# Supplementary information

# Residual polymer stabiliser causes anisotropic conductivity in metal nanoparticle 2D and 3D printed electronics

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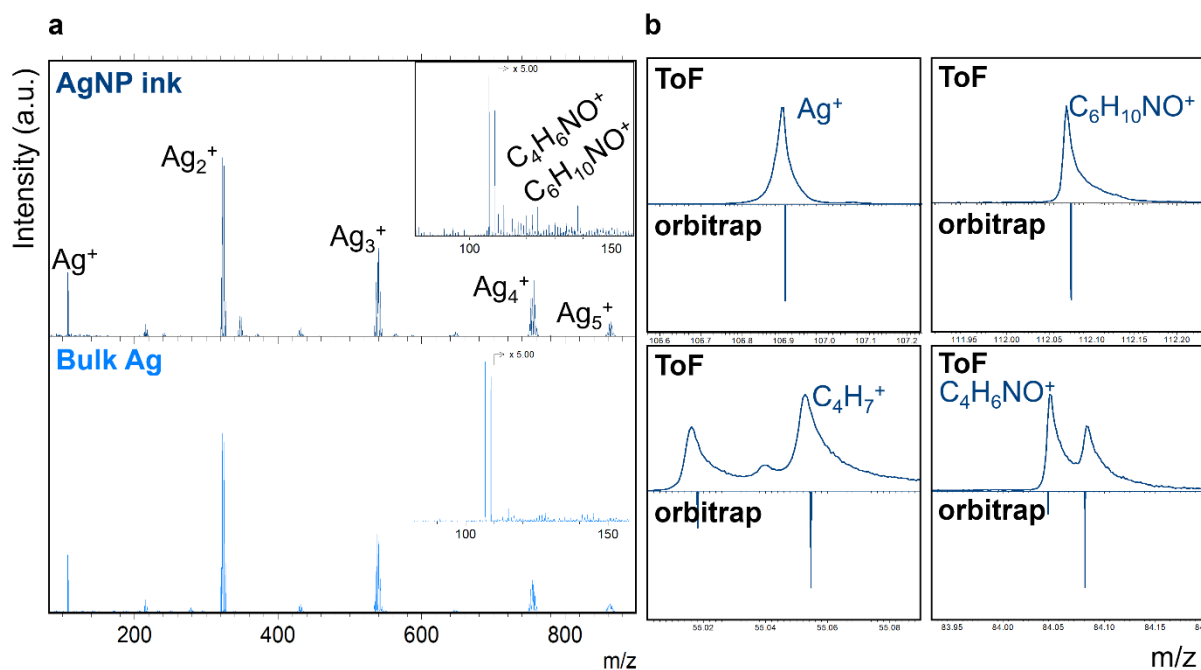
**Fig. S1** Unambiguous identification of PVP in inkjet-printed AgNPs (arbitrary intensities). **a** Measured spectra for AgNP (top) and reference bulk Ag (bottom). The inserts show a zoomed-in view with characteristic PVP peaks indicated. **b** High resolution view of peaks of main secondary ions of interest. The top curves showthe ToF-SIMS signal and the bottom curves show the orbiSIMS. The orbitrap data confirms that there is no interference within the ToF peaks of interest.
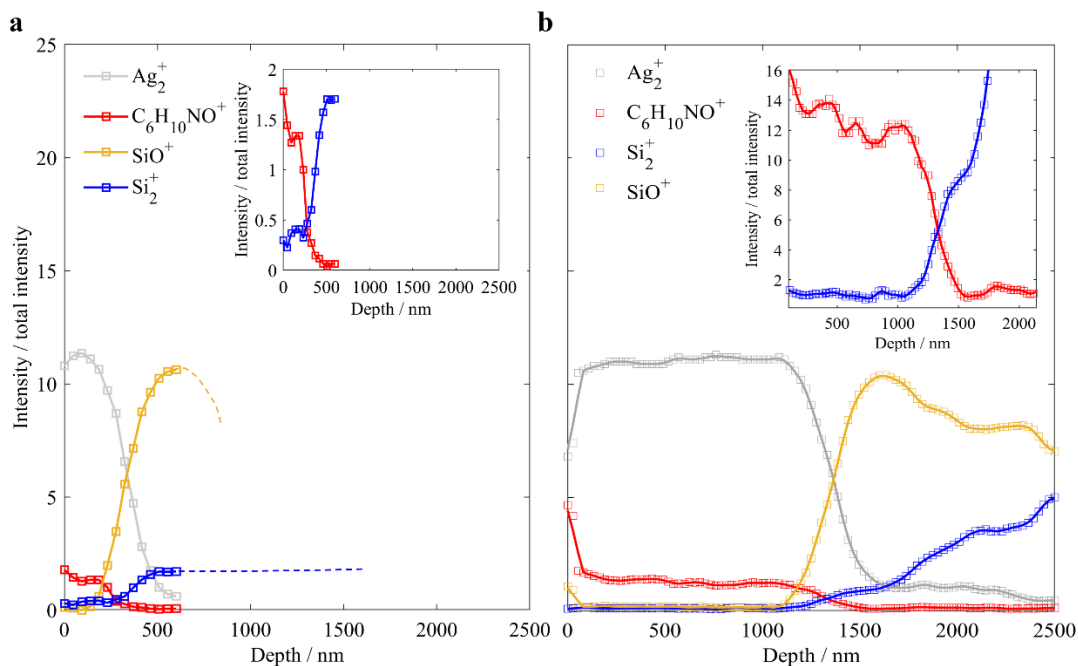


**Fig. S2** ToF-SIMS depth profiles of **a** 1 printed layer and **b** 4 printed layers of AgNP samples.

a



b

SIMS crater wall
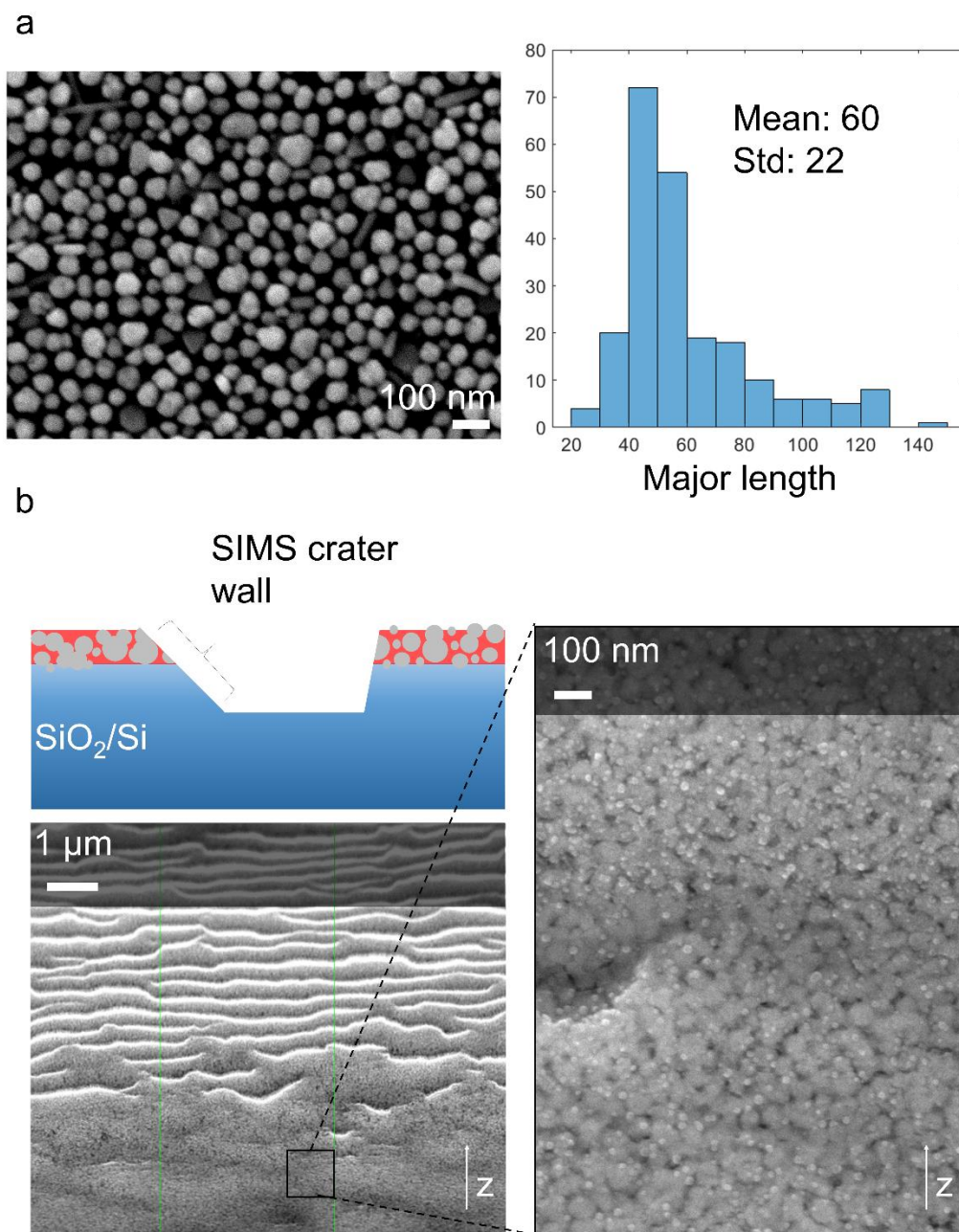
SiO$_2$/Si

100 nm

1 µm

z

z

**Fig. S3 a** Electron micrograph and AgNPs size distribution of the silver ink. **b** Electron micrograph of the ToF-SIMS crater wall after depth profiling.
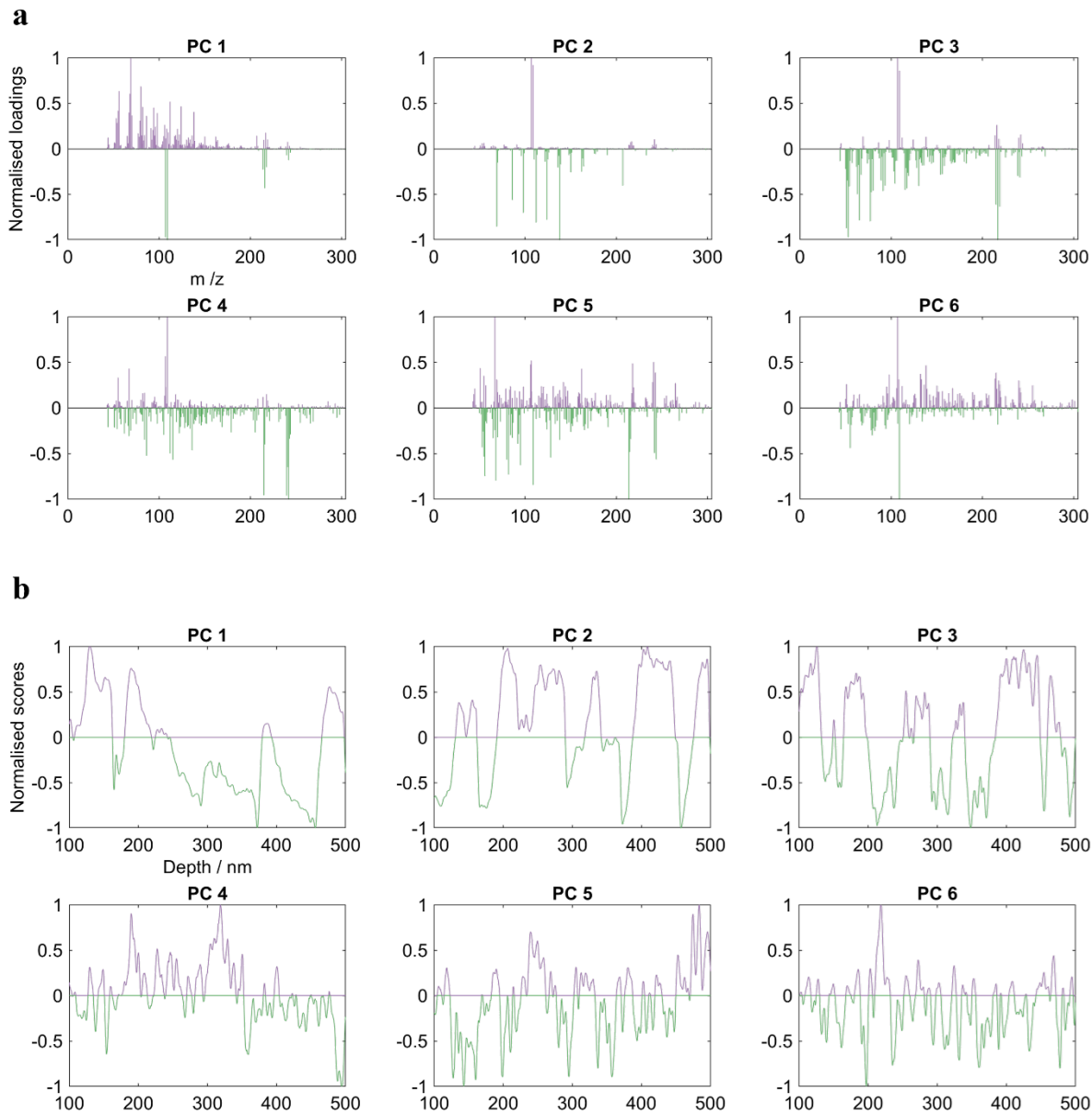
**a**



**b**



**Fig. S4** Principal component analysis results of the ToF-SIMS depth profiling data within a single printed layer of the AgNPs ink. Depth levels are used as observations and secondary ion mass peaks are used as variables. **a** Loadings. **b** Scores
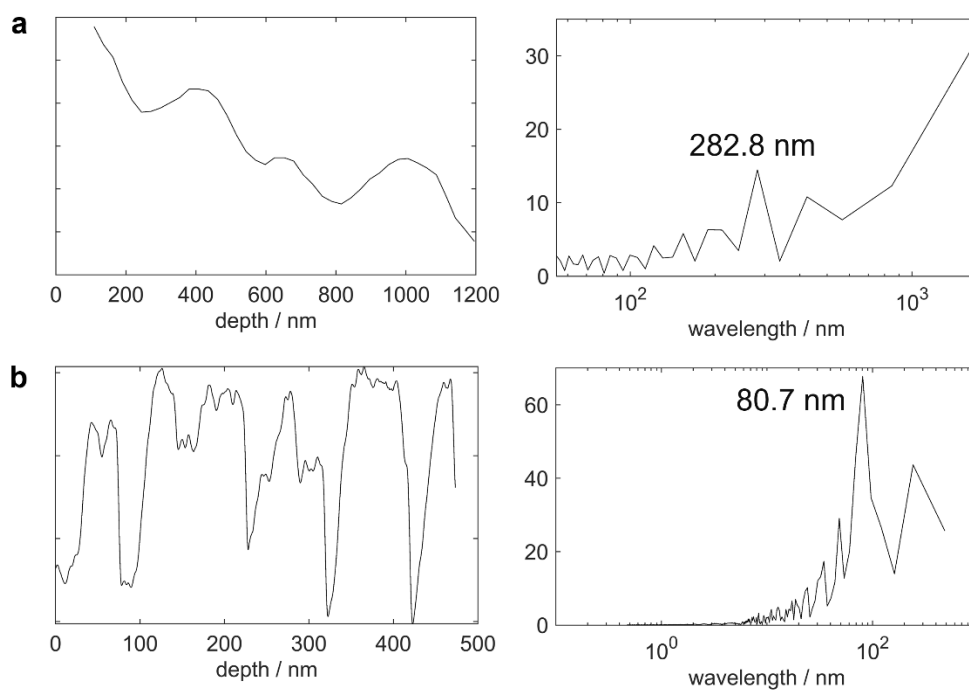
4

**Fig. S5:** Estimation of period of repeating patterns by Fast Fourier transforms of the ToF-SIMS depth profiling data within **a** 4 printed layers and **b** 1 printed layer (with higher depth resolution).
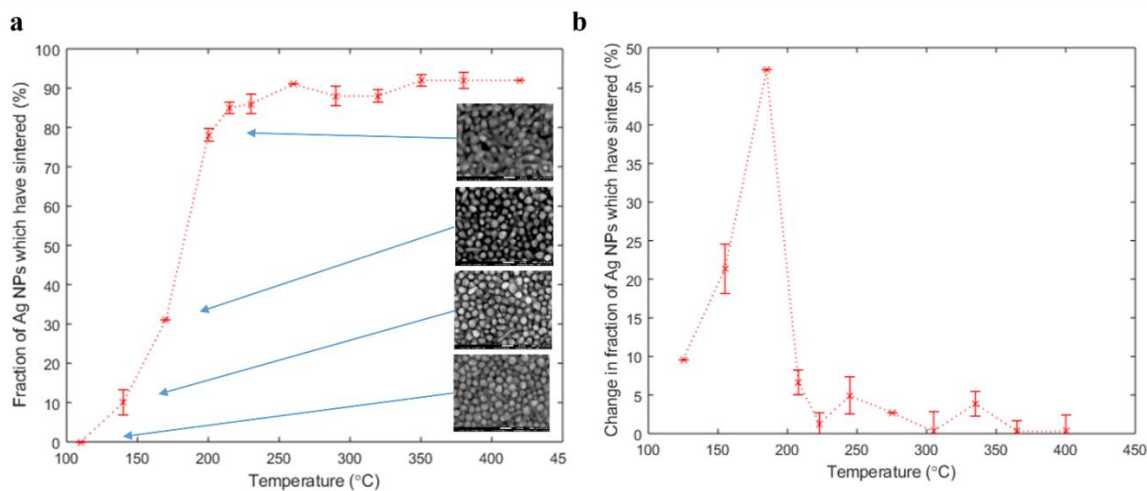


**Fig. S6: a** fraction of Ag NPs which have sintered against temperature. Exemplary images are included with arrow indications to the correspond data points. Error bars indicate standard deviation. **b** Change in fraction of Ag NPs which have sintered with increasing temperature. Error bars indicate standard deviation.
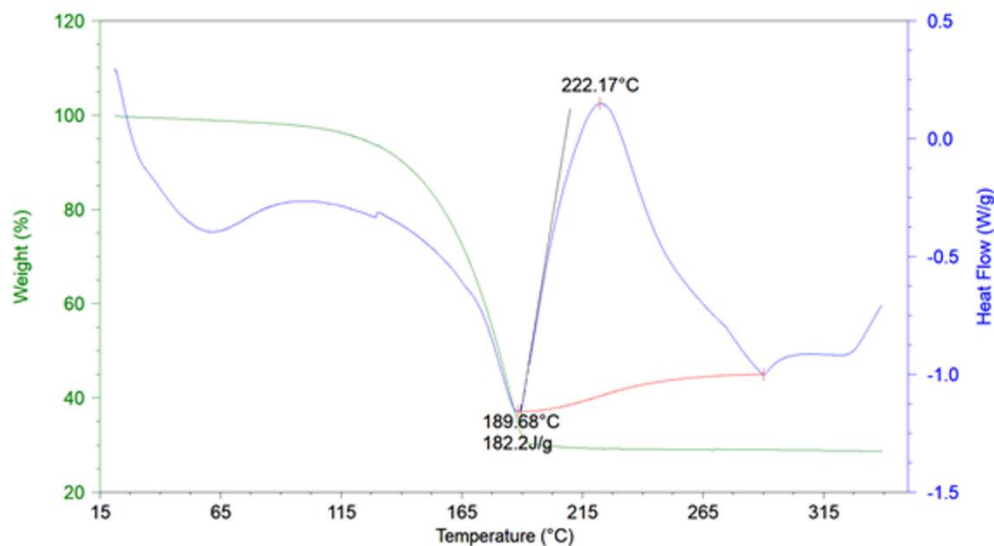
**Fig. S7** Simultaneous DSC/TGA measurements of the AgNP ink. Data reveal weight loss of approximately 70% by T = 190$^\circ$C. We attribute this to the evaporation of the solvent present in the ink. The DSC measurement shows an exothermic peak believed to be the result of NP sintering up to T = 290$^\circ$C.

**Table ST1**: XPS peak fitting for C1s spectra of printed AgNPs sintered at different

temperatures and corresponding estimated compositions.

|  | GROUP | POSITION(EV) | FWHM (EV) | AREA | CORRECTED AREA | ATOMIC CONC (%) |
|---|---|---|---|---|---|---|
| **RT** | C-C | 284.82 | 1.39 | 1687.44 | 2143.31 | 58.3 |
|  | N-C=O | 287.6 | 1.39 | 271.477 | 344.859 | 9.38 |
|  | C-N | 286.38 | 1.39 | 542.954 | 689.681 | 18.76 |
|  | C-O | 289.28 | 1.39 | 109.143 | 498.759 | 13.57 |
| **100$^O$C** | C-C | 284.78 | 1.27 | 1459.87 | 1854.25 | 63.13 |
|  | N-C=O | 287.42 | 1.27 | 172.05 | 218.552 | 7.44 |
|  | C-N | 286.2 | 1.27 | 344.1 | 437.082 | 14.88 |
|  | C-O | 288.89 | 1.27 | 93.506 | 427.291 | 14.55 |
| **150$^O$C** | C-C | 284.8 | 1.31 | 1805.19 | 2292.9 | 73.89 |
|  | N-C=O | 287.59 | 1.31 | 166.357 | 211.327 | 6.81 |
|  | C-N | 286.24 | 1.31 | 332.713 | 422.629 | 13.62 |

|  |  |  |  |  |  |
|---|---|---|---|---|---|
|  | C-O | 289.01 | 1.31 | 38.5496 | 176.163 | 5.68 |
| **230ᴼC** | C-C | 284.85 | 1.32 | 1345.51 | 1709.03 | 66.05 |
|  | N-C=O | 287.66 | 1.32 | 138.667 | 176.151 | 6.81 |
|  | C-N | 286.3 | 1.32 | 277.334 | 352.282 | 13.62 |
|  | C-O | 289.21 | 1.32 | 76.5669 | 349.895 | 13.52 |

**Table ST2**: XPS peak fitting for N1s spectra of printed AgNPs sintered at different temperatures and corresponding estimated compositions.

|  |  | POSITION (EV) | FWHM (EV) | AREA | CORRECTED AREA | ATOMIC CONC (%) |
|---|---|---|---|---|---|---|
| **RT SURFACE** | C-N-Ag | 397.83 | 1.25 | 114.064 | 294.412 | 63.82 |
|  | C-N | 399.79 | 1.61 | 64.7248 | 166.897 | 36.18 |
| **RT BULK** | C-N-Ag | 398.8 | 1 | 1.00E-20 | 2.58E-20 | 0 |
|  | C-N | 400.69 | 1.21 | 33.7063 | 86.8754 | 100 |
| **100 ᴼC SURFACE** | C-N-Ag | 399 | 1.54 | 133.438 | 344.199 | 71.42 |
|  | C-N | 400.8 | 1.7 | 53.4481 | 137.745 | 28.58 |
| **100 ᴼC BULK** | C-N-Ag | 398.01 | 1.7 | 57.7153 | 148.94 | 34.82 |
|  | C-N | 399.88 | 1.7 | 108.148 | 278.827 | 65.18 |
| **150 ᴼC SURFACE** | C-N-Ag | 398.04 | 1.7 | 164.003 | 423.311 | 65.79 |
|  | C-N | 400.51 | 1.7 | 85.3673 | 220.082 | 34.21 |
| **150 ᴼC BULK** | C-N-Ag | 398.09 | 1.7 | 98.3761 | 253.907 | 58.06 |
|  | C-N | 400.74 | 1.26 | 71.1677 | 183.447 | 41.94 |
| **230 ᴼC SURFACE** | C-N-Ag | 398.21 | 1.43 | 83.444 | 215.389 | 40.7 |
|  | C-N | 400.54 | 1.7 | 121.726 | 313.849 | 59.3 |
| **230 ᴼC BULK** | C-N-Ag | 398.23 | 1.7 | 29.3323 | 75.7025 | 23.68 |
|  | C-N | 400.57 | 1.38 | 94.6347 | 243.961 | 76.32 |