

Electronic Supplementary Information: Empirical evaluation of the TXRF detector field of view – a coffee-ring case study

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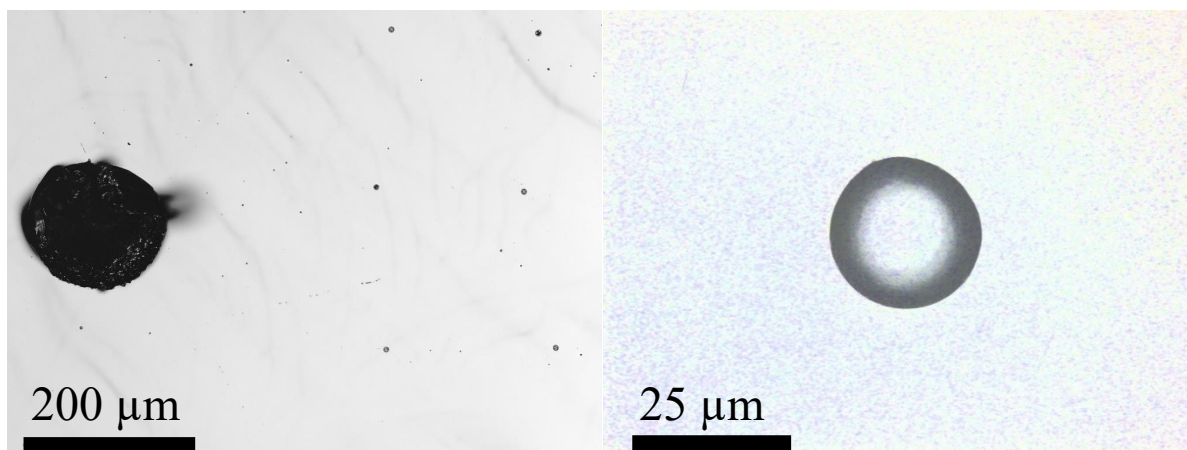
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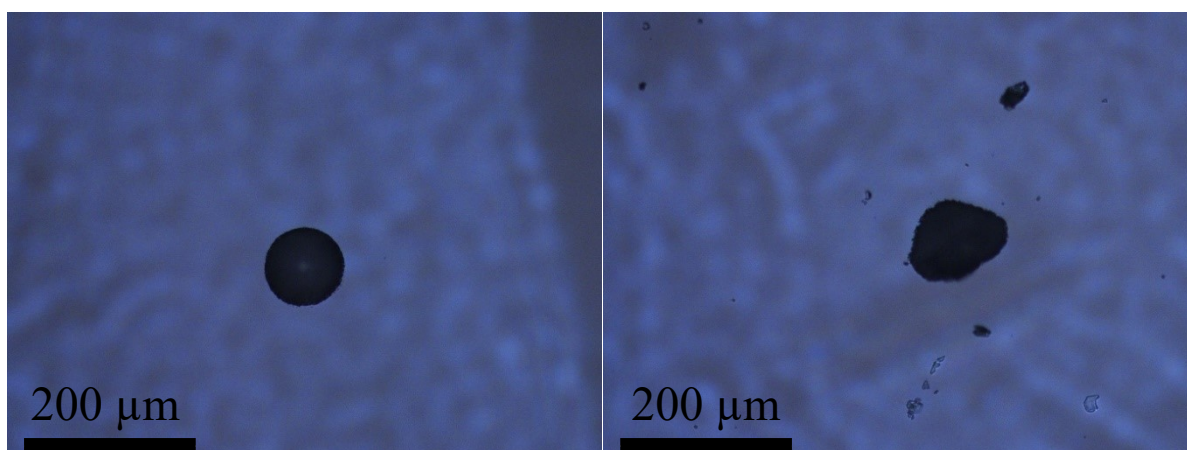
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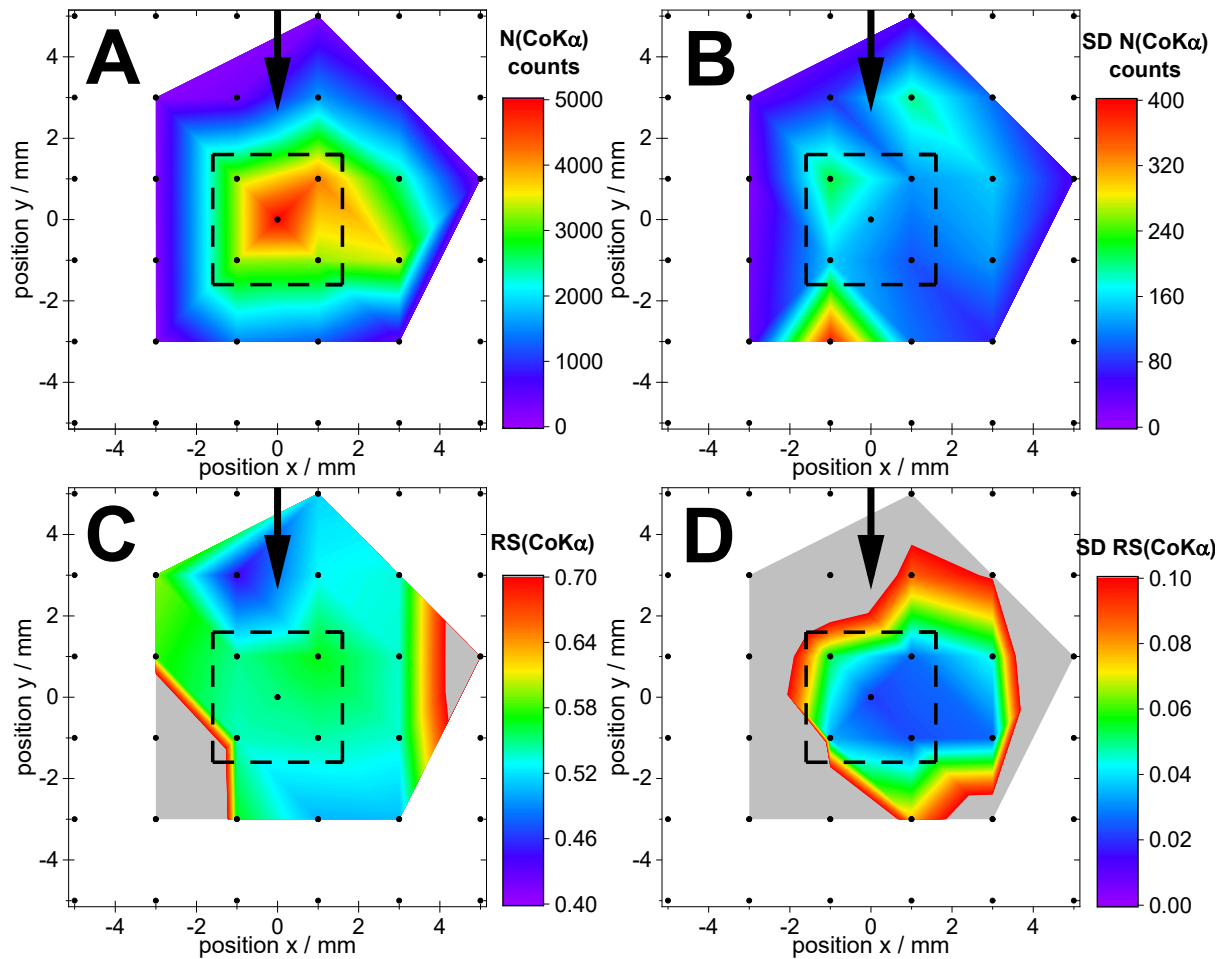


**Figure S1: Laser intensity images from confocal laser scanning microscopy of typical picoliter derived specimens. A large residue (150 μm diameter, 60 μm height) is shown along small residues (25 μm diameter, 9 μm height)**

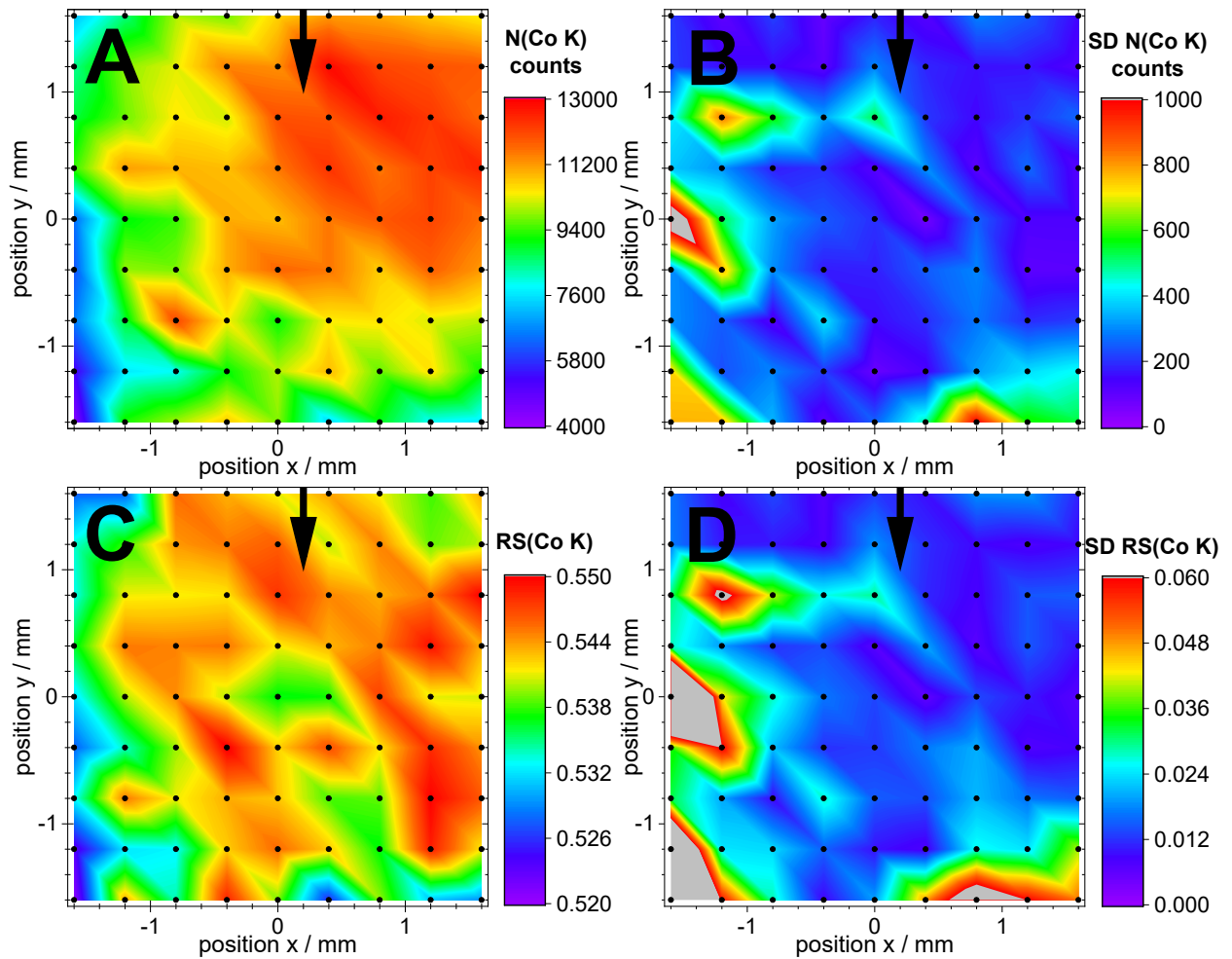


**Figure S2: Optical microscopy images of residues from the second series of picoliter derived specimens for the FOV determination with a) round shape and b) distorted shape.**

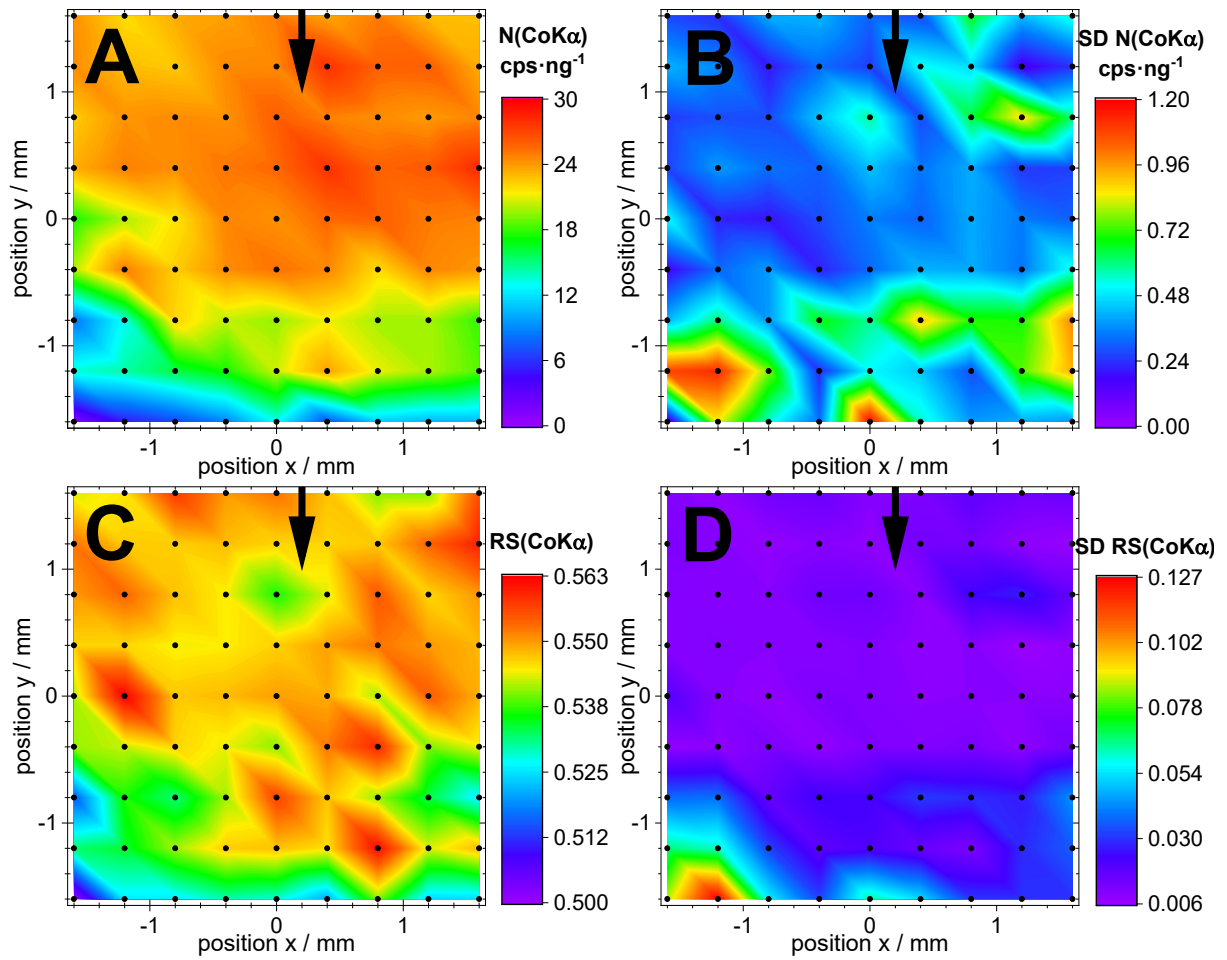
In general, colour maps show the net intensities of Co  $K\alpha$ -line, the standard deviation of the net intensities, and the sensitivities at each point relative to the Ga  $K\alpha$ -line. Each black dot represents the position of an individual sample.



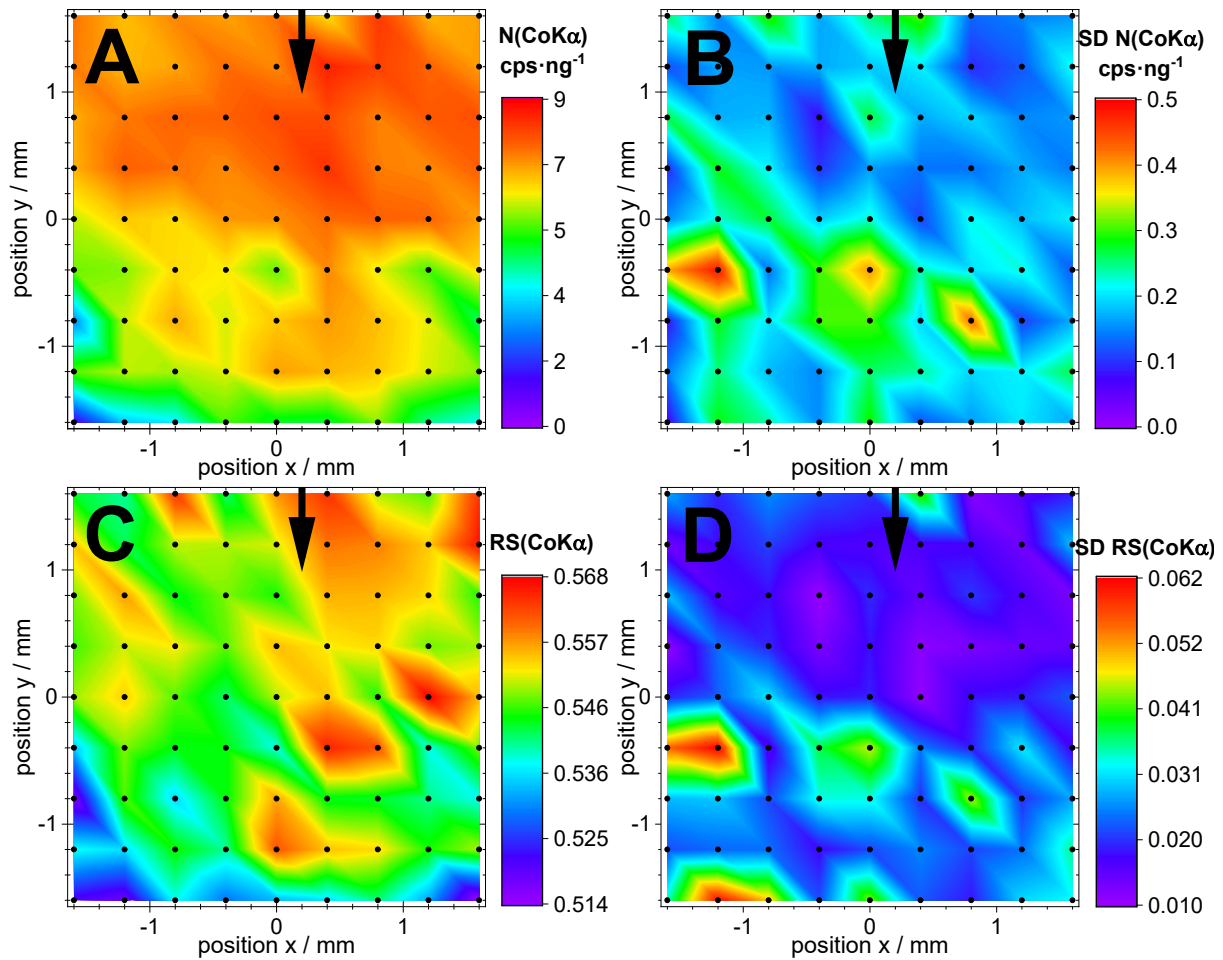
**Figure S3: Intensity and sensitivity distribution of Co  $K\alpha$ -lines for the first series. Net intensity (panel A), SD of the net intensity ( $n = 6$ , panel B), the local RS (panel C), and the SD of the local RS ( $n = 6$ , panel D). Each black dot represents the position of an individual sample. The arrows indicate the direction of the incident X-rays. Grey colour exceeds the scale, while white colour shows no valid data points.**



**Figure S4: Intensity and sensitivity distribution of Co K $\alpha$ -lines for the second series. Net intensity (panel A), SD of the net intensity ( $n = 6$ , panel B), the local RS (panel C), and the SD of the local RS ( $n = 6$ , panel D). Each black dot represents the position of an individual sample. The arrows indicate the direction of the incident X-rays. Grey colour exceeds the scale, while violet falls below the scale.**



**Figure S5: Merged intensity and sensitivity distribution of Co  $K\alpha$ -lines after alignment of detector unit and autosampler. Normalized intensity (panel A), SD of the normalized intensity ( $n = 6$ , panel B), the local RS (panel C), and the SD of the local RS ( $n = 6$ , panel D). Each black dot represents the position of an individual sample. The black arrow shows the direction of the incident X-rays.**



**Figure S6: Merged intensity and sensitivity distribution of Co  $K\alpha$ -lines with Goebel mirror optics after alignment of detector unit and autosampler. Normalized intensity (panel A), SD of the normalized intensity ( $n = 6$ , panel B), the local RS (panel C), and the SD of the local RS ( $n = 6$ , panel D). Each black dot represents the position of an individual sample. The black arrow shows the direction of the incident X-rays.**