

ERA Chair ISO-FOOD Stakeholder Workshop

"Recent Advances in Mass Spectrometry in Food, Environment and Health"

23th November 2015

Venue: Reactor Centre, Podgorica, Brinje 40, SI-1262 Dol pri Ljubljani

11:00 – 11:15 Welcome [Prof Milena Horvat] and introduction to session 1 [Dr David Heath]

Session 1: Focus on Policy, Industry, and Education

11:15 – 13:00

- **Dr Blaža Nahtigal** (EFSA):
"Working together with EFSA (European Food Safety Authority) to ensure food safety"
- **Dr Tatjana Zagorc** (GZS):
"The mission of the Chamber of Agricultural and Food Industry operating within The Chamber of Commerce and Industry of Slovenia"
- **Dr Francesca Lambertini** (Barilla):
"Relevant Food Chains Vulnerabilities vs current Analytical Methods: The Industrial Perspectives"
- **Prof Nives Ogrinc** (IJS):
"Stable isotopes in food authenticity and traceability: Industrial perspective"

13:00 – 13:30 Coffee Break

13:30 – 13:35 Introduction to session 2 [Prof Sonja Lojen]

Session 2: Focus on Science - Food Safety, Food Traceability

13:35 – 15:45

- **Prof Olivier Donard** (IPREM):
"Authenticity testing of wine and tea samples using ICP/ MC/ MS (Inductive Coupled Plasma / Multicollection / Mass-Spectrometry)"
- **Prof J. Ignacio García Alonso** (University of Oviedo):
"Atomic and molecular isotopic measurements using Mass Spectrometry"
- **Dr Matteo Perini** (FMACH):
"Stable isotope ratio analysis for protecting foods with denomination"
- **Prof Erik H. Larsen** (DTU Food):
"ICP-MS as a detector for characterization of nanoparticles in food and biological tissue"
- **Prof Janez Ščančar** (IJS):
"The use of stable isotopic tracers in speciation analysis at the Department of Environmental Sciences"

15:45 – 16:00 Q&A

Workshop close

Dr Blaža Nahtigal (EFSA)



Blaža Nahtigal holds a BSc, MSc and PhD in the field of food science from the University of Ljubljana, Biotechnical Faculty. She worked as a researcher at the Biotechnical Faculty in the Food Analysis Department, a secondary school teacher and a senior adviser for nutrition at the Ministry of Defence. Since 2006 she has worked at the Ministry of Agriculture, Forestry and Food in the field of food safety, food legislation and food standards – at the beginning at the Food Safety Directorate and now at the EU Coordination and International Affairs Service. She carries out tasks of EFSA Focal Point and Codex Contact Point for Slovenia. As an EFSA Focal Point she acts as the interface between the European Food Safety Authority and the national food safety authorities, research institutes, consumers and other stakeholders, ensuring the exchange of information on scientific outputs, data collection activities, coordinating scientific activities of relevance to EFSA at national level and strengthening national networking.

ABSTRACT: "Working together with EFSA (European Food Safety Authority) to ensure food safety"

The European Food Safety Authority (EFSA) was established by Regulation 178/2002 in 2002 as an independent source of scientific advice to support European policies and legislation, by performing risk assessment and communicating on risks associated with the "from farm to fork" food chain. EFSA is an open, innovative and collaborative partner adding value to society through science on existing and emerging food-related risks. EFSA's key values are scientific excellence, independence, openness, transparency and responsiveness.

Scientific cooperation is about enabling Member States (MS) and EFSA to work together for safer food, while strengthening consumer confidence. One of the bases for EFSA's effective functioning is the networking and cooperation with MS. The first aim of the cooperation is pooling knowledge and expertise through the EU with the support of networking of organisations operating within the fields of EFSA's mission, which includes data collection and data sharing, strengthening (inter)national networking and efficient use of scientific expertise in MS. Benefits for MS organisations include networking with other centres of expertise, dissemination of best practices, sharing and obtaining data of common interest, wider exposure of research findings and the possibility to obtain financial support for their activities.

On the basis of joint responsibility and by working together on food safety, the EFSA's vision is to move beyond the operation of scientific cooperation tools towards building a common risk assessment agenda with defined priorities to make best use of resources. A crucial aspect of success is common active engagement and co-operation at EU and national levels. The Advisory Forum, Focal Points and dedicated networks are key vehicles for data and information exchange. Advisory Forum concentrates on the strategic issues related to co-operation and networking, Focal Points provide support to EFSA's operational programmes, ensuring exchange of scientific information, cooperation through Article 36 and databases/networks of scientific experts, coordination scientific networks at national level and raising the visibility of EFSA.



Dr Tatjana Zagorc (GZS)



Biography: Born in 1970 in Murska Sobota, Slovenia. 1989–1995 undergraduate study of food technology at the Biotechnical Faculty of the University of Ljubljana, graduation in 1995 with a thesis entitled "Degradation of ergot alkaloids by yeasts"; 1995–1998 Master's study of biotechnology at the University of Ljubljana; 1998 Master's degree with a thesis entitled "Characterization of zymocid wine yeasts"; 1998 to 2001 Ph.D. study of biotechnology at the University of Ljubljana, 2001 earned doctoral degree with a thesis entitled "Heterologous protein expression in yeast".

The research study trail was marked with studies in Germany (Universität des Saarlandes) and Hungary (Department of Microbiology and Biotechnology, Corvinus University of Budapest). 1995–2001 young researcher at the Biotechnical Faculty; 2001–2005 independent advisor to the Chamber of Commerce and Industry of Slovenia; 2005 – Present the director of the Chamber of Agricultural and Food Enterprises of the Chamber of Commerce and Industry of Slovenia.

Bibliography: COBISS display comprises 44 units, including 4 scientific articles.

Additional duties: Building knowledge and experience on the economic and managerial skills. Sharing work experience as a lecturer and expert guest at numerous meetings, events, conferences organized by other domestic and foreign institutions. Representing interests and points of view of the food industry in a number of committees, supervisory committees, working groups, forums and consultative bodies of the ministries.

ABSTRACT: "The mission of the Chamber of Agricultural and Food Industry operating within The Chamber of Commerce and Industry of Slovenia"

The mission of the Chamber of Agricultural and Food Industry (CAFI) is: to merge, link and represent agricultural and food businesses in relation to the state Authorities and European industry associations; to develop positions and policies of social partners and facilitates and to develop the activities and flow of knowledge, ideas and best Slovenian and European practices in the industry. It provides technical assistance in the form of advice, education, information and training.

CAFI professional service represents the views of individual sectors at the national level. Since the business environment changes constantly, the membership in the EU associations requires fast transfer of information to companies. With specially adapted services for agricultural and food industry, we provide updated information on companies new developments in safety and food labelling, environmental protection, internal market EU and third markets and other policies that affect the business of agricultural and food industry. Training seminars, workshops and forums organized by the CAFI help members to actively monitor developments in the area of food, environmental and legislation. The traditional annual conference for managers of agricultural and food industry represents a cross-section of the situation and highlights current issues in the field of legislation and trends. Specialized sectoral conferences are oriented into the sectional developments in a particular industry.

Innovation is one of the key issues of all EU policies, thus within the CAFI a special competition Ecotrophelia is operating. On behalf of the companies, we take care that the competition involves students of biotechnology and other research areas to present their innovations and to develop new food products. It is expected that the experience gained within this completion would make them more competitive and interested for employers.



Dr Francesca Lambertini (Barilla)



As from 2011 Dott.ssa Francesca Lambertini is part of the Barilla Advanced Laboratory Research unit as a specialist in Emerging Contaminants.

She has a 5 year master degree in Food Science and Technology. She completed her academic education by obtaining a Ph.D. at the University of Parma, where she has been working as research fellow at the Department of Organic and Industrial Chemistry for several years. There she became skilled in different scientific areas concerning food chemistry, food safety and quality. In particular, she has experience in peptidomic/proteomic applications and liquid chromatography-mass spectrometry techniques.

She also has experience in teaching and project management. In 2009, thanks to an European project launched within the 7th Framework Programme of which Francesca managed the analytical activities, she has carried out part of her work at the AN Bakh Institute of Biochemistry of the Russian Academy of Science (Inbi) MOSCOW (RF), one of the most prestigious research centres in the country, where she deepened her experience in performing *in vitro* tests for the evaluation of biological and functional properties of food. The results of her research activities are more than 30 scientific papers, the majority of which are published in peer reviewed journals.

Her current activity is focused, at the global level, on emerging contaminants: naturally occurring compounds in raw materials, *de novo* formed during technological process and or those potentially migrating from different packaging materials, with the aim of guaranteeing the safety and authenticity of Barilla food products.

In particular, she will scout and support the development of new analytical tools to protect the core business, that contribute to the risk assessment and related mitigation actions along all the strategic supply chains.

ABSTRACT: "Relevant Food Chains Vulnerabilities vs current Analytical Methods: The Industrial Perspectives"

The integrity of European foods is under constant threat: deliberate food fraud exists due to motivations of financial gain, the likelihood of detection, and the balance between reward and penalty. At the same time, the consumer expects to buy products of which safety, quality and authenticity are assured. Furthermore, during the last ten years consumers have a renewed interest in foods strongly identified with a place of origin due to organoleptic-health-patriotism-environmental/animal welfare concerns - regional production enhancements, and so on. There is need for new harmonised methods and reference materials, consolidation of expertise, sharing of data, better anticipation on food fraud and guidance of future research: FoodIntegrity (FI) is a 5 years 12 million EU-FP7 funded project, comprising an inner core of 38 project participants from industry, academia, and research institutes. The work illustrated here is carried on within the activities connected to this important European Project and is related mainly to the selection and evaluation of the most relevant food chains vulnerabilities, observing them from the industrial perspective.

Its focus relies on: (i) bringing together available data on industrially exploited analytical tools for detection of food fraud; (ii) identifying reliable indicators/markers to use for horizon scanning of possible fraud events. Relevant feedbacks from either a number of different areas (vendor assurance, quality assurance, purchasing department, R&D, etc...) or a number of suppliers/co-packers and industrial stakeholders along many different supply chains were collected, rationalized and combined, with regard to the application of test methodologies, traceability issues, consumer issues and communication/media effects/repercussions. Useful information were selected, extracting from all the methods, according to the problems, which is considered the most reliable one and which are the gaps in the sense of industry monitoring and control needs.

This permits the facilitation of further prioritization-procurement setting phases and to better and exhaustively integrate extensive databases on analytical techniques and their application status/validation.



Prof Nives Ogrinc (IJS)



Nives Ogrinc obtained her BS and MSc degrees in physical chemistry from the Faculty of Chemistry and Chemical Technology University of Ljubljana. She received her PhD from the same faculty in 1997. Her PhD study was performed at Jožef Stefan Institute in the field of ecology using stable isotope approach to study carbonate system in different aquatic environments. Nives obtained a NATO-postdoctoral fellowship from 2000-2002 in the Department of Chemistry at Trent University, Peterborough, Ontario, Canada. This fellowship offered her possibilities to be involved in a larger research project on mercury (Hg) cycling in Canada (METAALICUS) using stable isotopes of Hg. She is also Associated Professor at the Jožef Stefan International Postgraduate School currently supervising 4

PhD students and deputy head of the Department of Environmental Sciences at Jožef Stefan Institute. Her research includes the use of stable isotopes in different environmental, archaeological and food studies. In food studies stable isotopes were used as tracers of the sources, origin and authenticity of various foodstuffs, such as honey, olive oil, wine, milk and fruit juice. She has published more than 100 papers, 10 book chapters, coordinated national and international projects and organized several workshops and conferences/symposiums. She is also a Vice President of The International Association for Sediment Water Science (IASWS), member of International Advisory Committee of International Society for Environmental Biogeochemistry (ISEB) and member of the Editorial board of the Journal of Soils and Sediments.

ABSTRACT: "Stable isotopes in food authenticity and traceability: Industrial perspective"

Guaranteeing the authenticity of products is vital to the food and beverage industry if it is to combat fraudulent misrepresentation or adulteration of premium products and at the same time maintaining consumer confidence. The natural variations of stable isotopes serves as a means of determining the origin of material, comparing its identity with that of other samples, or detect illegal additions. Hence Isotope Ratio Mass Spectrometry (IRMS) is a generally accepted technique for the authenticity control of food products and geographical origin determination. There are several practical applications for isotope testing. Milk and its products are tested to determine and verify the origin of cheese and butter products. It is possible to relate the origin of hormones in meat to the natural production by the animal itself or to animal feeding. Similarly, the origin of olive oil, honey and fruit juice used in production can be verified. Fraudulent addition of sugar, water or ethanol to wine can also be detected. Geographic identification requires the mapping and testing of samples known to originate from specific locations. In this presentation, some examples of practical applications of stable isotopes in Slovenian food industry will be outlined.



Prof Olivier Donard (IPREM)



Olivier Donard is currently the director of the UMR CNRS 5254 "Institut des Sciences Analytiques et de Physicochimie pour l'Environnement et les Matériaux" at the University of Pau (France). He is also now the director of the new centre for mass spectrometry MARSS (Centre of Mass Spectrometry for Reactivity and Speciation Science). His scientific expertise is in the field of analytical sciences promoting advanced analytical strategies for the speciation and isotopic signatures of metal and metal species in the environment. The objectives are to improve our understanding of the fate and impact of metals in the environment. He has published more than 200 research papers. He has given more than 120 international plenary or invited conferences around the world. He is or has been part of the editorial board of major international journals on analytical and environmental chemistry such as *Journal of Analytical Atomic Spectrometry*, *Analytica Chimica Acta*, *Analusis*, *Analytical and Bioanalytical Chemistry*, *Applied Organometallic Chemistry*, *Environmental Chemistry*. He has received a number of awards over time among them: Médaille de bronze du CNRS (Chimie) in 1989, the national price of the Division of Analytical Chemistry of the Société Française de Chimie (1993), and several innovation awards in analytical sciences and holds several patents.

ABSTRACT: "Authenticity testing of wine and tea samples using ICP/MC/MS (Inductive Coupled Plasma / Multicollection / Mass-Spectrometry)"

Light stable isotope (H, O) and selected non-traditional isotopes approaches (Sr, Pb) are already used to determine authenticity of food products. ICP/MC/MS is now recognized as a method of choice for the high precision measurement of non-traditional stable isotope ratios. Here, we present the benefits of combining the information of 2 isotopic systems to drastically improve the determination of the geographic origin and the authenticity of the samples analysed. Strontium isotope ratio reflects directly that of the soil and it is widely applied to trace geographic origin, while lead isotopes are extensively used to "fingerprint" important anthropogenic sources. This analytical strategy using 2 isotopic systems, one tracing the soil (Sr,...), the other one tracing the environmental ambient pollution (Pb, Hg,...), now allows us to obtain exceptional new information in terms of traceability. We have applied this new analytical strategy to discriminate with high precision the origin of prestigious wines and tea samples. This study represents the new potential and limits of a model based used for high-precision determination using combined non-traditional stable isotopes of Sr and Pb by MC-ICP-MS. Its application can be applied for determination of improved food origin, traceability and authenticity. Combining isotope ratios information with the elemental analysis data gives a complete tool to detect food frauds, including adulteration of high value products with cheaper substitutes, forgery and falsification. This analytical strategy was successfully applied to the task of finding the counterfeits in testing group of Bordeaux Grand Cru wines.



Prof. J. Ignacio García Alonso (University of Oviedo)



Professor J. Ignacio García Alonso obtained his PhD in analytical chemistry from the University of Oviedo, Spain in 1985 and subsequently became a postdoctoral fellow at the University of Plymouth, UK before returning to Oviedo in 1987. For five years he was a scientific officer of the European Commission, based in Karlsruhe, Germany and in 1995 returned to the University of Oviedo, where he is now Full Professor of Analytical Chemistry. He is head of the research group on Enriched Stable Isotopes at the University of Oviedo. Prof. Garcia Alonso is founding member of the spin-off company ISC-Sciences (www.isc-science.com) devoted to the synthesis and commercialisation of isotopically labelled

compounds particularly for speciation and food analysis. He is co-author of the recent book "Isotope Dilution Mass Spectrometry" published by the Royal Society of Chemistry in the UK.

His main research interest can be summarised as following:

- Metrology in Chemistry. Synthesis and application of isotopically labelled compounds (^{13}C , ^{81}Br , ^{37}Cl , ^{34}S , ^{119}Sn , ^{201}Hg , etc.). Development of instrumentation for post-column Isotope Dilution Mass Spectrometry and other analytical applications of IDMS. Quantitative proteomics.
- Metabolism studies. The use of enriched isotopes for metabolism studies (selenium, sulfur, iron, organotin compounds, etc.). Development of clinical tests based on enriched stable isotopes.
- Traceability studies. The use of a dual isotope procedure for traceability purposes. Labelling of manufactured products. Trans-generational marking of fish. Archaeological isotope ratio measurements.

ABSTRACT: "Atomic and molecular isotopic measurements using Mass Spectrometry"

Mass Spectrometry is increasingly employed as routine analytical technique in multitude of scientific fields from environmental analysis to food safety; not forgetting other fields such as metabolomics, quantitative proteomics or antidoping control. Modern ion sources allow the detection of almost all elements or compounds by Mass Spectrometry. One less known aspect of Mass Spectrometry is its capability to provide isotopic information on atoms and molecules. This isotopic information can be employed to gain further information on the samples or, in combination with enriched stable isotopes, to obtain very accurate concentrations by Isotope Dilution Mass Spectrometry (IDMS).

Natural variation in isotope compositions of Sr and Pb can be employed for the study of the origin of archaeological artefacts or food products. We have applied laser ablation in combination with multicollector ICP-MS to study the origin of asturian beans (Sr ratios) or copper artefacts (Pb ratios).

On the other hand, Isotope Pattern Deconvolution is a new mathematical tool based on multiple linear regression which can be employed in combination with enriched stable isotopes. This tool allows the determination of the molar fraction of different isotope patterns which contribute to the observed mass spectrum. For example in mineral metabolism studies on isotopic profile can be employed as metabolic tracer and a second isotopic profile as quantification tracers. In other studies, such as the marking of foods and living organisms, the two isotopic profiles can be added simultaneously to the sample at a given molar ratio. This molar ratio is constant and independent from the concentration of the natural abundance element in the sample.

We have applied this double tracer procedure for the transgenerational marking of trout and salmon and for the labelling of foods such as asturian beans.



Dr Matteo Perini (FMACH)



Matteo Perini (Trento, Italy, 12/08/1979) graduated in Pharmacy at the University of Padua, Italy and gained his Ph.D. in Agricultural Science and Biotechnology at the University of Udine, Italy. He is a member of the Italian Chemical Society and a councillor of the professional association of Chemists. Since 2003 he has been working as a researcher at the Agricultural Institute of San Michele all'Adige, now Fondazione Edmund Mach, where he is currently a supervisor of the 'Stable Isotope and Traceability' unit of the Centre for Technology Transfer. His main areas of research concern the application of stable isotope ratio analysis of bio-elements to food, aimed at characterising geographical origin and controlling and protecting quality and authenticity. He is the author of over 40 scientific papers (30 IF) and several communications at national and international conferences.

ABSTRACT: "Stable isotope ratio analysis for protecting foods with denomination"

European Regulations EC Nos. 510/2006 and 1151/2012 require protection against the mislabelling of foods with Protected Geographical Indication (PGI), Protected Designation of Origin (PDO) and Traditional Specialities Guaranteed (TSG). The number of these products is increasing year by year, reaching a total number of 1239 at the end of 2014 and Italy is the country with the highest number of designations (269). PDO, PGI and TSG foods can cost more than double the generic products imitating them and this remarkable price difference can induce the commercial temptation to use fraudulent designation labels not corresponding to the real production areas. In order to protect both the consumer and the honest producer from mislabelling fraud, it is desirable to develop objective and robust methods capable of discriminating the different types of products and usable to verify the authenticity of the marketed products with declaration of origin.

Among the possibilities, measuring the stable isotope ratios of bioelements seems to be one of the best candidates for this purpose because their variability is linked to the geographical and climatic characteristics of the provenance area.

The isotopic analysis has been successfully applied to PDO Italian cheeses and extra-virgin olive oils, PGI Aceto Balsamico di Modena and 'Made in Italy' tomato sauce.



Prof Erik H. Larsen (DTU Food)



Erik Huusfeldt Larsen, Ph.D. and leader of the NanoBioScience research group at the Technical University of Denmark, received his Ph.D. in analytical chemistry from University of Copenhagen (pharmacy) in 1993. He has held positions as research assistant, as associate professor University of Copenhagen and as professor of food chemistry at DTU-Food.

His field of research is toxic and essential trace elements and nanoparticles in food, in relation to human health and disease. Dr. Larsen has pioneered the science of speciation using hyphenated analytical techniques especially HPLC-ICP-MS. Since 2006 he has studied detection of nanoparticles in food and biological samples. For this he has applied field flow fractionation with on-line detection by light scattering and ICP-mass spectrometry.

During his 38 years as a scientist Dr. Larsen has published 95 scientific papers in peer-reviewed journals with an H-score of 33. He has given numerous lectures and invited lectures at international conferences.

ABSTRACT: "Characterization and detection of nanoparticles in food – An introduction"

Nanoparticles (NPs) of several elements and their compounds exist in food. Examples are NPs of silver or clay that have migrated from food packaging into food, or silica (consistency regulator) and titanium dioxide (colorant) used as food additives. Nanoparticles are used for their technological properties, but the safety of food has been questioned. The predominant health risk of NPs has been ascribed to their large specific surface area, where unwanted chemical reactions may take place (e.g. formation of reactive oxygen species). For this reason, not only chemical identity, but also metrics like size distribution and porosity are of importance in safety-based food control. From an analytical point of view, the detection of NPs in a complex matrix like food requires dedicated sample preparation and selective laboratory equipment. An analytical platform based on asymmetric flow field flow fractionation (AF4) coupled on-line to light scattering (LS), UV or fluorescence (FL) spectroscopies and ICP-MS was used for size separation and characterization of nanoparticles (NPs) in food. Furthermore, ICPMS in single particle (sp) mode was highly useful for off-line recording of the number-based size distribution of the size-separated NPs eluting from the AF4 separation module. Chicken meat containing silver NPs was enzymatically digested prior to AF4-ICP-MS analysis. The obtained fractograms showed a major nano-peak corresponding to AgNPs. Smaller peaks in the fractograms were ascribed to silver-containing molecules formed following partial dissolution of Ag NPs. The off-line use of spICPMS was instrumental for obtaining more detailed description of the size distribution and for simultaneous detection of a possible dissolved fraction of silver in collected fractions of the fractogram.

The take home messages are:

1. AF4 makes possible the separation of NPs of different sizes in an enzymatic extract of chicken meat
2. Light scattering has limited use in the complex mixture of NPs and digested protein because of its non-specific nature
3. ICP-MS is highly useful for selective detection of silver as dissolved low-molecular compounds and of silver as NPs
4. The discussed instrumental platform is potentially useful in future food monitoring and control activities once public legislation will appear in Europe



Prof Janez Ščančar (IJS)



Janez Ščančar has been actively involved in research for almost 20 years. In 1997 he joined the Jožef Stefan Institute, Ljubljana, Slovenia, obtained his PhD in biology from the University of Ljubljana in 2001 and, in this year, gained "Marie Curie" fellowship programme grant for postdoctoral research in CNRS, LCABIE - University of Pau, France. Currently, he is a Leader of Research Group for Environmental Inorganic Analytical Chemistry at the Department of Environmental Sciences, Jožef Stefan Institute. As Professor he is engaged in lecturing at the Jožef Stefan International Postgraduate School and at the University of Nova Gorica. His main research interests are investigations on the role of metal ions in the environment and living organisms by applying methods of chemical speciation. Among others, he has published 100 original scientific papers in analytical, environmental and life science journals.

ABSTRACT: "The use of stable isotopic tracers in speciation analysis at the Department of Environmental Sciences"

The role and impact of trace elements on the environment and living organisms depend fundamentally on their chemical forms. For illustration, hexavalent Cr is toxic, while trivalent Cr is believed to be an essential micronutrient and inorganic Sn species found in the environment represent no threat towards living organisms, while some organotin compounds (OTC) are among the most toxic chemicals ever introduced to the aquatic environment by man.

In last decades numerous analytical methods have been developed for the speciation of Cr and Sn in different sample matrices. Among them, those which are based on the hyphenation of high performance liquid chromatography (HPLC) or gas chromatography with inductively coupled plasma mass spectrometry (ICP-MS), for Cr or Sn, respectively are the most powerful and the most sensitive. Their analytical performances and applicability can be further expanded by precise isotope ratio measurement that enables the application of isotope dilution (ID) technique for the quantification of trace amounts of individual elemental species in various environmental and biological samples. Enriched stable isotopes can be also applied as tracers in investigations on the fate and role of a given element in the environment and living organisms or to monitor its species transformation during the analytical procedure.

Here, we are presenting new laboratory scale procedures for the synthesis of $^{50}\text{Cr(VI)}$, $^{53}\text{Cr(III)}$ and ^{117}Sn -enriched TBTCI spike solutions from ^{50}Cr or ^{53}Cr enriched oxide and ^{117}Sn -enriched metal, respectively. Their proper preparation and use to follow species transformations during analytical methods and in the environment is discussed.

