How Advances in Mass Spectrometry Are Helping the Food and Beverage Industry

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Mass spectrometry is an important tool for many industries, not least in ensuring the safety of our food and beverages. Hazards ranging from pesticides, to heavy metals and toxins can be identified using the technology, even if they are only present in minute quantities. Here Jenny Nelson tells us how advances in mass spectrometry (MS) have improved analysis potential and the important role it has played and will continue to play in ensuring the safety of the beverage industry.

Q: What advances in MS have had the biggest impact on your research?

A: Inductively coupled plasma triple quadrupole mass spectrometry (ICP-QQQ) has been a game changer. ICP-QQQ provides MS/MS capability which means we can remove spectral interferences with increased reliability and effectiveness through more controlled chemical reactions. MS/MS improves detection limits across the board, as well as providing access to isotopes and elements that we couldn't measure before with conventional quadrupole ICP-MS instruments.

Q: A lot of your recent work has focused on the beverage industry, could you tell us about some of the projects you have been involved in?

A: Our two most recent projects working on beverages have been with the Food and Drug Administration (FDA) studying arsenic speciation in wine. Arsenic exists in multiple forms in foods and beverages and not all forms have the same toxicity. The inorganic forms of arsenic (As(III) (arsenite) and As(V) (arsenate)), are the most toxic. Inorganic arsenic species are categorized as class 1 carcinogens. The FDA has established an action limit for inorganic arsenic in apple juice of 10 µg/kg (ppb), however, there are no regulations controlling the arsenic content of wine in the US. There are limits however in the EU and Canada. Europe (International Organisation of Vine and Wine, OIV) have set maximum acceptable limits for total arsenic in wine of 100 µg/L (ppb), and Canada (Vintners Quality Alliance VQA, Ontario) have set a limit of 200 µg/L (ppb). The first project was to extend the existing HPLC-ICP-MS method for determination of four arsenic species in fruit juice - US FDA Elemental Analysis Manual (EAM) 4.10 - to include wine. This work was recently published[1] in the Journal of Agricultural and Food Chemistry. The second was to develop an arsenic speciation method 10× faster than the current FDA 4.10 regulatory method. The methodology used in this study analyzed the inorganic arsenic species in the As(V) form. As(III) was intentionally oxidized to As(V) with hydrogen peroxide before analysis. By converting As(III) and analyzing all inorganic species as As(V), this method was able to separate from the other arsenic species monomethylarsonic acid (MMA) and dimethylarsinic acid (DMA). The total separation time was less than 2 minutes. This study[2] utilized oxygen reaction gas in the collision/reaction cell (CRC) of the ICP-QQQ to resolve the spectral interferences on arsenic. Some of the interesting results to readers would be the data on the market basket study.

Market Basket Wine Sample	Style	Cultivar	Region	Vintage	Alcohol (%v/v)	iAs	DMA	MMA	Sum of Species
S1	Red	Cabernet Sauvignon	North Coast	2009	13.5	17.13 ± 0.22	0.83 ± 0.03	<LOD	17.96 ± 0.25
S2	Red	Pinot Noir	Appellation Central Coast	2004	13.8	7.49 ± 0.15	0.30 ± 0.062	0.77 ± 0.32	8.56 ± 0.52
S3	White	Chardonnay	Santa Barbara County	2013	13.5	14.63 ± 0.40	0.80 ± 0.08	<LOD	15.43 ± 0.48
S4	Rose	Zinfandel	Napa and Sonoma	2013	10.5	25.03 ± 0.89	0.69 ± 0.26	0.47 ± 0.12	26.19 ± 1.27
S5	White	Chardonnay	Central Coast	2013	13.5	23.45 ± 1.12	0.32 ± 0.05	<LOD	23.77 ± 1.17

The table above shows quantitative results (µg/kg) for inorganic and organic arsenic species in five commercially available wines measured by LC-ICP-QQQ. In all cases, most of the arsenic was present as the inorganic forms (iAs). However, the arsenic levels were all much lower than the maximum allowable level of total arsenic in wine defined in Canada and Europe.

Q: What are the biggest challenges you face when applying mass spectrometry to food and beverage analysis?

A: Historically, the perception of ICP-MS has been that it is complicated and difficult to use, presenting its own set of challenges in the application of mass spectrometry to food and beverage analysis. However, modern ICP-MS instruments are much more user-friendly, with built-in auto-optimization and diagnostics capabilities. ICP-MS now provides analytical possibilities that extend the lab's capability beyond what's offered by the more traditional techniques we previously used.

In fact, ICP-MS greatly simplifies the analysis of foodstuffs, compared to the traditional analytical approaches. This would typically have involved AAS or ICP-OES for the major and nutrient elements, graphite furnace AAS for the toxic and trace elements, and a dedicated analyzer for mercury. All these analytes can now be measured – at much lower detection limits – in a single, fast, practically interference free ICP-MS measurement. So, the potential sample throughput with ICP-MS is much greater than before, and the cost per analysis is far lower. Plus, the method simplification in terms of sample preparation, calibration strategy, QC overheads, reporting, waste disposal etc., gives concrete benefits especially in commercial food labs.

Q: How do you think developments in mass spectrometry are likely to change the food and beverage industry in the future?

A: The removal of spectral interference provided by the ICP-QQQ system through MS/MS, has really changed things in the world of ICP-MS, enabling us to now develop methods around elements/metals that used to be challenging. One good example of this was a collaboration where we worked with Brian Jackson at Dartmouth University. The aim of this study[3] was to accurately measure arsenic and selenium in foods using Triple Quadrupole ICP-QQQ to remove doubly charged rare earth element (REE) interferences. REE levels in food samples are low, but crops grown in REE-enriched soils have the potential to have higher concentrations of these elements, leading to false positives for arsenic and selenium. It is known that arsenic and selenium can be difficult to quantify accurately by conventional single quadrupole ICP-MS, especially at low levels. This is because isotopes can suffer from multiple spectral interferences, from doubly charged ions of the REE (REE++), as well as polyatomic ions formed from the sample matrix and plasma. A quadrupole mass spectrometer separates ions based on mass-to-charge ratio (m/z), and so the REE++ ions appear at half their true mass, overlapping the singly charged analyte ions of arsenic and selenium. This table shows a comparison of single quadrupole (SQ) and triple quadrupole ICP-MS results for arsenic and selenium in food reference materials. Significant errors in the (uncorrected) single quadrupole results meant that correction equations had to be applied to improve the accuracy. Triple quadrupole ICP-MS provides better accuracy without requiring any correction equations, illustrating an important advantage of ICP-QQQ data vs. traditional SQ ICP-MS for this type of interference.

Additionally, analysis of nanoparticles in food is an emerging application, the development of which has greatly benefited from the advances in single particle inductively coupled plasma-mass spectrometry (sp-ICP-MS). As well as advances in the hardware in the ICP-MS, there have also been new software capabilities

| SRM | Certified | ICP-MSHe mode | | ICP-MSH$_2$ mode | | ICP-QQQO$_2$/ H$_2$ mass-shift |
		Uncorrected	Corrected	Uncorrected	Corrected	Uncorrected
Arsenic (mg/kg)						
NIST 1547	0.060±0.018	0.170±0.016	0.068±0.003*	0.113±0.004	0.079±0.004*	0.065±0.002*
NIST 1515	0.038±0.007	0.250±0.016	0.026±0.021*	0.126±0.005	0.047±0.004*	0.032±0.002*
Selenium (mg/kg)						
NIST 1547	0.120±0.009	0.394±0.04	0.113±0.02*	0.119±0.009*	0.119±0.009*	0.127±0.006*
NIST 1515	0.050±0.009	0.808±0.04	0.013±0.04*	0.050±0.003*	0.050±0.003*	0.047±0.006*

*95% confidence interval overlaps with the certified range

that have had to be developed to support this new application. I believe that advances in ICP-MS instrument sensitivity and sp-ICP-MS software will lead to this type of measurement soon becoming mainstream; regulators are already looking at how these novel nanomaterials should be monitored and controlled. Since this is a new hot topic, I foresee many advances in technology from the instrument vendors in the future as they gain a better understanding of the requirements of both their customers and the industry.

Dr Jenny Nelson was speaking to Dr Karen Steward, Science Writer for Technology Networks.

Jenny Nelson has been an Adjunct Professor in the Department of Viticulture and Enology at University of California, Davis since 2013 and is an Atomic Spectroscopy Research Scientist for the Applied Markets team at Agilent Technologies. Her research focus is in trace elemental analysis for the food and beverage industry. She has extensive experience in operating and method development for Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES), and speciation analysis for many sample matrices using GC-ICPMS and LC-ICPMS.

References

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