

1 Direct analysis of nanoparticles in organic solvents by ICPMS with microdroplet injection

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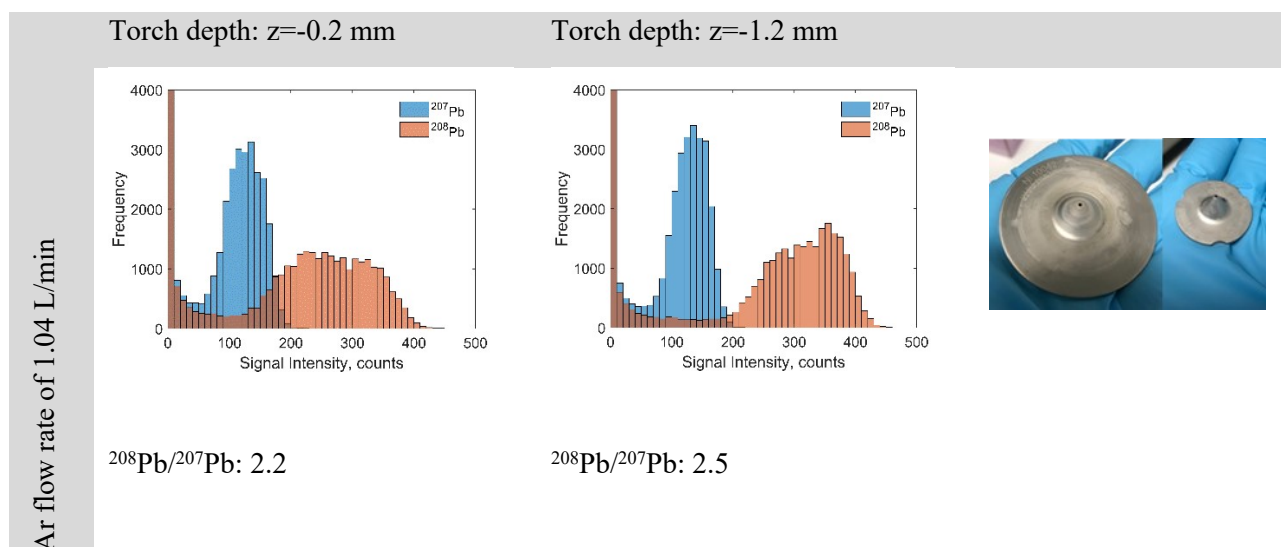
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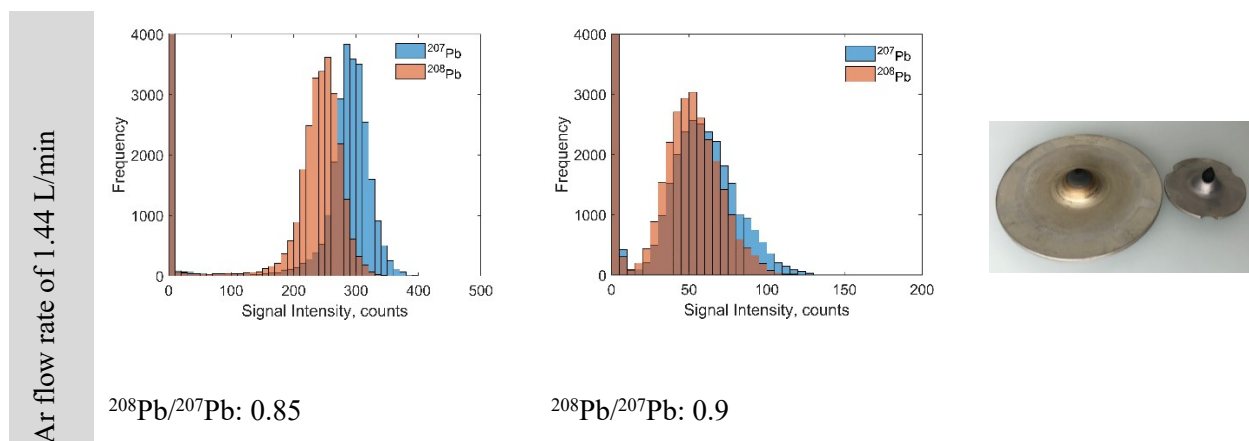
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9 Supplementary Information

10 To achieve the highest possible sensitivity and stability, carbon deposition should ideally be avoided.
11 Monitoring different isotopes of an element, additionally can help to identify and minimize the occurrence
12 of carbon-based molecular ions in the mass spectra. Figure S1 shows intensity histograms for ²⁰⁷Pb and
13 ²⁰⁸Pb, during experiments using different Ar gas flow rates and sampling depth positions. The natural
14 abundance ratio of ²⁰⁸Pb and ²⁰⁷Pb is 2.4, and deviations from this value indicate the presence of molecular
15 ions. It can be seen that the application of a higher Ar flow rate resulted in a signal intensity ratio of less
16 than 1, while using a lower gas flow rate achieved a better agreement. Images of the “Jet” sampler and X
17 skimmer cones are shown after operation with low and high Ar flow rates showing that soot formation
18 can be effectively avoided too.





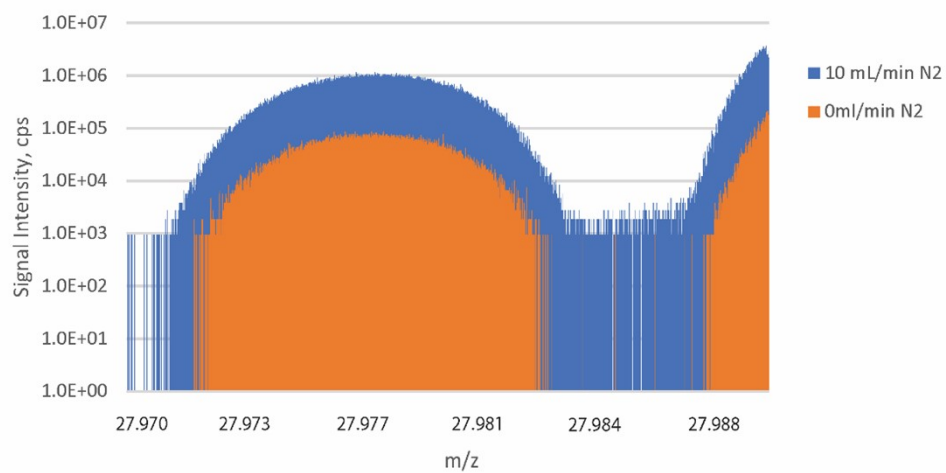
19 **Figure S1:** Histograms of ^{207}Pb and ^{208}Pb ion signal intensities for 4 different operating conditions.

20 **Solvent exchange procedure.** Ag NPs have been transferred to toluene via ligand replacement following
 21 the procedure reported elsewhere,³ with minor modifications. First, the aqueous solution of citrate-capped
 22 Ag NPs was concentrated by centrifugation to 1 mg/mL. 0.15 mL of this solution was mixed with 0.15
 23 mL of 10mM dodecanethiol in chloroform (2.4 $\mu\text{L}/\text{mL}$ or 2 mg/mL). 0.75 mL acetone was added to
 24 homogenize phases and the obtained solution was stirred at 50°C for 12 hours. After this ligand exchange,
 25 NPs were precipitated by centrifugation at 12100 x g for 2 minutes. The obtained pellet was re-suspended
 26 in 0.1 mL chloroform by sonication for 10 minutes. After that NPs were centrifuged again at 12100 x g
 27 for 2 minutes and finally re-suspended in 0.3 mL toluene by sonication for 5 minutes.

28 **MDG parameters**

29 **Table S1:** MDG operating parameters, for different solvents droplet generation. Droplets were dispensed
 30 at the frequency of 100 Hz. These settings were applied for a dispenser head with 50 μm nozzle.

Solvent	Triple pulse mode	Voltage, V	Width, ns	Delay, ns	Droplet size, μm
Toluene (DDT)	P1	44	36	31	35-37
	P2	76	23	35	
	P3	63	43	51	
Mesitylene (DDT)	P1	43	64	43	30-31
	P2	56	22	28	
	P3	44	44	80	
Water	P1	74	86	18	22
	P2	80	52	51	
	P3	55	49	37	



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33 **Figure S2:** Mass spectrum near $^{28}\text{Si}^+$ at an MRP of 4000 indicating that molecular ions do not contribute
34 substantially to the background signal.

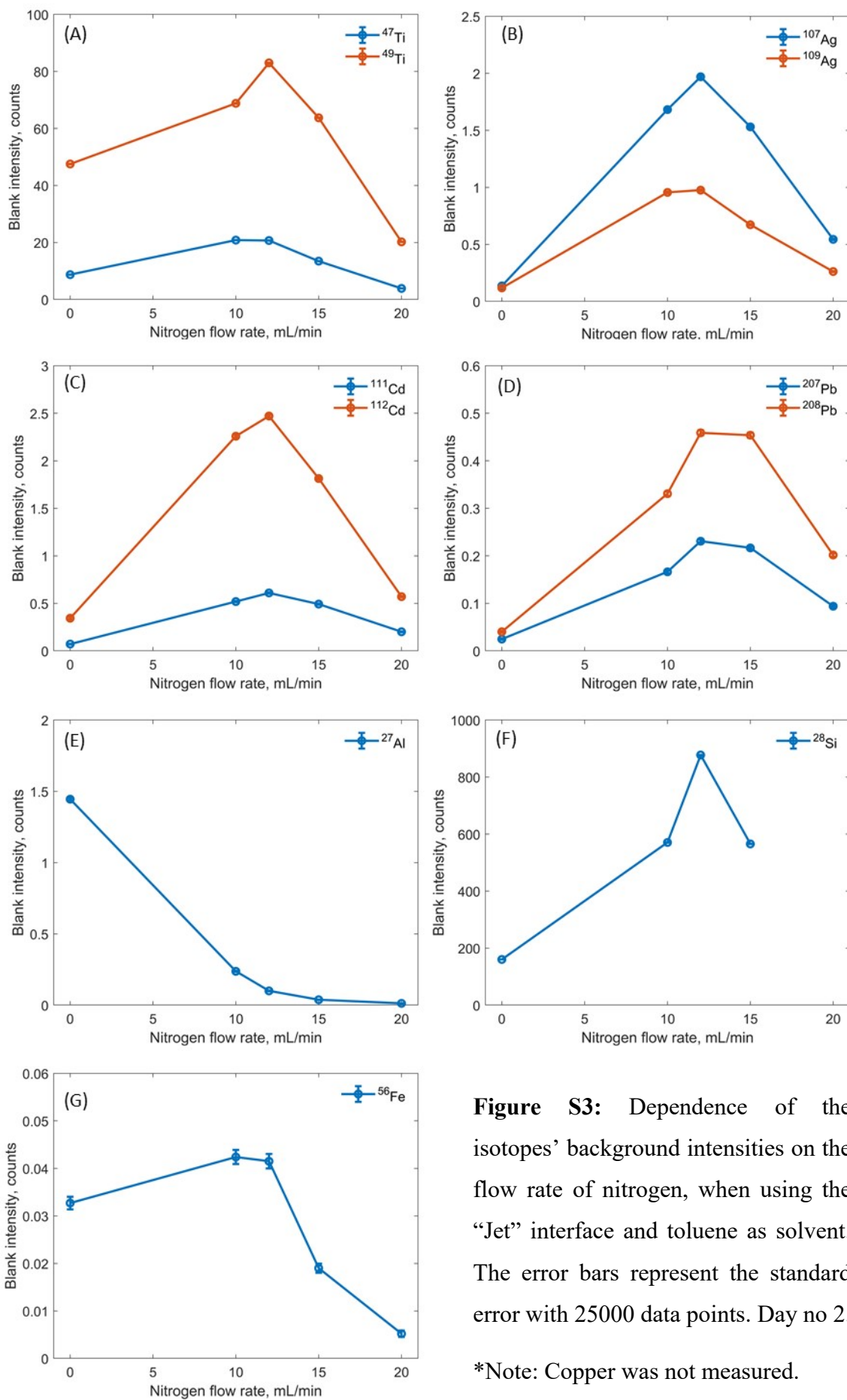


Figure S3: Dependence of the isotopes' background intensities on the flow rate of nitrogen, when using the "Jet" interface and toluene as solvent. The error bars represent the standard error with 25000 data points. Day no 2.

*Note: Copper was not measured.

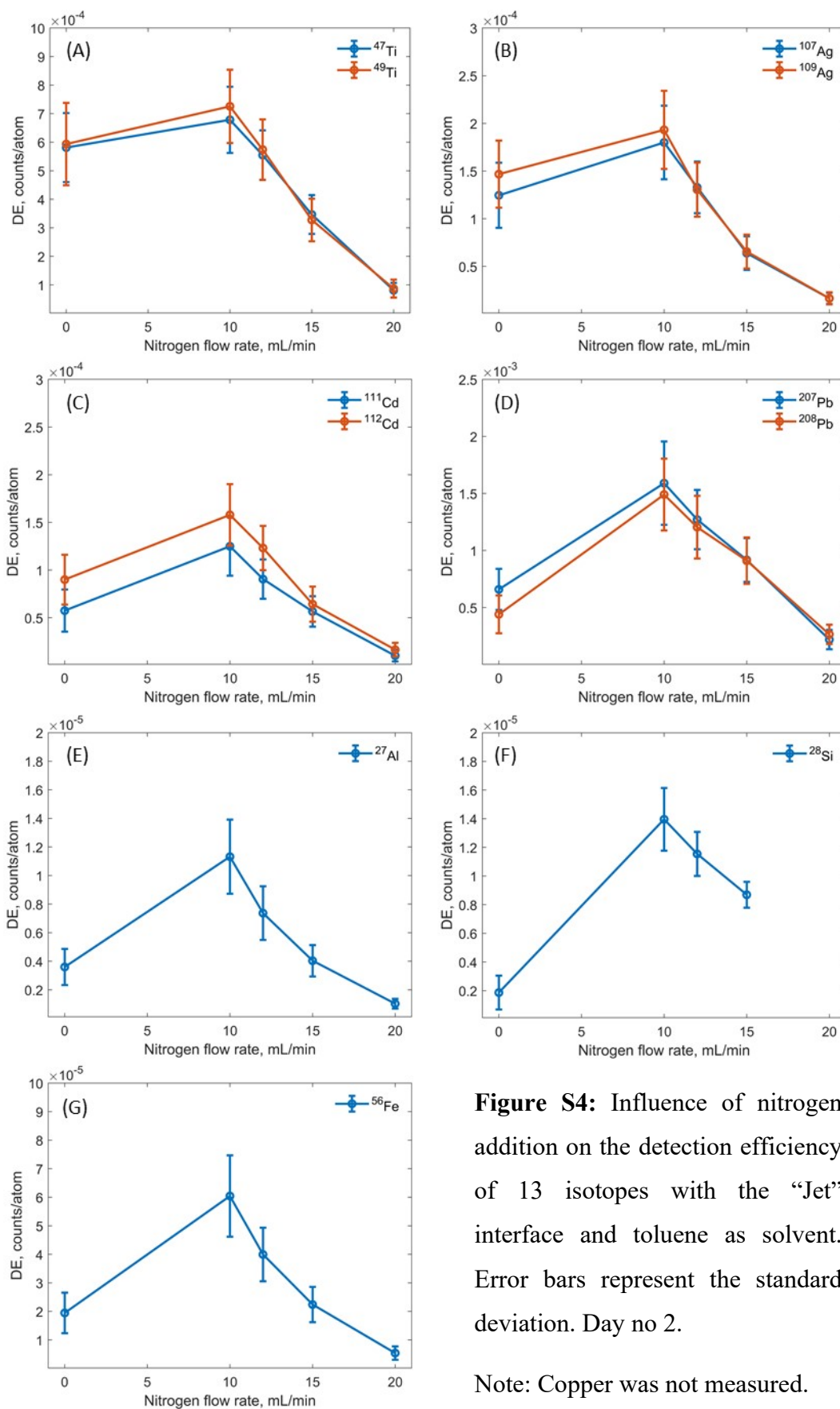


Figure S4: Influence of nitrogen addition on the detection efficiency of 13 isotopes with the “Jet” interface and toluene as solvent. Error bars represent the standard deviation. Day no 2.

Note: Copper was not measured.

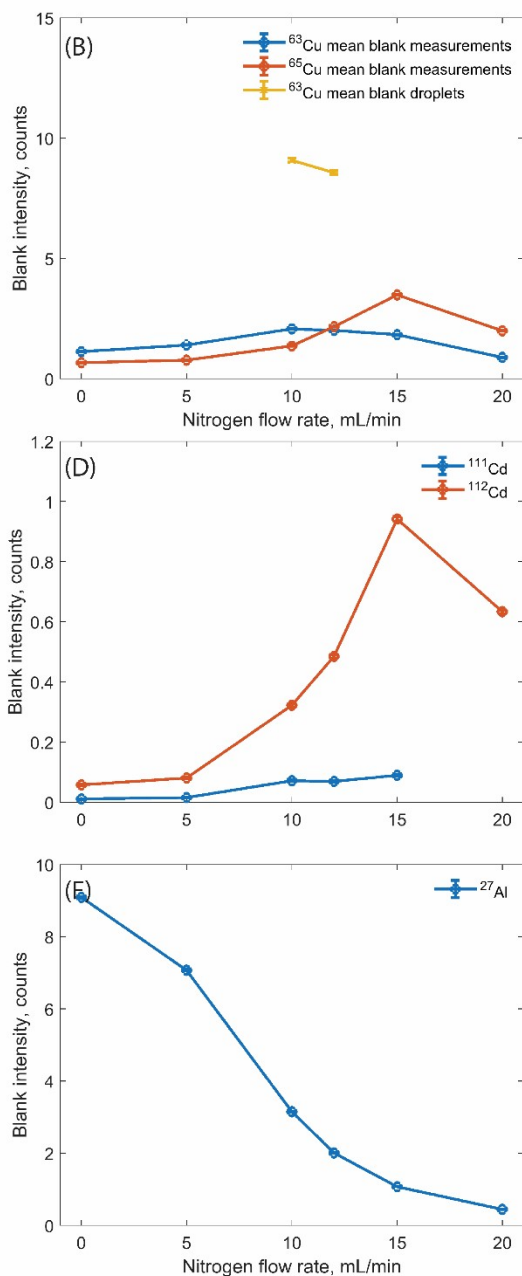
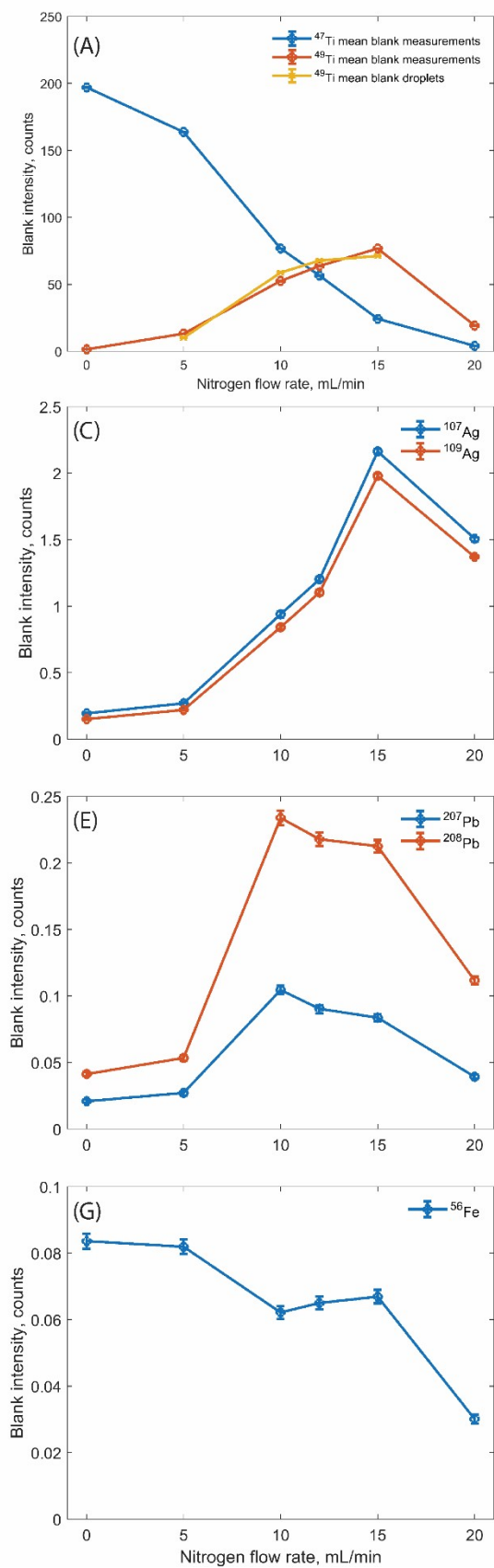


Figure S5: Dependence of the isotopes' background intensities on the flow rate of nitrogen, when using the "Jet" interface and mesitylene as solvent. The error bars represent the standard error with 2500 for ^{49}Ti and ^{63}Cu when measuring blank droplets and 25000 data points for the rest of isotopes measured as a mean of blank measurements.

Note: Si was not measured.

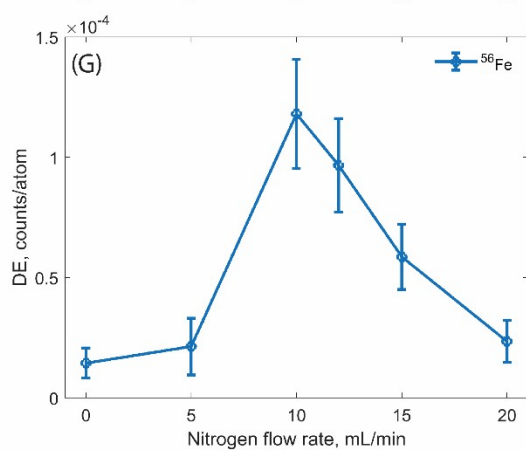
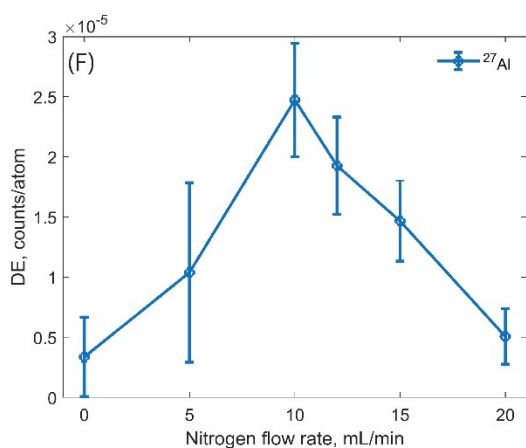
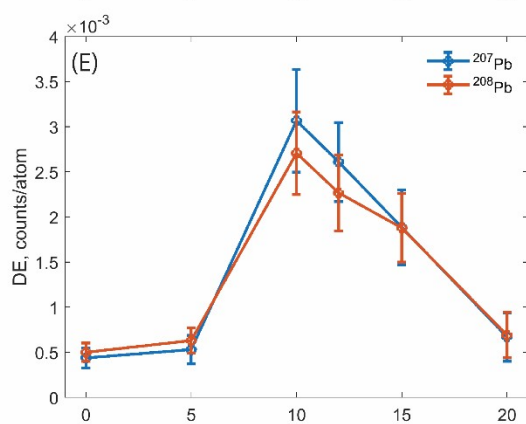
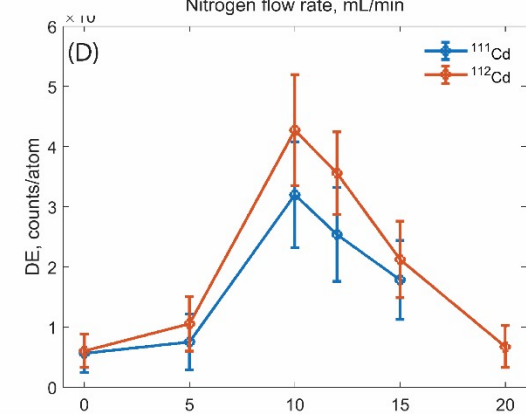
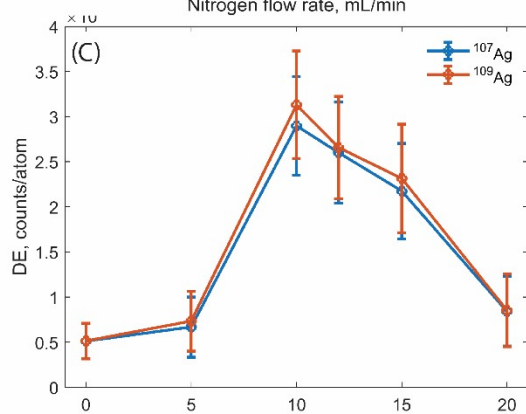
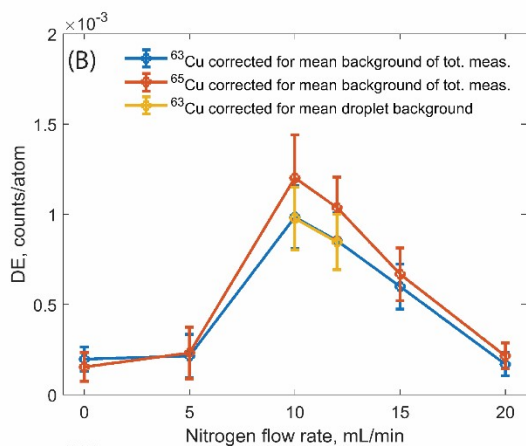
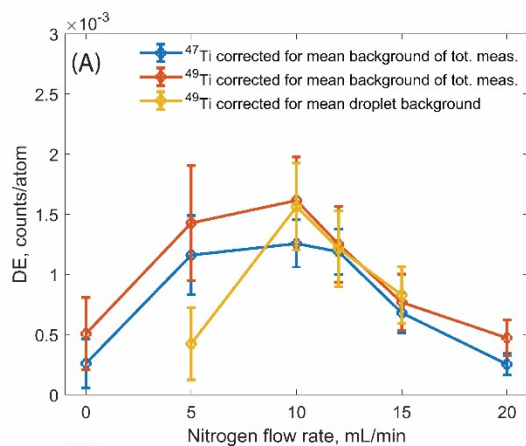
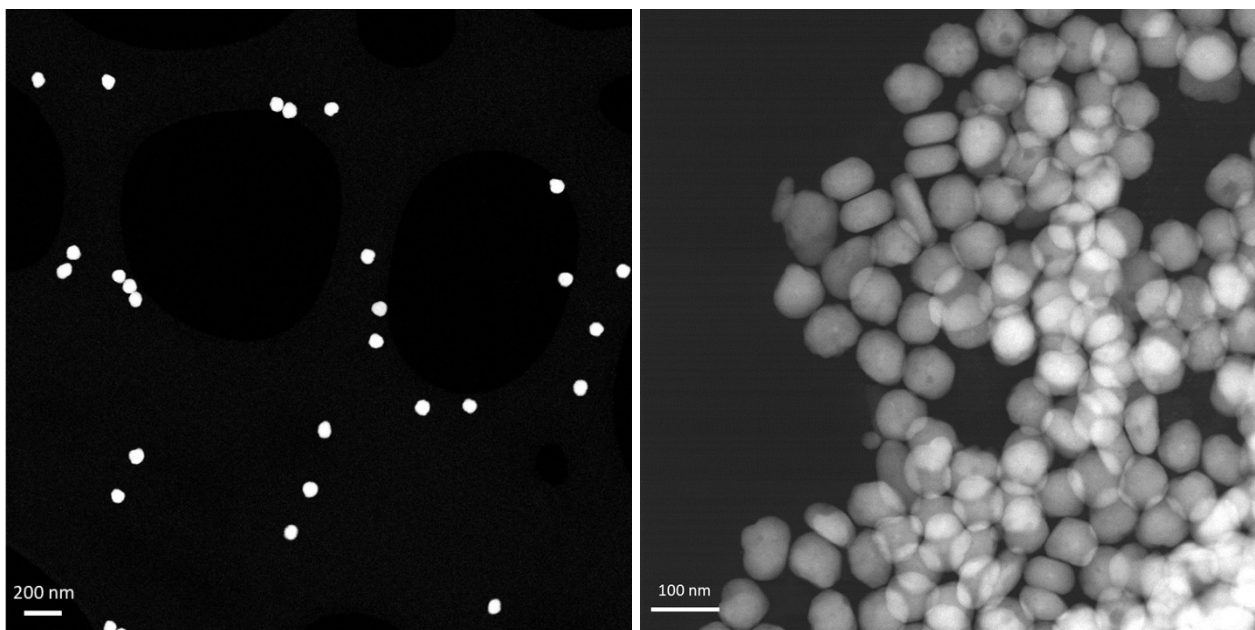


Figure S6: Influence of nitrogen addition on the detection efficiency of 13 isotopes with the “Jet” interface and mesitylene as solvent. Error bars represent the standard deviation.

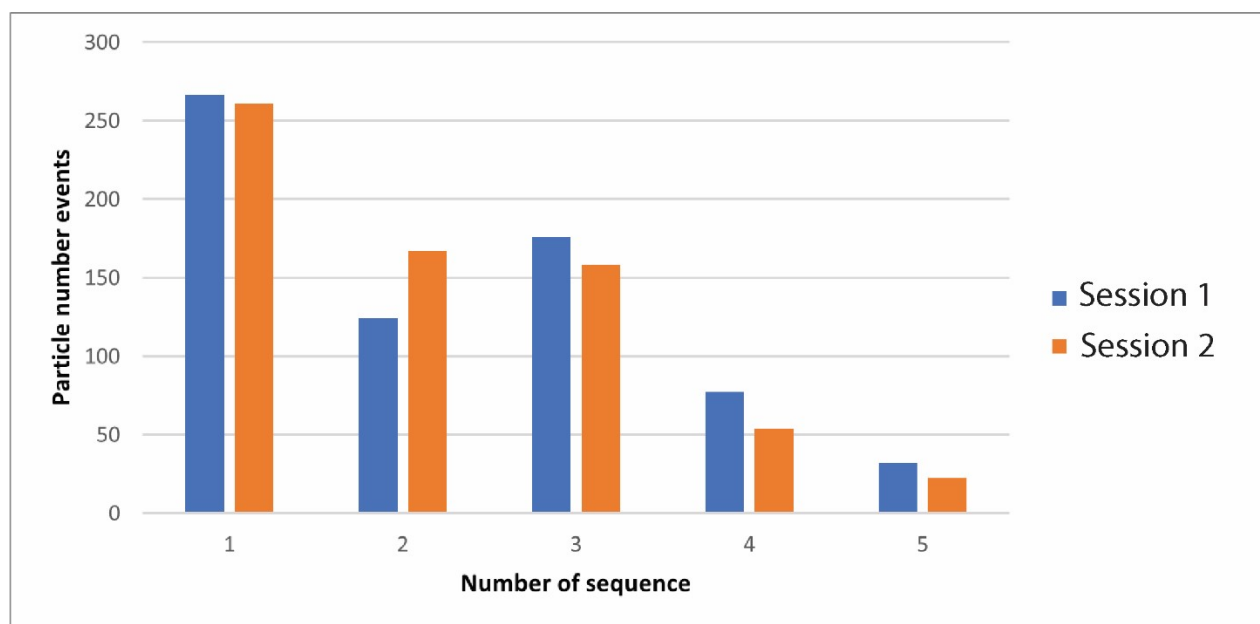
Note: Si was not measured.



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41 **Figure S7:** High angular annular dark field (HAADF) image of 80 nm Ag NPs deposited on TEM grids
 42 from Ag-NP dispersed in citrate solutions(left), and images of 80 nm Ag NPs suspended in toluene (right)
 43 after solvent exchange procedure.

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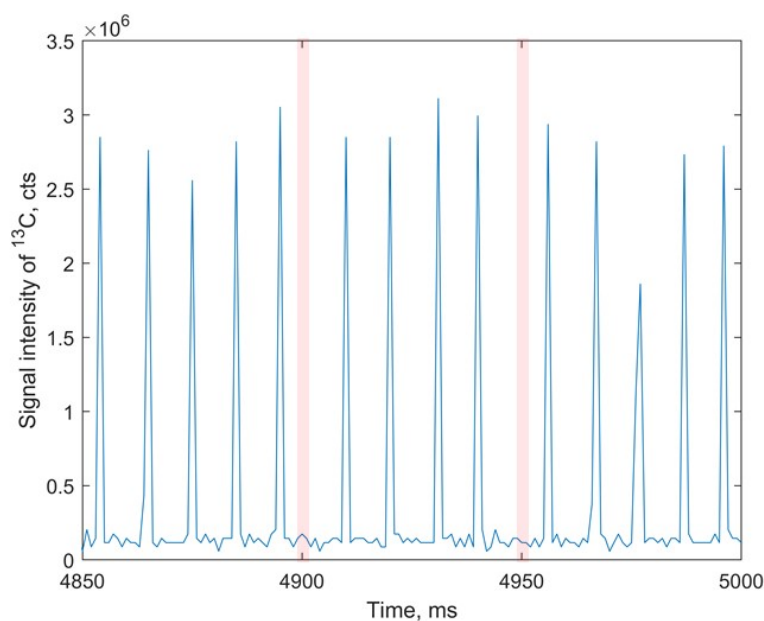


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46 **Figure S8:** Change of particle number events within two repeat measurement sessions. The total
 47 measurement time was 20 minutes each. “Measurement 1” represents the measurement data obtained
 48 directly after the preparation of the suspension, while “Measurement 2” represents the data obtained after
 49 sonication of the same suspension for 5 minutes. Measurement 1: (675 total), Measurement 2 (662 total).

50 TE values were determined at the beginning and in the end of measurement sequence by counting ^{13}C
 51 signal spikes arising from the introduced droplets when using organic solvents. With aqueous solvents in
 52 was added as droplet tracer. TEs were always calculated to be > 1 because of the flyback and settling
 53 times of the mass spectrometer after each scan. Figure S9 shows this as an example during a segment of
 54 150 ms for the $^{13}\text{C}^+$ signal. A single acquisition was contained of a sequence with 50 samples of 1 ms
 55 integration time.

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58 **Figure S9:** Time-resolved ^{13}C signals of individual microdroplets recorded when no nitrogen was used.
 59 The red bars indicate the flyback and settling time of the MS.

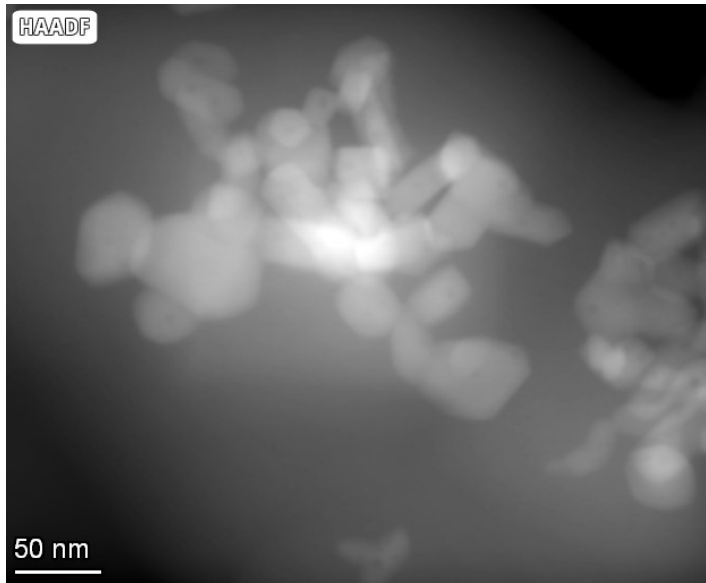
60 **Table S2:** Comparison data of measured TiO_2 NPs from sunscreen “B” sample suspended in different
 61 solvents. TiO_2 concentrations and total mass fraction present in the original sample were determined after
 62 digestion.

Solvent	Water*	Toluene	Toluene+DDT	Mesitylene	Mesitylene+DDT
Mean size, nm	50.3	57.3	57	44.6	65.1
Standard deviation, nm	22.5	17.8	13.8	14.3	12.9
PNC, NP g^{-1} #	2.20×10^{11}	2.74×10^{12}	2.85×10^{13}	1.18×10^{13}	8.34×10^{12}
Mass fraction, mg/g #	0.084	0.47	2.8	0.57	1.2
Recovery, % #	0.1	0.7	3.8	0.8	1.7
Mean intensity, cts	1040	495	510	210	540
Median background, cts	7	19	30	76	52

Droplet sizes of standard, μm	22	35	37	30	31
Abs. sensitivity, cts g^{-1}	3.8×10^{18}	1.5×10^{18}	1.7×10^{18}	1.4×10^{18}	1.3×10^{18}

63 *Defocused ion beam conditions; # calculated from only the first replicate (first 4 minutes of the
64 experiment).

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66

67 **Figure S10:** HAADF image of TiO_2 NPs from sunscreen “B” deposited on TEM grid from suspension in
68 mesitylene.

69 **Bulk analysis for TiO_2 in sunscreen**

70 The total Ti content in sunscreen was determined by digesting approximately 0.1 g of the sample with an
71 acid mixture of 1.25 mL nitric acid, 1.25 mL hydrogen peroxide and 0.25 mL hydrofluoric acid in a
72 Turbowave microwave system (MLS-MWS, Germany). The microwave power was increased from 800
73 to 1000 W in 20 minutes, and held at 1000 W for another 20 minutes. After the digest had cooled, further
74 dilutions were done in 1% HNO_3 . Quantification was carried out via standard addition calibration using
75 the sector field ICPMS instrument in medium resolution and with conventional nebulization.