High Matrix Analysis of As, Se, Cd, Hg, & Pb in Food Digestates Using Inductively Coupled Mass Spectrometry.

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Abstract

Increased regulations regarding the presence of toxic metals in food and beverages have become a fast growing analytical requirement which ultimately ensures their safety prior to consumption. Stricter regulations have been placed such as the Safe Drinking Water and Toxic Enforcement Act, also known as Prop 65, providing guidelines for food and beverage safety. The low detection limits achieved by ICPMS, along with ORS technology provide a reliable means of determining such toxic elements simultaneously and reliably.

Experimental

Agilent's 7700x ICP-MS was employed for this analysis. The 7700x incorporates Agilent's 3rd generation ORS, called the Octopole Reaction System (ORS^3). The ORS^3 was designed to use He mode with Kinetic Energy Discrimination (KED) as standard, although reaction gases such as H_2 can be also used. In addition, the High Matrix Interface (Figure 2) was employed, or HMI. This allows for more robust plasma conditions and the ability to dilute the samples via an Ar aerosol, eliminating the need for benchtop dilutions which may incorporate more background contamination.

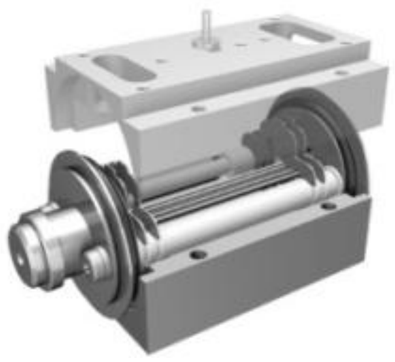
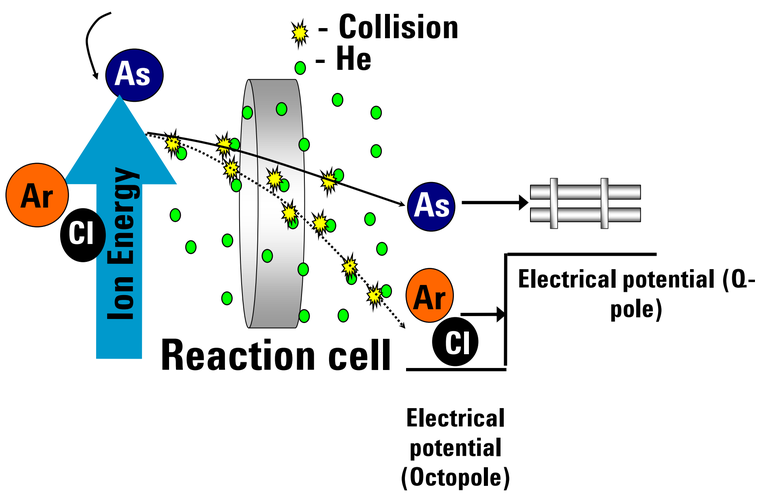


Figure 1 Schematic diagram of reaction cell



Plasma conditions were auto-tuned prior to analysis by selecting "Robust Plasma"in the ICP-MS MassHunter software. Robust plasma conditions provide a hot plasma (~1% CeO/Ce) with the addition of HMI, which introduces an Ar stream after the spray chamber, the oxide ratio was reduced to 0.5% CeO.Ce. Ion lens voltages were also auto-tuned for maximum sensitivity. The plasma and ion lens parameters are shown in Table 1.

Table 1. 7700x Instrument Operating Conditions

ICP-MS parameter	Value
RF power (W)	1550
Carrier gas (L min^{-1})	0.50
Dilution (HMI) gas (L min^{-1})	0.50
Extract 1 (V)	0
Extract 2 (V)	-200
Omega Lens (V)	-85
Omega Bias (V)	14.0
He flow (He mode)	4.0 ml min^{-1}
KED (He mode)	3 volts

The SRM materials were digested using a Milestone microwave digestion system with PTFE inserts. Approximately 0.5g of each SRM was weighed using an analytical balance. Dilutions shown in the results tables are the digestion dilution as the digested SRM's were analyzed with no further dilutions for analysis.

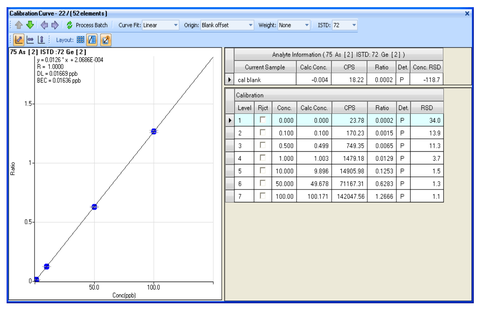
Results and Discussions

The calibration standards were prepared in a 1.0%HNO_3 and 0.5%HCl matrix. The data was acquired in He mode for As & Se, while Cd, Hg, & Pb were acquired in NoGas mode (no cell gases introduced into the ORS). All elements could certainly be acquired using He mode, but NoGas mode was utilized to achieve the best detection limits for the associated elements. Example calibration curves with estimated DL and BEC data are displayed.

Calibration Verification Standard Results

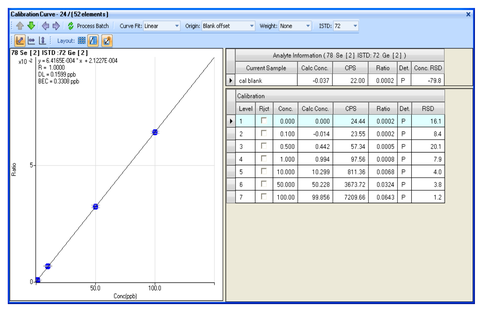
	NIST 1643e Results (ppb)		
	1643e ICV		
	Result	True Value	%Recovery
	1		
75 As [He]	59.155	58.98	100
78 Se [He]	11.340	11.68	97
111 Cd [NoGas]	6.3657	6.408	99
201 Hg [NoGas]	0.8341	n/a	
208 Pb [NoGas]	18.974	19.15	99

• As Calibration [He] (1%HNO_3 & 0.5% HCl) Calibration for ^{75}As at 0, 0.1, 0.5,1.0, 10.0, 50.0 & 100 ppb



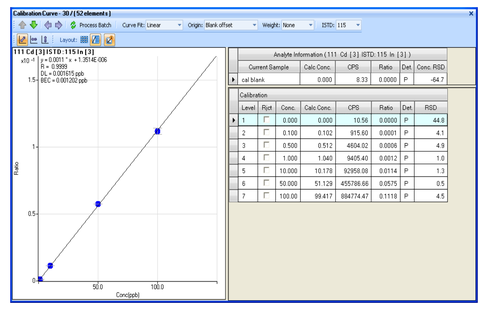
Gas Mode	Mass	Elem.	DL (ppb)	BEC (ppb)
He	75	As	0.017	0.016

• Se Calibration [He] (1%HNO_3 & 0.5% HCl) Calibration for ^{78}Se at 0, 0.1, 0.5, 1.0, 10.0, 50.0 & 100 ppb



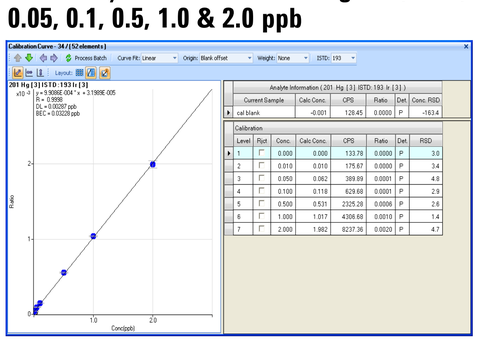
Gas Mode	Mass	Elem.	DL (ppb)	BEC (ppb)
He	78	Se	0.160	0.331

• Cd Calibration [No Gas] (1%HNO_3 & 0.5% HCl)Calibration for ^{111}Cd at 0, 0.1, 0.5, 1.0, 10.0, 50.0 & 100 ppb



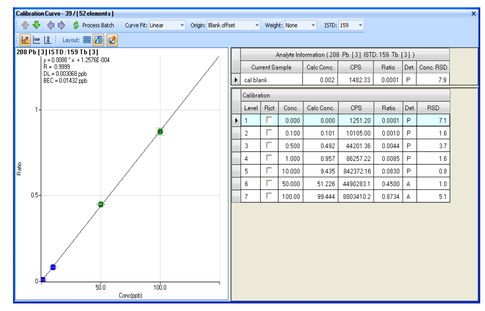
Gas Mode	Mass	Elem.	DL (ppb)	BEC (ppb)
No Gas	111	Cd	0.002	0.001

• Hg Calibration [NoGas] (1%HNO_3 & 0.5% HCl) Calibration for ^{201}Hg at 0, 0.01, 0.05, 0.1, 0.5, 1.0 & 2.0 ppb



Gas Mode	Mass	Elem.	DL (ppb)	BEC (ppb)
No Gas	201	Hg	0.003	0.032

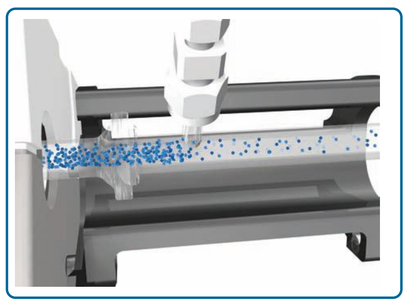
•Pb Calibration [No Gas] (1%HNO_3 & 0.5% HCl) Calibration for ^{208}Pb at 0, 0.1, 0.5, 1.0, 10.0, 50.0 & 100 ppb



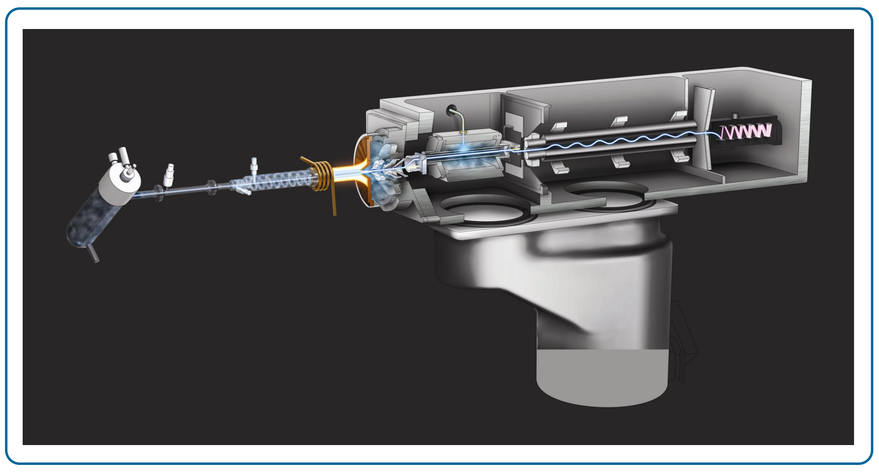
Gas Mode	Mass	Elem.	DL (ppb)	BEC (ppb)
No Gas	208	Pb	0.003	0.014

The low detection limits and BEC's acquired in the He mode, show the ability of the ORS to effectively remove the polyatomic interferences from the calibration matrix. Where interference equations would have to be used for a No Gas mode acquisition, the He mode provides a much simpler means of removing the polyatomics, resulting in lower DL's. This allows for future applications to be applied which require low determination of these elements that were previously difficult to determine in a high acid matrix.

	Food SRM Results (ppb)											
	SRM 1568a Rice Flour			SRM 2976 Mussel Tissue			SRM 1577c Bovine Liver			SRM 1570a Spinach Leaves		
	Result	True Value	%Recovery	Result	True Value	%Recovery	Result	True Value	%Recovery	Result	True Value	%Recovery
	93			99			94			106		
75 As [He]	263.80	290	91	13623	13300	102	19.711	19.6	101	66.473	68	98
78 Se [He]	349.50	380	92	1977.3	1800	110	2022.0	2031	100	128.48	117	110
111 Cd [NoGas]	21.066	22	96	821.96	820	100	96.339	97	99	2635.1	2890	91
201 Hg [NoGas]	6.0025	5.8	103	54.185	61	89	5.5658	5.36	104	24.114	30	80
208 Pb [NoGas]	5.3881	n/a		1048.0	1190	88	55.862	62.8	89	148.76	n/a	



Figures 2 & 3
Representations of HMI aerosol dilution and a cut away view of the Agilent 7700 ICPMS



Conclusions

Food analysis has been made simpler with the use of ICP-MS, which employs collision/reaction cell (CRC) technology. The new generation Octopole Reaction System (ORS^3) technology of the Agilent 7700x, using the inert gas helium, allows for elimination of polyatomic species such as $ArCl^+$, and $ArAr^+$ that otherwise interfere with the trace level measurement of As, and Se respectively. In addition, the high plasma temperature minimizes matrix suppression while maintaining ionization efficiency for those elements that are difficult to ionize, such as As, Se, Cd, & Hg, resulting in low detection limits. High matrix tolerance and polyatomic interference removal are essential for the analysis of trace elements in food and beverage digestates to assure accuracy and productivity in the food laboratory.

Germany, January 2011