transporting the sample gas to the PTR-MS instrument. Experience was gained in gas flow control, calibration and the practical concerns relating to VOC transport in gas transfer lines (e.g. importance of avoiding cold spots that can result in compound condensation). I also studied the theory of PTR-MS in addition to gaining practical experience in the application of the technique. By focusing on a discrete application (Real-time monitoring of oak toasting) I was able to collect a significant dataset within the time

period of the research placement. This data is currently being analysed for inclusion in a manuscript for an academic journal publication.

The importance of the toasting process in oak aroma development is widely recognised. That is, of the several processing stages in the production of oak maturation products the toasting process results in the most dramatic alteration of oak chemistry through hydrothermolysis and pyrolysis mechanisms. These reactions result in thermodegradation of the oak polysaccharides (cellulose and hemicellulose), lignin, polyphenols and lipids[17–19]. The objectives of the study were to elucidate the evolution of target oak aroma compounds during the toasting process and to demonstrate the potential of PTR-TOFMS for real-time monitoring of oak toasting systems.

Time was spent setting up and testing a suitable experimental system. This involved configuring gas flows, exhaust gas dilutions, setting up a mass calibration standard and transfer lines. Gas flows were calibrated using a bubble meter (**Figure 3**). An experimental plan was then developed and implemented based upon our preliminary findings. A detailed description of this work has been compiled in a draft manuscript to be submitted for publication in a suitable Analytical Chemistry journal following the data analysis currently underway. A picture of the experimental set-up is provided in **Figure 4**.



Figure 3: Calibrating gas flows with bubble meter



Figure 4: Convection toasting oven and sampling set-up

The toasting experiments were conducted over a time period chosen of sufficient length to elucidate the trends for aromatic development of the target compounds. Toasted samples were sealed after cooling in airtight bags (**Figure 5**) and stored for further (potential) analysis.



Figure 5: Oak stave samples after toasting

The mass spectrometer records a full mass spectrum within a fraction of a second. Thus the intensity of VOC's can be determined at any given time point – assuming compounds of interest are free from interference i.e. a given peak relates to one compound (one exact mass) or that nearby peaks (compounds) have a mass difference greater than the mass resolution of the instrument. For monitoring dynamic processes over time (as in the case of toasting), results can be plotted as Time-Intensity traces. An example trace is shown in **Figure 6**.

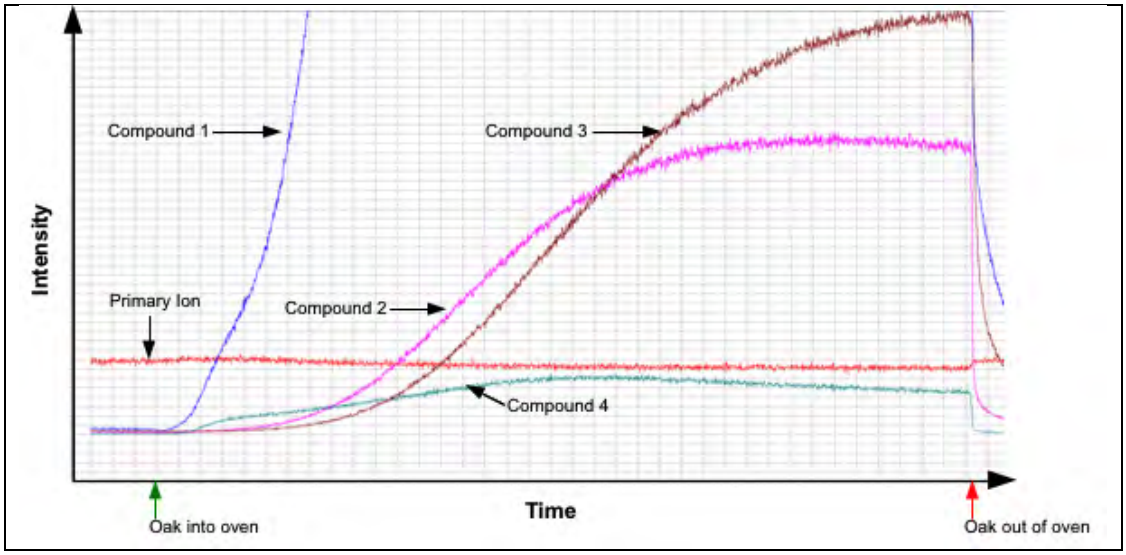


Figure 6: Example Time-Intensity trace from oak toasting via PTR-TOFMS

The potential of chemometric modelling to predict toasted profiles from green oak wood has been briefly examined. It should be possible to visualize the toasting process employing PCA as per previous work at ZHAW[14]. Alternative chemometric strategies exist that could facilitate prediction of compound levels through time – however, this would require quantitative PTR-MS analysis (i.e. beyond the scope of the preliminary qualitative study conducted in the current demonstration of "proof-of-principle").

Summary of PTR-MS applications to grape and wine industry

The application of PTR-MS to wine is complicated by the interference of ethanol with the H_3O^+ primary ions utilized in the standard PTR approach. However, PTR-MS can be applied using protonated ethanol clusters as reagent ions[20]. As this method results in complex mass spectra an alternative approach is to dilute the wine headspace with N_2 and then ionize using H_3O^+ primary ions[21]. This results in a simpler, faster method better suited to routine analysis. PTR-QMS was used to obtain rapid MS fingerprints of wine varietals, which were then successfully discriminated with a chemometric analysis (i.e. PCA). PTR-QMS has also been used for in vivo analysis of wine[22], wine contamination[16] and monitoring evolution of VOC's during grape must cooking (used in the production of many traditional Mediterranean food and beverages)[23]. Recently, instrument operating conditions have been investigated as a simpler way to control the ionization moving towards quantitative (PTR) analysis of high ethanol-containing samples[24].

Another relevant application used PTR-QMS for trace gas detection from fermentation processes in apples[25]. That study also compared PTR-QMS with a CO laser based photoacoustic detector (an alternative / established approach for trace gas analysis). PTR-QMS exhibited higher time resolution (<1 s) compared with photoacoustics (≈ 1 min) as well as allowing the simultaneous monitoring of a greater number of VOC's.

1st International Mass Spectrometry Summer School – Siena (Italy), 15-20th September 2013

The 1st International Mass Spectrometry Summer School (IMSS) was conducted by the International Mass Spectrometry Foundation (IMSF) in association with the Italian Chemical Society Division of Mass Spectrometry and took place in Siena (Italy), September 15-20th 2013. IMSS 2013 provided a six-day full immersion school aimed to give advanced education in mass spectrometry to graduate, PhD, post-doc students, and young scientists working in the areas of chemistry, biosciences, food, environment, and medicine. The school was truly international featuring 19 lectures from 8 different countries and 90 students from a total of 30 countries (**Figure 7**).

A summary of the school program is provided below:

- History and Future of Mass Spectrometry
- Ionization techniques: soft methods and new developments
- Ionization techniques for volatile molecules
- Analyzers (I): beam instruments
- Analyzers (II): Resolution, accurate mass measurements
- Coupling MS with separation techniques
- Tandem mass spectrometry (I)
- Tandem mass spectrometry (II) – Fundamentals
- Interactions of ions with electrons and surfaces
- Peptides - MS Imaging
- Ion mobility – Proteins
- Exercises on MS and MS/MS interpretation
- Short orals - Ion spectroscopy
- MS and life sciences
- MS and food

The IMSS provided a remarkable opportunity to network and engage with world leaders and visionaries in the field of mass spectrometry (MS). Beyond the lectures, these widely respected MS expert's made themselves freely available to one and all. Access to their wealth of experience and knowledge was available in an informal and inviting setting throughout the week. Such opportunities are rare – and would simply not be available through alternative venues such as a conference setting. My previous exposure to these Professors was limited to reading papers and watching their presentations on YouTube!

My ambitious research goals rely on forming an expert network and collaborating with “the right people” – those with the experience and vision to provide guidance. The IMSS has

provided such engagement in abundance. I have been able to delve into MS in an intensive manner and to network with MS peers and experts alike. The one-week intensive school provided far more than could ever be obtained through online learning or MS textbooks alone, and meeting the current and future leaders and visionaries in this field has been an inspirational experience. I now have the framework, structure, network and resources to further my learning in a more directed way.



Figure 7: Participants - 1st International Mass Spectrometry Summer School, Siena

I have been fortunate to attend the IMSS and the experience has certainly provided one of the highlights of my first year of PhD research. My attendance at the school was facilitated by a Fellowship from the IMSF covering travel expenses from Switzerland, accommodation and meals. Attendance would not have been possible without the IMSF Fellowship and GWRDC travel grant and their financial aid is gratefully acknowledged.

Tofwerk Visit 12th December 2013

Tofwerk (based in Thun, Switzerland) design and manufacture innovative Time-Of-Flight mass spectrometry instruments (Figure 8). Their products include robust field deployable instruments (deployed in ground, aircraft and ship-based measurement applications). Tofwerk also manufacture high-resolution ion mobility instruments that facilitate real-time analysis of VOC's in addition to a variety of interfaces that can accommodate different ionisation sources. The opportunity was taken to meet with Richard Knochenmuss (Director of R&D) and Michael Groessl (Application Scientist).

A fascinating and extensive tour of the facility was provided. I spent a number of hours with Michael, including a hands-on demonstration of instruments most relevant to my PhD research. Future work at ACROSS will focus on the development of a prototype sampling system to interface with a Tofwerk platform. Several possibilities exist here and the most promising methods will be short-listed following discussion with project supervisors and ACROSS peers (February 2014).

Time was also spent with one of the software engineers regarding a demonstration of Tofwerk data processing and analysis tools. In summary, a very productive meeting was had and plans for future collaboration in 2014 were discussed.

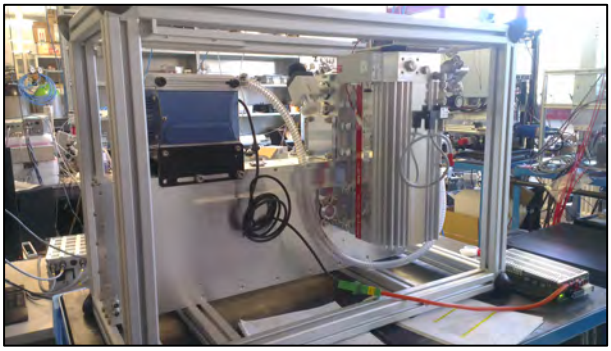


Figure 8: Instrument development at Tofwerk

Acknowledgements

I would like to thank my hosts at ZHAW, Professor Chahan Yeretzian, Dr Alexia Gloss, Dr Marco Wellinger and Sergio Petrozzi for kindly sharing their time and their research. I would also like to thank my fellow students at ZHAW for their hospitality, advice and humour. The IMSF are thanked for the Fellowship that enabled my attendance at the 1st International Mass Spectrometry School. Richard Knochenmuss, Michael Groessl, Marc Gonin and the Tofwerk team are also thanked for sharing their valuable time and thoughts regarding my PhD research. My project supervisors at ACROSS (Assoc. Prof. Robert Shellie and Prof. Michael Breadmore) are also thanked for their support and valuable guidance.

Budget Reconciliation

This is provided separately.

References

(1) Zardin, E.; Tyapkova, O.; Buettner, A.; Beauchamp, J. Performance Assessment of Proton-Transfer-Reaction Time-of-Flight Mass Spectrometry (PTR-TOF-MS) for Analysis of Isobaric Compounds in Food-Flavour Applications. *LWT - Food Sci. Technol.* **2014**, *56*, 153–160.

(2) Blake, R. S.; Monks, P. S.; Ellis, A. M. Proton-Transfer Reaction Mass Spectrometry. *Chem. Rev.* **2009**, *109*, 861–896.

(3) Özdestan, Ö.; Ruth, S. M. Van; Alewijn, M.; Koot, A.; Romano, A.; Cappellin, L.; Biasioli, F. Differentiation of Specialty Coffees by Proton Transfer Reaction-Mass Spectrometry. *Food Res. Int.* **2013**, *53*, 433–439.

(4) Hayward, S.; Tani, A.; Owen, S. U. E. M.; Hewitt, C. N. Online Analysis of Volatile Organic Compound Emissions from Sitka Spruce (Picea Sitchensis). **2004**, 721–728.

(5) Cappellin, L.; Soukoulis, C.; Aprea, E.; Granitto, P. PTR-ToF-MS and Data Mining Methods : a New Tool for Fruit Metabolomics. *Metabolomics* **2012**, *8*, 761–770.

(6) Mayhew, C. A.; Sulzer, P.; Petersson, F.; Haidacher, S.; Jordan, A.; Märk, L.; Watts, P.; Märk, T. D. Applications of Proton Transfer Reaction Time-of-Flight Mass Spectrometry for the Sensitive and Rapid Real-Time Detection of Solid High Explosives. *Int. J. Mass Spectrom.* **2010**, *289*, 58–63.

(7) Lindinger, W.; Hansel, A.; Jordan, A. On-Line Monitoring of Volatile Organic Compounds at Pptv Levels by Means of Proton-Transfer-Reaction Mass Spectrometry (PTR-MS) Medical Applications, Food Control and Environmental Research. *Int. J. Mass Spectrom.* **1998**, *173*, 191–241.

(8) Ruiz-samblás, C.; Tres, A.; Koot, A.; Ruth, S. M. Van; González-casado, A.; Cuadros-rodríguez, L. Proton Transfer Reaction-Mass Spectrometry Volatile Organic Compound Fingerprinting for Monovarietal Extra Virgin Olive Oil Identification. *Food Chem.* **2012**, *134*, 589–596.

(9) Blasioli, S.; Biondi, E.; Samudrala, D.; Spinelli, F.; Cellini, A.; Bertaccini, A.; Cristescu, S. M.; Braschi, I. Identification of Volatile Markers in Potato Brown Rot and Ring Rot by Combined GC-MS and PTR-MS Techniques: Study on in Vitro and in Vivo Samples. *J. Agric. Food Chem.* **2013**, *Article AS*.

(10) Wehinger, A.; Schmid, A.; Mechtcheriakov, S.; Ledochowski, M.; Grabmer, C.; Gastl, G. A.; Amann, A. Lung Cancer Detection by Proton Transfer Reaction Mass-Spectrometric Analysis of Human Breath Gas. *Int. J. Mass Spectrom.* **2007**, *265*, 49–59.

(11) Luchner, M.; Gutmann, R.; Bayer, K.; Dunkl, J.; Hansel, A.; Singer, W.; Strobl, F.; Winkler, K.; Striedner, G. Implementation of Proton Transfer Reaction Mass Spectrometry (PTR-MS) for Advanced Bioprocess Monitoring. *Biotechnol. Bioeng.* **2012**, *109*, 3059–3069.

(12) Herbig, J.; Gutmann, R.; Winkler, K.; Hansel, A.; Sprachmann, G. Real-Time Monitoring of Trace Gas Concentrations in Syngas. *Oil Gas Sci. Technol. - Rev. IFP Energies Nouv.* **2013**.

(13) Yeretzian, C.; Jordan, A.; Badoud, R. From the Green Bean to the Cup of Coffee : Investigating Coffee Roasting by on-Line Monitoring of Volatiles. *Eur. Food Res. Technol.* **2002**, *214*, 92–104.

(14) Wieland, F.; Gloess, A. N.; Keller, M.; Wetzel, A.; Schenker, S.; Yeretzian, C. Online Monitoring of Coffee Roasting by Proton Transfer Reaction Time-of-Flight Mass Spectrometry (PTR-ToF-MS): Towards a Real-Time Process Control for a Consistent Roast Profile. *Anal. Bioanal. Chem.* **2012**, *402*, 2531–2543.

(15) Jordan, A.; Haidacher, S.; Hanel, G.; Hartungen, E.; Märk, L.; Seehauser, H.; Schottkowsky, R.; Sulzer, P.; Märk, T. D. A High Resolution and High Sensitivity Proton-Transfer-Reaction Time-of-Flight Mass Spectrometer (PTR-TOF-MS). *Int. J. Mass Spectrom.* **2009**, *286*, 122–128.

(16) Jürschik, S.; Agarwal, B.; Kassebacher, T.; Sulzer, P.; Mayhew, C. A.; Märk, T. D. Rapid and Facile Detection of Four Date Rape Drugs in Different Beverages Utilizing Proton Transfer Reaction Mass Spectrometry (PTR-MS). *J. Mass Spectrom.* **2012**, 1092–1097.

(17) Jordão, A.; Ricardo-da-Silva, J.; Laureano, O.; Adams, A.; Demyttenaere, J.; Verhé, R.; De Kimpe, N. Volatile Composition Analysis by Solid-Phase Microextraction Applied to Oak Wood Used in Cooperage (Quercus Pyrenaica and Quercus Petraea): Effect of Botanical Species and Toasting Process. *J. Wood Sci.* **2006**, *52*, 514–521.

(18) De Simón, B. F.; Esteruelas, E.; Muñoz, A. M.; Cadahía, E.; Sanz, M. Volatile Compounds in Acacia, Chestnut, Cherry, Ash, and Oak Woods, with a View to Their Use in Cooperage. *J. Agric. Food Chem.* **2009**, *57*, 3217–27.

(19) Alanon, M. E.; Dıaz-Maroto, M. C.; Perez-Coello, M. S. Analysis of Volatile Composition of Toasted and Non-Toasted Commercial Chips by GC-MS after an Accelerated Solvent Extraction Method. *Int. J. Food Sci. Technol.* **2012**, *47*, 816–826.

(20) Boscaini, E.; Mikoviny, T.; Wisthaler, A.; Hartungen, E. Von; Tilmann, D. M. Characterization of Wine with PTR-MS. *Int. J. Mass Spectrom.* **2004**, *239*, 215–219.

(21) Spitaler, R.; Araghipour, N.; Mikoviny, T.; Wisthaler, A.; Dalla, J.; Tilmann, D. M. PTR-MS in Enology : Advances in Analytics and Data Analysis. *Int. J. Mass Spectrom.* **2007**, *266*, 1–7.

(22) Lasekan, O.; Otto, S. In Vivo Analysis of Palm Wine (Elaeis Guineensis) Volatile Organic Compounds (VOCs) by Proton Transfer Reaction-Mass Spectrometry. *Int. J. Mass Spectrom.* **2009**, *282*, 45–49.

(23) Dimitri, G.; Ruth, S. M. Van; Sacchetti, G.; Piva, A.; Alewijn, M.; Arfelli, G. PTR-MS Monitoring of Volatiles Fingerprint Evolution During Grape Must Cooking. *LWT - Food Sci. Technol.* **2013**, *51*, 356–360.

(24) Fiches, G.; Déléris, I.; Saint-Eve, A.; Brunerie, P.; Souchon, I. Modifying PTR-MS Operating Conditions for Quantitative Headspace Analysis of Hydro-Alcoholic Beverages. 2. Brandy Characterization and Discrimination by PTR-MS. *Int. J. Mass Spectrom.* **2013**, Online 4 December.

(25) Boamfa, E. I.; Steeghs, M. M. L.; Cristescu, S. M.; Harren, F. J. M. Trace Gas Detection from Fermentation Processes in Apples; an Intercomparison Study Between Proton-Transfer-Reaction Mass Spectrometry and Laser Photoacoustics. *Int. J. Mass Spectrom.* **2004**, *239*, 193–201.