

Table S1: Dissolved metal concentrations in runoff and rain in dissolved fraction (< 0.45 µm):

Date		Ag	As	Cd	Co	Cr	Cu	Mn	Mo	Ni	Pb	Se	Sb	Sr	Ti	Tl	V	Zn	Al	Ca	Fe
	QL	0,05	0,05	0,02	0,5	0,5	0,1	0,2	0,05	0,05	0,1	0,1	0,05	0,5	1	0,05	0,05	2	0,2	0,2	0,01
	Unit	µg/L																	mg/L		
	Method	ICP MS																	ICP OES		
24.07.2023		< LQ	2,74	0,04	0,6	5	50,3	35,8	5,92	3,68	0,5	0,2	5,04	34,9	3,7	< LQ	3,7	158,7			
02.08.2023		< LQ	3,1	0,03	< LQ	2,3	49,8	17,9	5,95	3,41	0,4	0,2	6,65	40,7	10,5	< LQ	3,17	93,5			
03.08.2023		< LQ	3,19	0,05	0,8	0,3	42	90,6	7,56	6,45	3,3	0,1	8,27	53,3	5	< LQ	2,2	261,6			
09.02.2024		< LQ	2,44	0,03	0,45	1,6	14,3	53,404	3,55	1,747	-0,1	< LQ	52,2	4,24	2,5	< LQ	1,2	53,211	< LQ	3,9	11,04
13.02.2024		< LQ	5,27	0,08	0,41	0,9	21,6	34,6	5,79	2,871	0,3	0,15	74,4	6,45	1,6	< LQ	2,3	62,757	< LQ	30,4	0,03
16.02.2024		< LQ	5,66	0,05	0,27	1,2	24,1	17,1	6,33	2,5	0,3	0,2	5,92	55,7	2,4	< LQ	2,5	38,9	< LQ	21,9	0,05
26.03.2024		< LQ	4,63	0,05	0,71	1,4	48,2	51	10,07	4,2	0,4	0,4	7,63	66,6	2,8	< LQ	2,14	115,3	< LQ	27,854	0,085
Rain.02.2024		< LQ	< LQ	< LQ	< LQ	< LQ	0,8	0,9	< LQ	< LQ	< LQ	< LQ	0,07	2,5	< LQ	< LQ	0,05	6,8	< LQ	0,429	< LQ

Detection of TiO₂:

The Ti was detected on O-mass shift mode using a combination of gas mode O₂ and H₂ to address potential interferences from ⁴⁸Ca: The first quadrupole (Q1) was set to pass only m/z 48, to allow ⁴⁸Ti⁺ (and any on-mass interferences (including ⁴⁸Ca) to enter the cell. The second quadrupole (Q2), which is located after the collision/reaction cell, was set to m/z 64 to pass the target product ion (⁴⁸Ti¹⁶O⁺) to the detector. Any potential native ion overlaps at m/z 64 (e.g. ⁶⁴Zn and ⁶⁴Ni) are rejected by Q1. Most of the primary interferences at m/z 48, such as ³²S¹⁶O⁺, ³⁰Si¹⁸O⁺, ³¹P¹⁶OH⁺, ¹²C¹⁸O₂⁺, can be avoided by measuring Ti as TiO⁺ in oxygen cell gas mode. However, some of the ⁴⁸Ca ions also react with oxygen to form ⁴⁸CaO⁺, which interferes with the ⁴⁸TiO⁺ product ions at m/z 64. Adding hydrogen gas can eliminate the Ca interference by converting CaO⁺ to CaOH⁺. TiO⁺ does not react in the same way with H₂ cell gas, so remains as the TiO⁺ product ion at m/z 64. Inter-isotope overlaps (such as ⁴⁶Ti¹⁸O and ⁴⁶Ca¹⁸O) can affect the ⁴⁸Ti¹⁶O measurement at m/z 64 when a single quadrupole or bandpass MS system is used. With MS/MS, however, these overlaps are avoided as the precursor ions (⁴⁶Ti and ⁴⁶Ca) are rejected by Q1 and so do not enter the cell to react.

Table S2: Threshold and ionic background (BG) for the characterization of Number, Mass and size of NPs in each sample

Elements	Date	D045		D[045µm-5KDa]	
		Threshold	BG	Threshold	BG
⁴⁸ Ti	24.07.2023	371.9	46.65	386.5	85.72
	02.08.2023	932.9	120.5	1028	155.8
	03.08.2023	706.6	116.6	936.9	172.6
	09.02.2024	527.7	60.8	674.2	66.68
	13.02.2024	740.4	74.16	724.1	87.94
	16.02.2024	428	64.68	491	77
	26.03.2024	48	18.39	165	32
	Rain.02.2024	11	0.26	13	0.37
⁵⁸ Fe	24.07.2023	30.15	11.07	59.13	28.02
	02.08.2023	31.9	12.18	43.12	17.52
	03.08.2023	34.06	13.33	65.68	28.84
⁵⁶ Fe	09.02.2024	1754	607.86	1721	660
	13.02.2024	2539.5	569.83	2397	699.26
	16.02.2024	1560	711.86	1758	836.33
	26.03.2024	464	194.63	605	284
	Rain.02.2024	14	1.22	21	4.50
⁶³ Cu	24.07.2023	287.7	175.8	927.2	599.4
	02.08.2023	288.2	180	452.8	289.5
	03.08.2023	237.2	139.1	608.7	392.8
	09.02.2024	131.7	68.72	158.80	85.88
	13.02.2024	157.7	87.58	262.90	153.40
	16.02.2024	159.8	90.19	232.50	132.67

	26.03.2024	177	96.48	198.60	122.60
	Rain.02.2024	16	2.38	18.00	3.45
⁶⁴ Zn	24.07.2023	100.8	36.37	230.7	131.6
	02.08.2023	74.03	36.29	94.28	49.32
	03.08.2023	112.5	54.94	189.4	114
	09.02.2024	72.52	34.75	74.23	35.83
	13.02.2024	89.98	44.58	134.00	72.05
	16.02.2024	63.98	30.69	76.73	38.75
	26.03.2024	77.00	40.45	87.00	46.57
	Rain.02.2024	25.00	7.10	30.00	10.35

Table S3 : Table of number concentration and mass of elements for the comparison between sample preparation:

Element	Date	Applied Threshold	particles/L (D045)	particles/L (D[045 μ m - 5KDa])	SD D045 (partciles/L)	SD D[045 μ M-5KDa] (particles/L)	Mass Median corrected D045	Median Mass (ag) corrected in D[045-5KDa]	SD D045 (ag)	SD D[045 μ M-5KDa] (ag)
48 Ti	24.07.2023	386,5	5,94E+08	1,97E+08			1322	1272		
	02.08.2023	1028	5,65E+08	3,15E+08			3483	3401		
	03.08.2023	936,9	3,07E+08	7,78E+07			3228	3155		
	09.02.2024	674,2	1,16E+08	8,65E+07	3,65E+06	2,29E+06	5407	5561	187	83
	13.02.2024	740,4	1,43E+08	7,04E+07	2,93E+06	2,42E+06	6641	6326	191	84
	16.02.2024	490,7	1,32E+08	8,65E+07	4,04E+06	4,36E+06	3918	3991	70	108
	26.03.2024	165	1,42E+08	1,80E+08	2,22E+07	3,40E+06	2487	1945	63	62
	Rain.02.2024	13	3,05E+07	5,08E+07	6,21E+06	4,16E+06	161	167	10	44
58Fe	24.07.2023	59,13	2,53E+07	6,36E+06			20918	22940		
	02.08.2023	43,12	9,34E+06	1,63E+07			43582	43440		
	03.08.2023	65,68	3,30E+06	5,31E+06			77305	107518		
56Fe	09.02.2024	1754	1,56E+08	1,32E+08	2,91E+06	4,36E+06	5701	5457	126	69
	13.02.2024	2539,5	1,06E+08	4,89E+07	3,89E+06	1,90E+06	12167	11218	208	337
	16.02.2024	1758	8,27E+07	8,77E+07	6,55E+05	4,41E+06	5679	5131	79	39
	26.03.2024	605	6,76E+07	1,33E+08	8,21E+06	1,04E+07	4349	3611	40	15
	Rain.02.2024	21	4,30E+08	6,48E+08	1,46E+07	1,89E+07	96	77	2	2

Element	Date	Applied Threshold	particles/L (D045)	particles/L (D[045 µm - 5KDa])	SD D045 (partciles/L)	SD D[045 µM-5KDa] (particles/L)	Mass Median corrected D045	Median Mass (ag) corrected in D[045-5KDa]	SD D045 (ag)	SD D[045 µM-5KDa] (ag)
63Cu	24.07.2023	927,2	1,65E+06	1,05E+08			2278	1122		
	02.08.2023	452,8	2,75E+06	1,13E+08			1137	554		
	03.08.2023	608,7	2,20E+06	5,52E+07			2134	700		
	09.02.2024	158,8	5,05E+06	1,46E+07	1,15E+06	4,02E+06	1220	514	38	38
	13.02.2024	262,9	2,88E+06	6,81E+06	7,69E+04	1,89E+06	2410	927	328	31
	16.02.2024	232,5	1,56E+06	1,27E+07	1,73E+05	4,39E+06	1938	824	210	59
	26.03.2024	198,6	1,40E+06	1,94E+06	4,62E+05	1,03E+06	2679	1570	302	220
	Rain.02.2024	18	1,12E+06	2,59E+06	0,00E+00	5,39E+05	97	90	10	10
64Zn	24.07.2023	230,7	9,62E+07	4,67E+07			3451	3437		
	02.08.2023	94,28	2,69E+07	2,96E+07			966	750		
	03.08.2023	189,4	3,85E+06	7,97E+06			2809	1412		
	09.02.2024	74,23	8,31E+06	7,97E+06	1,72E+06	3,68E+05	1564	1589	72	21
	13.02.2024	134	4,61E+06	4,02E+06	3,84E+05	1,09E+06	3395	2452	53	103
	16.02.2024	76,73	3,98E+06	4,36E+06	7,92E+05	1,29E+06	1928	1466	102	71
	26.03.2024	87	9,31E+05	2,62E+06	2,01E+05	8,22E+05	5931	4057	1221	424
	Rain.02.2024	30	0,00E+00	2,12E+06	0,00E+00	2,31E+06	0	73	0	31

Table S4: Elemental ratio: Concentration of Ti and V elements on 0.45 µm filter after 8-µm filtration)

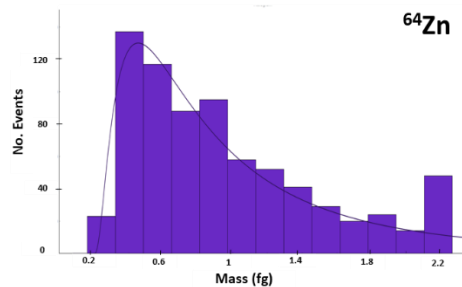
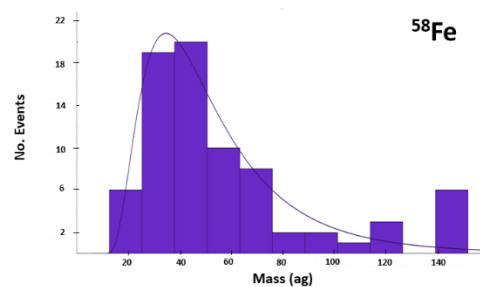
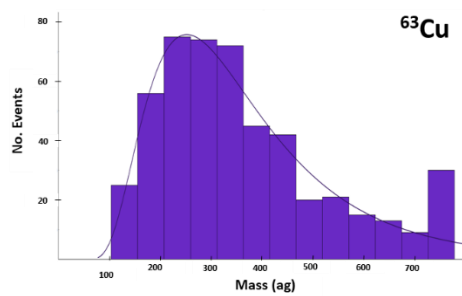
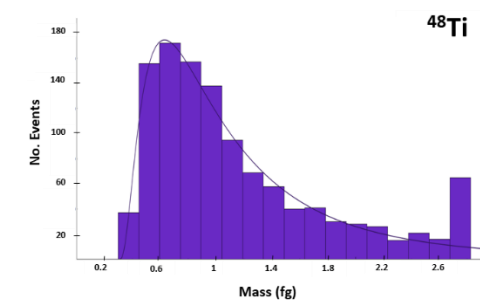
Date	Ti µg/L	V µg/L	(Ti/V) sample
24.07.2023	0,5	0,03	16,67
02.08.2023	21	0,41	51,22
03.08.2023	22,8	0,52	43,85
09.02.2024	8,5	0,191	44,50
13.02.2024	194,9	4,426	44,04
16.02.2024	66,8	2,18	30,64
26.03.2024	137,5	2,89	47,58
Rain.02.2024	4,32	0,05	83,72

Upper continental crust (UCC):

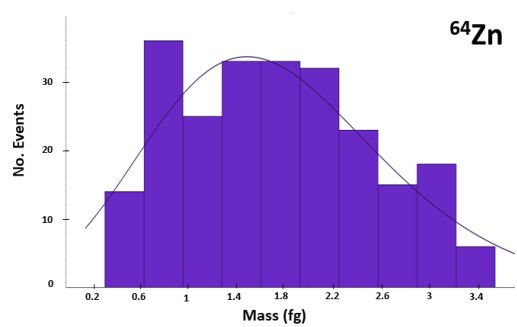
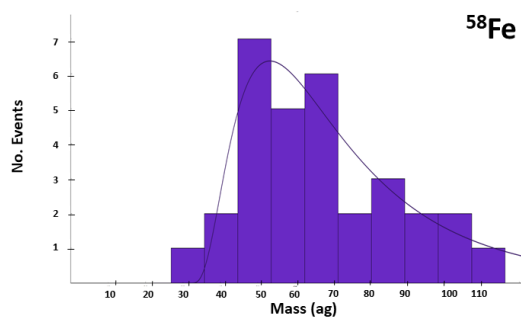
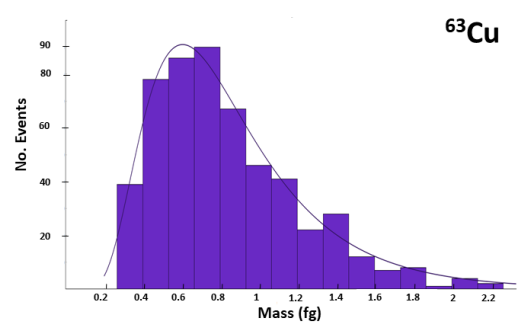
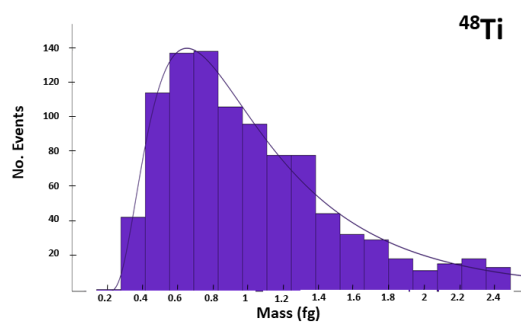
Study : Taylor and McLennan 2001	Ti (wt%)	V (ppm)	Ti/V
	0,39	110	35,455

MASS DISTRIBUTION:

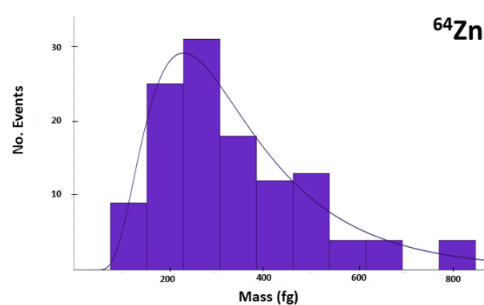
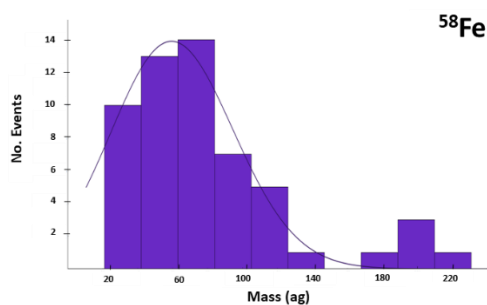
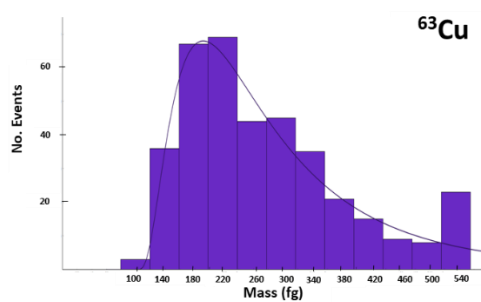
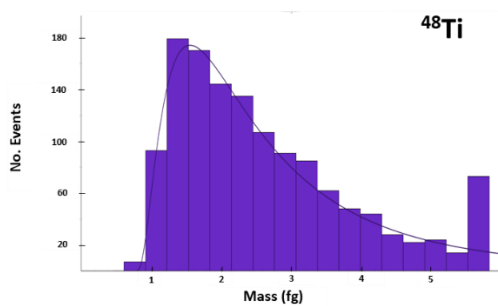
24-07-2023 D045



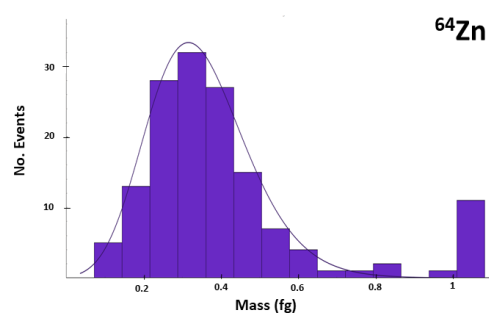
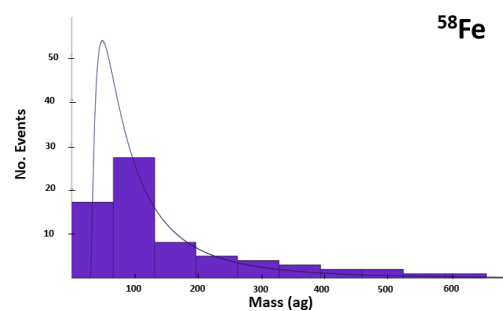
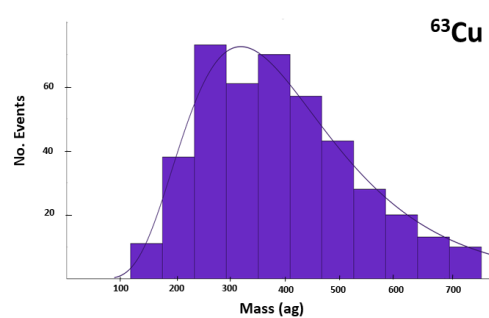
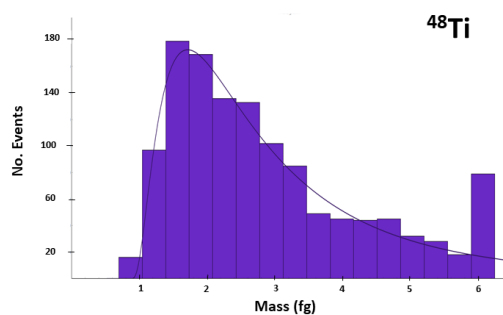
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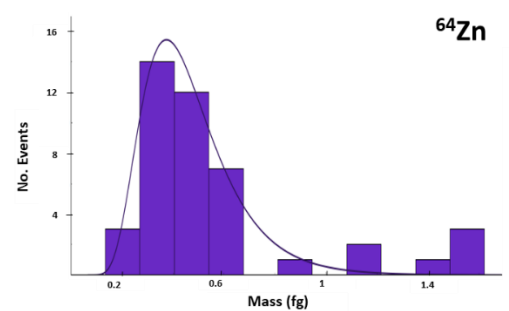
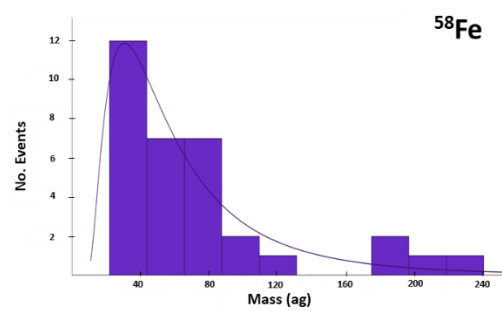
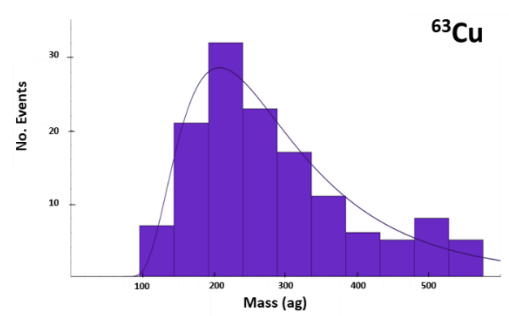
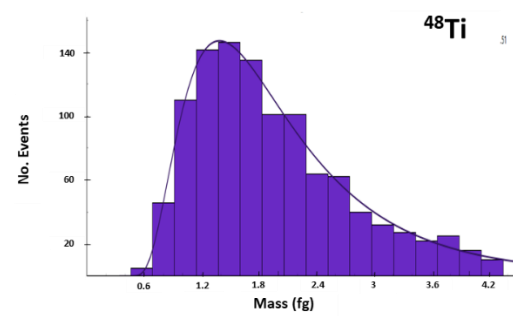
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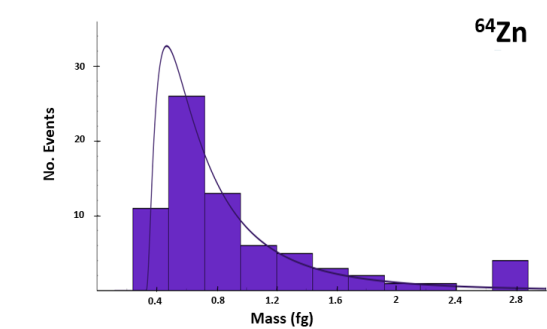
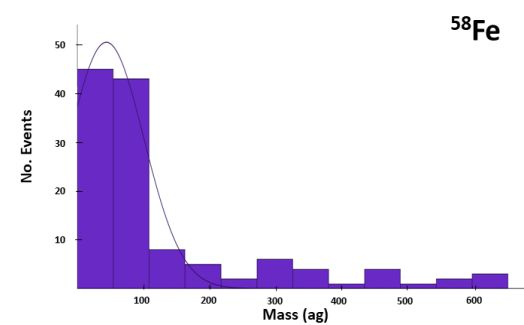
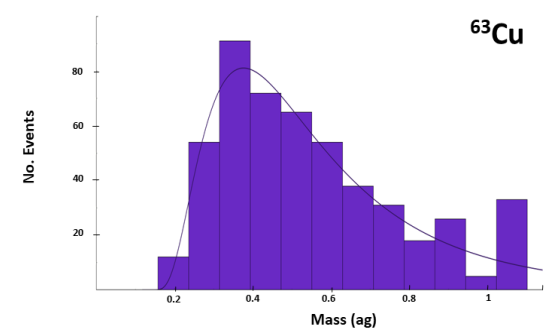
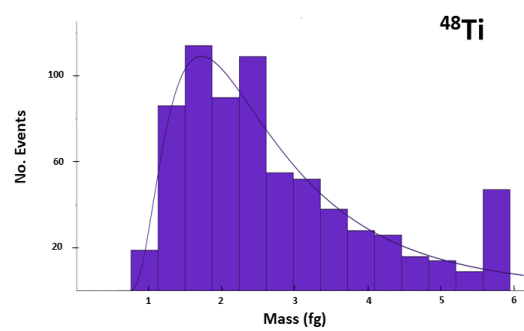
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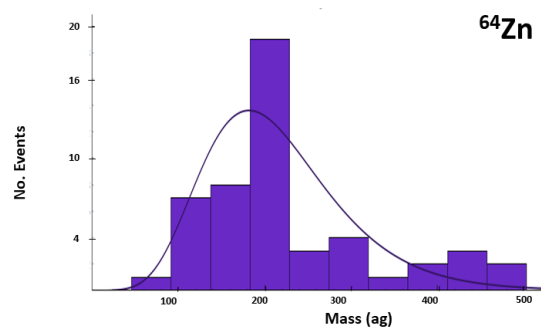
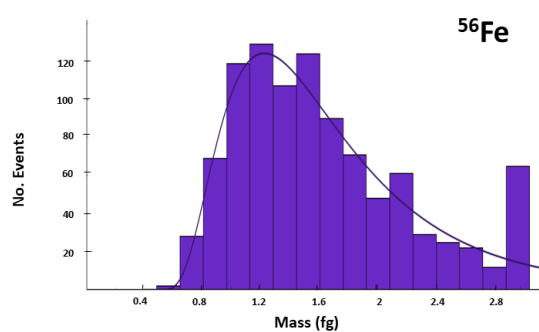
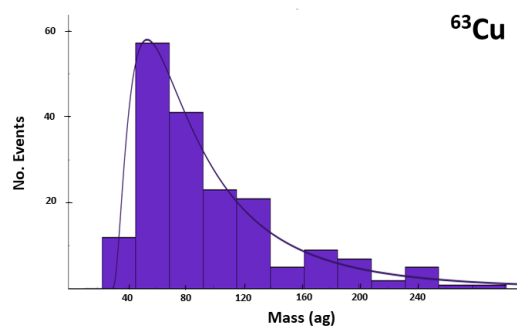
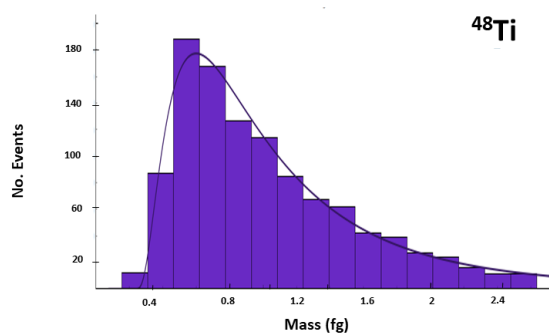
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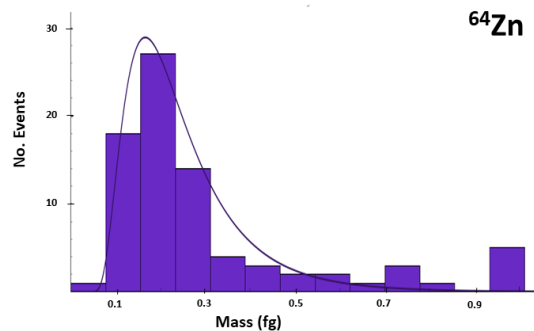
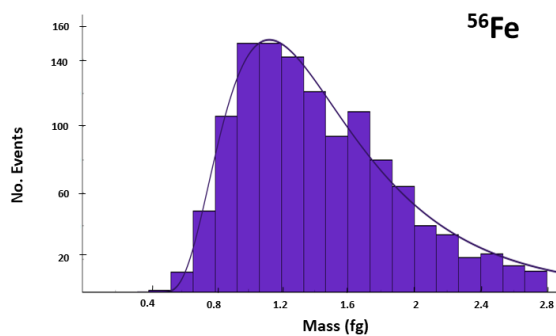
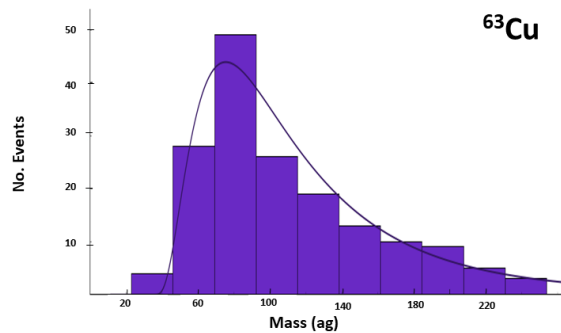
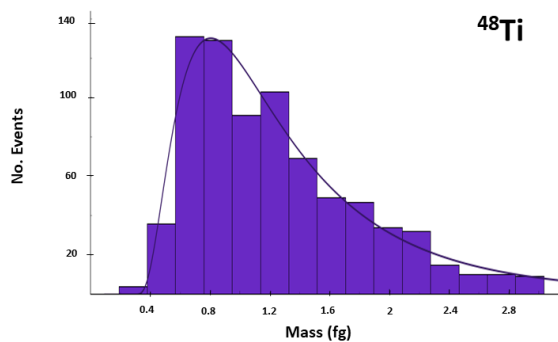
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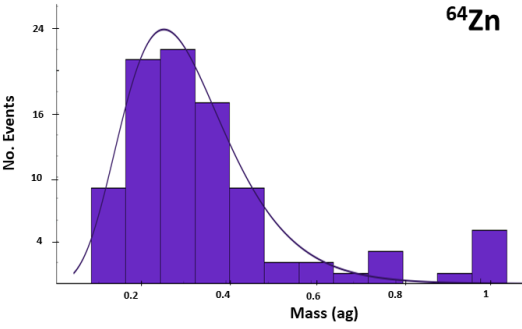
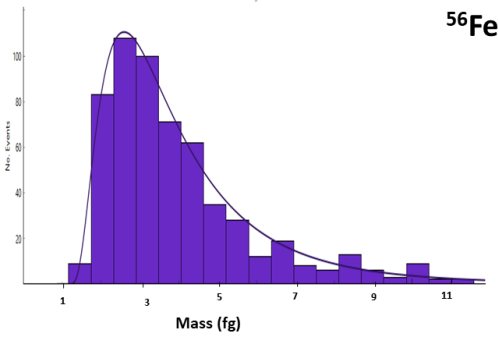
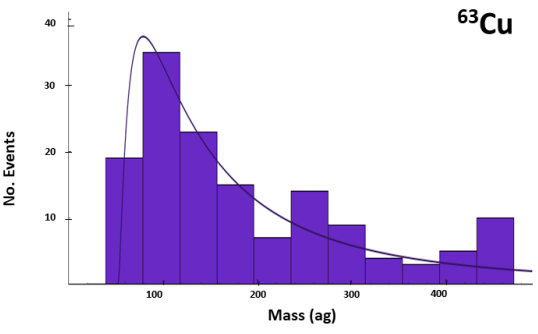
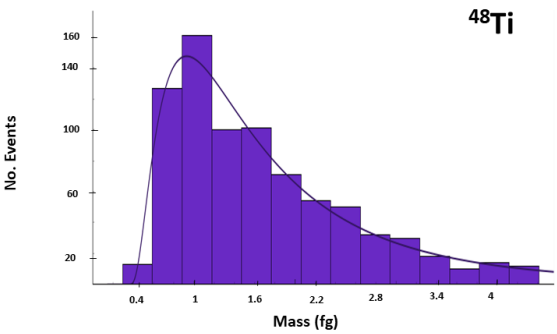
09-02-2024 D045



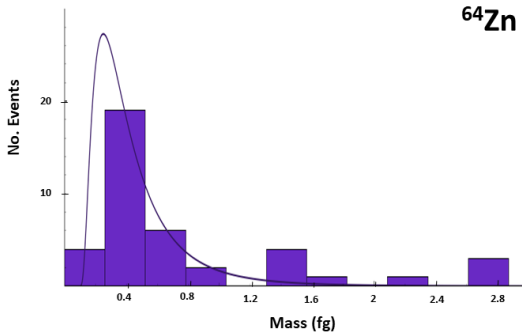
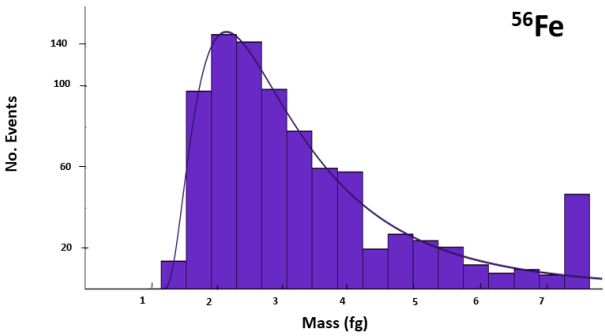
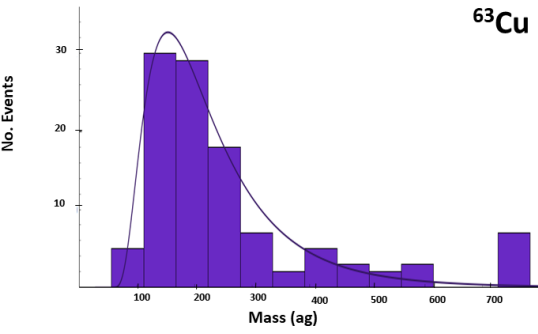
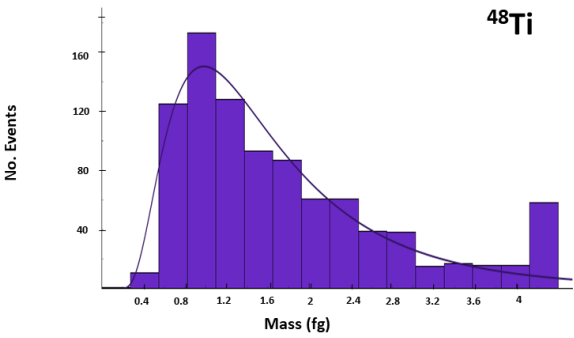
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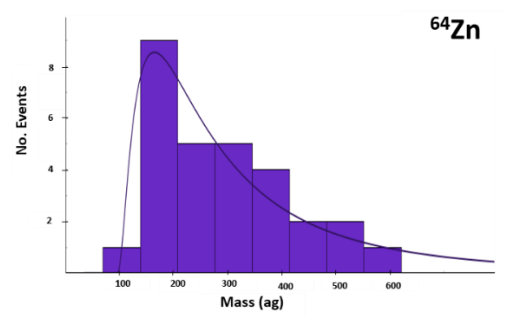
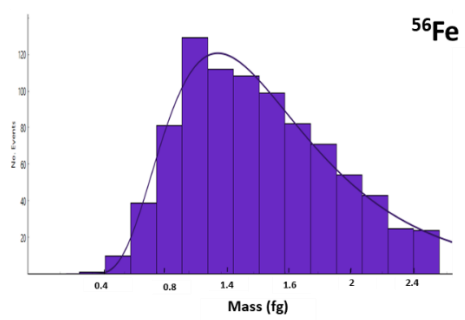
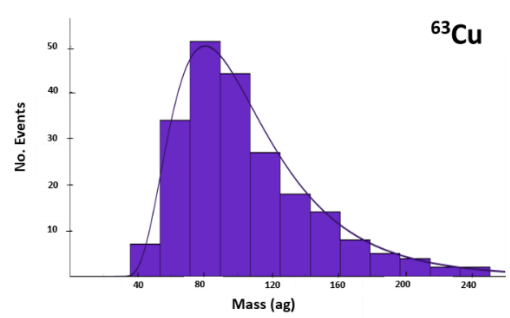
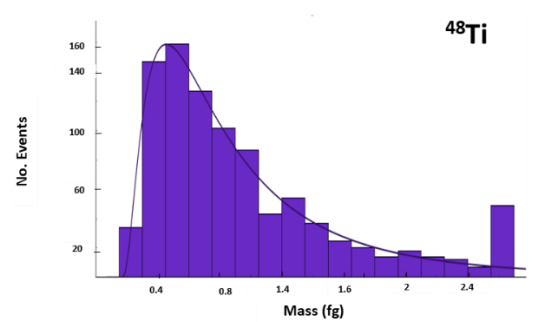
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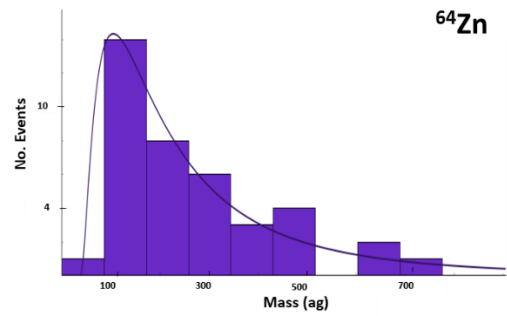
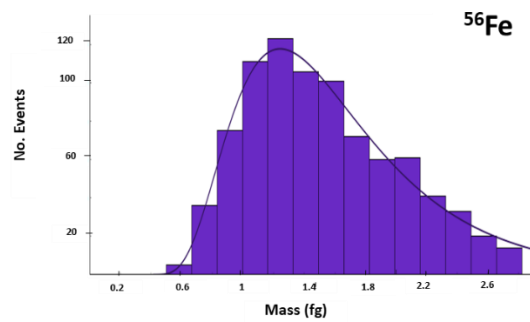
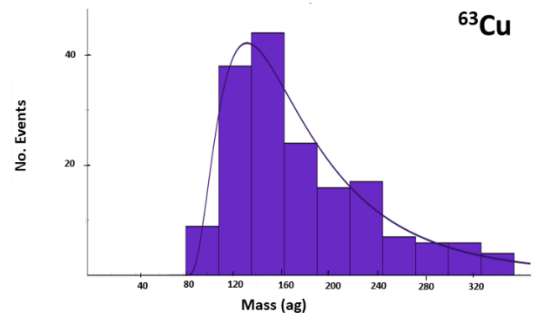
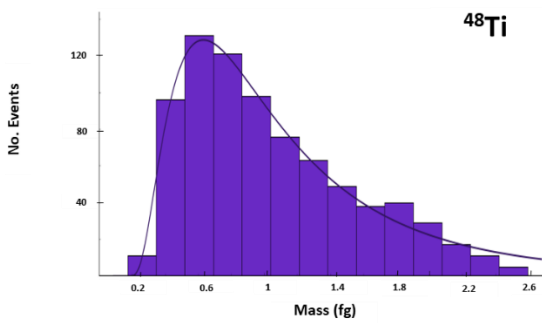
13-02-2024 D045-5kDa



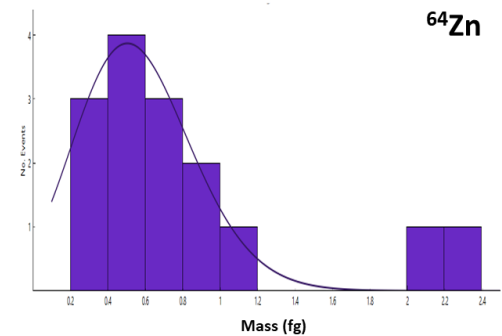
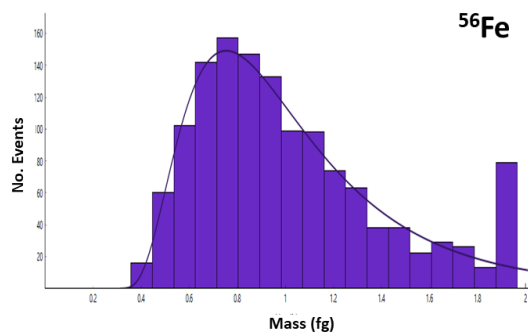
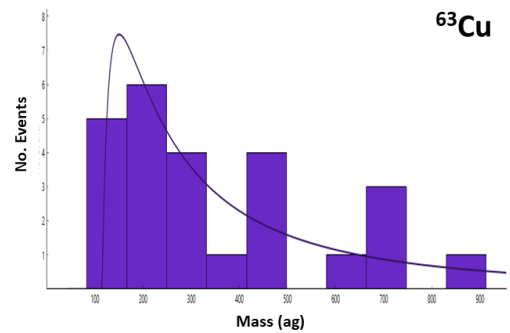
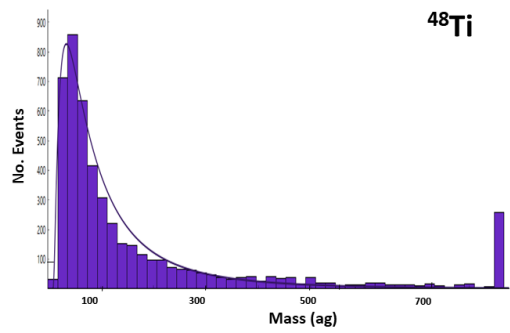
16-02-2024 D045



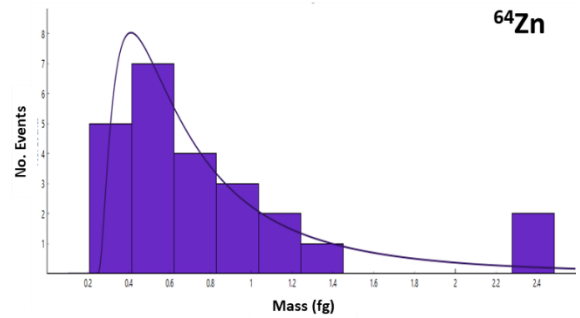
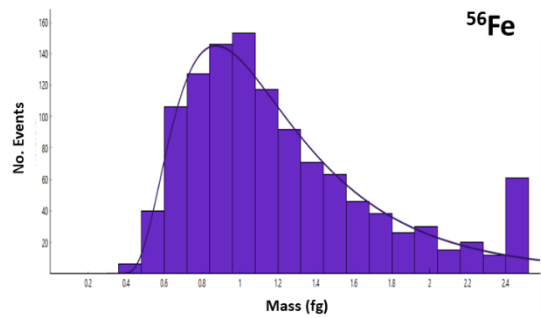
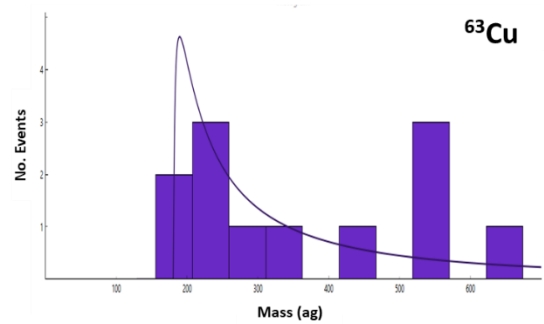
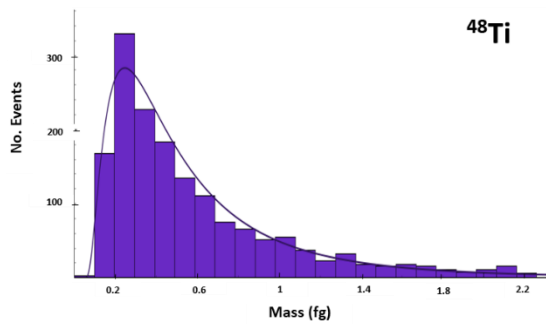
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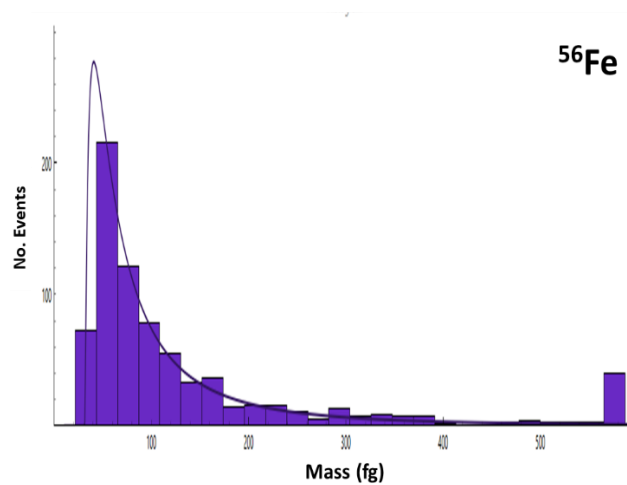
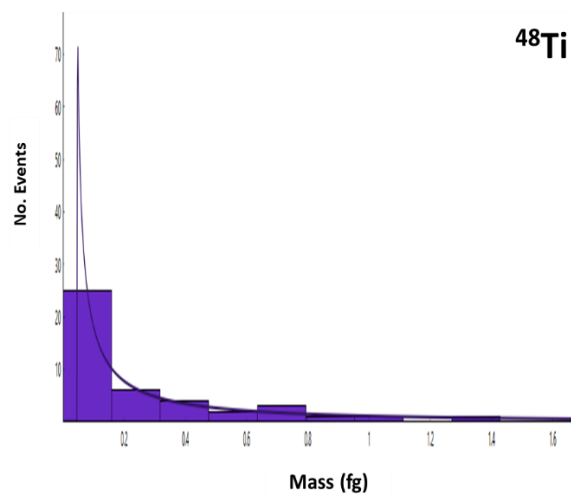
26-03-2024 D045



26-03-2024 D045-5kDa



Rain.02.24 D045



Rain.02.24 D045-5kDa

