GERMAN FEDERAL INSTITUTE
FOR RISK ASSESSMENT

BfR
Bundesinstitut für Risikobewertung

# Data intepretation

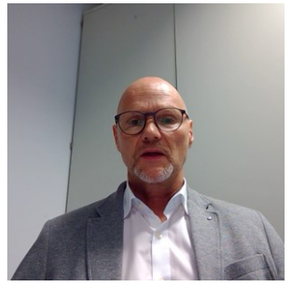
Carsten Fauhl-Hassek

# Significance of Stable Isotope Data for the Proof of Adulteration

**Chaptalization, Sweetening with Beet- and Cane-Sugar, Sugar Mixtures** → **$(D/H)_I$, R-Value $\delta^{13}C$**

**Addition of Water, Blending** → **$\delta^{18}O$, $(D/H)_{II}$**

**False Labelling of Origin Year of Vintage** → **$(D/H)_I$, $\delta^{13}C$ $(D/H)_{II}$, $\delta^{18}O$**



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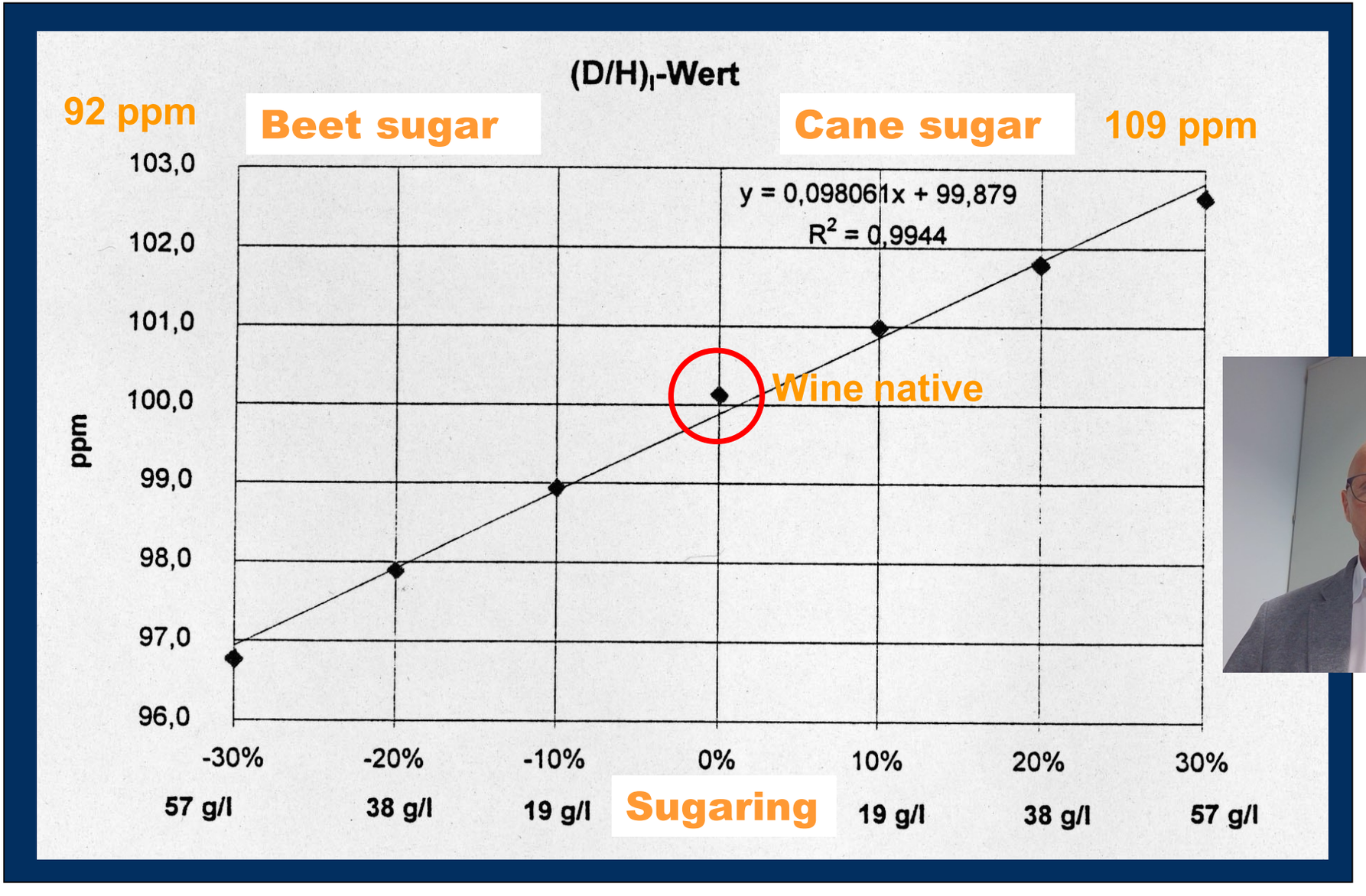
# $^2$H-NMR (SNIF-NMR)

## Chaptalisierung

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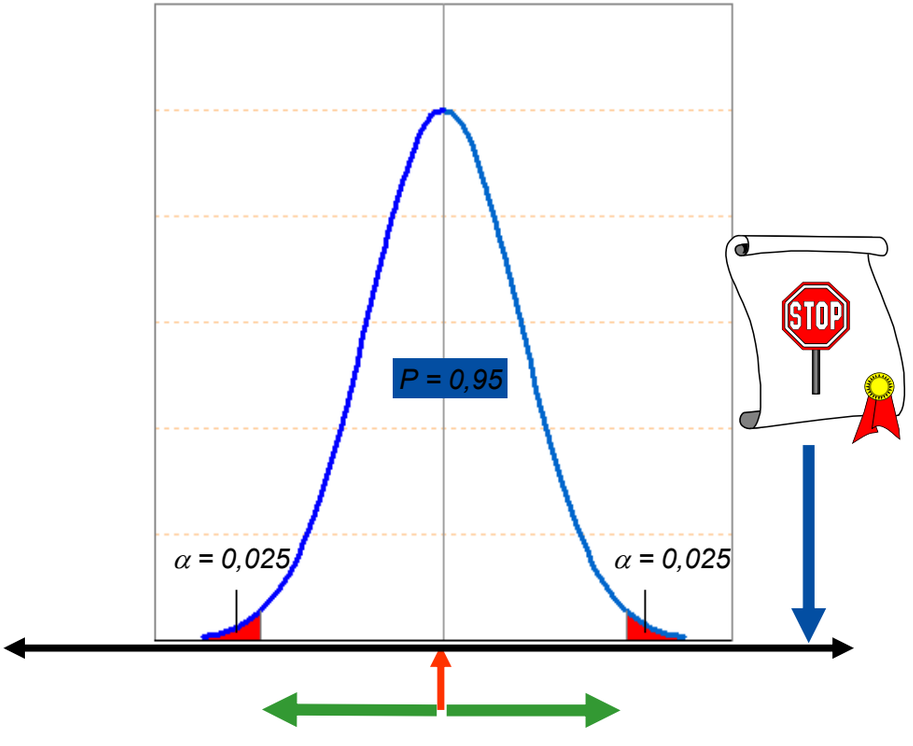
# Reference Data (banks)

**EU Regulation No. 555/2008**

**Stable Isotopes**

**Authentic or unsuspicious samples**




**± Student Factor x σ**

**Authenticity range**

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Guidelines, Minimum Requirements for the Use of EU Wine Data Bank in case of a suspected wine
**(Martin G.J. (OIV vert No. 985), Guillou & Reniero (2002)**

1. **Data from traceability: as much information as possible on the suspected wine sample**
2. **„Enough“ representative reference samples as close as possible to the wine sample**
3. **Computing of mean value, standard deviation, and confidence limit as a function of number of samples**
4. **If not „enough“ representative samples: selection of a set of samples with properties as close as possible**
5. **Meteorological data, discussion with other experts**
6. **Analytical validation of results**

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# Detection of Chaptalisation /Sweetening by $^{2}$H-NMR and $^{13}$C-IRMS

$\delta\ ^{13}C$ [‰] PDB Ethanol

-10
-12
-14
-16
-18
-20
-22
-24
-26
-28
-30

91 93 95 97 99 101 103 105 107 109 111

$(D/H)_I$ ppm Ethanol

natural range

Cut off range

- Beet Sugar (C3)
- Cane Sugar (C4)
- authentic wine
- Chaptalization with beet sugar
- Chaptalization with C3/C4-Sugar
- Chaptalization with cane sugar

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# Detection of Chaptalisation /Sweetening by $^{2}$H-NMR and $^{13}$C-IRMS

$\delta\ ^{13}C$ [‰] PDB Ethanol

-10
-12
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-16
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-20
-22
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-26
-28
-30

P = 0,95

$\alpha$ = 0,025

$\alpha$ = 0,025

91 93 95 97 107 109 111

1.96 σ

natural range

Cut off range

$(D/H)_I$ ppm Ethanol

- Beet Sugar (C3)
- Cane Sugar (C4)
- authentic wine
- Chaptalization with beet sugar
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- Chaptalization with cane sugar

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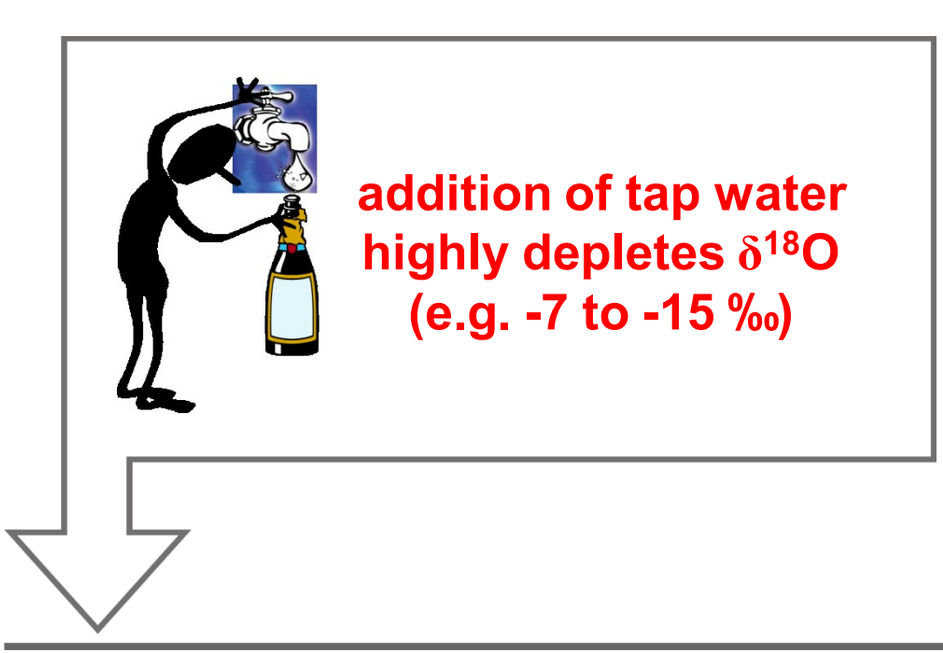
# Isotopic Analysis/$^{18}$O-Value

# Analysis of $\delta^{18}O$ by IRMS for Wine Authentication

- fictitious data set of $\delta^{18}O$-values:
  - selecting reference data (e.g. n = 44)
  - calculating mean, median, standard deviation
  - computing 95% confidence limits (two-tailed distribution)



## Significance interval of Student-t-distribution for one-sided testing and different significance levels (95, 97.5, 99 %)

| Number *n* reference samples | Interval (significance level P = 0.05) | Interval (significance level P =0.025) | Interval (significance level P = 0.01) |
|---|---|---|---|
| 3 | ± 2.920 s | ± 4.300 s | ± 6.960 s |
| 4 | ± 2.353 s | ± 3.180 s | ± 4.540 s |
| 5 | ± 2.132 s | ± 2.776 s | ± 3.747 s |
| 6 | ± 2.015 s | ± 2.571 s | ± 3.365 s |
| 8 | ± 1.895 s | ± 2.365 s | ± 2.821 s |
| 10 | ± 1.833 s | ± 2.262 s | ± 2.960 s |
| 20 | ± 1.729 s | ± 2.093 s | ± 2.539 s |
| 29 | ± 1.701 s | ± 2.048 s | ± 2.467 s |
| 51 | ± 1.676 s | ± 2.009 s | ± 2.403 s |
| 101 | ± 1.660 s | ± 1.984 s | ± 2.364 s |

# Analysis of $\delta^{18}O$ by IRMS for Wine Authentication

- **fictitious data set of $\delta^{18}O$-values:**
  - selecting reference data (e.g. n = 44)
  - calculating mean, median, standard deviation
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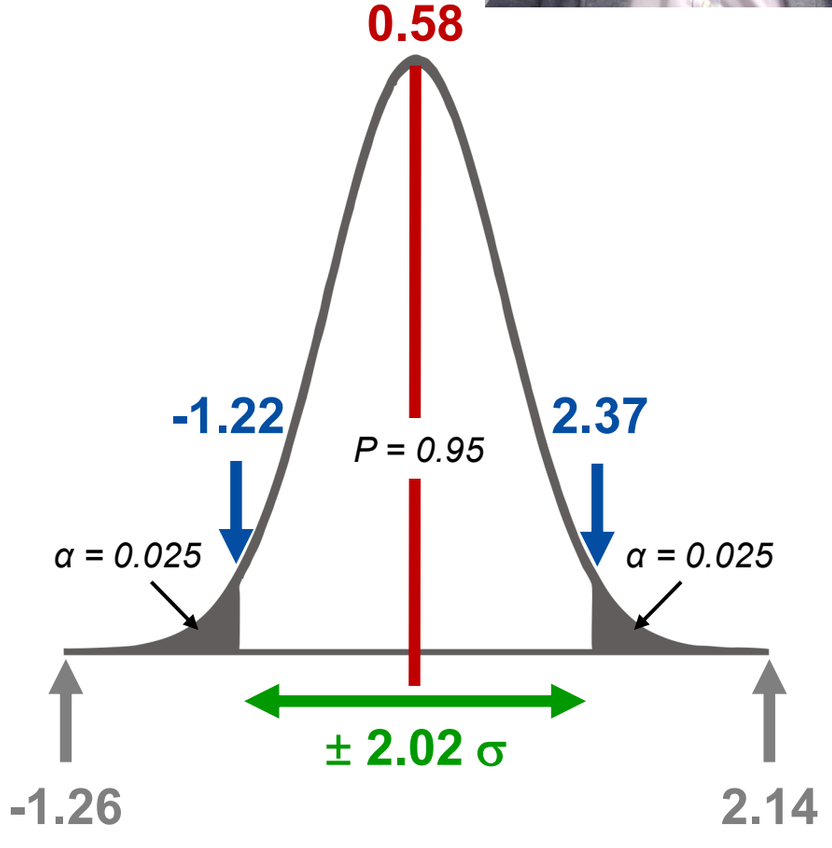
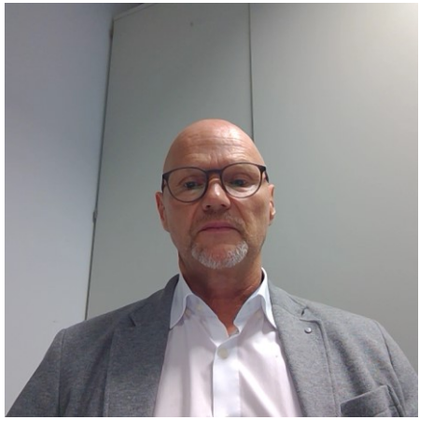
| | |
|---|---|
| Minimum data | -1.26 ‰ |
| Maximum data | 2.14 ‰ |
| Mean | 0.58 ‰ |
| Standard deviation $\sigma$ | 0.89 ‰ |
| Median | 0.82 ‰ |
| *Student factor* | 2.02 |
| 95% confidence limit$_{lower\ (-)}$ | -1.22 |
| 95% confidence limit$_{upper\ (+)}$ | 2.37 |



# Measurement Uncertainty and Decision Making

- definition of limits and compliance: **in authenticity testing control limits are usually experience values**
- 5 different situations from statistical point of view must be considered:


**a)**
result plus
uncertainty
within limits
**in compliance with control limit**

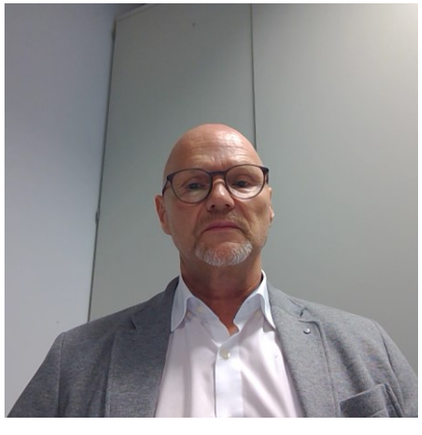


C. Fauhl (2006), *Mitteilungen Klosterneuburg*, **56**, 3–13.

# Measurement Uncertainty and Decision Making

- definition of limits and compliance: **in authenticity testing control limits are usually experience values**
- 5 different situations from statistical point of view must be considered:


**b)**
result within limits, but limit within uncertainty
**in compliance with control limits**



C. Fauhl (2006), *Mitteilungen Klosterneuburg*, **56**, 3–13.

# Measurement Uncertainty and Decision Making

- definition of limits and compliance: **in authenticity testing control limits are usually experience values**
- 5 different situations from statistical point of view must be considered:

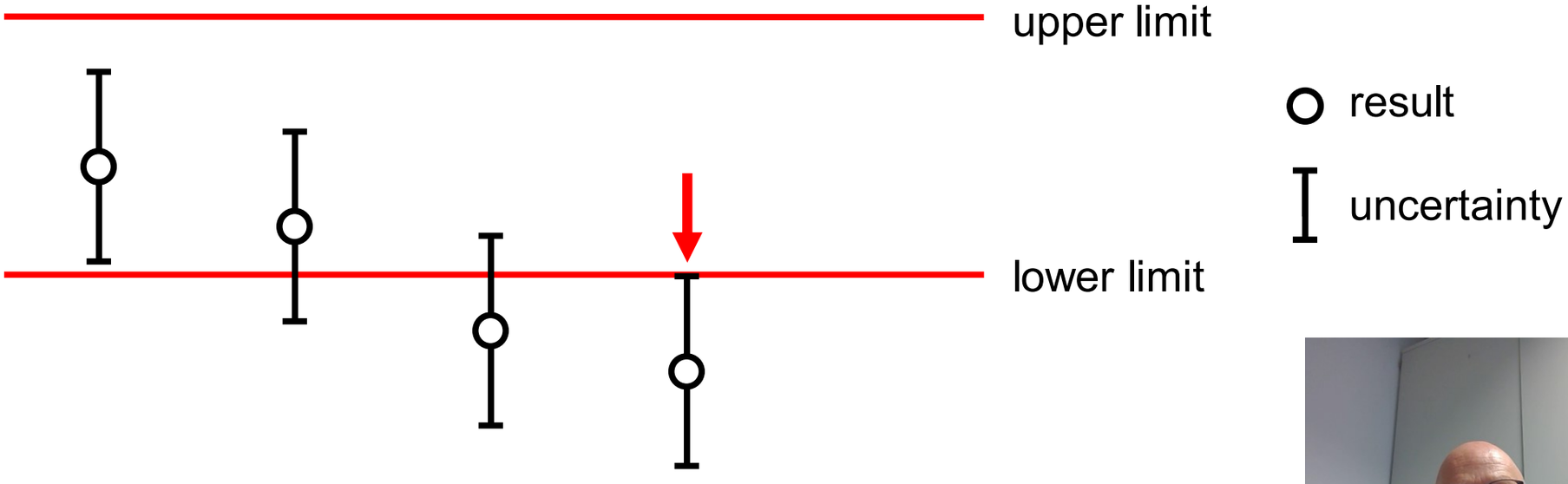

**c)**

result outside limits, but uncertainty within limits **"beyond reasonable doubt"**

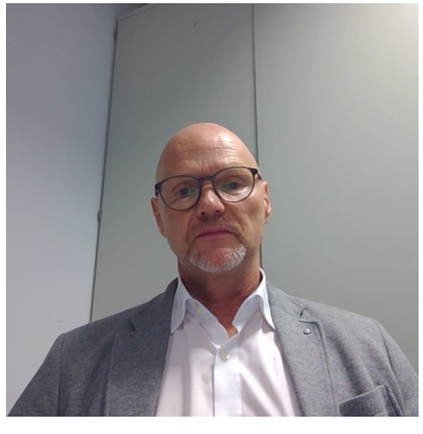
C. Fauhl (2006), *Mitteilungen Kloste*

# Measurement Uncertainty and Decision Making

- definition of limits and compliance: **in authenticity testing control limits are usually experience values**
- 5 different situations from statistical point of view must be considered:




**d)**
borderline situation
(decision limit)
**further action may become necessary**



C. Fauhl (2006), *Mitteilungen Klosterneuburg*, **56**, 3–13.

# Measurement Uncertainty and Decision Making

- definition of limits and compliance: **in authenticity testing control limits are usually experience values**
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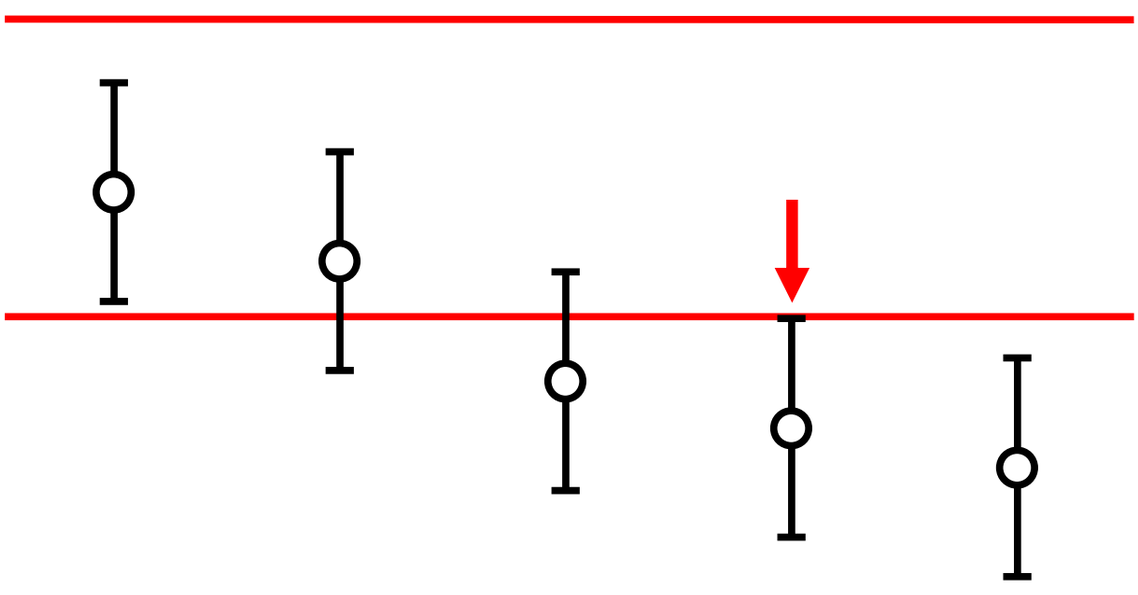



result

uncertainty

**e)**
result plus/minus uncertainty
without limits
**presents violation**

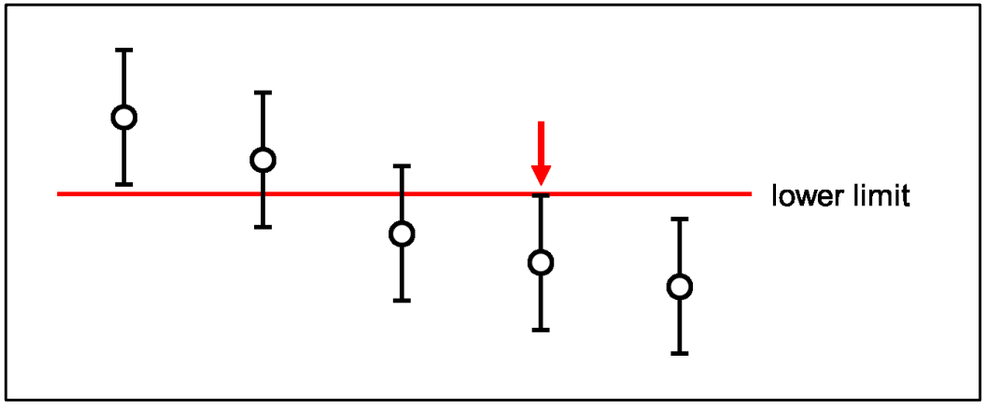

C. Fauhl (2006), *Mitteilungen Klosterneuburg*, **56**, 3–13.

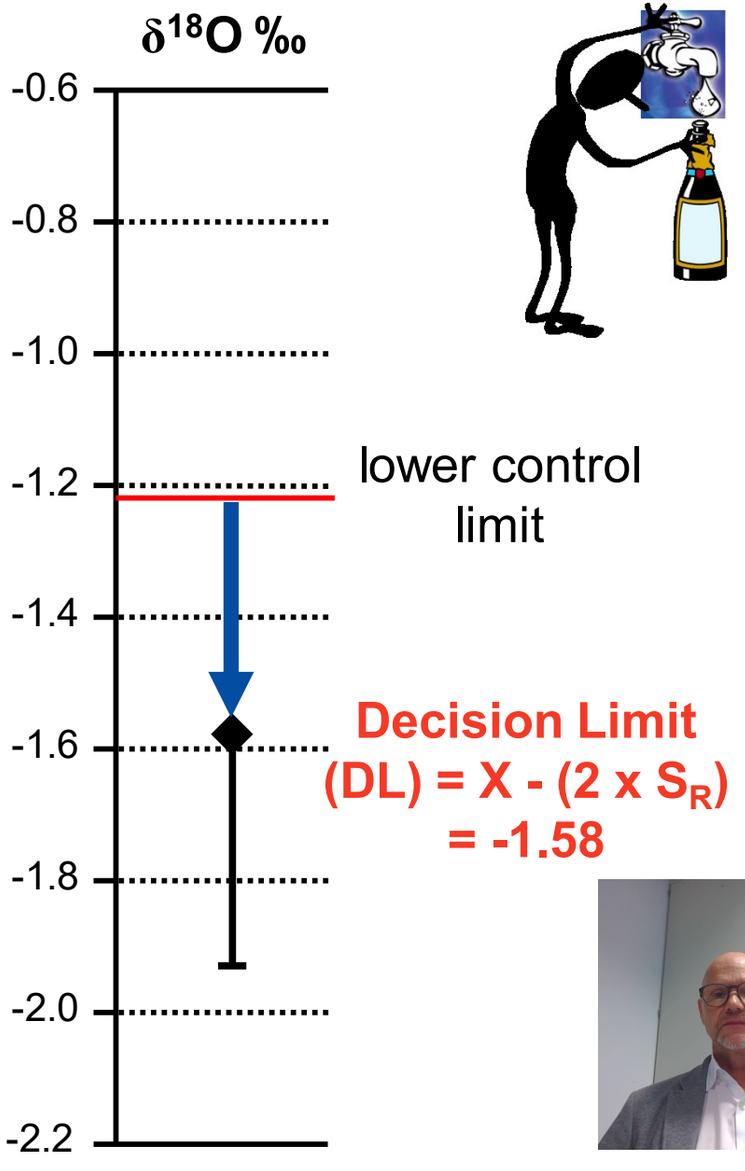
# Measurement Uncertainty and Decision Making e.g. Detection of Watering

- method for $\delta^{18}O$ determination of water in wines (Resolution OIV-Oeno 353/2009, Commission Regulation (EEC) 2676/90)

**R = 0.50 ‰**
**$S_R$ = 0.18 ‰**

- Expanded Measurement Uncertainty **(MU) = 2 x $S_R$ = 0.36 ‰**



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# Thank you for your attention

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