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Potential of gas-assisted time-of-flight secondary ion mass spectrometry for improving elemental characterization of complex metal-based systems

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SUPPORTING INFORMATION

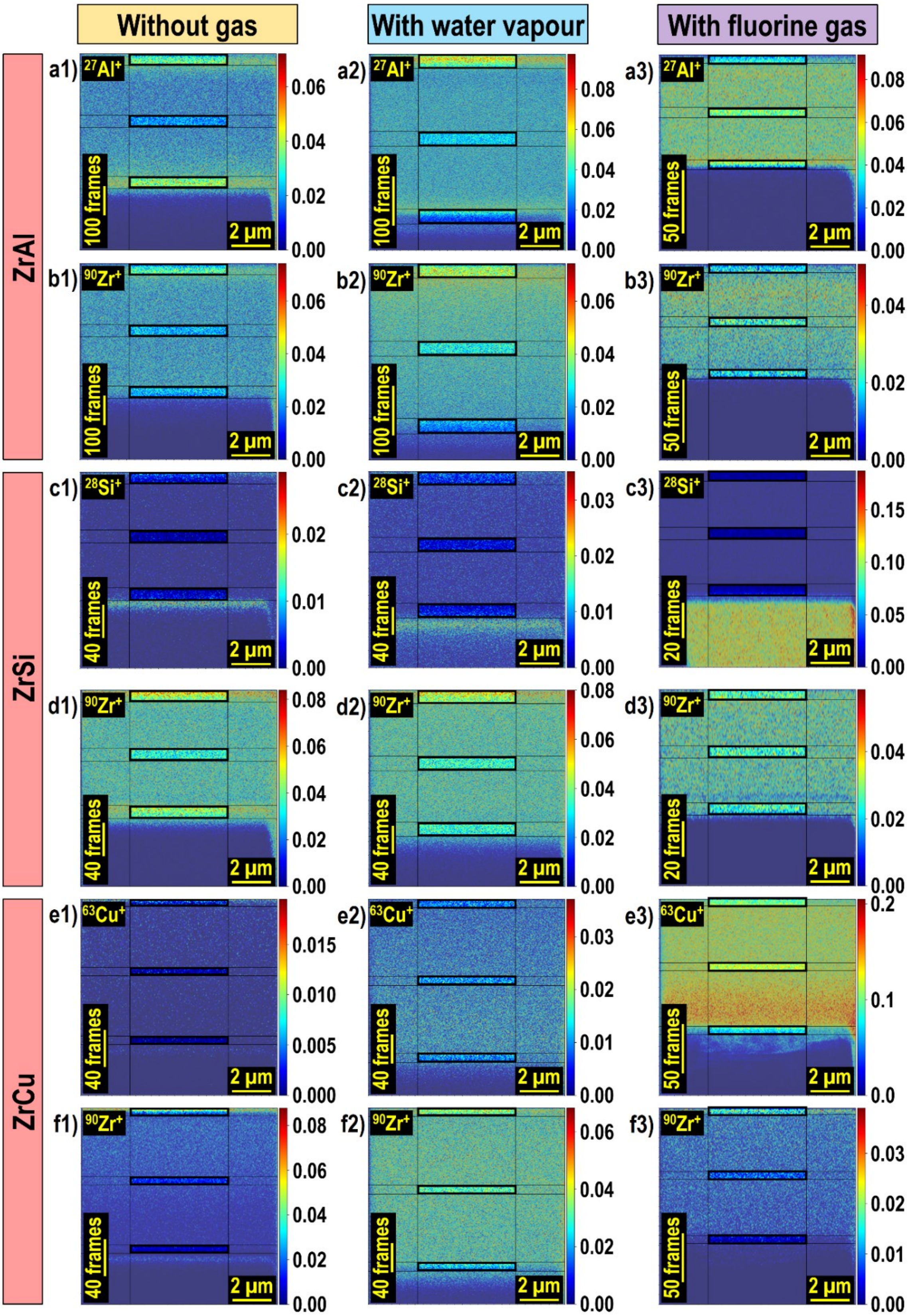

Figure S1. Elemental images in the lateral (*x*-*z*) plane of ZrAl, ZrSi and ZrCu alloys acquired under standard vacuum conditions (a1-f1), in the presence of water vapor (a2-f2) and fluorine gas (a3-f3). The black rectangles denote signal integration regions corresponding to 10 nm thickness of the measured thin films, which were used for generating the lateral (*x*-*y* plane) elemental images given in Figures S2-S4. The color scale is given in counts per pixel.

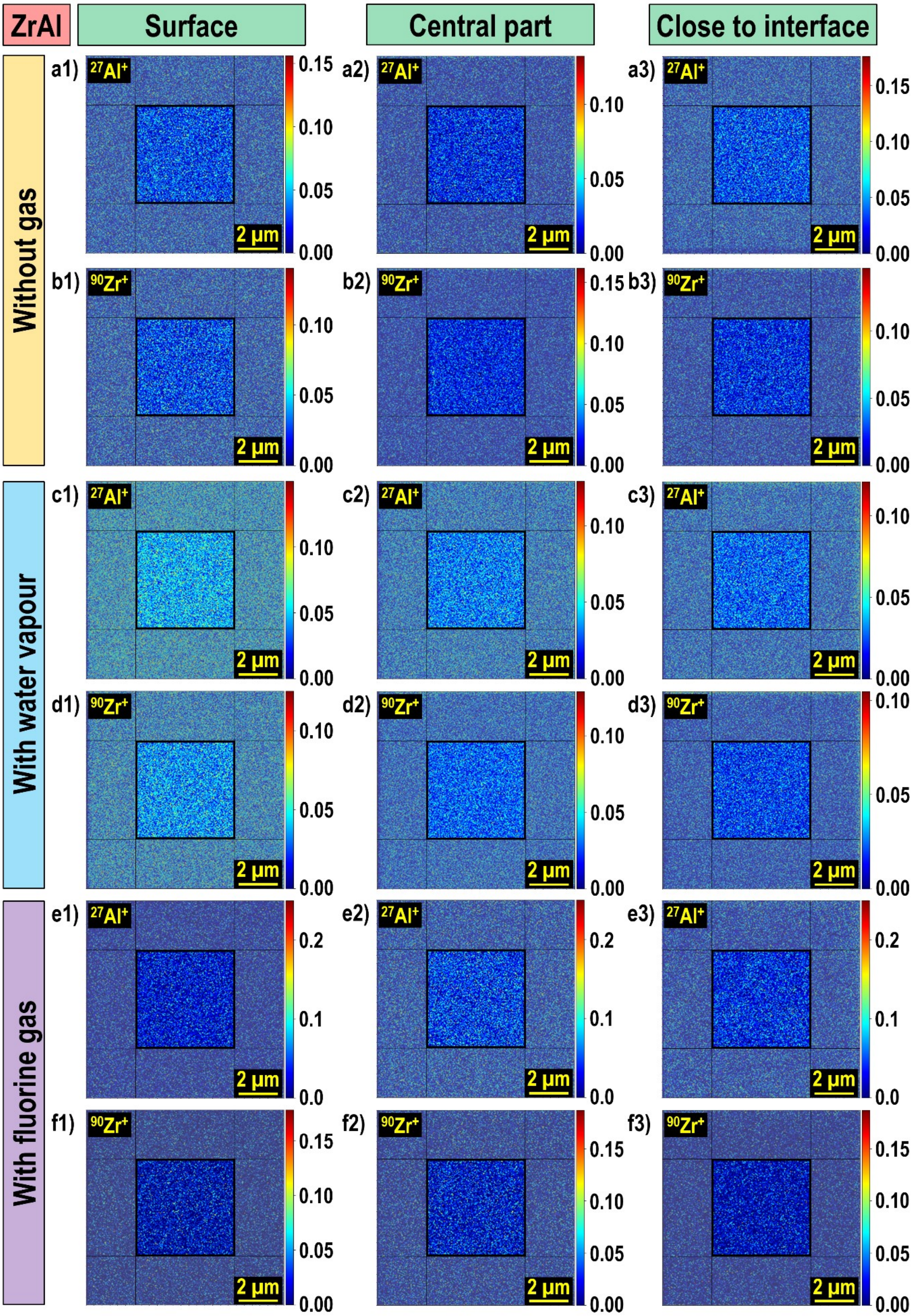

Figure S2. Elemental images in *x*-*y* plane of ZrAl acquired under standard vacuum conditions, in the presence of water vapor and fluorine gas. The black rectangle marks the central 5µm×5µm.

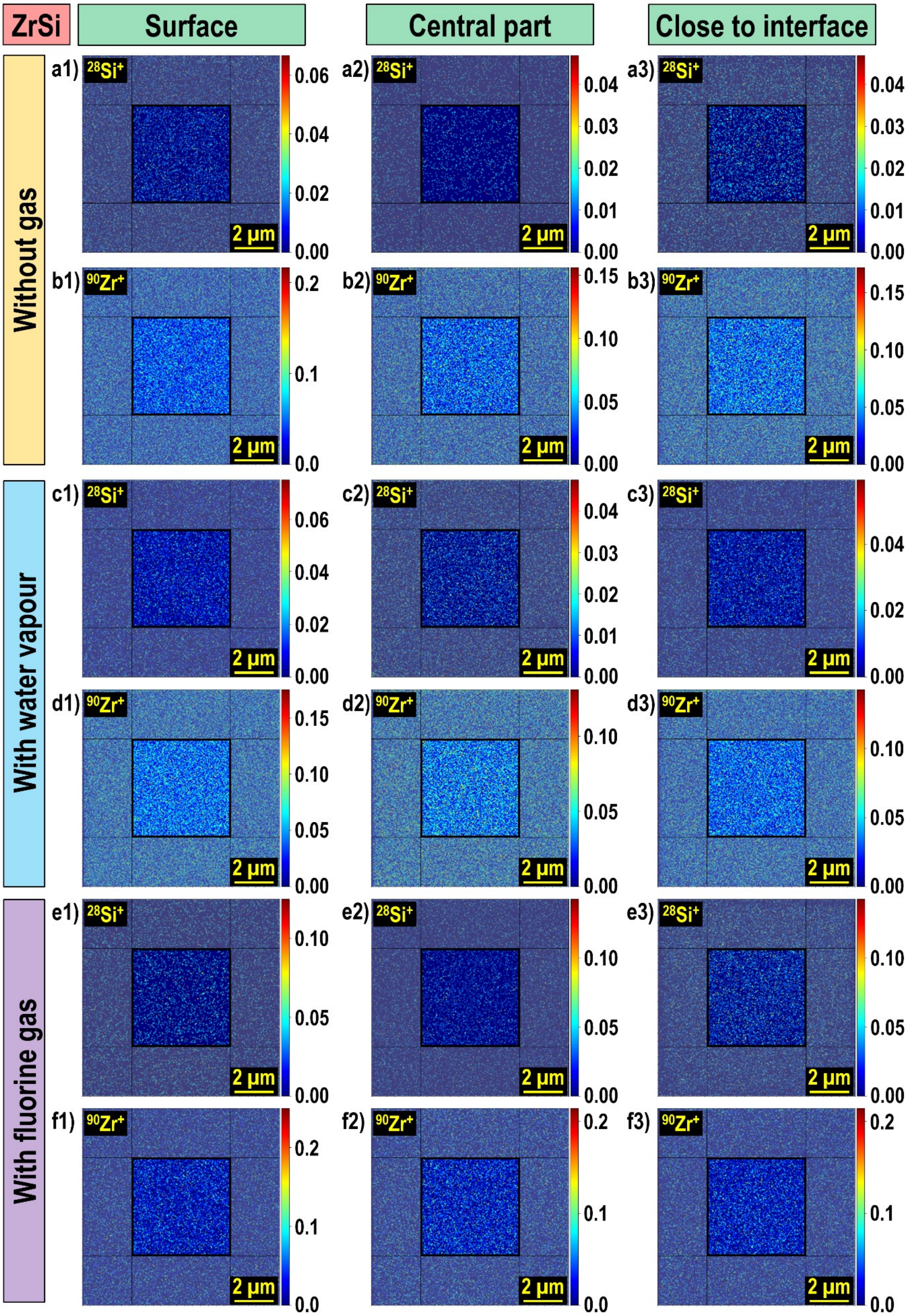

Figure S3. Elemental images in *x-y* plane of ZrSi acquired under standard vacuum conditions, in the presence of water vapor and fluorine gas. The black rectangle marks the central 5µm×5µm.

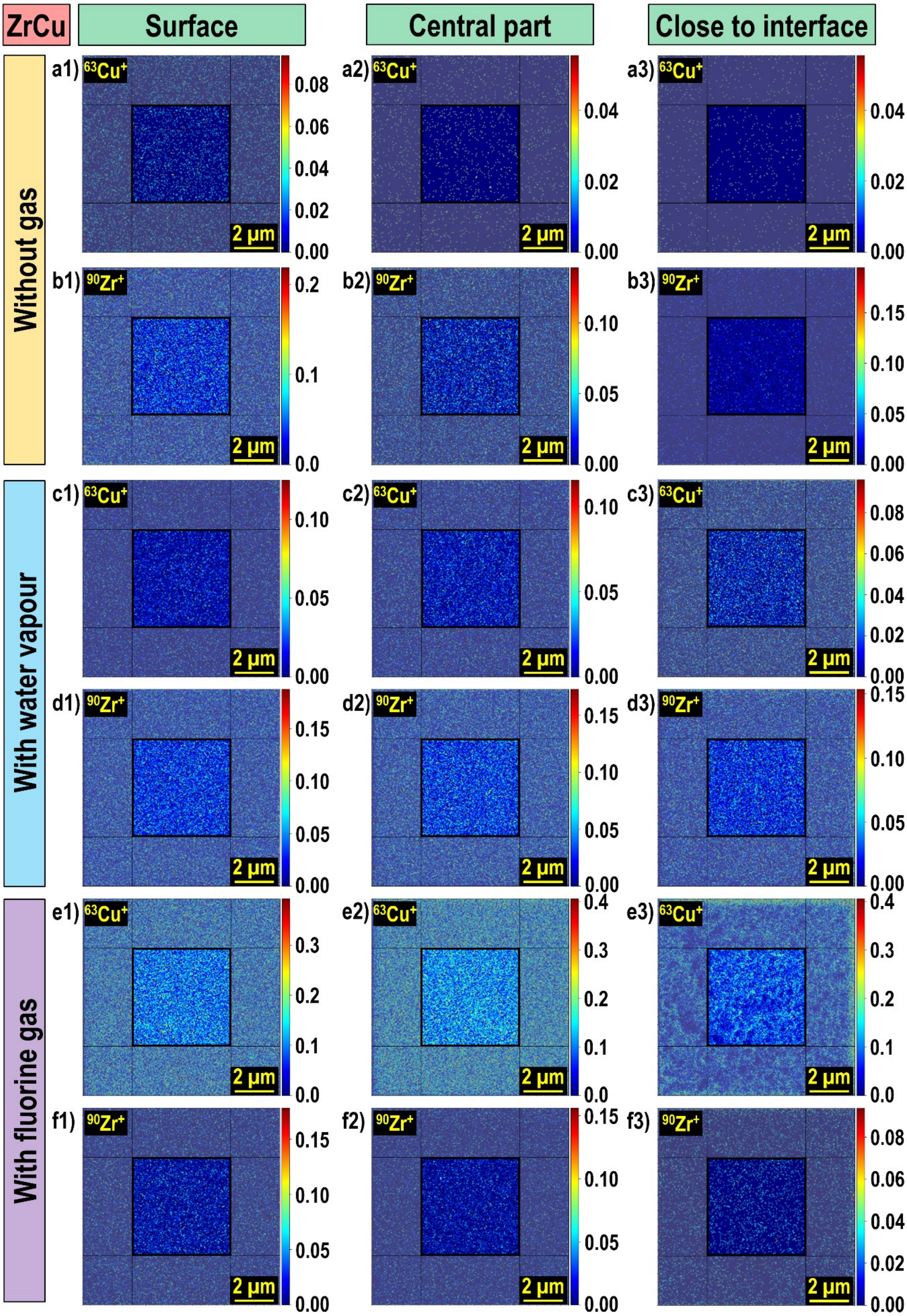

Figure S4. Elemental images in *x-y* plane of ZrCu acquired under standard vacuum conditions, in the presence of water vapor and fluorine gas. The black rectangle marks the central 5µm×5µm.

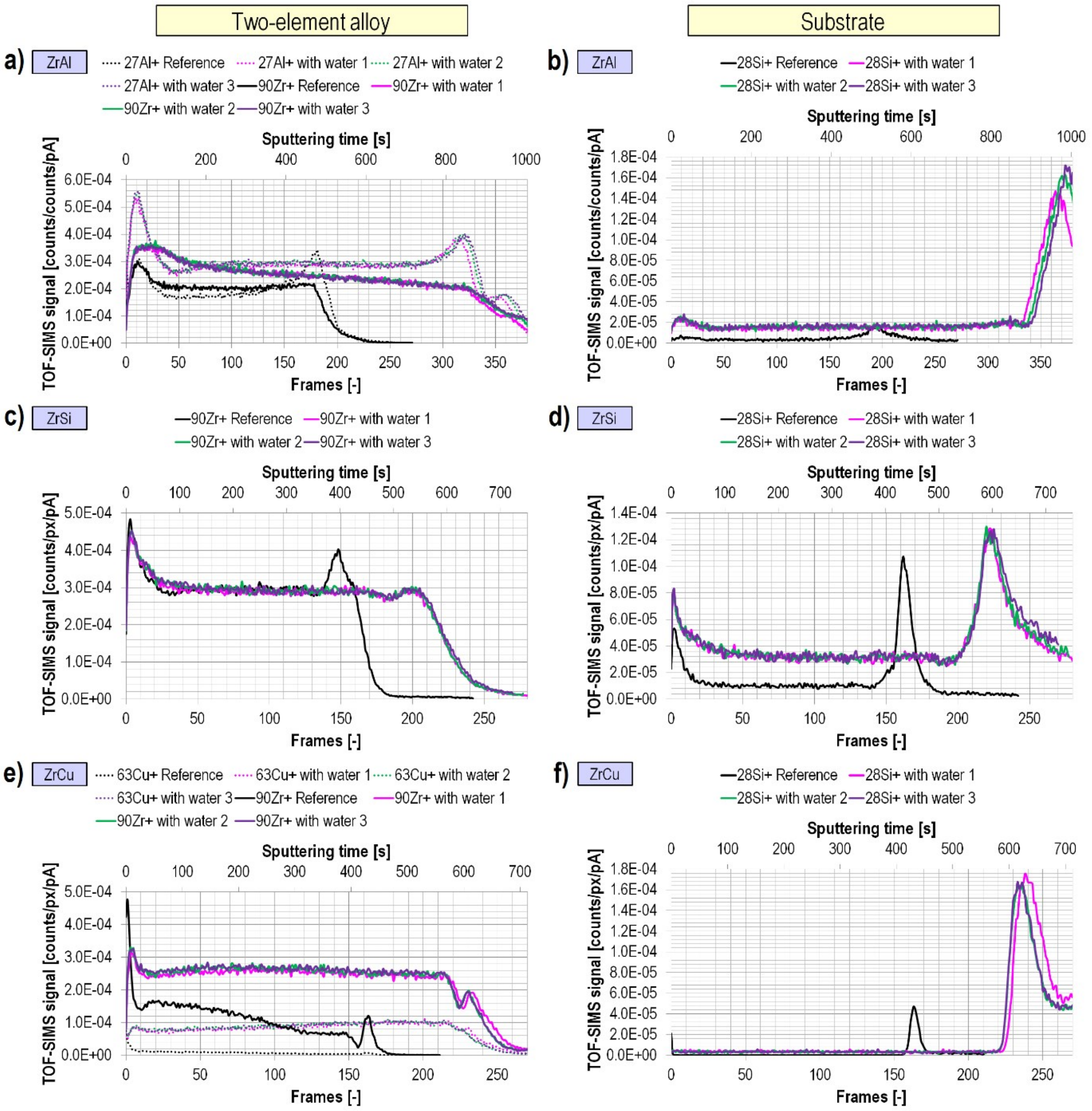

Figure S5. TOF-SIMS depth profiles of ZrAl, ZrSi and ZrCu samples obtained in the presence of water vapor. The signals of the most prominent isotopes of the thin films and the substrate are presented. The black lines represent reference measurements conducted under standard vacuum conditions and the colored lines show the results from water vapor-assisted measurements. Three measurements were performed to verify the reproducibility of the gas influence on the ionization efficiency.

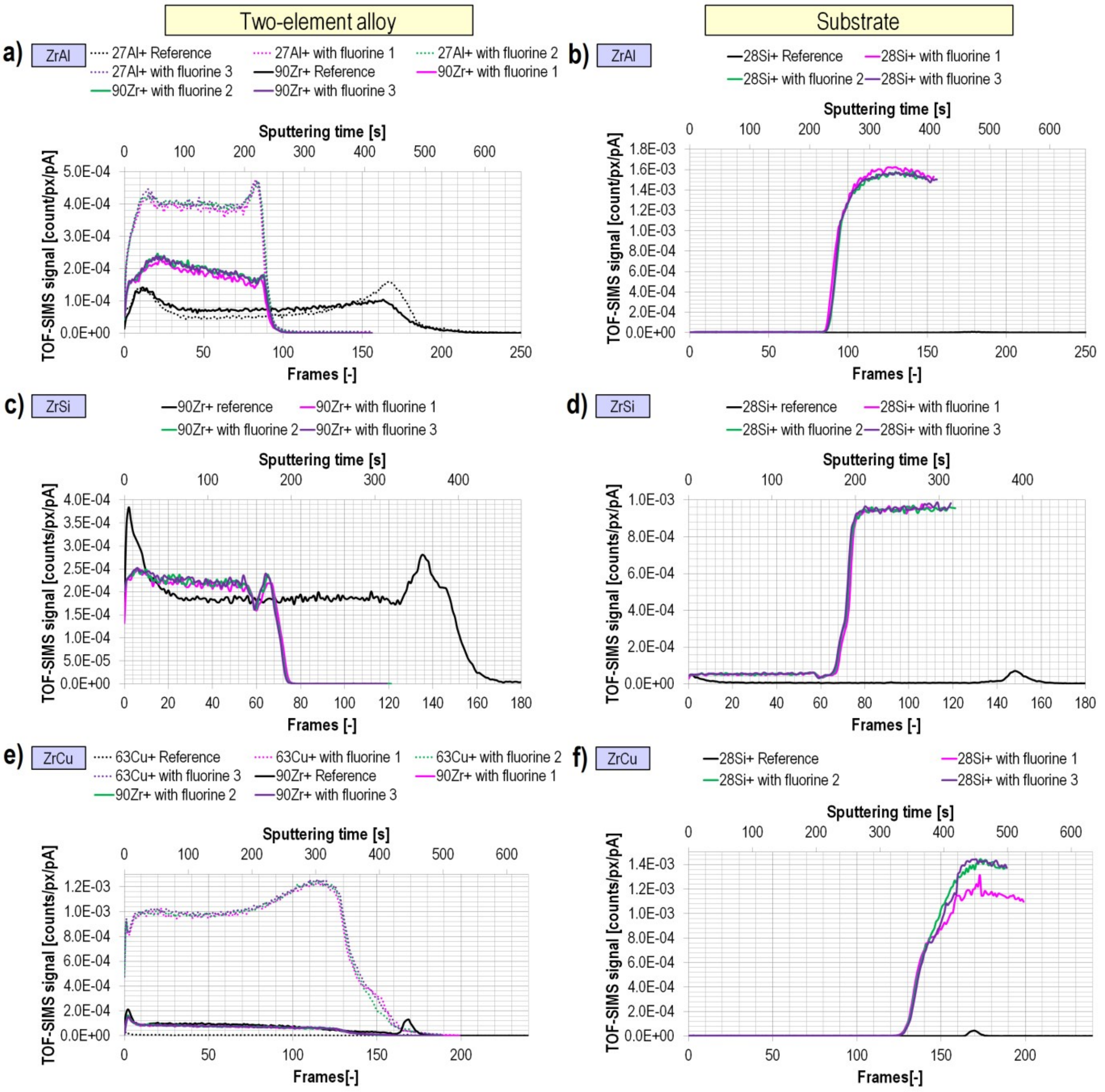

Figure S6. TOF-SIMS depth profiles of ZrAl, ZrSi and ZrCu samples obtained in the presence of fluorine gas. The signals of the most prominent isotopes of the thin films and the substrate are presented. The black lines represent reference measurements conducted under standard vacuum conditions and the colored lines show the results from fluorine gas-assisted measurements. Three measurements were performed to verify the reproducibility of the gas influence on the ionization efficiency.

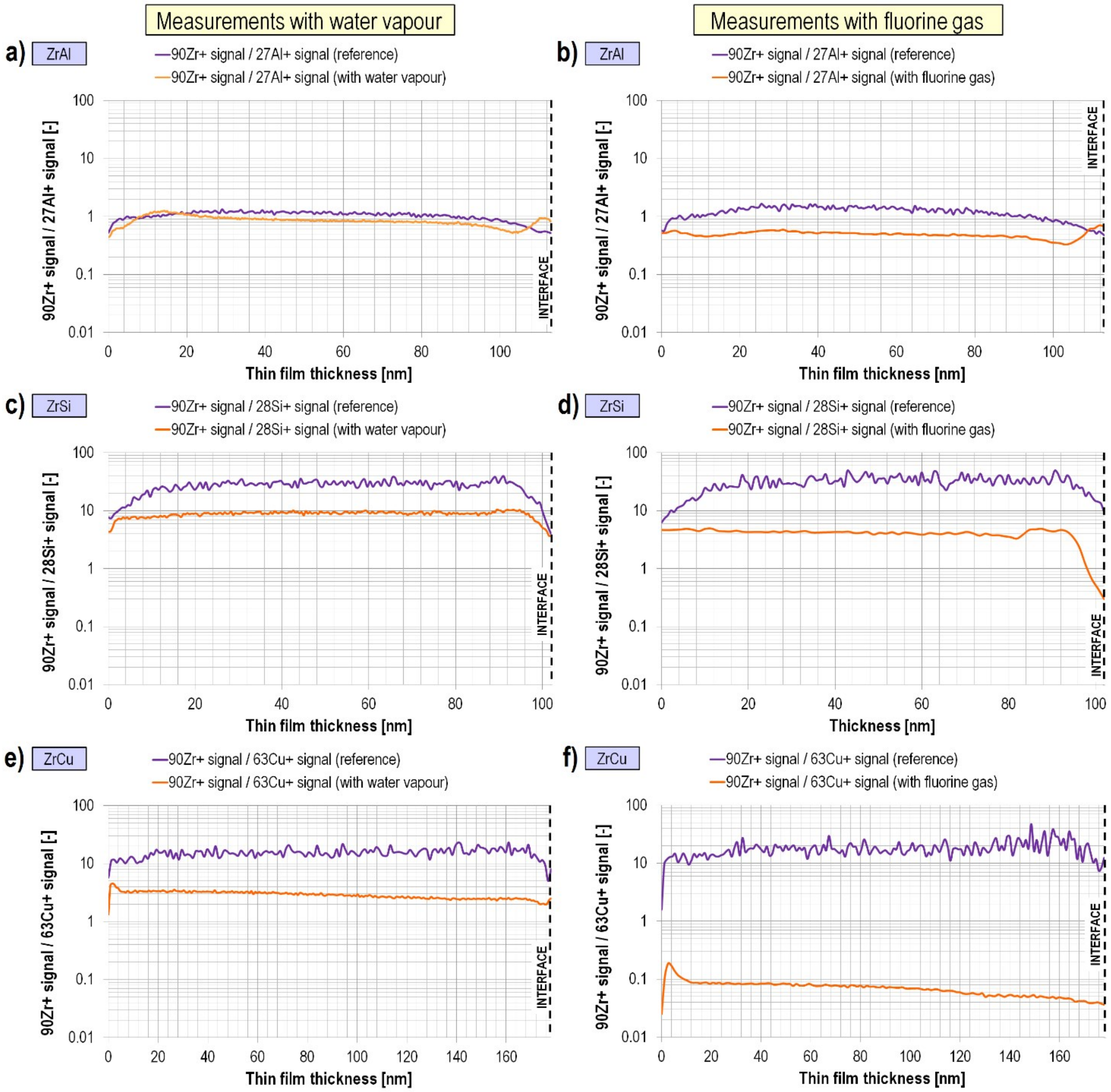

Figure S7. Distributions of the $^{90}Zr^+/^{x}M^+$ ratios across the ZrAl (a and b), ZrSi (c and d) and ZrCu (e and d) alloys. $^{x}M^+$ denotes $^{27}Al^+$, $^{28}Si^+$ and $^{63}Cu^+$ in the case of ZrAl, ZrSi and ZrCu, respectively. The plots are based on the data given in Figure 1. Note the logarithmic scale. This figure is also provided in the linear scale (Figure S8) for details.

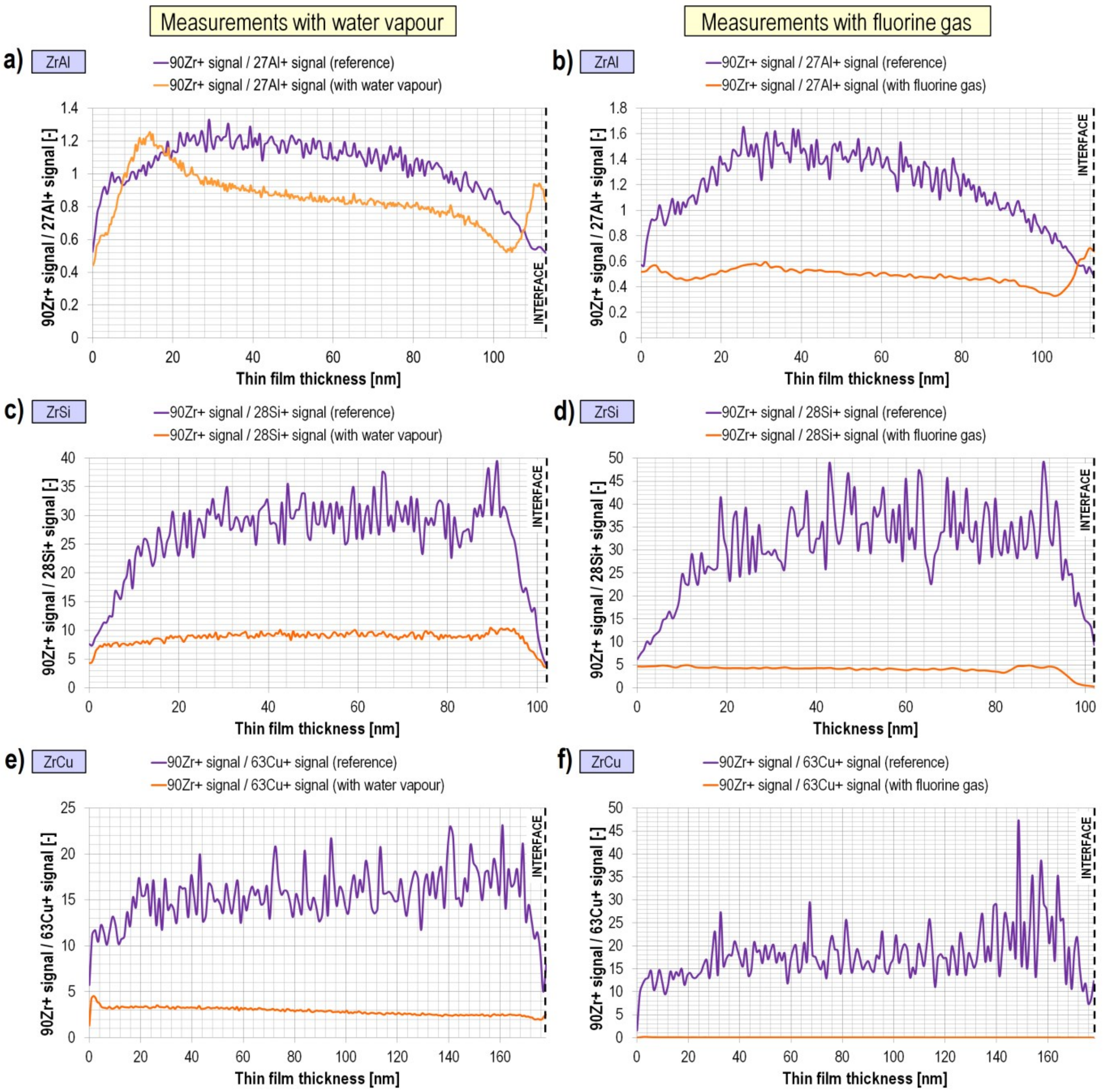

Figure S8. Distributions of the $^{90}Zr^+/^xM^+$ ratios across the ZrAl (a and b), ZrSi (c and d) and ZrCu (e and d) alloys. $^xM^+$ denotes $^{27}Al^+$, $^{28}Si^+$ and $^{63}Cu^+$ in the case of ZrAl, ZrSi and ZrCu, respectively. The plots are based on the data provided in Figure 1.

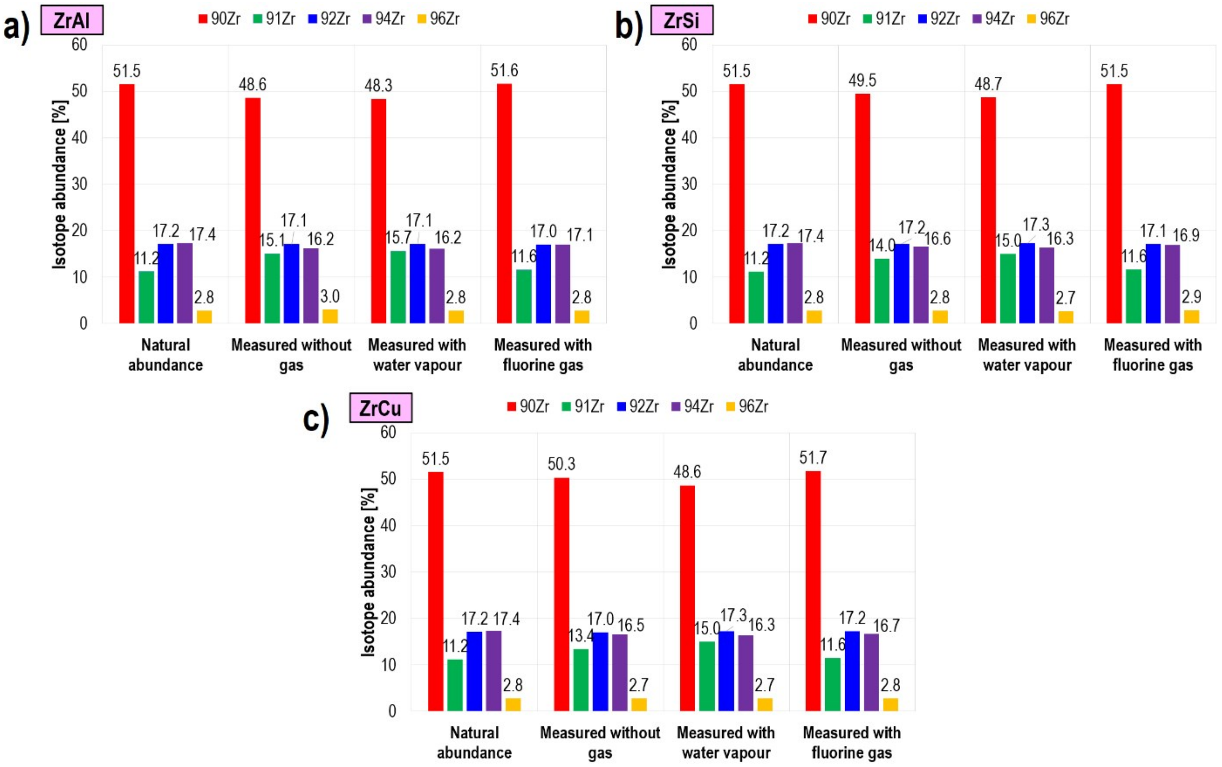

Figure S9. Zr isotope abundance measured in ZrAl (a), ZrSi (b) and ZrCu (c) under standard vacuum conditions, with water vapor and with fluorine gas in comparison to natural Zr isotope abundance.

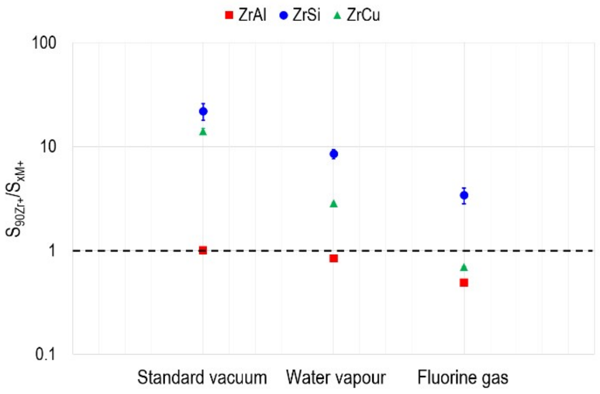

Figure S10. S_{90Zr+}/S_{xM+} (*M* stands for Al, Si and Cu and *x* represents 27, 28 and 63, for ZrAl, ZrSi and ZrCu, respectively) signal ratios obtained during the TOF-SIMS measurements conducted under standard vacuum conditions, in the presence of water vapor and fluorine gas. The data is given in the logarithmic scale.

Table S1. Summary of the results obtained during water-vapor assisted TOF-SIMS analysis (*wv*).

Alloy	Moment of reaching the interface [frames]		Total TOF-SIMS signal in the thin film [counts/pixel/pA/nm]			
	$t_{int,ref}$	$t_{int,wv}$	$S_{90Zr+,ref}$	$S_{xM+,ref}$	$S_{90Zr+,wv}$	$S_{xM+,wv}$
ZrAl	187±5	347±4	$(3.49\pm0.07)\times10^{-4}$	$(3.5\pm0.2)\times10^{-4}$	$(7.72\pm0.05)\times10^{-4}$	$(9.23\pm0.06)\times10^{-4}$
ZrSi	159±3	213±5	$(4.86\pm0.09)\times10^{-4}$	$(2.2\pm0.3)\times10^{-5}$	$(6.3\pm0.2)\times10^{-4}$	$(7.4\pm0.5)\times10^{-5}$
ZrCu	157±2	229±2	$(1.07\pm0.06)\times10^{-4}$	$(7.57\pm0.05)\times10^{-6}$	$(3.27\pm0.03)\times10^{-4}$	$(1.147\pm0.009)\times10^{-4}$

The moment of reaching the interface, t_{int}, and the total TOF-SIMS signal measured across the thin film, *S*, are provided. *M* denotes Al, Si or Cu in the case of ZrAl, ZrSi and ZrCu, respectively, and *x* stands for 27, 28 and 63, correspondingly. The values measured without any gas are marked with *ref* index. This data was used for the calculations given in Table 1.

Table S2. Summary of the results obtained during fluorine gas-assisted TOF-SIMS analysis (*f*).

Alloy	Moment of reaching the interface [frames]		Total TOF-SIMS signal in the thin film [counts/pixel/pA/nm]			
	$t_{int,ref}$	$t_{int,f}$	$S_{90Zr+,ref}$	$S_{xM+,ref}$	$S_{90Zr+,f}$	$S_{xM+,f}$
ZrAl	173±5*	91±2	$(1.28\pm0.04)\times10^{-4}$ *	$(1.18\pm0.08)\times10^{-4}$ *	$(1.51\pm0.02)\times10^{-4}$	$(3.10\pm0.03)\times10^{-4}$
ZrSi	126±2*	71±2	$(2.9\pm0.2)\times10^{-4}$ *	$(1.18\pm0.08)\times10^{-5}$ *	$(1.52\pm0.03)\times10^{-4}$	$(4.5\pm0.6)\times10^{-5}$
ZrCu	164±4*	138±5	$(6.8\pm0.3)\times10^{-5}$ *	$(4.6\pm0.2)\times10^{-6}$ *	$(5.57\pm0.09)\times10^{-5}$	$(8.0\pm0.3)\times10^{-4}$

Moment of reaching the interface, t_{int}, and the total TOF-SIMS signal measured across the thin film, *S*, are provided. *M* denotes Al, Si or Cu in the case of ZrAl, ZrSi and ZrCu, respectively, and *x* stands for 27, 28 and 63, correspondingly. The values measured without any gas are marked with *ref* index. This data was used for the calculations given in Table 2. *-data obtained from[1].

(1) Priebe, A.; Xie, T.; Bürki, G.; Pethö, L.; Michler, J. Matrix Effect in TOF-SIMS Analysis of Two-Element Inorganic Thin Films. *J. Anal. At. Spectrom.* **2020**. https://doi.org/10.1039/C9JA00428A.