

Nineteenth Biennial National Atomic Spectroscopy Symposium



2nd - 4th July 2018
St Mary's University, Strawberry Hill



BNASS is the flagship meeting for the Atomic Spectroscopy Group
of the Analytical Division, Royal Society of Chemistry

Preface

On behalf of the Organising Committee for the 19th Biennial National Atomic Spectroscopy Symposium (BNASS) may I extend a very warm welcome to all the participants at this years conference! I would like to thank all the members of the organising committee for their help, enthusiasm and dedication in making this BNASS 2018 a great meeting.

The philosophy of BNASS is to encourage interaction between delegates and we have therefore chosen a small university campus in an inspiring part of southern England and included a fully integrated social programme to stimulate discussion.

We are located next to Strawberry Hill House, the gothic revival villa built from 1749 by Horace Walpole (1717-1797), who was part of the “age-of-enlightenment”, an intellectual and philosophical movement that dominated the world of ideas in Europe during the "The Century of Philosophy". Science played an important role in Enlightenment discourse and thought. Many Enlightenment writers and thinkers had backgrounds in the sciences and associated scientific advancement with the overthrow of religion and traditional authority in favour of the development of free speech and thought.

Enjoy BNASS2018 and as we look to the future, take the opportunity to emulate the great scientific thinkers of the past.

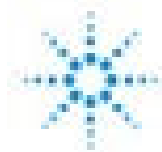
Organising Committee

Chairperson:	Dr Chris Harrington, SAS Trace Element Laboratory, Surrey County Hospital, Guildford
ASG Chair:	Dr Sarah Hill, Inorganic Analysis, Scientific Innovation, LGC, Teddington
Treasurer:	Dr Jackie Morton, Biological Monitoring, Health & Safety Laboratory, Buxton, Derbyshire
Vendors Exhibition and Sponsorship:	Dr Phil Riby, School of Chemistry, The University of Manchester, Oxford Road, Manchester

Acknowledgements

The Organising Committee wishes to express its grateful thanks to the following organisations for their generous platinum, gold and bronze support. BNASS 2018 would not be possible without their involvement and we strongly encourage all attendees to take some time out of the schedule and visit the Vendors Exhibition in the Student Union Hall.

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Workshop Sponsors

Workshop 1 sponsored by Eurachem:

Uncertainty and traceability for ISO accreditation will be led by two experts in this area: Marina Patriarca and Bertil Magnusson. This will take place in the main BNASS lecture theatre G7 on St Mary' Campus.



Workshop 2 sponsored by LGC, Postnova and Agilent Technologies:

Nanoparticle analysis by spICP-MS and FFF-ICP-MS will be led by Heidi Goenaga-Infante and colleagues at LGC. This will take place at LCG, Queens Road, Teddington. Transport will leave at 8:30 from St Mary's Reception. For those travelling directly LGC is a 5 min walk from Teddington train station.



General Information

Please See the BNASS Website for further information.

Venue: St Mary's University, Waldegrave Road, Strawberry Hill, Twickenham TW1 4SX. Please see the campus map at the back of this book. Access to the site is from Waldegrave Road via the middle gate, marked main reception. Signage will direct you to the registration desk in the Student Union Hall (marked J on the map).

Travel: trains run on a circular route from London Waterloo to Strawberry Hill, with 4 trains per hour Mon-Sat (2 ph on Sun). The station is a 5-10 min walk. London Underground, take the District Line westbound to Richmond and catch the R68 bus stop Z towards Hampton Court and alight at Michelham Gardens. There is a frequent bus service from Twickenham and Teddington train stations, both direct from London Waterloo.

Parking: there is limited parking at the venue which should be booked in advance via reception@stmarys.ac.uk cost is £2 per day, park in the bays marked "D". Alternatively there is unlimited off-road parking in the streets around the venue.

Registration: the registration desk is located in the Student Union Hall (J on map). Signage will direct you to the location. Registration is from 11:00 on Mon 2nd July.

Accommodation: for those people staying on campus check in is from 11:30 and keys can be picked up at the BNASS registration desk or if this is closed the main reception or security lodge. Accommodation is located in the De Marillac Halls of Residence, less than a 5 minute walk to conference venue (Za on map).

Internet Access: details of internet access will be available on arrival at the BNASS registration desk.

Catering: conference catering (tea and lunch) will be in the Student Union Hall at the times marked on the schedule. Details of breakfast for participants staying on-campus will be available at check in, or check the BNASS website.

Departure: will be after lunch on Wed 4th July, we wish everyone a safe onward journey.

Social Events

BNASS aims to be the most social event on the conference calendar. For BNASS 2018 we have organised two exciting events for you to enjoy and network with colleagues.

Ice Breaker on Mon evening: join us for a trip up the River Thames from Richmond to Hampton Court Palace, passing by Richmond Hill, Ham House, Orleans House, Strawberry Hill, Teddington Lock and Weir and finally arriving at Henry VIII's country palace. On arrival you will receive a free glass of bucks fizz, Cava or a soft drink, followed by a fish and chip supper (veggie option available).

Conference Meal: on Tues evening the conference meal will take place in the Waldegrave Suite at St Mary's University. The suite consisting of Drawing Room, Billiard Room and Bar was part of Strawberry Hill House and was built in the 18th century. Arrival at 19:00 for a 19:30 sit down meal. Live football will be available, to watch coverage of the World Cup in the bar area.

Instructions for Presenters

Poster Presentations: Posters will be displayed in the Students Union Hall (building J on campus map). The poster boards are 2m high by 1m wide and A0 sized posters in portrait orientation will fit comfortably. Velcro fasteners will be provided; no pins or staples should be used. Posters should be mounted by 13:00 on Monday July 2nd. Posters for Monday's session (16:30-17:30) should be placed on even numbered boards and those for Tuesday's session (15:05-16:00) on odd numbered boards.

Oral Contributions: It would be helpful to the Organisers if speakers could make themselves known to session chairs before the start of their particular session. Talks should be uploaded to the projection PC in plenty of time and the chair can help with this. Session chairs are asked to keep strictly to the scheduled timetable, which allows 40 minutes for keynote speakers and depending on the session, 20 or 30 minutes for contributed speakers (please check the schedule). Speakers are asked to allow time at the end for discussion.

Workshops: registration for the workshops will take place on Sun 1st July for students arriving then. Details will be sent to participants. Transport to LGC on Mon morning will leave at 8:30 from main reception.

Monday 2nd July		
	Time	BNASS Workshops
	Workshop 1 9:00-12:30	Uncertainty and Traceability for ISO Accreditation. Led by Marina Patriarca and Bertil Magnusson, Eurachem, St Mary's University Lecture Theatre G7
	Workshop 2 9:00-12:30	Nanoparticle Analysis Using spICP-MS and FFF-ICP-MS. Led by Heidi Goenaga-Infante. LGC, Queens Road, Teddington
	From 11:00	Registration, Students Union Hall
	From 11:30	Check into BNASS on-site accommodation, Students Union Hall
	From 12:30	Lunch, Student Union
Monday 2nd July		
		Main Programme, Main Lecture Theatre G7
	13:20-13:30	Welcome address: Chris Harrington , Chair, BNASS 2018 Organising Committee
Session 1: Clinical, Biomedical and Health Application. Chair: C. Harrington		
1	13:30-14:10	Keynote 1: Patrick Parsons , Director, Laboratory of Inorganic and Nuclear Chemistry, Wadsworth Center, New York State Dept. of Health, Albany. Quantifying the Rare Earth Elements in Human Bone by Triple Quad ICP-MS/MS: Method Optimization Parameters and Validation with Available CRMs
2	14:10-14:30	Elizabeth Leese , Health and Safety Laboratory, Buxton, Derbyshire. Exhaled Breath Condensate: A Novel Matrix for Biological Monitoring to Assess Occupational Exposure to Respirable Crystalline Silica
3	14:30-14:50	Calum Greenhalgh , Department of Chemistry, University of Loughborough. Oxaliplatin Imaging in A549 Cells by High Resolution Laser Ablation Inductively Coupled Plasma Mass Spectrometry
	14:50-15:30	Cream tea on the lawn (weather permitting)
Session 2: Metallomics. Chair: Jackie Morton		
4	15:30-16:10	Keynote 2: Wolfgang Maret , School of Life Course

		Sciences, King's College London A metallomics approach to human metal metabolism
5	16:10-16:30	Claudia Swart , Physikalisch-Technische Bundesanstalt, Braunschweig, Germany Reference Measurement Procedures to Elucidate the Role of Metalloproteins in Alzheimer's Disease
	16:30-17:30	Wine Reception and Poster Session 1: Biomedical, Quality Assurance and Instrumentation, Student Union and Bar Area
	18:30-23:00	ICE Breaker: Boat cruise up the Thames The coach will leave promptly at 18:35 and return to St Mary's University at 23:00.
Tuesday 3rd July		
		Main Programme, Main Lecture Theatre G7
Session 3: Current Innovations in Instrumental Analysis. Chair: Phil Riby		
6	9:00-9:40	Keynote 3: Mark Rehkamper , Department of Earth Science & Engineering, Imperial College, London. Isotope Ratios and Society
7	9:40-10:05	Phil Shaw , Ametek, Wrexham, Wales. Design considerations for a multi-collector ICP-MS with a multi-pole collision cell interference removal device
8	10:05-10:30	Ben Russell , National Physical Laboratory, Teddington. Comparison of tandem inductively coupled plasma mass spectrometry (ICP-MS/MS) for nuclear and gas particle metrology applications
	10:30-11:00	Tea Break and Vendors Exhibition, Student Union
9	11:00-11:40	Keynote 4: Wolfgang Muller , RHUL, Institute of Geosciences, Goethe-Universität Frankfurt Novel Applications in LA-ICP-MS
10	11:40-12:05	Giles Edwards , Surface Analysis Research Centre, University of Manchester. Development of novel compact carbon dating instrument based on Collinear Resonance Ionisation Spectroscopy (CRIS)
11	12:05-12:30	Simon Nelms , ThermoFisher Scientific, Hemel Hempstead.

		Advances in triple quadrupole ICP-MS for environmental and food analysis.
12	12:30-12:55	Rai Wahlen , Agilent Technologies, Cheadle Practical Benefits of Abundance Sensitivity Using ICP-QQQ
	13:00-14:00	Lunch: Manufacturers in the “Atomic Spectroscopy Dragon’s Den” Instrument manufacturers meet the Atomic Spectrometry Panel, Student Union
Session 4: New developments in Elemental Speciation. Chair: Steve Hill, University of Plymouth and Atomic Spectroscopy Group.		
13	14:00-14:40	Keynote 5: Joerg Feldman , TESLA, University of Aberdeen. Speciation Applications
14	14:40-15:05	Phil Riby , University of Manchester, The speciation of arsenic in antacid formulations as part of Q3D regulations
	15:05-16:00	Tea and Poster Session 2: Speciation, Nanoparticles, Environmental and Food Analysis, Student Union
15	16:00-16:30	Mesay Wolle , Centre for Food Safety and Applied Nutrition, US Food and Drug Administration. Solutions for challenges in arsenic speciation analysis in seafood and seaweed
16	16:30-17:00	Shaun Lancaster , PS Analytical, UK Mercury speciation using photochemical vapour generation with LC-UV-CV-AFS – A greener and more cost effective method.
17	17:00-17:30	Nunnapus Laitip , TESLA, University of Aberdeen. The simultaneous speciation of Se/Hg species in long-finned pilot whale (<i>Globicephala melas</i>)
	19:00-23:00	Conference Dinner Waldegrave Rooms, St Mary's University
Wednesday 4th July		
		Main Programme
Session 5: The Measurement of Nanoparticles. Chair: Liz Leese, HSL, Buxton		

18	9:00-9:30	Phil Shaw , Ametek, Wrexham, Wales. Detecting sub-10nm particles with greater accuracy using SP-ICP-MS in the presence of background signals due to ionic content of the element of interest in the sample.
19	9:30-10:00	Chris Harrington , SAS Trace Element Laboratory, Guildford. Characterization of Nanoparticles and Metal-protein Binding in Biological Fluids from Hip-replacement Patients.
20	10:00-10:30	Kenneth Nwoko , TESLA, University of Aberdeen. Selenium nanoparticles produced by the fungus <i>Aureobasidium pullulans</i> : Separation, detection and sizing by asymmetric flow field flow fractionation (AF4) with online ICP-MS
	10:30-11:00	Tea Break, Student Union
Session 6: Food and Environmental Applications. Chair: Chris Harrington		
21	11:00-11:30	Keynote 6: Marina Patriarca , Istituto Superiore di Sanità, Rome, Italy Harmonisation of Results for Determination of Nickel in Food: A New Analytical Challenge
22	11:30-12:00	Michael Ho Pan Yau , Government Laboratory, Hong Kong, China Inorganic Arsenic in Aquatic Products
23	12:00-12:30	Alá AlnaimatIn , University of Santiago de Compostela, Spain Vitro Study of the Bioavailability of Major and Trace Elements in Tea Samples
24	12:30-13:00	Christine Davidson , Department of Pure and Applied Chemistry, Strathclyde University. Bioaccessibility of potentially toxic element associated with plastic resin pellets collected from the River Forth, Scotland, UK
	13:00-13:05	Close and Final Remarks Dr Chris Harrington
	13:05	Lunch, Student Union and Depart

Keynote Speakers

Keynote Presentation 1

Quantifying the rare earth elements in human bone by triple quad ICP-MS/MS: method optimization parameters and validation with available CRMs

Patrick Parsons^{1,2}, Aubrey Galusha^{1,2}

¹New York State Dept of Health, Albany, USA. ²University at Albany, Albany, USA



Patrick Parsons gained his undergraduate (1978) and Ph.D. degrees (1983) from the University of London, England, under the direction of Professor Margaret Farago. He then moved to the USA as a Visiting Fellow at the National Institutes of Health, where he worked on platinum speciation in human body fluids. In 1986 he was

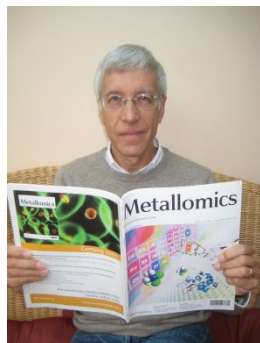
appointed Director, Lead Poisoning Laboratory, at the NY State Department of Health's Wadsworth Center, in Albany, New York. Dr. Parsons is currently Director of the Division of Environmental Health Sciences and Chief of the Laboratory of Inorganic and Nuclear Chemistry at Wadsworth. He also a Professor in the Department of Environmental Health Sciences at the University at Albany. For more than 35 years, Dr. Parsons has studied human exposure to trace elements using graphite furnace atomic absorption, inorganic mass spectrometry and X-ray fluorescence techniques. His research is currently supported by NIH and CDC grant funding. He has published more than 170 papers and 12 book chapters. Dr. Parsons is a Chartered Chemist and Fellow of the Royal Society of Chemistry. In 2018, he received the Gold Standard Award for Public Health Laboratory Excellence from the US-based Association of Public Health Laboratories.

Keynote Presentation 2

A metallomics approach to human metal metabolism

Wolfgang Maret

King's College London, London, United Kingdom



Wolfgang Maret FRSC is the Professor of Metallomics in the School of Life Course Sciences, Departments of Nutritional Sciences (research) and Biochemistry (teaching) at King's College London. He obtained his MSc (Dipl. Chem.) in chemistry and his PhD in Natural Sciences from Saarland University, Saarbrücken, Germany. After postdoctoral research at The University of Chicago (Department of Biophysics & Theoretical Biology) he briefly returned to his alma mater in Germany. His first faculty appointment (assistant professor) was in the Center for Biochemical and Biophysical Sciences and Medicine at Harvard Medical School, with an additional teaching appointment at The Bouvé College of Pharmacy, Northeastern University, Boston, MA. He then joined the University of Texas Medical Branch in Galveston, TX as an Associate Professor in the Institute of Nutrition (Department of Preventive Medicine & Community Health) and in the Department of Anesthesiology. In 2009, he accepted a position as Senior Lecturer in Iron Metabolism at King's. His research interests began with the catalytic mechanisms of metalloenzymes as investigated with spectroscopic and kinetic methods and continued with the role of metal and redox biology in health and disease, in particular liver disease, diabetes, and traumatic brain injury, and the molecular and cellular mechanisms of how metal ions control protein structure and function and how proteins control nutritionally essential elements and mitigate the effects of non-essential and toxic elements. From 2012-2014, he served as the president of the International Society for Zinc in Biology and from 2012-2016 as chair of the editorial board of the journal *Metallomics* of the Royal Society of Chemistry.

Keynote Presentation 3

Isotopic analysis of trace metals – from basic research to societal impact

Mark Rehkämper, Rebekah Moore

Mass Spectrometry and Isotope Geochemistry at Imperial College London, Department of Earth Science & Engineering, Imperial College London



Mark Rehkämper is an isotope geochemist with a particular interest in the development and application of novel techniques for trace metal isotope analysis. His research encompasses a diverse range of elements, including Fe, Cu, Zn, Mo, Cd, Tl and Pb, which he uses to address questions in planetary, Earth, environmental and life sciences. For example, he applies isotopic measurements to study cycling of anthropogenic Pb in the oceans, to elucidate the processes responsible for the depletion of volatile elements (such as Zn, Cd and Tl) in many planetary bodies including the Earth, to

examine the uptake of toxic Cd by crops, and investigate the role of Zn in the progression of breast cancer.

Mark is originally a chemist by training, with undergraduate studies in Germany at the Universities of Marburg and Heidelberg. His career in geochemistry commenced with a PhD project at the Max-Planck-Institute for Chemistry in Mainz. The doctoral studies, completed in 1995, were followed by stints at the Universities of Michigan and Münster, and at the ETH Zurich. He joined Imperial College London in 2005 and founded the department's MAGIC Research Centre (MASS spectrometry and isotope Geochemistry at IC London), which now encompasses a diverse team of 30 researchers.

Keynote Presentation 4

In-situ Rb/Sr dating by LA-ICP-MS/MS using SF₆ as reaction cell gas with internal normalization

Wolfgang Müller¹, David Evans²

¹ Institute of Geosciences, Goethe University Frankfurt, Frankfurt am Main, Germany (w.muller@em.uni-frankfurt.de), ² School of Earth & Environmental Sciences, University of St Andrews, UK



Wolfgang Müller is Professor of Geology and Palaeoenvironmental Research, at Goethe Universität Frankfurt, Germany. By using isotope analysis as a versatile toolkit, my research focuses on the close interplay between applications and the methodological developments necessary to achieve these goals. Over the years, my emphasis has been on spatially-resolved isotope and element ratio analysis, initially using conventional microsampling and more recently based on laser-ablation and/or SIMS. Good examples illustrating this interaction

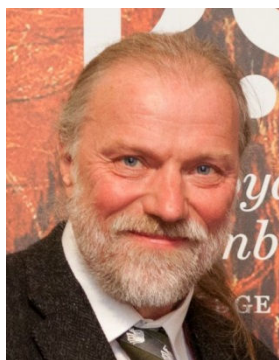
between application & methodology include 1) my earlier work on dating deformation, where we constrained for the first time directly duration and rates of shear zone activity (Science 2000), 2) the subsequent shift towards biominerals, including the multi-isotope tracing approach leading to the 'Origin and Migration of the Alpine Iceman' (Science 2003) or 3) the development of in-situ Hf isotope analysis including non-radiogenic ratios applied to the oldest minerals formed on Earth, the Jack Hills zircons (Science 2005).

Keynote Presentation 5

Elemental speciation is not only focussed on the traditional elements and methodologies: some examples and general concepts

Joerg Feldmann, Eva Krupp, Andrea Raab

Trace element speciation laboratory (TESLA), Department of Chemistry, University of Aberdeen, Aberdeen, United Kingdom.



Joerg Feldmann is Professor for Environmental Analytical Chemistry at the University of Aberdeen and Director of TESLA (Trace Element Speciation Laboratory) since 2004 after joining the University in 1997. He has studied chemistry and received his MSc and PhD from University of Essen, Germany before he became a Feodor Lynen Fellow (Alexander von Humboldt Foundation) in 1995, where he went to University of British Columbia, Canada.

His major interests are in describing processes in biology and in the environment for toxic and essential metals, metalloids and increasingly non-metals for that the molecular form of the elements need to be determined. His work on arsenic in rice was instrumental for the introduction of a legal maximum limit for inorganic arsenic in rice into EU law in 2016. TESLA demonstrated the first HPLC-ICPMS/ESIMS coupling in 2002 and in 2003 the first use of LA-ICPMS for bioimaging. He has given more than 150 keynote/plenary lectures worldwide and is on the editorial or advisory board of Environmental Chemistry (CSIRO), Analytical Bioanalytical Chemistry (Nature-Springer) and JAAS (RSC). He has published more than 250 peer-reviewed papers which attracted more than 13,000 citations (h-index 61). Recent Prizes and awards include the European Award for Plasma Spectrochemistry (2015), The RSC Interdisciplinary Prize and Medal (2016) and the election to become a Fellow of the Royal Society of Edinburgh (2018).

Keynote Presentation 6 and Workshop 1: Uncertainty and traceability for ISO accreditation

Harmonisation of results for determinations of nickel in food: a new analytical challenge

Marina Patriarca¹, Valeria Patriarca¹, Marilena D'Amato¹, Angela Sorbo¹, Paolo Stacchini¹, Maria Ciprotti², Laura Ciaralli², Timo Kapp³

¹NRL HMF Istituto superiore di sanità, Rome, Italy. ²EURL CEFAO Istituto superiore di sanità, Rome, Italy. ³Federal Office of Consumer Protection and Food Safety, Berlin, Germany



Marina Patriarca is a Senior Scientist at the Italian National Institute of Health. Her working experience involves analytical chemistry, with particular reference to atomic spectroscopy applied to biological and food

samples, and the application of metrology to analytical sciences. She is currently coordinating the activities of the Italian National Reference Laboratory for Heavy Metals in Food. Author of more than 100 scientific publications, she is a member of the Atomic Spectrometry Updates Board. She is an experienced trainer, at national and international level, on technical issues related to ISO/IEC 17025 and ISO/IEC 17043. Since 2005 she is representing Italy in Eurachem and is a member of various Eurachem Working Groups, as well as the Executive Committee. She is now serving as the Eurachem Chair.

Abstracts: Keynote and Contributed Presentations

Session 1 Clinical, Biomedical and Health Applications

Keynote Presentation 1

Quantifying the rare earth elements in human bone by triple quad ICP-MS/MS: method optimization parameters and validation with available CRMs

Patrick Parsons^{1,2}, Aubrey Galusha^{1,2}

¹New York State Dept of Health, Albany, USA. ²University at Albany, Albany, USA

The development of tandem mass spectrometry (MS/MS), coupled with inductively coupled plasmas (ICP) has opened up new possibilities for clinical and biological applications, where overcoming multiple matrix-based mass spectral interferences is challenging. While MS/MS, or "Triple Quad" technology has long been used in organic mass spectrometry, it is relatively new to inorganic mass spectrometry. One application of ICP-MS/MS in our laboratory was to determine Rare Earth Elements (REEs) in human bones, obtained post-mortem from patients that had received parenteral nutrition (PN) over a period of between 2 and 20 years (mean = 14y). The availability of ICP-MS/MS with an Octopole Reaction System (ORS) provided an opportunity to overcome the myriad of polyatomic interferences associated with REEs in bone. We used an Agilent 8800 ICP-MS/MS instrument to develop and optimize a method for quantifying 15 REEs in human bone. Four ORS gas modes (He, H₂, O₂ + no gas), and 3 internal standards (Rh, Ir, and Bi) were explored. Polyatomic interferences were evaluated for 30 REE isotopes. The paucity of biological reference materials certified for the REEs presented a challenge for method validation, yet we found 7 CRMs that provided an assessment of accuracy and two bone SRMs to evaluate comparability with published values. The final method leveraged mass-shifting with O₂, as well as on-mass detection with H₂. On average, REEs in PN bones were at least 15x higher than the "control" group. Trace amounts of five REEs were detected in all 18 "control" bones.

Exhaled breath condensate: A novel matrix for biological monitoring to assess occupational exposure to respirable crystalline silica

Jackie Morton, James Staff, Elizabeth Leese

Health & Safety Executive, Buxton, United Kingdom

Biological monitoring is a useful way of determining overall exposures to chemical substances; however in the case of respirable crystalline silica (RCS) this has not been analytically feasible in conventional biological matrices. The aim of this study was to investigate the utility of exhaled breath condensate (EBC) as a potential biological matrix in which to determine exposure to RCS.

Firstly it was established that RCS particles could be qualitatively determined using single particle inductively coupled plasma mass spectrometry (spICP-MS). After this a small pilot study was undertaken collecting EBC from quarry workers, foundry workers and occupationally unexposed persons. The samples were then analysed using both spICP-MS, ICP-MSMS and transmission electron microscopy (TEM).

The results showed that EBC samples obtained from the quarry workers and the foundry workers contained silica particles of various sizes. Silica particles were detected in the occupationally unexposed persons but at significantly lower levels.

This is the first study to report EBC as a potential biological matrix that allows differentiation of RCS concentrations between samples from workers and occupationally unexposed controls. The results obtained confirmed the presence of RCS in EBC by both spICP-MS and TEM. However, there are difficult analytical challenges still to be overcome before this can be used as a biological monitoring method to determine workplace exposure; these are currently being investigated.

Oxaliplatin imaging in A549 cells by high resolution Laser Ablation Inductively Coupled Plasma Mass Spectrometry

Calum Greenhalgh, Amy Managh

Loughborough University, Loughborough, United Kingdom

Metallodrugs containing non-endogenous metals are commonly used in the treatment of several forms of cancer. Oxaliplatin is one such platinum-based

metallodrug, which works by penetrating the nucleus of cancerous cells and forms DNA adducts that prevent cell proliferation. Monitoring Oxaliplatin uptake and activity can provide insight into its efficacy and help improve future treatments¹, but bulk measurements on cell populations could obscure vital information about heterogeneity in uptake across the cell samples.

In the present work, A549 cells, a model of human lung adenocarcinoma, were doped with concentrations of between 5µM and 50µM oxaliplatin. Using a prototype NWR Image 266nm laser ablation system, the cells were imaged with a laser spot size of 1-2µm. High Pt responses were found accumulated within the nuclei of the cells, suggesting preferential localisation of the drug to areas of high DNA concentrations. The NWR image system coupled to SF-ICP-MS allowed for not only a spatial resolution down to 1µm, but also a greater sensitivity and speed of analysis due to the high efficiency of the Direct Concentric Injector² technology used.

1. A. Zayed *et al.*, *International Journal of Mass Spectrometry*, 2011, 307: 70-78.
2. D.N. Douglas *et al.*, *Analytical Chemistry*, 2015, 87: 11285-11294.

Session 2: Metallomics

Keynote Presentation 2

A metallomics approach to human metal metabolism

Wolfgang Maret

King's College London, London, United Kingdom

Quantitative analysis of single or a few chemical elements in blood samples is a mainstay in clinical chemistry. However, this approach misses out on critical information that determines the balance between health and disease. For some metal ions, it is unclear whether they are indeed essential for humans, e.g. chromium(III). Concentrations in blood do not necessarily reflect the concentrations in tissues. Metal concentrations can differ significantly among tissues and metals can be distributed heterogeneously in a tissue. For many elements, we do not know the normal concentrations in a healthy individual and what defines a deficiency or an overload. With the exception of very specific indications such as poisoning, non-essential metal ions usually are not analysed in a clinical setting. Yet, many additional elements are present in humans and have either beneficial or detrimental functions. Some of them are present at higher concentrations than essential elements. Due to new

manufacturing practices, we are exposed to some metal ions, to which we have never been exposed before in the history of mankind. It becomes increasingly important to monitor this exposure. With regard to all these issues elemental analysis has to gain additional dimensions. In the London Metallomics Facility at King's, we are beginning to address some of these issues by mapping/imaging metal ions in tissues during the life cycle and by employing a metallomics approach to look at many chemical elements simultaneously and to understand their interactions.

Reference measurement procedures to elucidate the role of metalloproteins in Alzheimer's Disease

Claudia Swart, Julia Gleitzmann, Susann Loddeke, Christine Brauckmann
Physikalisch-Technische Bundesanstalt, Braunschweig, Germany

Alzheimer's disease (AD) is one of the main challenges for the healthcare systems of aging societies worldwide. Metalloproteins are likely to be involved in or released by the body during the development of AD. As the regulation of Fe containing proteins is an important factor for the function of the brain, the Fe transport and storage proteins receive special attention. Besides these proteins, ferroxidases such as ceruloplasmin (CER) are also involved in Fe regulation by oxidising Fe to the less toxic ferric state which can be bound, for example, by transferrin. Furthermore, CER is a Cu storage protein and Cu is thought to be involved in the formation of b-amyloid oligomers. Another important protein involved in the prevention of oxidative stress is superoxide dismutase. As it seems that damage of the neurons through oxidative stress is also involved in the process of AD, these proteins are promising candidates for monitoring the progress of the disease. The low concentrations of these proteins require new strategies for the quantifications in samples with challenging matrices and small available sample volumes such as CSF and brain homogenate. Species-specific isotope dilution mass spectrometry methods are developed for the quantification of the named metalloproteins via their metal content using ICP-MS for the detection. The coupling with liquid chromatography ensures the separation of the analyte from interfering matrix.

Acknowledgement: 15HLT02 has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

Session 3 Current Innovations in Instrumental Analysis

Keynote Presentation 3

Isotopic analysis of trace metals – from basic research to societal impact

Mark Rehkämper, Rebekah Moore

Mass Spectrometry and Isotope Geochemistry at Imperial College London,
Department of Earth Science & Engineering, Imperial College London

The application of isotopic techniques for radiometric dating, to characterize system conditions and the tracing of material transport goes back to the early 20th century. The methods that underpin such basic research have made huge advances in the last 100 years, driven by interest to investigate novel sample types and isotope systems as well as new developments in both theory and analytical instrumentation. Most recently, the quick but robust and highly precise isotope analyses afforded by MC-ICP-MS, the double spike technique and other innovations in methods, have spurred isotopic investigations of numerous trace metals and widespread application of novel 'non-traditional' stable isotope systems in earth, environmental and planetary sciences. In addition, such analytical techniques offer significant scope for interdisciplinary trace metal isotope research, as in life and medical sciences. For example, the methods promise to deliver new understanding of trace metal uptake and metabolism, which may be harnessed to support improvements in food safety and the diagnosis of medical conditions. The techniques can also be applied in high-sensitivity trace metal tracing studies with enriched stable isotopes. This presentation reviews such recent advances in isotopic research, by discussing investigations of (i) Pb isotopes to quantify anthropogenic pollution in the oceans, (ii) Zn stable isotope variations associated with breast cancer, (iii) Cd accumulation in crops using Cd isotopes, and (iv) the fate of engineered nanomaterials in complex environmental systems.

Design considerations for a multi-collector ICP-MS with a multi-pole collision cell interference removal device

Phil Shaw, Mark Mills

Nu Instruments, Wrexham, United Kingdom

Multi-collector ICP-MS (MC-ICP-MS) has been used for 20 years with little change to the basic configuration of a forward geometry magnetic sector ICP-MS with an array of faraday and ion counting detectors used to simultaneously collect the signals from multiple ions over a narrow mass range. Whilst collision cells are commonly used in quadrupole ICP-MS to remove interferences, the specific needs of multi-collection have historically made the collision cell impractical for precise isotope ratio work.

This work will describe the fundamental difficulties in using RF multipole devices as reaction cells for MC-ICP-MS and the design criteria of how such a device can be implemented to minimise the fundamental effects leading to poor data quality. The design of the Nu Sapphire MC-ICP-MS will be described showing removal of interferences whilst preserving the instrument's transmission for mid and high mass isotopes (Mg to U).

One of the fundamental issues with collision cells is the loss of signal at low masses due to scattering which is then compounded by the more significant mass bias effects of the RF multipole due to the relative mass differences being much greater. This new design will describe how the Sapphire uses a novel "dual-path" mechanism where the ion beam from the ICP interface can be directed past the collision cell at high voltage and then into the standard mass spectrometer source slit so data can be collected in the same manner as conventional MC-ICP-MS with the same sensitivity and precision.

Comparison of tandem inductively coupled plasma mass spectrometry (ICP-MS/MS) for nuclear and gas particle metrology applications

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The commercial availability of ICP-MS/MS has been proven to offer improved removal of isobaric, polyatomic and tailing interferences compared to other instrument designs. The instrument is fitted with two quadrupole mass filters,

separated by a collision-reaction cell. The quadrupole prior to the cell enables the user to mass filter the ion beam prior to the cell, improving understanding of the cell chemistry, whilst also improving the abundance sensitivity compared to single quadrupole instruments. The collision-reaction cell can be operated with multiple gases for removal of isobaric and polyatomic interferences, reducing or even eliminating the need for comparatively time-consuming offline chemical separation.

This study compares the capabilities of different ICP-MS/MS instruments in the fields of Nuclear Metrology and Gas and Particle Metrology at the National Physical Laboratory. Firstly, the benefits of ICP-MS/MS have been demonstrated for low-level measurement of multiple radionuclides, including ^{90}Sr , ^{93}Zr , ^{135}Cs , ^{151}Sm , ^{226}Ra and ^{236}U . The reduced reliance on offline cell separation and rapid measurement compared to decay counting techniques offers a higher sample throughput for end users in the nuclear industry. For several radionuclides, different instruments are compared with regards to sensitivity and interference removal capability. The optimal instrument setup is investigated using stable element standards, followed by active testing. Additionally, the classic determination of ^{56}Fe in environmental samples has been compared on two different ICP-MS/MS instruments. The effects of cell gas flow rate (He) and energy discrimination voltage on sensitivity and detection limit have been investigated.

Keynote Presentation 4

In-situ Rb/Sr dating by LA-ICP-MS/MS using SF₆ as reaction cell gas with internal normalization

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The Rb/Sr geochronometer is one of the oldest isotopic dating techniques (1). Given the 1) ubiquitous occurrence of datable minerals such as micas, 2) the comparatively high concentrations of Rb and Sr and 3) the strong elemental fractionation, Rb/Sr dating has become a common dating tool, particularly for metamorphic rocks. Owing to the isobaric decay of ^{87}Rb to ^{87}Sr , no mass spectrometric separation of the two nuclides has been possible given the

required mass resolution of 286000 ($M/\Delta M$), making ‘true’ in-situ dating without chemical separation so far impossible. However, the application of reaction cell ICPMS (2) and recently ‘triple-quadrupole’ -ICP-MS/MS (3) provides a paradigm shift for in-situ Rb/Sr geochronology. We present an evaluation of the use of a 2nd generation ‘triple-quadrupole’ ICP-MS/MS (Agilent 8900 ICP-QQQ) coupled to the RESolution prototype LA system (193 nm) for in-situ Rb/Sr dating of micas. Importantly, we utilize SF₆ as reaction gas in mass shift mode because it has the highest selectivity between Rb⁺ and Sr⁺ ions (4). We find at optimum SF₆ gas flow (i.e. maximized signal/background) that $\geq 96\%$ Sr⁺ ions convert into SrF⁺, with the SrF⁺-signal (MS/MS-mode) remaining $>1/3$ of that in single-quadrupole mode, vital in achieving precise Sr-isotopic ratios. Crucially, even at 87Rb/86Sr-ratios $\gg 104$, no RbF⁺-ions are detectable (monitored at Sr-free $m/z=104$ (85Rb19F)). No adverse effect of SF₆ on low-level S-analyses is found.

White mica samples of known age but contrasting Rb/Sr-ratios (granite gneiss (very high Rb/Sr) and phengitic schist (moderate/low Rb/Sr)) were chosen for initial method setup (5). We utilize normal exponential mass bias correction ($88\text{Sr}/86\text{Sr}=8.37521$), use ⁸⁴Sr (besides all other Sr-isotopes) as an accuracy monitor and achieve accurate ⁸⁴Sr/⁸⁶Sr-ratios within error of naturally-invariant 0.0565. We evaluate the extent of observed Rb/Sr elemental fractionation using known age samples. The corresponding results of *rapid in-situ* dating of single white mica grains in thin section will be presented, besides a discussion of limitation and potential.

1. Hahn et al. *Chemiker-Zeitung* **67**, 55-56 (1943).

2. Moens et al. *JAAS* **16**, 991-994 (2001).

3. Bolea-Fernandez et al. *JAAS* **31**, 303-310 (2016). 4. Cheng et al. *Anal. Chim. Acta* **627**, 148-153 (2008). 5. Müller et al. *J. Geol. Soc.* **156**, 261-278 (1999).

Development of novel compact carbon dating instrument based on Collinear Resonance Ionisation Spectroscopy (CRIS)

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Traditional carbon dating techniques based on isotope ratio accelerator mass spectrometry are expensive, experimentally complex and access to

instrumentation is often associated with excessive lead times. The use of CRIS as an alternative method affords unparalleled interference suppression when compared to RIMS for example. This is achieved by effectively decoupling the inlet electron cyclotron resonance ion source from the resonance ionisation spectroscopy by means of a charge exchange cell. The instrument employs a variety of ion optics including initial multi-collector magnetic sector mass selection and a linear ion trap to increase duty cycle; the sample inlet is a flash GC nitrogen/carbon elemental analyser.

The CRIS technique was initially developed at CERN in the ISOLDE facility for the analysis of exotic nuclei. The instrument at the University of Manchester is configured for the analysis of carbon isotopes but can easily be tuned for other nuclei and offers a state-of-the-art alternative technique for various forensic, dating and food security applications.

Advances in triple quadrupole ICP-MS for environmental and food analysis

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Following its commercial introduction in the 1980's, ICP-MS revolutionised trace elemental analysis by providing fast, multi-element detection for a wide range of applications. Early in its development, however, polyatomic interferences derived from combination of the sample components and the plasma gas were found to limit the performance of the instrumentation. Furthermore, it was observed that isobaric overlap from isotopes of other elements having the same mass as the element of interest also caused significant interference. Development of collision cell technology for interference removal provided a major improvement, but even this innovation couldn't fully remove every polyatomic interference or solve the problem of isobaric interferences.

With the advent of triple quadrupole ICP-MS, a new level of interference removal has been achieved. The implementation of an additional quadrupole before the collision cell of the instrument allows pre-filtering of the ion beam to selectively transmit only the masses of interest, which alleviates the problem of unwanted side interference production in the cell through collisions between other masses in the sample and the cell gas. This pre-filtering capability also allows selective chemical reactions to be conducted in the cell to enhance

polyatomic interference removal and, in many cases, solve the problem of isobaric overlap.

In this presentation, the latest advances in triple quadrupole ICP-MS technology and how these apply to routine analysis will be described. The enhanced performance provided by this technique will also be discussed, with a particular focus on its applicability in routine analysis of environmental and food samples.

Practical benefits of abundance sensitivity using ICP-QQQ

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Abundance sensitivity is a measure of the contribution from a large matrix mass peak next to the target analyte mass peak. The abundance sensitivity for quadrupole based instrumentation can typically be around 5×10^{-7} to 1×10^{-7} and higher in Sector Field systems (although this can partially be compensated for by increasing resolution) – it is essentially the measure of peak tailing from the matrix element peak.

This poster will demonstrate the improvement in abundance sensitivity when using a MS/MS capable ICP-QQQ system operating using two tandem mass separations (one before and one after the collision reaction cell) – giving abundance sensitivity $< 1 \times 10^{-10}$ with examples such as manganese in a whole blood matrix and neptunium in a uranium matrix.

Session 5: Key Developments in Speciation

Keynote Presentation 5

Elemental speciation is not only focussed on the traditional elements and methodologies: some examples and general concepts

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This keynote lecture will introduce briefly the concept of elemental speciation and will give an overview what has become routine analysis for elements such

as arsenic, mercury or selenium. Then a few challenges will be highlighted, which need other concepts in order to identify the molecular structure of the element in question. When does the general concept of a hyphenated technique for speciation analysis does not work and which concept will be followed. Additionally it will be illustrated that the availability to new instruments will give new opportunities for elements which are not necessarily associated with elemental speciation analysis.

The speciation of arsenic in antacid formulations as part of Q3D regulations

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The analysis of As in pharmaceutical formulations is a requirement under the Q3D regulations. These regulations discuss speciation analysis although little work has been carried out. Arsenic speciation analysis was performed using HPLC-ICPMS equipped with a reverse phase C18 (Phenomenex 5u 250x4.60mm) column and a mobile phase consisting of 10mM tetrabutyl ammonium phosphate (TBA), 20mM potassium phosphate monobasic (KH₂PO₄) and 2% methanol at pH=6. Four arsenic compounds; [arsenite](#) (As (III)), arsenate (As (V)), monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA) were successfully separated using the described method. The arsenic species were detected at m/z 75 with a Thermo X-series ICP-MS. The method was validated for linearity, accuracy and precision. The limits of detection and limits of quantification for the four compounds were: As (III): 0.095ng/ml, 0.278ng/ml, As (V): 0.119ng/ml, 0.362ng/ml, MMA: 0.122, 0.353 ng/ml and DMA: 0.118, 0.336ng/ml respectively. A selection of antacids were analysed and some products showed a total concentration of arsenic of about 800 ng/g. The arsenic was extracted using CEM SP-D microwave with a multistep heating program where the maximum temperature was 95°C. Water and 0.3M phosphoric acid (H₃PO₄) were used as extraction media and H₃PO₄ was found to be more efficient in extracting the arsenic species. The percentage extracted for all products was more than 90% in comparison with the total concentration obtained from the reverse aqua regia extraction of the samples. As (III) was the dominant species in 5 of the 6 analysed products.

Solutions for challenges in arsenic speciation analysis in seafood and seaweed

Mesay Wolle, Sean Conklin

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Seafood and seaweed contain arsenic in any of several dozen different chemical forms. While inorganic arsenicals (iAs) are classified as Group I carcinogen and some organoarsenicals (such as arsenobetaine) exhibit exceedingly low toxicity, the potential risk associated with other forms of arsenic, particularly arsenosugars and arsenolipids, is yet to be fully elucidated. This complex distribution and toxicity of arsenic suggest that assessment of the risk associated with seafood and seaweed containing arsenic based only on iAs monitoring may not provide sufficient information. Analyses should aim at capturing a full picture of the distribution of arsenicals. Such comprehensive speciation analysis requires reliable and robust methods. Numerous methods are reported for arsenic speciation analysis in seafood and seaweed. In a recent study at the US Food and Drug Administration, several of the sample preparation and chromatographic methods were evaluated. [1] In the presentation, the challenges encountered in most methods, which relate to extraction efficiency, effect on the native chemical forms of analytes, efficiency in separation and quantification of the extracted analytes, and method reproducibility will be discussed. Solutions will be outlined to solve most of the challenges. Optimum conditions identified for the speciation analysis of seafood and seaweed arsenic will be discussed along with their application in analysis of samples and reference materials of finfish, crustaceans, molluscs and seaweed. [2]

1. M. M. Wolle, S. D. Conklin, *Anal. Bioanal. Chem.* (2018) <https://doi.org/10.1007/s00216-018-0906-0>
2. M. M. Wolle, S. D. , *Anal. Bioanal. Chem.* (2018) <https://doi.org/10.1007/s00216-018-0910-4>

Mercury speciation using photochemical vapour generation with LC-UV-CV-AFS – A greener and more cost effective method.

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A reliable method for the analysis of mercury species is cold vapour generation of mercury coupled with atomic fluorescence spectrometry. The most commonly used method of cold vapour generation involves oxidising all organic mercury species to inorganic mercury (Hg^{2+}), followed by a reduction to elemental mercury (Hg^0) with tin(II) chloride or sodium borohydride. However, this method uses a plethora of chemicals which is costly and prone to error, as well as instrumental issues due to the complex wet chemistry necessary.

Another pathway is photochemical vapour generation (PVG), which has been used in the past in conjunction with atomic fluorescence spectrometry (AFS) as an alternative method of cold vapour generation. PVG has previously been applied to total mercury measurements using UV with formic acid and acetic acid. PVG promises a much simpler and more cost effective approach with fewer and more environmentally friendly chemicals, achieving results that are comparable to the chemical vapour generation approach.

Here, we apply acetic acid PVG to speciation measurements to provide a simpler analysis of methylmercury in three selected matrices: seafood, hair, and sediment. In total, 9 certified reference materials were analysed to assess the accuracy and precision of the method. A comparison was made between PVG and CVG methods, which showed that the PVG method provided sensitivities equal to that of the CVG method. In addition, 14 yellowfin Tuna samples were analysed using acetic acid PVG and compared with an analysis using GC-AFS, which showed good agreement of results between the two methods.

The simultaneous speciation of Se/Hg species in long-finned pilot whale (*Globicephala melas*)

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Biomagnification of mercury (Hg) level has been found in the marine food chain from seawater to predatory fish, hence it is anticipated that Hg would accumulate in high concentrations in cetaceans. Its toxicity has been concerned but selenium (Se) is known to bind to Hg and may act as a detoxifier. If sufficient Se is taken up then it might suppress the toxic potential of Hg, by

binding Hg to selenoproteins. In this study, the interaction between Hg and Se was evaluated. A method of affinity high-performance liquid chromatography (AF-HPLC) hyphenated to inductively coupled plasma (quadrupole) mass spectrometry (ICP-qMS), was used for quantitative simultaneous speciation of Se/Hg species in tissues of a long-finned pilot whale (*Globicephala melas*). Se species were expected to be glutathione peroxidase (GPx), selenoprotein P (SeP) and selenoalbumin (SeAlb). Muscle, liver, kidney, and brain in different ages of pilot whale were studied. The results revealed that different selenoprotein fractions bind to Hg in the different tissues of the whales of different ages.

Session 5: Nanoparticles

Detecting sub-10nm particles with greater accuracy using SP-ICP-MS in the presence of background signals due to ionic content of the element of interest in the sample.

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The biological impact of nanoparticles is generally accepted to be more critical for particles <20nm in size with some researchers citing <10nm being the point at which nanoparticles start to induce DNA damage. This make the ability to detect and characterise the size distribution of smaller particles more critical in environmental and biological samples.

It has been established for some years that data acquisition times (dwell times for Single Particle ICP-MS) need to be shorter than the duration of the signal seen from a nanoparticle in ICP-MS and that the shorter the dwell time, the more accurate will be the distinction of a particle from the background signal.

This work will describe the benefits of using a desolvating nebuliser to improve the signal to background by compressing the signal from a nanoparticle into a shorter duration and increasing the ion transmission so more counts/ng are seen for each particle. We will also describe the use of signal smoothing and characterisation of the background immediately before a particle event to improve the accuracy of particle peak detection and reduce the incidences of false positive detection.

Size detection limits of 4.5nm for Au, 4.4nm for CeO₂, 3.8nm for Ag and 7nm for TiO₂ have been measured. Distributions of single nanometre sized particles are now possible, even in the presence of a reasonable amount of ionic background.

Characterisation of nanoparticles and metal-protein binding in biological fluids from hip-replacement patients

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Hip replacements are used to improve the quality of life of people with orthopaedic conditions, but the use of metal-on-metal (MoM) arthroplasty has led to poor outcomes for some patients. These problems are related to the generation of micro- to nanosized metal wear particles containing Cr, Co or other elements. The current analytical methods used do not provide sufficient information to understand the size or composition of the wear particles generated *in vivo*. In this feasibility study, asymmetric flow field-flow fractionation (AF4) and liquid chromatography (HPLC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) were used to investigate the metal protein binding and the size and composition of wear metal particles present in serum and hip aspirates from MoM hip replacement patients.

Enzymolysis was used to degrade synovial fluid samples collected from the hip-joints of patients with MoM hip-replacements made from a Co-Cr-Mo alloy. Fractograms obtained by AF⁴-LS-ICPMS demonstrated that the bio-fluids contained not only NPs, predominantly containing Cr, but also a dissolved fraction of metals, which were bound to albumin and transferrin. The composition of the NPs released from the MoM hip-replacements showed that Co was selectively released and became associated with albumin, whereas Cr from the alloy largely remained in the NPs. To further confirm the results, spICPMS was used to determine the number-based size distribution of the NPs, which had a diameter of approximately 100 nm (LOD) to 400 nm for the Cr-containing NPs, and approximately 35 (LOD) to 100 nm for the Co containing NPs.

Selenium nanoparticles produced by the fungus *Aureobasidium pullulans*: Separation, detection and sizing by asymmetric flow field flow fractionation (AF4) with online inductively coupled plasma mass spectrometry (ICPMS).

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Selenium is an economically important but rarely occurring element, used in manufacture of semi-conductors, photocells, glass, and pigments. Its low natural abundance has heightened supply security fears leading to the exploration of environmentally sustainable ways for its production. Here, we report the detection and sizing of selenium nanoparticles obtained from a fungus, *Aureobasidium pullulans* grown in a liquid nutrient medium amended with 1 mM Na₂SeO₃ for 10 days at 25°C. We developed an optimised AF4 separation method in aqueous mode (0.2% Novachem as eluent, and an exponential elution crossflow of 4 mL min⁻¹), with online coupling to ICPMS for element specific detection of selenium on m/z 78. Integration of the MALS peak with the Postnova® AF2000 MT software resulted to two size distributions with radii of gyration (R_g) ranging from 55-65 nm, and 66-80 nm; with a good data fit across all 21 angles using a spherical model. This positively correlates with single particle ICPMS data which showed a narrow size distribution with a median particle diameter of 70 nm. Our study thus highlights the possibility of a sustainable method for the biological sequestering of selenium from the solution in the form of pure elemental selenium. It also demonstrates the robustness of hyphenated ICPMS techniques for the characterization of such natural nanoparticles in complex biological media.

Session 6: Food and Environmental Applications

Keynote Presentation 6

Harmonisation of results for determinations of nickel in food: a new analytical challenge

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¹NRL HMF Istituto superiore di sanità, Rome, Italy. ²EURL CEFAO Istituto superiore di sanità, Rome, Italy. ³Federal Office of Consumer Protection and Food Safety, Berlin, Germany

Recently, the European Food Safety Authority (EFSA) issued a scientific opinion on the risks to human health arising from the presence of nickel (Ni) in foodstuffs and drinking water. Based on the examination of data on reproductive and developmental toxicity in experimental animals, a tolerable daily intake of 2.8 mg Ni / kg body weight was identified, to be further reduced in case of susceptibility to allergic reactions. At present EU legislation sets no limit for the content of Ni in foods, whereas the level of Ni in drinking water intended for human consumption and in natural mineral waters must not exceed 20 µg/L. Since occurrence data for different food groups and geographical areas are limited, a monitoring plan involving all Member States was launched in 2016 (CR (EU) 2016/1111). EU and national reference laboratories (EURLs, NRLs) have the task to support official control laboratories in producing comparable results, using proficiency tests to assess laboratories' performance. In this occasion, two NRLs collaborated to organize two joint proficiency tests for Ni in vegetable matrices. An additional test was carried out on freeze-dried mussels, a test material prepared by the EURL-CEFAO as part of their activities. Information was collected regarding test methods used by the participants, quantification limits and measurement uncertainty. Analytical performance was assessed by z-scores against consensus values using criteria defined by the NRLs. In general, the outcome of these exercises indicated comparability of analytical results across the two networks, thus satisfying the prerequisite for the EFSA data collection.

Inorganic arsenic in aquatic products

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Recently, a comprehensive review on the Food Adulteration (Metallic Contamination Regulations) has been conducted in Hong Kong. With a view to enhancing food safety for the protection of public health and keeping the regulation abreast of the international standards, a number of amendments on the existing regulations have been proposed. The proposed amendments increase the number of maximum levels (MLs) to 145 compared to the 16 MLs listed in the existing regulations. The increase of MLs is to align with Codex principle and modern international regulatory trends of specifying metallic contamination standards.

Inorganic arsenic in aquatic products is one of the newly added specific food item with a proposed maximum permitted level of 0.5 mg/kg. However, the proficiency test for determination of inorganic arsenic in aquatic product is very limited in the market. To support the local testing industry, the Government Laboratory, Hong Kong, China (GLHK) will organize a proficiency test program for determination of inorganic arsenic in aquatic product. Details of the preparation of test material will be presented. The newly developed method for analyzing inorganic arsenic in aquatic products will also be discussed.

***In Vitro* Study of the bioavailability of major and trace elements in tea samples**

Alá S. Alnaimat, María Carmen Barciela-Alonso, Paloma Herbello-Hermelo, Elena Peña-Vázquez, Raquel Domínguez-González, Pilar Bermejo-Barrera

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Total contents of 34 elements in tea leave samples and their infusions were studied. Tea leaves samples were digested by microwave-assisted acid digestion. Rb, Ba, Al, Fe, Zn, Si, Ca, Mg, Mn, Mo, Sr and P were determined using ICP-OES. Li, Be, Ti, Ga, Ag, Hg, Cd, Cs, Pt, Bi, Tl, Pb, As, Cr, Co, Ni, V, Se, Sn and Sb were determined by ICP-MS, while K was determined using FAES. The detection limits ranged from 0.1 ng g⁻¹ to 16.6 µg g⁻¹. The extraction efficiency of each element was estimated as the ratio of its concentration in tea infusion to the total concentration in tea leaves; the values ranged from 0 to 97%. The

accuracy of the method was evaluated using INCT-TL-1 Tea Leaves and Rye Grass certified reference materials. The analytical recoveries were also calculated, with values near to 100% for all the elements. Bioavailability of toxic and essential metals in tea samples has been assessed in terms of an *in vitro* dialyzability protocol. Gastric simulation (using pepsin solution) and intestinal simulation (using a solution of pancreatin and bile salts) were used to perform the *in vitro* study.

Topics: Essential and Toxic Metals, *In-vitro* Bioavailability, ICP-MS, ICP-AES, AES, Tea

The authors wish to thank the Xunta de Galicia (Grupo de Referencia Competitiva 6RC2014/2016) for financial support. This program is co-funded by FEDER (UE).

Bioaccessibility of potentially toxic element associated with plastic resin pellets collected from the River Forth, Scotland, UK

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The presence of microplastics in the marine environment is of global concern. As well as causing physical damage to marine organisms, pellets act as a potential vector for transfer of pollutants into the biosphere. To assess the importance of this pathway, analytical procedures are needed to estimate the bioaccessibility of potentially toxic elements associated with ingested plastics in the gastro-intestinal tracts of sea creatures such as fish.

Plastic pellets were collected from the foreshore at Limekilns, River Forth, Scotland, UK.

They were air-dried, sieved, rinsed with deionised water, classified using ATR-FTIR analysis, and then subjected to two bioaccessibility tests. Pellets were extracted following either the simplified bioaccessibility extraction test (SBET) usually applied to estimate human oral bioaccessibility of PTE in soil (0.4 M glycine at pH 1.5) or the procedure recommended by Pena-Icart *et al.*,¹ to assess the bioavailability of sediment-bound PTE to fish (0.1M HCl). Extracts were analysed for As, Cd, Cr and Zn using an Agilent 7700x ICP-MS instrument.

Higher concentrations of all analytes were extracted using the SBET procedure than with dilute HCl. For most analytes, the bioaccessible concentration associated with polyethylene pellets was greater than that associated with polypropylene. Percentage bioaccessibility, as calculated relative to results of digestion in 20% *aqua regia*, was greatest for Pb (around 80% using the SBET and 65% using dilute HCl) and least for Cr (< 10% by both methods).

1. M Pena-Icart, C Mendiguchia, M E Villaneuva-Tagle, M S Pomares-Alfonso and C Moreno, Marine Pollution Bulletin, 2014, **89**, 67-74.

Monday Poster Session 1: Biomedical, Quality Assurance and Instrumentation

Exact determination of Ferritin as a potential marker for Alzheimer's disease by ID-ICP-MS

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According to estimates over 6 million people are affected in the European Union by neurodegenerative diseases which pose a big challenge to the health care systems. In an ageing population the diagnosis and treatment of these diseases are gaining more and more importance. With about 70% the most common form of dementia is Alzheimer's disease (AD). Determination of the biomarkers for AD (most established are β -amyloid peptide and τ -protein) is generally performed using immunoassays or optical methods which often lead to incomparable results. Besides the established biomarkers, metalloproteins are under discussion as potential clinical markers. For example, ferritin (FER) levels in cerebrospinal fluid (CSF) are in correlation with brain iron levels which are increased in AD. A promising approach for the quantitative determination of FER via its S-content in CSF is species-specific isotope dilution inductively coupled plasma mass spectrometry (SS-ID-ICP-MS) as it is a primary measurement method and gives results that are traceable to the International System of Units (SI). To perform SS-IDMS, a protein reference and an adequate spike material are needed. As there is no FER reference material commercially available, pure native FER is characterized in-house for the use as reference. A recombinantly produced FER enriched in ^{34}S acts as spike.

Acknowledgement: This project has received funding from the EMPIR programme co-financed by the Participating-States and from the European Union's Horizon 2020 research and innovation programme.

Simultaneous quantification of Fe and Se, at clinically relevant concentrations, in brain tissue using LA-ICP-MS: tissue homogenate preparation and Se signal enhancement

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Disruption to iron homeostasis at regional or cellular levels in the brain has been implicated in excessive formation of reactive oxygen species (ROS)¹. This can lead to abnormal A β peptide aggregation and the formation of senile plaques resulting in cell death, which are hallmarks of neurodegenerative diseases. Contrastingly, selenium containing proteins have antioxidant properties and play a role in neuroprotection and regulation of these ROS².

Due to the contrasting roles played by Fe and Se in the brain there is an increasing interest in the ability to quantitatively map these elements simultaneously in micro-sections of brain tissue. However their natural concentrations in the brain vary from low ppb for Se to hundreds of ppm for Fe. This causes many analytical challenges; such as the lack of sufficiently stable and homogeneous matrix-matched calibration standards and the large concentration gap between co-located Fe and Se.

This work describes an optimised protocol for producing tissue homogenates spiked with inorganic Fe and Se and/or their high molecular weight species including Ferritin and Selenoprotein P. Main considerations to produce calibration standards, which are sufficiently both stable so can be re-used from batch to batch and, homogeneous (RSD of 15% and 19% for Fe and Se, respectively) will be highlighted. Finally, method development to increase the signal-to-noise ratio for Se using ICP-carbon addition approaches will be discussed.

1 J. F. Collingwood and M. R. Davidson, *Front. Pharmacol.*, 2014, **5**, 191.

2 D. Xiubo *et al.*, *Curr. Top. Med. Chem.*, 2016, **16**, 835

Chronic kidney disease of unknown origin in sugarcane industry: metals analysis in biological samples

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In Central America, there is an epidemic of Chronic Kidney Disease of unknown cause (CKDu), also referred as Mesoamerican Nephropathy (MeN). In the last 15 years it has been estimated that CKDu has caused the premature death of approximately 20,000 individuals, mainly young males, who work in physical intensive manual labour, hot climate agriculture such as sugarcane cultivation and sugar production. Sufferers reach end stage renal disease before the age of fifty. Over the last two decades there has been a progressive increase in CKDu and the work presented here is part of a study investigating different possible causative factors.

Following site visits to different locations in Nicaragua, urine samples were collected from 330 workers at both the start and end of the harvest season. This include of workers who did and did not exhibit kidney function decline, as well as from two different geographical locations.

In this part of the project a range of elements were analysed in the urine samples by ICP-MS. Whilst the results from the metals analysis showed elevated urinary aluminium, cadmium, copper and silicon levels, no correlation with kidney function status was observed.

As yet there is still no clear evidence as to what is the leading cause of kidney failure and multiple pathways have been proposed. The levels of elements determined here provide an association with metals exposures however this is not in every worker and more work is needed to understand this further.

Total element determination in the brains of different mouse models of Alzheimer's disease, by ICP-MS.

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Alzheimer's disease (AD) is the most common cause of dementia, and is a growing health concern worldwide, with no cure or disease modifying therapy. It is pathologically characterised by the presence of neurofibrillary tangles of tau protein, and β -Amyloid plaques within the brain, however, evidence also suggests that metals play a role in disease mechanisms. This work used ICP-MS to determine the total element concentrations of various elements within the brains of four different mouse models: 3 AD disease models and one Wild Type (WT) control. The disease models overexpressed Tau and β -Amyloid, with varying levels of gene expression and pathological development. This work used pig brain for method development and aimed to establish if pig brain would have potential as a reference material for an inter-laboratory study, with a reproducibility of 10%). This talk will present data gathered, and discuss possible reasons for changes in elemental concentrations.

Multi-element determination in populations of single cells by quadrupole ICP-MS

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Recent advances in analytical technology enabling the analysis of single cells has resulted in increased interest in this field of research. Previously, elemental quantification in life science research has been performed by a series of processes including culturing large numbers of cells, preparing cell extracts, and defining analyte concentrations as an average value in cell extractions. However, this method assumes that the cell population is homogenous, and therefore might miss minority cell clusters which exhibit significant differences. In contrast, single cell analysis allows cells to be injected individually, enabling us to understand the detailed elemental profiles of cell clusters. Single cell

analysis using ICP-MS is performed by suspending cells in solution to separate them, vaporizing and ionizing the cells using an Ar plasma and detecting the resulting ion cluster as a signal pulse at the ICP-MS detector lasting less than 1 msec. Elemental concentrations in the cells are determined from the peak areas. We have developed a new sample introduction system comprising a total consumption nebulizer and spray chamber which greatly improves the transmission efficiency of μm size particles and has enabled us to quantify the concentrations of P, Ca, Fe, and Zn at ag/cell level in bakery yeast cells (*Saccharomyces cerevisiae*). Newly developed software monitors 16 elements within the same batch, and calculates the analyte concentrations in the cells automatically. In this presentation, we will show the fundamental results based on the new hardware and software development for the single cell analysis.

EURACHEM: A Focus for Analytical Chemistry in Europe

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Eurachem (www.eurachem.org) is a network of organisations within Europe designed to a) establish a system for the international traceability of chemical measurements and b) promote good quality practices in analytical sciences. Currently represented in 33 European countries, it aims to provide a forum for analytical scientists, laboratory staff and those interested in using the results of analytical measurements, to discuss common problems and develop informed and considered approaches to both technical and policy issues.

Members and stakeholders meet once a year at the Eurachem General Assembly. An Executive Committee and several topical Working Groups pursue

the organisation's stated goals throughout the year, often in cooperation with other organisations. Participation is open and channeled through national representatives.

Eurachem's main output is authoritative guidance documents, promoted through dedicated events which are also designed to provide opportunities for collecting feedback. Beside the guides, information leaflets, *i.e.* short briefing documents on specific topics, are intended to inform a wide audience, including laboratory staff, managers and laboratory customers. This poster, presented by the members of the Eurachem Executive Committee, aims to summarise current Eurachem activities, inform readers about the available guidance and attract active participation.

Reliable Estimates of Measurement Uncertainty Obtained from External Quality Assessment Schemes: A Case Study

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The estimate of measurement uncertainty (MU) is a requirement for the competence of testing, calibrating and clinical laboratories (ISO/IEC 17025, ISO 15189). The Nordtest approach provides a model for robust MU estimate applicable in single, routine, analytical laboratories using information collected from the procedures in place for the quality assurance of results. In laboratory medicine, external quality assessment schemes (EQAS) typically consist of numerous samples to be analysed at regular intervals over a given period and including duplicates unknown to the participants. Beside scoring performance on the individual items, these data can be exploited to provide the information needed for the estimate of MU according to the Nordtest approach.

In this study, data from EQAS for lead in blood, designed to provide participants with 24 items including 12 unknown duplicates, over a cycle of one year, were analysed to determine laboratory intermediate precision and bias variability. These components were combined to determine the MU of the laboratory results over the concentrations range. The reliability of this approach was successfully tested using the individual estimates of MU to calculate zeta-scores (a type of score where the deviation from the assigned value is compared with the MU of the laboratory result) for the results provided by the same participants in the first six months of the following EQAS cycle. This approach provides robust estimates of MU from data already available as part of EQAS and allows laboratories to fulfil the need for periodic review of such estimates.

The use of External Quality Assurance in improving the methods used for clinical trace element analysis in liver biopsy samples

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Running since 2012-13 the solid matrix EQA scheme provides specimens for laboratories that undertake the analysis of solid samples for copper and iron. The scheme is offered by UK NEQAS for Trace Elements in Guildford to 18 participants worldwide.

Clinically, in patients suspected of having Wilson Disease or genetic haemochromatosis, a liver biopsy sample (<5 mg) may be taken for the determination of copper or iron respectively, to aid diagnosis. To ensure accurate testing methods in these complex determinations this scheme sends out small mass (10 - 20 mg) powdered samples of animal organs or other suitable organic solid materials, which are analysed by the participants for their copper and iron content. The analytical procedure used requires the organic materials sent to be converted to a liquid prior to analysis; this step can be carried out in a number of ways using various combinations of reagents and heating methods. It was felt that this complex step lead to significant errors being introduced due to contamination or under-recovery of the analyte from the matrix.

Over the last year and a half, in addition to the solid samples analysed, the laboratories also tested pre-digested samples prepared by the EQA program. Some samples were spiked to concentrations which better reflect clinically relevant levels (Reference ranges in tissue: Cu >250 ug/g, Fe > 1508 ug/g dry weight). This study aims to determine the source of the error and attempt to offer advice on best practice.

Development of new certified reference materials for SI-traceable $^{13}\text{C}/^{12}\text{C}$ isotope amount ratio measurements

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Reference materials (RMs) play a key role in calibration of isotope ratio mass spectrometers, assigning property values and the transfer of measurement accuracy between different laboratories and over time. A long-standing problem associated with the latter function of isotopic RMs stems from the fact that many RMs used in differential, or delta value, isotope ratio measurements lack a straightforward link to the International System of Units (SI). Instead, traceability in delta value isotope ratio measurements is established to scale-defining artefacts which are recognised as International Standards and represent the end members of the traceability chain for the measurements.

$d^{13}\text{C}$ delta measurements are a good example of a situation where it gets increasingly more difficult for practitioners to achieve comparability of measurement results. Establishing traceability of $d^{13}\text{C}$ delta measurements to the SI as a stable metrological reference system can be a sustainable solution for ensuring comparability of measurement data. In this work, we have produced and characterised three new glycine RMs certified for $^{13}\text{C}/^{12}\text{C}$ isotope amount ratios and $d^{13}\text{C}_{\text{VPDB}}$ delta values, covering a wide range of ~54 ‰ ($^{13}\text{C}/^{12}\text{C}$ isotope amount ratios with expanded uncertainties in parentheses are 0.010642(30), 0.010821(30) and 0.011227(32), respectively). $^{13}\text{C}/^{12}\text{C}$ isotope ratio measurements were performed by both multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) and flow injection analysis-chemical oxidation-isotope ratio mass spectrometry (FIA-CO-IRMS) using a calibration strategy based on the use of synthetic isotope mixtures gravimetrically prepared from well characterised, highly ^{13}C -enriched and ^{13}C -depleted glycines.

New RMs will be invaluable in improving comparability of $\delta^{13}\text{C}$ delta measurements.

Determination of total fluorine of organofluorine compounds in cookware using high-resolution graphite furnace molecular absorption spectrometry.

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Fluorine has a very high ionisation potential of 17.42 eV that has a high tendency to obtain a negative charge (1). Fluoride is an essential for human health and can protect from dental decay and promotes healthy bones. Humans are exposed to fluoride through food and drinking water and by breathing air (2). According to World Health Organization, the recommended limit of fluoride in drinking water between 0.8 and 1.0 mg/L (3). European Food Safety Authority has recommended the fluorine intake 0.05 mg/kg of body weight per day for children and adults (4). Perfluorinated compounds (PFCs) are xenobiotics and have been detected in the blood of wildlife and humans worldwide. They pose great threats to human health due to its persistence and bioaccumulative effects, PFCs have become the hot topic in recent years (5, 6). PFCs have found in cookware, fast-food containers, carpet cleaning solutions, beverage cups, and microwave popcorn bags (7). In this study, the absorption of calcium monofluoride (CaF) molecule has been applied for the determination of fluorine of organofluorine compounds and high-resolution continuum source graphite furnace molecular absorption spectrometry has been employed. The rational line at 606.432 nm was used for measuring the molecular absorption (1). The pyrolysis and atomization temperatures were 500 °C and 2100 °C. The method was used to determine the total fluorine rather than fluoride, which includes polar organofluorine and nanoparticles. The values were found in cookware samples by using water extraction between 534 and 1900 ug/L

Improved data acquisition speeds for high resolution ICP-MS

Phil Shaw

Nu Instruments, Wrexham, United Kingdom

High resolution magnetic sector ICP-MS has become the favoured instrument for many laser ablation applications due to the high sensitivities seen in dry

aerosol sampling and the flat topped peak characteristic of the magnetic sector mass spectrometer.

Recent improvements to laser ablation sample cells have prompted requests for even faster data acquisition for wide if not full mass spectra, without sacrificing the sensitivity benefits of the magnetic sector when used in dry aerosol mode. This work will describe new data acquisition modes available with the recently released fast magnet power supply and controller. It has been possible to increase the magnetic field ramping and fall-back speeds to obtain spectra up to uranium in 105ms leading to an acquisition rate of 9.5Hz.

With a fixed magnet cycle time, the acquisition time of each mass is governed by the number of isotopes chosen for the method and the allowable range of the deflectors used to jump from one isotope to another. This work will describe the “LinkScan” technique which has been used for many years successfully in multiple laser ablation labs and the modification of the deflector scan range made to improve the duty cycle further for this technique.

Laser-Induced Breakdown Spectroscopy of Actinides: Elemental and Isotopic Analysis for Nuclear Forensics

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Laser-induced breakdown spectroscopy (LIBS) permits real time elemental analysis of a material irrespective of its nature, physical state or environment. The ability to perform contact-free or stand-off analysis of materials by this method offers significant advantages for applications which require the interrogation of hazardous materials contained within controlled or inaccessible environments. This capability is a particularly attractive feature for applications in the nuclear industry and in the field of nuclear forensics. The LIBS technique demonstrates many of the attributes required of a field-deployable method: these include accurate and rapid analysis, no (or minimal) sample preparation and the ability for remote operation. Whilst the technique is capable of identifying all elements in a sample on the basis of their atomic / ionic emission spectra, applications in isotopic analysis present a greater challenge and are only feasible for elements at the extremities of the periodic table (e.g. hydrogen

and uranium). Furthermore, isotopic LIBS requires the use of high resolution spectrometers which have poor light throughput and lack portability.

This presentation will focus on the development of a system based on the use of tuneable diode laser absorption spectroscopy (TDLAS), in conjunction with LIBS, for isotopic analysis of uranium. This ‘hyphenated’ approach (LIBS-TDLAS) will provide information regarding the elements present in the samples of interest by LIBS whilst TDLAS will be used to ascertain the $U^{235}:U^{238}$ isotopic ratios. This approach offers potential applications in nuclear forensics investigation as it can provide information on the provenance of materials containing uranium (e.g. uranium ore concentrates and processed material). The feasibility of the LIBS-TDLAS approach has been demonstrated by detecting lithium in a laser-produced plasma using diode laser absorption spectroscopy at 670.78 nm. ©British Crown Owned Copyright 2018/AWE

Improving the accuracy of nuclear decay data using tandem inductively coupled plasma mass spectrometry (ICP-MS/MS)

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The accuracy and precision of nuclear decay data underpins all applications of nuclear science, including radiometric dating, climate modelling, nuclear medicine and decommissioning of nuclear sites. However, many of these data were collected decades ago and large uncertainties remain, which limits the measurement precision achievable. Advances in mass spectrometric methods can be combined with established decay counting techniques to reduce the uncertainties in nuclear decay data of multiple long-lived radionuclides, offering benefits to a range of end users.

This project presents the methodology for measurement of half-life values for long-lived radionuclides using a combination of decay counting and ICP-MS/MS. This includes determination of isotopic composition, as well as weighing of the source material and measurement of the activity concentration. Isotope dilution techniques allow for the measurement of the relative abundance of radionuclides by spiking of a reference solution, eliminating errors related to

signal intensity and is therefore a useful technique in such high-precision isotope analysis.

The aim of this project is to improve the accuracy of half-life values for priority long-lived radionuclides, focusing on naturally occurring ^{238}U and ^{232}Th . Both these radionuclides have geochronological applications involving large timescales, in which changes to the uncertainty of decay data are significant. The methodology developed will be applicable to other natural and anthropogenic radionuclides that suffer from similar decay data limitations.

Tuesday Poster Session 2: Elemental Speciation, Nanoparticles, Environmental and Food Analysis

A metrology strategy for the accurate determination of chromium (VI) in water ususing HPLC-ICP-MS with species-specific isotope dilution analysis

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Trivalent [Cr(III)] and hexavalent [Cr(VI)] chromium are commonly observed species in the environment and their redox state is known to interconvert. Cr(VI) is highly toxic and recognised as a carcinogen. Therefore, procedures for the SI traceable quantification of Cr(VI) in the presence of the other Cr species are required.

In this work, a reversed phase HPLC separation method that enabled baseline separation of Cr(III) and Cr(VI) within 15 minutes was developed with Cr isotope detection by ICP-MS. Quantification of Cr(VI) was undertaken by species-specific double spiking single isotope dilution with HPLC-ICP-MS. To achieve this, $^{50}\text{Cr(III)}$ and $^{53}\text{Cr(VI)}$ -enriched spikes were produced and characterised *in-house*. Using this method, the Cr(VI) mass fraction of a water sample from the Aquacheck Proficiency Testing (PT) Scheme was found to agree well with the assigned value.

The same separation method was used in combination with species-specific double isotope dilution analysis and this measurement capability was demonstrated through participation in an international inter-laboratory key

comparison study (CCQM K124) for Cr(VI) in drinking water. Spiking, dilution (1:6) and stabilisation were achieved in one step by the gravimetric addition of an appropriate amount of $^{53}\text{Cr(VI)}$ to the sample to achieve a target isotope ratio of 1 for $^{52}\text{Cr(VI)}/^{53}\text{Cr(VI)}$. A relative expanded uncertainty of 1.42% ($k=2$) was achieved for Cr(VI) at $62.88 \pm 0.90 \mu\text{g kg}^{-1}$. The value reported by LGC was in good agreement with the key comparison reference value.

Quantification and Identification of Perfluoroalkyl Compounds using HPLC simultaneously coupled to ICPMS/MS and ESI-Orbitrap-MS

Tengetile Nxumalo, N. Laili A Jamari, Abdullah Akhdhar, Andrea Raab, Eva M. Krupp, Jorg Feldmann

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Perfluoroalkyl compounds (PFCs) have been detected in many different environmental samples. A trend which has been noted is that the commonly measured PFC species in different environmental samples account for only a small fraction of the extractable organofluorines present in these samples. These unknown fluorinated organic compounds, which might be abundant in the environment present a pronounced basis of uncertainty for ecological and humans health risk assessment, and thus their identification and characterisation is vital. The main challenge in the identification of these fluorinated compounds is the lack of a fluorine specific detector. In this work we show the use of ICP-MS/MS as a fluorine specific detector for chromatography to determine PFCs individually. PFC species were separated using reverse phase high performance liquid chromatography (RP-HPLC) and simultaneously detected using ICP-MS/MS and orbitrap mass spectrometry employing electrospray ionization operated in the negative mode.

Fluorine detection with ICPMS/MS? A concept of metal-fluorine polyatomic ions

Nor Laili Azua Jamari, Jan Frederik Dohmann, Arne Behrens, Andrea Raab, Eva Krupp, Joerg Feldmann

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Detection of fluorine by inductively-coupled plasma mass spectrometry (ICPMS) is impossible due to the high ionisation potential of fluorine (17 eV). Only small amount of F^+ generated in the argon plasma (15 eV) and high background at m/z 19 due to $^{16}O^{1}H_3^+$ ions restrict the measurement of fluorine with ICPMS. However, through the concept of polyatomic ion interference forms in the plasma, fluorine could be quantified in sub-ppm range. Different metals were evaluated to find the most promising metal-fluorine polyatomic ion ($M-F^+$). Three main characteristics: high bond energy with fluorine, relative low bond energy with oxygen and low second ionisation potential play a role in the formation of $M-F^+$. Barium-fluorine polyatomic ion (BaF^+) at mass-to-charge ratio (m/z) 157 exhibit the highest sensitivity for fluorine detection. Two mechanisms were proposed involving fluorine atom and negative fluorine ion with barium. The method was further developed for fluorine speciation by coupling the high-performance liquid chromatography (HPLC) with ICPMS-triple quad mass spectrometry (ICPMS/MS) and electrospray ionisation mass spectrometry (ESI-MS). Different fluorine compounds exhibit similar sensitivity regardless the structure, which indicates the ICPMS/MS method is fluorine specific detection. ICPMS/MS method able to detect any fluorine compounds which ESI-MS not able to do so. This novel method could be a possible method for analysing unknown fluorine compounds present in environmental and biological samples. Application of this method on the real sample will be presented in the talk.

Sulphur compounds in *Allium* plants and data mining for sulphomics

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Allium vegetables like garlic and shallots are universally consumed because of their flavour, but also as traditional medicine. Both flavour and beneficial health effects are attributed to S-alk(en)yl-L-cysteine sulfoxides, a group of secondary sulphur metabolites.^[1] Further insight into the sulphur metabolism of *Allium* plants is desirable to find connections between fertilisation and these metabolites.

Common analysis methods for these precursor compounds involve the use of species specific standards for quantification and identification. In contrast to

this, a coupled HPLC-ICP-MS/ESI-MS system was used in this project to gain elemental, molecular and quantitative information simultaneously.

This poster presents the results of a study examining the influence of different levels of sulphur fertilisation on *Allium* plants. The plants were grown hydroponically with excess sulphate in the nutrition solution. Principle component analysis will be used as a method to find variation in the dataset and could help to find patterns in how the fertilisation influences different metabolites or metabolite groups. An additional focus is on the analysis of the high resolution MS data. The program Dynamic Cluster Analysis (DCA) can be used for the detection of compounds containing heteroatoms like sulphur in HR-MS data without elemental information from an ICP-MS. The manual and automated data mining approaches will be described and compared.

^[1] J. Feldmann, K. Bluemlein, E.M. Krupp, M. Mueller, B.A. Wood, Metallomics study in plants exposed to arsenic, mercury, selenium and sulphur: in Metallomics – the science of biometals, M.A. Zezzi (Ed.), Springer, accepted.

Water-soluble arsenic compounds in the tissue of stranded pilot whales

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Arsenic compounds are recognized as potential toxins. It is found that arsenic is widely contaminating the marine environment, with higher concentrations than in terrestrial organisms. Arsenic can be divided in organic arsenic and inorganic arsenic compounds and can be also categorised into water-soluble and lipid-soluble arsenic species. This study investigates the presence of arsenic species in kidney and brain tissue of pilot whales. Samples were extracted to analyse water soluble arsenic and lipid soluble arsenic species. Total water soluble arsenic compounds in the samples were determined by ICP-MS. The compounds were analysed and identified with high performance liquid chromatography separation with simultaneous detection by both inductively coupled plasma mass spectrometry and electrospray ionization mass spectrometry (HPLC-ICPMS/ESI-MS). The investigated compounds are methylarsonic acid (MA), dimethyl arsonate (DMA), trimethylarsine oxide (TMAO), arsenobetaine (AB), arsenosugars, arsenolipids and others unknown species.

A direct online solid phase extraction high performance liquid chromatography inductively coupled plasma mass spectrometry for methylmercury in rice

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Rice is a staple food that easily accumulates trace metals in the grain, including mercury in a neurotoxic form as methylmercury (MeHg) which possibly contribute MeHg exposure risk to rice consumer¹. However, the MeHg content in rice is in trace levels², and the sample preparation for determination can be complicated and time-consuming. A simple and reliable method consisted of online preconcentration or solid phase extraction high performance liquid chromatography cold vapor atomic fluorescence spectrometry (SPE-HPLC-CV-AFS)³ was developed. In this work, the online pre-concentration part consisted of a sulfur-based sorption material for solid phase extraction part is hyphenated to high performance liquid chromatography inductively coupled plasma mass spectrometry (SPE-HPLC-ICP-MS) and improves the LOD and LOQ to 0.08 ng kg⁻¹ and 0.26 ng kg⁻¹ for methylmercury (as Hg) using 40 ml MeHg standard. Then, MeHg concentration in polished (white) and unpolished (brown, red, black) from Thailand was studied and show a difference between types of the grain.

1. Gong, Y. *et al.* Bioaccessibility-corrected risk assessment of urban dietary methylmercury exposure via fish and rice consumption in China. *Sci. Total Environ.* **630**, 222–230 (2018).
2. Brombach, C.-C. *et al.* Methylmercury varies more than one order of magnitude in commercial European rice. *Food Chem.* **214**, 360–365 (2017).
3. Brombach, C.-C. *et al.* Quick and robust method for trace determination of MeHg in rice and rice products without derivatisation. *Anal. Methods* **7**, 8584–8589 (2015).

Chemical Speciation of Antimony using voltammetry in Natural Systems

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The increased use of the metalloid antimony (Sb) has led to many environmental soils and groundwater contamination problems and understanding their biogeochemical cycling is of prime importance to predict potential contamination issues. The speciation of Sb is however often limited to the differentiation of oxidation states and identification of stable organic

species by techniques such as ICP and LC-MS. The detection and identification of more reactive, relatively weak complexes that can play a preponderant role in the transport of these elements are however much less known. One of the aims of this study is to use voltammetry to look at the complexation of antimonite Sb(III) with model ligands. Speciation predictions were obtained using Visual Minteq and using complexation data compiled with Filella and May (2005). Results from pseudopolarographic experiments of Sb(III) on gold electrode gave a wave that was found to be independent of the Sb(III) concentration, but dependent on pH and deposition time as expected. In the case of EDTA and DTPA, two waves were observed at pH 3 and were attributed to the reduction of Sb(III) and of the 1:1 complex, Sb-EDTA or Sb-DTPA. In the former case, stability constant determined experimentally matched those reported by Filella while in the latter case, the stability constant determined experimentally was found 100 times stronger than previously reported. In the case of tartaric acid and glutathione, one wave was observed suggesting the presence strong complex, that cannot be reduced within the deposition potential range tested (-1 V).

Characterization of natural Hg nanoparticles in gas condensate samples: TEM, AF4-ICP-MS, sp-ICP-MS and LA-ICP-MS

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The diversification of feedstock supply in the petroleum industry has led to an increased use of heavy crude oils and gas condensates; many of these more difficult duties contain significant amounts of mercury. The impact of mercury on industrial equipment can be serious, including equipment corrosion¹, catalyst poisoning² and particulate emissions.

These concerns have led to the development of mercury removal units as well as analytical methods for the determination of total mercury; however, the efficiency of the mercury removal units strongly depends on its speciation, which is still debated right now regarding gas condensates³. In this regard, the possible presence of mercury-containing nanoparticles is of concern.

Asymmetric flow field-flow fractionation (AF4) is one of the most promising techniques for particles separation, but it has never been applied to petroleum matrices. We are here presenting a novel method to separate nanoparticles

from the dissolved fraction in a “real” gas condensate sample with AF4 using THF as the carrier liquid. The coupling with ICP-MS has highlighted the presence of several elements (Hg but also Fe, P, As, V, Ni and Co) in the nanoparticulate fraction, while TEM imaging confirmed the presence of a large size range (15 to more than 400 nm) of irregularly-shaped nanoparticles. The size of the Hg metallic “core” has been estimated to 60-80 nm using Single Particle-ICP-MS. Finally, LA-ICP-MS imaging showed that Hg particles can sometimes coexist with other elements such as S or As.

Selenium nanoparticles produced by the fungus *Aureobasidium pullulans*: Separation, detection and sizing by asymmetric flow field flow fractionation (AF4) with online inductively coupled plasma mass spectrometry (ICPMS).

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Selenium is an economically important but rarely occurring element, used in manufacture of semi-conductors, photocells, glass, and pigments. Its low natural abundance has heightened supply security fears leading to the exploration of environmentally sustainable ways for its production. Here, we report the detection and sizing of selenium nanoparticles obtained from a fungus, *Aureobasidium pullulans* grown in a liquid nutrient medium amended with 1 mM Na₂SeO₃ for 10 days at 25°C. We developed an optimised AF4 separation method in aqueous mode (0.2% Novachem as eluent, and an exponential elution crossflow of 4 mL min⁻¹), with online coupling to ICPMS for element specific detection of selenium on m/z 78. Integration of the MALS peak with the Postnova® AF2000 MT software resulted to two size distributions with radii of gyration (R_g) ranging from 55-65 nm, and 66-80 nm; with a good data fit across all 21 angles using a spherical model. This positively correlates with single particle ICPMS data which showed a narrow size distribution with a median particle diameter of 70 nm. Our study thus highlights the possibility of a sustainable method for the biological sequestering of selenium from the solution in the form of pure elemental selenium. It also demonstrates the

robustness of hyphenated ICPMS techniques for the characterization of such natural nanoparticles in complex biological media.

Nanoparticle analysis in cosmetic samples by multi-element screening function of spICP-MS

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Nanoparticles (NPs) are widely used in paints, food colorants, cosmetics, pharmaceuticals, and many other applications. Due to their high refractive index, TiO₂ and ZnO NPs are common ingredients in sun protection products used to guard against UV exposure. However, the fate of NPs in the environment and the potential for toxic effects once absorbed into the body are not yet well understood. Therefore, a method to accurately measure NPs in various matrices is required.

The relatively recent development of Single Particle ICP-MS (spICP-MS) provides a powerful tool to characterize the NP content of dispersed samples. spICP-MS is used to measure the target element signals generated from individual NPs in the solution analyzed. This approach allows the simultaneous determination of the number, concentration, and size distribution of particles present, as well as the dissolved element concentration.

In order to detect and characterize nanoparticles of unknown composition, a Fast Time Program Analysis (FTPA) function has recently been developed for the ICP-MS MassHunter software. FTPA measures multiple elements sequentially by spICP-MS mode within a single sample measurement. This provides a rapid screening analysis to quickly identify the elements associated with the NPs in the sample, and thereby gain understanding of the NPs' origin.

In this study, several elements such as Ti, Zn and Si in sunscreen samples were measured using the FTPA function in spICP-MS mode. The method was also applied to measure sunscreen ingredients in swimming pool water samples. The application of the method to cosmetic and environmental samples will be discussed.

CACO-2 IN VITRO MODEL OF HUMAN GASTROINTESTINAL TRACT FOR STUDYING ABSORPTION OF TITANIUM DIOXIDE NANOPARTICLES FROM SEAFOOD SAMPLES

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Titanium dioxide nanoparticles (TiO₂ NPs) are used in industry, as an inorganic UV filter in sunscreens and personal care products, and also as a food additive (E171). The huge increase in the use of nano-based products, mainly metallic NPs, implies the presence of nanomaterials in the environment, and hence, the unintentional human ingestion through water or foods (gastrointestinal, GI, tract is the main pathway of NPs intake in humans) [1].

The presence of TiO₂ NPs in seafood samples was firstly established using an ultrasound assisted enzymatic hydrolysis procedure and sp-ICP-MS analysis. Several clams, cockles, mussels, razor shells, oysters and variegated scallops, which contain TiO₂ NPs, were subjected to an *in vitro* digestion process [2]. The selected GI model was Caco-2 cells because of the development of membrane transporters that are responsible for the uptake of chemicals [3]. Parameters as trans-epithelial electrical resistance (TEER) and permeability of Lucifer Yellow were studied for establishing monolayer integrity. TiO₂ NPs transport and apparent permeability through GI-epithelial barrier (0-2 hours) have been assessed by sp-ICP-MS.

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Alkaline Digestion as a Sample Pre-Treatment for Titanium Dioxide Nanoparticles Extracted from Surimi and Seafood Samples

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The remarkably increase in the use of nanoparticles (NPs) in many applications implies a need to evaluate their impact on human health and environment [1]. Titanium dioxide nanoparticles (TiO_2 NPs) are hugely used in industry, as an inorganic UV filter in sunscreens and personal care products, and also as a food additive (E171) [2].

TiO_2 NPs in surimi and seafood samples have been studied using an alkaline digestion. Some alkaline extractions have been reported in the literature [3] but there are not data regarding TiO_2 NPs extraction from food matrices. Optimum extraction conditions imply 2 mL of TMAH 10% (v/v) and sonication (ultrasound water-bath) for 2 hours. Repeatability, limit of detection and analytical recovery with TiO_2 NPs standards of different sizes were studied. TiO_2 NPs presence in different types of clams, cockles, mussels, razor shells, oysters and variegated scallops and surimi samples (11 samples) have been previously confirmed by an ultrasound assisted enzymatic extraction and sp-ICP-MS analysis. They also were analyzed for total titanium (ICP-MS after acid digestion).

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Assessment of Zinc Oxide Nanoparticles in Textiles by Single Particle ICP-MS

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The modification of textile fibres with nanoparticles (NPs) offers to customers clothing with innovative properties. Thus, metallic NPs provide protection against ultraviolet light (TiO₂ NPs, ZnO NPs), water resistance (SiO₂ NPs, ZnO NPs), antimicrobial activity (Ag NPs, TiO₂ NPs, MgO NPs, CaO NPs, CuO NPs), and flame retardant characteristics (ZnO NPs, SiO₂ NPs, TiO₂ NPs) [1-3]. However, the release of these NPs from textiles can occur during laundering, and they can therefore reach wastewater treatment plants. NPs can be accumulated in sewage sludge, by-product which is commonly used as a fertilizer. Otherwise, NPs can migrate through sweat and can penetrate into the skin, being a risk for human health. The development of methods for assessing NPs in textiles is therefore necessary.

In the current communication, a simple extraction pre-treatment (sonication with water as a solvent) has been used for isolating ZnO NPs from textiles before sp-ICP-MS assessment. The whole method has been optimized and validated, and it has been applied to several clothing.

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The effect of sample drying on the operational speciation of potentially toxic elements in sediment using the modified BCR sequential extraction procedure

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The BCR sequential extraction procedure is widely used to determine the operational speciation of potentially toxic elements in soils and sediments. When applying the approach, a dichotomy exists between maintaining a sample's intrinsic speciation, and pre-treating the sample to make it stable and amenable to standard laboratory operations such as sieving, cone-and-quarterming etc. Sample drying in particular has been reported to cause redistribution of analytes to more readily extractable forms. A common compromise is to air-dry samples at < 25 °C. However, many studies report findings based on extraction of sediments subjected to much harsher pre-treatment regimes.

In order to assess the effects of sample drying on the operational speciation of PTE in sediment, the modified BCR sequential procedure was applied to samples obtained from the catchment of the River Derwent (an area impacted by historical mining and smelting) following various pre-treatment regimes. Samples were analysed as received, air-dried, freeze-dried, and following oven drying at 60°C and 110°C. Extracts were analysed for As, Cd, Cu, Fe, Mn Ni, Pb, U and Zn using an Agilent 7700x ICP-MS instrument.

Different changes in operational speciation occurred for different analytes. Freeze-drying increased the proportion of Pb associated with the exchangeable and acid soluble fraction. In general the proportion of Cd, Cu and Zn associated with the oxidisable phase increased on drying up to 60°C but decreased at 110°C. Manganese and Fe were less affected by drying, whereas the behaviour of As differed between samples.

Seasonal investigation of potentially toxic elements in the vicinity of a major e-waste recycling site in Lagos, Nigeria

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Alaba International Market is one of the oldest and largest e-waste recycling site in Nigeria. The e-wastes are recycled crudely with minimal regard to environmental impact. The influence of these activities on the concentrations of potentially toxic element in and around the site is of concern and requires investigation.

Soil samples from the vicinity of the Alaba e-waste recycling site in Lagos were collected during wet, intermediate and dry seasons for two years. They were dried, sieved and subjected to microwave-assisted aqua regia digestion. The digests were analysed for Cu, Cr, Fe, Mn, Pb and Zn and using an Agilent 7700x ICP-MS instrument.

The results of the pseudototal analysis showed that the concentrations of the potentially toxic elements were higher than permissible limits recommend by the Nigerian Federal Environmental Protection Agency Act (1991). Higher concentrations were generally recorded in the dry seasons. Levels were dependent upon proximity to the recycling site and activities carried out there.

Comparison of on-site field measured inorganic arsenic in rice with laboratory measurements using a field deployable method: method validation

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A commercial arsenic field kit designed to measure inorganic arsenic (iAs) in water was modified into a field deployable method (FDM) to measure iAs in rice. While the method had been validated to give precise and accurate results in the laboratory, its on-site field performance has not been evaluated. This study was designed to test the method on-site in Malawi in order to evaluate its accuracy and precision for the determination of iAs on-site by comparing on-site iAs results with those obtained using validated reference method; and to obtain original data on iAs in Malawian rice. The method was validated by using the established laboratory-based HPLC-ICP-MS/MS. Statistical tests indicated there were no significant differences between on-site and laboratory iAs results determined using the FDM ($p=0.263$, $\alpha=0.05$) and between on-site results and results determined using HPLC-ICP-MS/MS ($p=0.299$, $\alpha=0.05$). Furthermore,

both FDM and HPLC-ICP-MS/MS analyses gave low false positive (9.1% and 0%) and low false negative (3% and 0%) results for samples with low (<100 µg/kg) and high (>100 µg/kg) iAs values respectively. The findings strongly indicate that results obtained in the field using FDM are reproducible (high precision) with reference methods in a laboratory. This method also allows quick (within 1 hour) and efficient screening of iAs concentrations in rice on-site.

Direct, Rapid Analysis of Undiluted Seawater using ICP-MS with an Aerosol Dilution System

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The analysis of seawater presents numerous analytical challenges – the typical elemental targets are at low concentrations and the seawater matrix concentration usually precludes direct measurement by ICP-MS. Approaches usually involve some form of matrix elimination either by liquid-liquid or solid liquid matrix elimination and preconcentration. Whilst these approaches usually work for the majority of elements, they tend to be time consuming, expensive and require user expertise.

With the greater sensitivity of modern ICP-MS instrumentation a simple dilution approach can often be used to reduce the total dissolved solids (TDS) levels typical of seawater (~3%) to that more compatible to ICP-MS (~0.2-0.3%). Usually, a 1:10 or 1:15 dilution is used and whilst this can work well there is a possibility of introducing contamination from the diluent and/or making an error during the dilution step; additionally, the preparation step requires time and a degree of expertise.

An alternative approach is to use so-called “aerosol dilution” whereby the matrix loading within the plasma is reduced in the aerosol phase - in effect diluted using clean, dry argon. This “High Matrix Introduction” (HMI) system is demonstrated with loop injection for the application of direct, undiluted seawater analysis by ICP-MS.

Effect of fertiliser choice on elemental composition of bere barley crops

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Elemental/isotopic compositions of skeletal remains can be used to investigate past diets and geographical origins of people and animals. Fertilisation of crops has been shown to cause difficulties for such studies, as it can influence the composition of the crops to mimic other foods, such as meat (in case of $\delta^{15}\text{N}$). Particularly the effects of seaweed fertilisation on crops require further research, with relevance not only to archaeology, but also to nutritional sciences and food chemistry.

A fertilisation trial was undertaken on Orkney, where selected plots of bere barley were fertilised with seaweed (10 t/ac and 20 t/ac), NPK fertiliser (50 kg N/ha) or left unfertilised. Yield, and grain, husk and straw elemental compositions were determined by MP-AES (Mg, K, Ca, Mn, Fe, Cu, Zn and Sr) and ICP-MS (B, V, Cr, Co, Ni, Zn, As, Br, Sr, Mo, Cd and Pb). Concentrations of B, Sr, As, Mn and Cd were elevated in at least some parts of the plants in the seaweed-fertilised crops compared to unfertilised samples; however, Mo and Br appear to be less concentrated in seaweed- and NPK-fertilised crops than in unfertilised crops. This is likely attributable to the effects of soil chemistry. Principal component analysis of these results showed a clear separation of the three different fertilisation treatments (seaweed, NPK and no fertiliser) on the basis of As, Mo, Mn, Sr, B and Cd concentrations (PC1 53 %, PC 2 22 %), indicating that seaweed fertilisation significantly impacts the chemical composition of crops.

Elemental analysis of maize impacted by the cement industry in North-Central Nigeria

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Maize is one of the most significant cereal grains in the world and is a foremost staple diet of many Nigerians and Africans eaten by people with variable socio-economic circumstances and food inclinations¹. Maize also serves as feed for domestic animals and its production has surpassed the traditional cereals like millet and sorghum. It is hypothesized that it could also pose a risk to human health and environmental harm depending on the farming location.

Plants serve as the initial step of a metal's route to entering the food chain of humans and animals from the soil². Therefore, the concentration of nutritionally, toxicologically and environmentally-important major, minor and trace elements in the edible parts of a plant denote accessible load that could enter the food chain through plants².

In this study, maize grains were sampled from five farmlands including control during the maize growth season in an area of active cement manufacturing in North-Central Nigeria. We have analysed a range of essential and toxic elements using MP-AES and ICP-MS to assess the impact of the cement factory in the vicinity, and in a control site. The results are aimed at generating data for impact studies which could be useful for improving food quality.

Keywords: Maize; Cement factory; Essential elements; Toxic elements; Trace Elements

¹ https://www.afdb.org/fileadmin/uploads/afdb/Documents/Events/DakAgri2015/Cereal_Crops-Rice_Maize_Millet_Sorghum_Wheat.pdf

² <http://onlinelibrary.wiley.com/doi/10.1002/fes3.24/full>

³ The impact of Obajana cement company as a growth pole in Obajana, Kogi State, Nigeria, D. Musa and D. Kpanache, *Ethiopian Journal of Environmental Science and Management*, **2014**, 7(1), 73-81

Total elemental analysis of food samples with ICP-OES and ICP-MS

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The measurement of toxic, essential and nutritional elements in food has, through regulatory drivers and today's health-conscious consumers, become a routine part of food quality monitoring. Alongside regulatory compliance, it is necessary to monitor potentially toxic contaminants that could enter the food chain via a series of pathways including, but not limited to, industrial pollution or environmental contamination. For these reasons, it is essential to have a

simple, robust, multi-elemental analysis method for detecting and quantifying major and minor concentrations of elements in food.

ICP-OES and ICP-MS are sensitive and rapid techniques with wide linear dynamic range and as such are ideal tools for the analysis of trace and major analytes in food together in one analytical run. The principal challenge for trace elemental ICP-based techniques are interferences that stem from the complex food matrix, the reagents used to prepare the sample and the plasma source. This paper reviews different strategies, including collision/reaction cell (CRC) approaches in triple quadrupole ICP-MS, for the accurate analysis of trace elements in food sample matrices. The accuracy of the techniques reviewed is demonstrated by the analysis of food based certified materials following microwave digestion.

Overview of applications for ICP-MS in Food Industry services.

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Campden BRI specialises in providing analytical services to the Food and Drink industries, encompassing testing of food, beverages, food additives, pet and animal feeds, packaging and migration from packaging; for both toxic and nutritional elements. Traditionally applied for low-level toxic element screening, we employ ICP-MS to analyse abundant nutritional elements including sodium and equivalent salt content using sensitivity reduction strategies. Simultaneous measurement of major and trace elements also has application in Food Authenticity and identification of unknown substances for Flavour and Taint investigations and Foreign Body identification. ICP-MS is also applied to speciation analysis particularly for inorganic arsenic and selenium.

