

Turmeric fraud: rapid authenticity screening using benchtop analytical instruments

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Introduction

Turmeric is the powdered rhizome of the *Curcuma Longa* plant and is used for culinary and medicinal purposes. As one of the **most common examples of spice adulteration**, turmeric fraud is facilitated by the complex and dispersed nature of the commodity's supply chains and is motivated by **economic opportunity**. Dyes such as lead chromate and metanil yellow, in addition to exogenous bulking agents, have been found adulterating commercial turmeric samples, presenting significant health risks.^{1,2}

On-site colourimetric tests that are unreliable and do not screen for unknown entities are currently used to detect turmeric adulteration. Untargeted techniques such as **ATR-FTIR** have been used for food authenticity screening and **¹H NMR** is emerging as another untargeted approach. Since turmeric is composed of **~5% curcuminoids** (**Figure 1**) that produce distinct chemical markers for analysis, these analytical techniques can be proposed for turmeric authenticity analysis. However, the costs associated with high-field NMR render it unfavourable for many within the food industry whereas **benchtop NMR is cheaper and more accessible**.

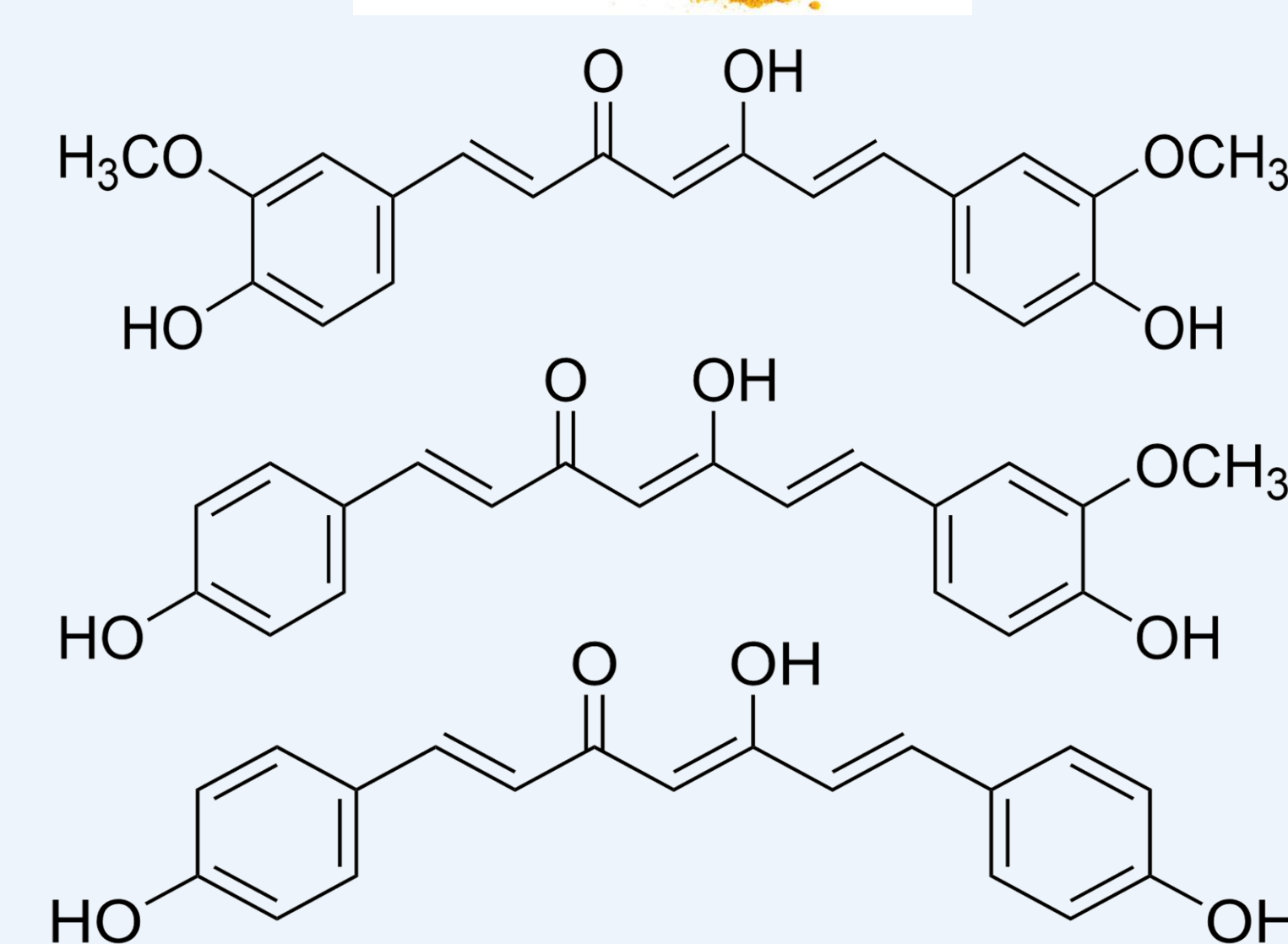


Figure 1: Structures of curcumin (top), demethoxycurcumin (middle), bisdemethoxycurcumin (bottom)

Objective

Currently, there are **no harmonised methods** for authentication, and this work addresses a key gap in the interest of food safety. Our **aim** is to evaluate the use of bench top analytical instrumentation as rapid authenticity screening approaches to turmeric fraud identification. For this, 77 samples (32 from a domestic online market and 45 from an overseas online market) of turmeric were analysed through ATR-FTIR and **benchtop 43 MHz ¹H NMR**. For ATR-FTIR, the samples were analysed in biological triplicate, yielding 231 spectra, and for 43 MHz ¹H NMR, the samples were analysed in biological and technical triplicate respectively, yielding 693 spectra. Chemometric analysis was performed on these spectra.

Results

1. Method optimisation

43 MHz ¹H NMR spectra were acquired using **ultrasonication-assisted extraction** in acetone-d₆ and DMSO-d₆. As shown in **Figure 2**, the acetone-d₆ spectrum (left) illustrates greater peak resolution in the region of the aromatic curcuminoid protons (6-8 ppm), and a sharper curcuminoid methoxy singlet (3.9 ppm) that is more distinguishable from the water region than in DMSO-d₆ (right). Based on these factors, **acetone-d₆ was selected** as the solvent for all subsequent extractions for NMR spectral acquisition.

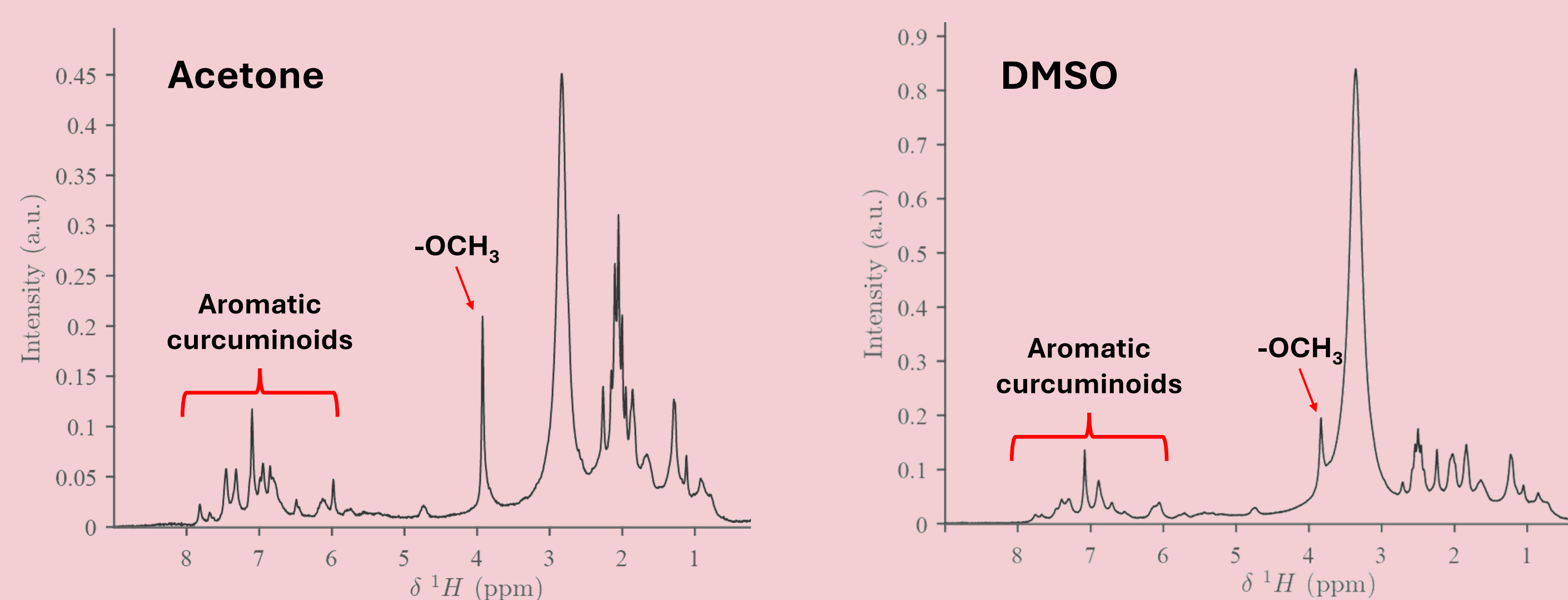


Figure 2: ¹H NMR spectrum of turmeric extracted in acetone-d₆ (left) and DMSO-d₆ (right). Spectra were acquired on the 43 MHz Magritek Spinsolve.

2. 43 MHz ¹H NMR

From the PCA plot (**Figure 3**), several trends were observed. First, the **domestic turmeric samples** formed a relatively tight central cluster. Many of the **overseas turmeric samples** were distributed away from the central region. This indicated that some samples formed a **chemically distinct region**.

Tighter clustering was observed between biological triplicates, indicating a **high degree of reproducibility**, which suggested the protocol used was robust and yielded consistent results.

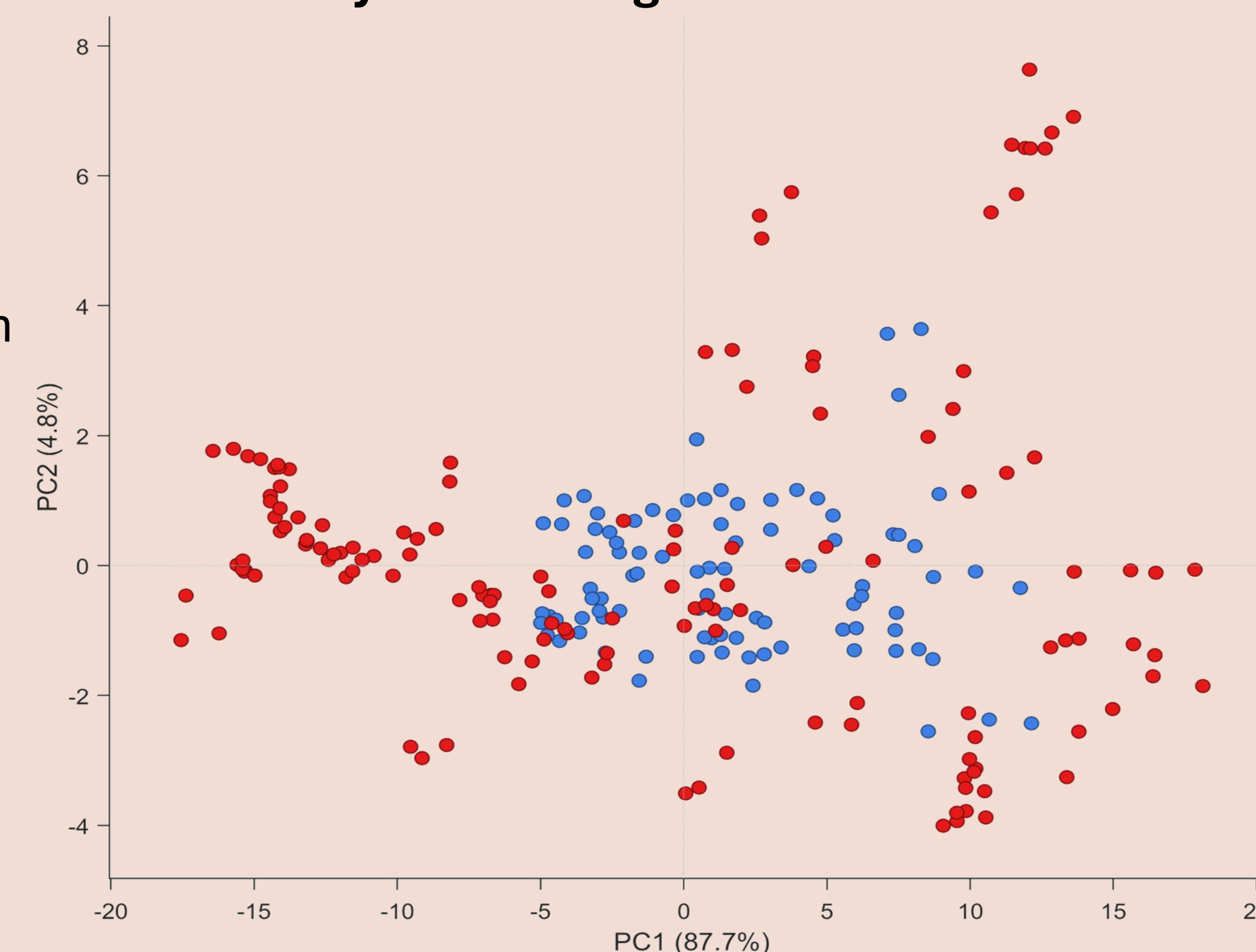


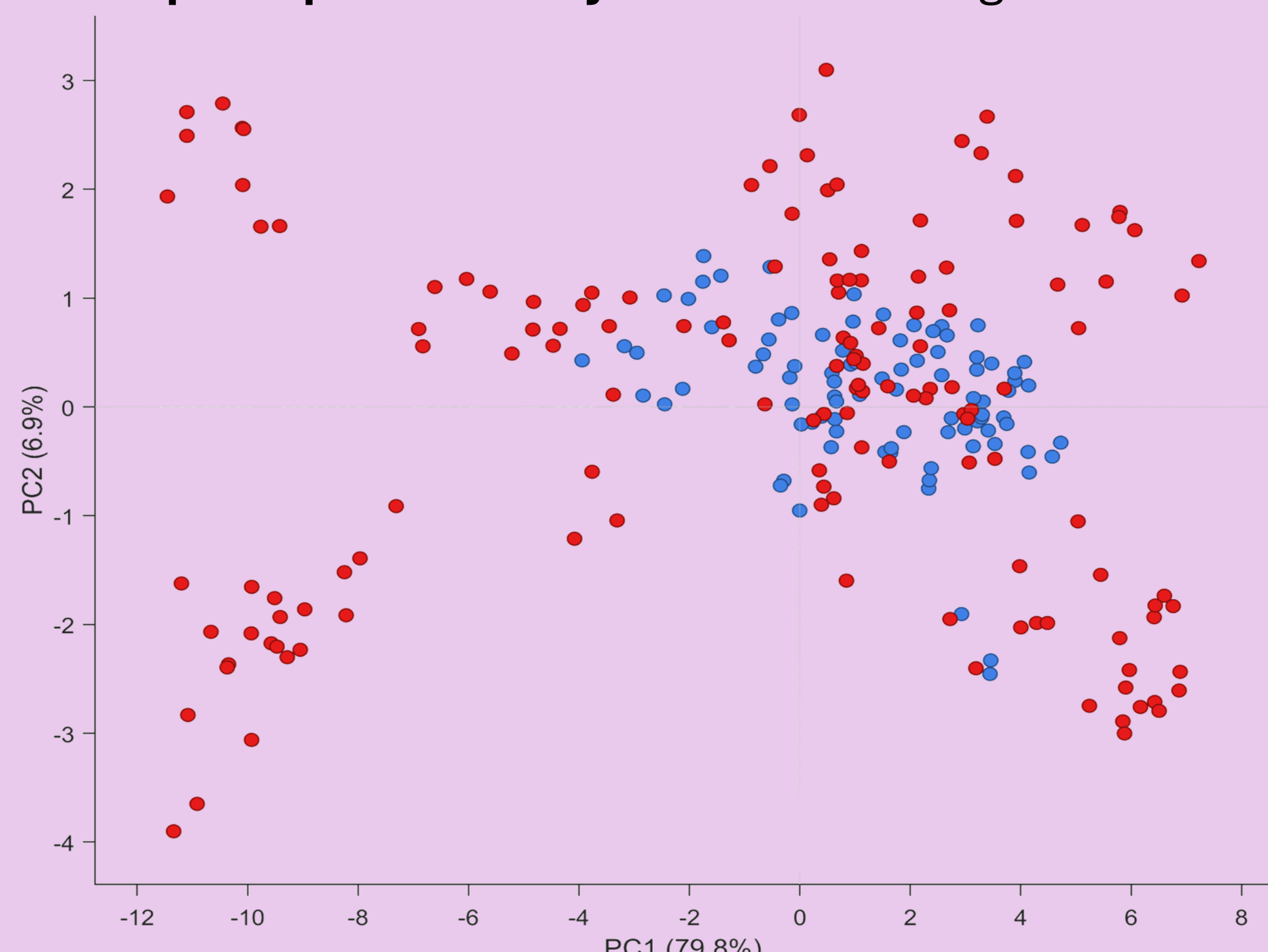
Figure 3: PCA scores plot for 77 turmeric samples analysed in biological triplicate via 43 MHz ¹H NMR. Domestic online samples are in **blue**, overseas online samples are in **red**.

3. ATR-FTIR

From the PCA plot (**Figure 4**), the **domestic samples** again formed a tight central cluster, consistent with the grouping in the NMR scores plot (**Figure 3**). The **overseas outliers** in the FTIR analysis were also consistent with those in the NMR analysis. Strong **intra-sample reproducibility** was observed again between biological replicates.

By drawing the same conclusions from two independent untargeted analytical methods, there is likely meaningful chemical variation and grouping between both sample sets.

Figure 4: PCA scores plot for 77 turmeric samples analysed in biological triplicate via ATR-FTIR. Domestic online samples are in **blue**, overseas online samples are in **red**.



Conclusions and future directions

Current work: exploratory analysis

- Chemometric pipeline elucidated – regions of interest pinpointed and analysed for two methods.
- Intra-sample reproducibility** observed.
- Complementarity exhibited between FTIR and NMR.
- Little to no sample preparation** required.
- Cross-complementarity will be further demonstrated by data analysis such as **canonical correlation analysis**.

Next stage: diversifying & standardising methodology

- Benchtop mass spectrometry to be added to the workflow.
- This will allow more facile detection of inorganic adulterants.
- Once methods have been standardised, an **authentic reference database** will be constructed which encompasses natural variability.
- One-class classification approaches can then be used to detect genuine outliers.