

10-YEAR OVERVIEW OF HALOANISOLE AND HALOPHENOL PROFICIENCY TESTING IN WINE

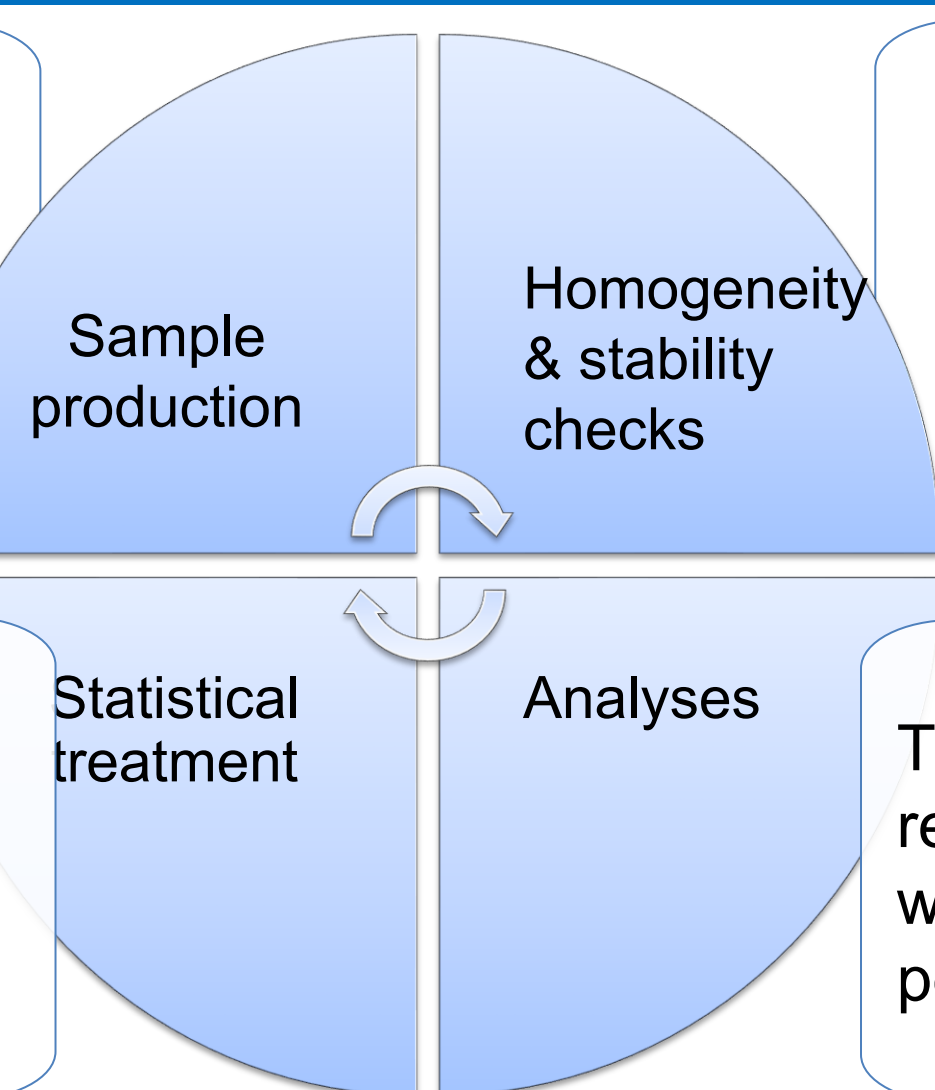
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INTRODUCTION

Haloanisole (HA) contamination is a major concern for wine quality because these highly odor-active compounds can irreversibly affect wine aroma. Trace concentrations of 2,4,6-trichloroanisole (TCA), 2,3,4,6-tetrachloroanisole (TeCA), pentachloroanisole (PCA), and 2,4,6-tribromoanisole (TBA) are sufficient to produce musty or mouldy off-flavours [1]. Although these compounds share similar sensory characteristics, their odour detection thresholds differ. HA are not naturally present in wine. They are formed by microbial O-methylation of their corresponding halophenols (HP), which originate from contaminated corks, treated wood, environmental contamination, or certain sanitizing agents used in wineries [2]. Since the early 2000s, growing awareness of HA and their precursors has increased the demand for their analysis in wines and spirits [3]. Consequently, proficiency testing (PT) schemes have been developed in accordance with the requirements of ISO 17043 standard [4] to support laboratory accreditation and ensure the quality and reliability of analytical results. The results from PTs conducted between October 2015 and June 2026 are presented in this study. During this period, an average of 5 PTs were organized annually.

DESIGN & IMPLEMENTATION

Wines and spirits are spiked with HA and HP at different concentrations. The spiked product is then handled using a specific equipment to ensure homogeneity during the sampling and correctly conditioned to ensure the stability of the manufactured samples.



After the production and before the shipment to the laboratories, the homogeneity and stability of the samples for the duration of the test are checked, according to requirements of the ANNEX B of ISO 13528 standard [5].

The statistical treatments were conducted according to ISO 13528 standard [5]. The assigned values (x_{pt}) were estimated using the means of all results (except incoherent ones), obtained from the application of robust algorithm A.

The laboratories participating in PTs are required to return their results, via a dedicated website after a period of 3 weeks, specifying the performed method.

Performances of each laboratory were evaluated using a tolerance value, set by the Technical Committee, by calculating z-scores (z). The z-score (z_i) for a result x_i is calculated as :

$$z_i = (x_i - x_{pt}) / \sigma_{pt}$$

Where:

x_i is the result indicated by the laboratory

x_{pt} is the assigned value

σ_{pt} is the standard deviation for proficiency assessment (which corresponds to half the tolerance value).

The results can then be classified as follows:

$|z| \leq 2$: acceptable
 $2 < |z| < 3$: warning signal
 $|z| \geq 3$: not acceptable.

Figure 1. Description of main steps of PTs

RESULTS & DISCUSSION

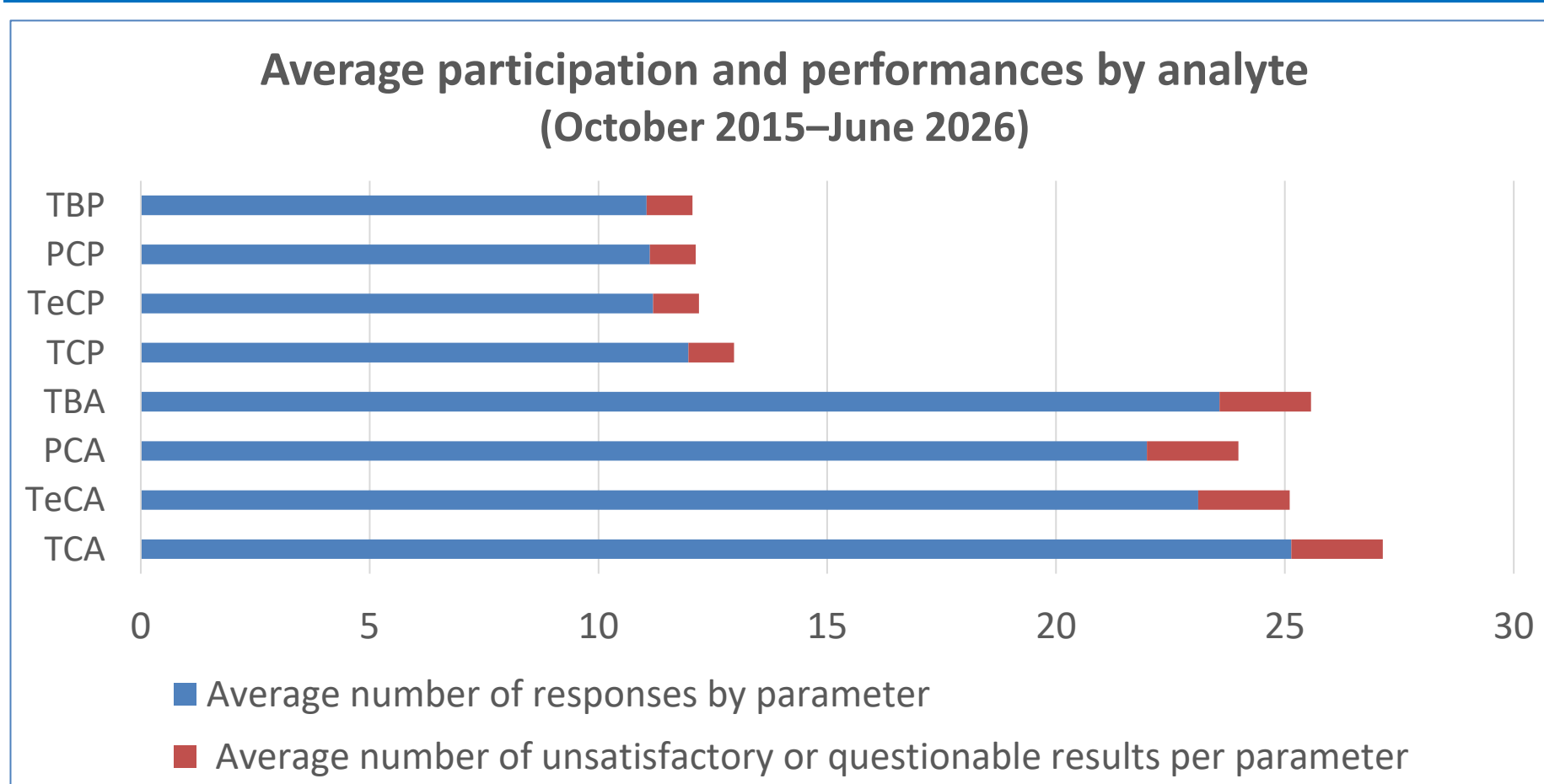


Figure 2. Average number of returned results and laboratories performances by analyte from October 2015 to June 2026

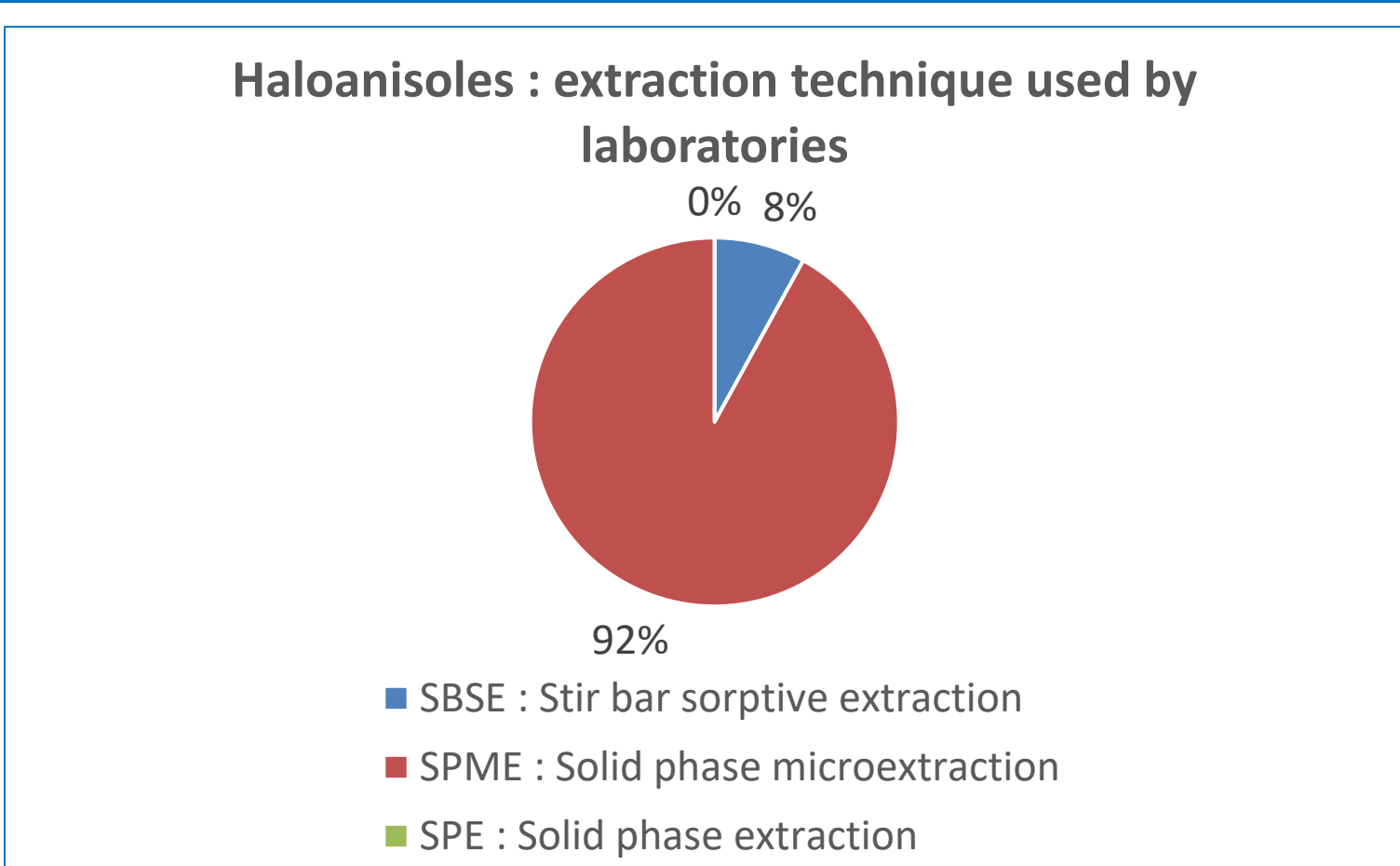


Figure 3. Extraction techniques indicated by laboratories for HA extractions

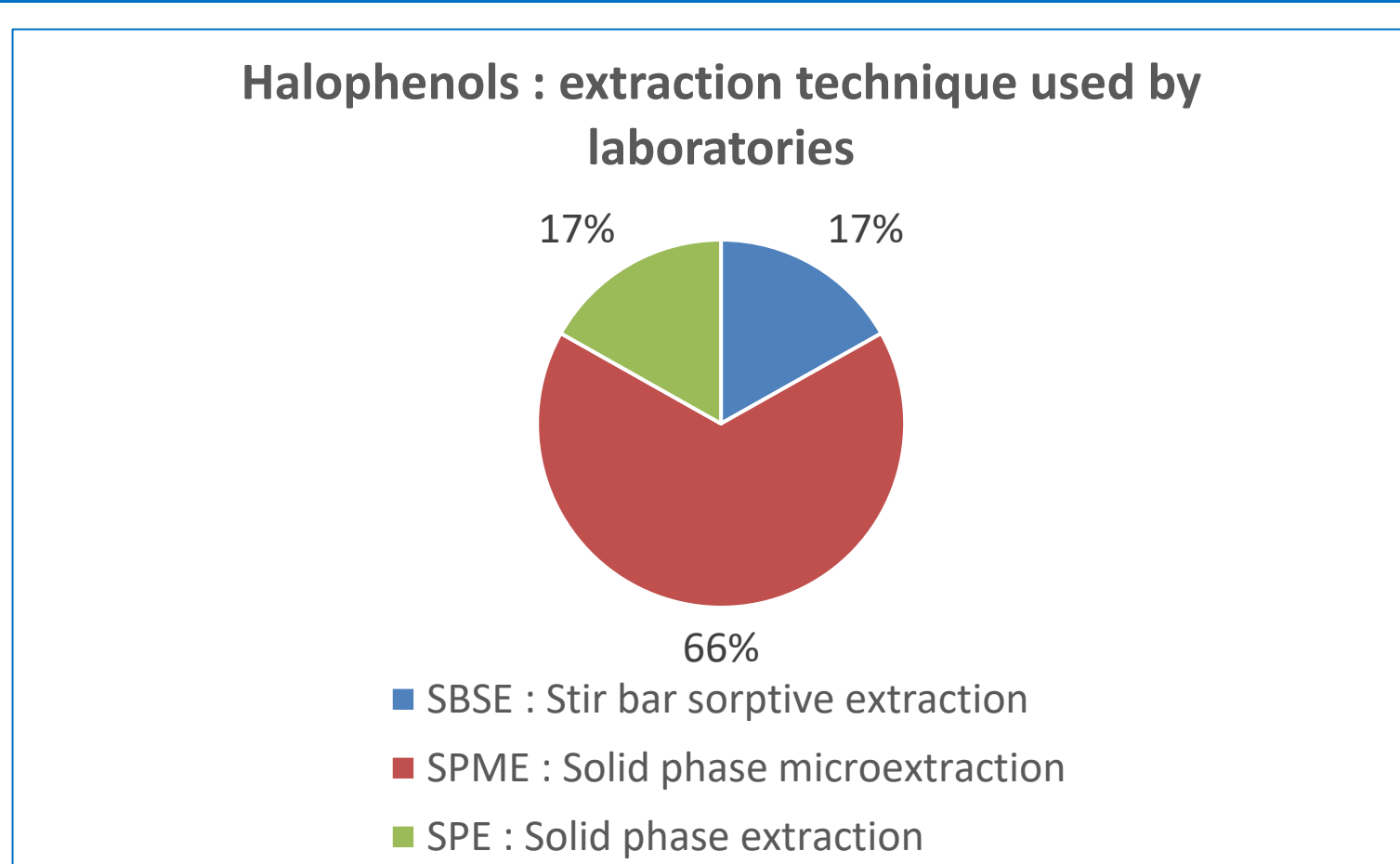


Figure 4. Extraction techniques indicated by laboratories for HP extractions

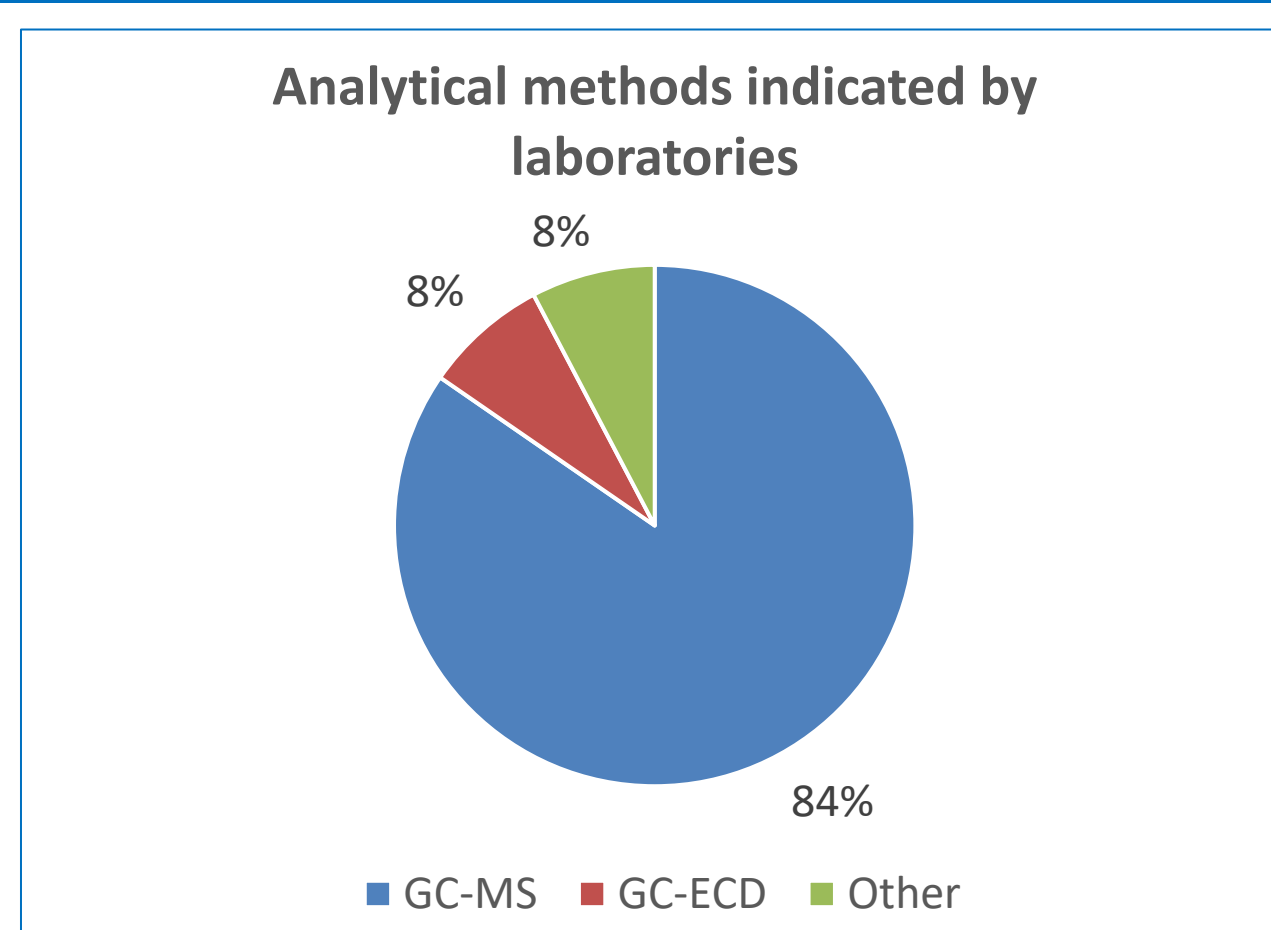


Figure 5. Analytical methods used by laboratories for HA and HP analyses

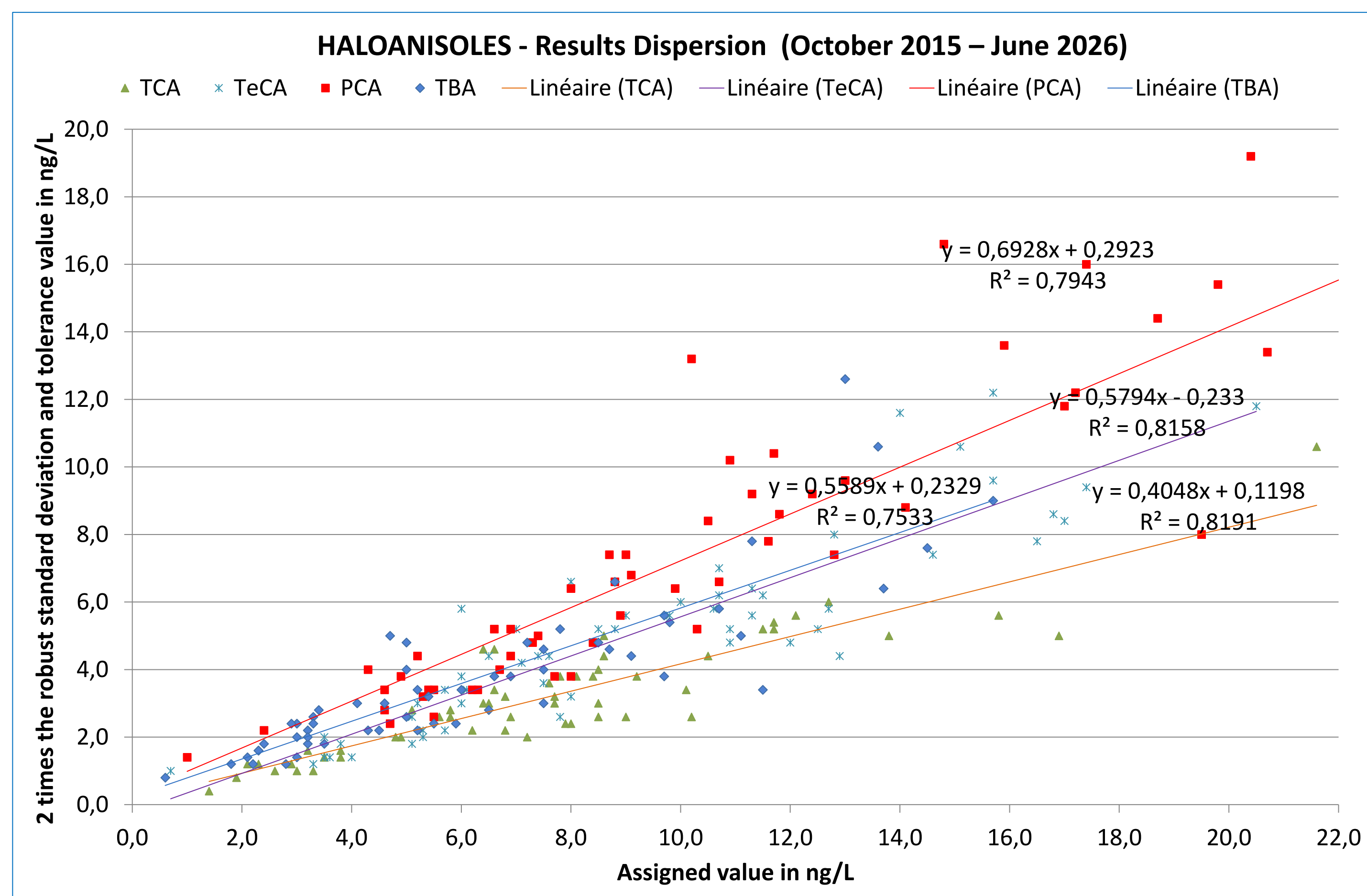


Figure 6. Results dispersion as a function of the assigned value for HA analyses (PT from October 2015 to June 2026)

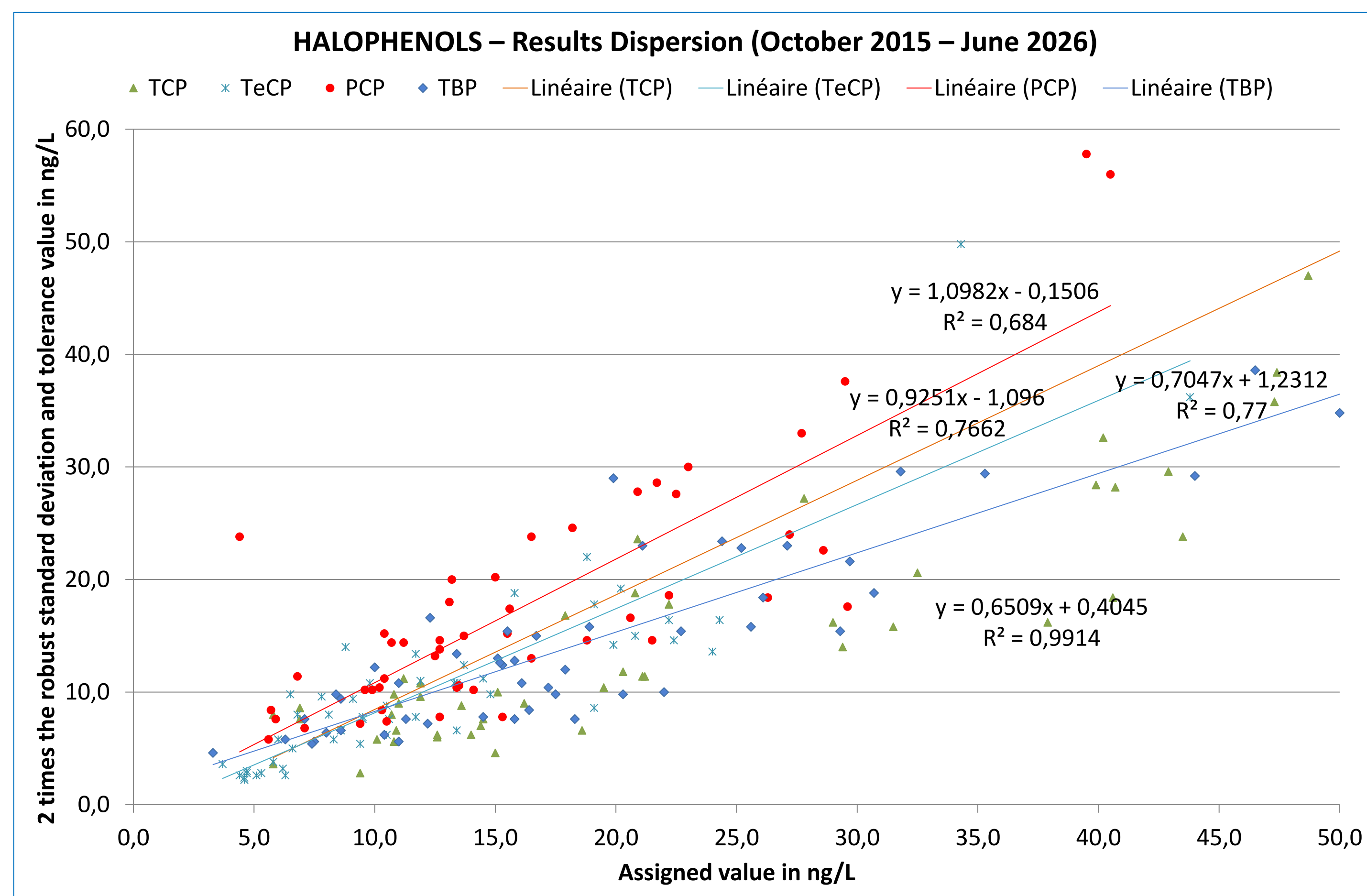


Figure 7. Results dispersion as a function of the assigned value for HP analyses (PT from October 2015 to June 2026)

Average participation from October 2015 to June 2026 is stable and varies from 27 laboratories for TCA and 12 for TeCP, PCP and TBP. Most laboratories use SPME as the extraction method and GC-MS for compounds quantification. No method-related effect was observed for this studied period. Based on the tolerance values defined by the specialist committee as performance targets, the results are satisfactory, with an average of between 1 and 2 laboratories with questionable or unsatisfactory. However, the dispersion of the results remains high, particularly for PCA and all HP. Graphs on Figures 6 & 7 plot twice the robust standard deviation according to the assigned value obtained on the PT from October 2015 to June 2026 for all HA & HP: the variability in results is close to 100 per cent for some compounds. There may be several sources of dispersion, including the different extraction techniques used by laboratories, SPME fiber type and age, extraction temperature and time, GC column selection, mass spectrometer sensitivity, calibration and blank control, internal standard quality and the low spiking concentrations. No matrix effect was detected: Figure 8 shows results' dispersion for TCA highlighting the different analyzed products (white, red, fortified, rosé wines and spirits). No trends were identified based on the matrix analyzed and these results were confirmed the other compounds analyzed.

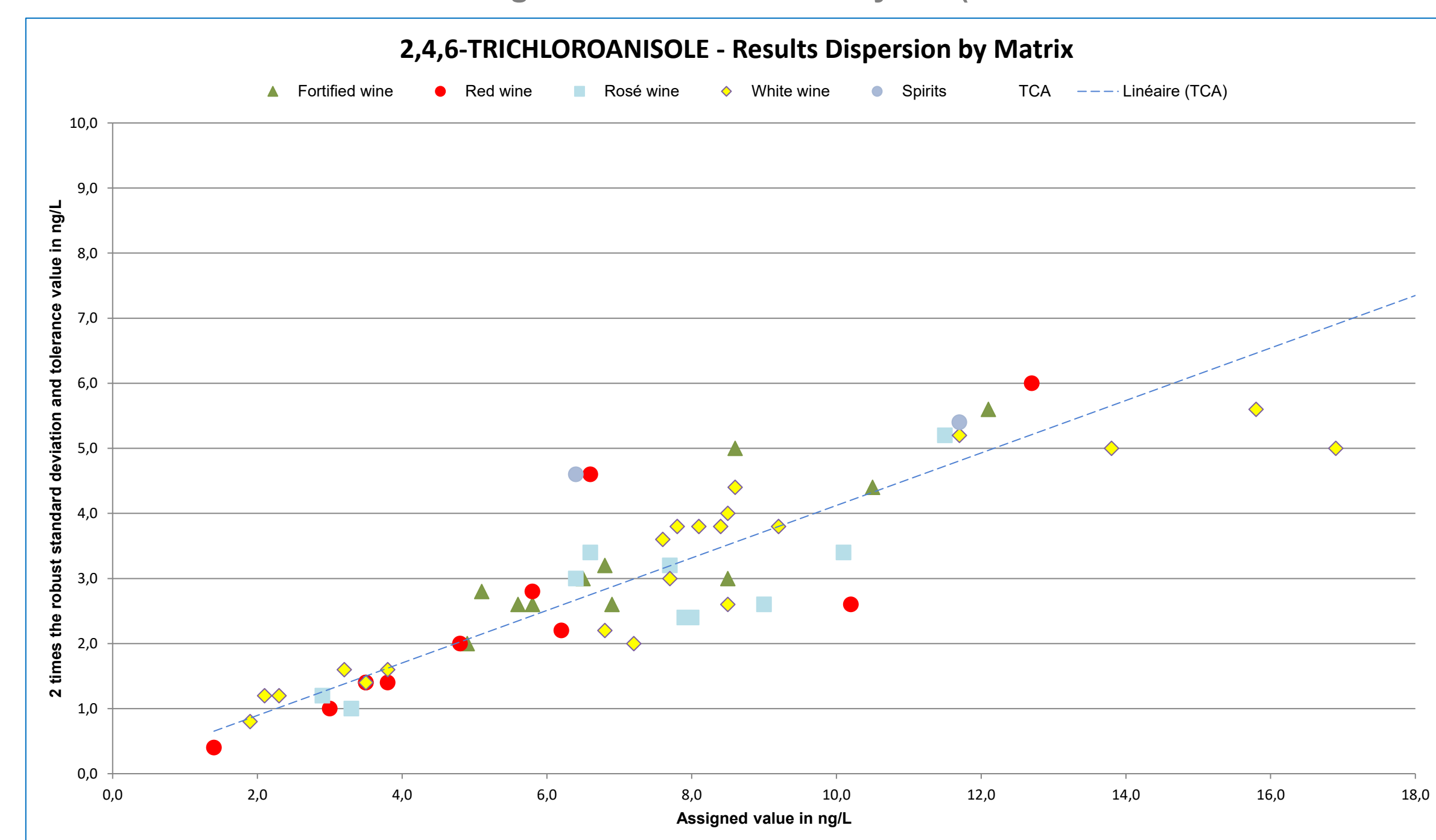


Figure 8. Results dispersion by matrix for TCA analyses (PT from October 2015 to June 2026)

CONCLUSION

Analysis of haloanisoles and halophenols can be considered a mature field, and competent laboratories routinely produce reliable results. The remaining challenges are not identifying the compounds but quantifying them accurately at parts-per-trillion levels while preventing contamination and controlling matrix effects. There is, in fact, still considerable dispersion in the results, particularly for halophenols and PCA. TCA remains the analyte that laboratories analyze with the highest level of proficiency.

REFERENCES

- Buser H. R., Zanier C. and Tanner H. (1982) Identification of 2,4,6-trichloroanisole as a potent compound causing cork taint in wine. J. Agric. Food Chem. 30:359-362
- Chatonnet P., Bonnet S., Boutou S. and Labadie M.D. (2004) Identification and responsibility of 2,4,6-tribromoanisole in musty, corked odors in wine. J. Agric. Food Chem. 52:1255-1262
- Callejón R.M., Ubeda C., Ríos-Reina R., Morales M.L. and Troncoso A.M. (2016) Recent developments in the analysis of musty odour compounds in water and wine: A review. Journal of Chromatography A. 1428:72-75
- ISO/IEC 17043:2023 - Conformity assessment — General requirements for the competence of proficiency testing providers.
- ISO 13528:2022 - Statistical methods for use in proficiency testing by interlaboratory comparisons.