Supplementary Material

Comparison of optical techniques and MeV SIMS in determining deposition order between optically distinguishable and indistinguishable writing tools

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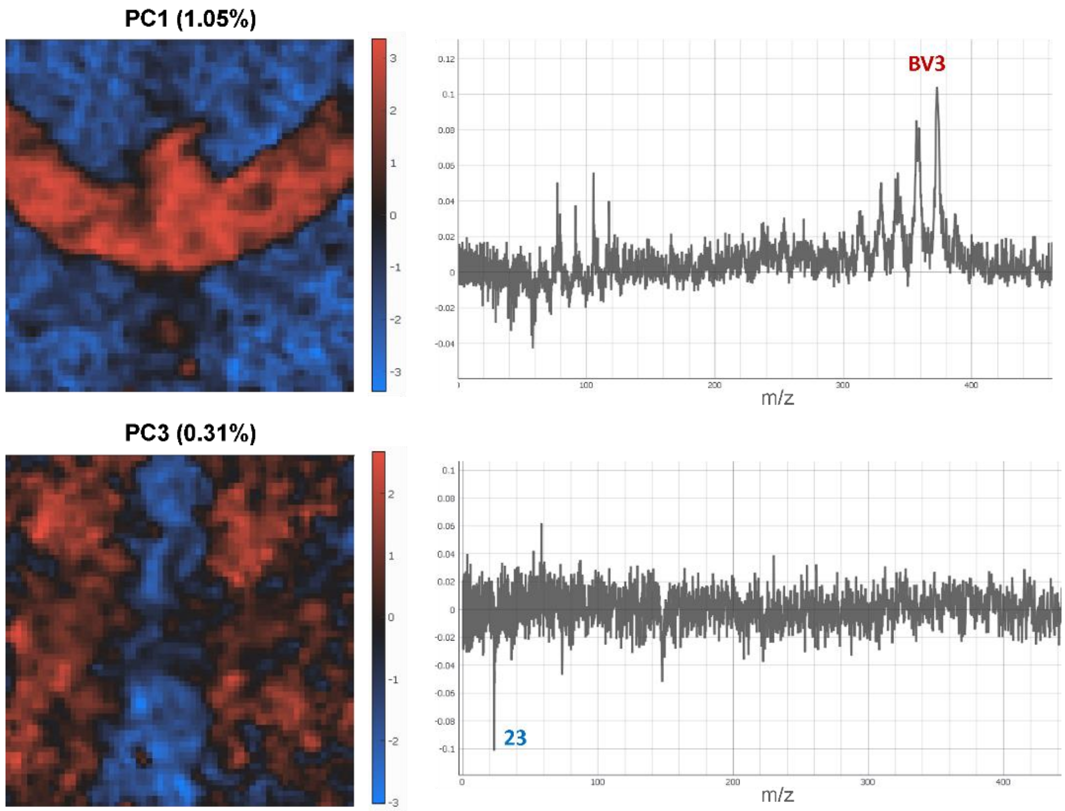

*Figure S-1. PCA results for **fountain pen over BIC** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC3), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.8 was applied. All calculated principal components were autoscaled.This sample had a low number of counts collected.*

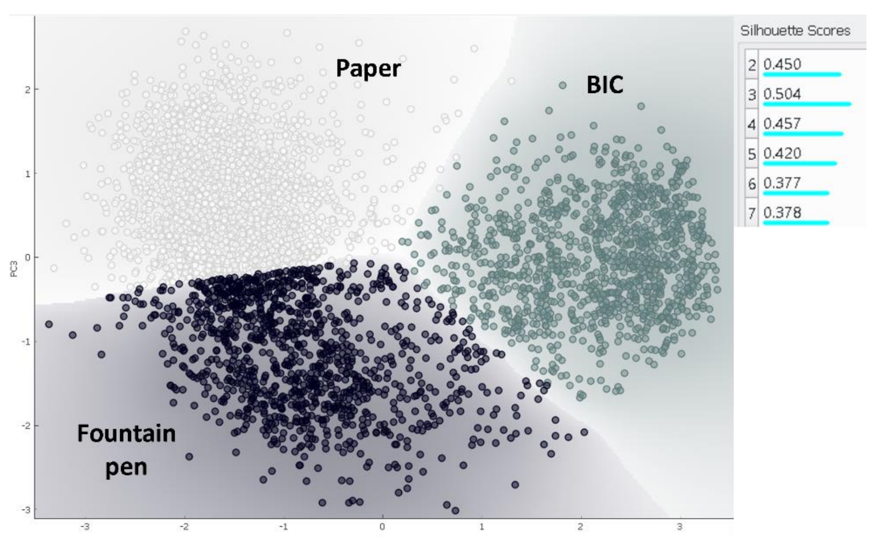

Figure S-2. K-means clustering on pixels represented in autoscaled PC1-PC3 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to BIC ink, fountain pen ink and paper.

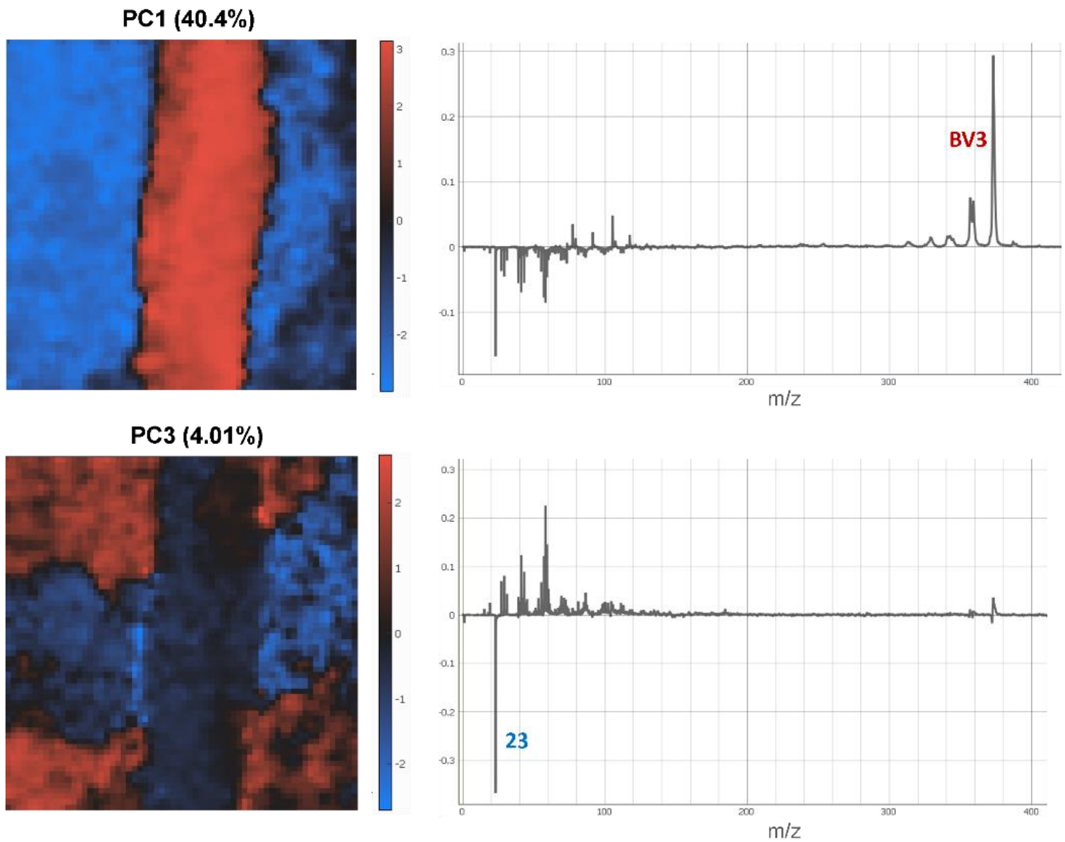

*Figure S-3. PCA results for **BIC over fountain pen** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC3), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.8 was applied. All calculated principal components were autoscaled.*

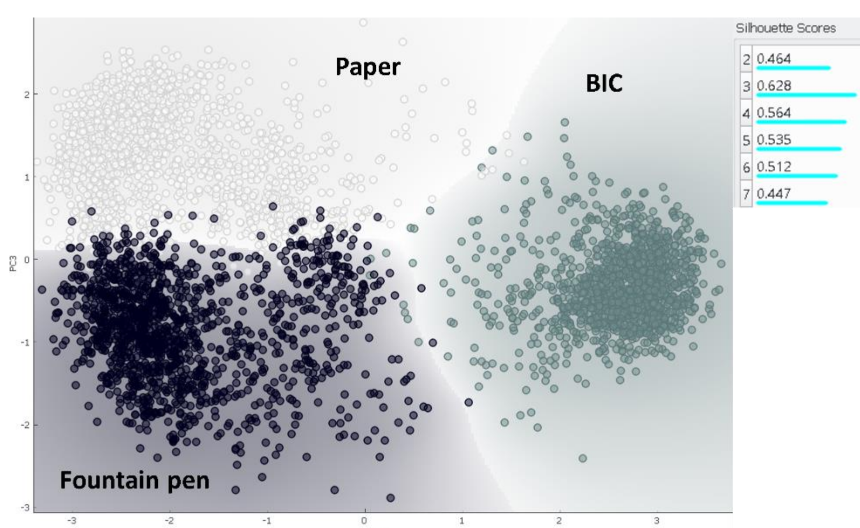

Figure S-4. K-means clustering on pixels represented in PC1-PC3 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to BIC ink, fountain pen ink and paper.

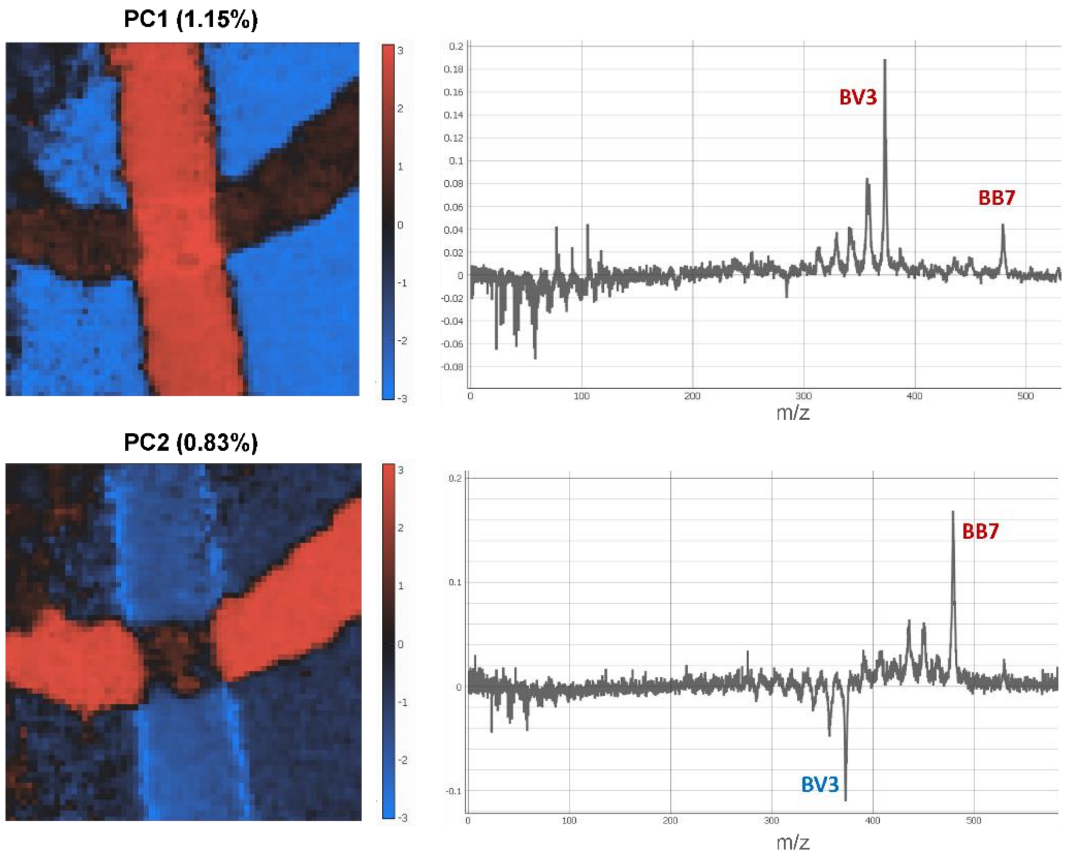

*Figure S-5. PCA results for **BIC over Pilot** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC2), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by Poisson scaling + mean centering. A Gaussian smoothing filter with SD=0.6 was applied. All calculated principal components were autoscaled.*

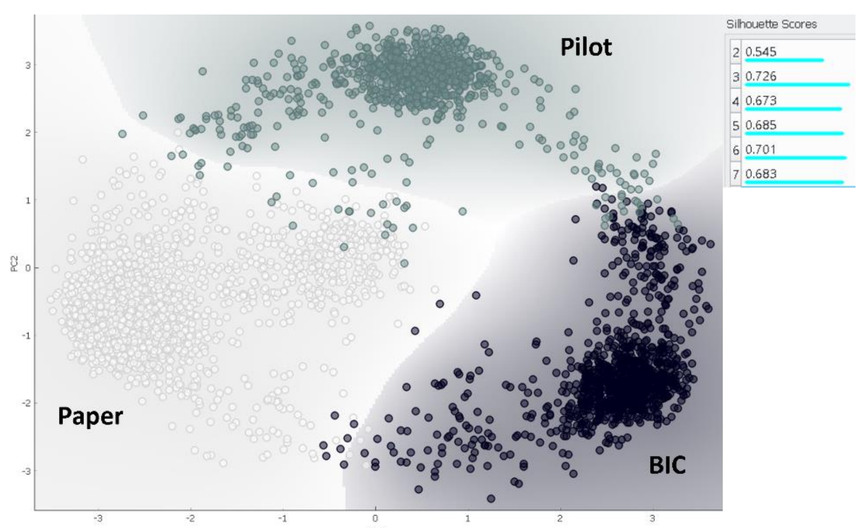

Figure S-6. K-means clustering on pixels represented in PC1-PC2 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to BIC ink, Pilot ink and paper. Higher number of clusters separates the paper cluster into multiple regions, probably due to morphology.

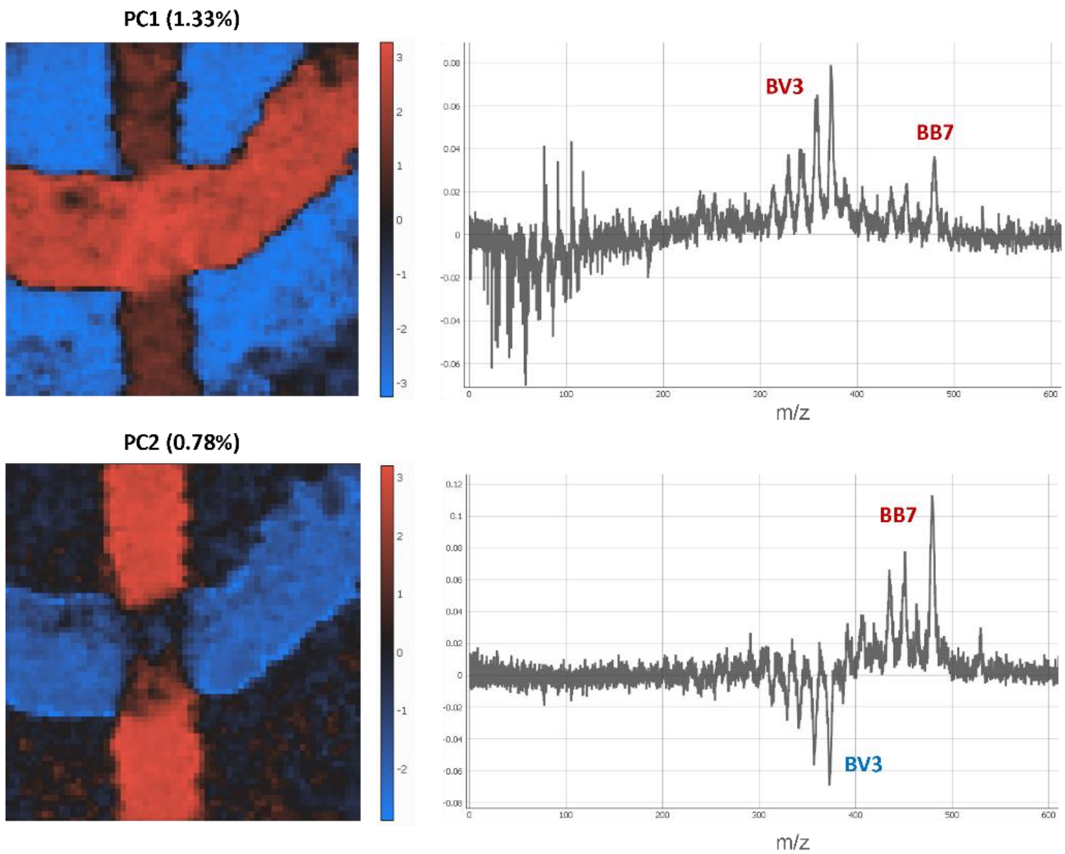

*Figure S-7. PCA results for **Pilot over BIC** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC2), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by Poisson scaling + mean centering. A Gaussian smoothing filter with SD=0.6 was applied. All calculated principal components were autoscaled.*

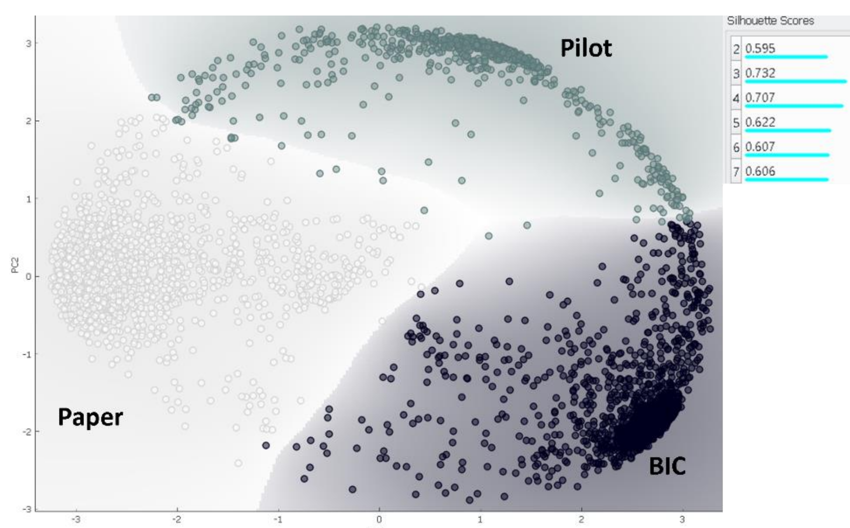

Figure S-8. K-means clustering on pixels represented in PC1-PC2 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to BIC ink, Pilot ink and paper. The second highest silhouette score (4 clusters) separates the paper cluster into two regions, probably due to morphology.

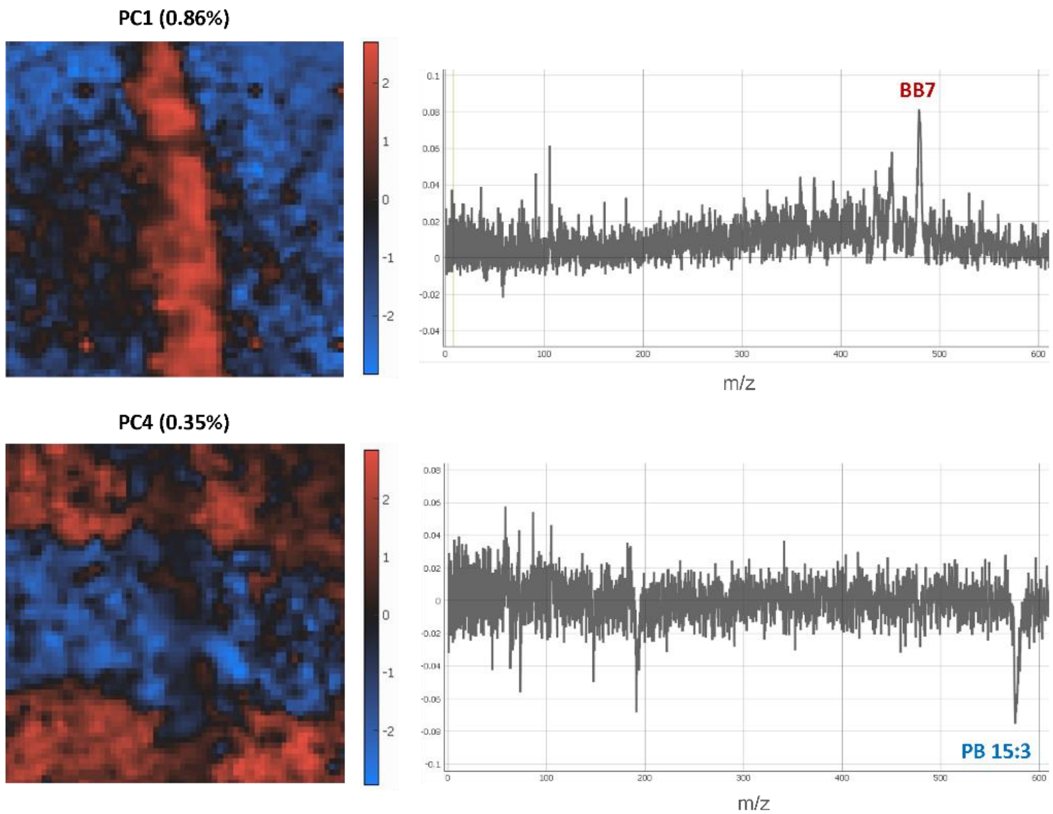

*Figure S-9. PCA results for **Pilot over Trodat Printy** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC4), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.8 was applied. All calculated principal components were autoscaled. This sample had a low number of counts collected.*

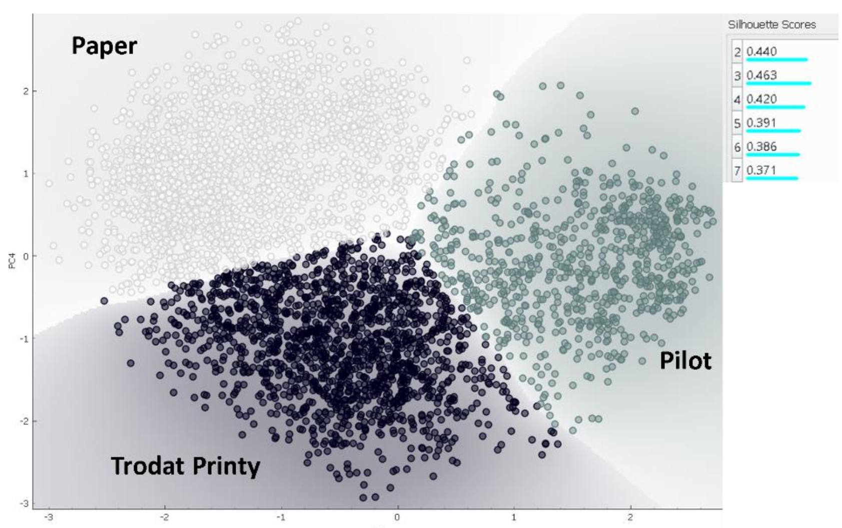

Figure S-10. K-means clustering on pixels represented in PC1-PC4 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to Pilot ink, Trodat Printy ink and paper.

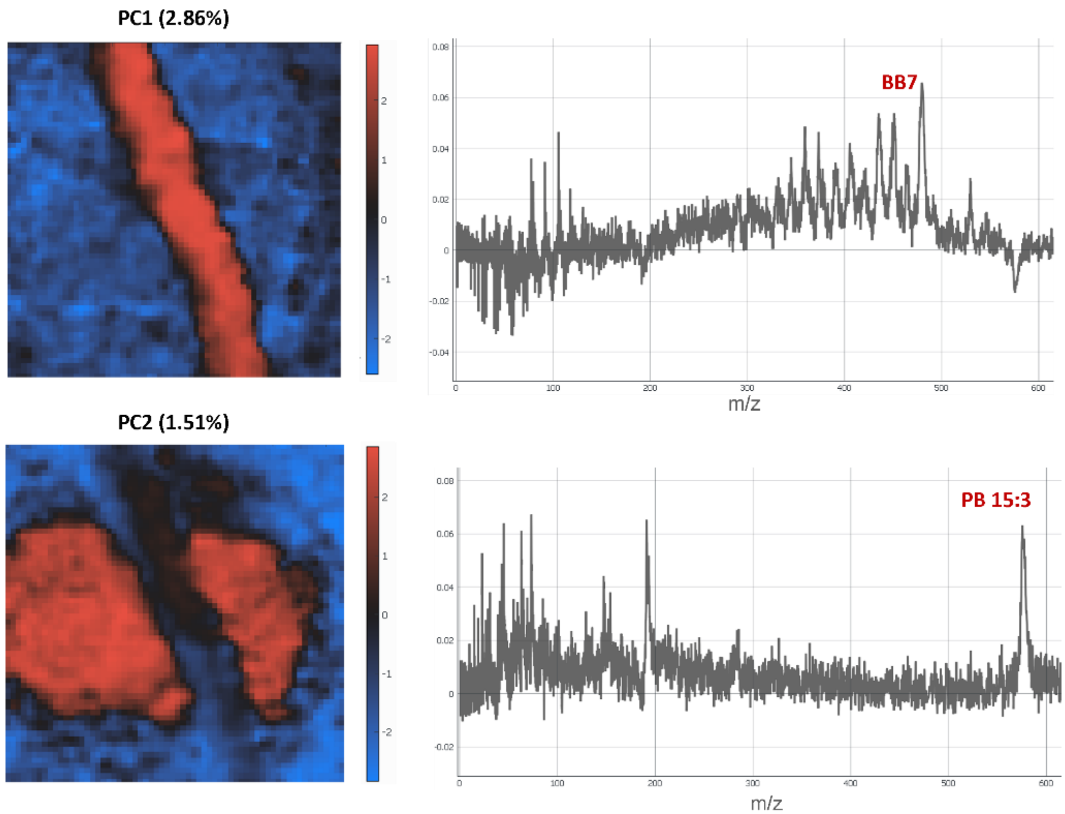

*Figure S-11. PCA results for **Trodat Printy over Pilot** combination. Scores (left) of the ink-descriptive principal components (PC1 and PC2), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.8 was applied. All calculated principal components were autoscaled.*

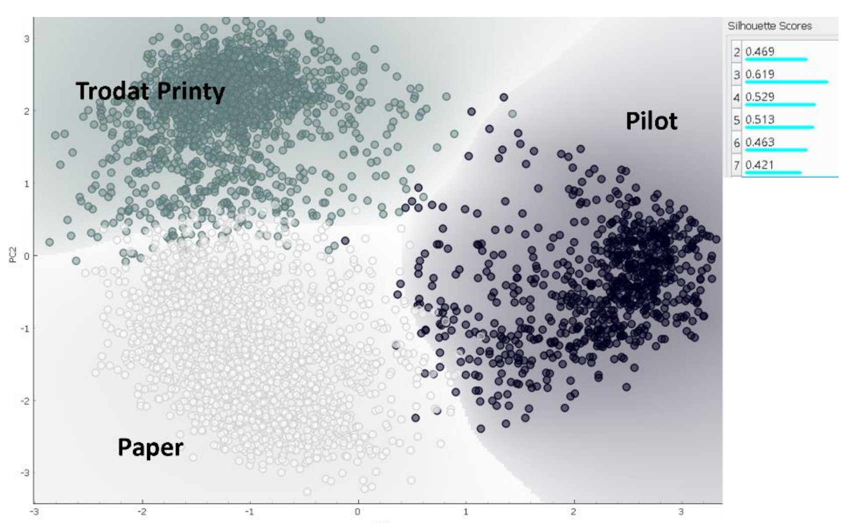

Figure S-12. K-means clustering on pixels represented in PC1-PC2 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to Pilot ink, Trodat Printy ink and paper.

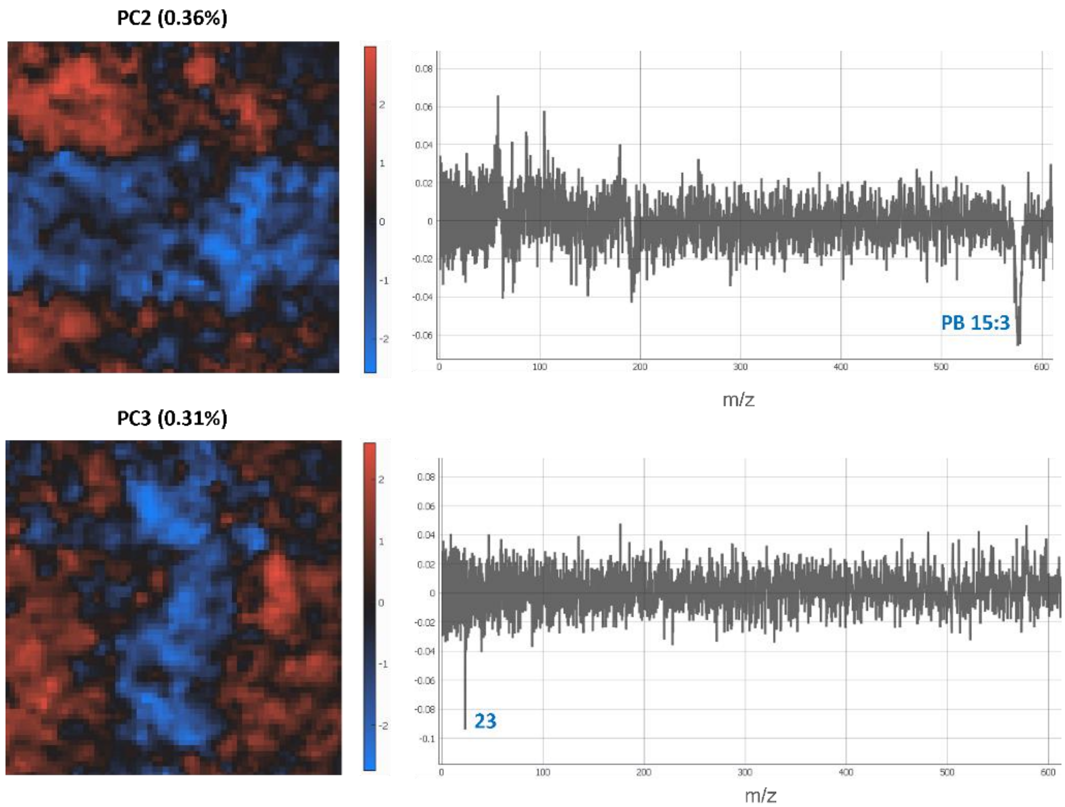

*Figure S-13. PCA results for **fountain pen over Trodat Printy** combination. Scores (left) of the ink-descriptive principal components (PC2 and PC3), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.8 was applied. All calculated principal components were autoscaled. This sample had a low number of counts collected.*

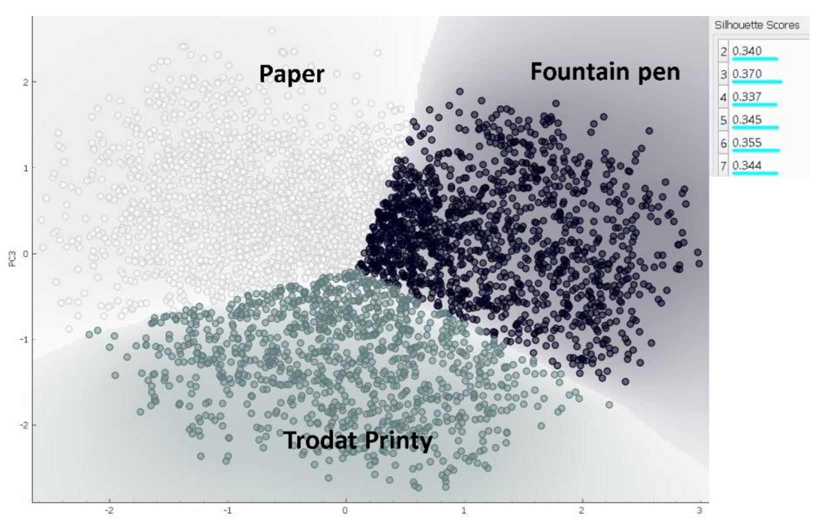

Figure S-14. K-means clustering on pixels represented in PC2-PC3 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to fountain pen ink, Trodat Printy ink and paper.

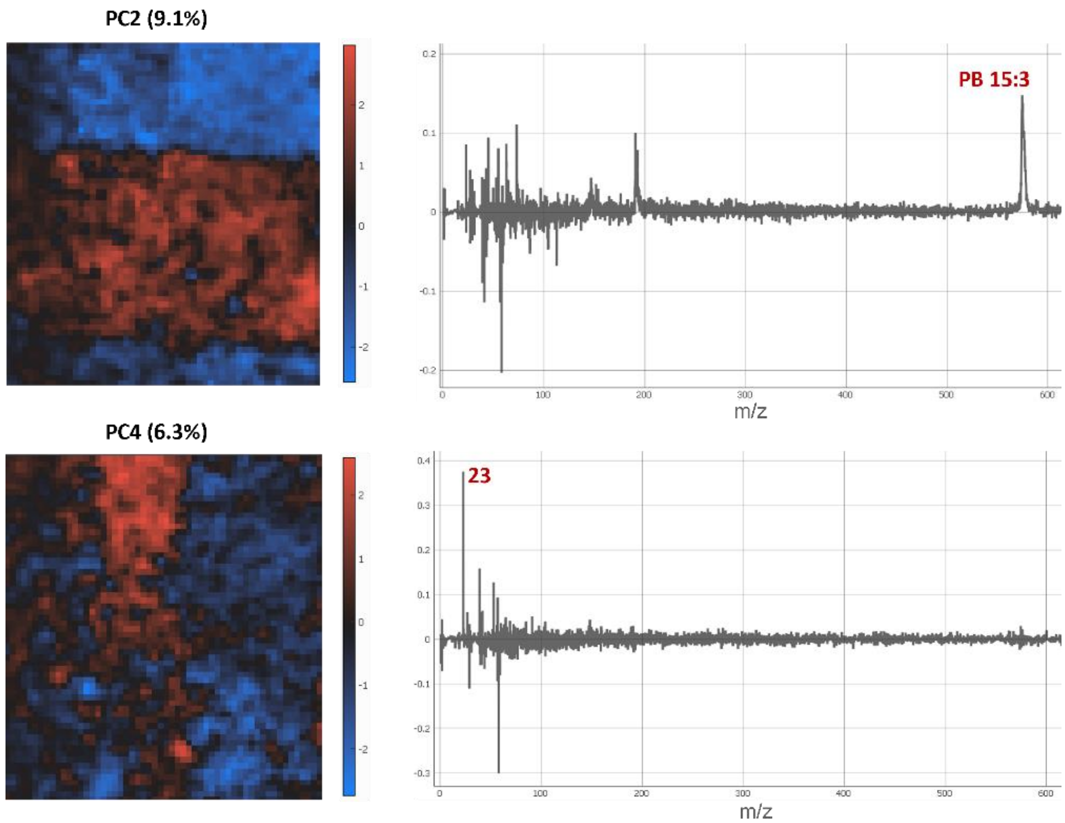

*Figure S-15. PCA results for **Trodat Printy over fountain pen** combination. Scores (left) of the ink-descriptive principal components (PC2 and PC4), and their corresponding loading plots (right) with ink-determining species highlighted. Raw data was first normalized to total counts and binned by a factor of 2, then pre-processed by square root scaling + mean centering. A Gaussian smoothing filter with SD=0.9 was applied. All calculated principal components were autoscaled. This sample had a low number of counts collected.*

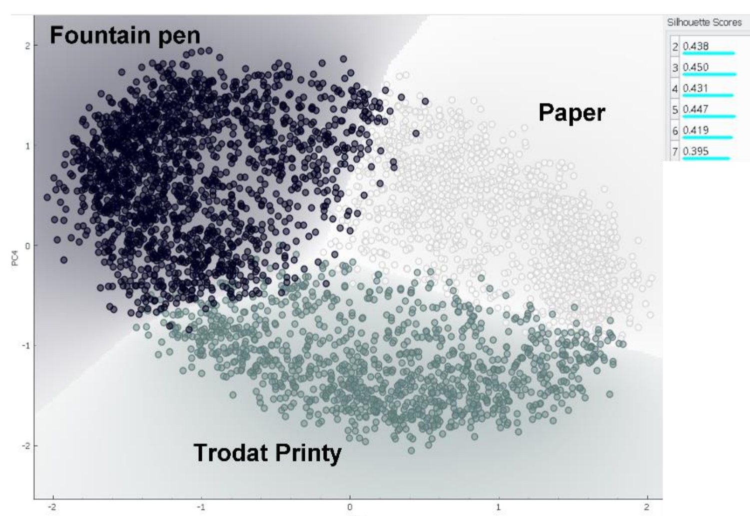

Figure S-16. K-means clustering on pixels represented in PC2-PC4 score plot. Optimal number of clusters (three) is determined from the highest silhouette score, corresponding to fountain pen ink, Trodat Printy ink and paper.

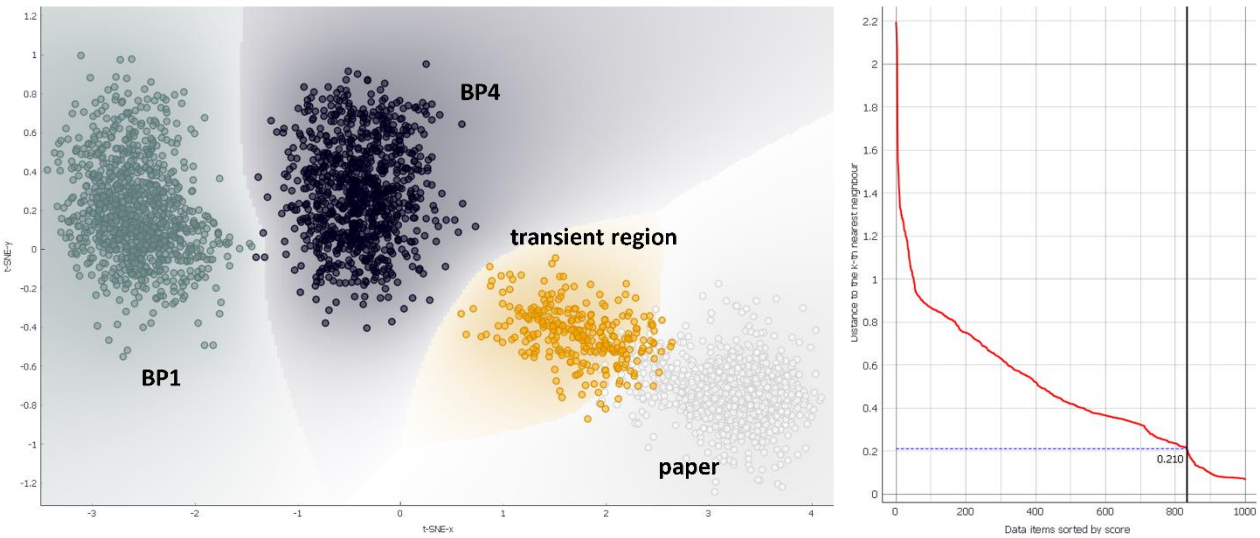

*Figure S-17. T-SNE results for **BP1 over BP4 combination**. Clustered pixels originating from BP1, BP4, paper, and a transient region, represented in t-SNE space (left). Perplexity parameter for t-SNE was conditioned to preserve global structure, combining two different perplexity values (50 and 500) to try preserve both the local and global structure. Clustering was performed with DBSCAN code within Orange software (density based clustering). Optimal number of clusters is defined by selecting the neighborhood distance parameter to the value in the first "valley" (right).*

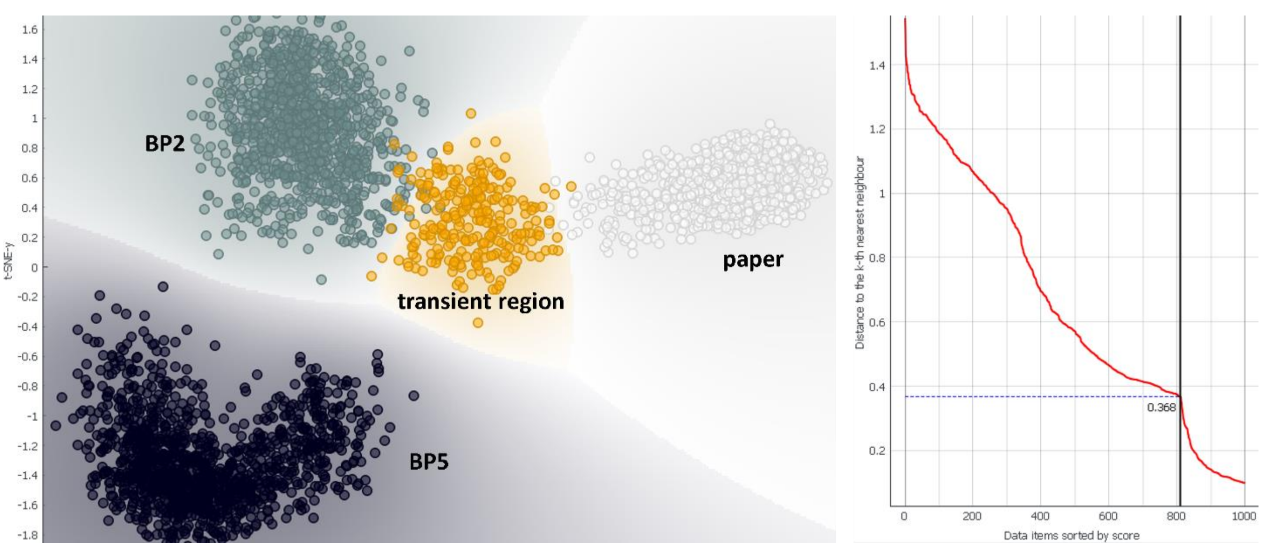

*Figure S-18. T-SNE results for **BP5 over BP2 combination**. Clustered pixels originating from BP5, BP2, paper, and a transient region, represented in t-SNE space (left). Perplexity parameter for t-SNE was conditioned to preserve global structure, combining two different perplexity values (50 and 500) to try preserve both the local and global structure. Clustering was performed with DBSCAN code within Orange software (density based clustering). Optimal number of clusters is defined by selecting the neighborhood distance parameter to the value in the first "valley" (right).*

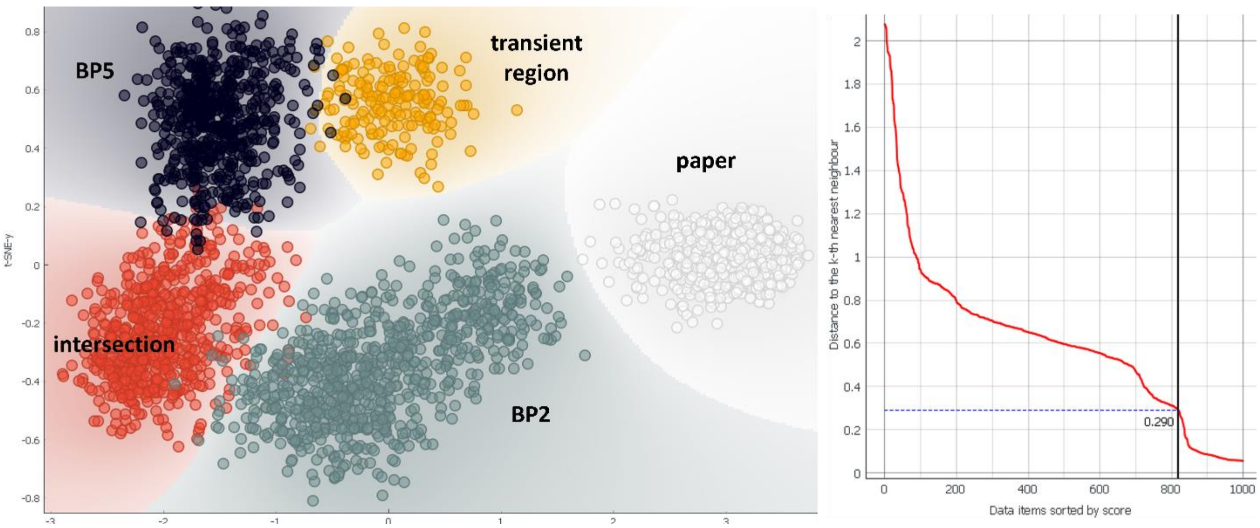

*Figure S-19. T-SNE results for **BP2 over BP5 combination**. Clustered pixels originating from BP2, BP5, paper, transient region, and intersectionregion is represented in t-SNE space (left). Perplexity parameter for t-SNE was conditioned to preserve global structure, combining two different perplexity values (50 and 500) to try preserve both the local and global structure. Clustering was performed with DBSCAN code within Orange software (density based clustering). Optimal number of clusters is defined by selecting the neighborhood distance parameter to the value in the first "valley" (right).*