

Assessment of results against limits -practical example-

Laying down enforcement limits for chemical analysis (X_{max} and X_{min})

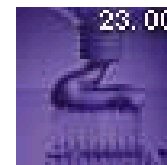
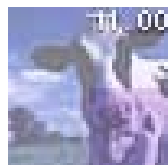
Klaas Strikwerda

Inspectorate for Health Protection and Veterinary Public
Health, Groningen, The Netherlands



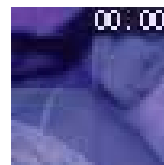
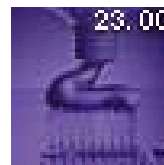
Presentation

- Introduction Inspectorate
- Why limits of enforcement
- Approach of laying down limits
- Results of the approach-**examples**



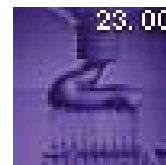
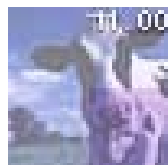
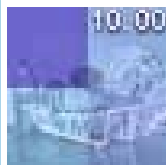
Introduction/Tasks

- Enforcement and promotion of compliance with regulations
- Investigations health hazards situations
- Advising policy making authorities
- Investigations consumers complaints
- Developments and publication of methods



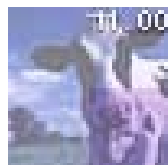
Workfield

- Food and commodities act
- Meat inspection act
- Livestock act
- Experiment on animals act
- Dangerous machinery act
- Pesticide act
- Environmentally hazardous substances act
- Tobacco act



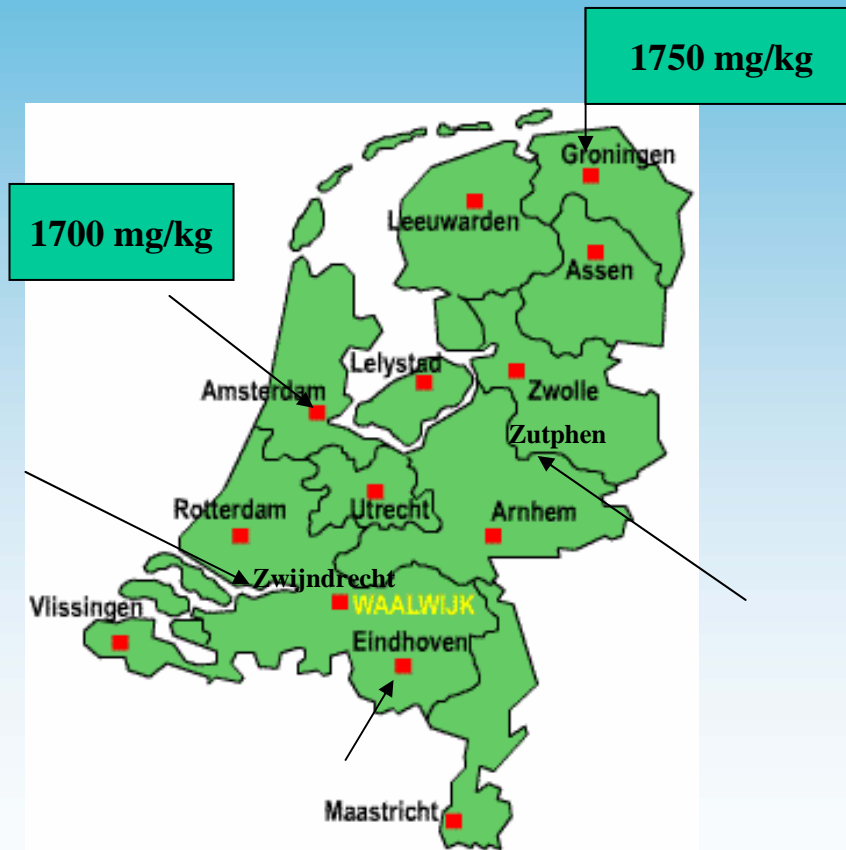
Special tasks

- * Primary and horticultural products
- * Composite food products
- * Veterinary products
- * Non-food product safety
- * Non-food chemistry



5 Regional Inspectorates

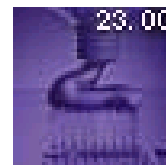
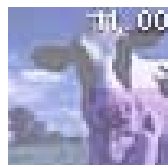
Different enforcement limits



Enforcement limits

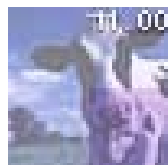
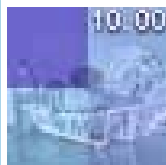
WHY ?

- Be sure, 5 laboratories of the inspectorate enforce on the same way, with the same quality, with a confidence of 95%
- **Work with the same (concern-)uncertainty**



Uncertainty

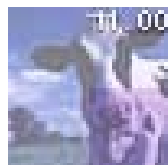
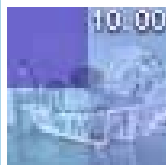
- No analytical method gives the exact value or content of an measurand (analyte).
- We make (little) mistakes such as:
 1. Systematically errors
 2. Random errors



Validation

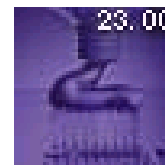
- Recovery
- Specificity
- Reproducibility
- Limit of detection
- Uncertainty

Test always: Robustness



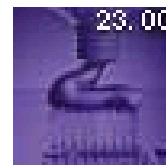
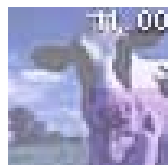
Tools for enforcement limits

- Organise proficiency test
- Use reference materials



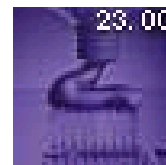
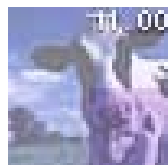
Criteria CHEK proficiency studies

- Test accredited methods
- Desires of the regions
- Possibilities



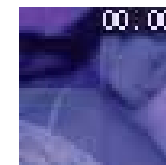
What kind of proficiency tests?

- Food
- Non Food
- Microbiological



Examples of proficiency tests

- Histamin in fish
- Alcohol/methanol in wine
- Aflatoxins in nutproduct
- Glutamic acid in soup
- Parabens in cosmetics
- Hydrochinon in cosmetics
- Salmonella spp in milk





• Certified Secondary Reference example^m material (CSRM) Specification

Glutamic acid in chips

Product

Batch	: Proficiency study 292
Matrix	: Bolognese chips
Date of production	: June 2004
Storage life	: June 2005
Store temperature	: - 20° C
Glutamic acid	: 0.639% m/m
Uncertainty	: 0.034% m/m



Description of the sample

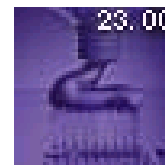
10 gram homogeneous well-crushed and minced Bolognese chips in vacuum-sealed sachets.

How to use

The material is intended for analytical purposes. Samples should be stored unopened < -20°C.

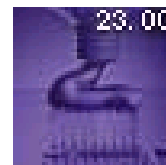
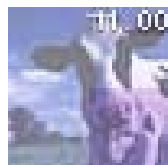
Used methods

A detailed technical report of the analytical procedures and treatment of the analytical data is available (Proficiency study 292, oktober 2004).



Analytical measurement and uncertainty HOW?

- $R \Rightarrow$ proficiency studies
(reproducibility between labs)
- $R \Rightarrow$ Shewhart charts
(within lab reproducibility)
- Formula of Horwitz

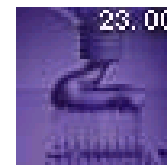


Estimation of R HOW ?

Proficiency studies

- > S_R = standard deviation estimates for interlaboratory reproducibility
- > $2.8 S_R$ = interlaboratory reproducibility
- > $2.8 S_R = R$

CHEK organised more than 300 proficiency studies



Estimation of R

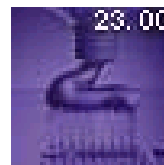
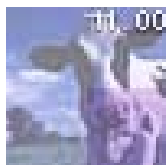
HOW?

Use data of SHEWHART charts

-> S_1 = standard deviation estimates for intralaboratory reproducibility

-> $1.6 * 2.8 * S_1$ = interlaboratory reproducibility

-> $1.6 * 2.8 * S_1 = R$



Estimation of R HOW?

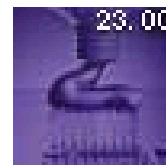
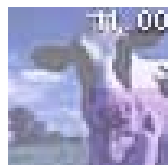
Use the formula of Horwitz
(calculated from > 100 proficiency studies)

$$R = X_{\text{limit}} * 2.8 * 2^{(1-0.5 \log c)/100}$$

c: absolute concentration, f.e. 10% is c=0.1)

x_{limit} : legal limit

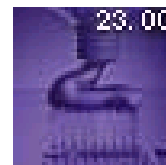
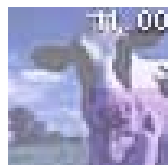
criterion: use a validated method



Enforcement limit = $X_{\min/\max}$

X_{\max} : the value of a certain parameter, resulting from analyses, above which is a sample regarded as rejectable with a probability of 95% (upper limit)

X_{\min} : under limit



X_{\max} and X_{\min}

$$X_{\max/\min} = X_{\text{limit}} \pm \frac{0.84 R_1}{2} \quad (\text{duplicates})$$

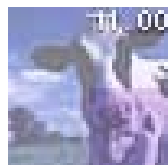
$$X_{\max/\min} = X_{\text{limit}} \pm \frac{0.84 R_1}{\sqrt{2}} \quad (1 \text{ analysis})$$

X_{limit} = legally required maximum/minimum value

literature:

ASTM standard D 3244-74 (2002)

NEN 3206



Example X_{\max}/\min Horwitz

$$R = X_{\text{limit}} * 2.8 * 2^{(1-0.5 \log c)}/100$$

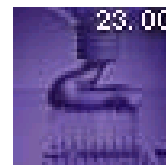
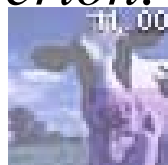
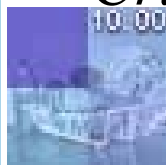
$$X_{\text{limit}} = 1 \%$$

$$C = 10^{-2}$$

$$R = 1 * 2.8 * 2^2 / 100 = 0.112$$

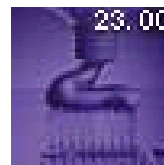
$$X_{\max} = 1 + 0.59 * 0.112 = 1.066\%$$

Criterion: use a validated method



Examples $X_{\max/\min}$ proficiency studies

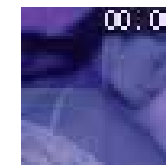
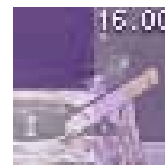
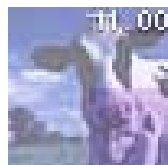
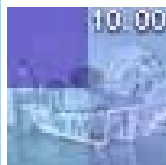
component	matrix	Legal limit	R	X max/min (1 analysis)
Acesulfaam-K	Lemonade	400 mg/l	40.5 mg/l	423.9 mg/l
Benzoic acid	Salad	1500 mg/kg	152 mg/kg	1590 mg/kg
Cadmium	Canned tomatoes	0.1 mg/kg	0.040 mg/kg	0.124 mg/kg
Alcohol	Beer	4 % (m/m)	0.15 % (m/m)	3.915 % (m/m)



Examples Xmax/min

Interlaboratory reproducibility

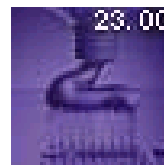
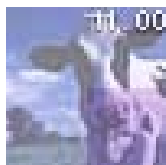
component	matrix	(Legal) limit	R ($R_i * 1.6$)	X max/min (1 analysis)
Propanol	Winter-product	20%	4.27%	22.52%
d-limonene	Household-product	1%	0.14%	1.08%
Activ chlor	Desinfectant	30%	0.88	30.52%



Summary

Calculation of the enforcement limits:

- Use R calculated/estimated from:
 1. Proficiency studies
 2. Shewhart charts (reference materials)
 3. Horwitz



Conclusion

