NMR OF WINES
CONSUMER AND INDUSTRY PROTECTION AGAINST FRAUD AND SABOTAGE

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INTRODUCTION

The Bruker company has developed several lines of application of the proton NMR (Nuclear Magnetic Resonance) technique in the control and analysis of wine and, Estación Enológica de Haro (EEH), as a partner, has collaborated with them in it. The Wine-Profiling™ equipment, which allows obtaining the "fingerprint" of a wine, has a versatility that makes it possible to adapt the analysis to the specific needs of the client, since, it can be used both for self-control and for the detection of fraud, or the improvement of the production process, among other purposes, opening up a range of very important possibilities at the service of the wine sector. What really makes this equipment different, is the consistency check of wines by origin and variety. The EEH is the only Spanish laboratory that has Wine-Profiling™ and is also Bruker's exclusive partner in the creation of the Spanish wine database, and with which the predictive models used throughout the world are developed.

MATERIAL AND METHODS

The Comunidad Autónoma de La Rioja acquired the Wine-Profiling™ by Bruker in 2014, an innovative solution for the analysis of wine using NMR spectroscopy.[1] The main objective of the action was to establish Estación Enológica de Haro, with the help of new NMR facility, as a reference lab for wine authenticity and quality determination in Spain, as partner of the Bruker NMR database network.

Figure 1. Wine-Profiling™ equipment.

Until then there had been no method to verify the consistency of the origin of a wine while at the same time giving us analytical information about over 50 of its metabolites. All of these in less than 20 minutes and with less than 1 ml of sample (**Figure 2**). Bruker Company obtained ISO.17025 accreditation for this methodology in 2015, and quantification methodology is a official IV type analysis in OIV for same metabolites (OIV-MA-AS316-01)
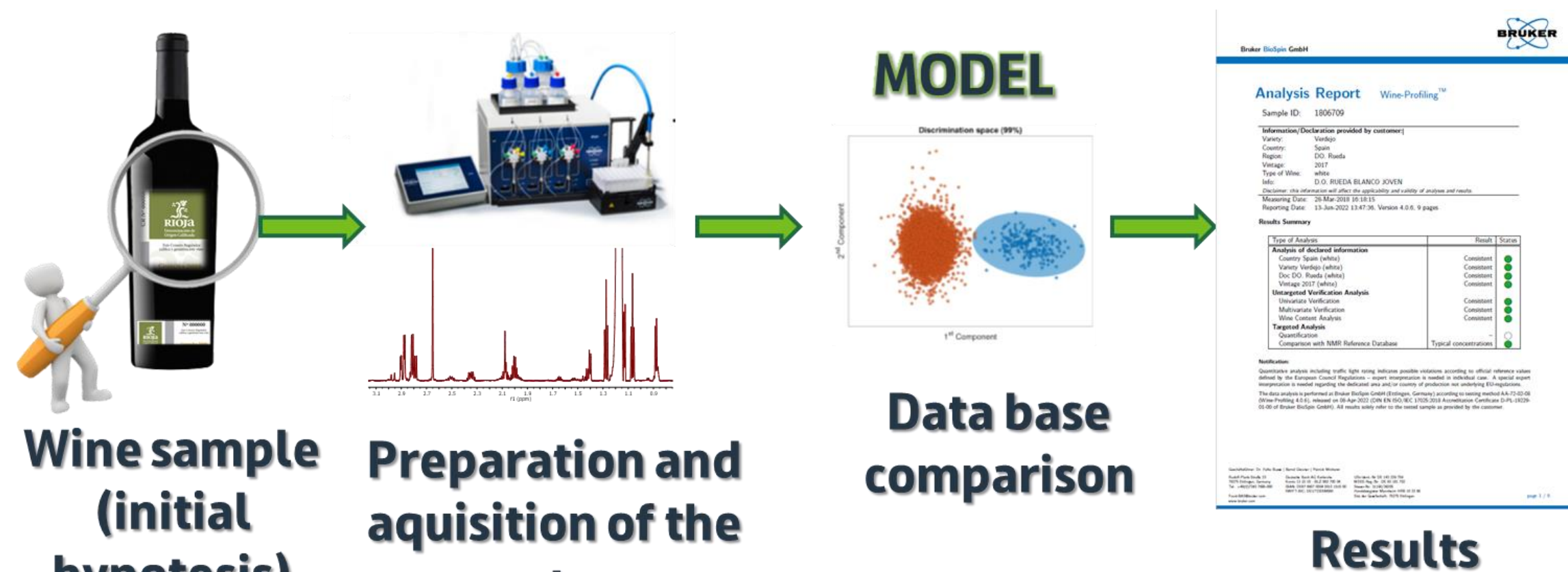

Figure 2. Wine-Profiling™ analytical process.

In order to verify the consistency of a wine, the equipment must compare its spectrum with a wine database of variables such as variety, origin, country and so on (**Figure 2**) and a initial hypothesis is needed. For the results to be reliable, the samples that make up the database must be authentic and with certified traceability. Moreover, one needs to know what area is being tested in order to choose the type of wine as well as adapt the selection to the necessities and peculiarities of each region.
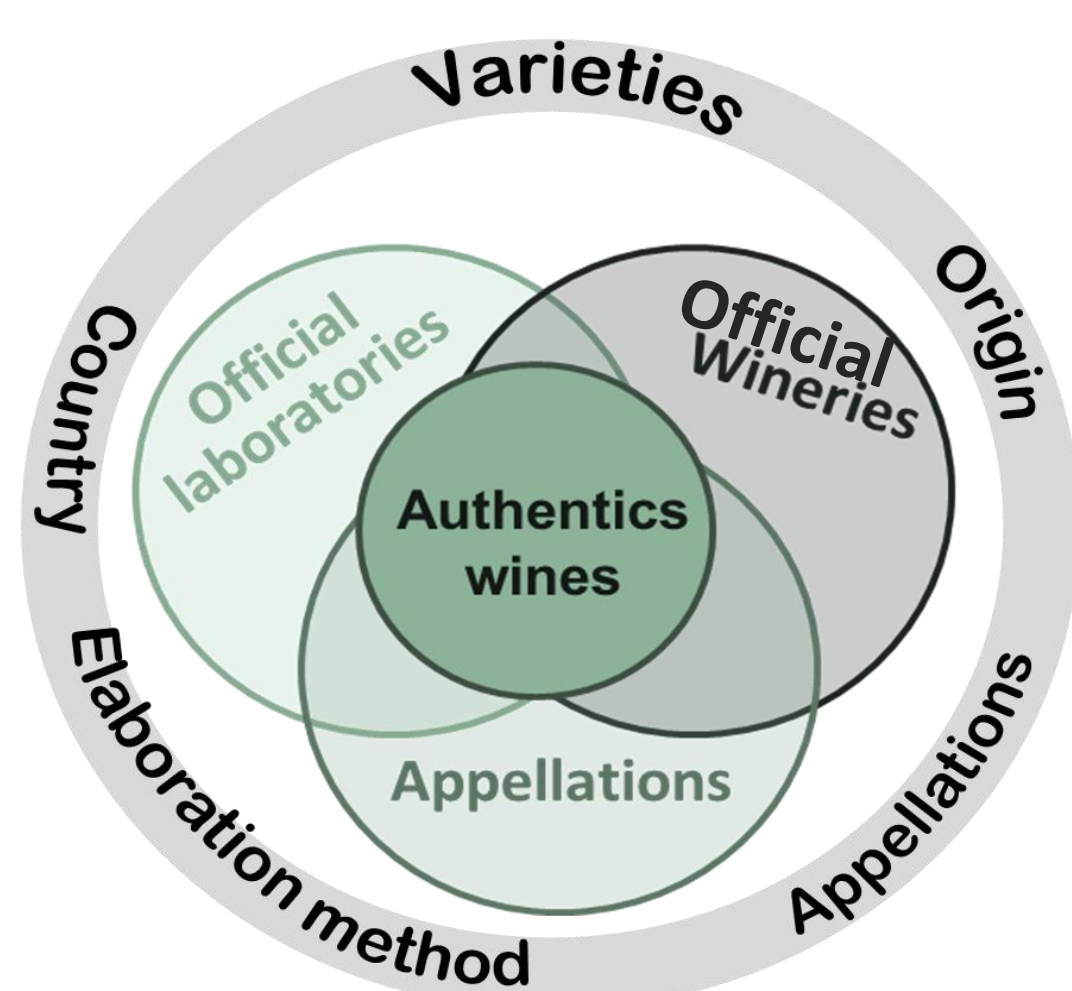

Figure 3. Samples collection for Data-Base.

To this end the EEH is working with the Bruker Company in developing a database of Spanish wines. Different Spanish institutions, which can guarantee traceability and security of samples taken, have assisted with the collection of samples.

In fact all the samples given to the EEH have been collected either by other Official Laboratories similar to Haro, or by Regulatory Bodies of the controlled denominations or appellations all over Spain. Each of these partners has chosen samples of known traceability in terms of their grape variety, winemaking technique and regional typicality.

RESULTS

The starting point was to produce the most general model, that of Spain. This model needed to include those wines that were readily available on the domestic as well as the international market. As a result, wine-producing regions and denominations with high production and exports were given priority. This was followed by those regions with a wide range of samples. As a result only a few denomination regions will have a certification model to begin with. However, in future the vast majority of these will be certifiable by this technique as the database will be in a state of constant development.

All wine was analyzed in EEH lab and with these spectra the modeling was developed by Bruker BioSpin in Germany. A brief explanation about the methodology is described in the **Figure 4**.
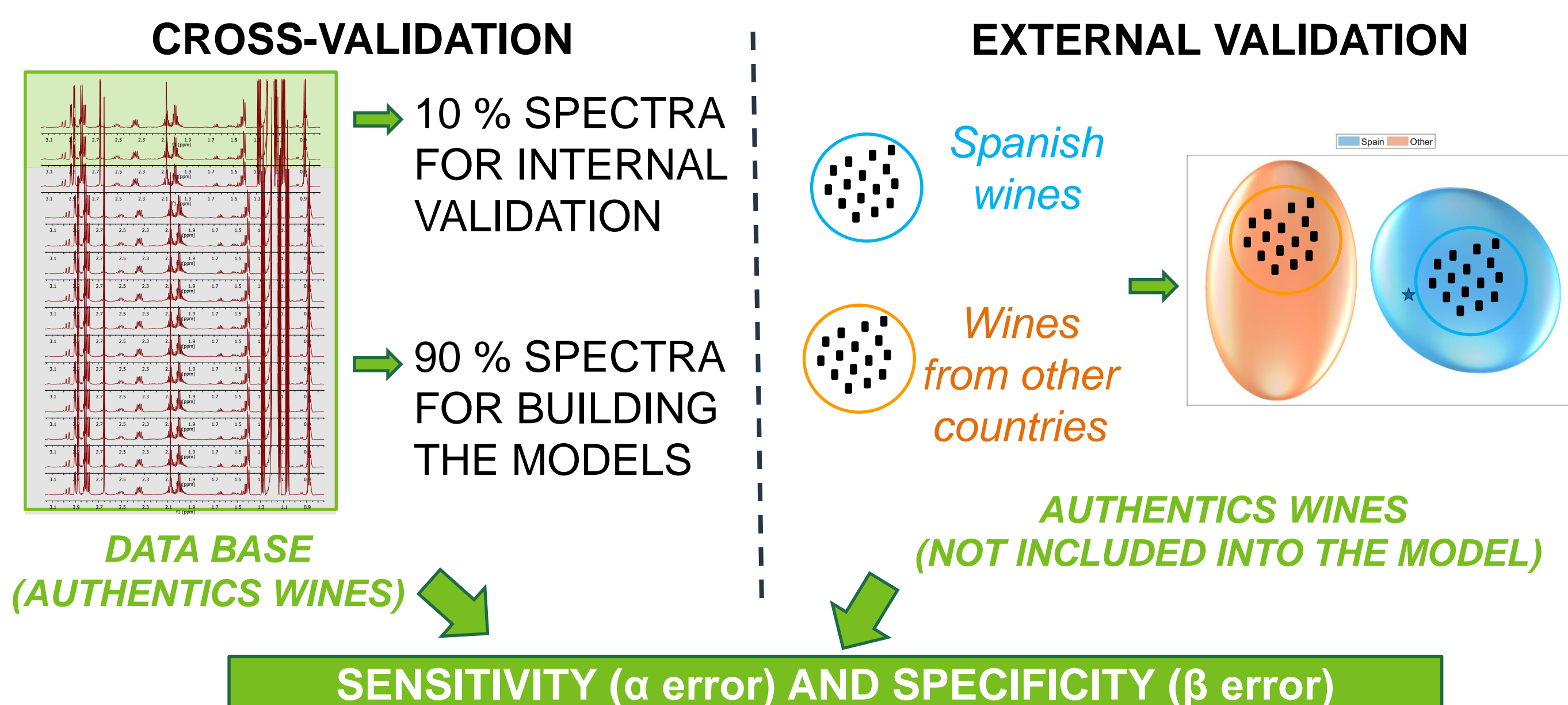

Figure 4. Modeling process. Type of validations.

A **balance** between these two properties, which are inversely proportional, is needed, and always looking for obtaining a **α error low** (all authentic Spanish wines recognized as a Spanish wine) and the minimization of both errors without breaking the balance.

The latest models of Wine-Profiling equipment supplied by Bruker contain around 7000 samples of Spanish wines from the main quality wine production areas. These samples have been used to make models as shown in the **Table 2**.

Table 2. Models of origin and variety red, white and rosé wines.

	RED WINE	sensitivity	WHITE WINE	sensitivity	ROSÉ WINE	sensitivity
ORIGIN	España	99.0	España	99.0	España	99.0
	DOCa. Rioja	99.0	DOCa. Rioja	99.0	DOCa. Rioja	99.1
	DO. Navarra	98.8	DO. Rías Baixas	99.1		
	DO. Ribera del Duero	98.9	DO. Rueda	99.0		
	DO. Ribera de Guadiana	97.6	DO. Valencia	99.3		
	DO. Valencia	99.1				
	DO. Bierzo	99.3				
VARIETY	Tempranillo	98.8	Albariño	98.9	Tempranillo	99.1
	Garnacha T.	98.8	Viura	98.5		
	Monastrell	96.1	Verdejo	98.9		
	Cabernet Sauvignon	98.9	Chardonnay B.	98.0		
	Merlot Noir	98.8	Sauvignon B.	99.0		
	Pinot Noir	99.0	Moscatel	99.0		
	Syrah	97.8	Riesling	99.0		
	Mencía	98.7				

REAL CASES

Regulatory Bodies of the controlled denominations. Protection against irregular use of the brand of a Spanish denomination of origin (DO) (Figure 5 A, B). PCA and modeling were used for detecting the origin of the possible fraud.
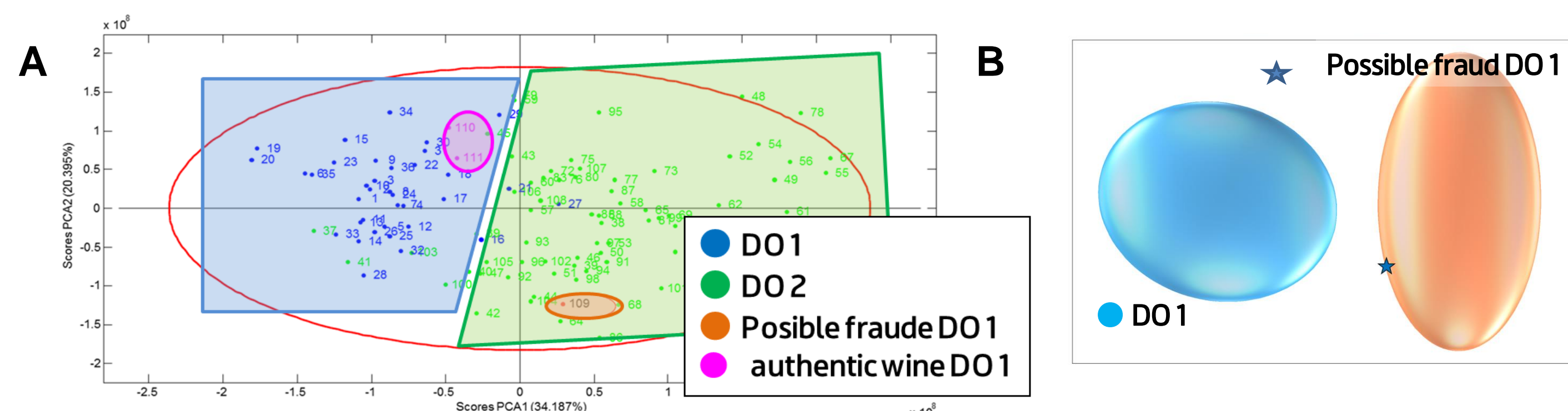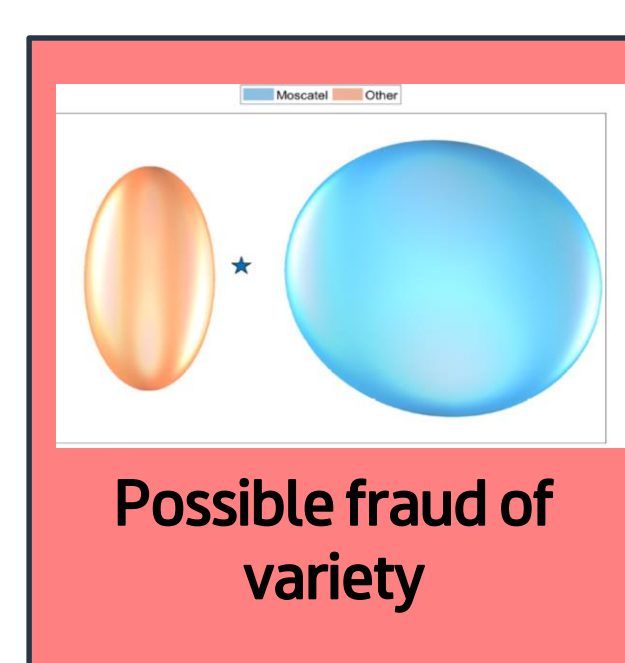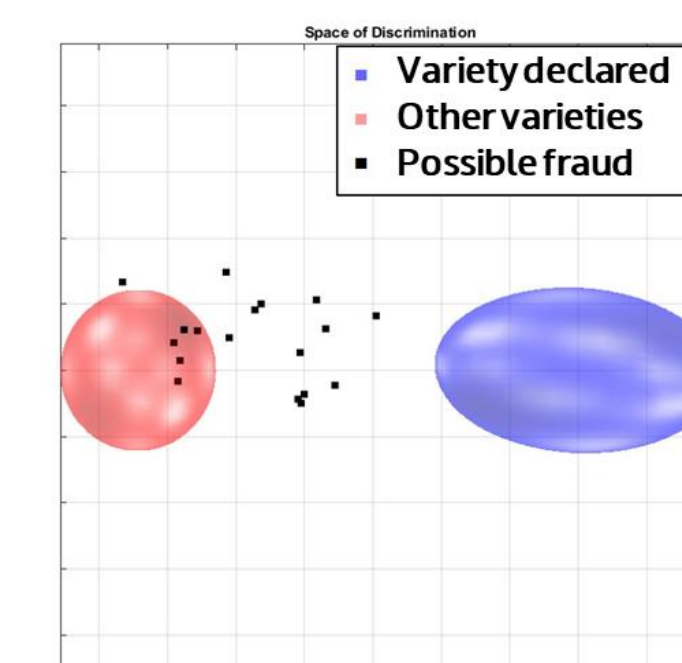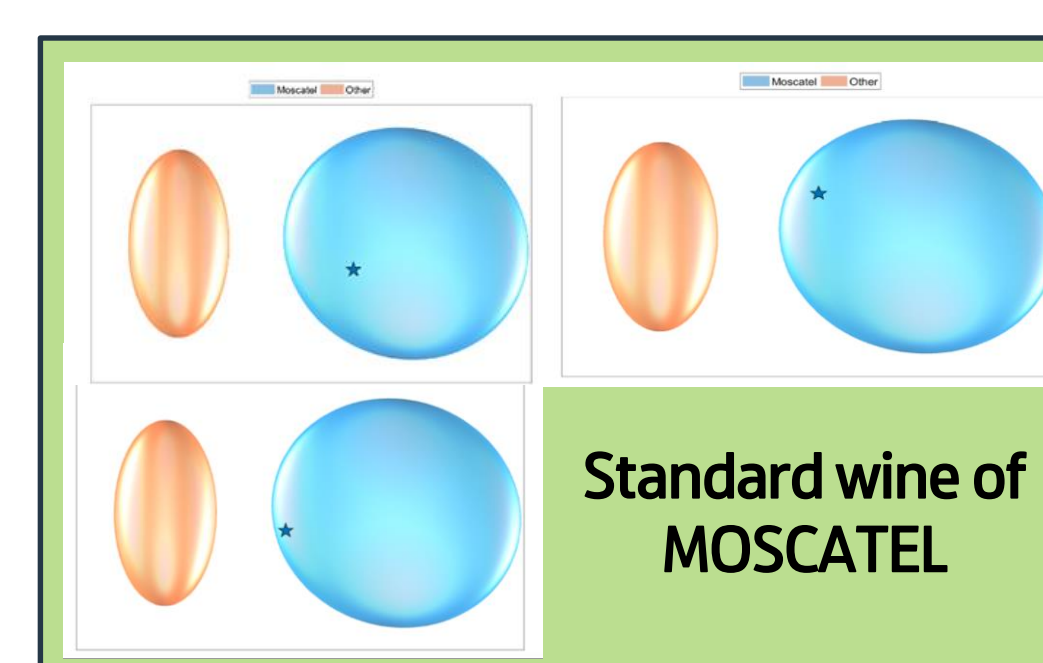

Figure 5. Examples of applications fraud with DO A) score plots PCA; B) Model Wine-Profiling™.

Protection to consumer against fraud in label with the variety declared (Figure 6)

A) Fraud official department   **B) Judicial Police**

CONCLUSION

With these 7000 Spanish wines 3 models of country Spain (red, white and rosé wines), 11 models of denomination of origin and 16 models of typically varieties in Spain, have been built with a high sensibility. Almost all have a high specificity and sensitivity, most of them have a sensitivity more than a 99.0%.

Nowadays, it's an essential tool to police, fraud official department and Regulatory Bodies of the controlled denominations, for detecting fraud and protect to consumer of wine.

References

[1] R. Godelmann, F. Fang, E. Humpfer, B. Schütz, M. Bansbach, H. Schäfer, M. Spraul *J. Agric. Food Chem.* **2013**, 61, 5610–5619.