Clean and efficient extraction method of TiO_2 nanoparticles from commercialized sunscreens (supporting information)

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List of ingredients for each tested sunscreen as provided on the packaging

S1: Rewe Feuchtigkeits-Sonnenspray

Aqua, C12-15 Alkyl Benzoate, Octocrylene, Alcohol, Glycerin, Titanium dioxide, Butyl Methoxydibenzoylmethane, VP/Hexadecene copolymer, Stearyl Dimethicone, Panthenol, Butyrospermum Parkii Butter, Ethylhexylglycerin, Tocopheryl Acetate, Microcristalline Cellulose, Trimethoxycaprylylsilane, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Disodium EDTA, Cellulose Gum, Sodium Hydroxide, Carbomer.

S2: Rewe Feuchtigkeits-Sonnencreme

Aqua, Octocrylene, Alcohol, C12-15 Alkyl Benzoate, Glycerin, Titanium dioxide, Butyl Methoxydibenzoylmethane, Prophyheptyl, Caprylate, Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, VP/Hexadecene copolymer, Tricontanyl PVP, Stearyl Dimethicone, Panthenol, Butyrospermum Parkii Butter, Tocopheryl Acetate, Ethylhexylglycerin, Trimethoxycaprylylsilane, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Carbomer, Sodium Hydroxide, Xanthan Gum, Disodium EDTA, Tocopherol.

S3: Real,- Quality Sonnenmilch

Aqua, Alcohol denat., Octrocrylene, Glycerin, C 12-15 Alkyl Benzoate, Butyl Methoxydibenzoylmethane, Ethylhexyl Salicylate, Titanium Dioxide (nano), Dicaprylyl Carbonate, Tocopheryl Acetate, VP/Hexadecene copolymer, Panthenol, Silica, Parfum, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Ethylhexylglycerin, Sodium Hydroxide, Carbomer, 1,2-Hexanediol, Caprylyl Glycol, Xanthan Gum, Disodium edta, Dimethicone, Citral, Benzyl Alcohol, Linalool, Citronellol, Tocopherol.

S4: Real,- Quality Sonnencreme

Aqua, Octrocrylene, C 12-15 Alkyl Benzoate, Glycerin, Butyl Methoxydibenzoylmethane, Titanium dioxide (nano), Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Potassium Cetyl Phosphate, Triacontanyl PVP, Dicaprylyl Carbonate, Cetearyl Alcohol, Tocopheryl Acetate, Panthenol, Phenoxyethanol, Butylene Glycol, Parfum, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Polyglyeryl-2 Sesquiisostearate, Methylparaben, Aminomethyl Propanol, Simethicone, Sodium Benzoate, Xanthan Gum, Disodium EDTA, Salvia Triloba Leaf Extract, Helianthus Annuus Seed Oil, Citric Acid, Citral, Benzyl Alcohol, Litchi chinensis Pericarp Extract, Linalool, Citronellol, Tocopherol.

S5: Biotherm Lait Solaire:

Aqua, C 12-15 Alkyl Benzoate, Octocrylene, Propylene Glycol, Glycerin, Ethylhexyl Salicylate, Isohexadecane, Butyl Methoxydibenzoylmethane, Titanium dioxide, Nylon-12, Zea Mays Starch, Alcohol denat., Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, PEG-100 Stearate, Potassium Cetyl Phosphate, Glyceryl stearate, Synthethic wax, Stearic acid, Triethanolamine, Phenoxyethanol, Dimethicone, Caprylyl Glycol, Terephthalylidene Dicamphor Sulfonic Acid, Aluminium Hydroxide, Limonene, Xanthan Gum, Acrylates/C10-30 Alkyl Acrylate Crosspolymer, Disodium EDTA, Linalool, Tocopherol, Vitreoscilla Ferment, Citrus Grandis Extract, Citronellol, Citral, benzyl Alchol, Parfum.

S6: Nivea Sun Pflegende Sonnenmilch

Aqua, Butylene Glycol Dicaprylate/Dicaprate, Glycerin, C12-15 Alkyl Benzoate, Butyl Methoxydibenzoylmethane, Octocrylene, Titanium Dioxide, Alcohol Denat., Bis-Ethylhexyloxyphenol Methoxyphenyl Triazine, Dicaprylyl Carbonate, Cetearyl Alcohol, Sodium Phenylbenzimidazole Sulfonate, Cetyl Alcohol, C18-36 Acid Triglyceride, Glyceryl Stearate SE | Diethylhexyl Butamido Triazone, Ethylhexyl Methoxycinnamate, Tocopheryl Acetate, PEG-40 Castor Oil, Sodium Cetearyl Sulfate, Hydrogenated Coco-Glycerides, Xanthan Gum, VP/Hexadecene Copolymer, Trimethoxycaprylylsilane, Trisodium EDTA, Ethylhexylglycerin, Phenoxyethanol, Methylparaben, Propylparaben, Linalool, Benzyl Alcohol, Limonene, Benzyl Benzoate, Hydroxyisohexyl 3-Cyclohexene Carboxaldehyde, Hexyl Cinnamal, Benzyl Salicylate, Butylphenyl Methylpropional, Alpha-Isomethyl Ionone, Eugenol, Citronellol, Coumarin, Parfum..

S7: Sundance Sonnenmilch

Aqua, Octocrylene, Alcohol denat., Glycerin, C12-15 alkyl benzoate, Butyl methoxydibenzoylmethane, Ethylhexyl salicylate, Titanium dioxide, Dicaprylyl carbonate, Tocopheryl acetate, Silica, Panthenol, Bis-ethylhexyloxyphenol methoxyphenyl triazine, Triacontanyl PVP, VP/Hexadecene copolymer, acrylates/C10-30 alkyl acrylate crosspolymer, Parfum, Sodium hydroxide, Ethylhexylglycerin, Maltodextrin, 1,2-Hexanediol, Caprylyl glycol, Carbomer, Xanthan gum, Dimethicone, Citric acid, Disodium EDTA, Limonene, Alpha-isomethyl ionone, Camellia sinensis leaf extract, Benzyl alcohol, Tocopherol..

S8: Garnier Ambre Solaire Resisto Sonnenschutz-Milch

Aqua, C12-15 Alkyl Benzoate, Alcohol Denat., Isohexadecane, Ethylexyl Salicylate, Propylene Glycol, Titanium Dioxide, Cyclohexasiloxane, Butyl Methoxydibenzoylmethane, PEG-30 Dipolyhydroxystearate, BIS-Ethylhexyloyphenol Methoxyphenyl Triazine, Octocrylene, Glycerin, Cyclopentasiloxane, Lauryl PEG/PPG-18/18 Methicone, Terephthalylidene Dicamphor Sulfonic Acid, Synthetic Wax, Ethylhexyl Triazone, Tocopherol, Dodecene, Triethanolamine, Silica, Poloxamer 407, Dimethicone, Ammonium Polyacryldimethyltauramide/Ammonium Polyacryloyldimethyl Taurate, Simmondsia chinensis oil/Jojoba Seed oil, Pentasodium Ethylenediamine Tetramethylene Phosphonate, Drometrizole Trisiloxane, Isopropyl Lauroyl Sarcosinate, Isostearyl alcohol, Caprylyl Glycol, Disteardimonium Hectorite.

S9: Alverde Sonnencreme Jojoba

Aqua, Titanium Dioxide, Cocoglycerides, Helianthus Annuus Seed Oil, Isoamyl Laurate, Polyglyceryl-2 Dipolyhydroxystearate, Glycerin, Polyglyceryl-3 Polyricinoleate, Helianthus Annuus Seed Cera, Simmondsia Chinensis Seed Oil, Magnesium Sulfate, Olea Europaea Fruit Oil, Alumina, Stearic Acid, Glyceryl Caprylate, Levulinic Acid, Tocopherol, p-Anisic Acid, Sodium Levulinate.

S10: Babylove Sonnencreme

Aqua, Zink oxide (nano), Hydrogenated polyisobutene, Poly-glyceryl-2 dipolyhydroxystearate, Titanium dioxide (nano), Glycerin, Hydrogenated Polydecene, Hydrogenated poly 6-14 olefin, Butylene glycol, Glyceryl oleate, Tocopheryl acetate, Butyrospermum parkii butter, Magnesium sulfate, Panthenol, Aluminum hydroxide, Ethylhexylclycerin, Stearic acid.

S11: Baby sebamed Sonnenschutzlotion

Aqua, C12-15 Alkyl Benzoate, Cetearyl Isononanoate, Octocrylene, Glycerin, Propylene Glycol, Polyglyceryl-2 Dipolyhydroxystearate, Ethylhexyl Salicylate, Butyl Methoxydibenzoylmethane, Diethylamino Hydroxybenzoyl Hexyl Benzoate, Panthenol, Dimethicone, Titanium Dioxide, Diethylhexyl Butamido Triazone, Magnesium Sulfate, Tocopheryl Acetate, Phenoxyethanol, Zinc Stearate, Cera alba, Glyceryl Oleate, Bis-

Ethylhexyloxyphenol Methoxyphenyl Triazine, Parfum, Silica, Ethylhexylglycerin, Sorbic Acid, Inulin, Lecithin.

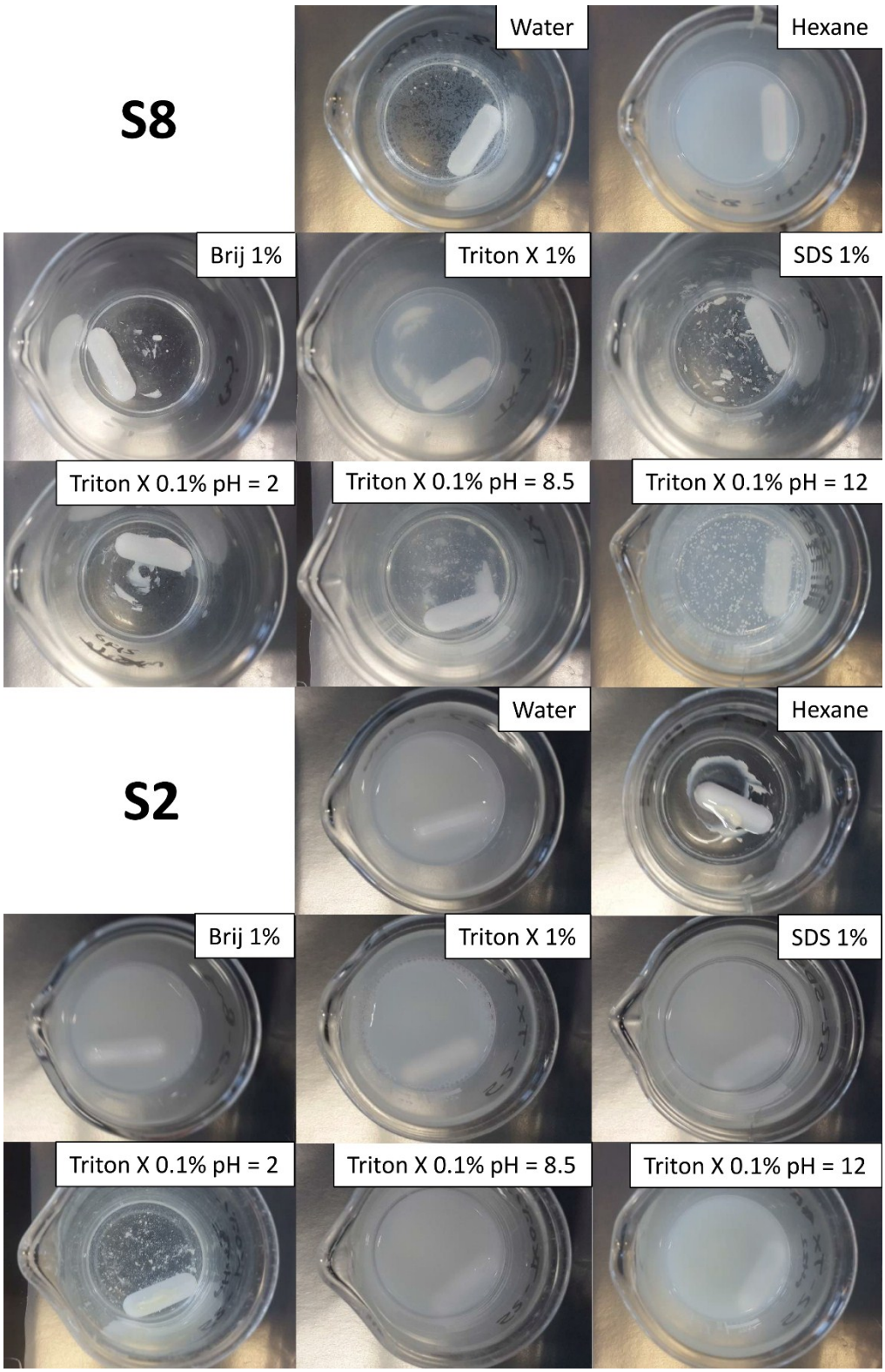
Method validation for the quantification of TiO_2 in sunscreens

In order to confirm that the proposed digestion procedure effectively dissolved our samples and that matrix effects could be ignored, we perform a matrix matched calibration curve with our external standards (P25 powder Degussa) with masses of TiO_2 in the digestion beakers ranging from 0.01 to 10 mg of TiO_2 standard and a standard addition with 0,5 and 1 mg of TiO_2 added to S5. The data evaluation was performed using Excel. The recovery of the method was determined using the counts values obtained from the standard addition samples using the external calibration curve and knowing the expected added masses of TiO_2. The average recovery was 104%. The slopes obtained using external calibrants and standard addition (SI-table 1) did not differ significantly (t-test, $p = 0.697$). Therefore, we consider the possible matrix effects as negligible. The recovery for ionic standards (Ti dissolved in 0.1% HF, SCP, Germany) was interestingly lower than for TiO_2 (76%). This may be due to the sorption of Ti ions on the glass beakers used for the digestion. Therefore, we decided to use TiO_2 standard as calibrants, since it is chemically closer to our target analytes and avoid an absolute error in the determination of the concentration.

SI-Table 1: Slopes for the calibration curves using external standards (P25 powder, 9 concentrations) and using a standard addition procedure using S5 (three concentrations). Standard deviations are determined over 4 replicates. Regression factors were determined for the combined replicates.

	External calibration	Standard addition	Ratio in %
Average slope in mg^{-1}	6.08	6.4	95
Standard Deviation	0.02	1.6	
R^2	0.9988	0.9656	

Sunscreens suspension step



SI-Figure 1: Picture of S5 and S2 (50 mg each) suspended in, from left to right and from top to bottom, in 10 mL pure water, n-hexane, Brij L35, Triton X-100, sodium dodecyl sulfate (SDS) (the three latter 1 % (w/w) in water), and Triton X-100 (0.1 % (w/w) in water) at pH = 2, 8.5 (without pH adjustment), and 12 and stirred at room temperature for 30 min.

Dynamic light scattering experiments

The minimal required sonication time was determined using particles extracted from sunscreen 5 and further diluted in 1 % Triton X-100 aqueous solution at a concentration of 41.8 mg L^{-1}. 10 mL of diluted suspension was transferred into PP centrifuge tubes. Each tube was exposed in a sonication bath for different amount of time and measured directly after sonication using dynamic light scattering. Particle size decreased from 0 to 15 min sonication time and staid constant between 15 and 30 minutes (**SI-table 1**). Therefore, a sonication of 5 min was chosen since longer sonication would not have further reduced particle size.

SI-Table 2: average hydrodynamic diameters of particles extracted from S5 measured using dynamic light scattering after different sonication times. Standard deviations were determined from three measurement replicates.

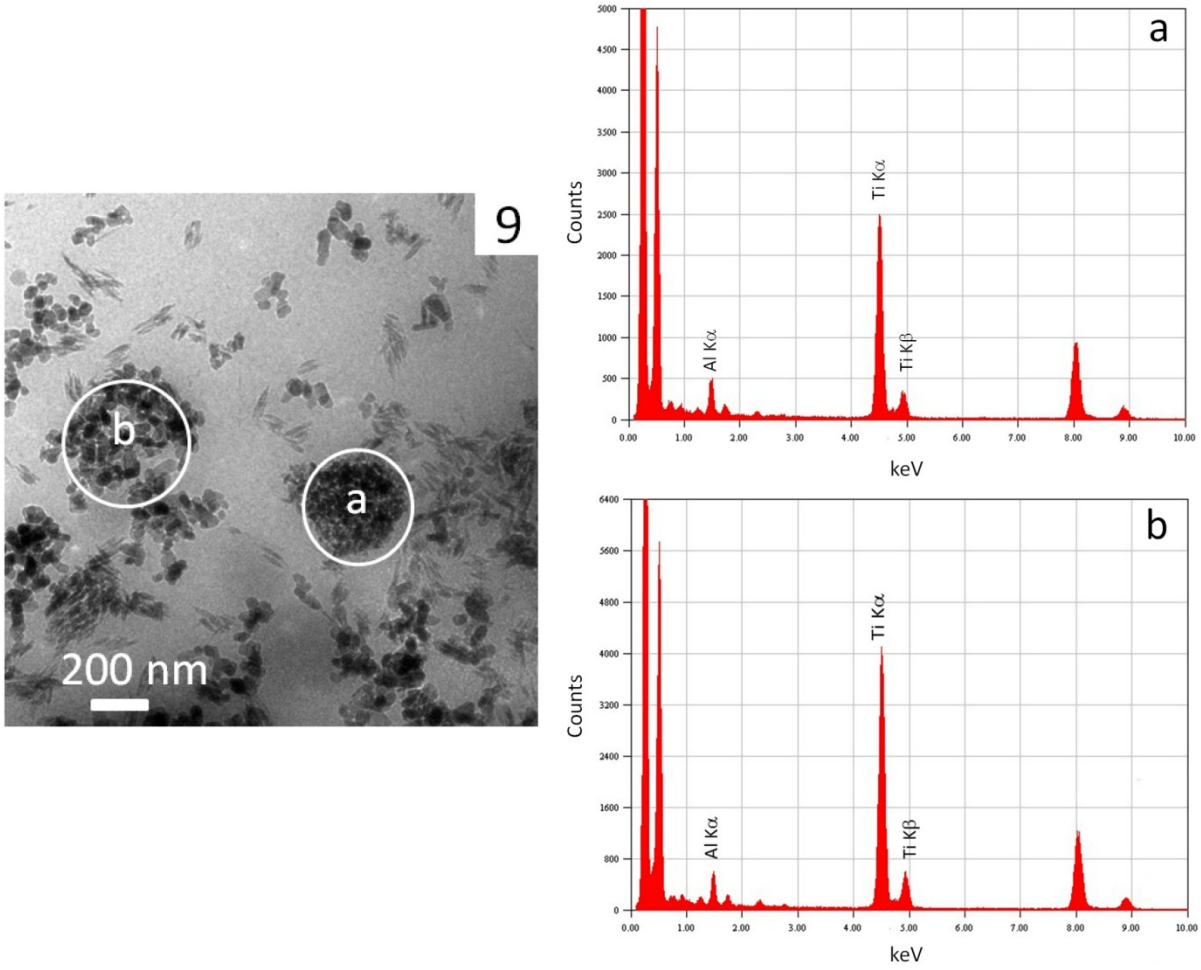
Sonication Time (min)	**0**	**5**	**10**	**15**	**20**	**30**
Average	131.3	125.2	120.7	111.8	115.7	114.8
Standard Deviation	7.7	5.9	4.2	4.4	3.7	4.1

Furthermore, we observed that the dilution ratio had a significant influence on the size measured using dynamic light scattering. Therefore, we measured the size of particles extracted from S5 after dilution at different ratios in 1 % Triton X-100 aqueous solution. Dilution rates higher than 1:300 resulted in poor accuracy of the size estimation due to low scattered light intensity. Each sample was ultrasonicated for 15 min prior to size determination. Particle size decreased with increasing dilution rate until 1:200 and no further decrease in size was observed at a dilution rate of 1:300 (**SI-table 1**). Particles were most probably completely disagglomerated after ultrasound treatment. However, they were not stable and started to agglomerate as soon as sonication stopped. The lower the particle concentration is, the lower is the agglomeration rate. Therefore, decreasing particle concentration improved size measurement by slowing agglomeration rate until its effect on the size determination is negligible. Thus, we chose a dilution rate of 1:200 for all DLS measurements as it warranted a operatively stable suspension and a high scattered light intensity.

SI-Table 3: average hydrodynamic diameters of particles extracted from S5 measured using dynamic light scattering after dilution at different rates. Standard deviations were determined from three measurement replicates.

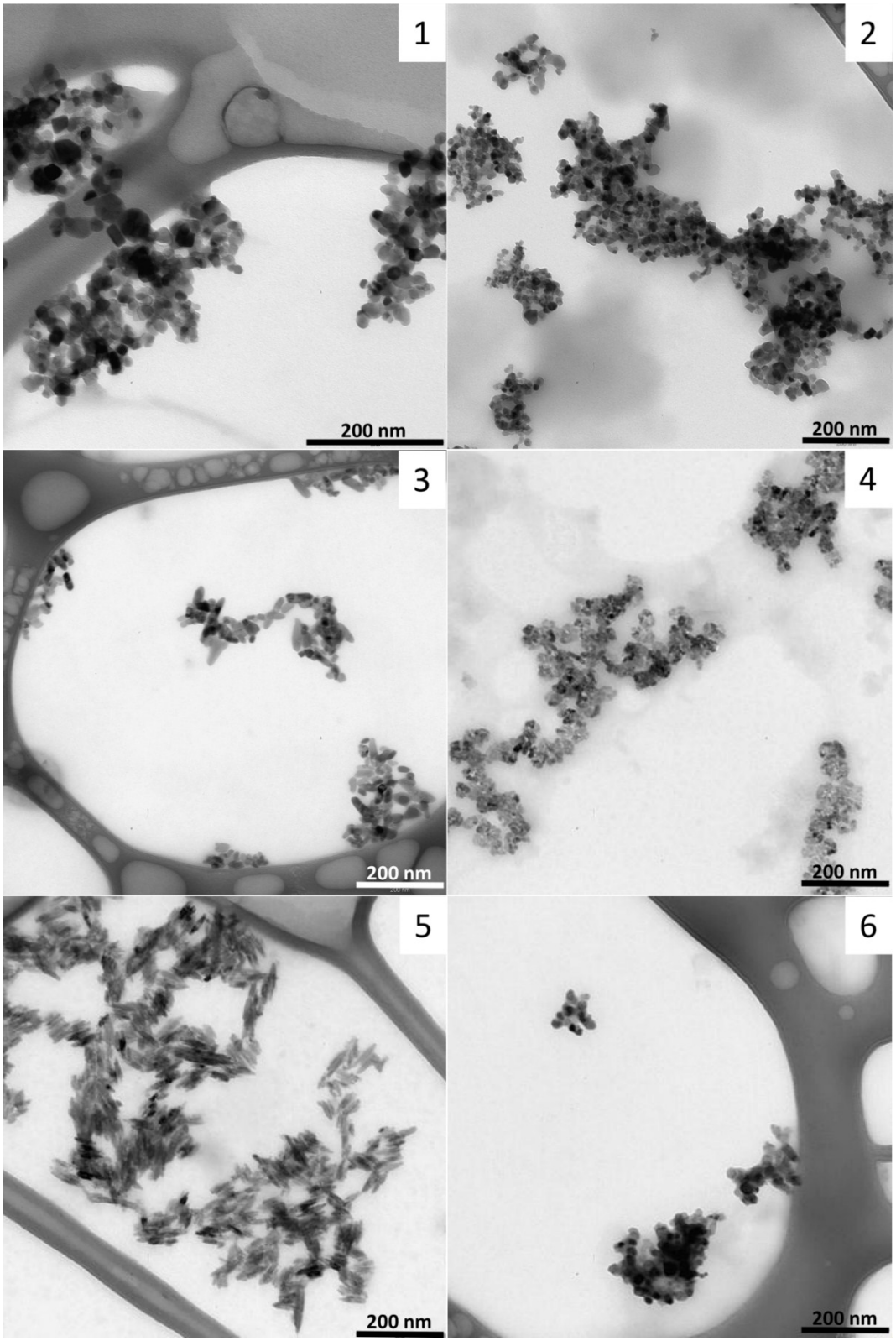
Dilution rate	1:10	1:20	1:50	1:100	1:200	1:300
Average	99.1	65.5	54.5	28.1	24.5	24.5
Standard Deviation	3.2	2.7	2.4	1.3	1.1	1.5

Cryogenic transmission electron microscopy

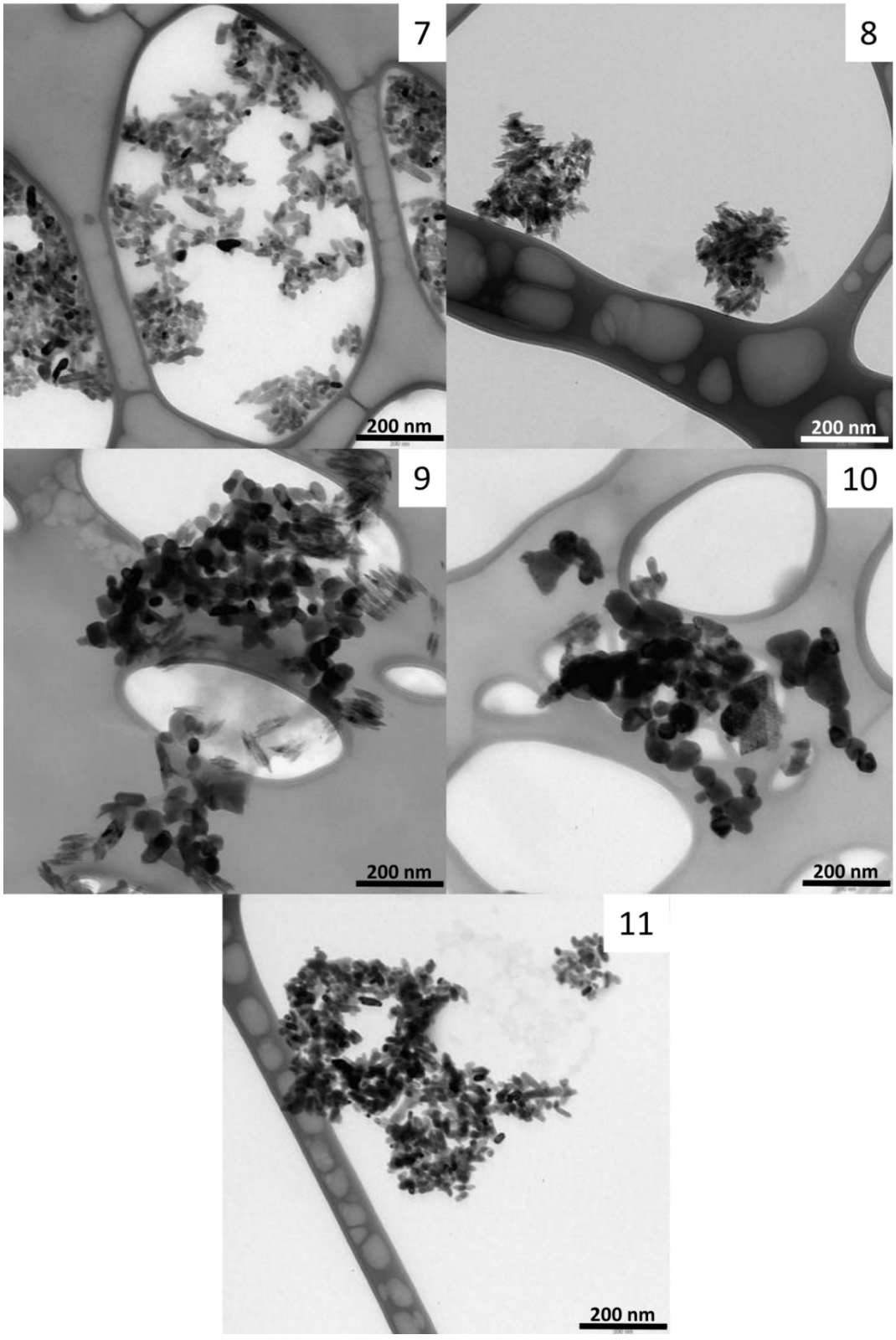


SI-Figure 2: Image and the corresponding EDX-spectra of TiO_2 particles from S9 obtained using transmission electron microscopy in cryogenic mode. The length of the scale bar is 200 nm. The peaks at 0.25 (C K_α), 0.5 (O K_α), 8 (Cu K_α), and 9 (Cu K_β) keV in the EDX spectrum correspond to C and O present in sunscreen's components (water and organic molecules) and the carbon coating of the sample grid. and to Cu from the grid itself, respectively.

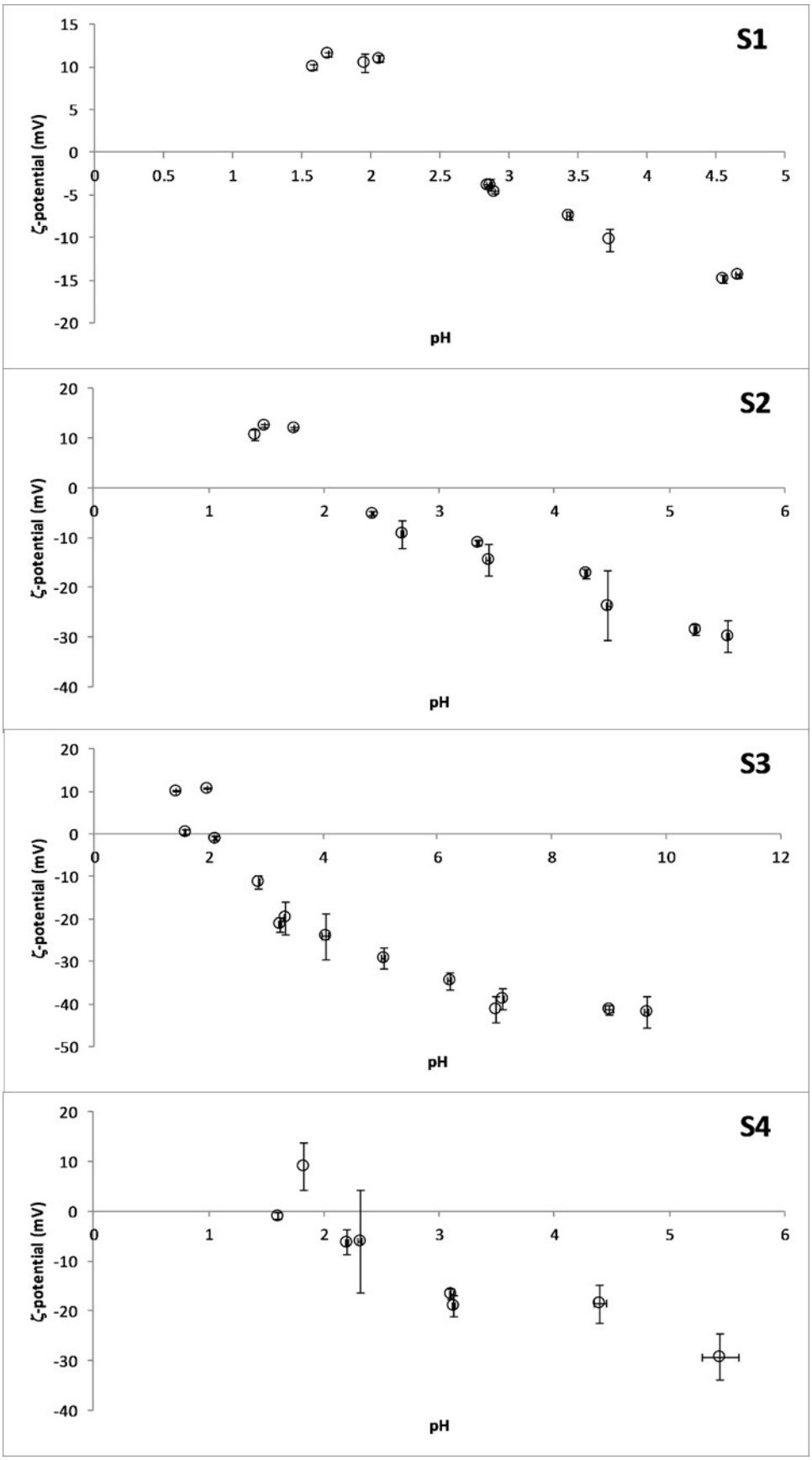
Transmission electron microscopy



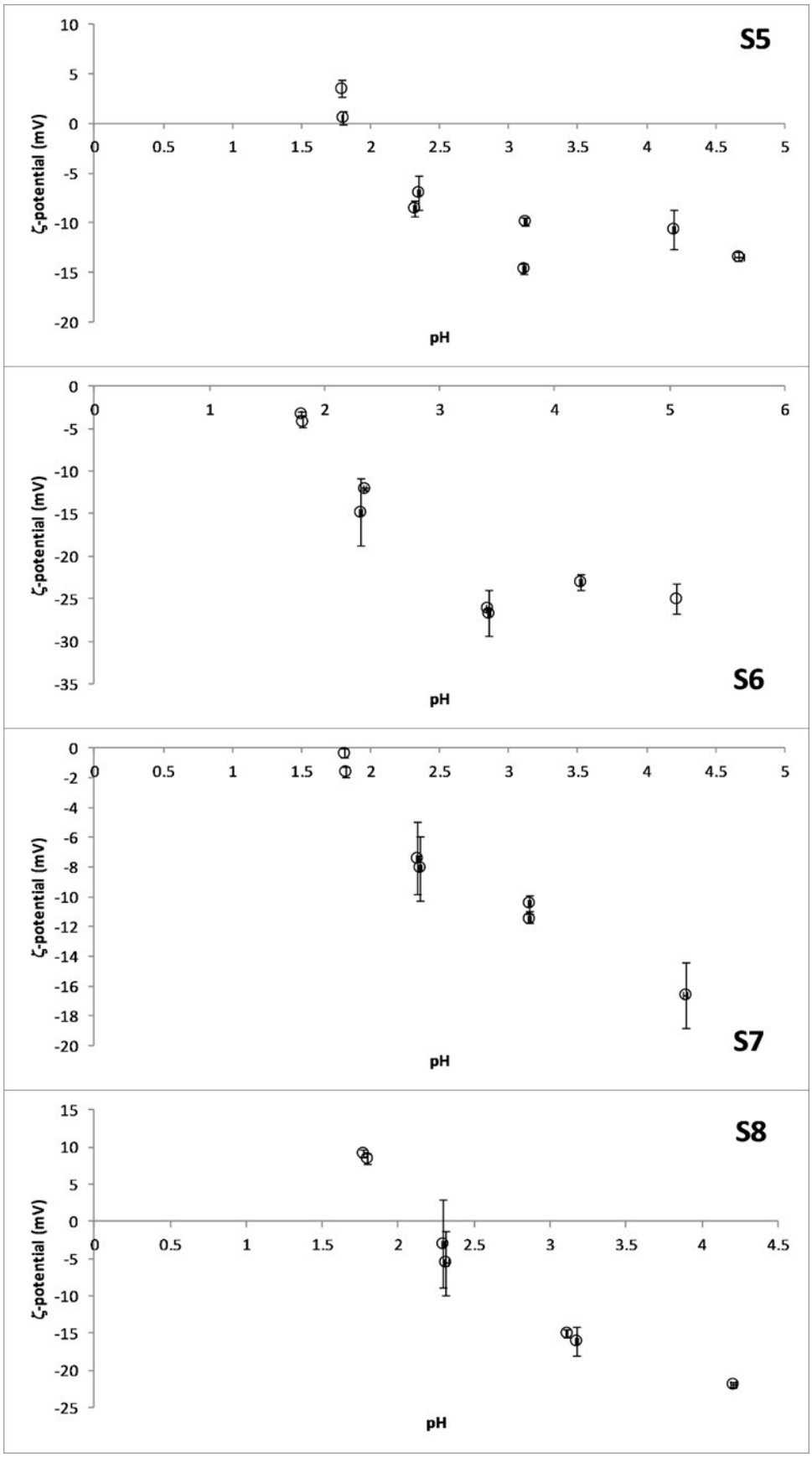
SI-Figure 3: Representative images of extracted inorganic nanoparticles from eleven commercial sunscreens obtained using transmission electron microscopy. The sunscreen number is given on the upper right corner. The length of the scale bar is 200 nm.



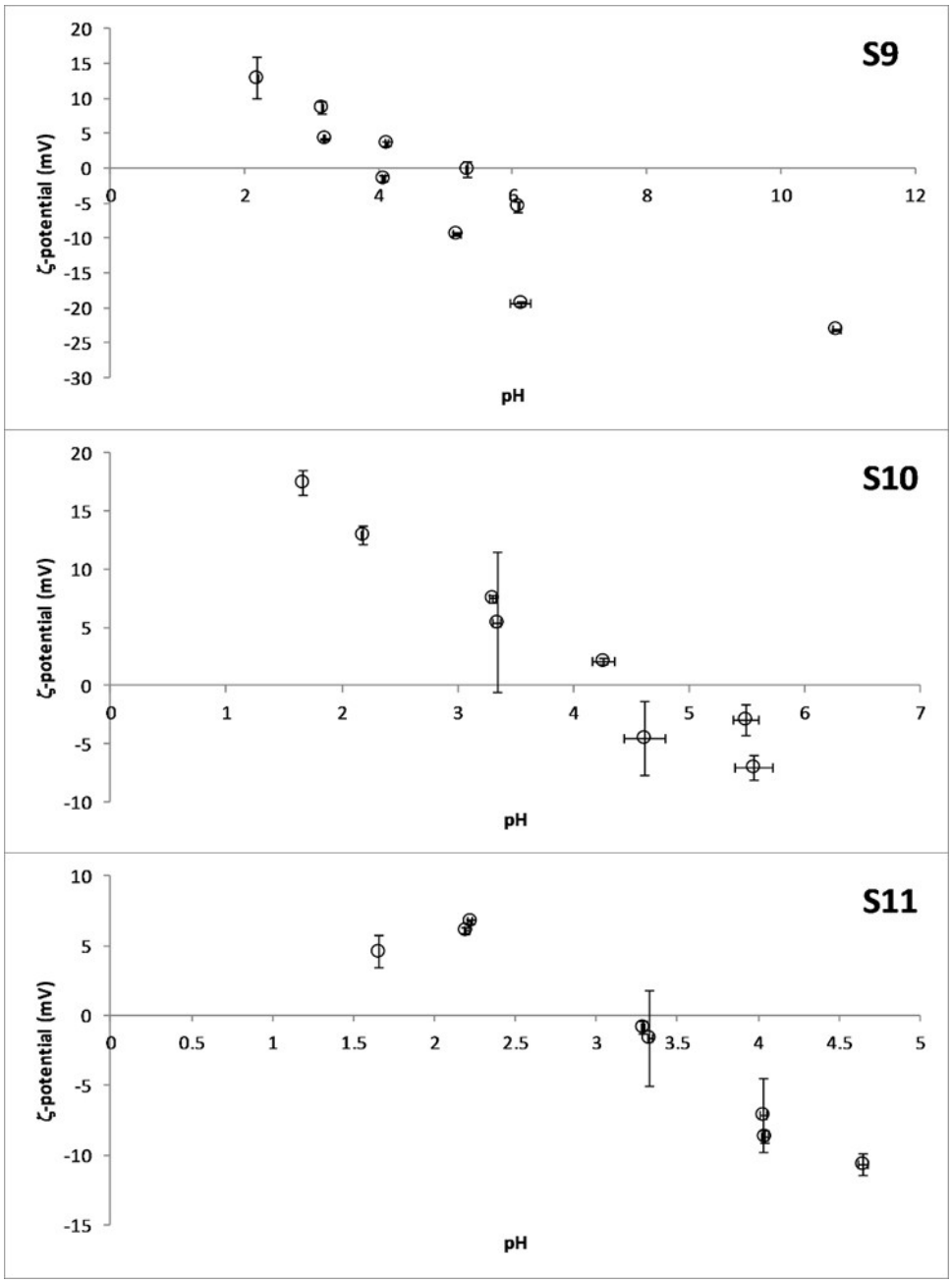
SI-Figure 3: Continuation and end.



SI-Figure 4: ζ-potential measurements at different pH values of nanoparticles extracted from sunscreens and suspended in a 10 mM solution containing 0.1 % Triton X-100. These data were used for calculating isoelectric points.



SI-Figure 4: Continuation.



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174 **SI-Figure 4: Continuation and end.**

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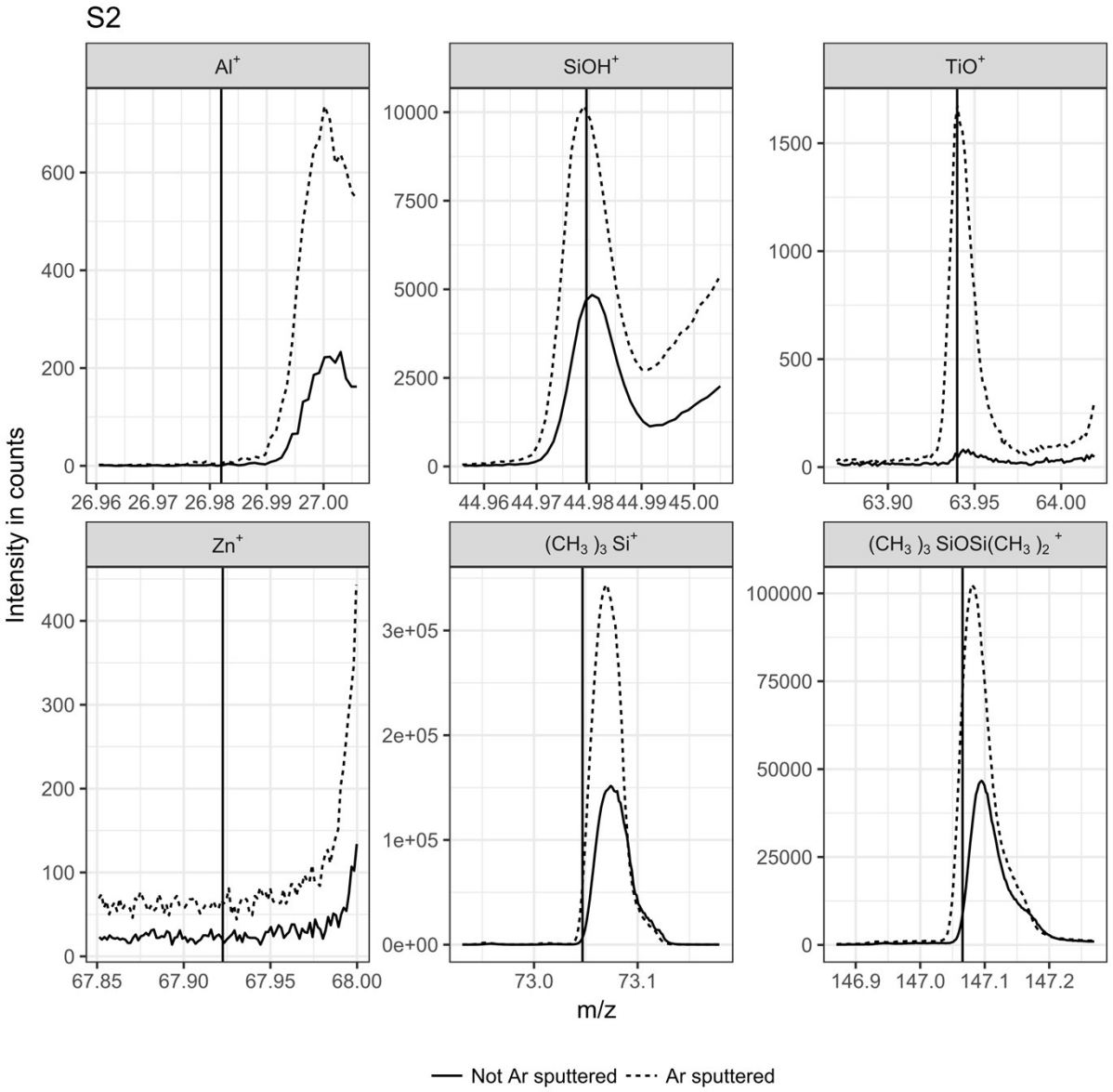

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178 **SI-Figure 5: ToF-SIMS signal intensities obtained before (full line) and with (dashed line) Ar-clusters**
179 **sputtering for the sunscreens extracts S2. Vertical lines indicate the exact mass expected from the**
180 **respective ions or fragments; from left to right: $^{27}Al^+$, $^{28}SiOH^+$, $^{48}TiO^+$, $^{68}Zn^+$, $(CH_3)_3Si^+$, and**
181 **$(CH_3)_3SiOSi(CH_3)_2^+$. The two latter are characteristic fragments for polydimethylsiloxane.**

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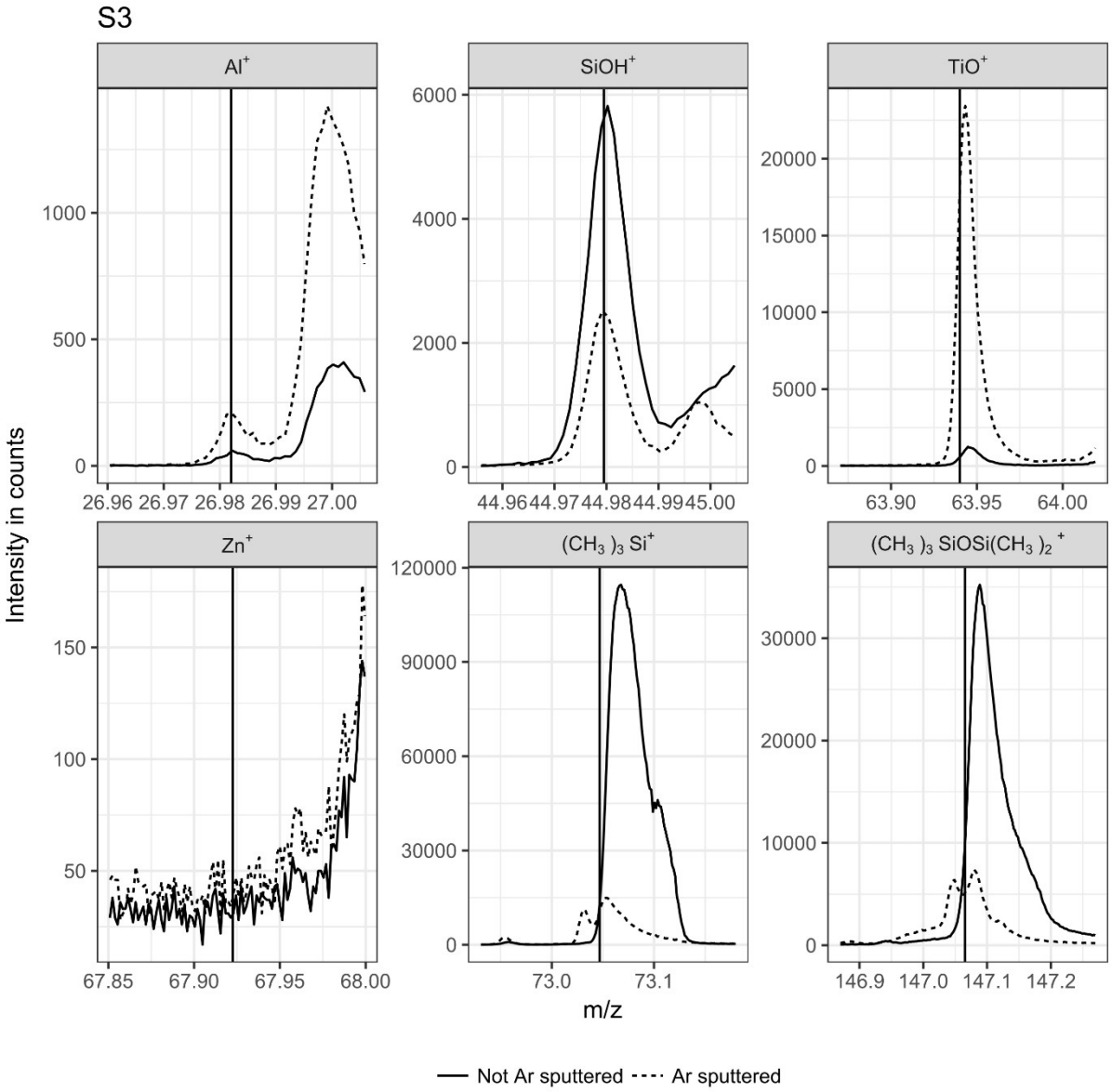

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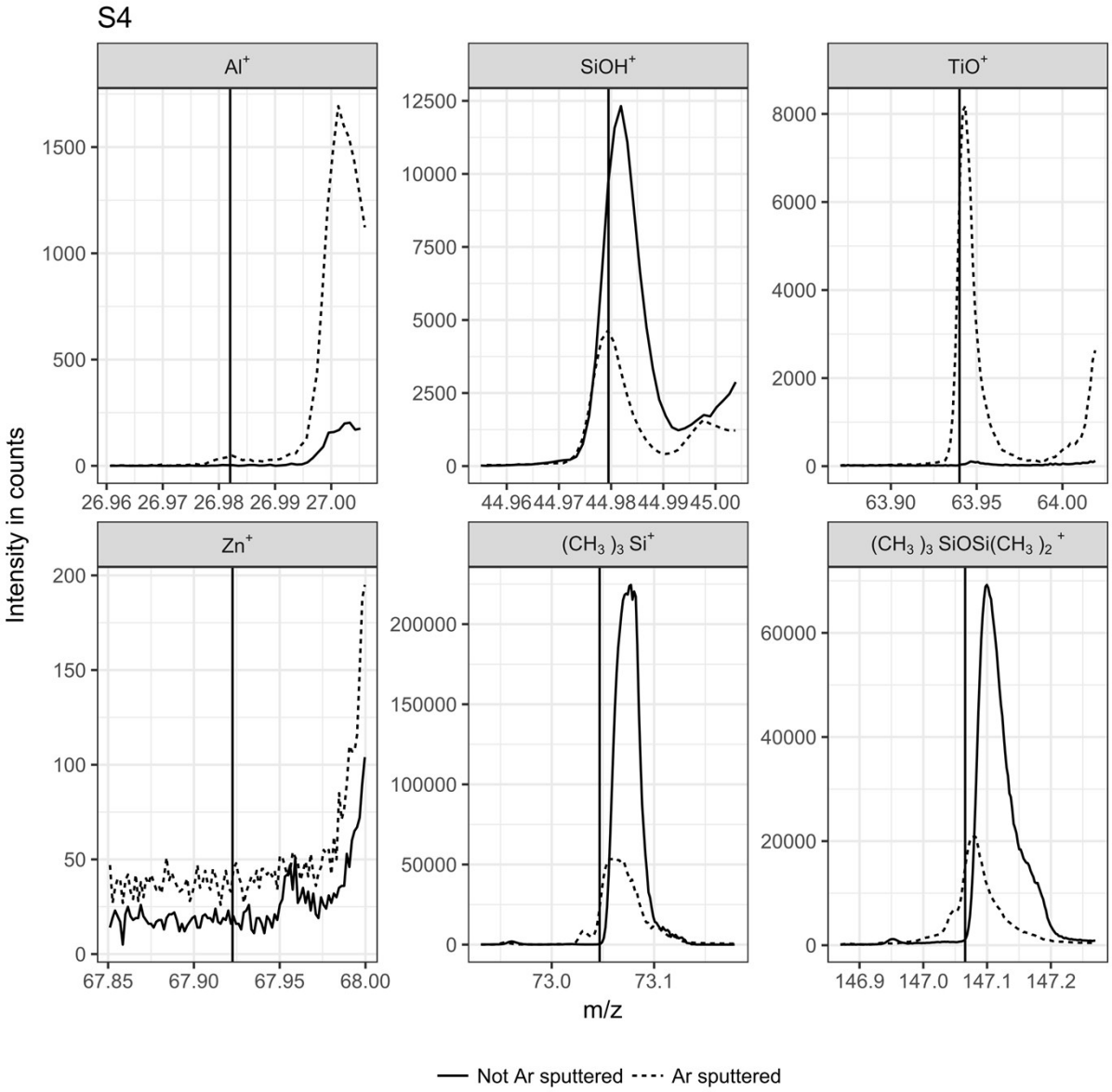
184 **SI-Figure 6: ToF-SIMS signal intensities for the sunscreens extracts S3. See SI-figure 5 for more details.**



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186 **SI-Figure 7: ToF-SIMS signal intensities for the sunscreens extracts S4. See SI-figure 5 for more details.**

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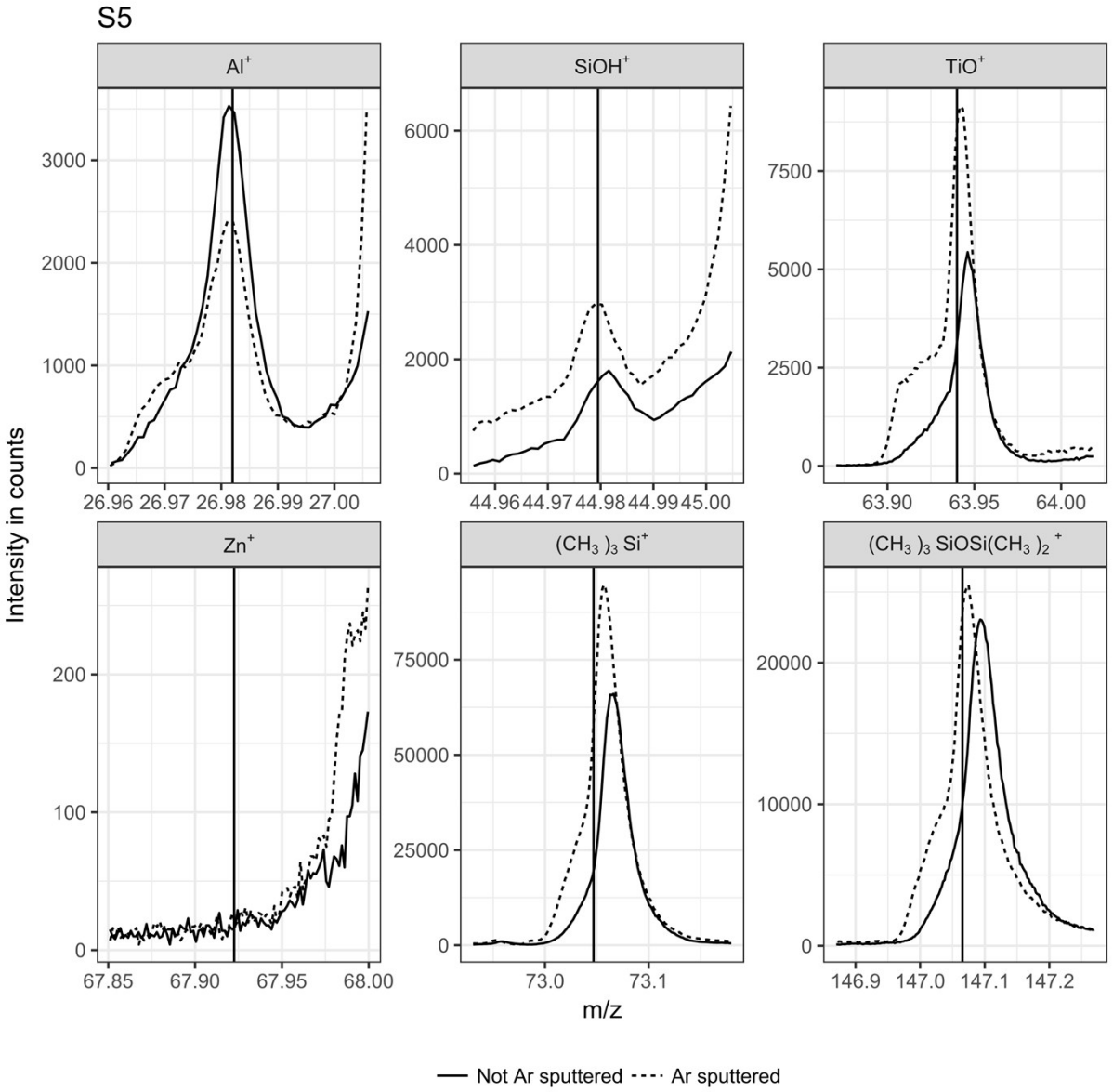

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189 **SI-Figure 8: ToF-SIMS signal intensities for the sunscreens extracts S5. See SI-figure 5 for more details.**

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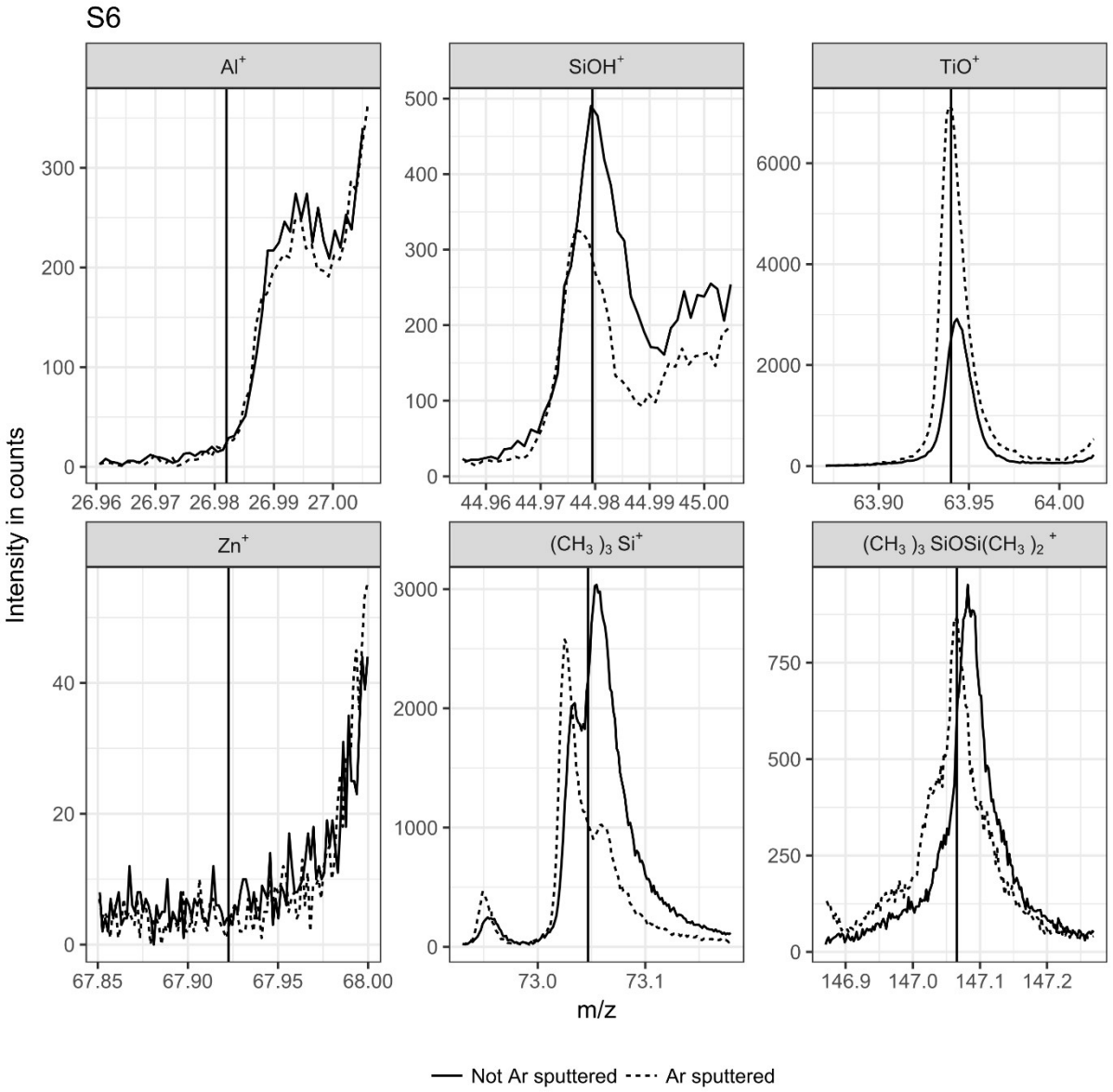

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192 **SI-Figure 9: ToF-SIMS signal intensities for the sunscreens extracts S6. See SI-figure 5 for more details.**

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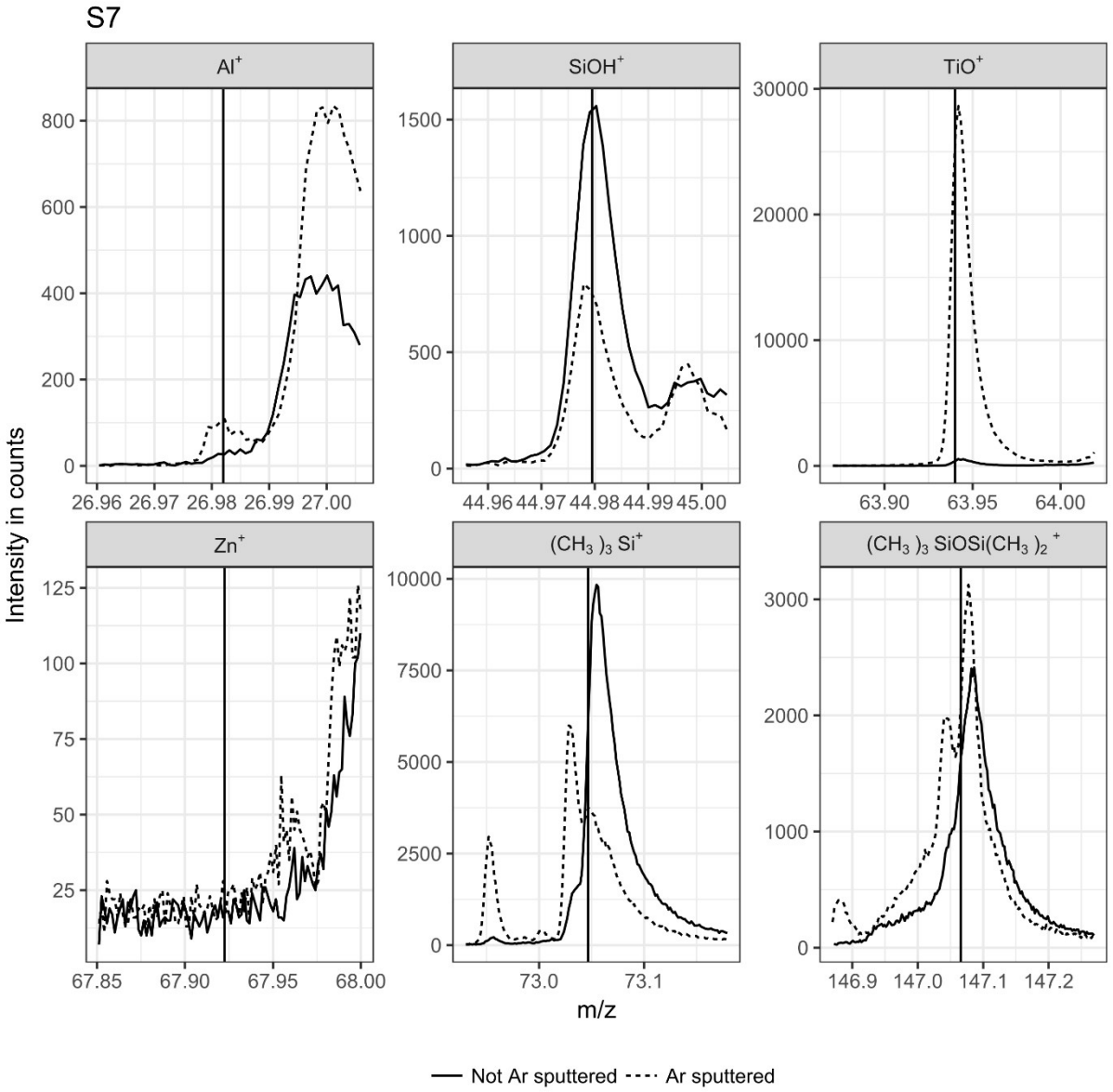

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195 **SI-Figure 10: ToF-SIMS signal intensities for the sunscreens extracts S7. See SI-figure 5 for more details.**

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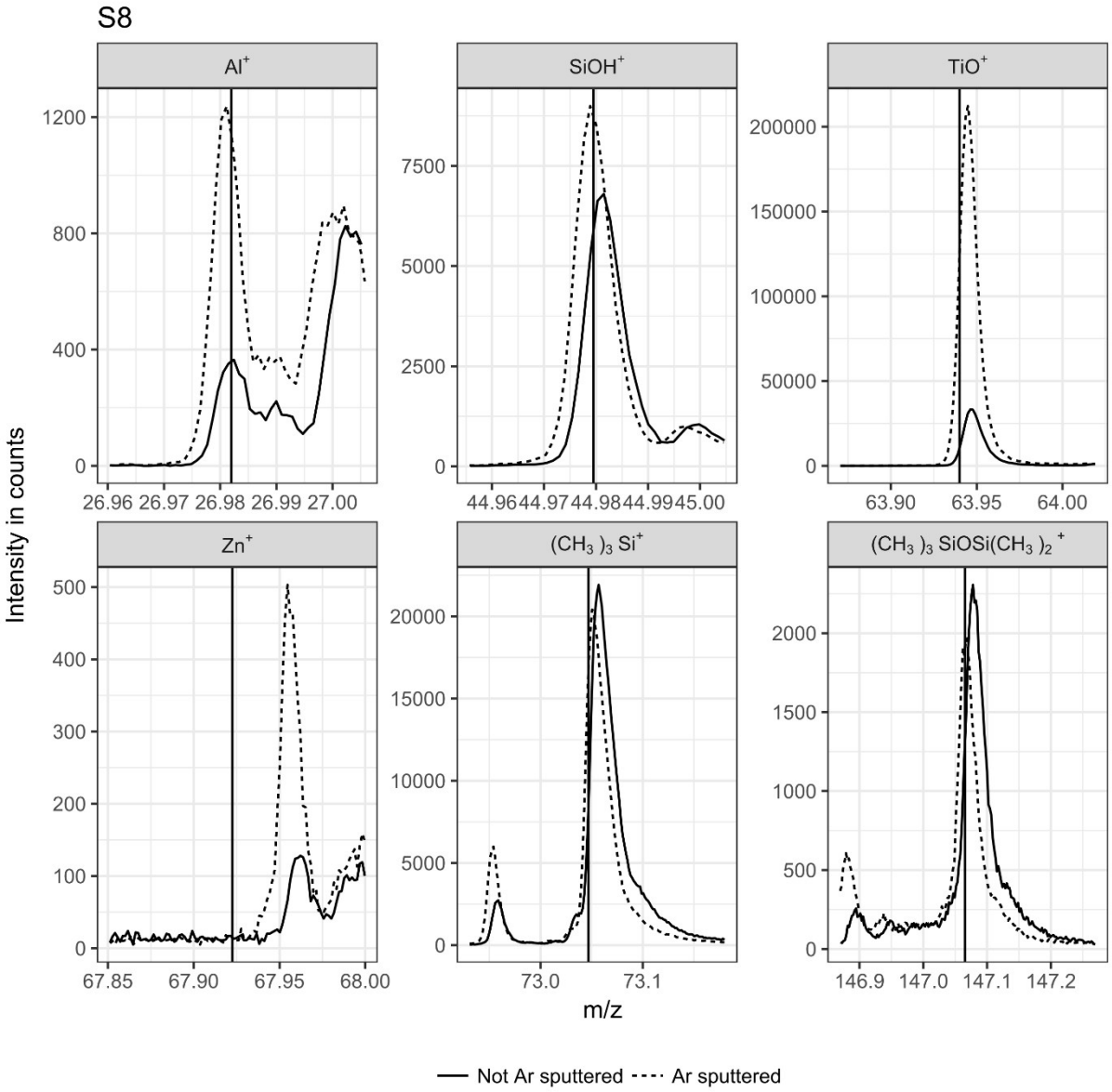

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198 **SI-Figure 11: ToF-SIMS signal intensities for the sunscreens extracts S8. See SI-figure 5 for more details.**

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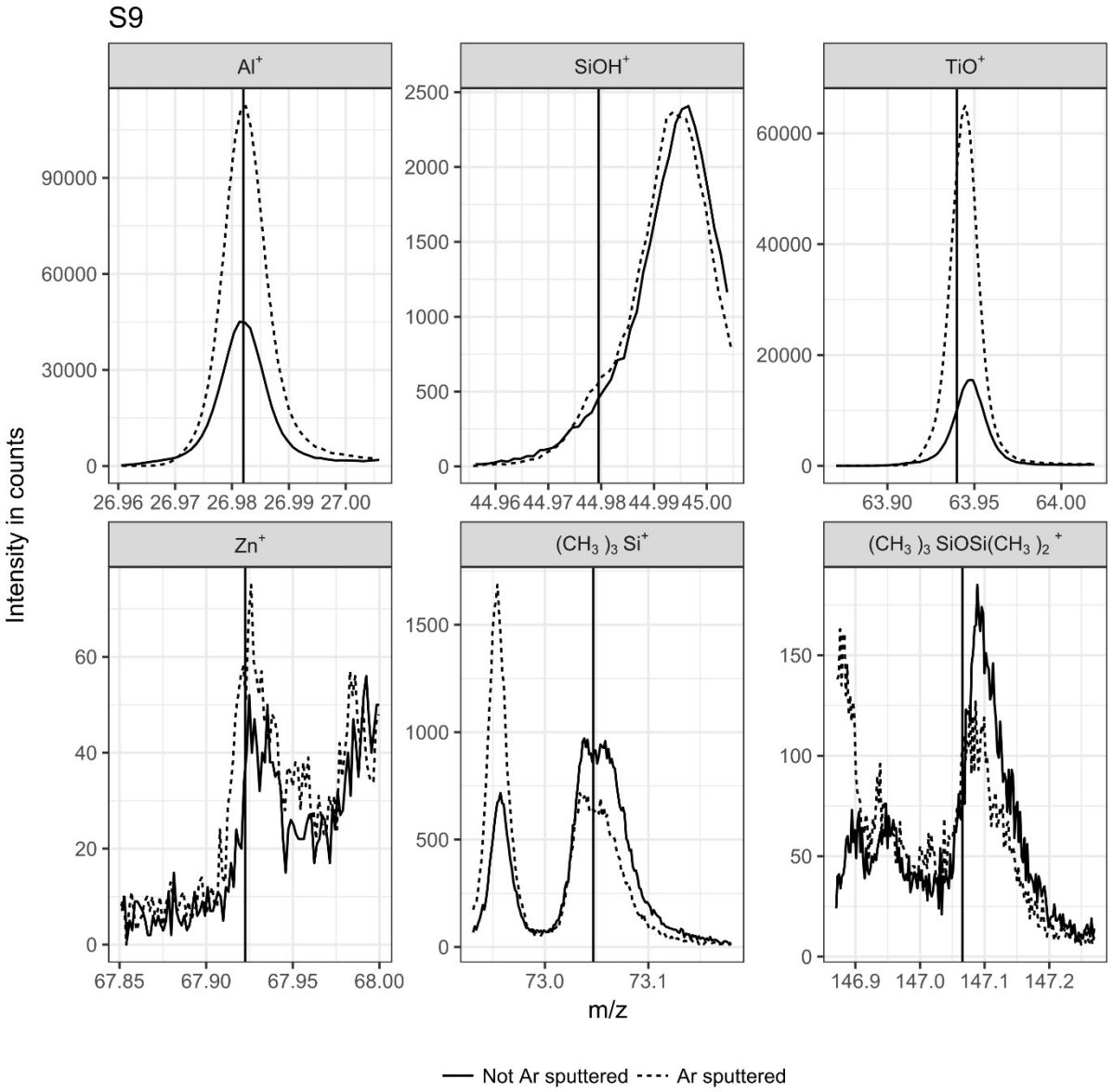

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201 **SI-Figure 12: ToF-SIMS signal intensities for the sunscreens extracts S9. See SI-figure 5 for more details.**

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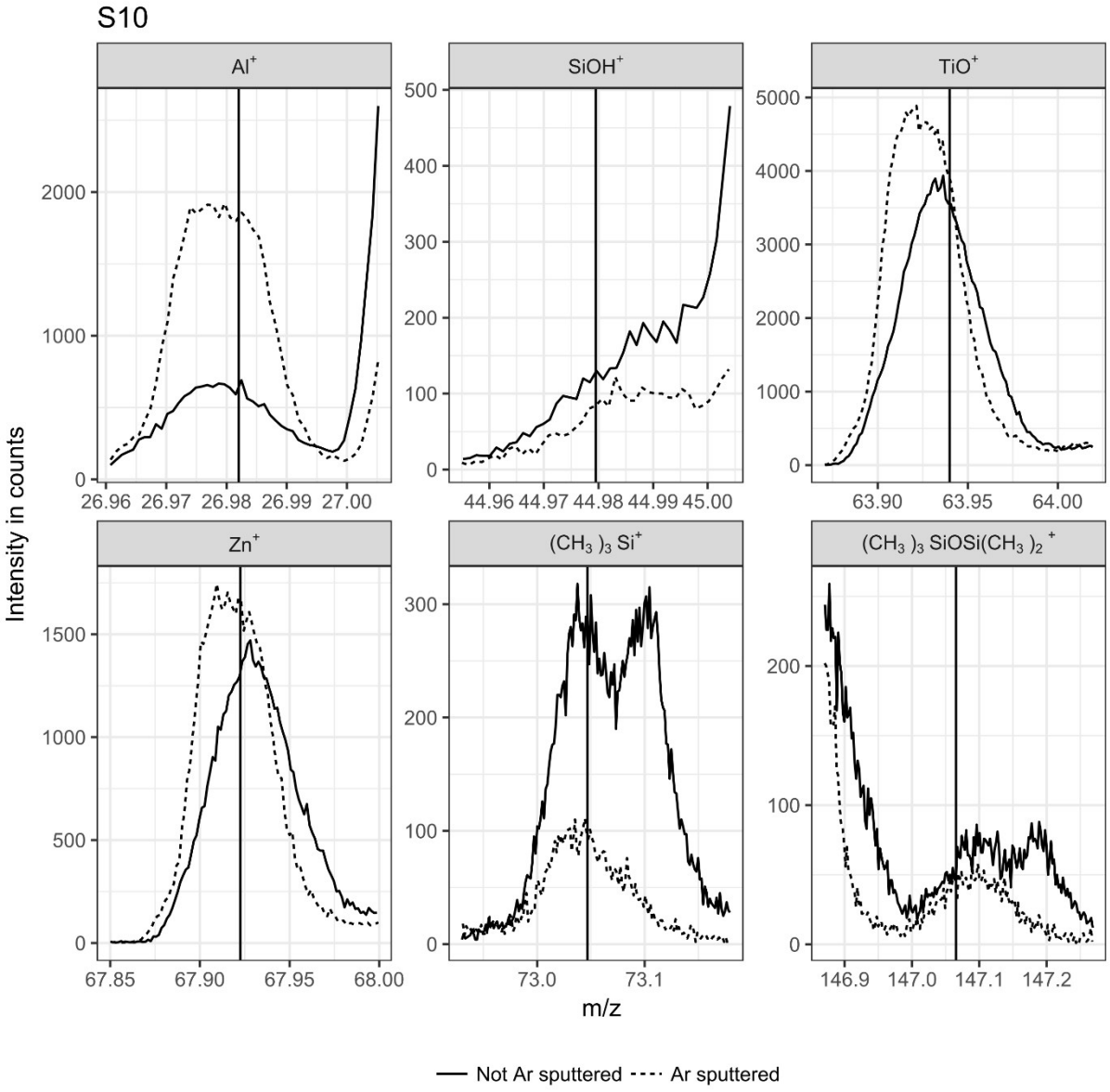

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204 **SI-Figure 13: ToF-SIMS signal intensities for the sunscreens extracts S10. See SI-figure 5 for more details.**

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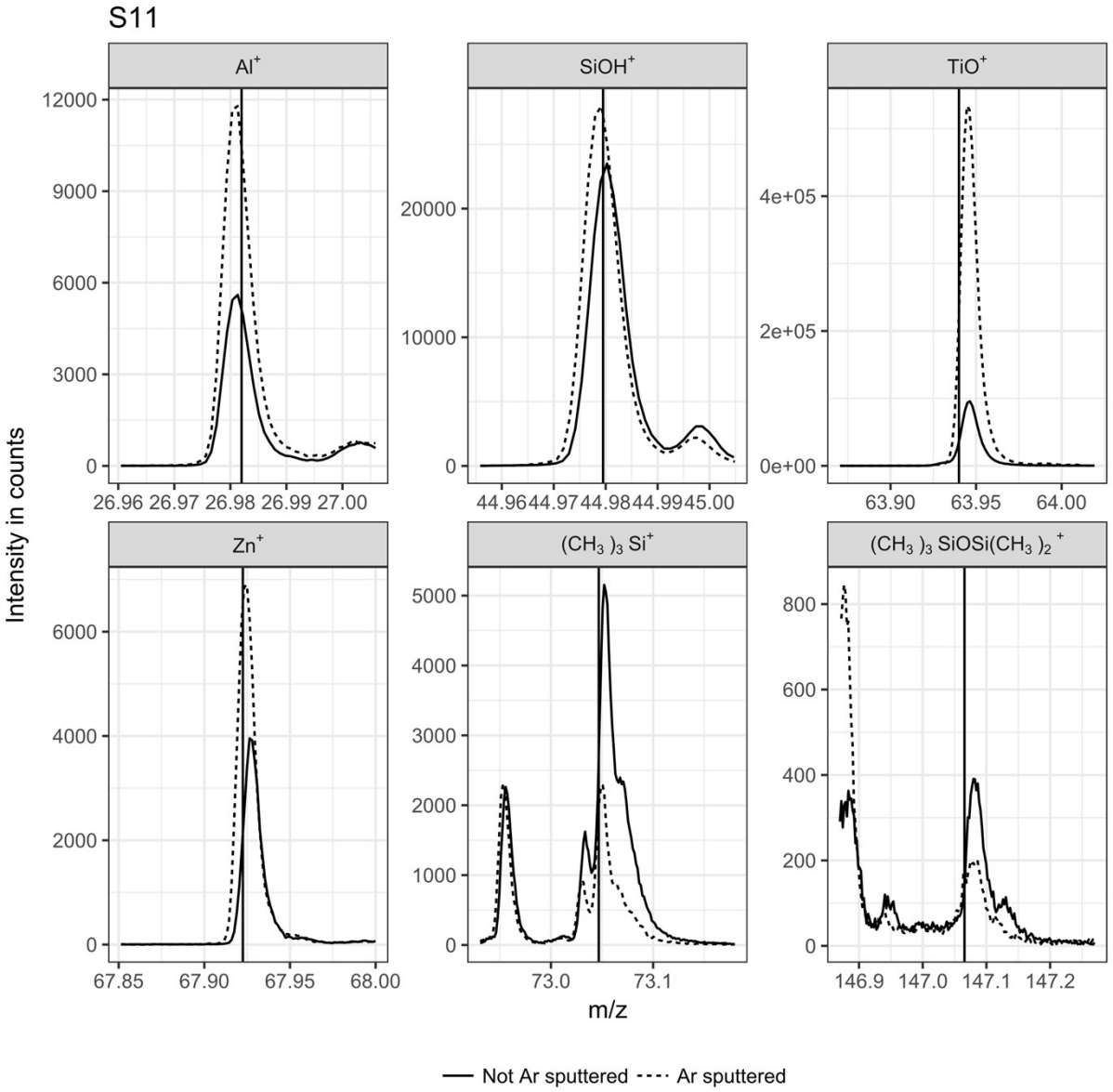

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207 **SI-Figure 14: ToF-SIMS signal intensities for the sunscreens extracts S11. See SI-figure 5 for more details.**

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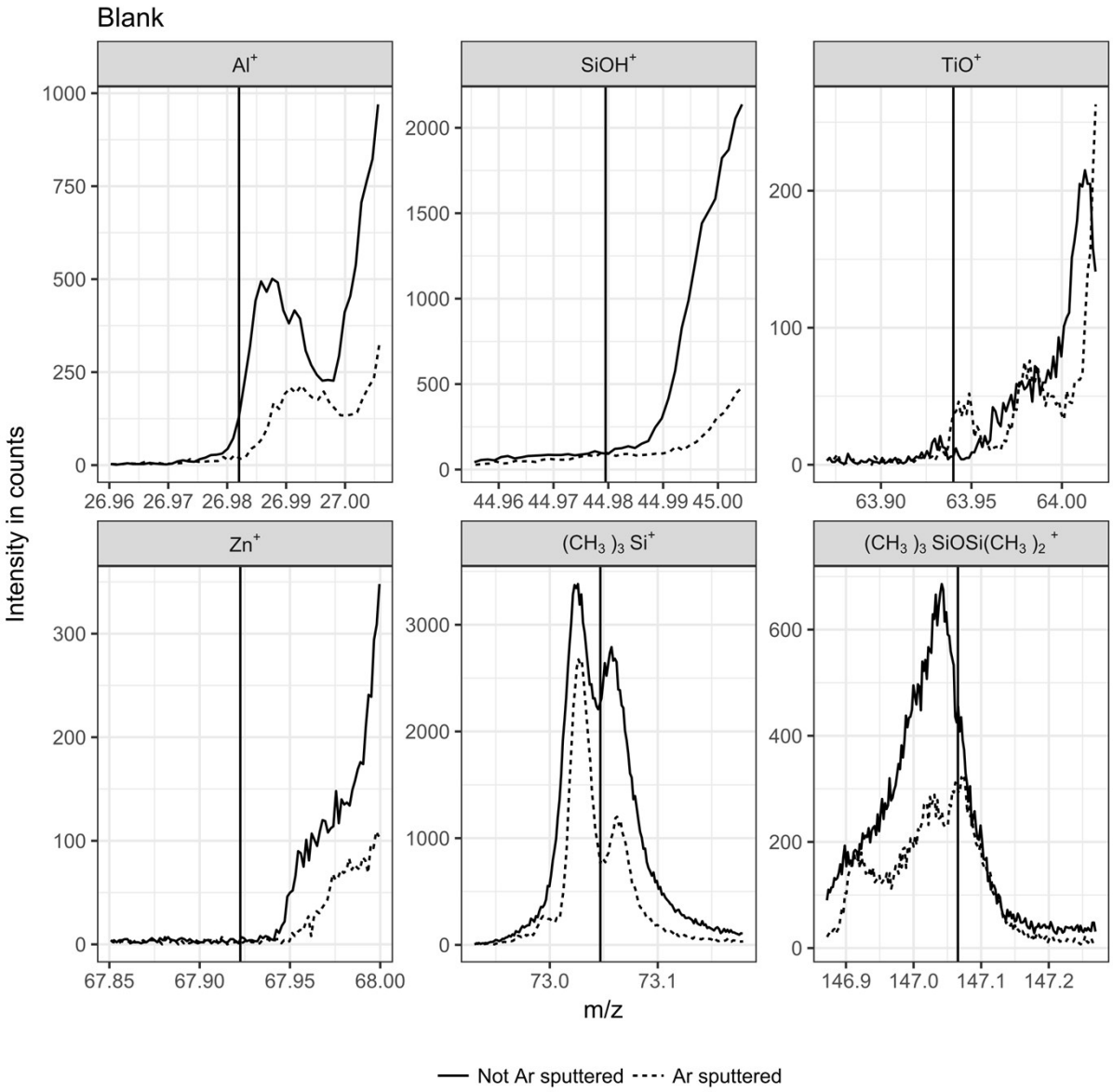

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210 **SI-Figure 15: ToF-SIMS signal intensities for the blank sample. See SI-figure 5 for more details.**