Supplementary Information for Integration of Capillary Vibrating Sharp-Edge Spray Ionization as a Nebulization Device for ICP-MS

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Contents

Table 1: ICP-TOFMS and cVSSI tuning parameters.

Experiment	**Flow Rate Study** (Fig. 3)	**Input Study Device 1** (Fig. 4)	**Input Study Device 2** (Fig. S5)	**Calibration** (Fig. S6)	**Long Term Stability** (Fig. 5)
Nebulization Conditions					
F_{piezo} (kHz)	95.45	94.9-95.5	96.96	96.2	95.2
V_{piezo} (V_{p-p})	24.75	19.80-26.40	14.19/ 23.76	24.75	24.75
Sample Flow Rate (µL/min)	5-50	15	15	15	15
ICP-MS Conditions					
Carrier Gas Flow (L/min)	0.120	0.115	0.184	0.144	0.115
Curtain Gas Flow (L/min)	0.79	0.82	0.738	0.89	0.82
Auxiliary Flow (L/min)	1.03	1.03	1.19	1.03	1.03
Cool Flow (L/min)	13.8	13.8	14.7	13.8	13.8
Injector Diameter (mm)	1.5	1.5	1.5	1.5	1.5
Sampling Depth (mm)	5.90	6.06	6.32	6.04	6.06
Plasma Power (W)	1550	1550	1500	1550	1550
Collision Cell Gas H_2 (mL/min)	4.8	6.2	4.1	6.0	6.2
Notched m/z	17.2, 30.95, 37.89, 39	17.2, 30, 37.85, 39	18.4, 20.5,31 38	17.2, 31, 37.85, 39	17.2, 31, 37.85, 39
Mass-Spectral Averaging Period (ms / spectrum)	1.20	300	300	300	300

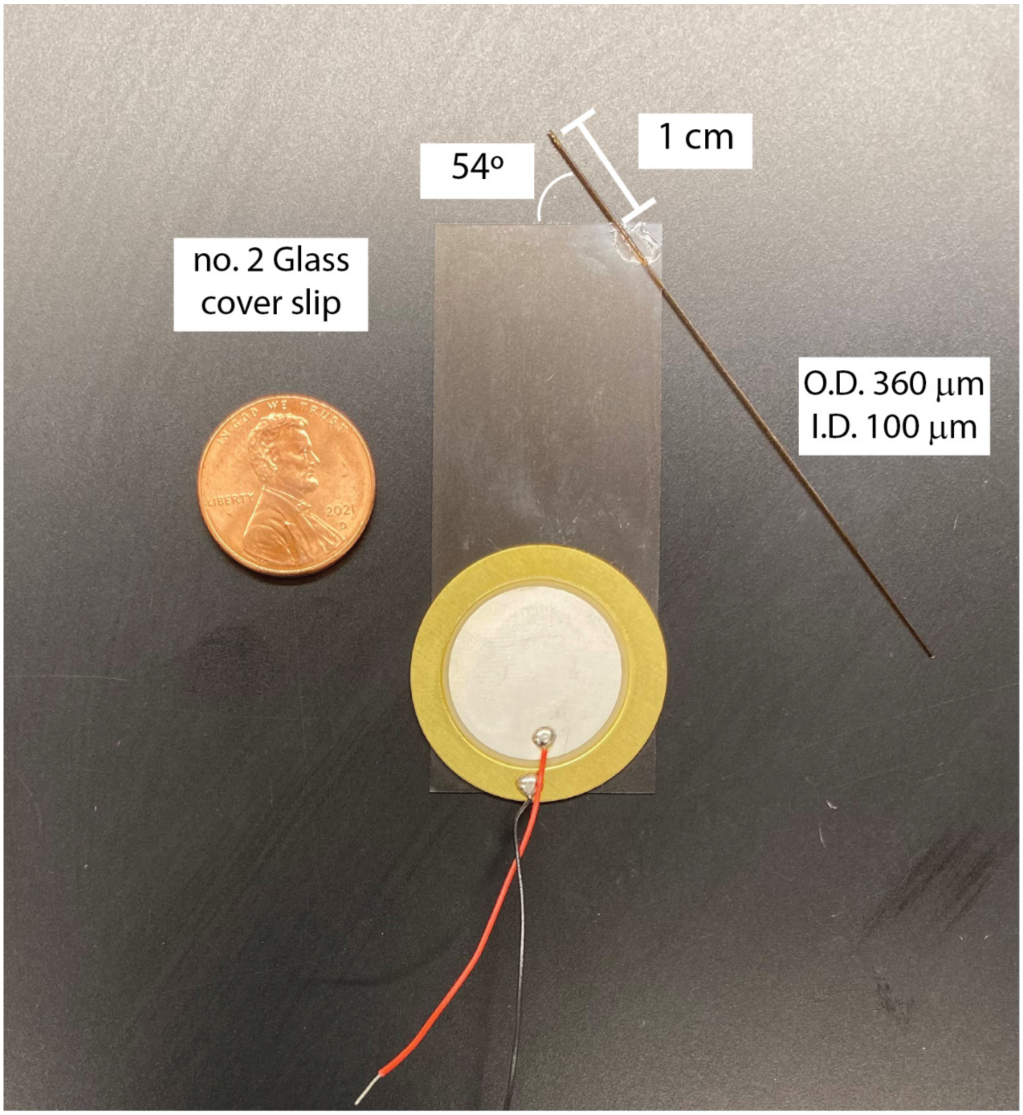

Figure S1: Image of cVSSI nebulization device with optimized geometry. USA penny is added for scale.

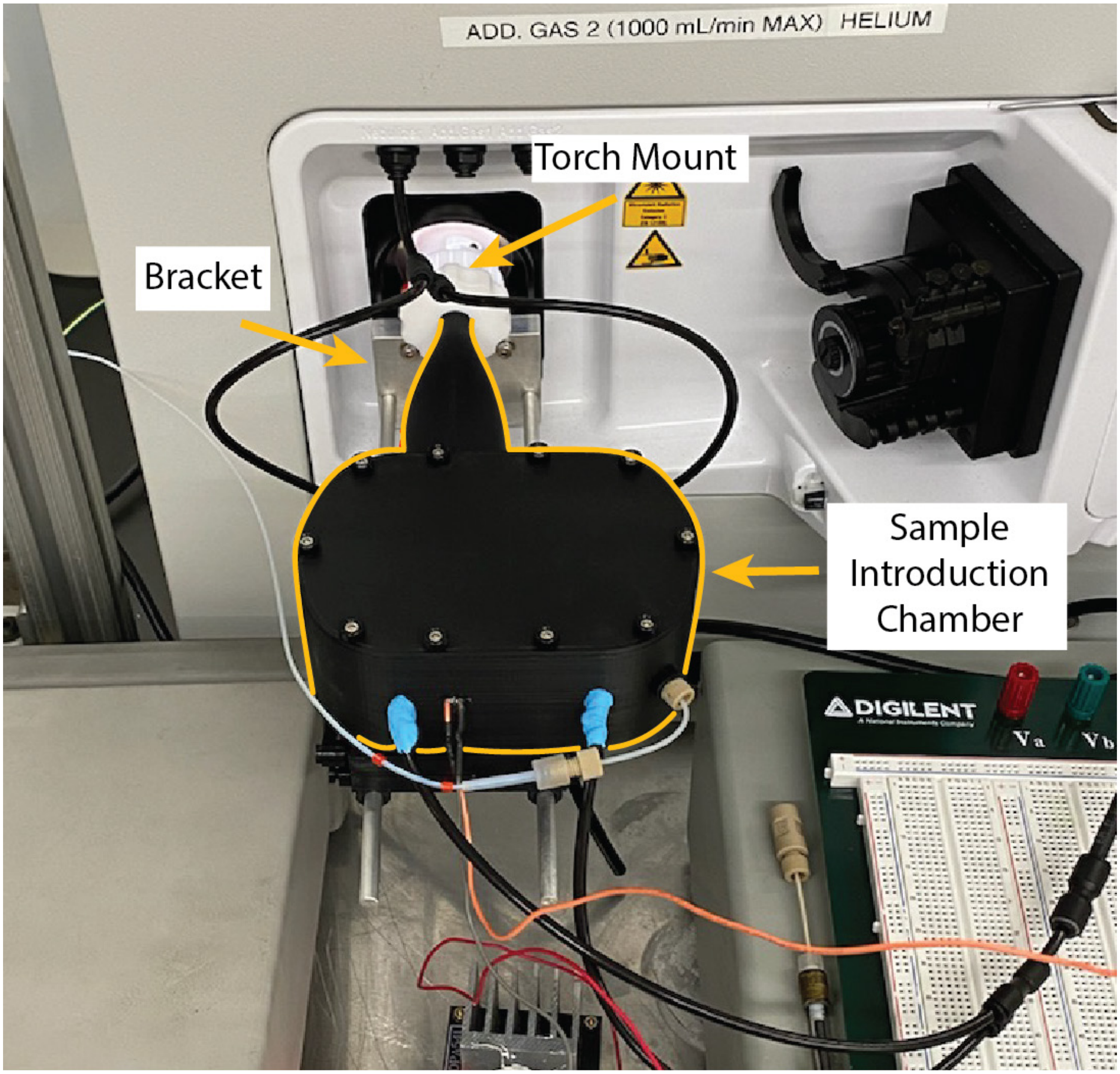

Figure S2: Image of cVSSI sample introduction system on ICP-TOFMS instrument.

Droplet Sizing Procedure

Droplets were sized using immersive sampling.[1] The sample solution was dyed with black water-based ink (Waterman Paris, Paris, France). A petri dish was filled with mineral spirits, and sample solution was nebulized at f_{piezo}=96.5 kHz and V_{piezo}= 24.75 V. The outlet of the cVSSI capillary was held about 1 cm above the surface of the immersion fluid (mineral spirits) to collect nebulized droplets. Pictures of the droplets were taken on a Nikon Multizoom AZ1000 bright field microscope (Nikon Instrument Inc., Melville, NY, USA) at 40x magnification. A USAF1951 positive test target (ThorLabs, Newton, NJ, USA) was used for microscope scale calibration, and droplet diameters were found using ImageJ (US National Institutes of Health, Bethesda, MD, USA) with the ParticleSizer plugin.[2] All droplets with aspect ratios of 1.1 and greater were excluded from sizing. This process was carried out for droplets collected at flow rates from 5-50 µL/min.

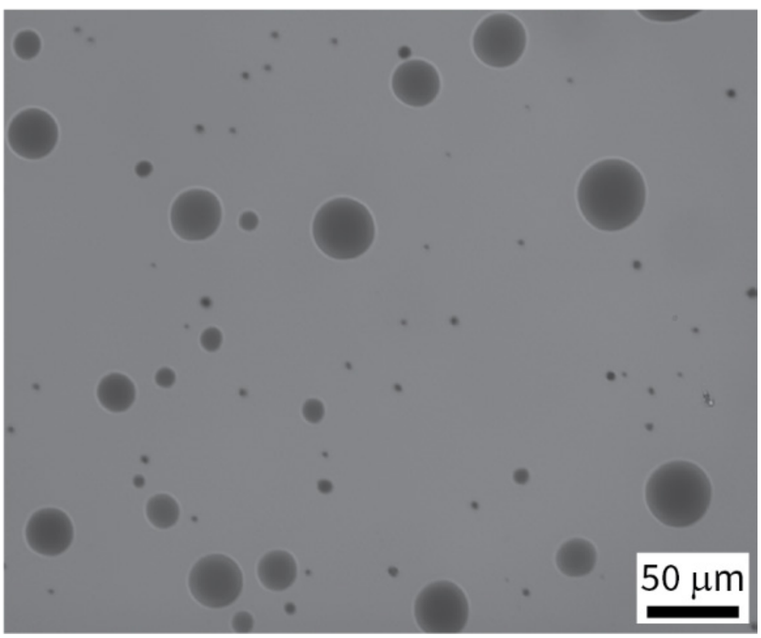

Figure S3: Microscope image (40x magnification) of droplets after immersive sampling. cVSSI conditions: liquid flow rate of 15 µL/min, f_{piezo}=96.5 kHz, and V_{piezo}= 24.75

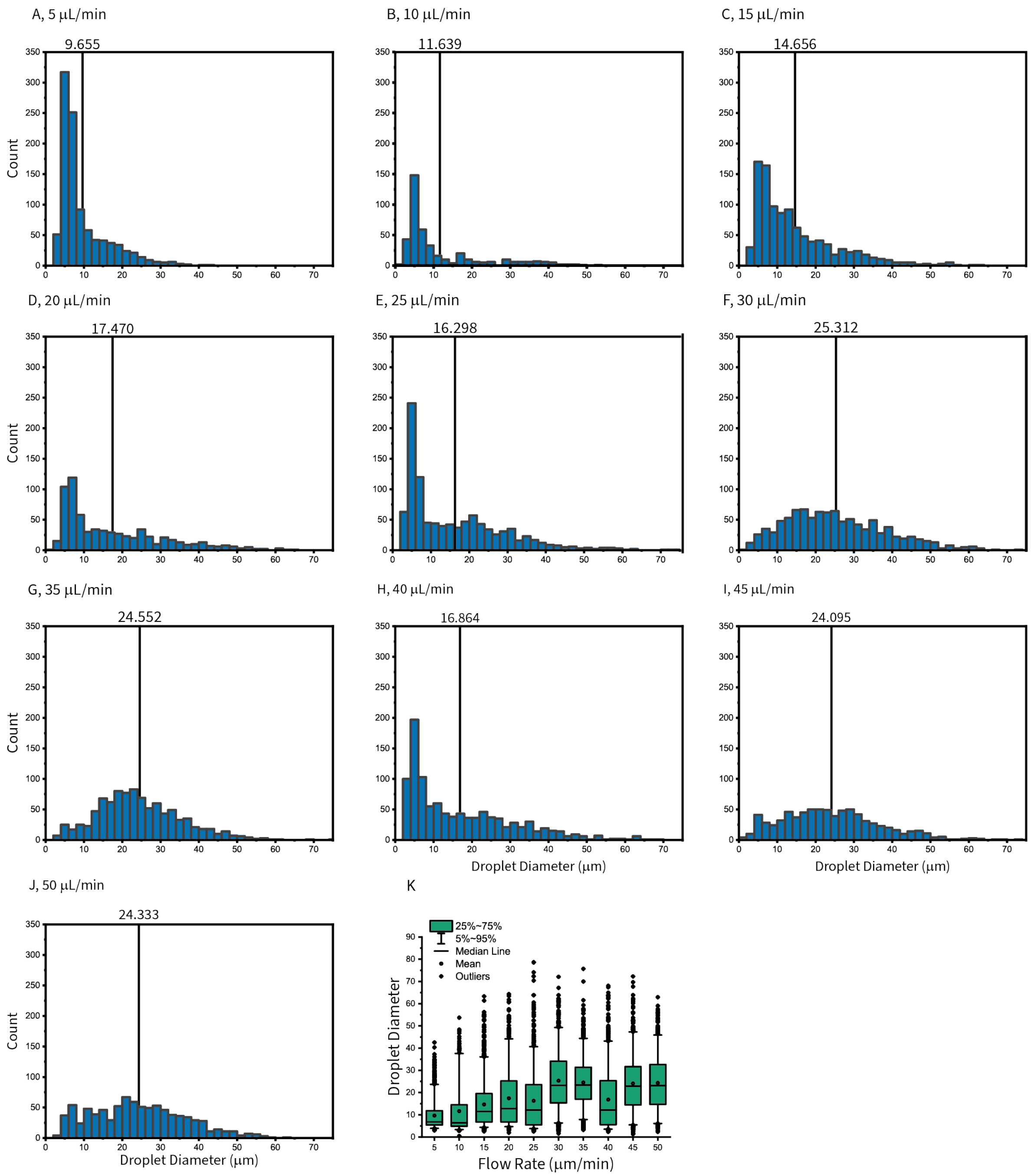

Figure S4: (A-J) Droplet size distributions across flow rates from 5-50 µL/min. Vertical lines indicate the mean droplet size. (K) Box and whisker plots comparing droplet size distributions at all flow rates.

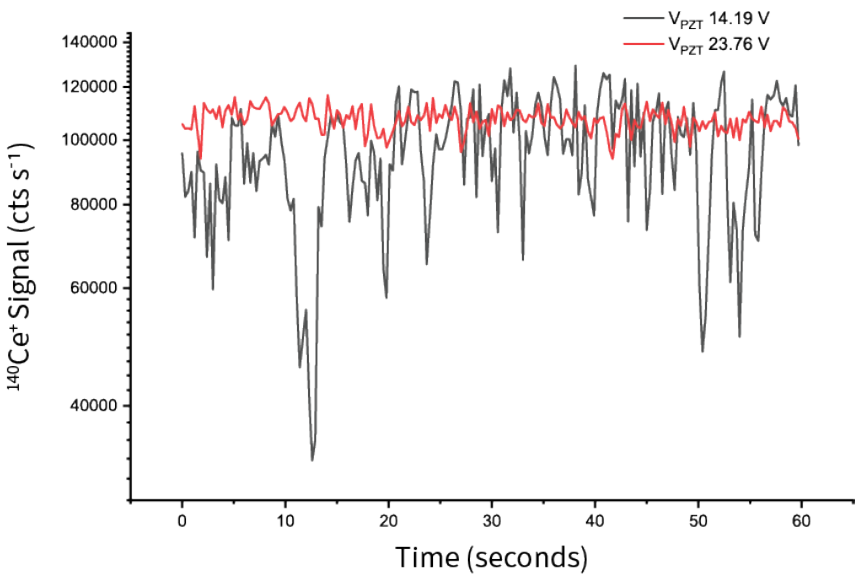

Figure S5: Time traces collected for $^{140}Ce^+$ at two different voltage inputs. The relative standard deviation (RSD) at V_{piezo}=14.19 V_{p-p} was 20.32% and at V_{piezo}=23.76 V_{p-p} the RSD measured was 4.02%. f_{piezo}=96.96 kHz for both measurements. Transport gases were also held constant for both acquisitions.

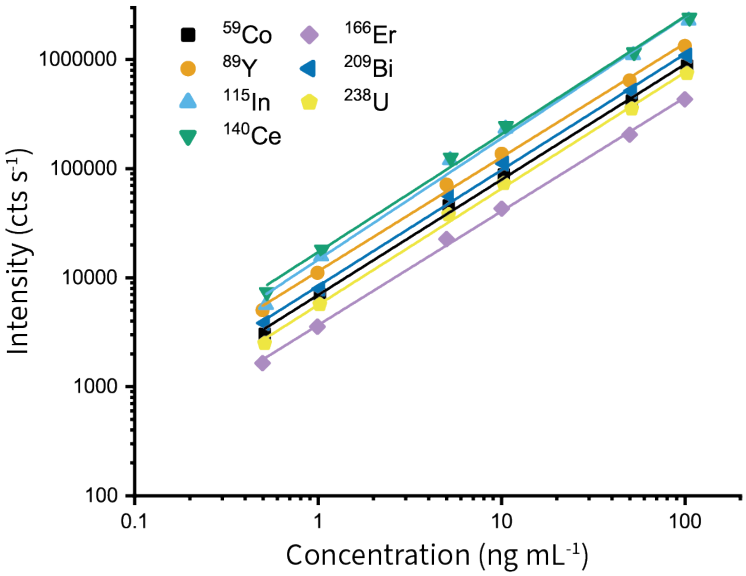

Figure S6: Multi-element calibration curve collected with cVSSI sample introduction system. Average RSD is 16%.

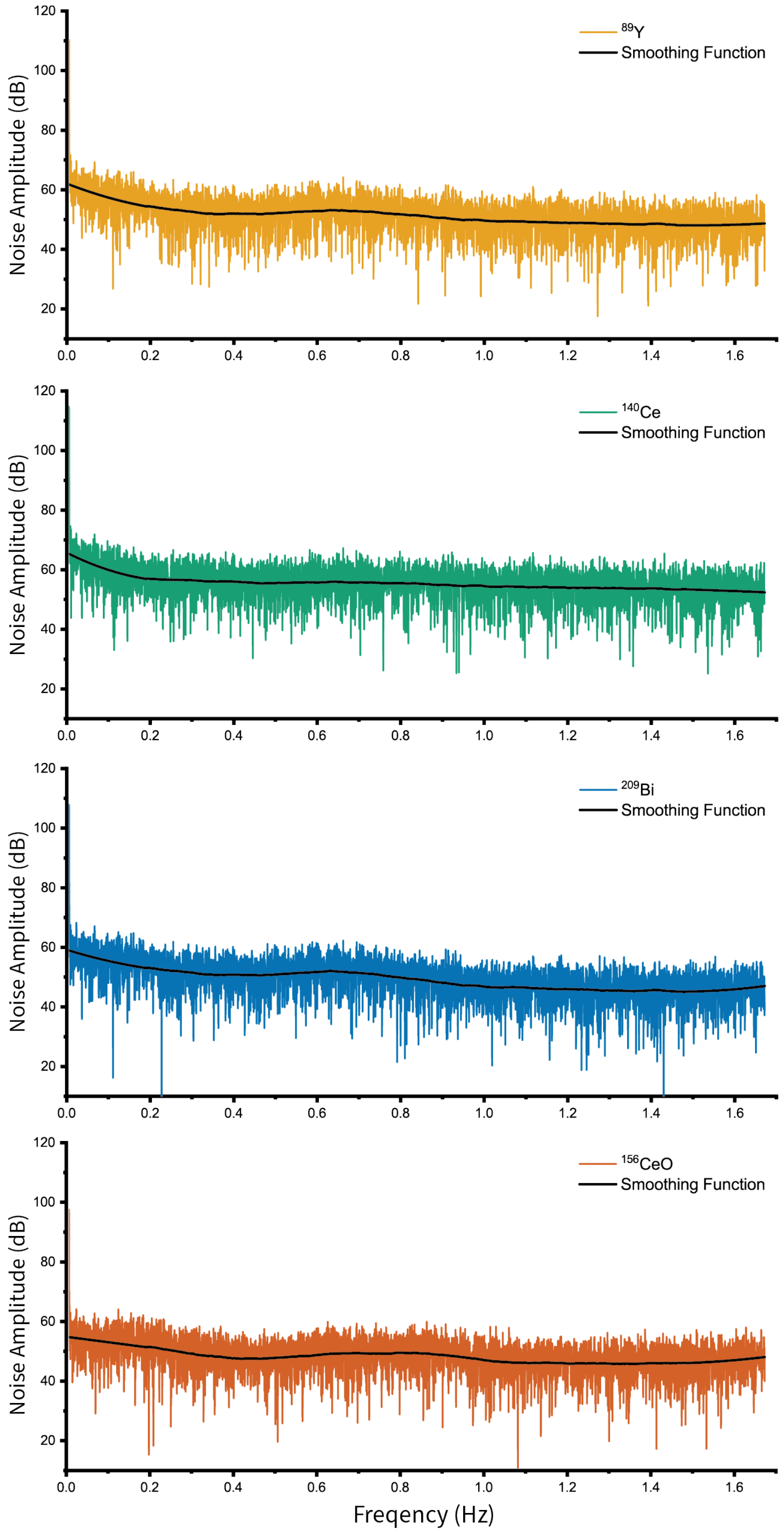

Figure S7: Noise power spectra created from long term stability acquisition. Savitzky-Golay smoothing function shown in black.

Citations

1. J. H. Rupe, *Symposium on Combustion and Flame, and Explosion Phenomena*, 1948, **3**, 680-694.
2. Thorsten Wagner. (2016). ij-particlesizer: ParticleSizer 1.0.1. Zenodo. 10.5281/zenodo.56457 (https://zenodo.org/badge/latestdoi/18649/thorstenwagner/ij-particlesizer)