SUPPLEMENTARY INFORMATION

Quantitative on-line LC-SERS of purine bases

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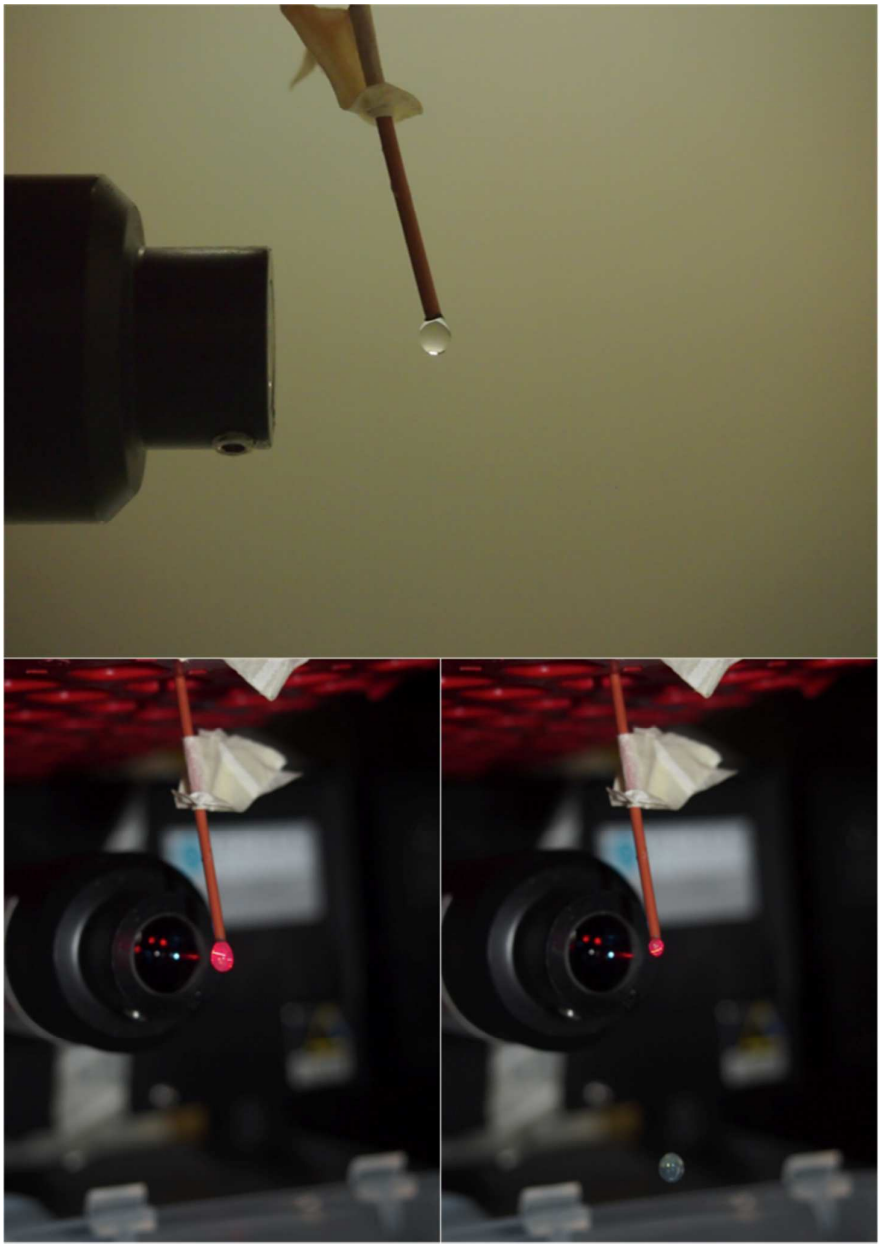

Figure S1. Photographs of the SERS detector during analysis with the enclosure removed. Side view of the sample droplet forming at the end of the LC tubing in front of the laser aperture (top), front-on view (lower left) and a new droplet forming in the laser path as soon as the previous droplet has fallen (lower right).

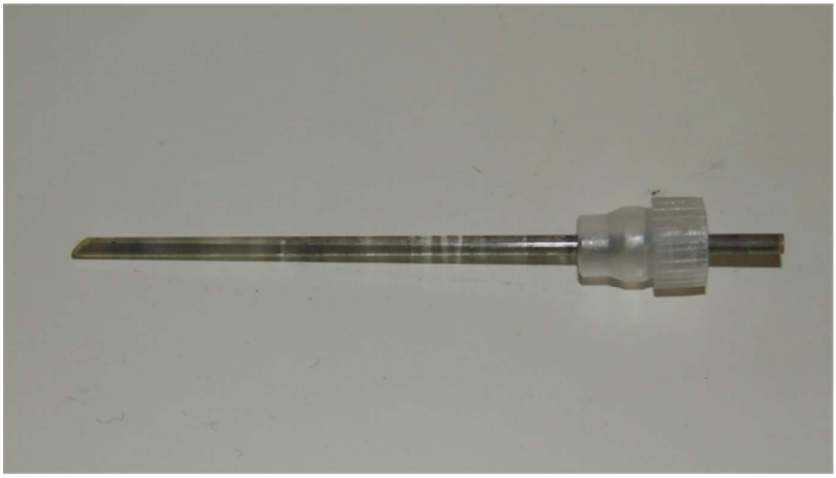

Figure S2. Quartz capillary used for LC-SERS analysis, showing the inside of the tube coated with silver.

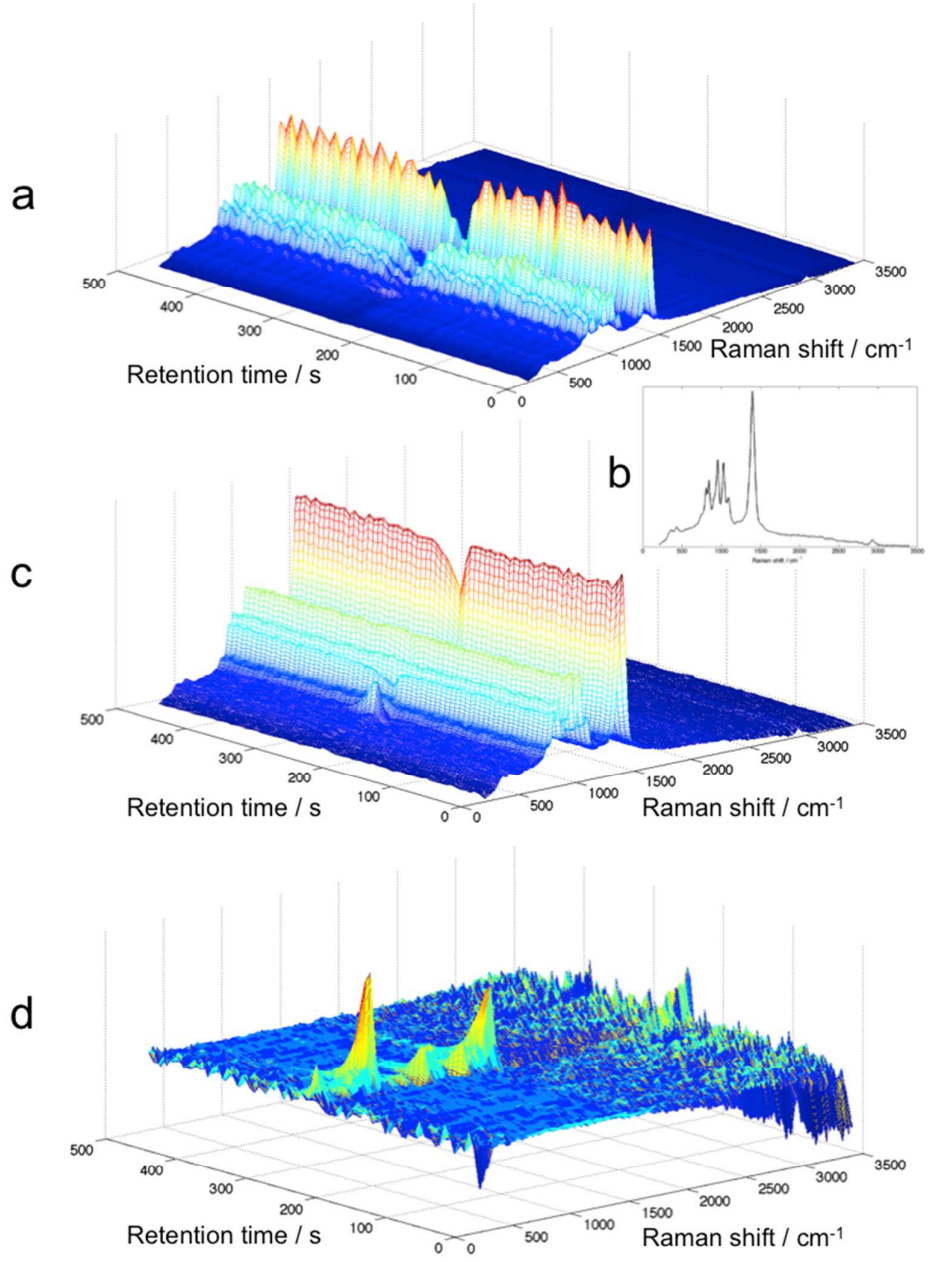

Figure S3. Extracting useful information from the LC-SERS data. (a) shows a 3D plot of the raw data obtained from a LC-SERS injection. In this case the sample is 5 x 10^{-5} M guanine. The spectra are clearly dominated by the vibrations of the Ag nanoparticles' citrate capping species, shown in (b). This becomes more apparent when the spectra are normalised against the total signal (c). A loss of signal intensity is observed when the analyte displaces the citrate on the surface. Normalisation against the mean blank spectrum (entirely citrate peaks) revels the relatively low-intensity guanine spectrum (d).

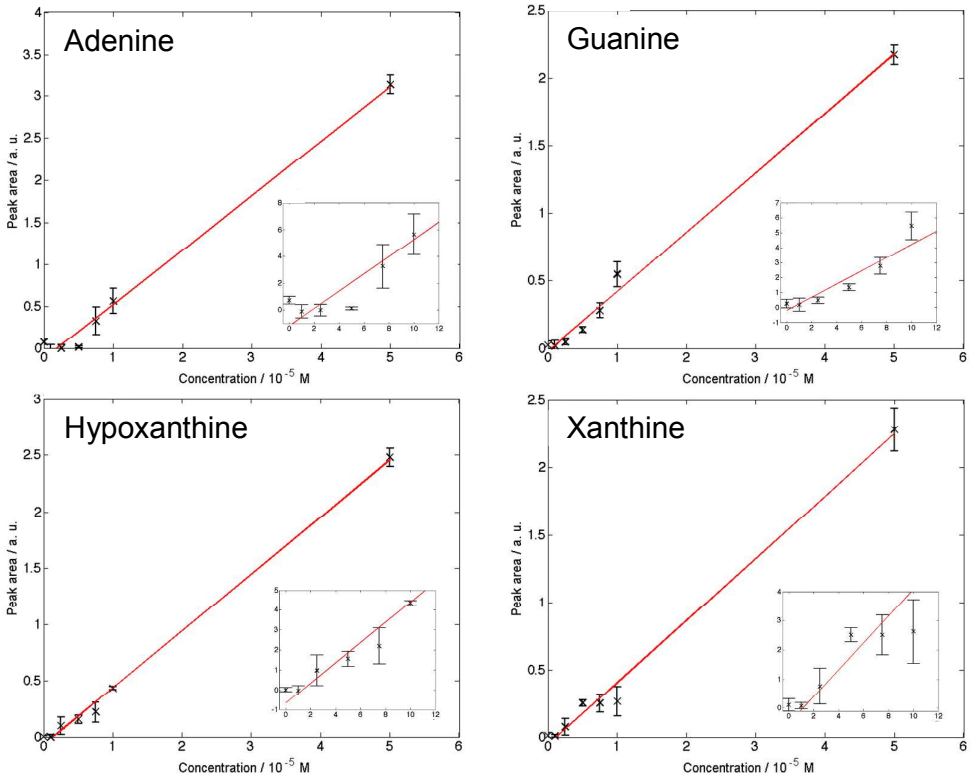

Figure S4. Calibration plots for injections of the **individual** nucleobases using **UV** detection. The mean UV peak area (n = 3) is shown with error bars equal to one standard deviation. Insets show a close-up of the main plot in the low concentration region.

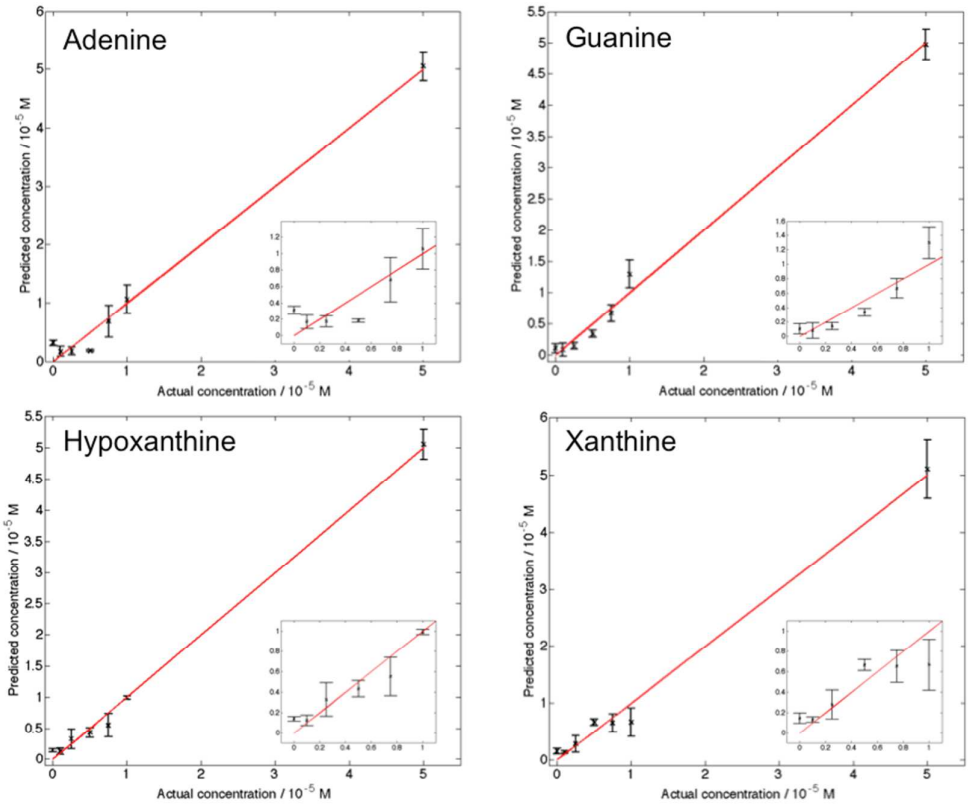

Figure S5. Plots of mean (n = 3) predicted concentration against actual concentration for each of the four nucleobases using leave-one-out calibration. All data are from injections of **individual** nucleobase samples using **UV detection**. Error bars show one standard deviation. Insets show a close-up of the main plot in the low concentration region.

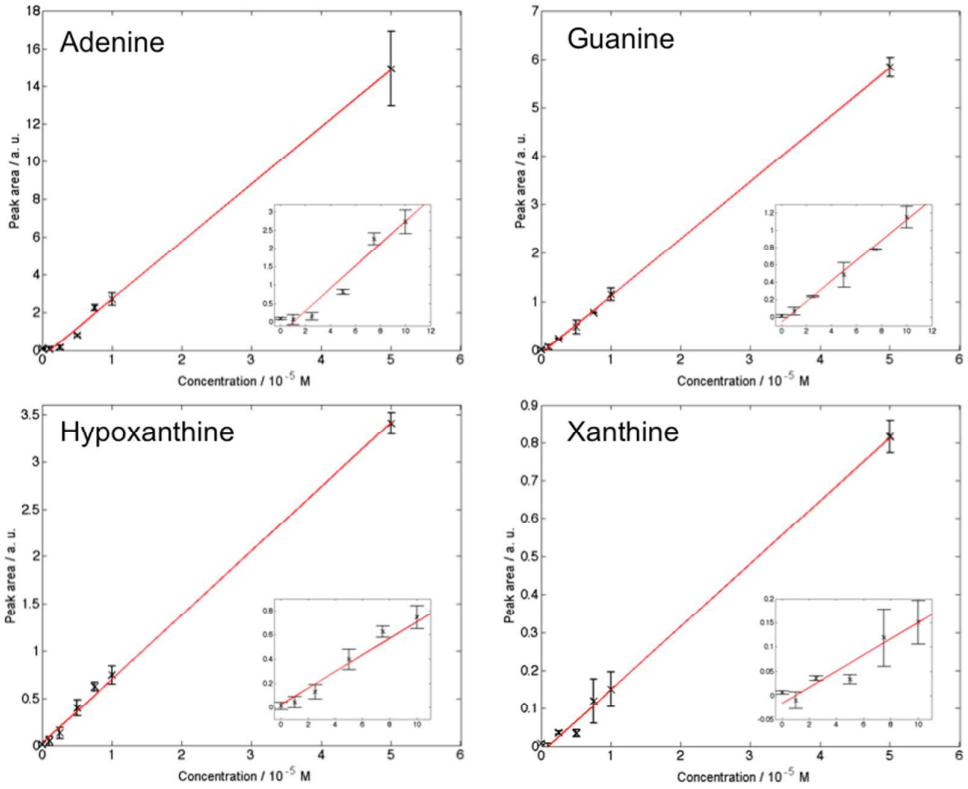

Figure S6. Calibration plots for injections of the **individual** nucleobases using **SERS detection**. The mean SERS peak area (n = 3) at the relevant wavelength (see Table 1) is shown with error bars equal to one standard deviation. Insets show a close-up of the main plot in the low concentration region.

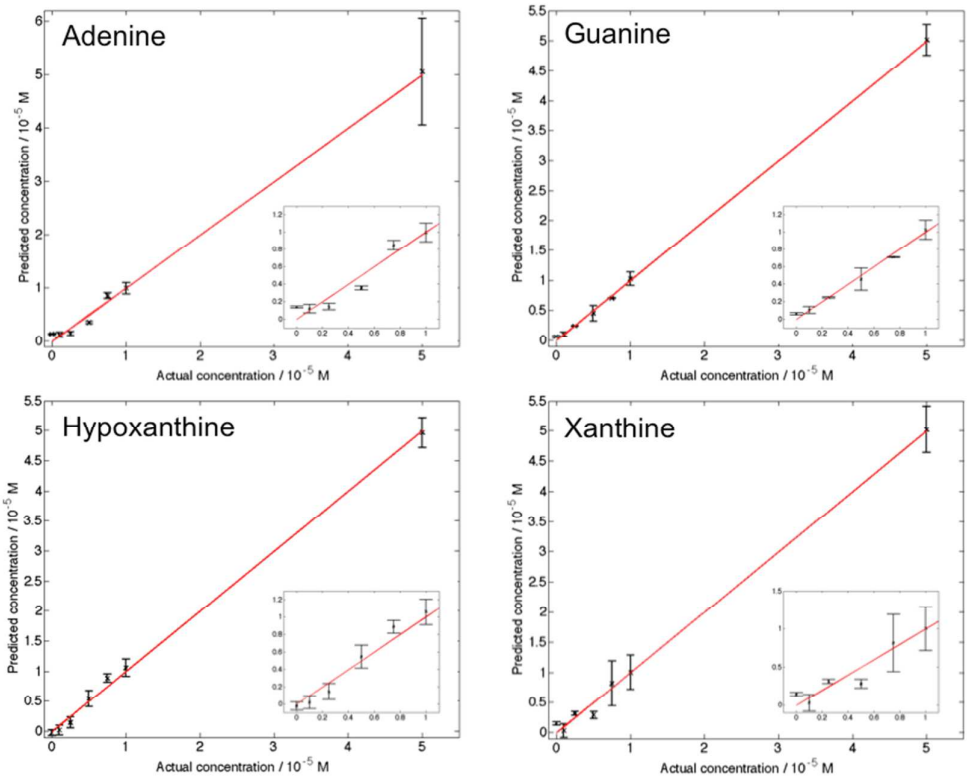

Figure S7. Plots of mean (n = 3) predicted concentration against actual concentration for each of the four nucleobases using leave-one-out calibration. All data are from injections of **individual** nucleobase samples using **SERS detection**. Error bars show one standard deviation. Insets show a close-up of the main plot in the low concentration region.

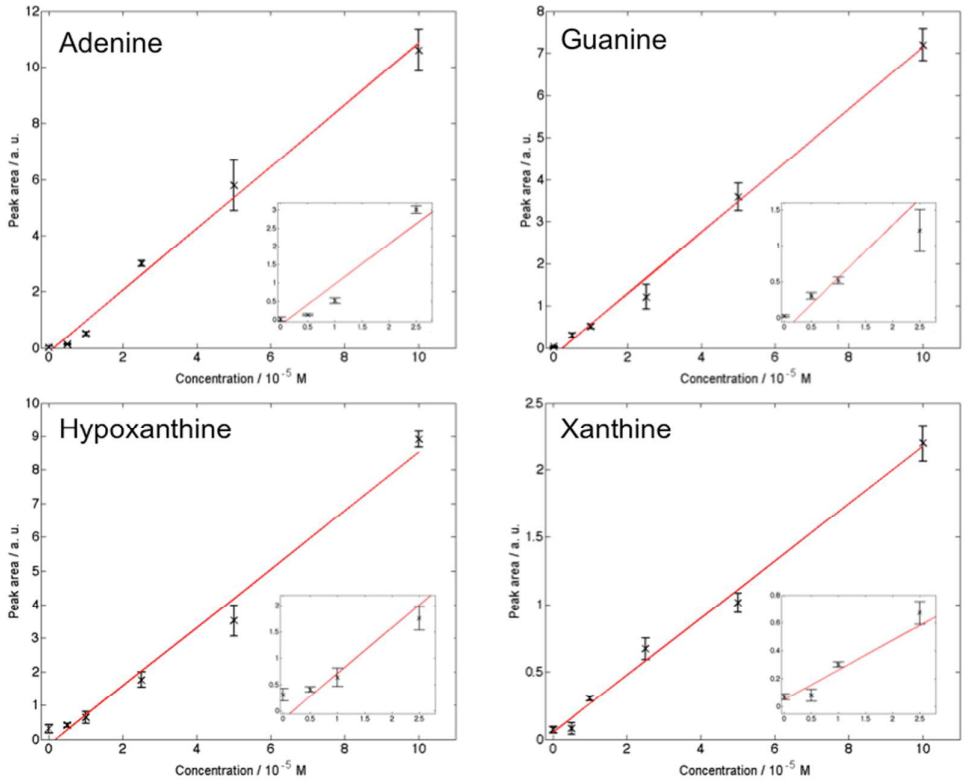

Figure S8. Calibration plots for injections of **mixtures** of nucleobases using **SERS detection**. The mean SERS peak area (n = 3) at the relevant wavelength (see Table 2) is shown with error bars equal to one standard deviation. Insets show a close-up of the main plot in the low concentration region.