Portable through bottle SORS for the authentication of extra virgin olive oil

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Table S1 For SORS as there was limited sample then mixtures within the same bottle were prepared at two volume levels. This table describes the volumes generated for these various binary mixtures.

Mixture series for EVOO-sunflower oil			Mixture series at lower total volumes		
EVOO (%)	Sunflower oil (%)	Total vol. (mL)	EVOO (%)	Adulterant* (%)	Total vol. (mL)
0	100	9	10	90	28
10	90	10	20	80	14
20	80	11.25	25	75	11.2
25	70	12	40	60	7
40	60	15	50	50	6
50	50	18	60	40	7.5
60	40	22.5	70	30	10
70	30	30	80	20	9
80	20	45	90	10	18
90	10	90			

* For sunflower oil, pomace olive oil and refined olive oil.

Fig. S1 Pictures of the Heath Robinson constructed wooden holder with a Resolve and commercially available clear glass bottle *in situ*. Data were collected in "Thick, Colored or Opaque" mode for SORS.

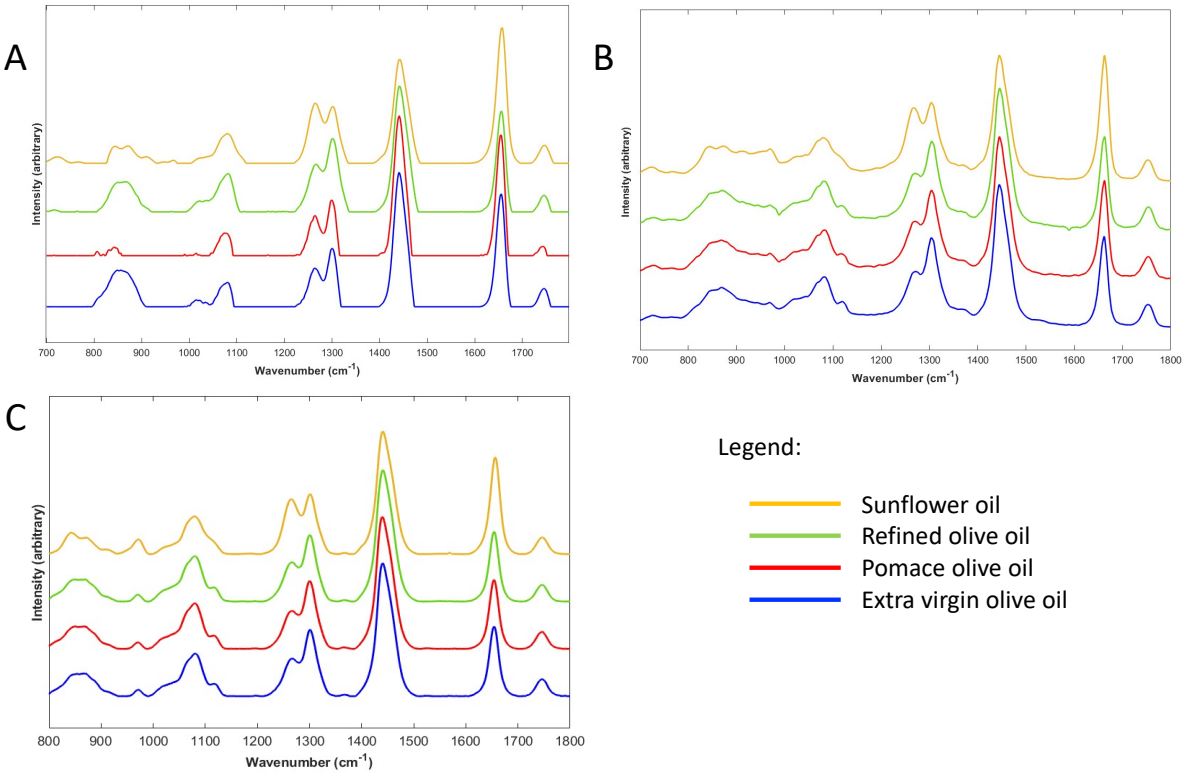

Fig. S2 Conventional Raman spectra of olive oil and the adulterants. These were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm. Spectra are offset in the y-axis so that the features can be more easily observed.

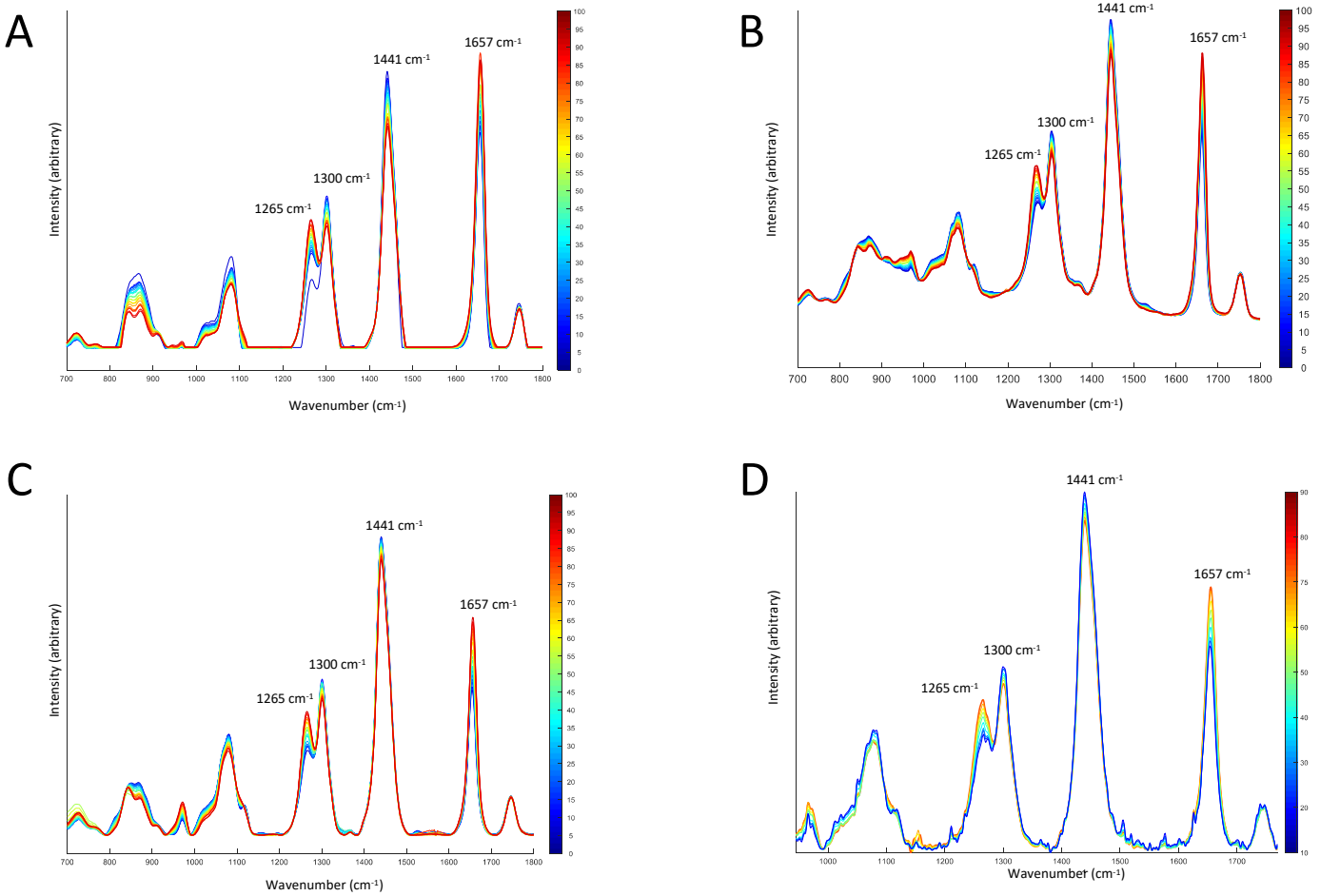

Fig. S3 Raman and SORS spectra showing the adulteration of authentic EVOO with **sunflower oil**. These Raman spectra were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. The adulteration has been performed in increments as depicted in the rainbow colour gradient bars within these figures, with the gradient from blue for pure EVOO to red for pure **sunflower oil**. The key vibrations that change are highlighted: increasing levels of sunflower oil in the mixtures result in increase in the intensity of two strong peaks at 1265 cm^{-1} and 1657 cm^{-1}, and decrease in the intensity of peaks at 1300 cm^{-1} and 1441 cm^{-1}.

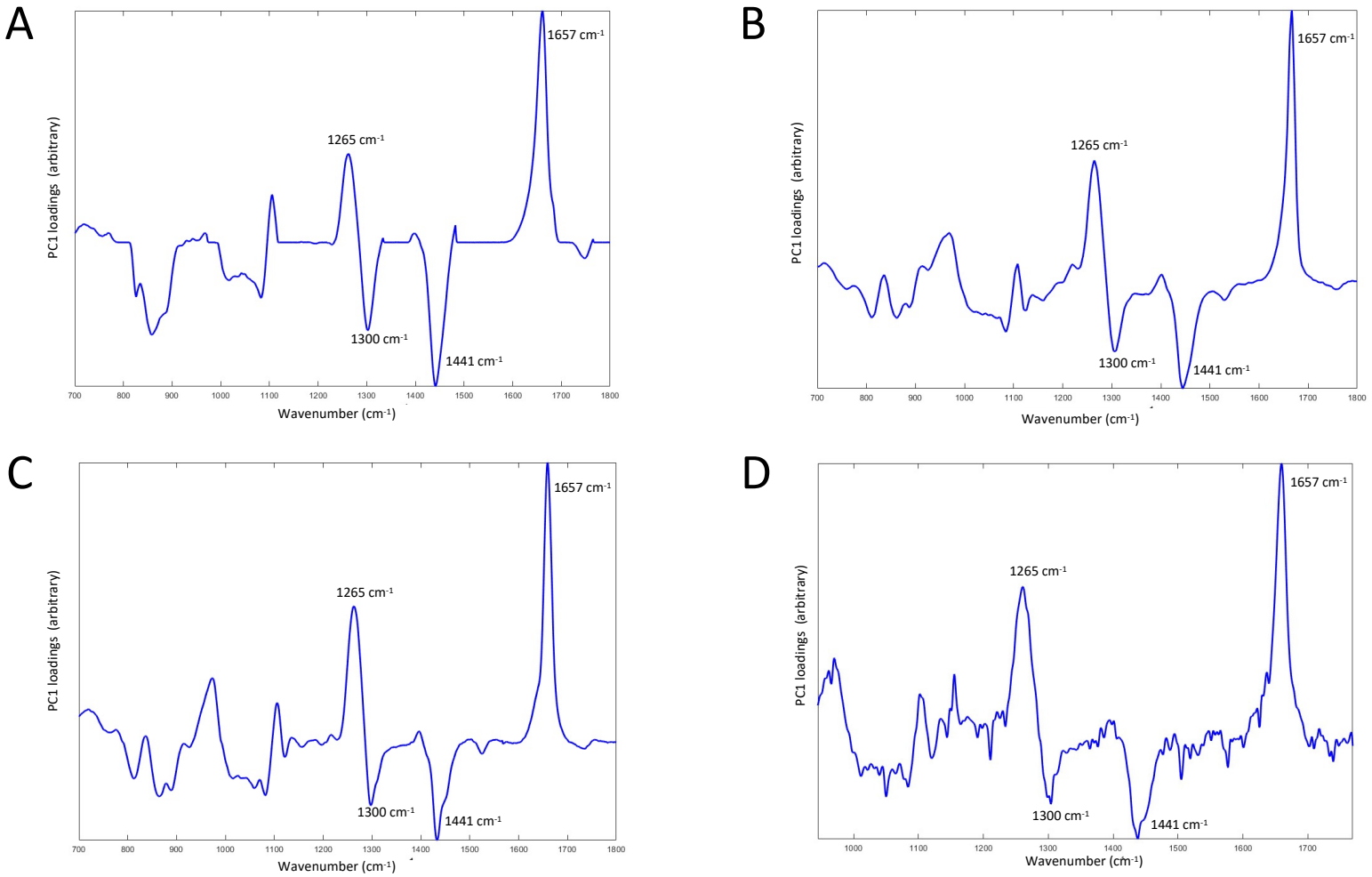

Fig. S4 PCA loadings plots on Raman spectral data collected showing the adulteration of authentic EVOO with **sunflower oil**. These correspond to the PCA scores plot shown in Fig. S5. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. The key vibrations that change are highlighted: peaks due to sunflower oil are in the positive side of PC1 loadings at 1265 cm^{-1} and 1657 cm^{-1}, and peaks due to EVOO in the negative side of PC1 loadings at 1300 cm^{-1} and 1441 cm^{-1}.

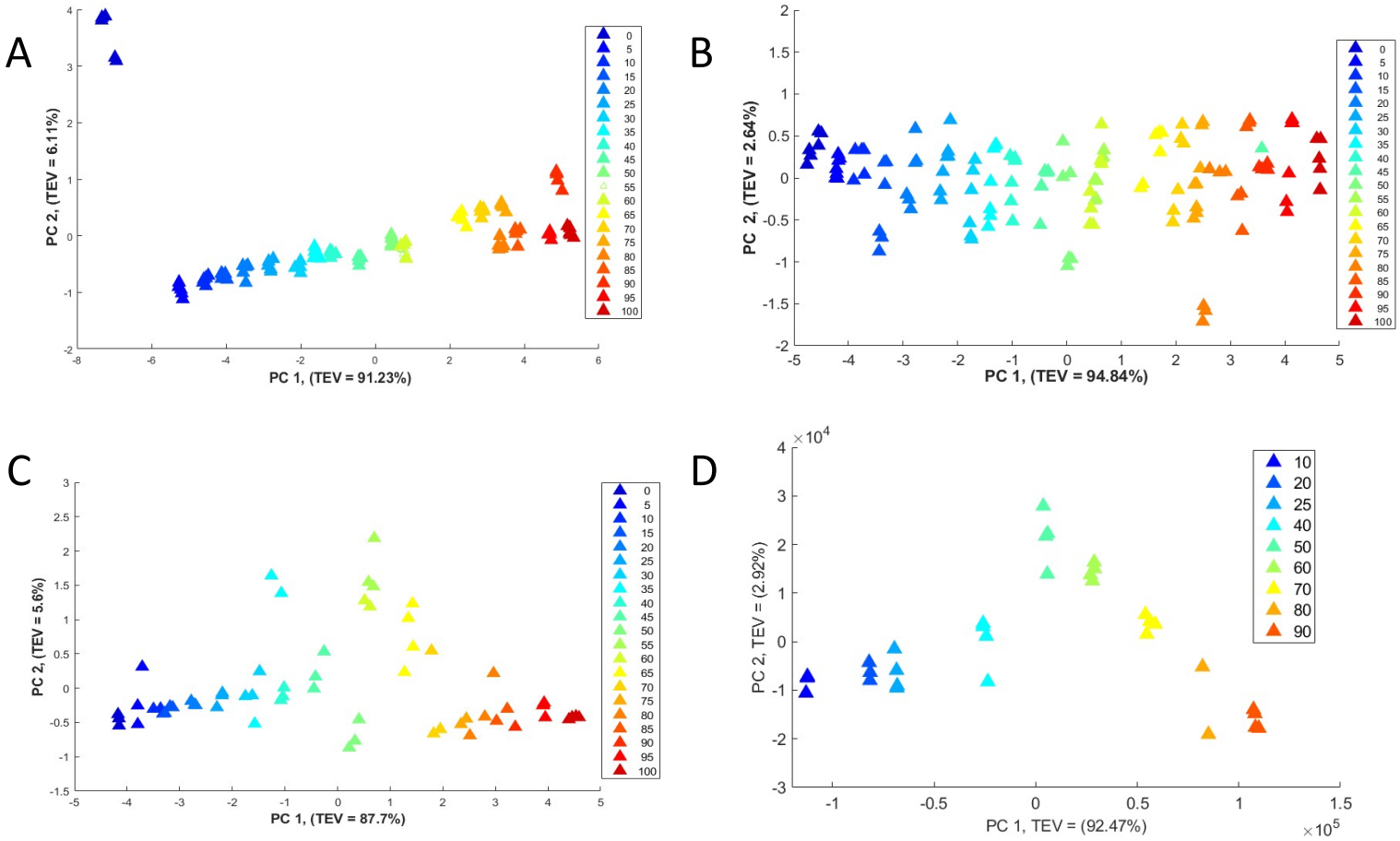

Fig. S5 PCA scores plots on Raman spectral data collected showing the adulteration of authentic EVOO with **sunflower oil**. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. The adulteration has been performed in increments as shown in the rainbow colour gradient bars within these figures, with the gradient from blue for pure EVOO to red for pure **sunflower oil**. The values in parentheses on the axes labels are the total explained variance (TEV) for each principal component (PC).

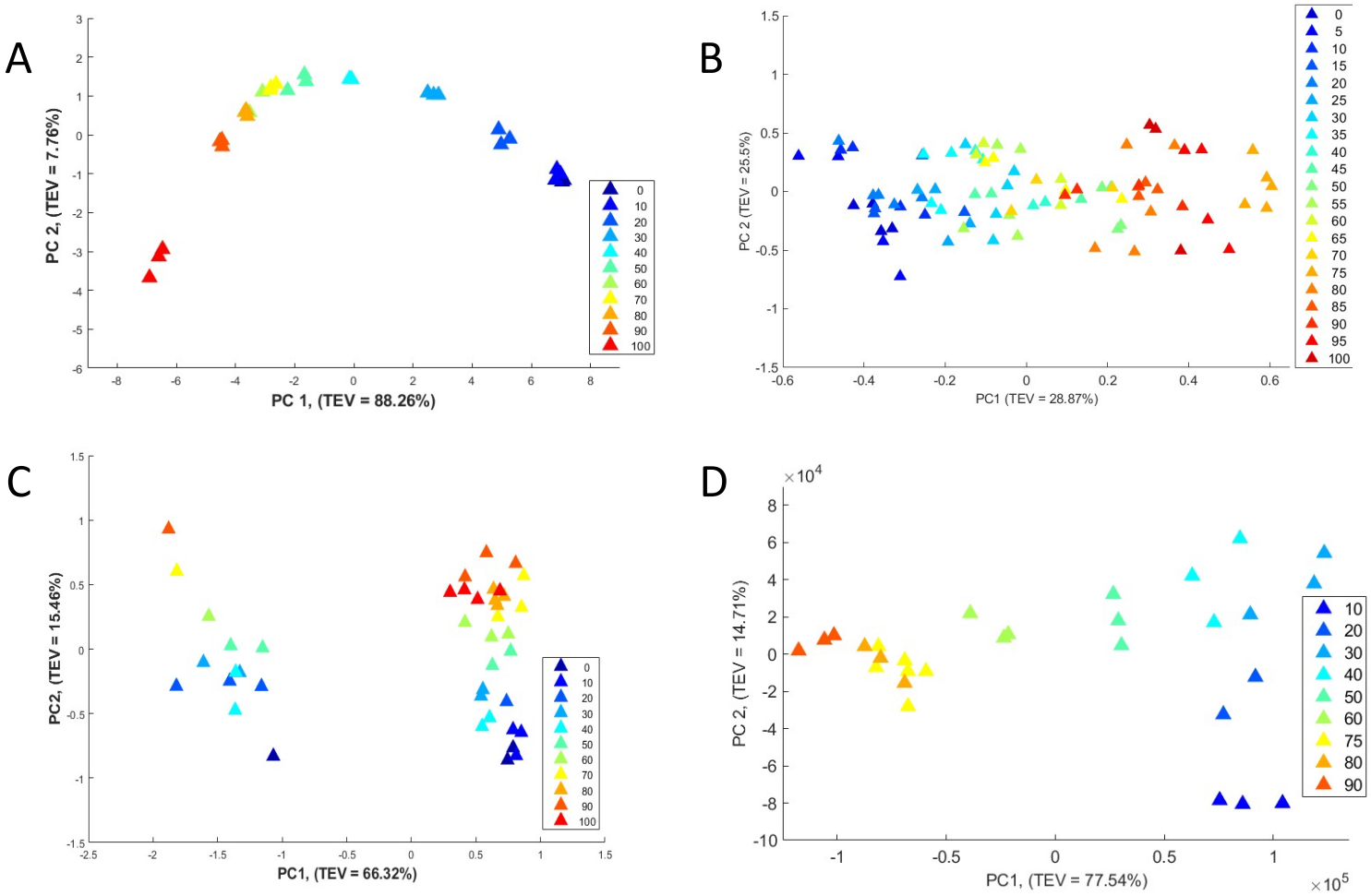

Fig. S6 PCA scores plots on Raman spectral data collected showing the adulteration of authentic EVOO with **pomace olive oil**. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. The adulteration has been performed in increments as shown in the rainbow colour gradient bars within these figures, with the gradient from blue for pure EVOO to red for pure **pomace olive oil**. The values in parentheses on the axes labels are the total explained variance (TEV) for each principal component (PC).

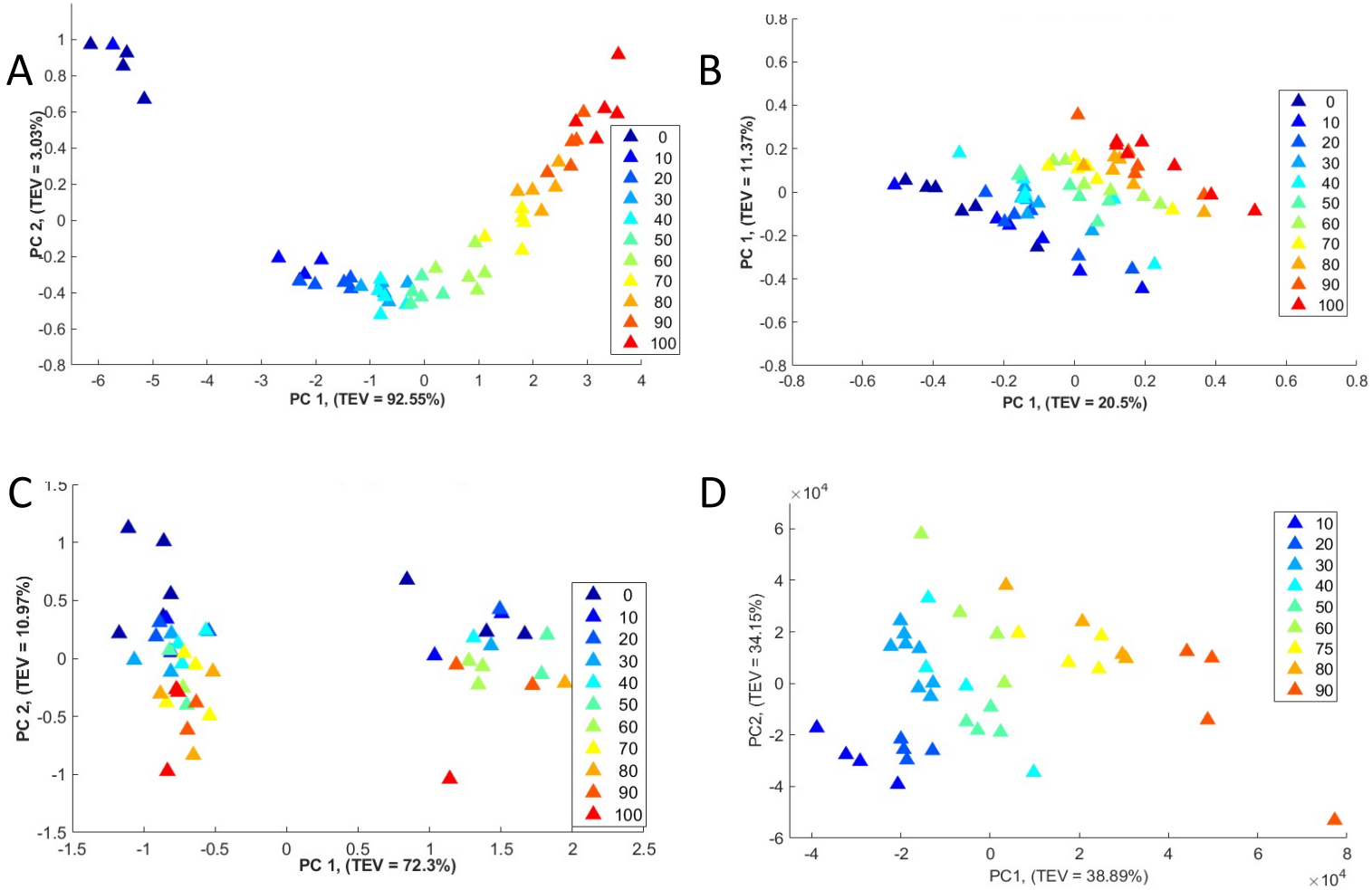

Fig. S7 PCA scores plots on Raman spectral data collected showing the adulteration of authentic EVOO with **refined olive oil**. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. The adulteration has been performed in increments as shown in the rainbow colour gradient bars within these figures, with the gradient from blue for pure EVOO to red for pure **refined olive oil**. The values in parentheses on the axes labels are the total explained variance (TEV) for each principal component (PC).

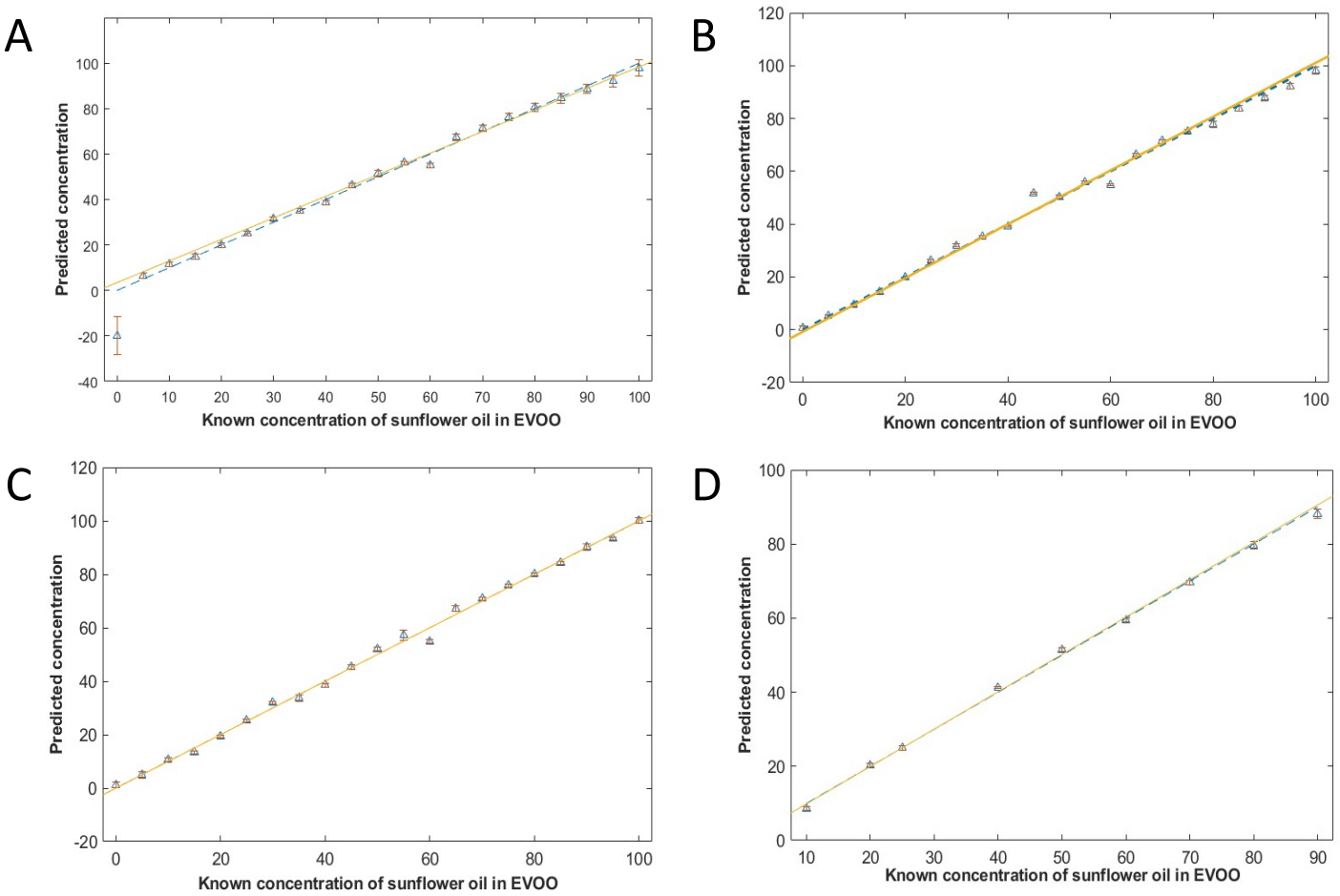

Fig. S8 PLSR prediction model plots comparing the predicted actual concentrations for the **sunflower oil** against the known level of this adulterant in EVOO. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. PLSR was conducted using bootstrap validation (n =1000) and this figure shows the results from the test 1000 test sets only (i.e., not the training data used for model construction). The symbols depict the means of the test set predictions with standard deviation error bars. The yellow solid line is the line of best fit from these models and the blue dotted line the expected $y = x$ line which would be from a perfect model.

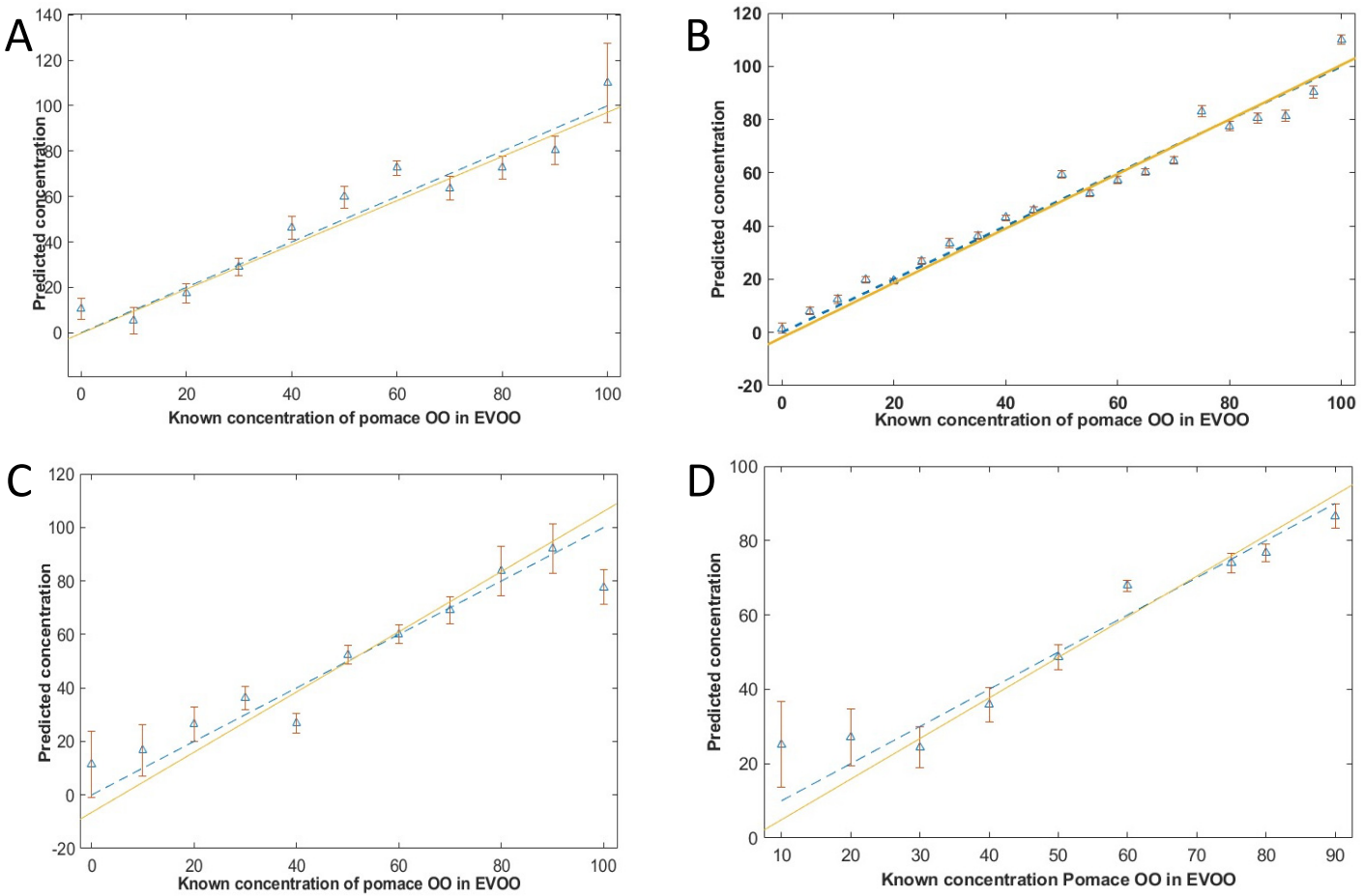

Fig. S9 PLSR prediction model plots comparing the predicted actual concentrations for the **pomace olive oil** against the known level of this adulterant in EVOO. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. PLSR was conducted using bootstrap validation (n =1000) and this figure shows the results from the test 1000 test sets only (i.e., not the training data used for model construction). The symbols depict the means of the test set predictions with standard deviation error bars. The yellow solid line is the line of best fit from these models and the blue dotted line the expected $y = x$ line which would be from a perfect model.

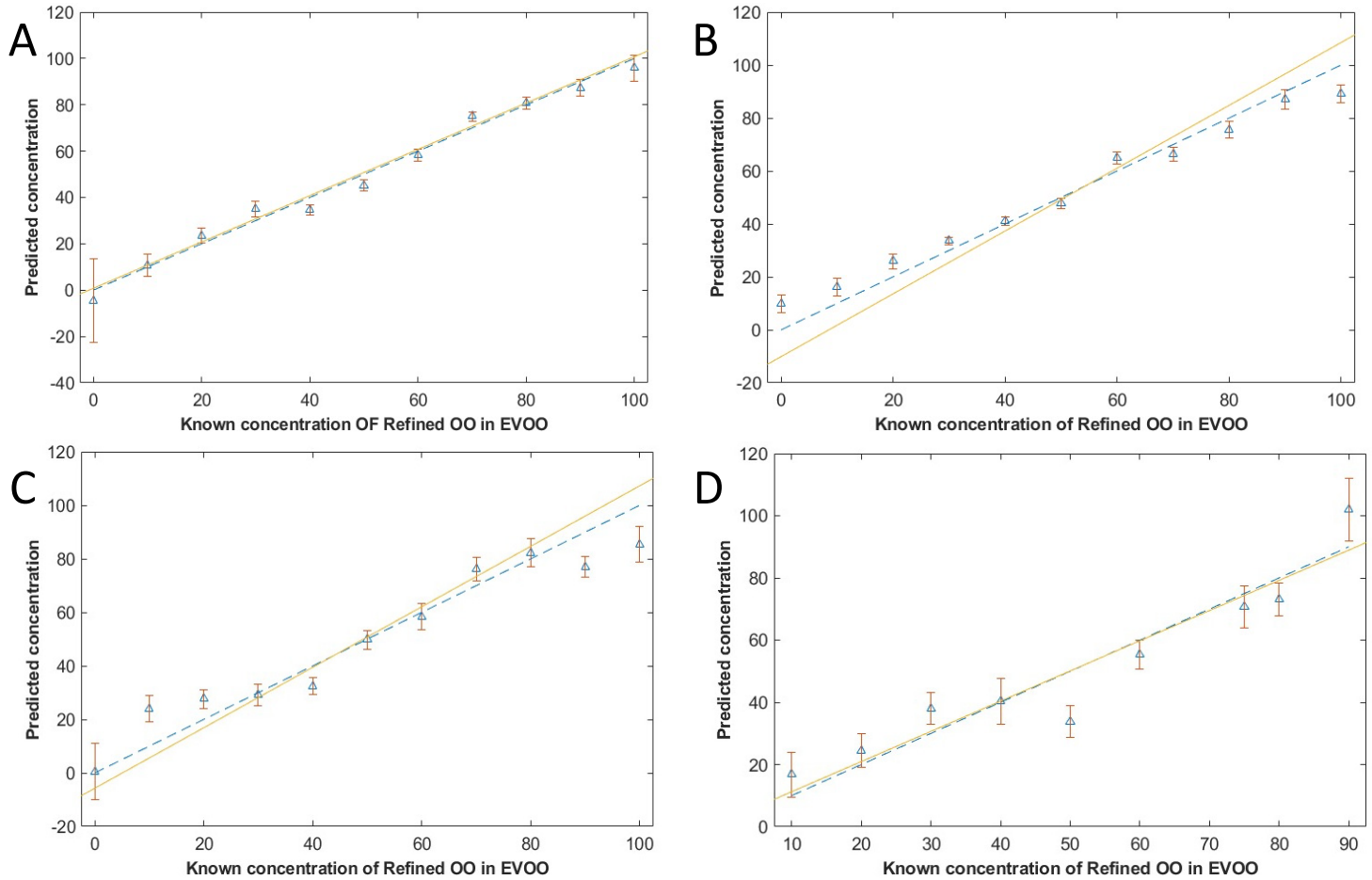

Fig. S10 PLSR prediction model plots comparing the predicted actual concentrations for the **refined olive oil** against the known level of this adulterant in EVOO. Raman data were collected in vial mode at (A) 785 nm, (B) 1064 nm and (C) 830 nm, as well as (D) directly through an olive oil bottle using SORS with 830 nm excitation. PLSR was conducted using bootstrap validation (n =1000) and this figure shows the results from the test 1000 test sets only (i.e., not the training data used for model construction). The symbols depict the means of the test set predictions with standard deviation error bars. The yellow solid line is the line of best fit from these models and the blue dotted line the expected $y = x$ line which would be from a perfect model.