# Supplementary material

## Enhancing verapamil traces determination from biological matrices by bar adsorptive microextraction

Camilla Fonseca Silva[1,2], Mariana Foles Mendes[2], José Manuel Flôrencio Nogueira[2,*], Keyller Bastos Borges[1,*]

[1] Departamento de Ciências Naturais, Universidade Federal de São João del-Rei, Campus Dom Bosco, Praça Dom Helvécio 74, Fábricas, 36301-160, São João del-Rei, Minas Gerais, Brazil.

[2] Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.

*Corresponding author:

Prof. Keyller Bastos Borges, PhD, Departamento de Ciências Naturais, Universidade Federal de São João del-Rei, Campus Dom Bosco, Praça Dom Helvécio 74, Fábricas, 36301-160, São João del-Rei, Minas Gerais, Brazil

*e-mail: keyller@ufsj.edu.br

Prof. José Manuel Florêncio Nogueira, PhD. Centro de Química Estrutural, Institute of Molecular Sciences, Departamento de Química e Bioquímica, Faculdade de Ciências, Universidade de Lisboa, Campo Grande, 1749-016 Lisboa, Portugal.

*e-mail: jmnogueira@ciencias.ulisboa.pt

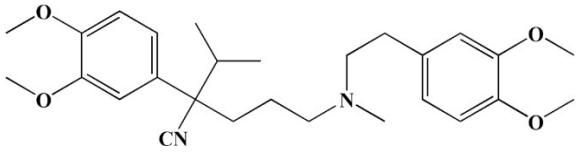
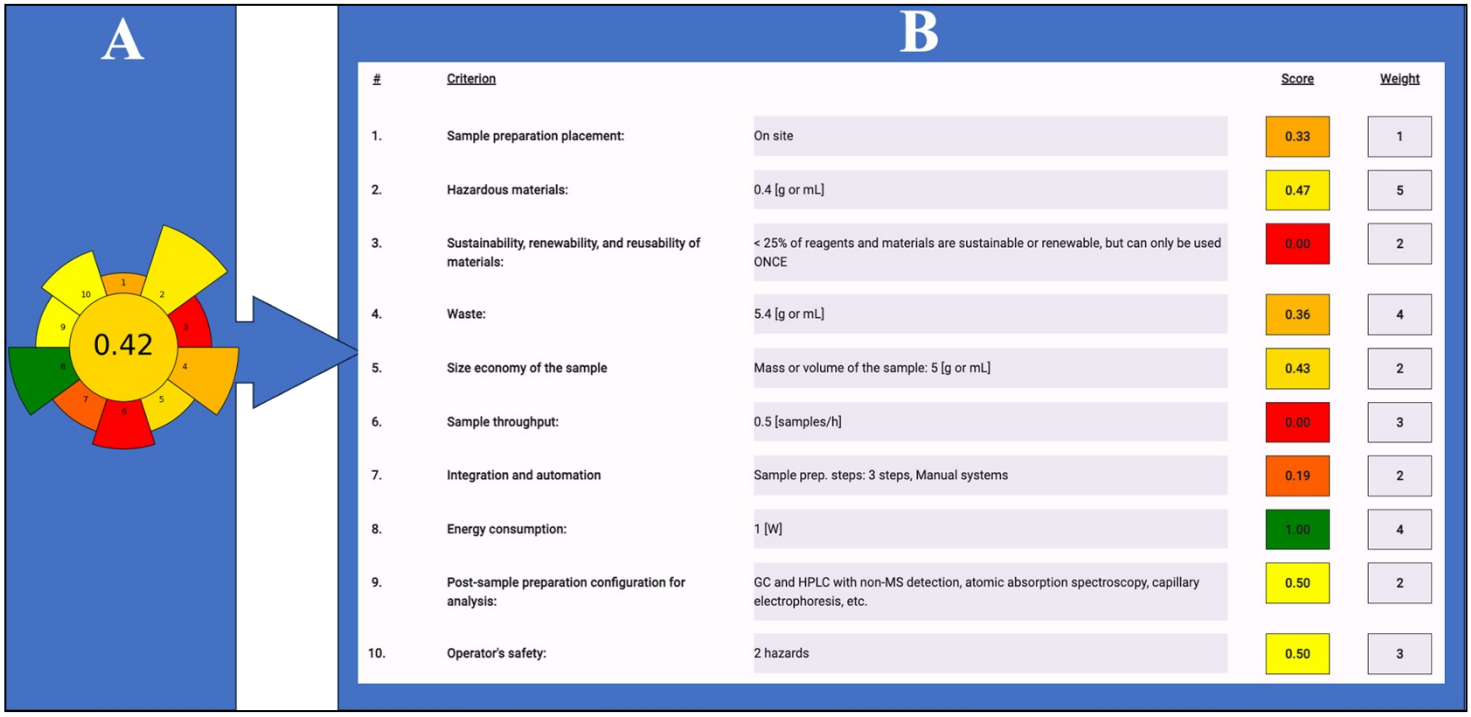



**Figure S1.** Chemical structure of the VER molecule.




| # | Criterion | | Score | Weight |
|---|---|---|---|---|
| 1. | Sample preparation placement: | On site | 0.33 | 1 |
| 2. | Hazardous materials: | 0.4 [g or mL] | 0.47 | 5 |
| 3. | Sustainability, renewability, and reusability of materials: | < 25% of reagents and materials are sustainable or renewable, but can only be used ONCE | 0.00 | 2 |
| 4. | Waste: | 5.4 [g or mL] | 0.36 | 4 |
| 5. | Size economy of the sample | Mass or volume of the sample: 5 [g or mL] | 0.43 | 2 |
| 6. | Sample throughput: | 0.5 [samples/h] | 0.00 | 3 |
| 7. | Integration and automation | Sample prep. steps: 3 steps, Manual systems | 0.19 | 2 |
| 8. | Energy consumption: | 1 [W] | 1.00 | 4 |
| 9. | Post-sample preparation configuration for analysis: | GC and HPLC with non-MS detection, atomic absorption spectroscopy, capillary electrophoresis, etc. | 0.50 | 2 |
| 10. | Operator's safety: | 2 hazards | 0.50 | 3 |

**Figure S2. (A)** Graphical results from the AGREEprep analysis calculated by emulator version *online;* **(B)** Criteria and data input for each subcategory with the final scores and weight employed for the BAμE procedure.

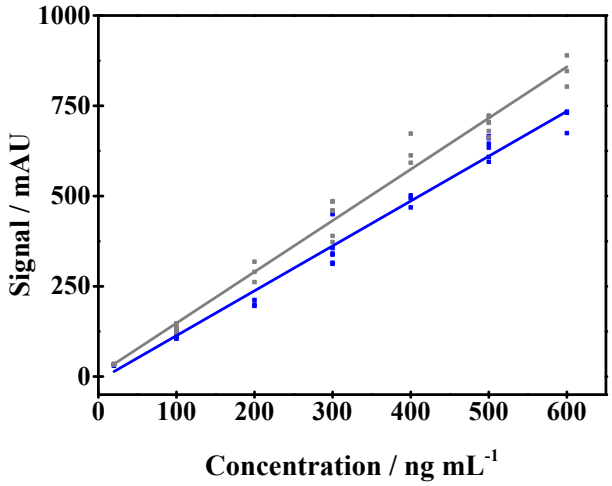



**Figure S3.** Analytical curves obtained for each method. In blue: STRATA-CN, in gray: ENVI-18.

**Table S1.** Main characteristics of the evaluated polymeric phases

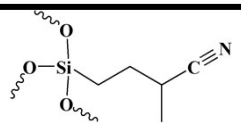
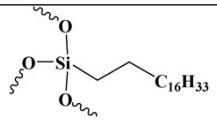
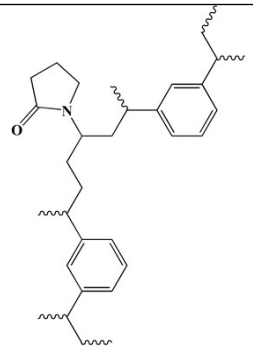
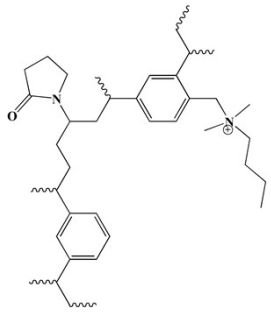
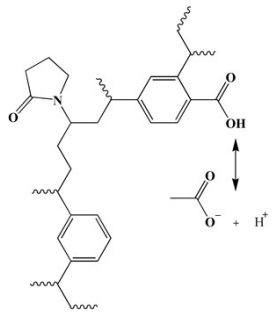
| Commercial name | Chemical structure | Separation mode | Type of analyte | Surface area ($m^2$ $g^{-1}$) | Particle size (µm) | Pore size (Å) |
|---|---|---|---|---|---|---|
| **STRATA-CN** |  | Normal phase | More polar | 500 | 55 | 70 |
| **ENVI-18** |  | Reverse phase | More apolar | 475 | 45 | 60 |
| **Oasis HLB** |  | Reverse phase | Polar e apolar | 810 | 30 | 80 |
| **Oasis MAX** |  | Reverse phase and strong anionic exchange | Acids | 830 | 30 | 80 |
| **Oasis WCX** |  | Reverse phase and strong cationic exchange | Bases (including quaternary amines) | 750 | 30 | 80 |

**Table S2.** Precision and accuracy of the analytical methods

| **Method** | **STRAT-CN** | | | **ENVI-18** | | |
|---|---|---|---|---|---|---|
| **Nominal concentration / ng mL$^{-1}$** | **100** | **300** | **500** | **100** | **300** | **500** |
| | | | **Intra-day / n[a] = 6** | | | |
| **Concentration analyzed / ng mL$^{-1}$** | 90.97 | 307.12 | 487.88 | 86.14 | 274.37 | 502.02 |
| **Precision / %RSD [b]** | 7.35 | 11.06 | 3.32 | 9.08 | 14.36 | 4.45 |
| **Accuracy / %RE [c]** | -9.03 | 2.38 | -2.42 | -13.87 | -8.54 | 0.40 |
| | | | **Inter-day / n[a] = 6** | | | |
| **Concentration analyzed / ng mL$^{-1}$** | 94.33 | 296.47 | 502.91 | 93.62 | 292.50 | 492.72 |
| **Precision / %RSD[b]** | 1.15 | 6.87 | 2.73 | 11.04 | 14.33 | 3.79 |
| **Accuracy / %RE[c]** | -5.67 | -1.18 | 0.58 | -6.38 | -2.50 | -1.46 |

[a] n = number of repetitions; [b] %RSD = mean relative standard deviation; [c] %RE = mean relative error