Electronic Supplementary Material (ESI) for Journal of Analytical Atomic Spectrometry.

Supplemental information

1. SIMION modeling of $^{45}Sc^+$ and $^{238}U^+$ ion trajectories at different lens voltages.

SIMION was used to simulate ion trajectories from the skimmer through the ion optics. For the ion trajectory simulations shown in Figure S1, a SIMION Lua workbench user program for space charge was used. Ions were specified to have initial angles of 0 to 4° at the skimmer orifice. The simulation included 5000 $^{40}Ar^+$ ions with an ion kinetic energy of 3.08 eV and a weighting factor of 2 per ion. The simulation also included 5000 Sc^+ (KE=3.08 eV) or U^+ (KE=8.4 eV) ions, each with a weighting factor of 3.33×10^{-5}. The weighting factors determine the fraction of the total current that each simulated ion trajectory represents. The actual current in the positive ion beam is expected to be about 1500 µA. However, the simulation did not converge when a total ion current greater than about 50 µA was used. The total ion current was specified to be 6.6 µA for the SIMION simulation because the optimum lens voltages from the simulation then best matched the experimentally determined lens voltages (within 1 V or less) as a function of analyte ion mass.

The ions were assumed to originate at the skimmer orifice (i.e. no transition from a neutral beam to a positive ion beam was included). The simulations in Figure S1 are intended only to show the trends in ion beam focusing for ions with different m/z at different lens voltages.

When the lens voltage is set to focus light ions at the aperture to the third vacuum stage (such as $^{45}Sc^+$, Fig. S1a), then heavy ions (such as $^{238}U^+$, Fig. S1b) are not focused well. When the lens voltage is set to focus heavy ions (such as $^{238}U^+$, Fig. S1d) at the aperture to the third vacuum stage, then light ions (such as $^{45}Sc^+$, Fig. S1c) are not focused well.

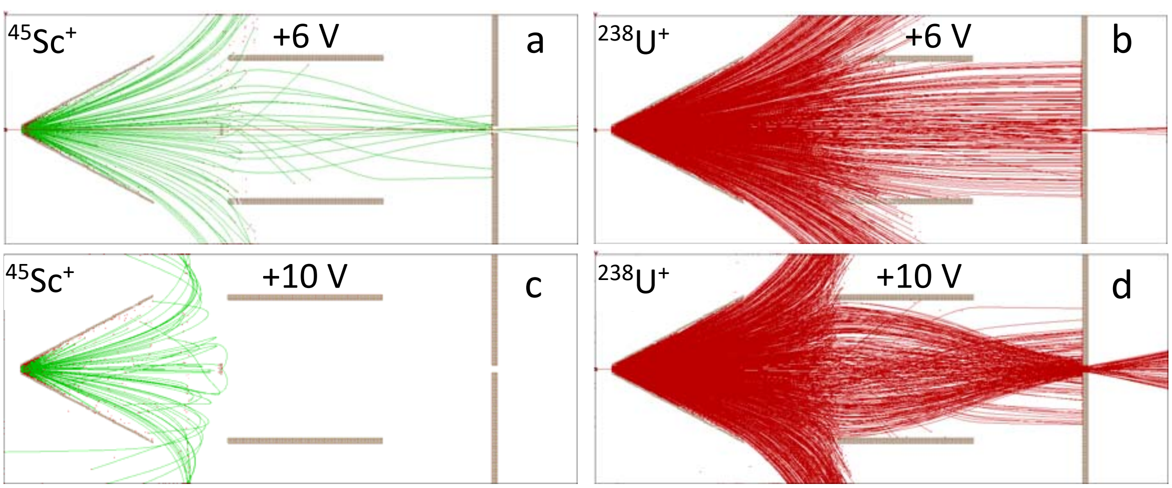

Figure S1. Ion trajectories calculated using SIMION. (a) $^{45}Sc^+$ ions with a lens voltage of 6 V. 32 of 5000 Sc^+ ion trajectories passed through the orifice into the third vacuum stage. (b) $^{238}U^+$ ions with a lens voltage of 6 V. 144 of 5000 $^{238}U^+$ ion trajectories passed through the orifice into the third vacuum stage. (c) $^{45}Sc^+$ ions with a lens voltage of 10 V. 0 of 5000 Sc^+ ion trajectories passed through the orifice into the third vacuum stage. (d) $^{238}U^+$ ions with a lens voltage of 10 V. 836 of 5000 $^{238}U^+$ ion trajectories passed through the orifice into the third vacuum stage.

2. Reproducibility of no matrix solution signals

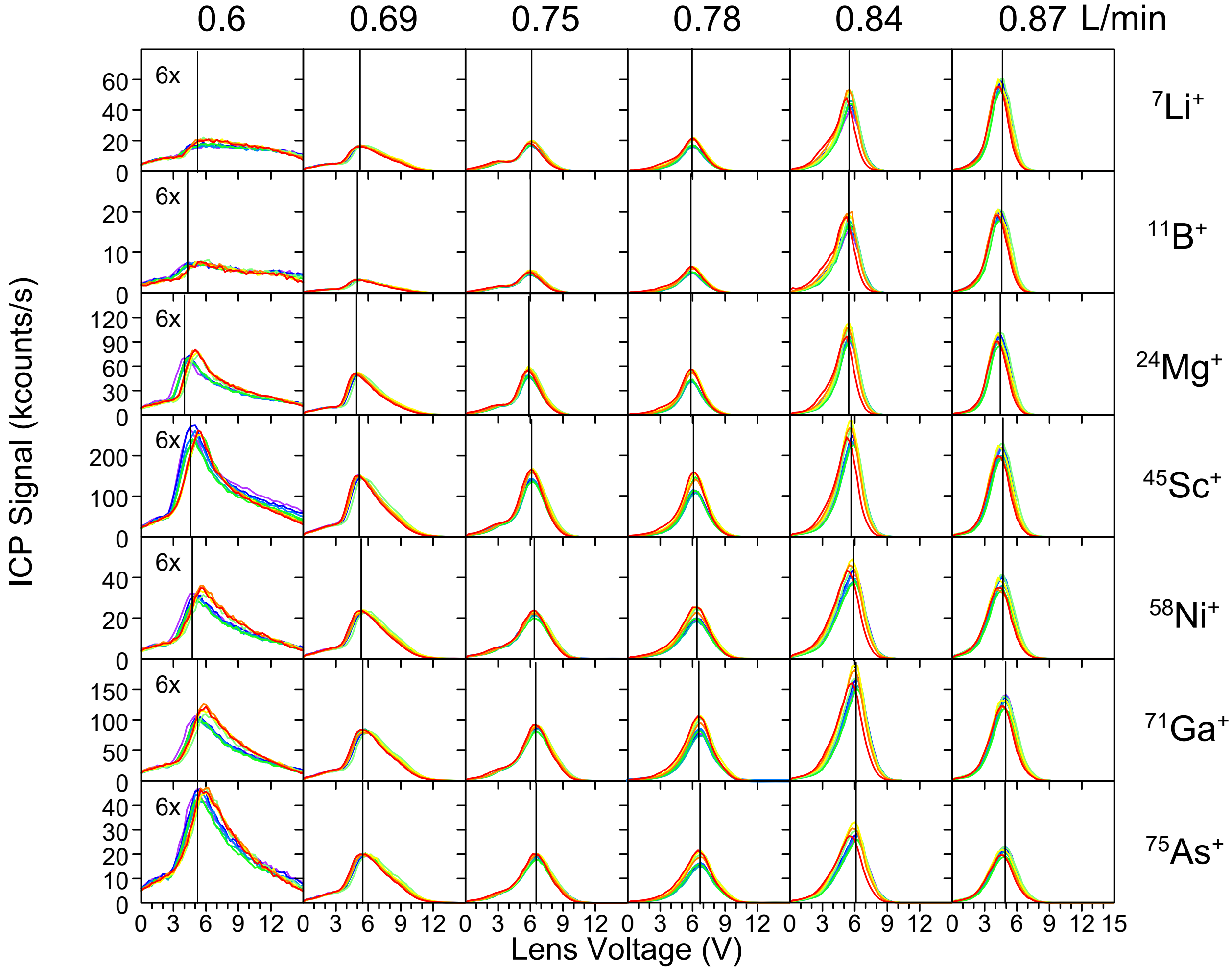

Figure S2. At each nebulizer gas flow rate, nine measurements of ICP-MS signal versus lens voltage from a 20 ppb multi-element solution. Measurements were made before and after each of the solutions containing one of the eight matrix elements at a concentration of 5 mM. Order: prior to any matrix (——), after Na (——), after Cu (——), after Y (——), after In (——), after Cs (——), after Tb (——), after Lu (——), after Tl (——). Analytes are listed on the right. The intensities measured at a nebulizer gas flow rate of 0.6 L/min were multiplied by 6 prior to plotting. Vertical lines indicate optimum lens voltage for first measurement without matrix.

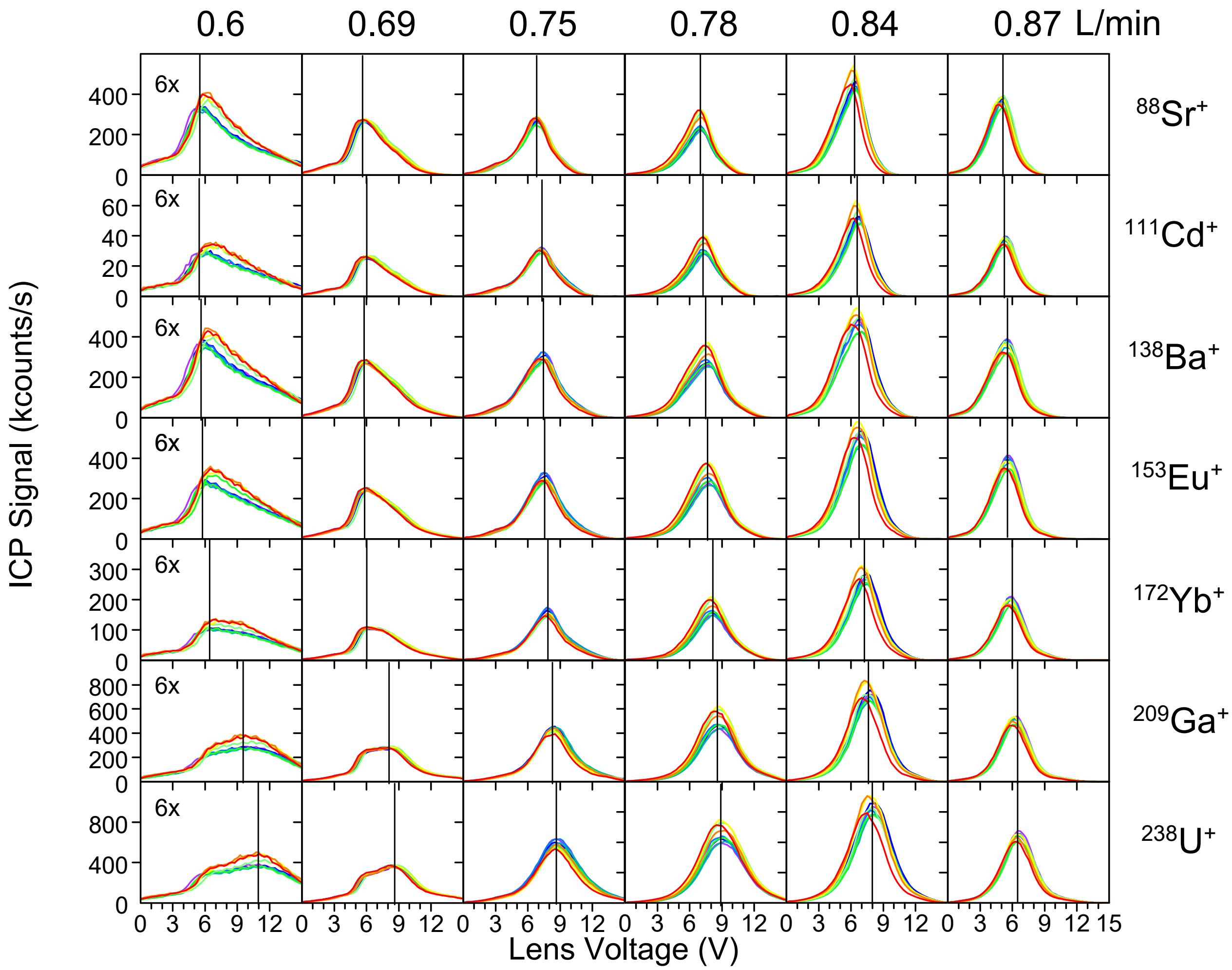

Figure S3. At each nebulizer gas flow rate, nine measurements of ICP-MS signal versus lens voltage from a 20 ppb multi-element solution. Measurements were made before and after each of the solutions containing one of the eight matrix elements at a concentration of 5 mM. Order: prior to any matrix (——), after Na (——), after Cu (——), after Y (——), after In (——), after Cs (——), after Tb (——), after Lu (——), after Tl (——). Analytes are listed on the right. The intensities measured at a nebulizer gas flow rate of 0.6 L/min were multiplied by 6 prior to plotting. Vertical lines indicate optimum lens voltage for first measurement without matrix.

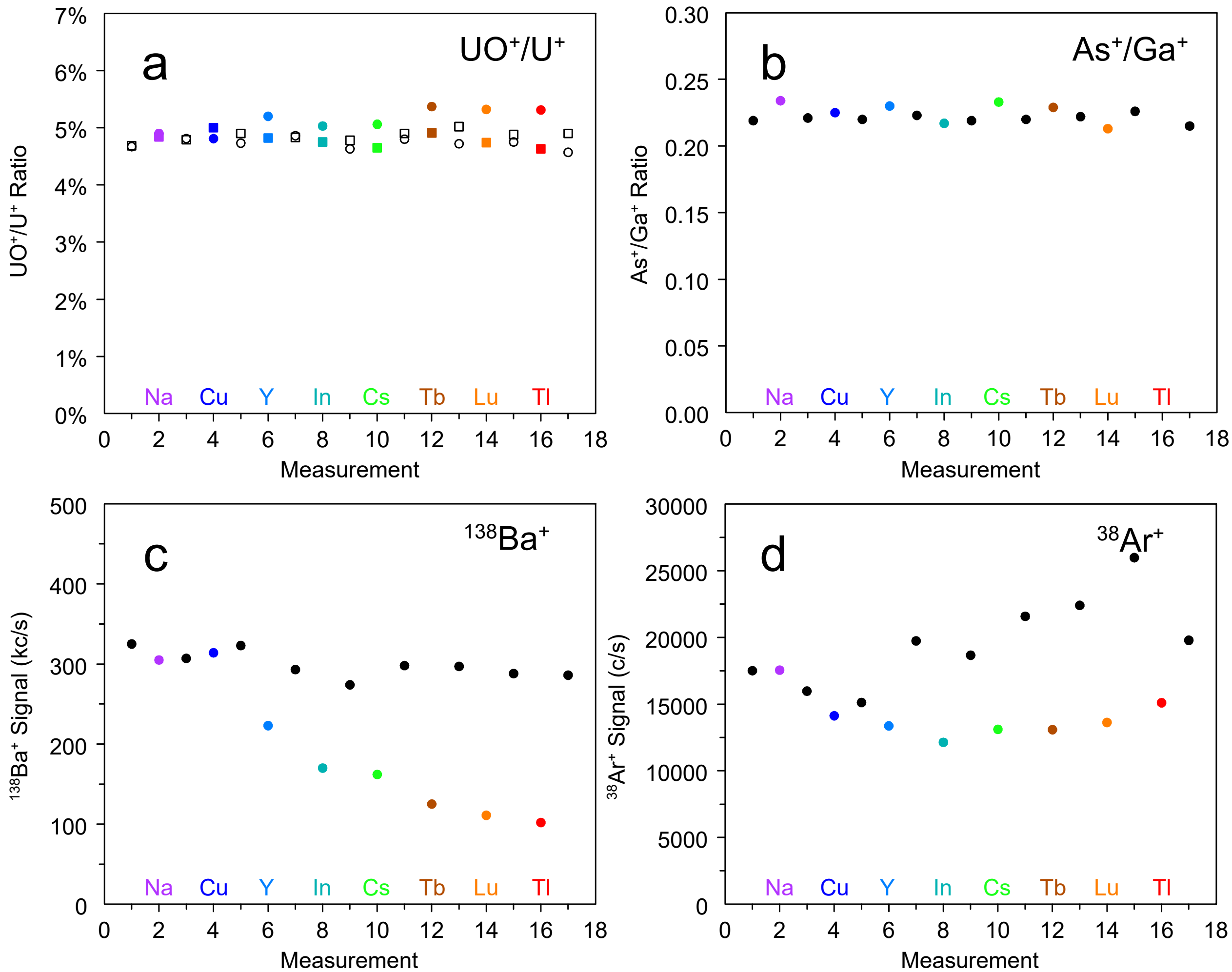

Figure S4. Measurements of: (a) UO^+/U^+ intensity ratio, (b) As^+/Ga^+ intensity ratio, (c) $^{138}Ba^+$ intensity and (d) $^{38}Ar^+$ intensity before, during and after measurement of solutions containing 5 mM of one of the eight matrix elements at a nebulizer gas flow rate of 0.75 L/min. Black symbols indicate signals produced from solutions without an added matrix element. Circles indicate signals at the lens voltage that produced the largest signal in the absence of an added matrix element. Squares indicate the ratio of the sum of UO^+ intensities over all lens voltages to the sum of U^+ intensities over all lens voltages.

3. Matrix effects on 14 analyte ion signals as a function of lens voltage

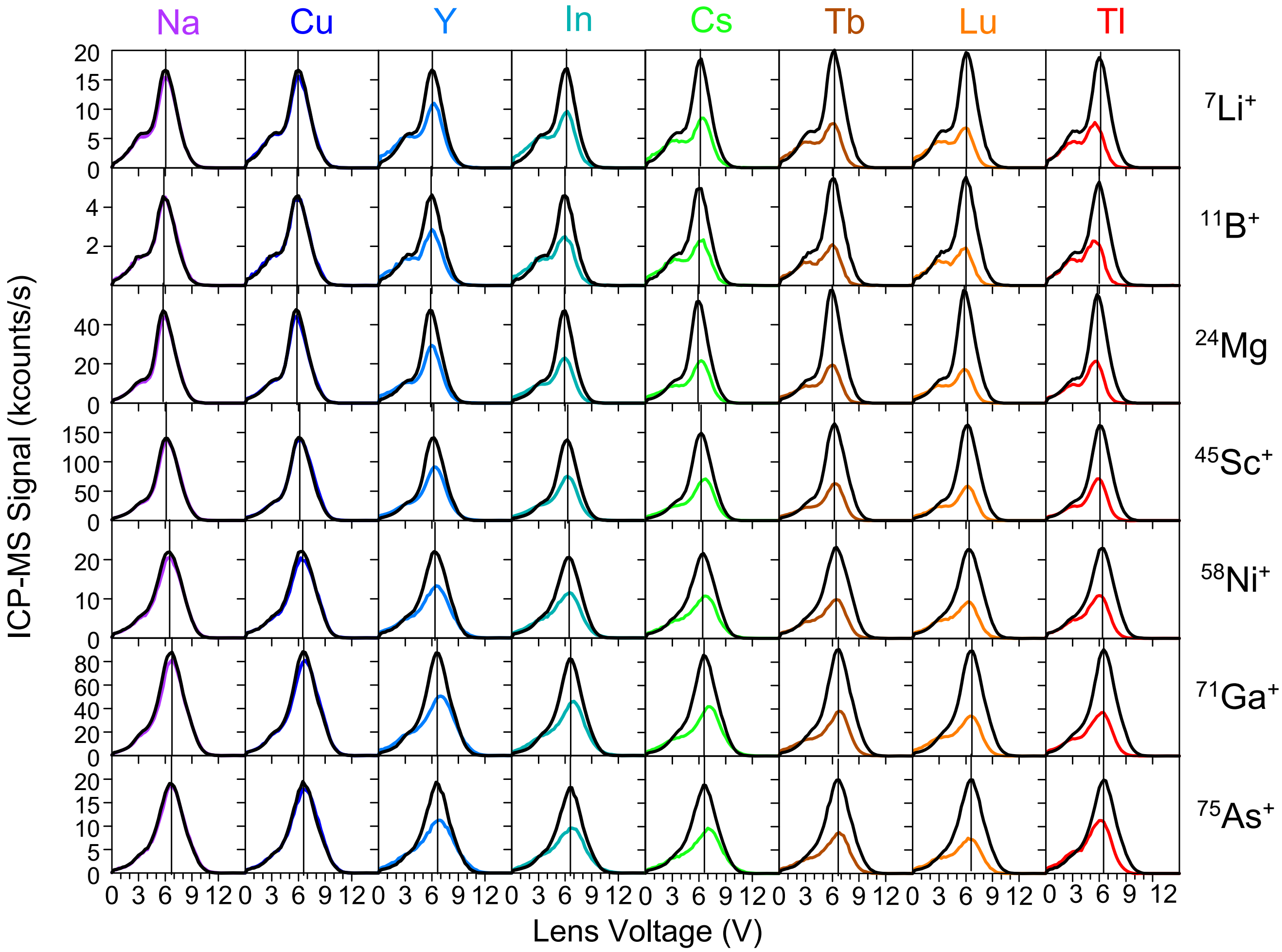

Figure S5. ICP-MS signals as a function of lens voltage in the absence (black line) and presence of 5 mM matrix element at the optimum nebulizer gas flow rate. Matrix elements listed on top. Analytes listed on the right. Tl solution contains As contamination that contributes significantly to the signal measured at m/z 75.

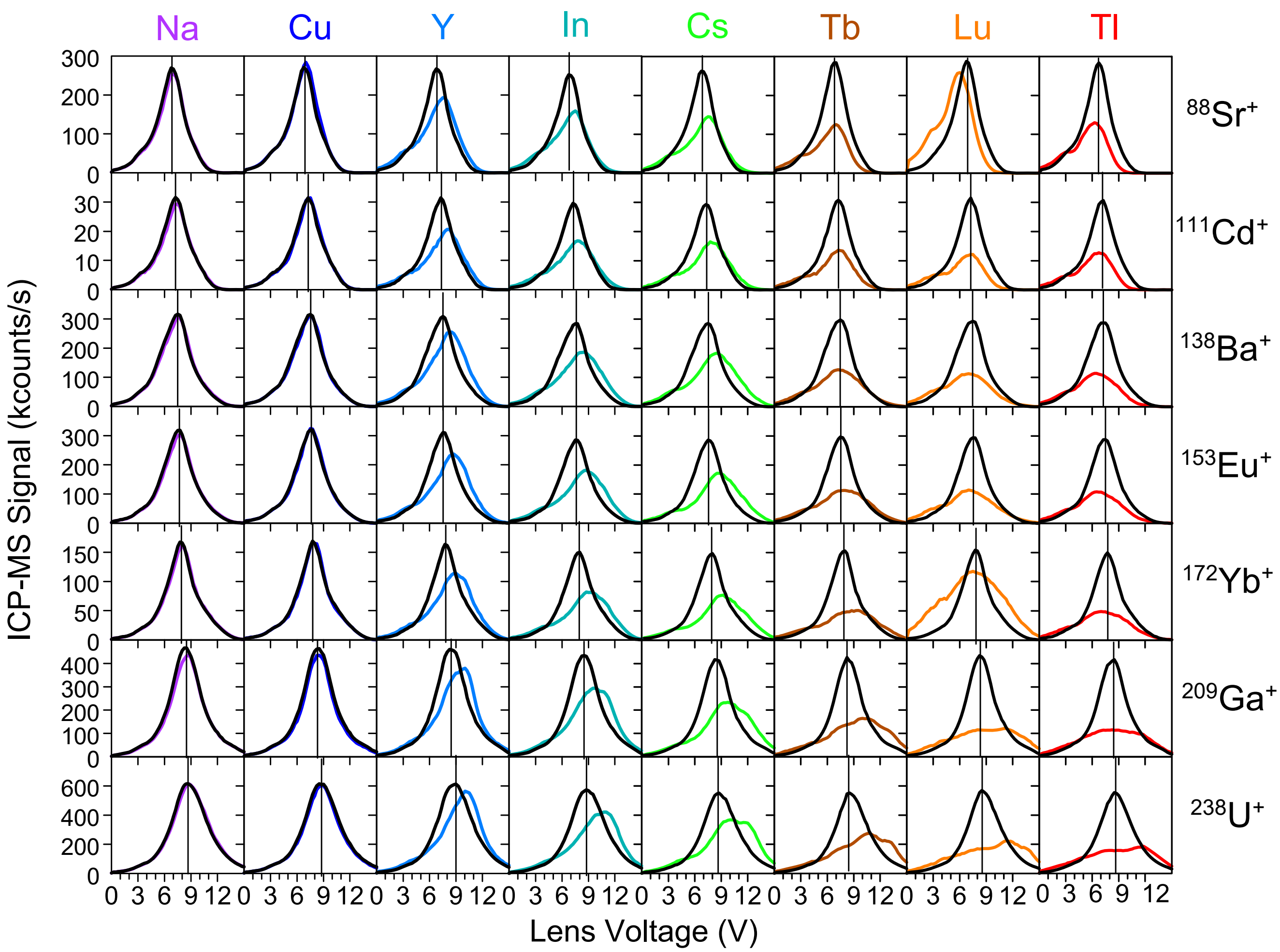

Figure S6. ICP-MS signals as a function of lens voltage in the absence (black line) and presence of 5 mM matrix element at the optimum nebulizer gas flow rate. Matrix elements listed on top. Analytes listed on the right. Lu solution produces a significant Lu^{2+} signal at same m/z as $^{88}Sr^+$. Lu solution contains Yb contamination that contributes a significant signal at m/z 172.

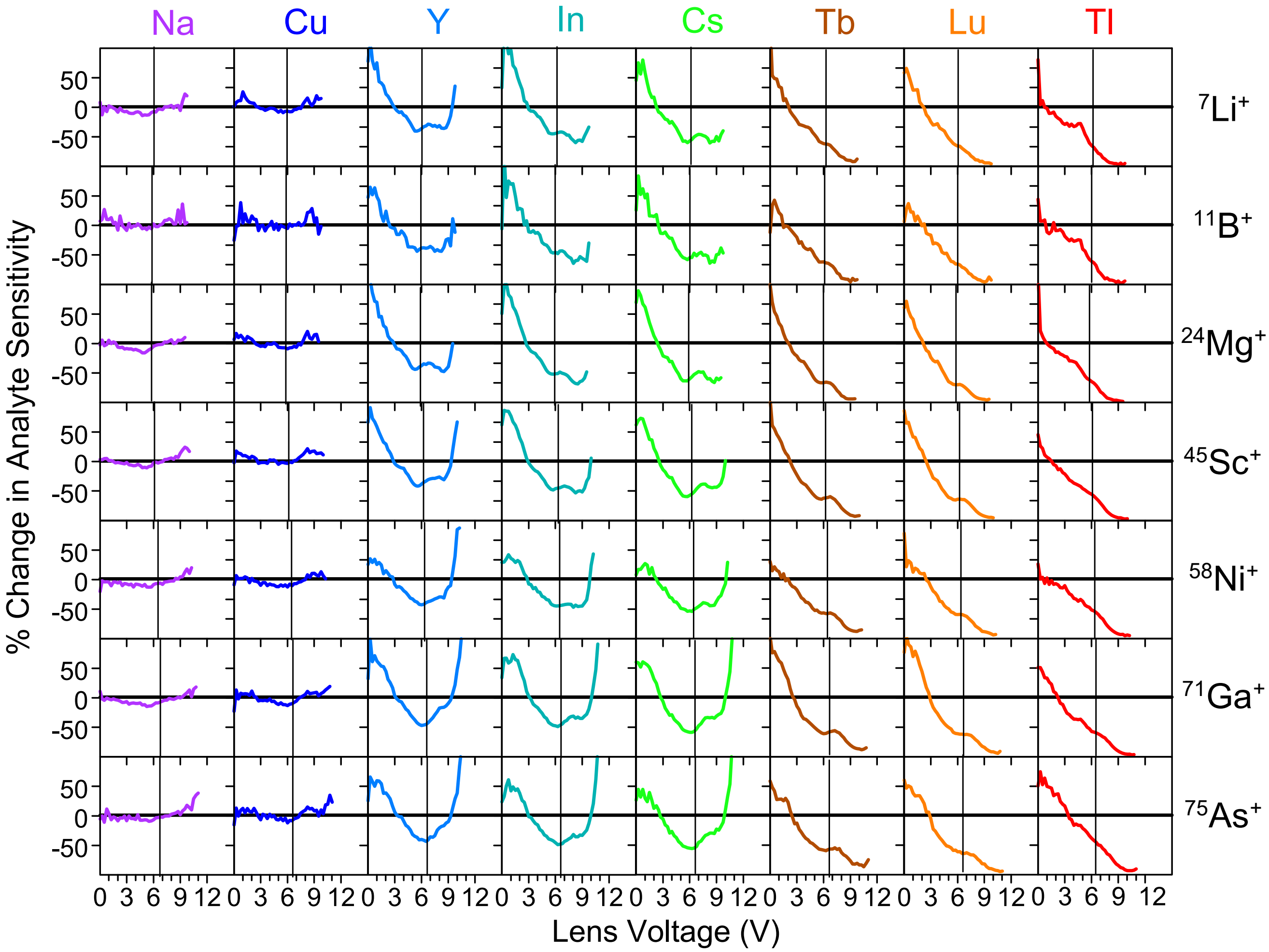

Figure S7. Matrix induced change in ICP-MS sensitivity as a function of lens voltage at the nebulizer gas flow rate. Matrix elements listed on top. Analytes listed on the right.

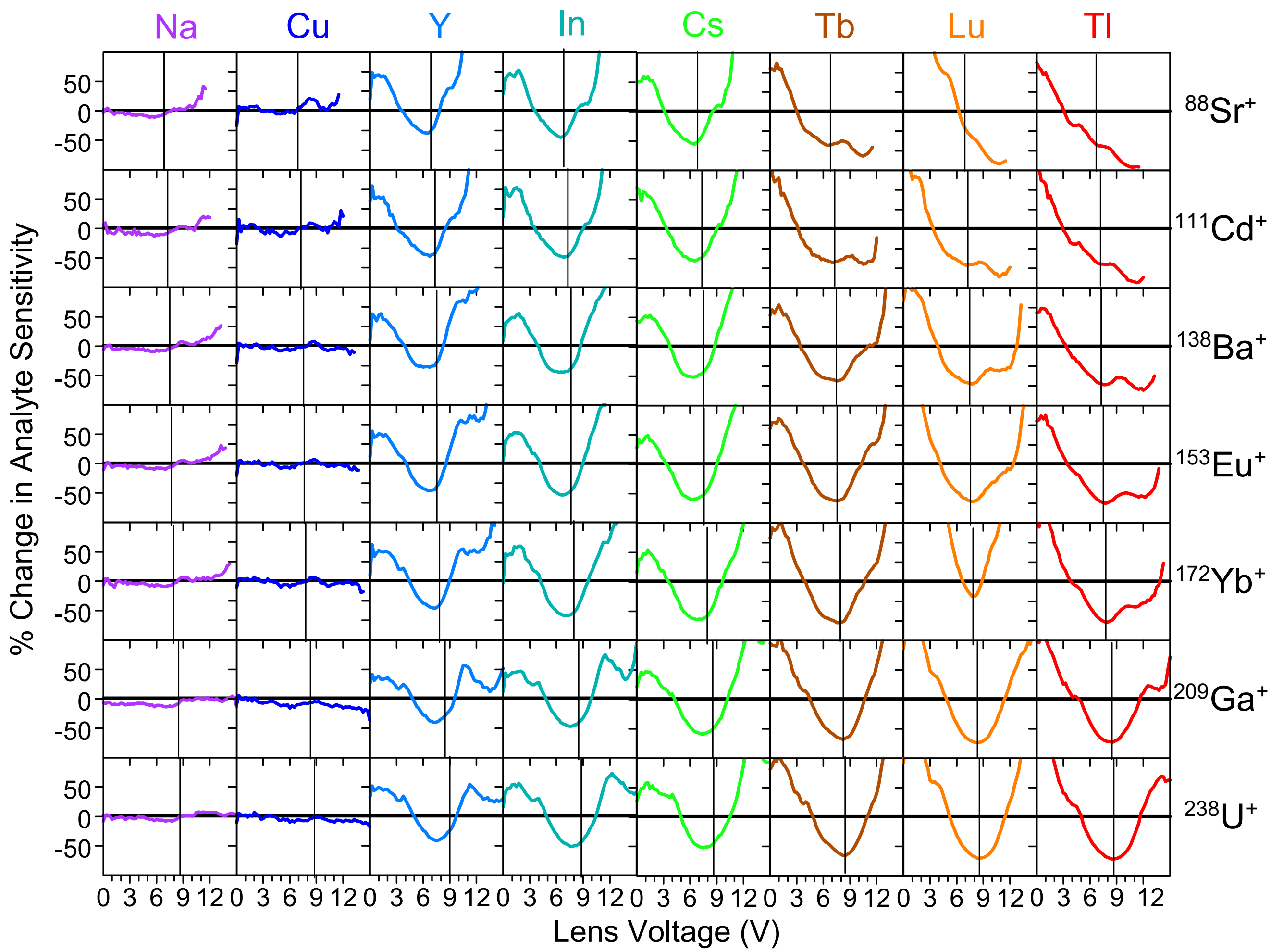

Figure S8. Matrix induced change in ICP-MS sensitivity as a function of lens voltage at the optimum nebulizer gas flow rate. Matrix elements listed on top. Analytes listed on the right.

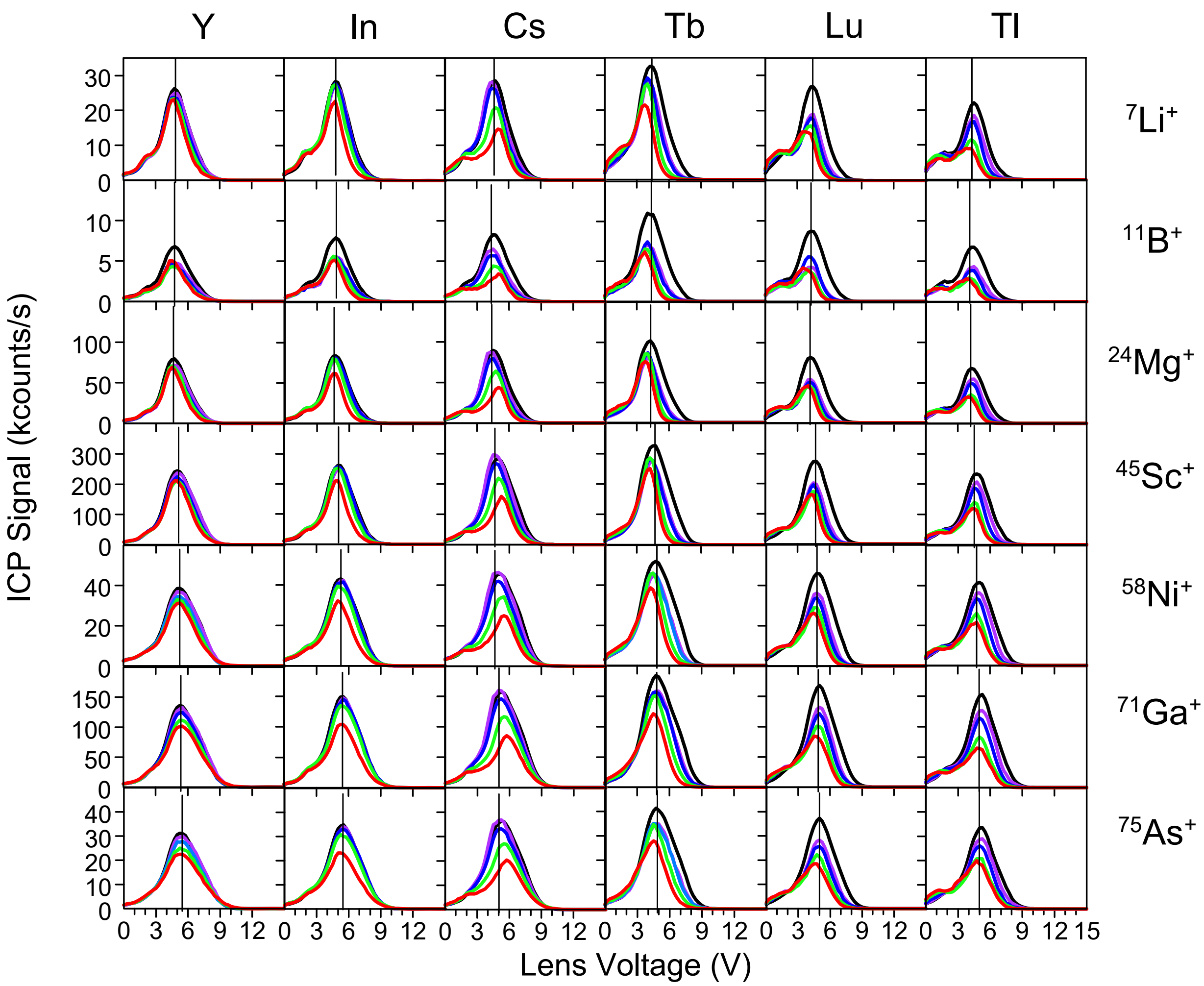

Figure S9. ICP-MS analyte ion signals as a function of lens voltage at the optimum nebulizer gas flow rate in the absence (——) or presence of 0.5 (——), 1.0 (——), 2.5 (——) and 5 (——) mM matrix element. Matrix elements listed on top. Analytes listed on the right.

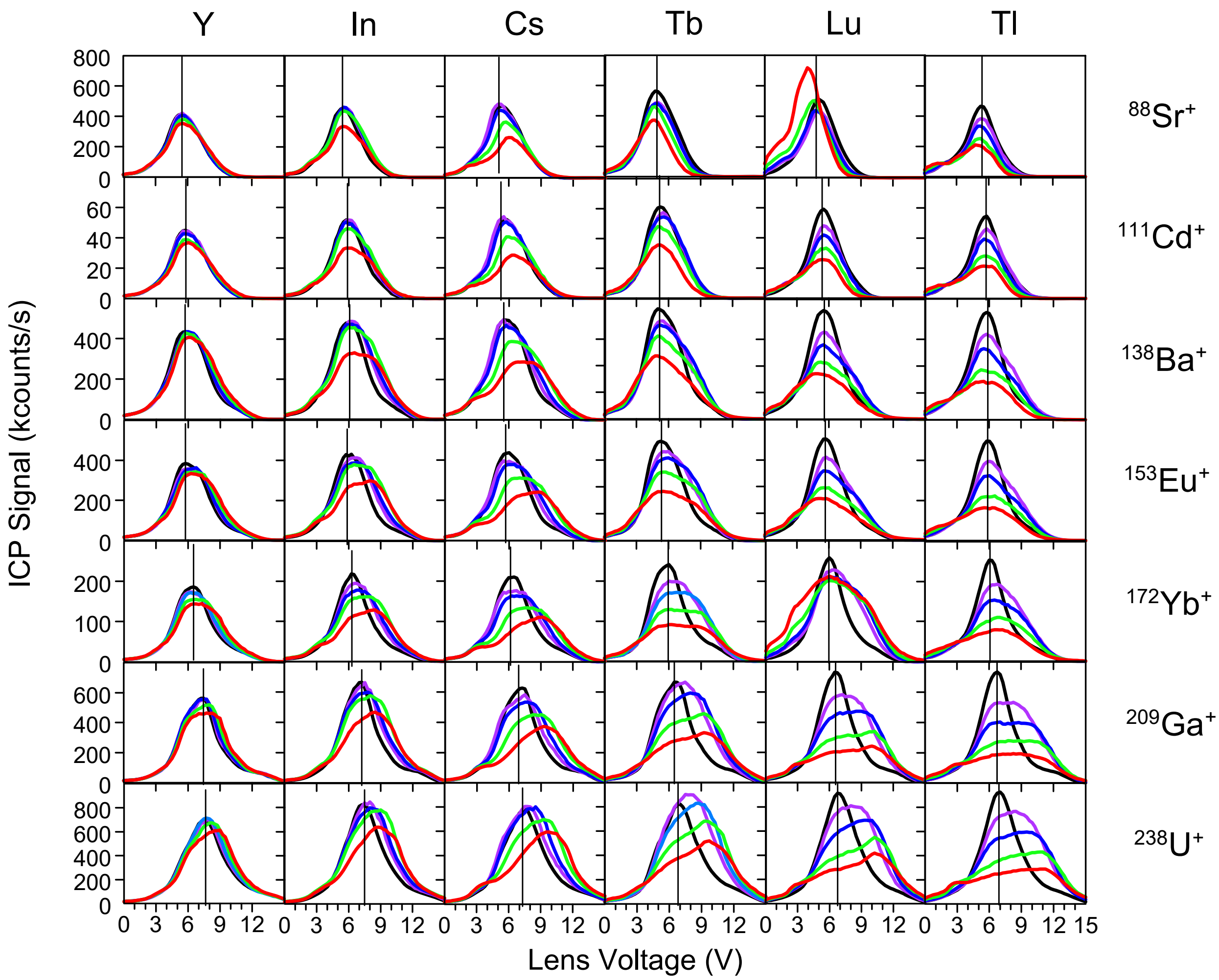

Figure S10. ICP-MS analyte ion signals as a function of lens voltage at the optimum nebulizer gas flow rate in the absence (——) or presence of 0.5 (——), 1.0 (——), 2.5 (——) and 5 (——) mM matrix element. Matrix elements listed on top. Analytes listed on the right. $^{88}Sr^{+}$ data with Lu matrix not shown due to spectral overlap (Lu^{2+}). $^{172}Yb^{+}$ data with Lu matrix not shown due to Yb contamination.

4. Matrix effects as a function of nebulizer gas flow rate and lens voltage

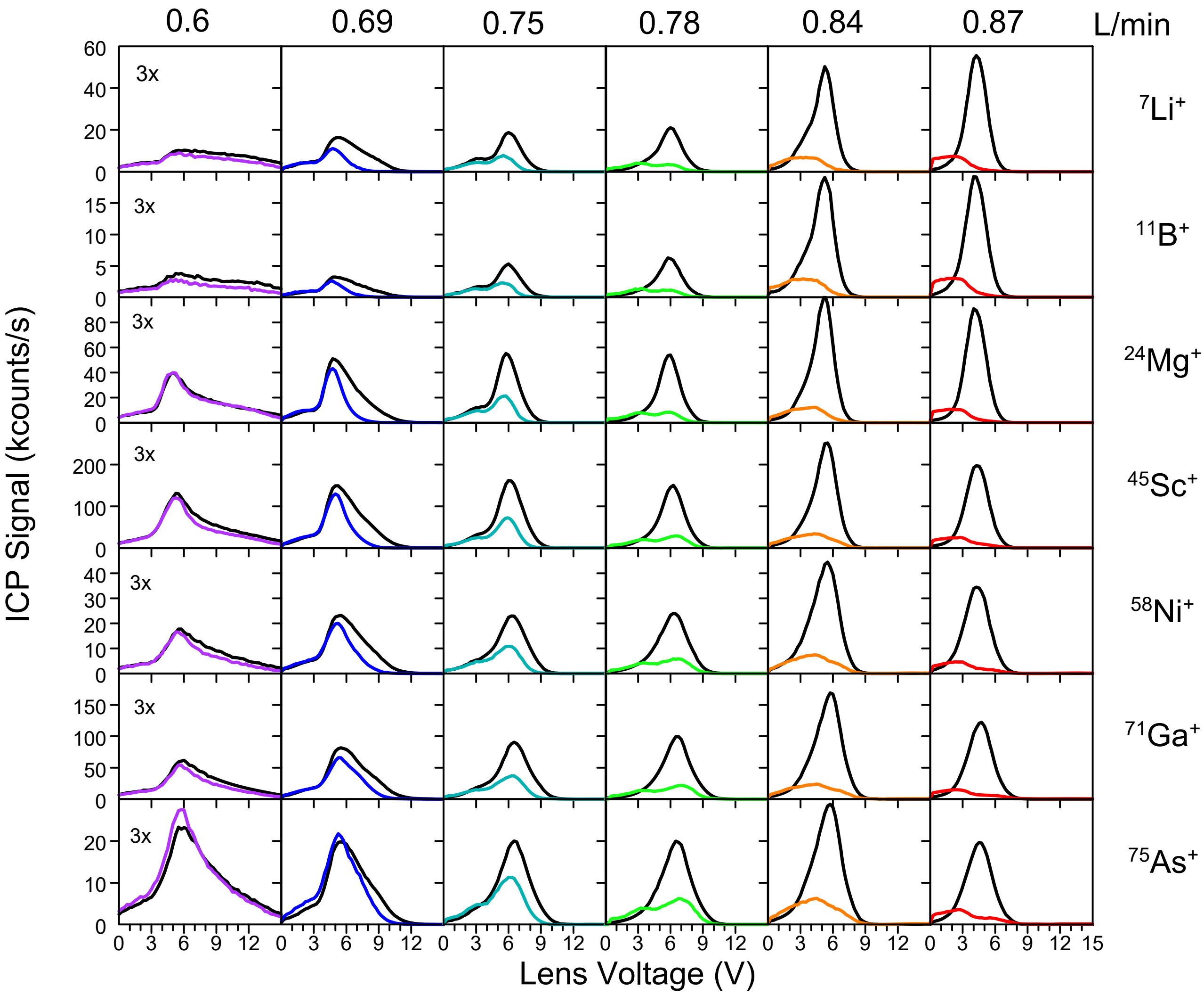

Figure S11. Analyte signals in the absence and presence of a 5 mM Tl at different nebulizer gas flow rates.

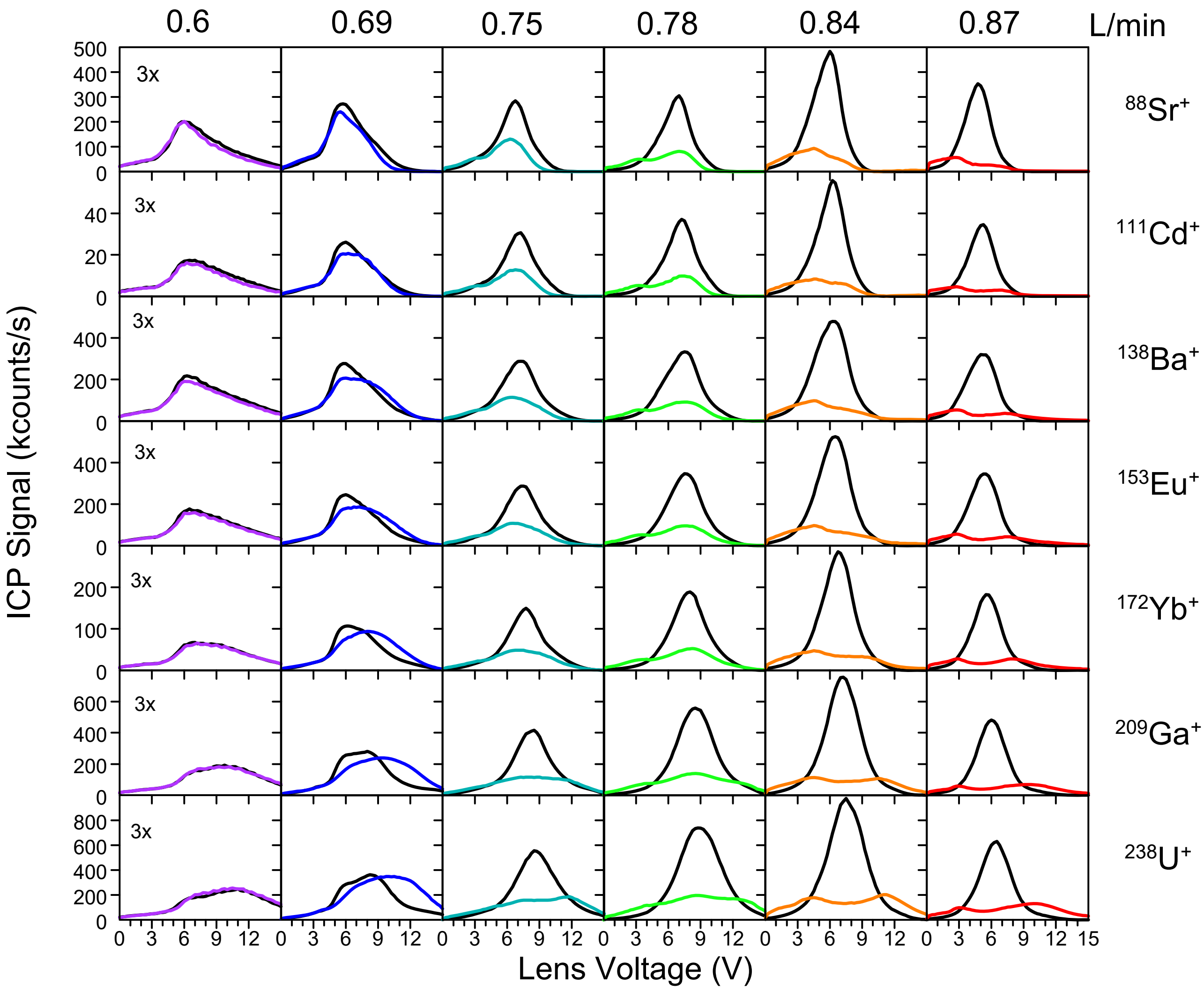

Figure S12. Analyte signals in the absence and presence of a 5 mM Tl at different nebulizer gas flow rates.

Table S1. UO^+/U^+ intensity ratio, As^+/Ga^+ intensity ratio and Ar^+ signal at different nebulizer gas flow rates.

Nebulizer gas flow rate (L/min)	UO^+/U^+	As^+/Ga^+	$^{38}Ar^+$ (c/s)	$^{40}Ar^+$ (Mc/s)*
0.6	3.5%	0.452	124,956	208
0.69	3.6%	0.248	160,600	268
0.75	4.8%	0.231	17,500	29
0.78	5.3%	0.232	8,070	13
0.84	7.8%	0.194	7,040	12
0.87	10.6%	0.187	9,210	15
0.9	28.8%	0.144	2,000	3

*Estimated assuming ^{38}Ar natural abundance of 0.06%, ^{40}Ar natural abundance of 99.6%
Data at each nebulizer gas flow rate were measured on different days
The As^+/Ga^+ signal intensity ratio increases with plasma temperature (As ionization energy is 9.8 eV. Ga ionization energy is 6.0 eV.)