Quartz Crystal Microbalance with Dissipation monitoring analysis of wine polyphenols

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1.Introduction

Polyphenols, a large group of compounds, are vital in winemaking, impacting various aspects like quality, color, and taste [1]. Traditional analysis methods for polyphenols are costly and time-intensive, prompting wineries to seek alternative approaches.

Figure 1. Polyphenols winemaking process.

Quartz Crystal Microbalance with Dissipation Monitoring (QCM-D) is a gravimetric sensor, that uses a piezoelectric resonator to generate acoustic waves at a specific frequency (resonance frequency). Variations in resonance frequency, caused by mass adsorption or desorption, facilitate the study of surface phenomena [2].

We developed powerful approach for polyphenols detection. Four functionalizations for QCM-D sensors were investigated: **Bovine Serum Albumin** (**BSA**); **Gelatin type A from porcine skin** (**Gel-A**); the synthetic low-molecular-weight peptide **Istatine-5** (**Ist-5**); and a peptide fragment of the **Murine Salivary Protein-5** (**MP5**).

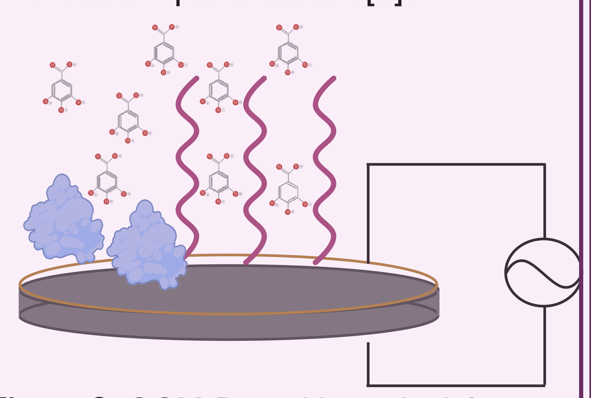

Figure 2. QCM-D working principle.

2.Experimental methods

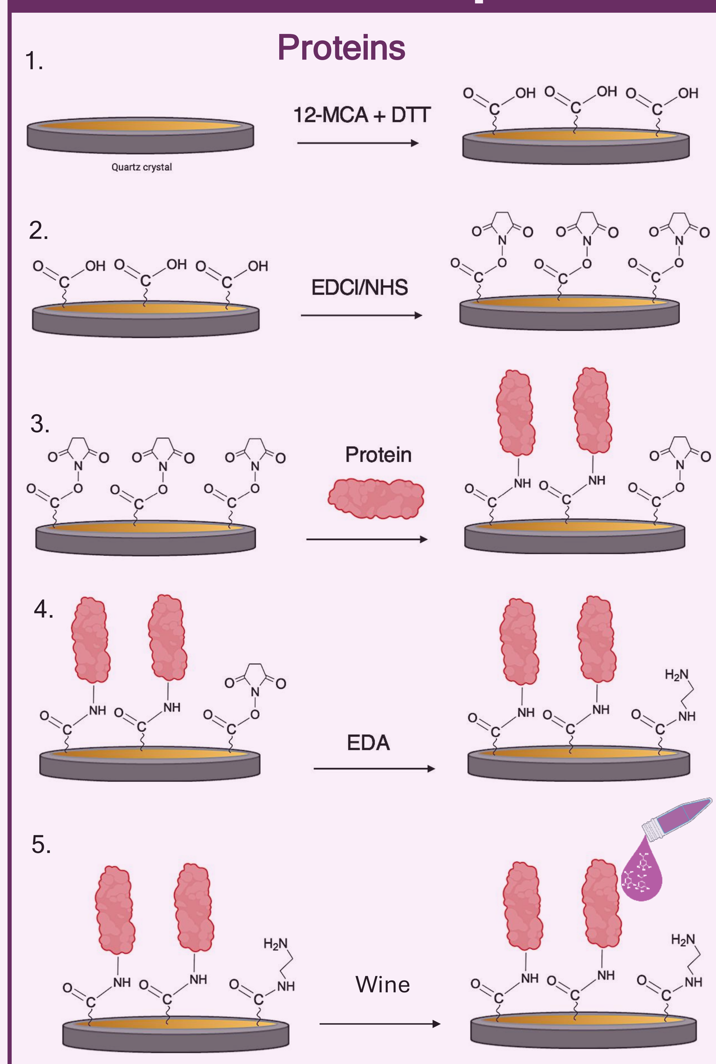

Figure 3. Sensor functionalization using proteins and sample detection: 1. Adlayer formation; 2. Coupling; 3. Protein immobilization; 4. Blocking; 5. Sample detection [3].

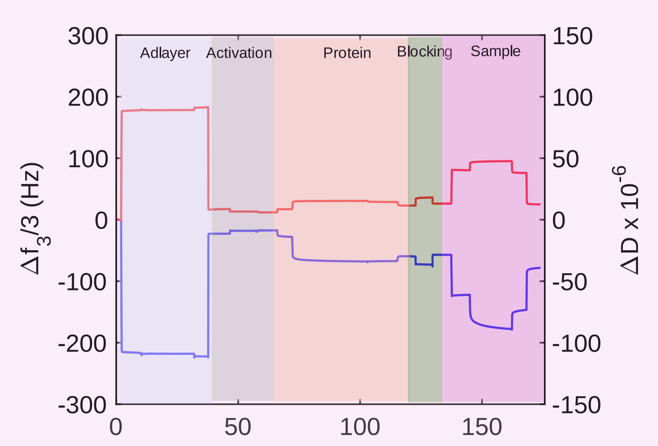

Figure 4. Typical $\Delta f_3/3$ (Hz) (blue line) and ΔD_3 (red line) traces over time during sensor functionalization with proteins and sample detection.

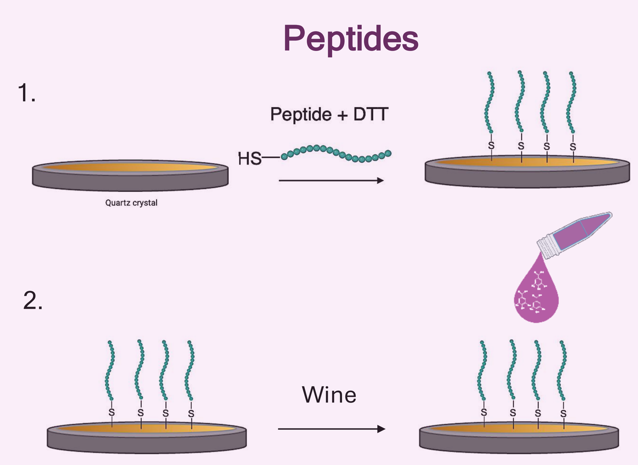

Figure 5. Functionalization process and sample detection using peptides: 1. Peptide immobilization; 2. Sample detection.

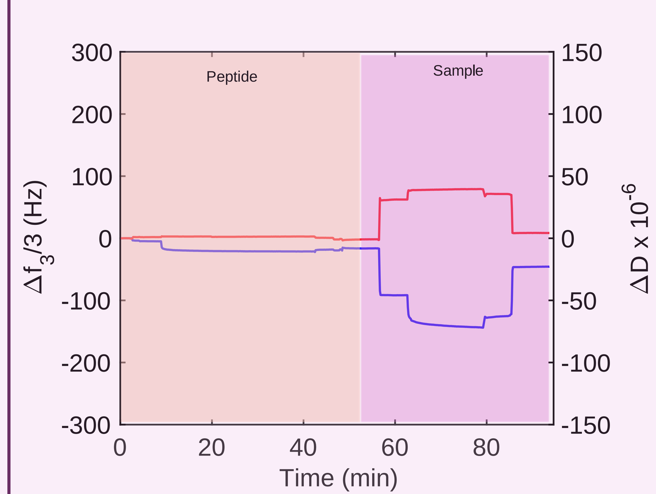

Figure 6. Typical $\Delta f_3/3$ (Hz) (blue line) and ΔD_3 (red line) traces over time during sensor functionalization with peptides and sample detection.

3.Surface functionalization

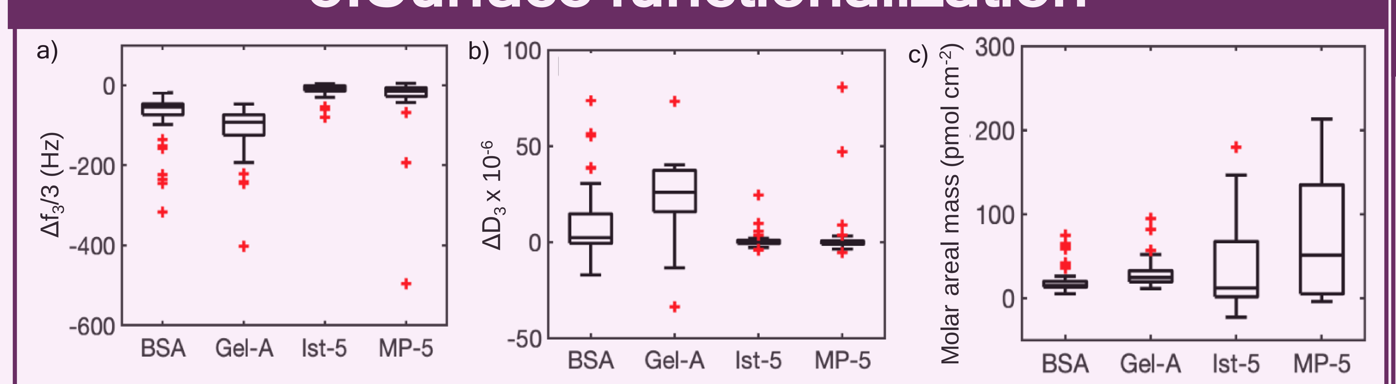

Figure 5. Characterization of the functionalized sensors: a) $\Delta f_3/3$ (Hz); b) ΔD_3 ; c) Molar areal mass (pmol cm^{-2}). N_{BSA} = 39, N_{GelA} = 32, N_{Ist5} = 30 and N_{MP5} = 30 [4]. Regarding the proteins, the functionalization protocol mirrors that detailed in experimental procedure section, omitting the blocking step.

4.Detection of polyphenols in aqueous solutions

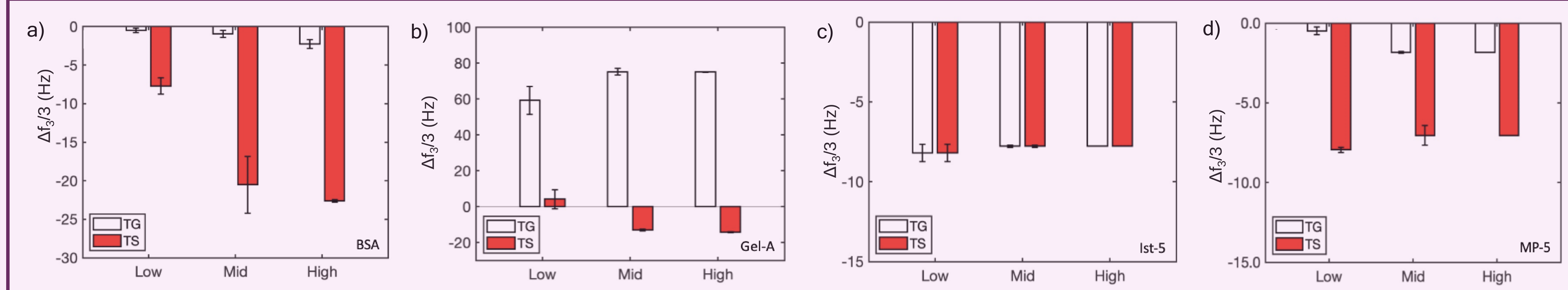

Figure 6. Detection of polyphenols in aqueous solutions: $\Delta f_3/3$ (mean ± SE) vs. sample concentration (Low = 0.02 g L^{-1}, Mid = 0.1 g L^{-1}, High = 0.19 g L^{-1}) in (**a**) BSA, (**b**) Gel-A, (**c**) Ist-5, (**d**) MP5, N=2 [3]. Regarding the proteins, the functionalization protocol mirrors that detailed in experimental procedure section, omitting the blocking step.

5.Detection of polyphenols in artificial wines

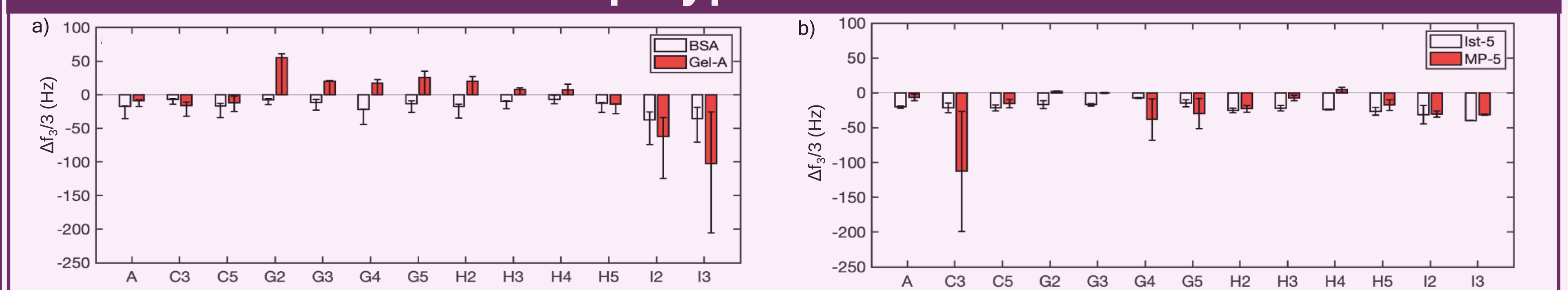

Figure 7. Detection of polyphenols in artificial wines: $\Delta f_3/3$ (mean ± SE) observed with different wine samples in (a) proteins, (b) peptides, N=2 [4]. Regarding the proteins, the functionalization protocol mirrors that detailed in experimental procedure section, omitting the blocking step.

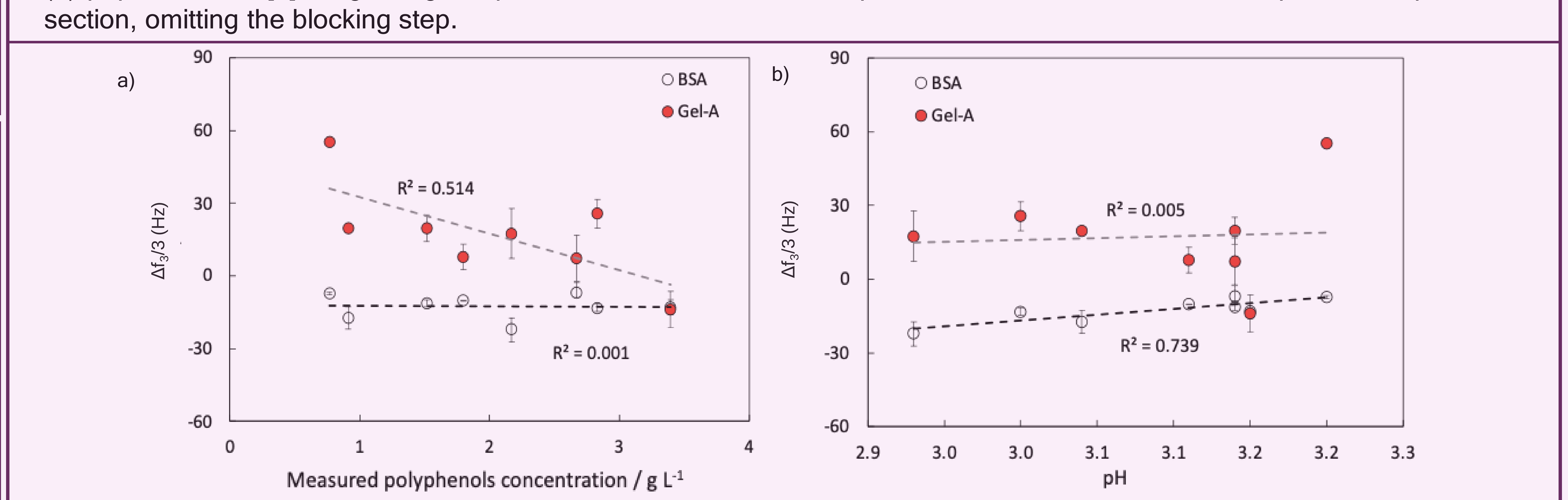

Figure 8. Detection of polyphenols in artificial wines added with gallic tannins: (**a**) as a function of measured polyphenols concentration, (**b**) as a function of measured pH, N=2 [4]. Regarding the proteins, the functionalization protocol mirrors that detailed in experimental procedure section, omitting the blocking step.

6.Detection of polyphenols in red wines

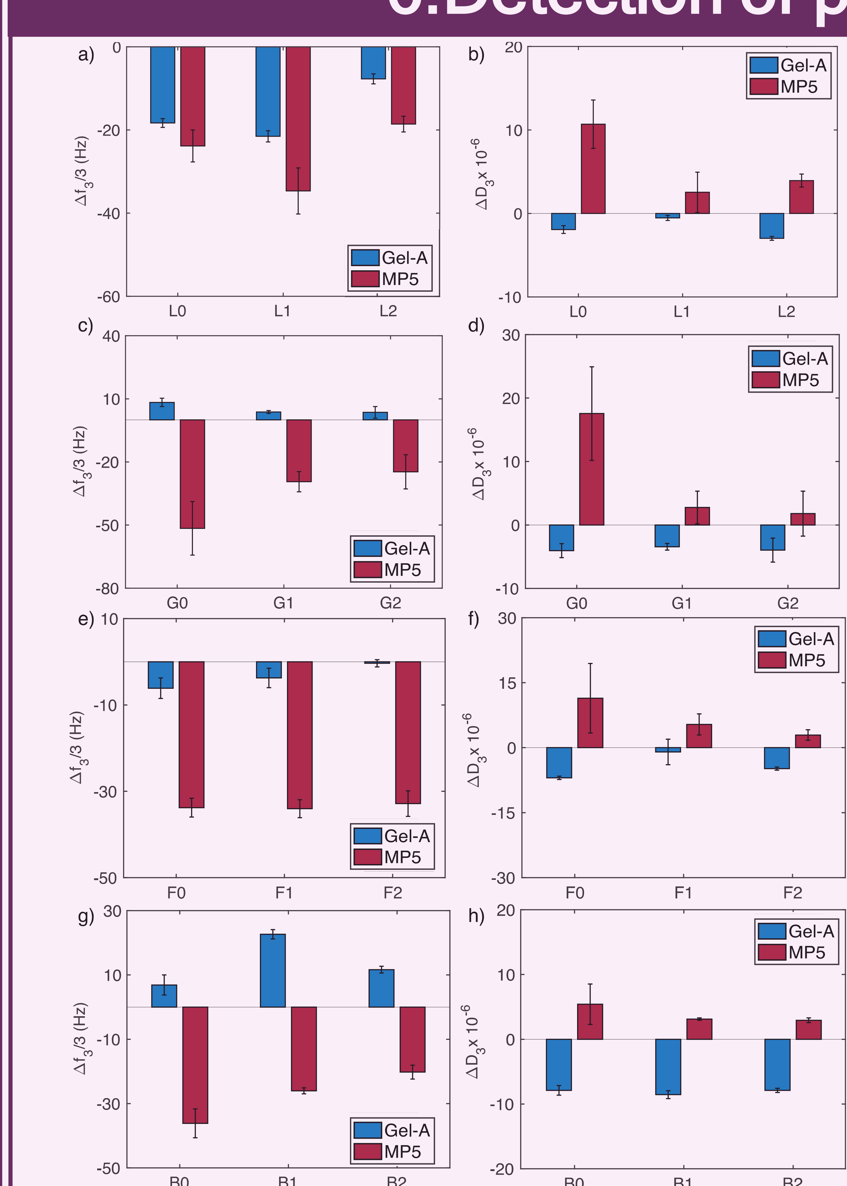

Figure 9. Detection of polyphenols in red wine samples. a), c), e), g) $\Delta f_3/3$ (mean ± SE) values with Gel-A and MP5 (blue and red respectively) and b), d), f), h) ΔD_3 (mean ± SE) values with Gel-A and MP5 (blue and red, respectively), N=4.

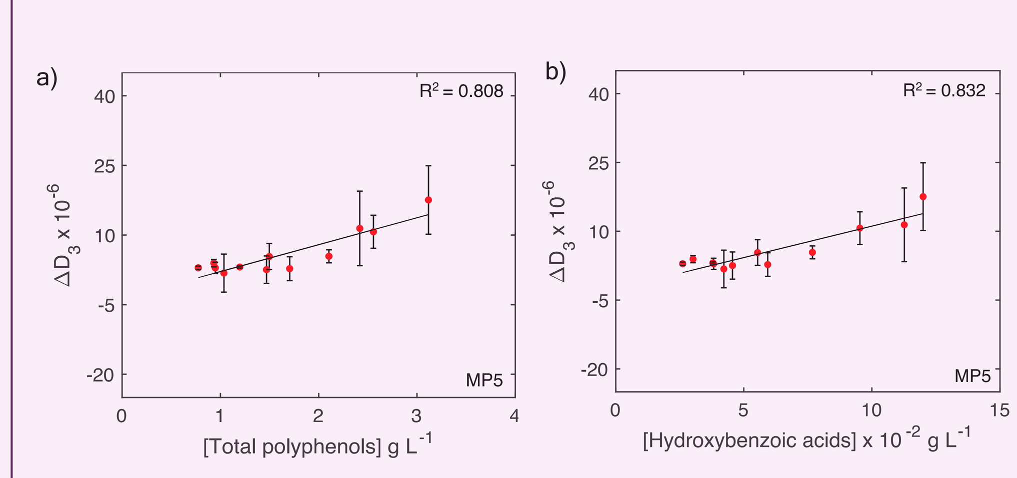

Figure 10. Dissipation shift (ΔD_3, mean ± SE) as a function of: a) total polyphenols concentration, b) hydroxybenzoic acids concentration in sensors functionalized with MP5, N=4.

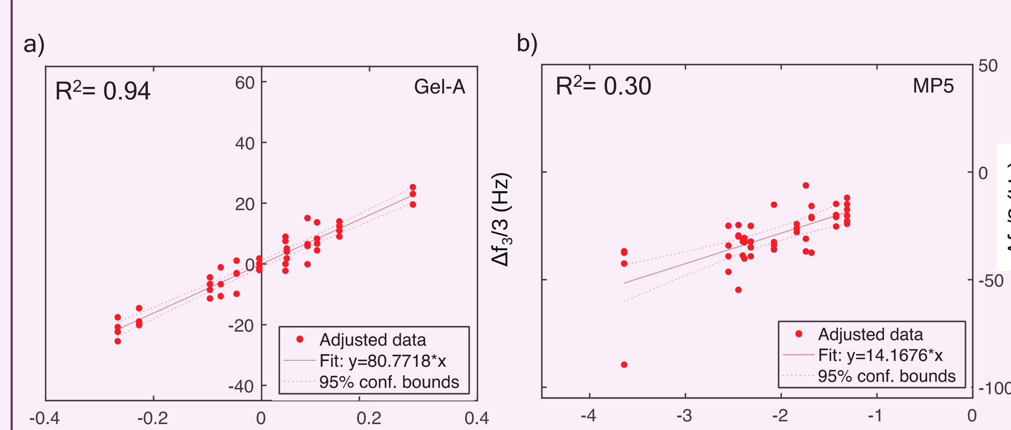

Figure 11. Multilinear regression model. The the fit of 14 independent variables (different polyphenolic species in the wine matrix) against the dependent variable, $\Delta f_3/3$ (Hz), is shown.

7.Conclusions and Acknowledgements

- The functionalization of the quartz crystals was correctly obtained with all the tested probes. The functionalizations demonstrated promising performance in the analysis of polyphenols both in aqueous solutions of and in artificial wines. Using Gel-A, a linear trend was observed between the frequency shift and total polyphenols concentration in artificial wines added with gallic tannins.
- Gel-A and MP5 also confirmed their potential in the analysis of polyphenols in red wines. In sensors functionalized with MP5 a linear trend was highlighted between dissipation shift and both total polyphenols and hydroxybenzoic acid concentration.
- The multilinear regression model revealed that the frequency response obtained with Gel-A was determined by the combined effect of the different polyphenolic subfamilies in the wine matrix.
- Our research paves the way for the potential future applications of these strategies in oenology field.

This research was funded by the Italian Ministry of University and Research (MUR) with the project 'VioLOC – Wine and Oil Analysis 4.0: development of a Lab-On-Chip with remote connectivity' FISR 2019, Grant FISR2019-03020.

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