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Determination of wine authenticity and geographical origin by measuring non-exchangeable hydrogen stable isotopes in wine ethanol with EIM-IRMS® methodology in combination with $\delta^{18}\text{O}$ values obtained from wine water

By authors:

Ivan Smajlovic and Mirko Glavanovic
SG Isotech, IL, US

ivan@sgisotech.com , mirko@sgisotech.com

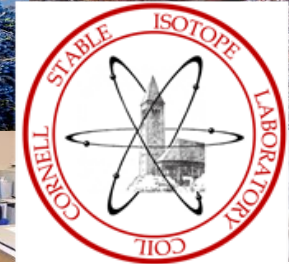
Kimberlee L. Sparks and Prof. Jed P. Sparks,
Cornell University, Ithaca, NY, EEB

kls37@cornell.edu , jps66@cornell.edu

Prof. Slobodan Jovic
Faculty of Agriculture, Belgrade, Serbia
jovics@agrif.bg.ac.rs



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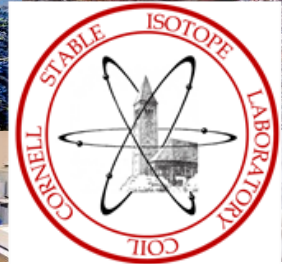


Introduction

- SG Isotech is a privately owned company which specializes in wine authenticity, verification and identification.

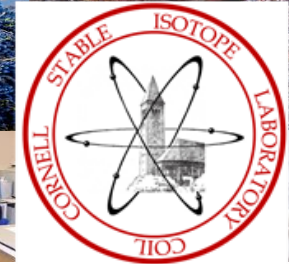
<http://bottleCONTENT.com>





Follow up with our previous work

- SG Isotech has developed, verified, patented, published and standardized a new isotope method (EIM-IRMS[®]) capable of uncovering counterfeit wine and adulteration practices used in wine production.
- Scientific paper was previously published in Natural Product Research:
Ethanol isotope method (EIM) for uncovering illegal wine (2012) by Smajlovic, I., Sparks, K.L., Sparks, J.P., Leskosek Cukalovic, I., & Jovic, S.,. DOI: 10.1080/14786419.2012.673610. Natural Product Research

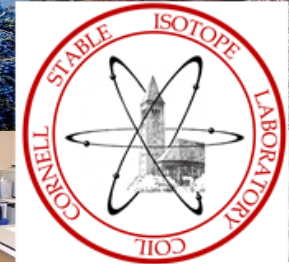


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EIM-IRMS[®] method

- EIM-IRMS[®] method gives us information about non-exchangeable hydrogen stable isotopes in ethanol, so we have established new parameter as δD_n value in ethanol (‰ vs. V-SMOW).

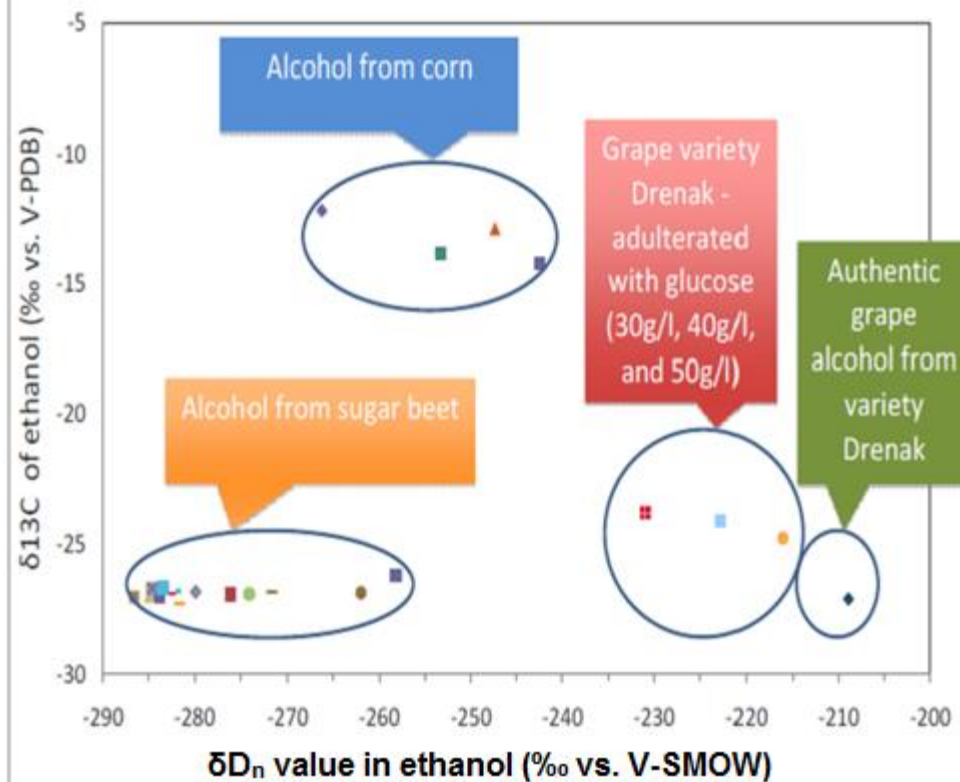


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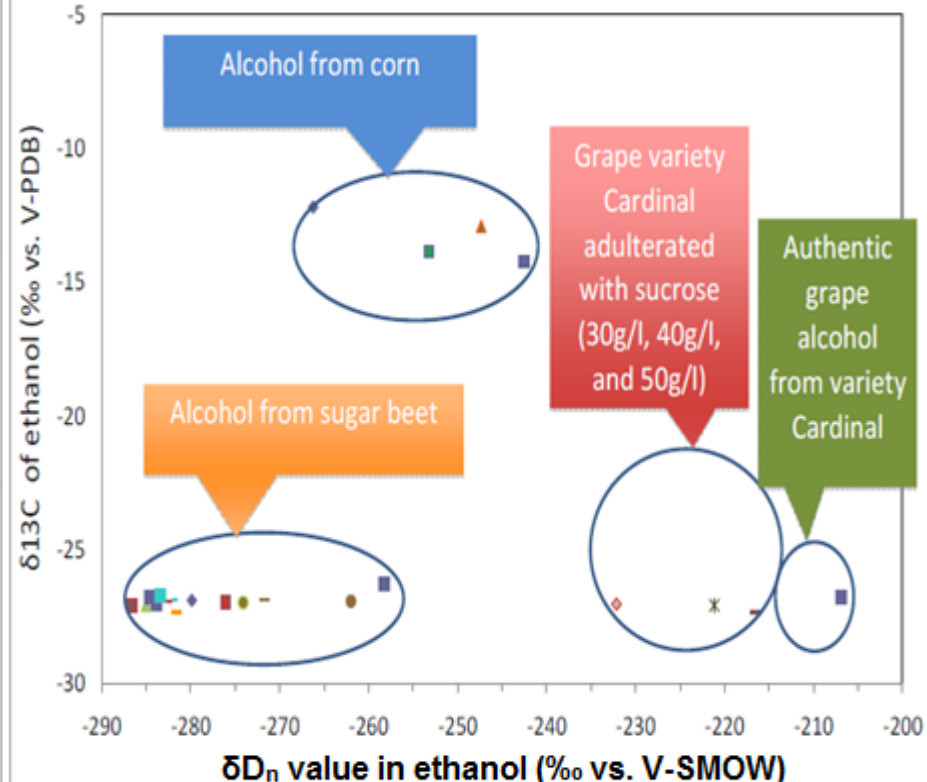
EIM-IRMS[®]

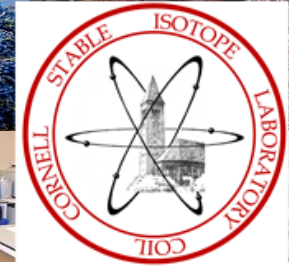
Graphical preview of different sugar addition to grape must

Addition of Glucose to Grape Must - variety Drenak



Addition of Sucrose to Grape Must - variety Cardinal



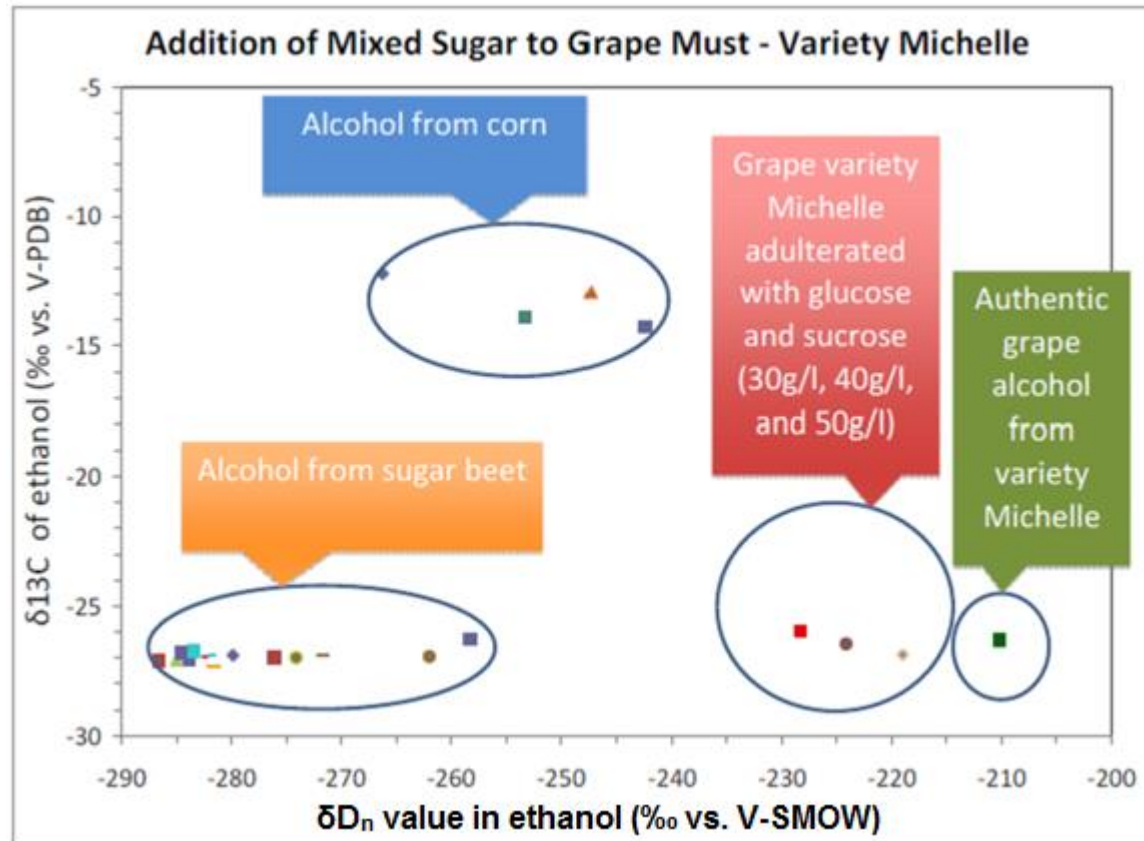


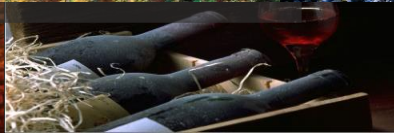
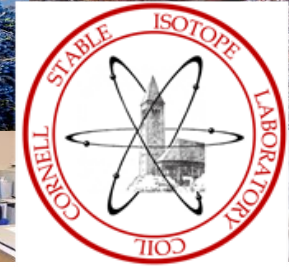
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Results

Graphical preview of mixed sugar addition to grape must





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More results from wine samples

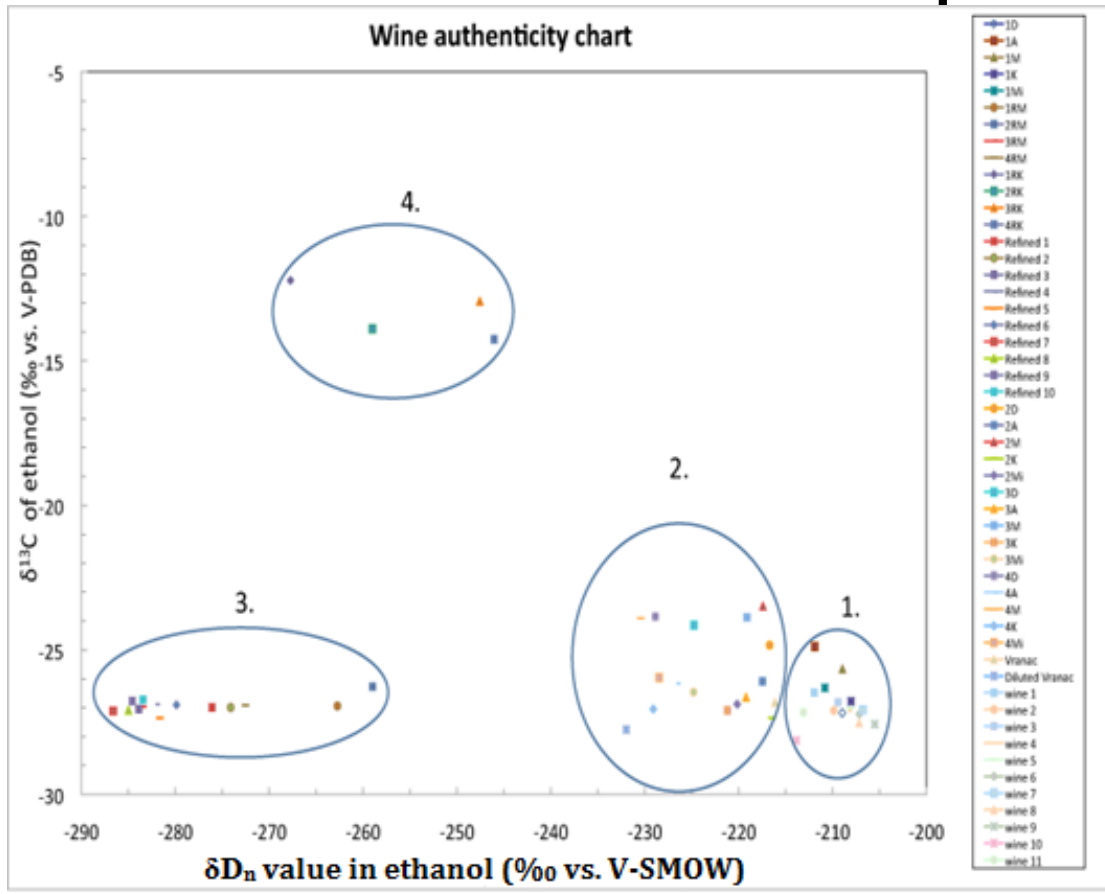
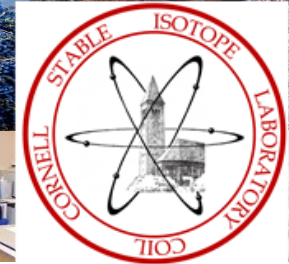
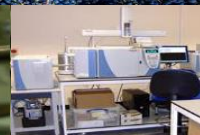


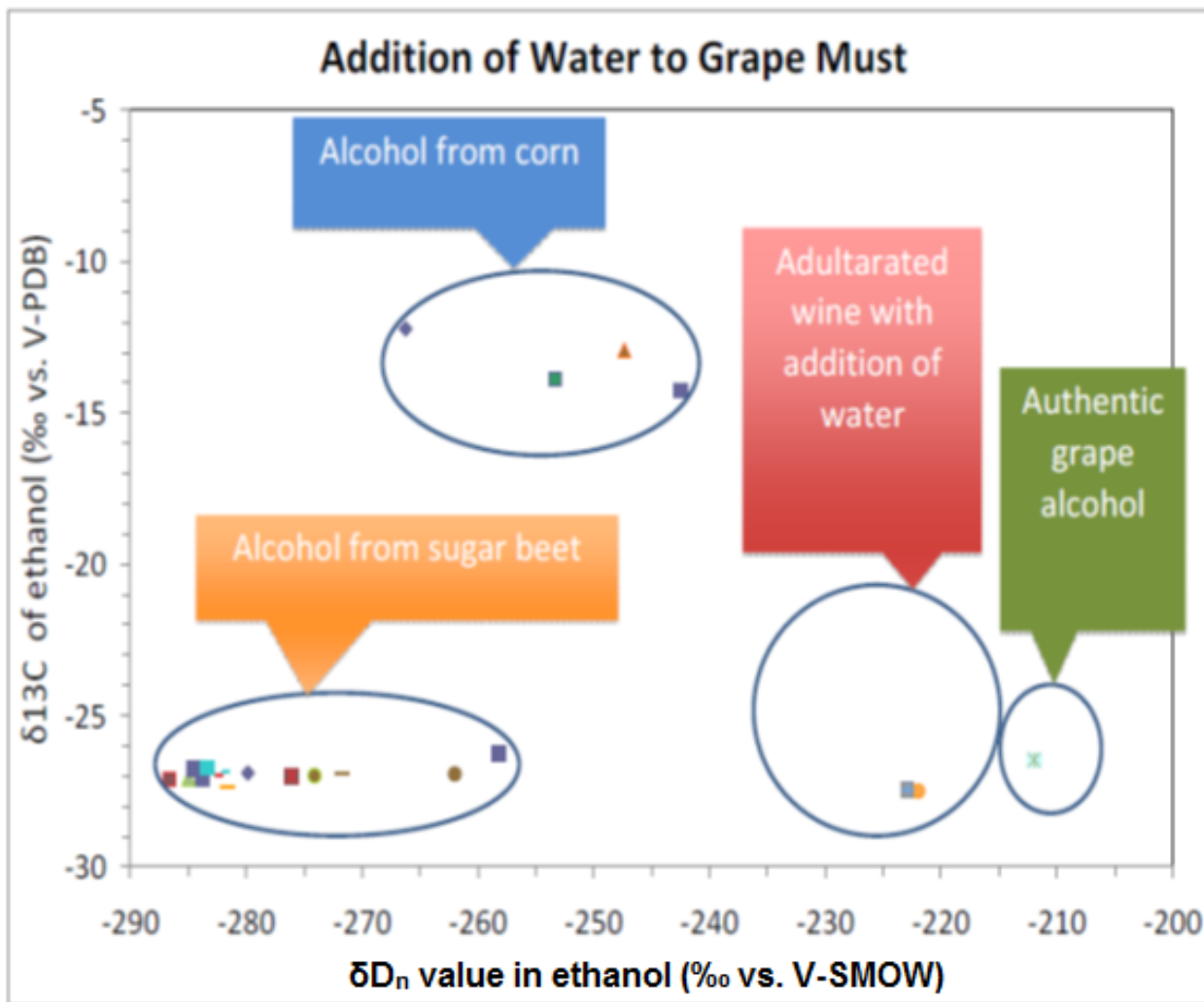
Figure 6: δD values for authentic grape varieties (area 1), grape varieties with added sugar or water (area 2) and ethanol from sugar beet (area 3) and from corn (area 4).



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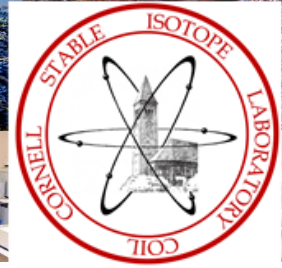


EIM-IRMS® can also detect addition of water to grape must

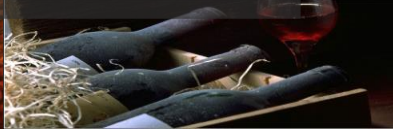




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Detection Of Illegal Watering Of Grape Must



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Detection of Illegal Water Addition to Grape Must

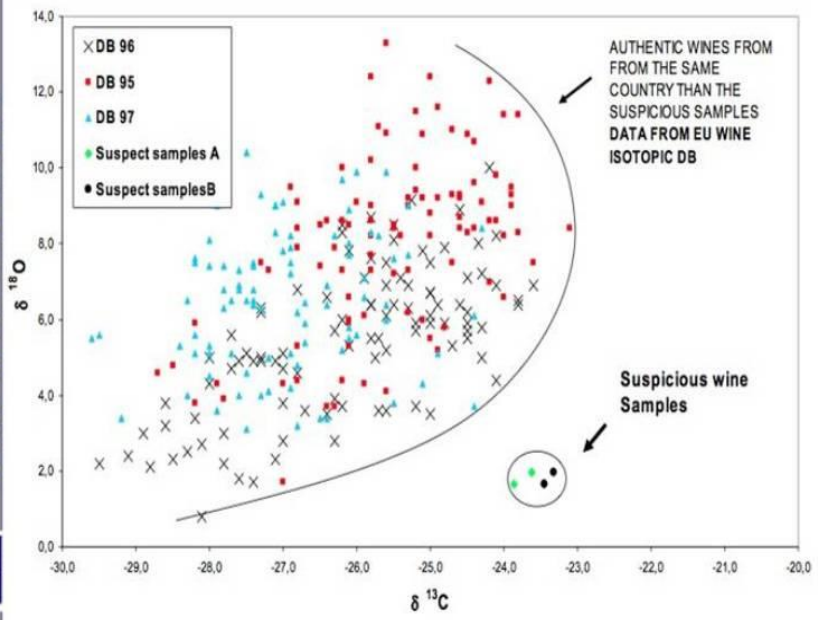
EU Official Equilibration Method
 $\delta^{18}\text{O}$ in wine water vs. $\delta^{13}\text{C}$ in ethanol

EIM-IRMS® Method

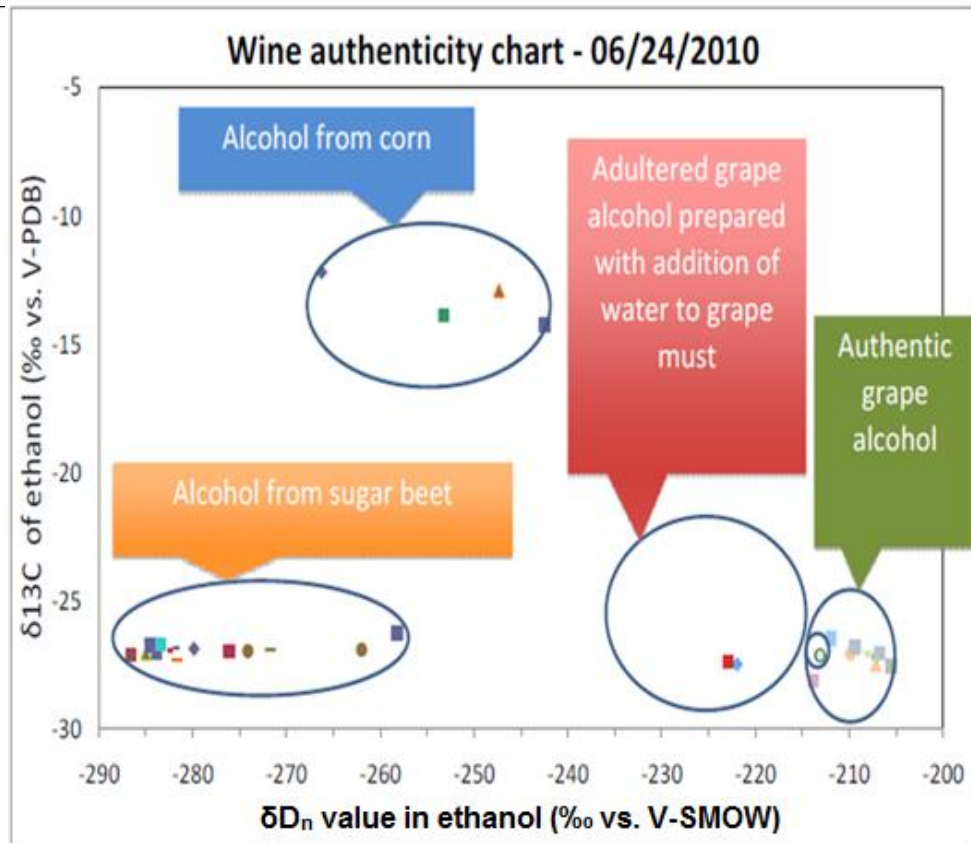
Joint Research Centre



Example: use of isotope ratios for the detection of adulteration of wine

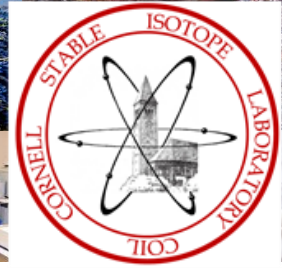


27-28 Mars 2006 - 4th International Workshop on Water in Food, Brussels BEVABS

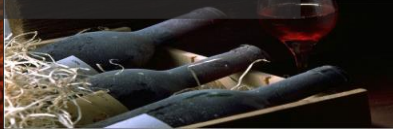




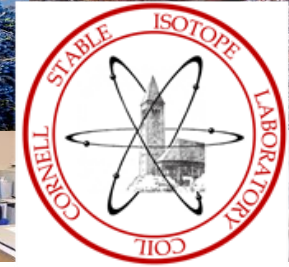
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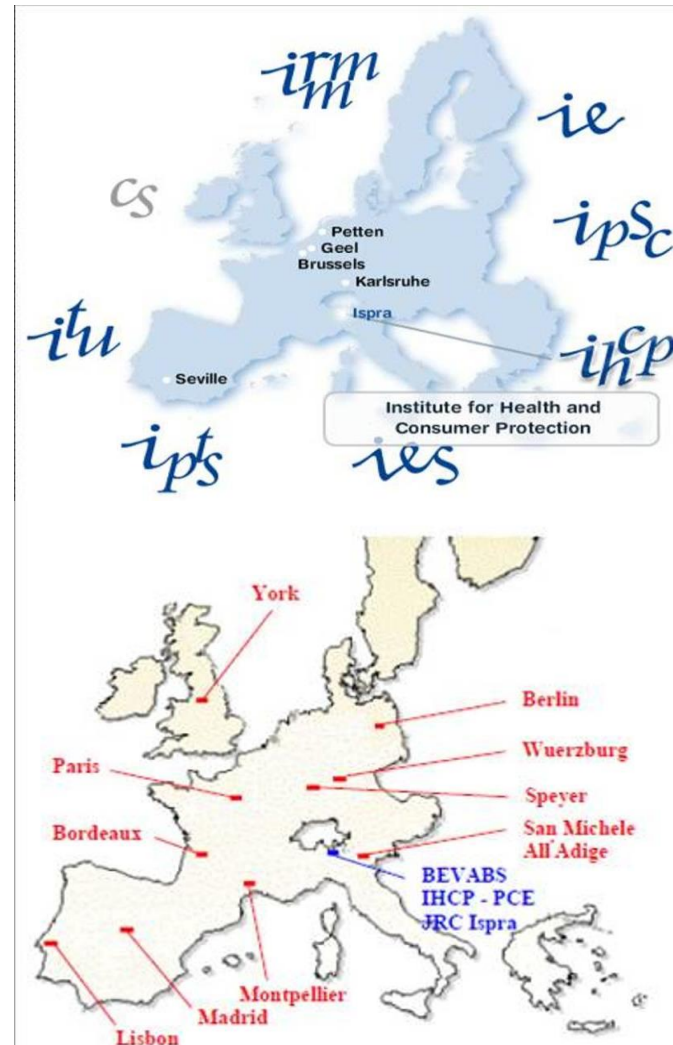
Overview Of The Present Quality Control Of Wine



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Overview of the present wine quality control actions

Based on SNIF-NMR® methodology, the European Commission has founded BEVABS located at IHCP (member institute of JRC), in Italy (Ispra), and a network of National Referent Laboratories throughout the E.U. to prepare European isotopic wine databanks, used to guarantee the geographical origin and authenticity of all European wines with a designated origin.

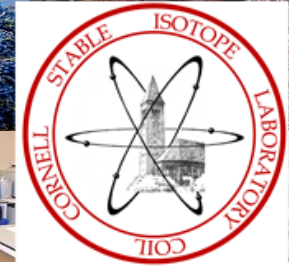




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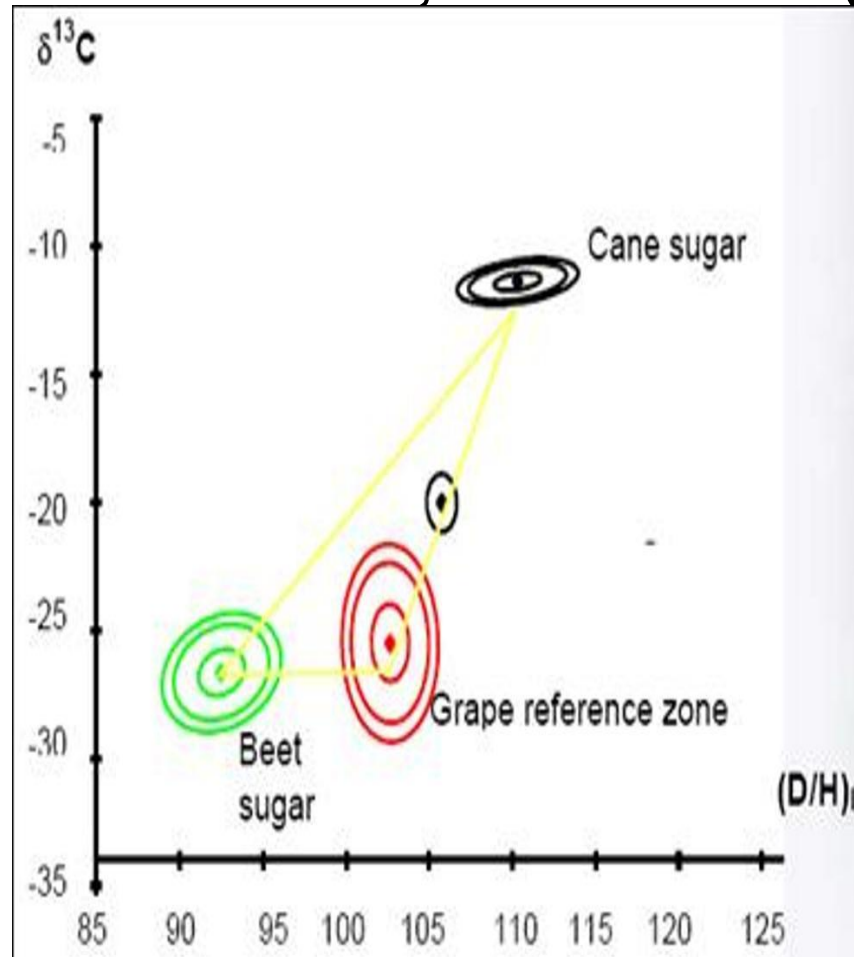
SNIF-NMR[®] Feedback

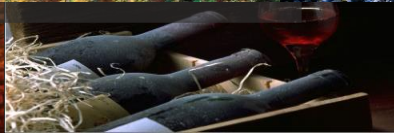
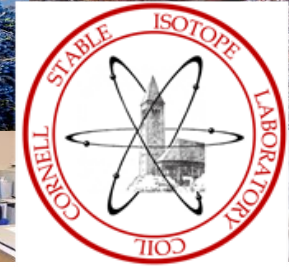
- As stated by Claude Guillou, the Team Leader of BEVABS, and his associates Segebarth Nicolas, Alonso-Salces Rosa-Maria and Skordi Eleni from IHCP (Institute for Health and Consumer Protection) in the Scientific and Technical Report which was published under the title “Analysis and Characterization of Alcoholic Products” in JRC (Joint Research Center) Bulletin (2008):
- “...A sample is considered problematic if its ethanol (D/H)₁ value falls out of the natural range. In the case of wine for instance, values under 99 ppm to 105 ppm **are suspicious**. If average values for (D/H)₁ are considered, then an evaluation of the detection limit for ethanol addition can be made for the different possible ethanol sources (Table 1). This is only indicative since **with this approach the addition of beet ethanol to a wine with high (D/H)₁ value (105 ppm) would be detected only if its proportion is superior to 50%! If the geographic origin of the wine is known, then the natural (D/H)₁ range can be reduced and the detection limit refined: it is case-to-case work necessitating supplementary information on the wine (grape growing region, for instance). With this method, addition to wine of ethanol from distilled wine or fruit wines (apples, etc.) cannot be detected (all fruit alcohols have similar D/H ranges). **If the ethanol added comes from grain, it will be detected only if its proportion is higher than 70%.****”



SNIF-NMR[®] Values For Ethanol With Different Botanical Origin

Y axis: IRMS $\delta^{13}\text{C}$, V.S. X axis: $(\text{D}/\text{H})_i$



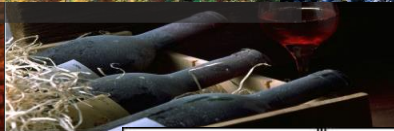


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EIM-IRMS[®]

Detection of Adulteration in Known and Unknown Wine Samples





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In the meantime EIM-IRMS® was standardized and accepted at the Institute for standardization of Republic of Serbia and published in Official Gazette of Republic of Serbia.

ТЕХНИЧКА
СПЕЦИФИКАЦИЈА

SRPS TS E.M8.031

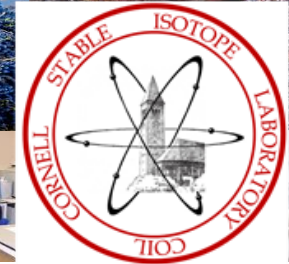
Новембар 2011.

Вино — Одређивање релативног односа неизменљивих атома деутеријума и водоника у етанолу применом инструменталне технике TC/EA - IRMS

Wine — Determination of relative ratio of non-exchangeable hydrogen and deuterium atoms in ethanol by means of instrumental technique TC/EA - IRMS

Овај документ има статус нацрта техничке спецификације. У току јавне расправе коришћенима је на располагању ради достављања примедба и предлога. Подлогам је изменама и стога се на њога не може поклапати док се не објави као техничка спецификација.

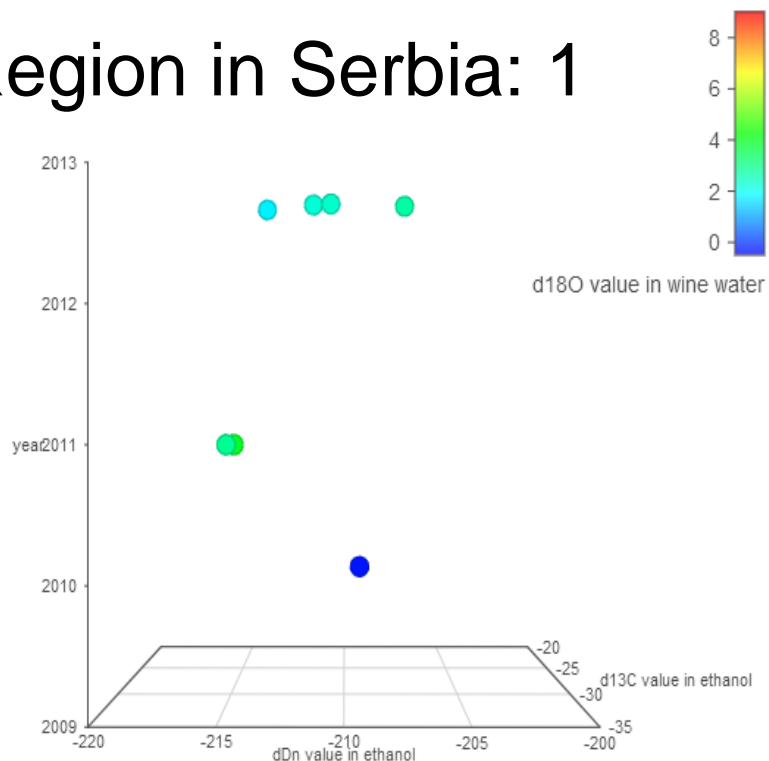
1 од 2



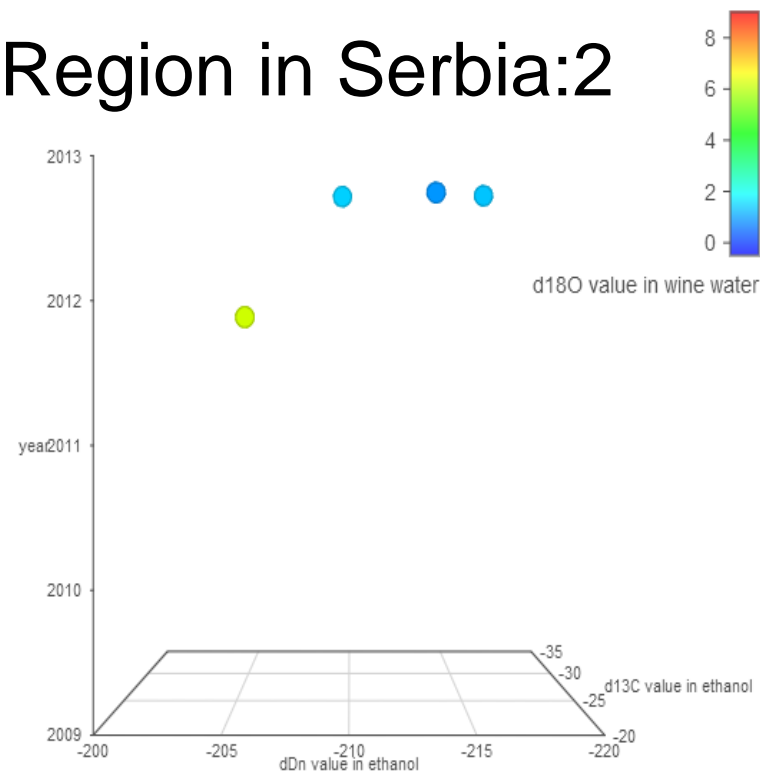
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δD_n value in ethanol in combination with $\delta^{18}O$ value in wine water as a proof of botanical and geographical origin of wine

Region in Serbia: 1



Region in Serbia: 2

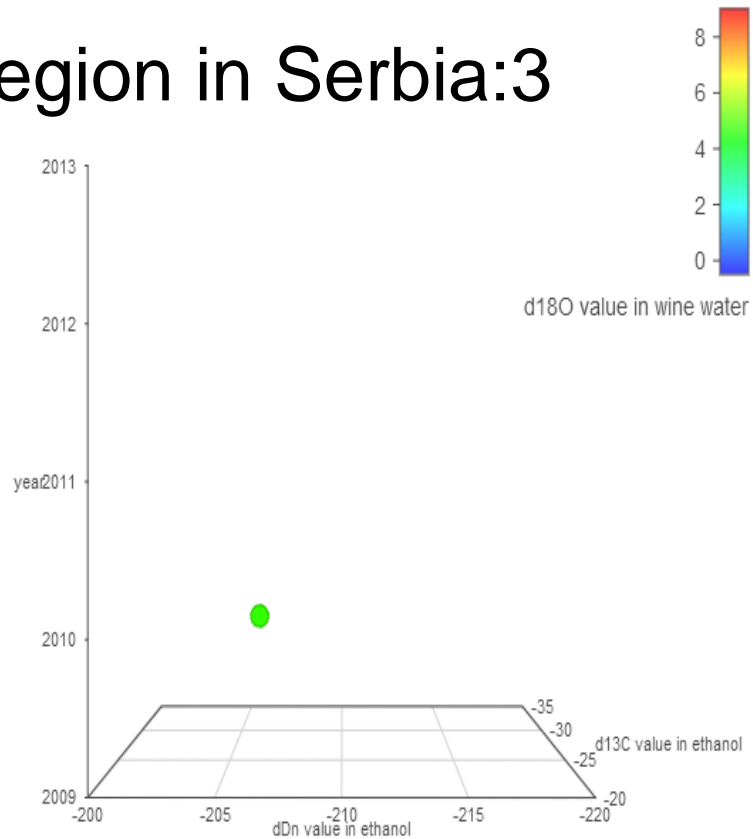


All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale

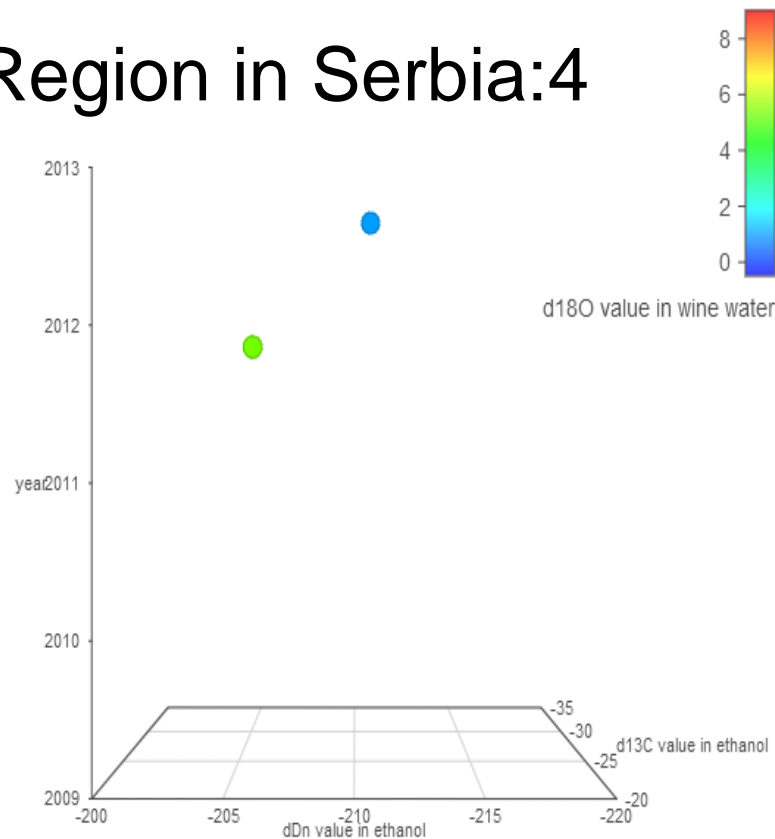


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Region in Serbia:3



Region in Serbia:4

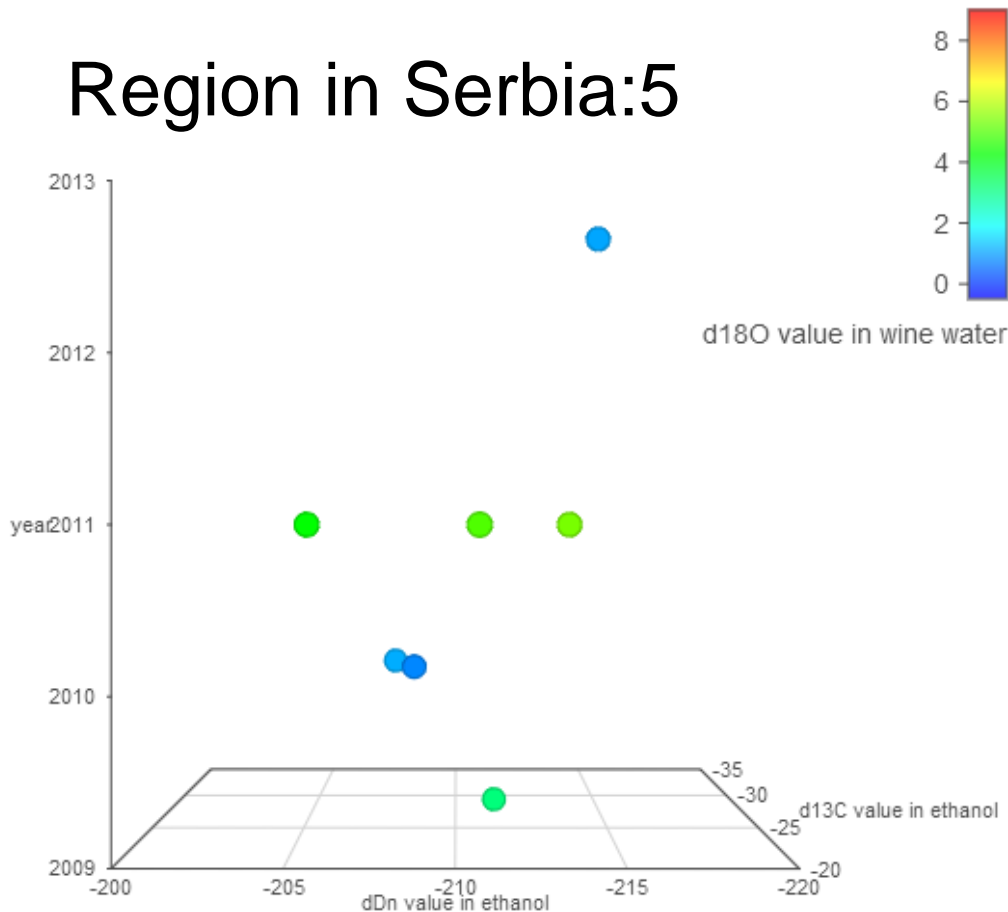


All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale

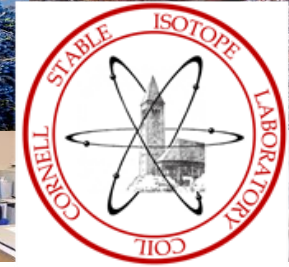


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Region in Serbia:5

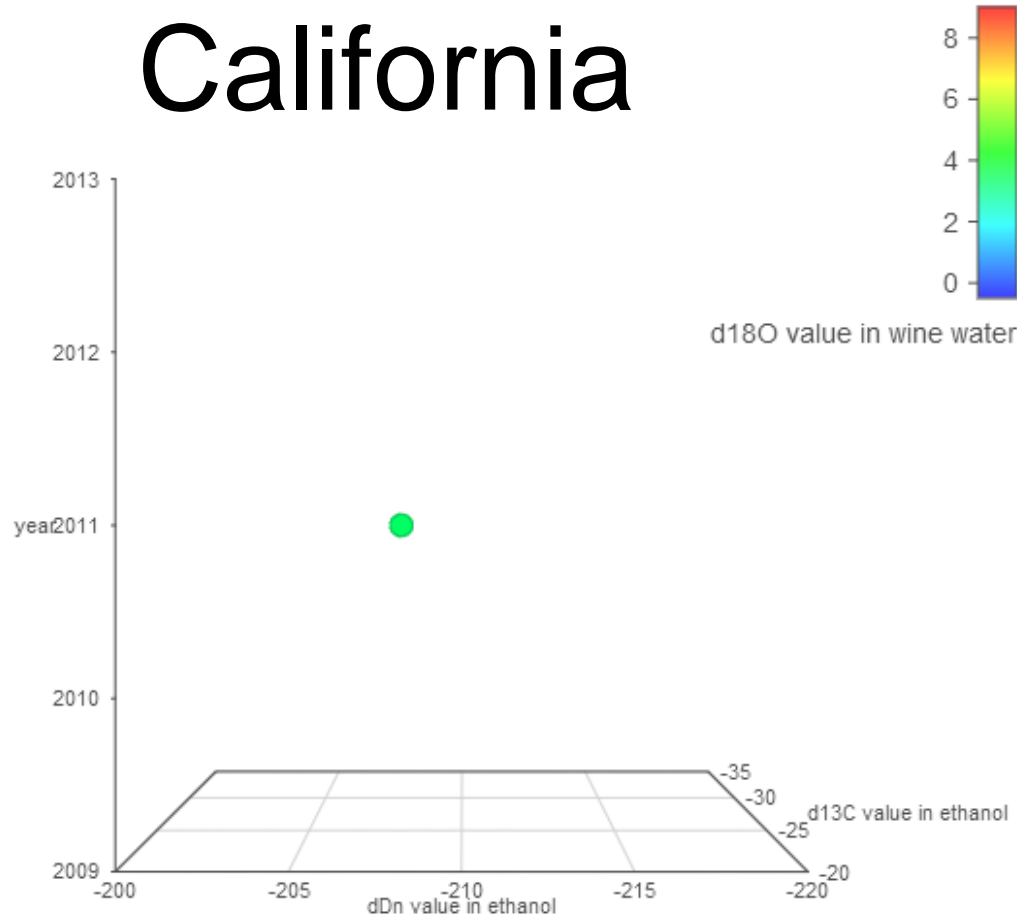


All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale

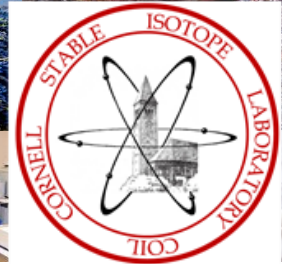


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California



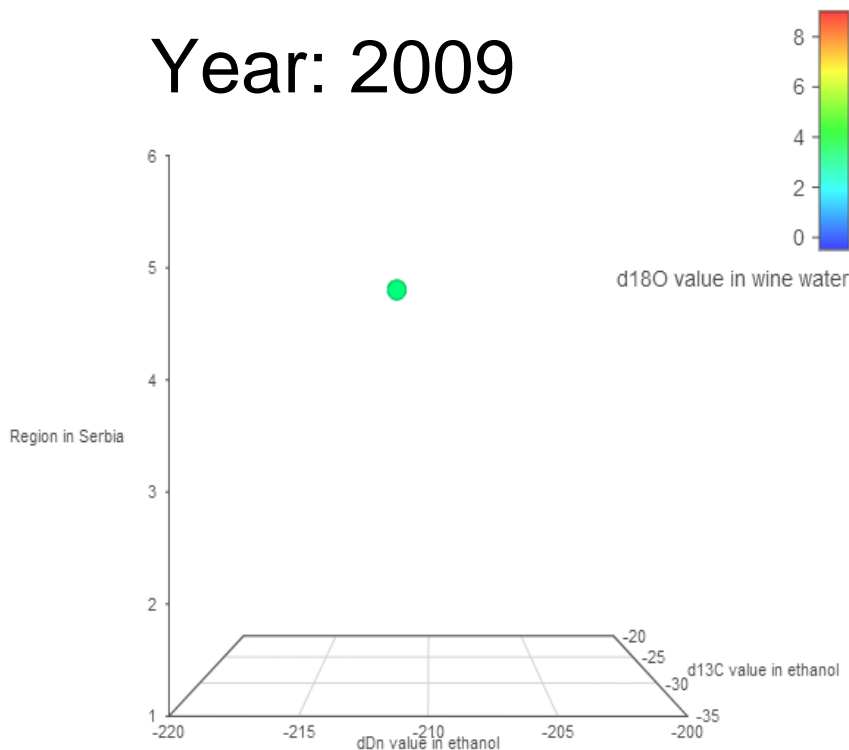
All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale



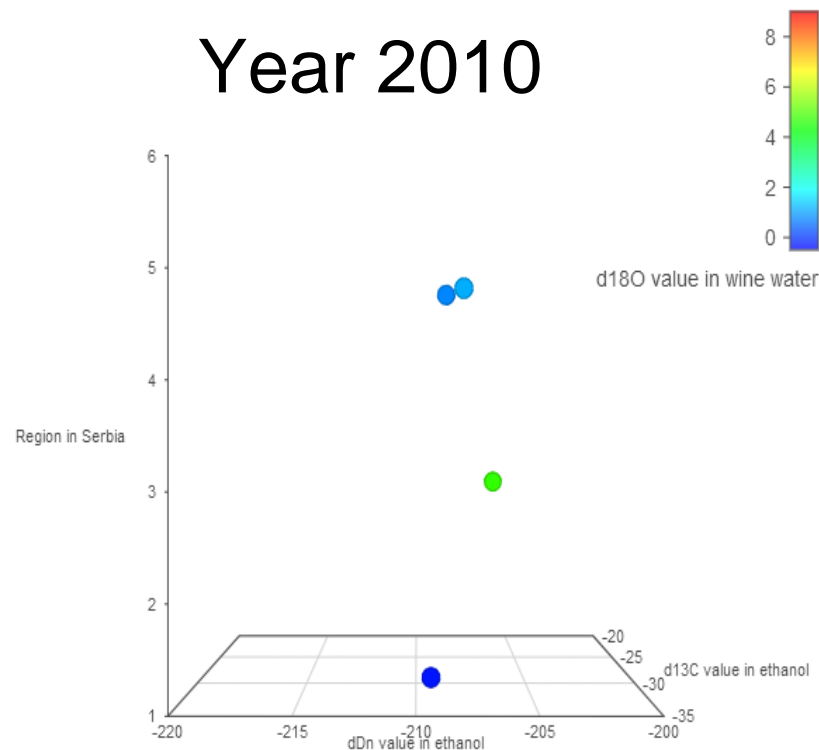
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Wine samples in Serbia Year vs. region

Year: 2009



Year 2010



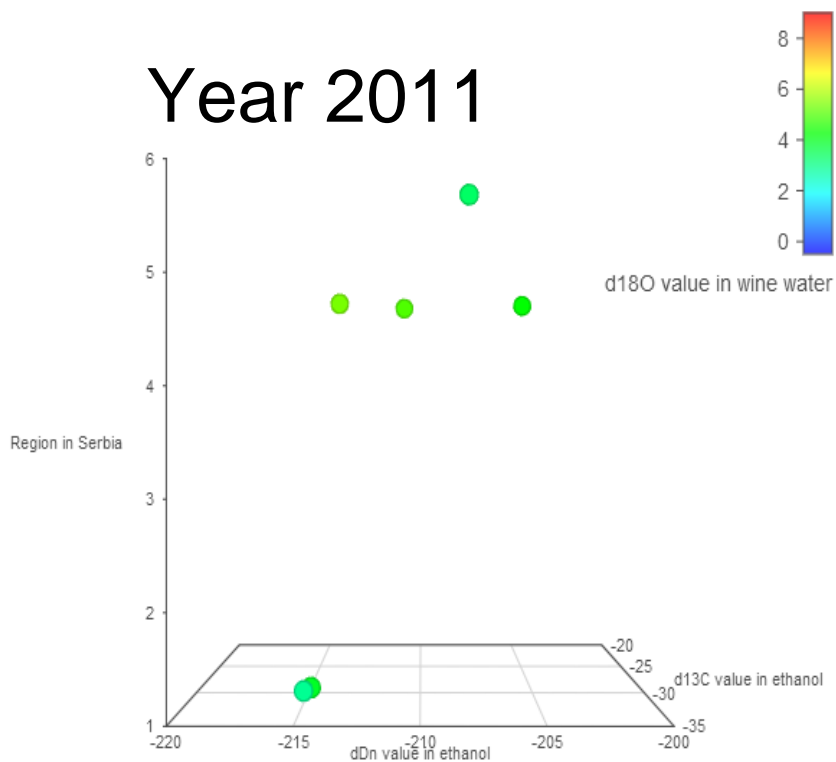
All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale



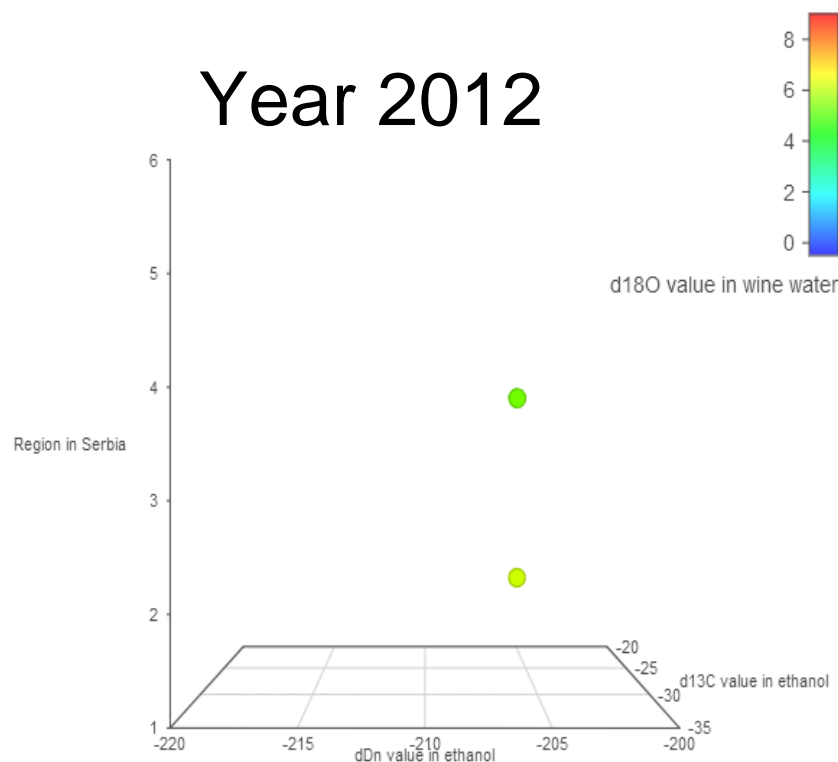
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Wine samples in Serbia Year vs. region

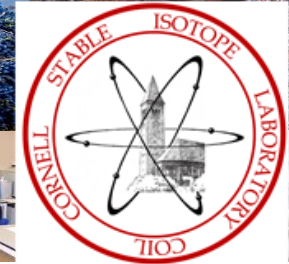
Year 2011



Year 2012

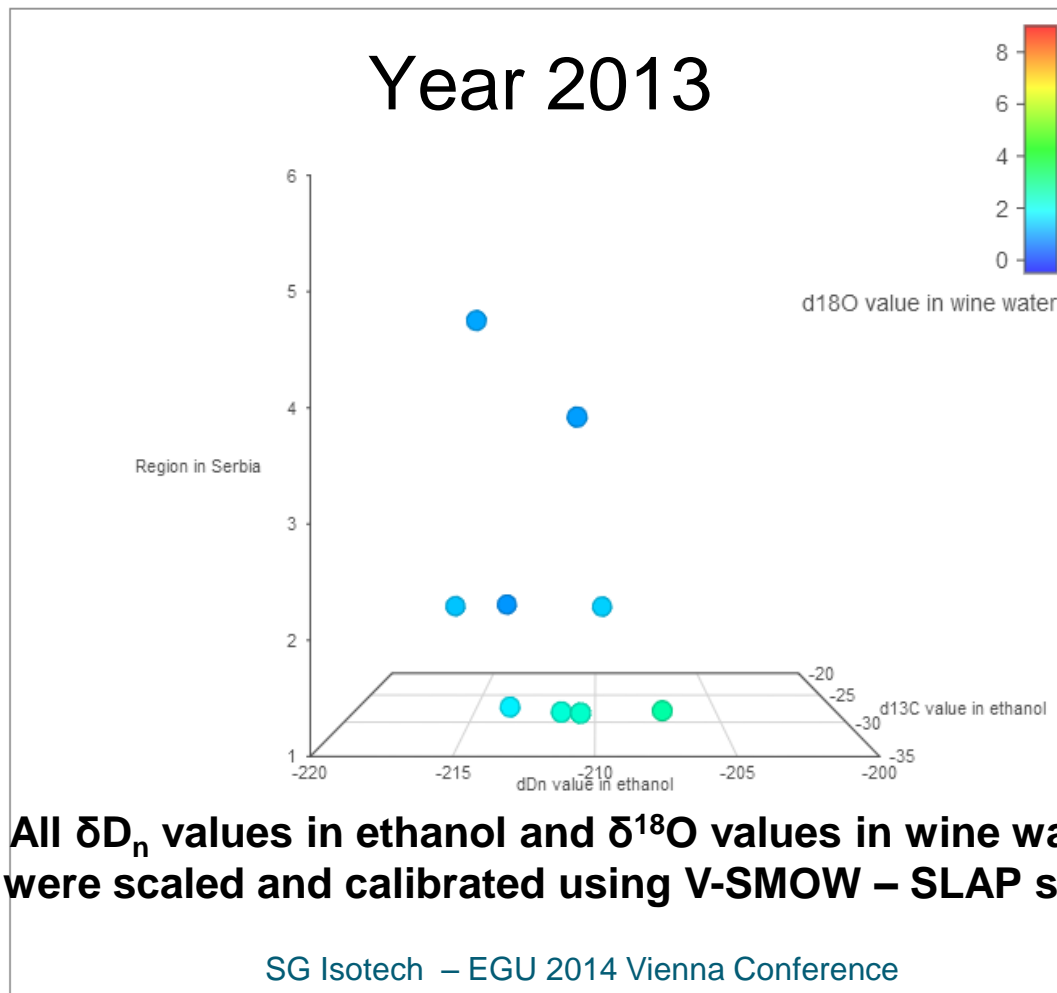


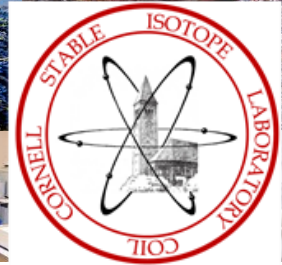
All δD_n values in ethanol and $\delta^{18}O$ values in wine water were scaled and calibrated using V-SMOW – SLAP scale



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Wine samples in Serbia Year vs. region

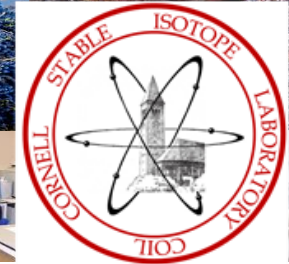




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Sumarized

- δD_n value in ethanol primary gives information about production practices – addition of sugar and/or addition of water
- $\delta^{18}O$ value in wine water gives information about source of the wine water – added water or grape water and information about geographical location and local climate.
- If δD_n value in ethanol is in range of -205 to -215 ‰ vs. V-SMOW, then $\delta^{18}O$ value in wine water can be true and it gives correct information about origin of that wine.
- Our assumption is that If the local climate for specific year was warmer and drier, $\delta^{18}O$ value in wine water would be incriedes. This would be a result of isotopic fractionation of plant water from the grape berries which would grape vine use to continue photosintesis and production of sugar. This process would be influenced by KIE as lighter fractions of plant water would be used in photosintesis process and that would be the reason for $\delta^{18}O$ value in wine water incrisement.
- If the local climate for specific year was colder and with more rain, then final $\delta^{18}O$ value in wine water would be lower, as plant would not be under stress and use water from the grape berries but water from the rooth, and grape berries water would stay more balanced and lower – isotopic perspective.



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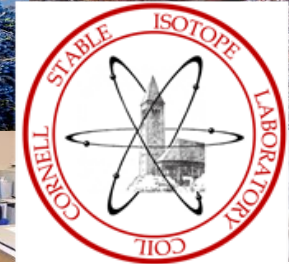


Further activities

- As European Union is preparing for big reforms in wine sector starting from January 2016th and the major challenge will be in connection with liberalization of planting rights and more restrictive rules on chaptalization, EIM-IRMS® can make a contribution in increasing the competitiveness as a quick response to detecting the authenticity of the wine at the European market (imported and domestic).
- We are open to future partnerships and cooperations with laboratories which would be interested in working with us and join our scientific team, so that we could together build an open source isotopic wine data base which could be easily used by all laboratory partners in our network.

To get in touch with us you can contact our team on their e-mail addresses (look at first page of this presentation), or call Ivan Smajlovic

on +381 64 22 95 680



Fingerprint your wine[®]



EIM-IRMS[®] Conclusion

- More accurate results in less than 2 minutes.
- Significant cost savings
- Many more samples can be analyzed per day
- EIM-IRMS[®] means:

“ONE INSTRUMENT FOR ALL ISOTOPIC ANALYSIS OF WINES”



SG Isotech, Inc.



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Thank you for your attention

Questions?