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Autor: Gremaud, Gérard / Pfammatter, Elmar / Piantini, Umberto

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Classification of Swiss Wines on a Regional Scale by Means of a Multi-Isotopic Analysis Combined with Chemometric Methods*

Gérard Gremaud, Swiss Federal Office of Public Health, Berne

Elmar Pfammatter, Kantonales Laboratorium Wallis, Sion

Umberto Piantini and Sylvie Quaille, Haute école valaisanne, Sion

Introduction

In the last ten years, some new regulations for the analysis of wines have been adopted by the European Union (EEC 2676/90, EEC 2348/91, EEC 822/97, EEC 2729/2000). These regulations introduced among others some new analytical tools, based on stable isotope techniques, for the detection of frauds such as false declaration of origin, watering or addition of exogenous sugars. All the wine producing countries of the EU must deliver yearly a number of samples which is proportional to the size of their vineyard. The samples are analysed using the methods described in the above mentioned regulations and the results are centralised in a databank at the EU Joint Research Center at Ispra (Italy). In order to catch up with these efforts, we designed a project to develop in Switzerland the adequate analytical tools and know-how required to assess the authenticity of wines. This paper reports on the first results obtained in Switzerland, on authentic samples of fermented musts from the 2000 vintage, applying the methods described in the above mentioned regulations.

Stable isotope ratio analysis methods have been recognised in recent years to provide one of the most innovative source of information for the authenticity assessment of foodstuffs and especially for wines (1–4). These analytical methods

* Enhanced version of the oral communication from Dr Umberto Piantini at the 113th meeting of the Swiss Society of Food and Environmental Chemistry, Mendrisio (Switzerland) 31 August 2001

encompass determination of the site-specific $^2\text{H}/^1\text{H}$ ratios of ethanol in wine, the measurement of $^{18}\text{O}/^{16}\text{O}$ on wines water, and also some other isotopic measurements such as $^{13}\text{C}/^{12}\text{C}$ ratio measurements on wine ethanol. Using these methods, various countries have reported interesting results regarding the authenticity of geographic origin. In Italy, *Monetti* (5) and *Versini* (6) who submitted 445 resp. 1496 authentic samples to $^2\text{H}/^1\text{H}$, (NMR), and $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ (IRMS) analysis were able to clearly distinguish wines from the southern (Calabria, Sicily, Puglia) and northern part of Italy (Trentino, Piemont). Nevertheless, adjacent districts could not be separated. The statistical treatment used were MANOVA and LDA (Linear Discriminant Analysis). Applying on 50 slovene wines the same measurements but with a different statistical treatment (Principal Component Analysis, PCA and Kohonen Artificial Neural Network, KANN) *Kosir* (7) could easily separate the coastal vineyard of Slovenia from its continental counterparts but could not differentiate between districts belonging to the same region (Sava and Drava). The same methods, plus trace metal analysis, allowed a separation at 98.5 % confidence of wines from Burgundy, Alsace, Loire Valley and Beaujolais typical appellations (8). Finally, using site-specific NMR and with $^{13}\text{C}/^{12}\text{C}$ ratio of fermentative ethanol, combined with LDA, *Gimenez* (9) found out that a good separation of red wines from district of Valencia (Spain) was easily feasible for some vintages but more difficult for others.

In Switzerland the site-specific measurements of isotopic ratios using NMR methodology has been introduced in 1997 for the first time in the canton of Wallis (Valais) and validated using local samples of fermented musts. Two years later, an IRMS system, allowing measurements of $^{18}\text{O}/^{16}\text{O}$, was also available in the same canton. In autumn 2000, grapes originating from the most important wine-growing regions of Switzerland (VS, VD, NE, GE, BE, ZH, AG, SH, GR, TI) were collected and then submitted to a controlled fermentation. The resulting wines were then analysed according to the relevant EU regulations. The ethanol fraction was measured using site-specific ^2H -NMR and the wine itself was submitted to $^{18}\text{O}/^{16}\text{O}$ -IRMS analysis (see materials and methods).

The major objective of this study was to verify that the combination of the two above mentioned isotopic methods can be used, with the help of an appropriate statistical treatment, to assess and validate the origin of wines coming from different wine-producing CH regions.

Materials and methods

In all, 75 sampling sites from ten cantons of Switzerland (Valais (VS), Vaud (VD), Zürich (ZH), Graubünden/Grisons (GR), Tessin (TI), Berne (BE), Neuchâtel/Neuenburg (NE), Aargau/Argovie (AG), Schaffhausen/Schaffouse (SH) and Genève (GE) have been considered in this study. Four wine varieties, characteristic of the local wine production, were chosen on these sites and they were Riesling \times Sylvaner (=Müllerthurgau, 13 sites), Pinot noir (=Blauburgunder, 19 sites), Merlot

(14 sites) and Chasselas (29 sites). For each wine variety, 10 kg of representative grapes were picked at the suitable ripening state. Harvested grapes were pressed, according to the local procedure of vinification, to the same yield in must (70% w/w). After addition of solution of SO₂ (1 ml/1 kg), the musts were allowed to settle and then fermented by a selected *Saccharomyces Cerevisiae* strain between 18°C and 21°C. The fermentation was allowed to act till all the sugar contained in the wine was transformed in alcohol. Almost the same procedures and the same *S. Cerevisiae* strain are used on most of the production sites of Switzerland. The decanted wines were stored at 4°C, in a fridge. Before NMR analysis, the samples of wines were distilled with an automatic distillation device, according to the standard EU protocol 822/97 (extraction with a Fischer column yields >98% and ethanol content of distillates at least 92%). The NMR measurements were carried out between April and July, in the year following the harvest.

NMR-measurements

The measurements were performed using a VARIAN Gemini 2000 NMR spectrometer equipped with a 10 mm probe operating at 46.089 MHz for ²H. An internal standard N,N-tetramethylurea (TMU) with a known isotopic content (bureau des références (BCR) of Bruxelles) was used. Measurements were done according to the standard protocol of EU 822/97. 304 Transients were accumulated with 12000 data points over a 1500 Hz spectral width and with a 90° rf pulse and proton decoupling (WALTZ). Temperature was 303 K and the acquisition time was 4.0 s (4 times the relaxation time). For each sample, this set of accumulation was repeated 10 times. Free induction decay (FID) signals were converted by a Fourier transform with sensitivity enhancement (2.0 Hz line broadening). The D/H ratios were measured by recording the intensities of the deuterium signals corresponding to the methylene and methyl sites of ethanol and of TMU and the ratios were calculated and expressed in ppm according to the following formulas of the Journal officiel des Communautés Européennes 03/10/1990 part 5:

$$(D/H)_I = 1.5866 \cdot \frac{\text{height}_{\text{CH}_2\text{DCH}_2\text{OH}}}{\text{height}_{\text{TMU}}} \cdot \frac{m_{\text{TMU}}}{m_{\text{distillate}}} \cdot \frac{(D/H)_{\text{TMU}}}{t}$$

$$(D/H)_{II} = 2.3799 \cdot \frac{\text{height}_{\text{CH}_3\text{CHDOH}}}{\text{height}_{\text{TMU}}} \cdot \frac{m_{\text{TMU}}}{m_{\text{distillate}}} \cdot \frac{(D/H)_{\text{TMU}}}{t}$$

The Exel program performed calculation of the mean and standard deviation. Besides the absolute parameter (D/H)_I and (D/H)_{II}, a relative parameter *R* derived from intensity measurements of the deuterium signals of methylene and methyl sites of methanol has been calculated according to the following formula:

$$R = 3 \cdot \frac{\text{height}_{\text{CH}_3\text{CHDOH}}}{\text{height}_{\text{CH}_2\text{DCH}_2\text{OH}}}$$

IRMS-measurements

The measurements were done using a Finnigan Delta-Plus XL mass spectrometer. The selected method (10) to measure the isotopic $^{18}\text{O}/^{16}\text{O}$ ratio of wines of different origins was performed by the gas bench II system. By equilibrating 0.5 ml of the wine's sample during 18 hours at 26.8°C with a gas mixture (0.4% CO_2 in helium), the $^{18}\text{O}/^{16}\text{O}$ ratio was determined by mass spectrometry from ionic currents of m/z 46 ($^{12}\text{C }^{16}\text{O }^{18}\text{O}$) and m/z 44 ($^{12}\text{C }^{16}\text{O }^{16}\text{O}$), measured on the carbon dioxide equilibrated with the water in wine.

All results were reported as deltas ‰ relative to the Vienna-Standard mean Ocean water (V-SMOW) standard as cited elsewhere (11):

$$\delta \text{‰} = 1000 \times [R_{\text{sample}} - R_{\text{V-SMOW}}] / R_{\text{V-SMOW}}$$

The local working standard was the tap water from Sion, collected in February 2001, and measured at $-13.9 \delta \text{‰}$ vs V-SMOW (confirmed by measurement in an independent laboratory). In order to calibrate and compare our data, standards wines (measured in the official EU laboratory, JCR, Ispra) were also analysed.

Statistical treatment of the data: Linear discriminant analysis (LDA)

Among the multivariable statistical techniques, the relatively simple LDA method (12), which maximizes the variance between categories and minimizes the variance within categories was found to be the most adequate tool. LDA makes the hypothesis that the distribution is multivariate normal and that the covariance matrix of each category (dispersion of the category) is not significantly different from one case to another. The mahalanobis distances of each object from the centroids of the categories are computed, the object resulting assigned to the category with lowest distance. The LDA calculations and corresponding schemes were obtained using the statistical software Statistica.

Titles of the European regulations cited

- | | |
|---------------|---|
| EEC 2676/90 | detecting enrichment of grape musts, concentrated grape musts, rectified concentrated grape musts and wines by application of NMR of deuterium. |
| EEC 2348/91 | establishing of a data bank for the results of analyses of wines products by NMR of deuterium. |
| EEC 822/97 | amending regulation EEC 2676/90 determining Community methods for the analysis of wines. |
| EEC 2729/2000 | commission regulation laying down detailed implementing rules on controls in the wine sector |

Results

Site-specific NMR D/H isotopic measurements on the ethanol molecule

For all samples from the 2000 vintage considered and irrespective of the sort of grapes (whites and reds together), values for D/H_I on ethanol molecule (methyl site)

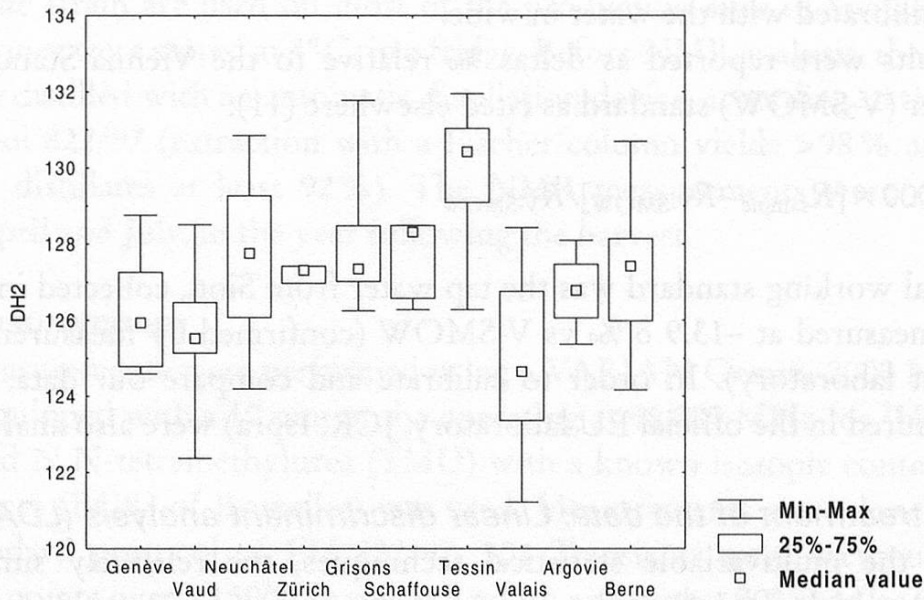


Figure 1 2H -NMR measurements of the D/H_{II} ratio on samples from the most relevant wine-producing regions of Switzerland

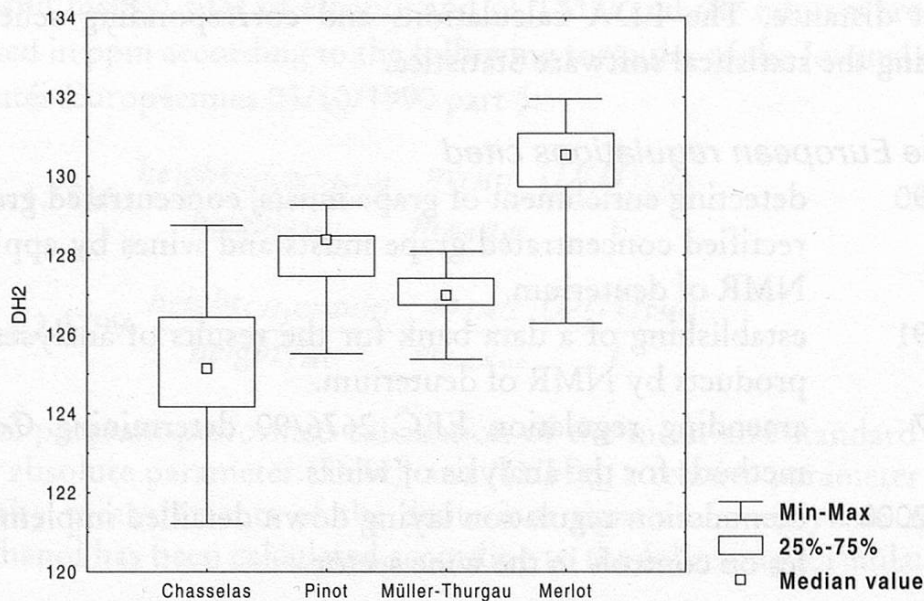


Figure 2 2H -NMR measurements of the D/H_{II} ratio: impact of the wine variety

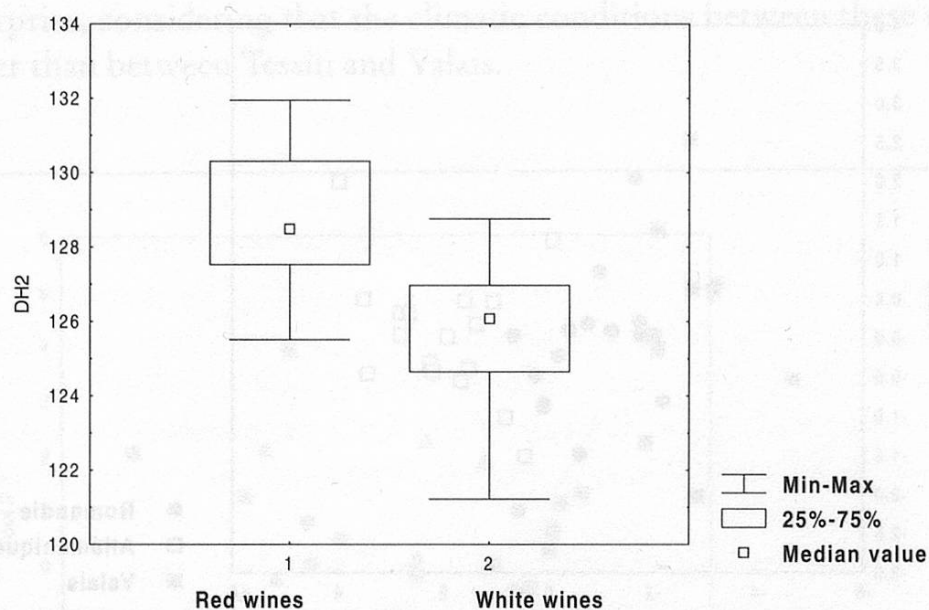


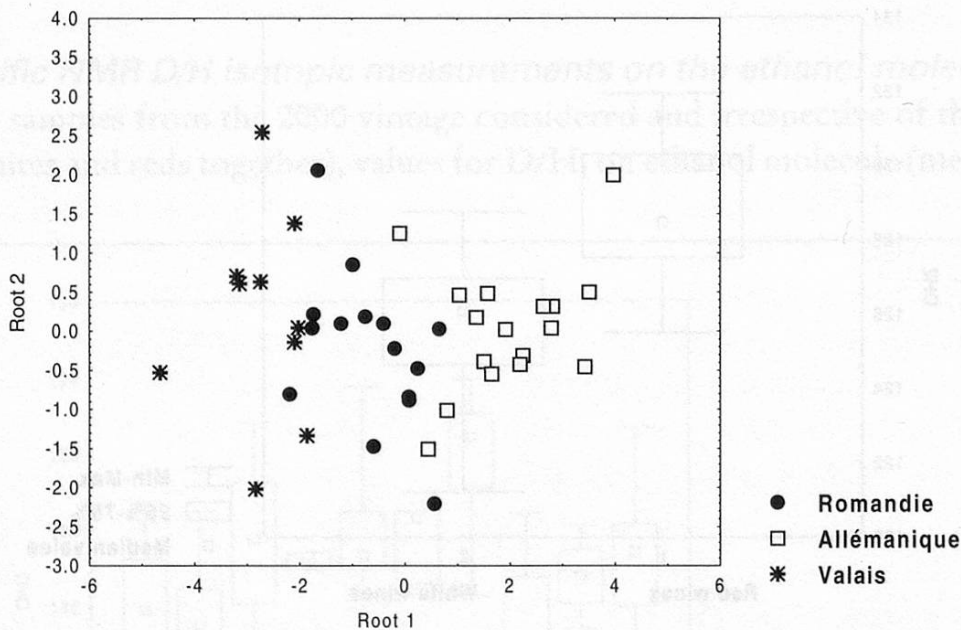
Figure 3 $^2\text{H-NMR}$ measurements of the $\text{D}/\text{H}_{\text{II}}$ ratio: impact of the wine colour

ranged from 98.5 ppm to 103.5 ppm. For $\text{D}/\text{H}_{\text{II}}$ (methylene site of the ethanol molecule) the range was 121 to 132 ppm. The wines originating from Valais have the lowest values lying between 123 and 127 ppm, wines from the Romandie and the eastern Switzerland (allémannique) show values between 126 and 129 ppm while wines from Tessin exhibit the highest values (128 and 131 ppm).

In our case, the isotopic ratios $\text{D}/\text{H}_{\text{II}}$ proved to be much more influenced by the geographic origin of the sample than the $\text{D}/\text{H}_{\text{I}}$ ratios. Therefore we kept only $\text{D}/\text{H}_{\text{II}}$ for further group definition. Box-plot representation of $\text{D}/\text{H}_{\text{II}}$ values following the production zones is given in figure 1. As we can see, samples from Valais are clearly lighter (lower $\text{D}/\text{H}_{\text{II}}$ values) than those from Tessin. To assess the impact of wine variety (red or white) a second Box plot graph was performed following varietal characteristics. As shown in figure 2 and 3 white wines varieties (Chasselas, Riesling (=Müllerthurgau) exhibit clearly lower (lighter) enrichments as red varieties Pinot (=Blauburgunder) and Merlot).

Combination with the $^{18}\text{O}/^{16}\text{O}$ IRMS isotopic measurements on the wine

The $^{18}\text{O}/^{16}\text{O}$ ratios were found to be spread on range of about 7 δ ‰ (–5–+2 δ ‰ vs V-SMOW). These data were not used as such but combined with NMR data by use of LDA. This statistical manipulation of the data emphasizes the differences among the wine-producing areas. The defined area for the wines originating from Valais and Tessin clearly show different and distinct graphical regions with the exception of two values originating from the canton of Graubünden. In fact, after control, these two values belong to a region of Grisons situated to the south of the Alp (Monticello area) i.e in Tessin. After reattribution of these two data in the cor-



NB: The only one sample (Chardonnay) from the group "Tessin" (Monticello Area) is not represented on this scatterplot due to the statistical treatment.

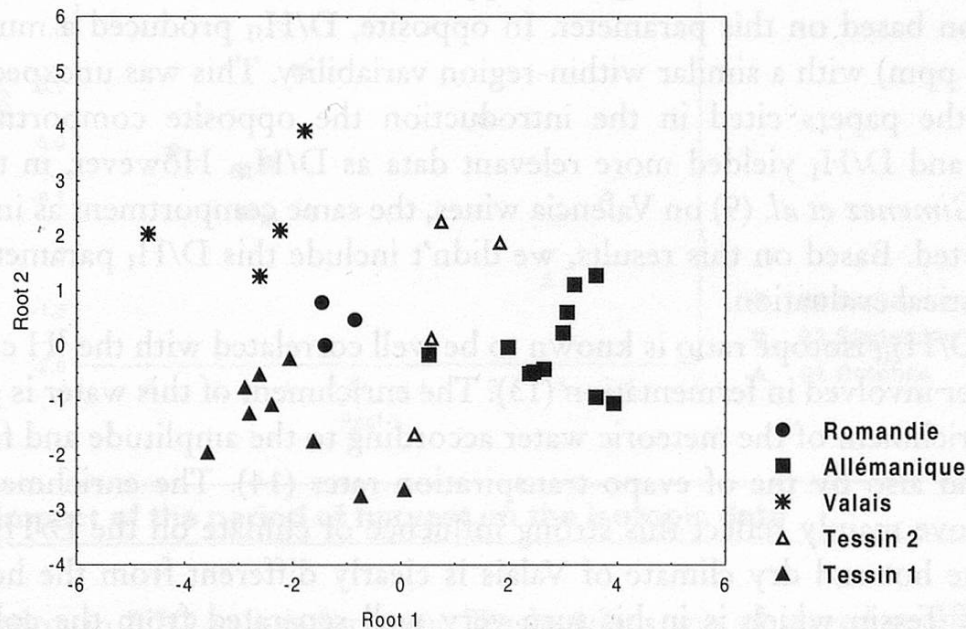
Figure 4 Discriminant analysis of white Swiss wines (vintage 2000) scatterplot of canonical scores from combination of ^2H -NMR and ^{18}O -IRMS measurements

rect geographical area, the separation was better. Based on these results, we classified the wines in four groups: Valais, Tessin, eastern Switzerland (allémanique) and western Switzerland (romandie). The scatterplot of canonical score (fig. 4 and fig. 5) show the situation for white and red wines. To check the relevance of our classification, we performed a re-attribution of the samples using the classification function of the Systat[®] software. The results are shown in table 1. As we can see, 94% of the red wine samples and 85% of the white wine samples were correctly attributed. The major problem occurring by the re-attribution of white wine samples was due to four samples from Romandie that were wrongly classified in Wallis.

Discussion

The differences in precipitations and temperatures are the most important factors affecting the isotopic data. The very good separation of wines originating from regions located south of the Alps (Tessin) from those originating from north of the Alps (Valais) is explained by the fact that they benefit of very different weather conditions. The canton of Valais exhibits values that are characteristic for a warm and dry climate, whereas Tessin, shows values that correspond to a warm and wet climate. Sample from Tessin are also well distinguished from those coming from the central part of Switzerland. On the other hand, the separation among wines from

the western part of Switzerland (Romandie) with the eastern part is not so easy. This is not a surprise, considering that the climatic conditions between these regions are much closer than between Tessin and Valais.



NB: Tessin 1 samples were harvested on 21st and 22nd September 2000, Tessin 2 on 4th October 2000

Figure 5 Discriminant analysis of red Swiss wines (vintage 2000) scatterplot of canonical scores from combination of ²H-NMR and ¹⁸O-IRMS measurements

**Table 1
Reclassification results for Swiss wines samples vintage 2000**

	<i>White wines</i>				<i>Apparent correct classification (%)</i>
	<i>Allémanique</i>	<i>Romandie</i>	<i>Tessin</i>	<i>Valais</i>	
Allémanique	15	2	0	0	88
Romandie	1	9	1	4	60
Tessin	0	0	1	0	100
Wallis	0	1	0	9	90
	<i>Red wines</i>				<i>Apparent correct classification (%)</i>
	<i>Allémanique</i>	<i>Romandie</i>	<i>Tessin</i>	<i>Valais</i>	
Allémanique	11	0	1	0	92
Romandie	0	3	0	0	100
Tessin	1	1	11	0	85
Wallis	0	0	0	4	100

Site specific (D/H)_I and (D/H)_{II} ratios measurements

The hydrogen isotope ratio of the methyl group of the NMR ethanol signal depends strongly on the botanical origin of the plant and is often used as a discriminant factor for origin assessment (1–9). The range of values recorded on all our samples, independently of the wine variety, was very narrow (≈ 4 ppm). Because of the spread of data within each region (≈ 2 ppm), this was too narrow to allow any discrimination based on this parameter. In opposite, D/H_{II} produced a much wider range (≈ 8 ppm) with a similar within-region variability. This was unexpected as in most of the papers cited in the introduction the opposite compartment was observed and D/H_I yielded more relevant data as D/H_{II}. However, in the paper from by *Gimenez et al.* (9) on Valencia wines, the same compartment as in our case was reported. Based on this results, we didn't include this D/H_I parameter in the final statistical evaluation.

The (D/H)_{II} isotope ratio is known to be well correlated with the ²H content of plant water involved in fermentation (13). The enrichment of this water is governed by the enrichment of the meteoric water according to the amplitude and frequency of rain and also by the of evapo-transpiration rates (14). The enrichments mentioned above mainly reflect this strong influence of climate on the D/H_{II} isotope ratios. The hot and dry climate of Valais is clearly different from the hot-humid climate of Tessin which is in his turn very well separated from the cold-humid climate of the eastern Switzerland.

The wine variety plays only a secondary role in the isotopic fractionation phenomena as compared to the geographical effect.

¹⁸O/¹⁶O ratios in wine water (IRMS)

The ¹⁸O-IRMS results obtained on the wine allowed, by combination with NMR data, to distinguish wines coming from our four zones of production. The large (≈ 7 ‰) range is due to the very diverse landscape which characterizes Switzerland. In comparison, typical ranges in France and Germany are 4–5‰ (15–17). The lowest values observed are typical of alpine regions. Similarly, *Rossmann* (15) observed for Bodensee wines (Germany) much lower values (-4 to -5 ‰ vs V-SMOW) than for other German wines, which were around -1 ‰ vs V-SMOW. The main factor which affects the $\delta^{18}\text{O}$ IRMS values of the wine water is the origin of this water. During the evapo-transpiration processes in the plant, the heavier ¹⁸O isotope remains in the liquid phase to a higher extent than the ¹⁶O isotope. Because of this effect, water in grapes are enriched in ¹⁸O when compared to the ground water. The amount of ¹⁸O in the precipitation also depends on the latitude: it decreases from the equator to the poles. Finally the altitude also plays an important role, and mountain waters exhibit lower concentration in ¹⁸O than those from plains. Ground water mostly reflects the enrichment of meteoric water, averaged on long periods. As mentioned above for NMR data, the $\delta^{18}\text{O}$ value of wine water also are strongly influenced by changing climatic conditions. Thus a signifi-

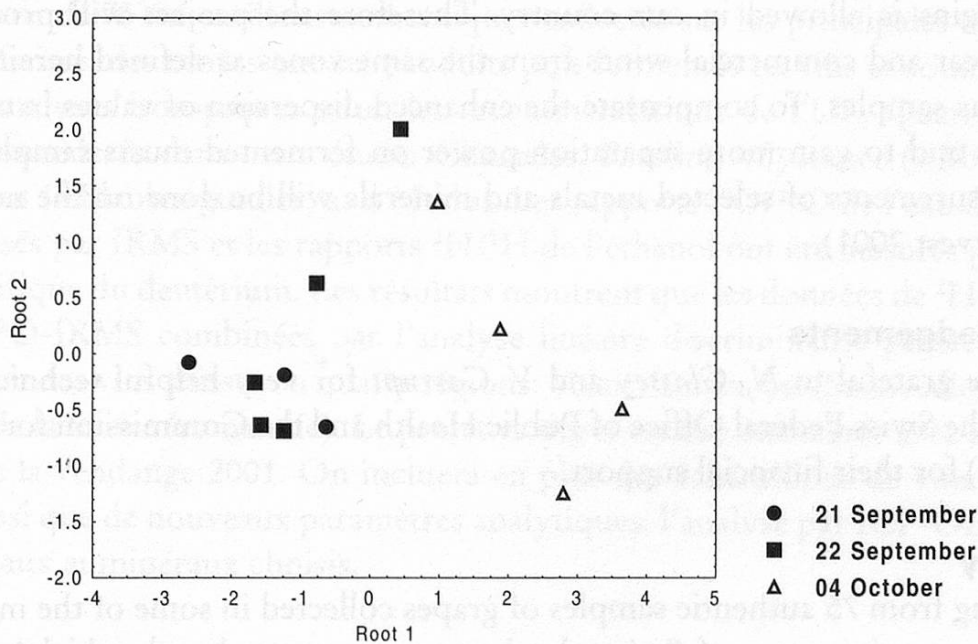


Figure 6 Impact of the period of harvest on the isotopic data

cant depletion in $\delta^{18}\text{O}$ values for some Tessin wines was observed resulting from grapes which were harvested just after a period of important meteoric watering (fig. 6). This phenomenon was also described by *Rossmann et al.* (15) on wine samples from Pfaltz (Germany) and where the δ ‰ values plunged from +2 δ ‰ vs V-SMOW (1st of sept.) down to -3 δ ‰ vs V-SMOW (15th of oct.). The data obtained for Switzerland are similar to those found for the neighbouring countries, and the North-South increase of δ -values is confirmed.

Conclusions

Switzerland is a small country but, due to the presence of the Alps, it encompasses a wide pattern of pedological and climatological conditions. In this study we could demonstrate that these differences were large enough to allow a good separation of some regions of the Swiss vineyard. The combination of $^{18}\text{O}/^{16}\text{O}$ ratios of wine-water (IRMS) and $^2\text{H}/^1\text{H}$ ratios of ethanol (site-specific ^2H -NMR) and appropriate data analysis techniques offers an interesting analytical tool to investigate the origin and authenticity of Swiss wines. These techniques allowed us to define four production areas within Switzerland: canton of Tessin, canton of Valais, western part of Switzerland (Romands) (GE, VD, NE), and eastern part of Switzerland (allémaniques) (BE, ZH, AG, SH, GR). The measured parameters being mostly influenced by climate conditions, the limits of the zones followed geophysical parameters (elevation, position relative to the Alps, distance to the sea) and not political subdivisions. However, the question is not yet settled as we produced our wines starting with authentic samples of musts. Commercial wines are more complex, as

mixing, within legally defined limits, of different vintages, different colours, and different origins is allowed in our country. Therefore the project will proceed for another year and commercial wines from the same zones as defined herein will be included as samples. To compensate the enhanced dispersion of values in commercial wines and to gain more separation power on fermented musts samples, ICP-OES measurements of selected metals and minerals will be done on the next campaign (harvest 2001).

Acknowledgements

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Summary

Starting from 75 authentic samples of grapes collected in some of the most relevant wine-growing areas of Switzerland, musts were produced, which were fermented in wines and submitted to two stable isotope analyses following the relevant EU methods. Four wine varieties were considered in this study: Chasselas, Riesling × Sylvaner (=Müllerthurgau), Pinot (=Blauburgunder) and Merlot. The $^{18}\text{O}/^{16}\text{O}$ ratio of wine-water was analysed using IRMS and the $^2\text{H}/^1\text{H}$ ratios of ethanol molecule were measured using site-specific ^2H -NMR. The results show that a combination of the ^2H -NMR and $^{18}\text{O}/^{16}\text{O}$ -IRMS data and linear discriminant analysis allowed a separation of Swiss wines in four main regions: Valais, Tessin, eastern (German) and western Switzerland (romandie). This project will go on for another year, including also commercial wines and will ICP-OES measurements of selected metals and minerals as further analytical parameters.

Zusammenfassung

Aus 75 authentischen Proben von Weintrauben, die aus den wichtigsten Weinanbaugebieten der Schweiz stammten, wurde deren Saft gewonnen und zu Wein fermentiert. Die Analyse erfolgte mittels zweier Stabil-Isotopen-Methoden nach relevanten EU Richtlinien. Vier Rebsorten wurden untersucht: Chasselas, Riesling × Sylvaner (=Müllerthurgau), Pinot (=Blauburgunder) und Merlot. Das $^{18}\text{O}/^{16}\text{O}$ Verhältnis im Wasser des Weins wurde mittels IRMS und das $^2\text{H}/^1\text{H}$ Verhältnis der Ethanolmoleküle wurde durch ort-spezifische ^2H -NMR erfasst. Die Ergebnisse zeigen, dass eine Kombination der ^2H -NMR mit den $^{18}\text{O}/^{16}\text{O}$ -IRMS Daten durch die Linear Discriminant Analysis die Einteilung der inländischen Weine in vier Regionen erlaubt: Wallis, Tessin, Ost- (deutsche Schweiz) und Westschweiz (Romandie). Das Projekt wird auch im nächsten Jahr mit Proben von der Ernte 2001 weitergeführt und durch zusätzliche Analysen von Proben handelsüblicher Weine erweitert. Die ICP-OES Messungen von ausgewählten Metallen werden die analytischen Parameter ergänzen.

Résumé

A partir de 75 échantillons authentiques collectés sur les principales zones viticoles de Suisse, des moûts ont été produits puis fermentés en vins et soumis à deux types d'analyses isotopiques selon les recommandations de l'UE. Quatre cépages ont été considérés dans cette étude: Chasselas, Riesling × Sylvaner (=Müllerthurgau), Pinot (=Blauburgunder) and Merlot. Les rapports $^{18}\text{O}/^{16}\text{O}$ de l'eau du vin ont été analysés par IRMS et les rapports $^2\text{H}/^1\text{H}$ de l'éthanol ont été mesurés par RMN site-spécifique du deutérium. Les résultats montrent que les données de ^2H -NMR et de $^{18}\text{O}/^{16}\text{O}$ -IRMS combinées par l'analyse linéaire discriminante permettent une séparation des vins suisses en quatre régions: Valais, Tessin, est (Suisse allémanique) et ouest de la Suisse (romandie). Le projet va durer encore une année avec les échantillons de la vendange 2001. On inclura en plus des échantillons de vins du commerce ainsi que de nouveaux paramètres analytiques: l'analyse par ICP-OES de certains métaux et minéraux choisis.

Key words

Swiss wine, Stable isotopes, Authenticity, Site-specific NMR, IRMS, Geographical origin

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Corresponding author: Dr Gérard Gremaud, Office fédéral de la santé publique, CH-3003 Berne, E-mail: gerard.gremaud@bag.admin.ch