Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

19.11.2019

UNCERTAINTY FROM SAMPLING OF TRACE EXPLOSIVES AMOUNTS AND DETECTION BY ION MOBILITY SPECTROMETRY

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Outline

1. Introduction
- Security checks and air cargo

2. Method
- Ion mobility spectrometry as ETD-method
- Logistic regression

3. Results
- Comparison of POD0.9 in dependence of deposition and sampling
- Measurement uncertainty for Boolean results

4. Conclusions and Summary

Introduction

- Loading of approximately 2.3 Mt airfreight at German airports in 2019

January to June 2019, https://www.destatis.de/DE/Presse/Pressemitteilungen/2019/08/PD19_320_464.html

- 50% of the total airfreight is transported in civil aviation planes

- Protection against threats on air traffic security

- Regulatory responses in D / EU → increased freight controls, restructuring “secure supply chain”

MergeGlobal Inc.: Global Air Freight: Demand Outlook and its Implications, Lizenz: Creative Commons by-nc-nd/3.0/de, Bundeszentrale für politische Bildung, 2009, www.bpb.de

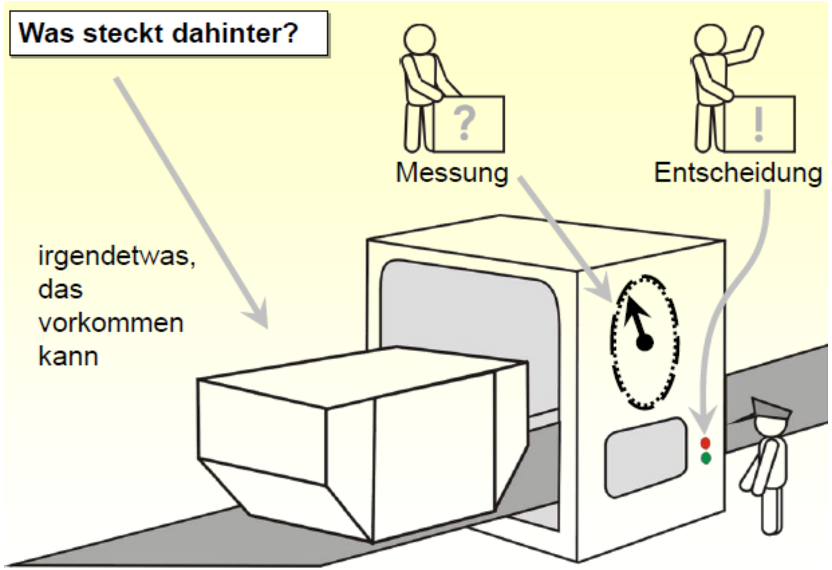
"Al-Qaeda publishes recipe for easy-to-make bomb that would evade airport check that 'any determined Muslim can prepare'". *Daily Mail,* Retrieved on https://www.dailymail.co.uk/news/article-2905276/Al-Qaeda-publishes-recipe-easy-make-bomb-evade-airport-check-determined-Muslim-prepare.html, 2019-11-17.

Regulations for air cargo and mail screening

Cargo and mail shall be screened by at least one of the following methods

- hand search
- x-ray equipment
- Explosive detection systems (EDS)
- Explosive detection dogs (EDD)
- Explosive trace detection (ETD)
- visual check
- metal detection equipment (MDE)

→ Waybill content must match the x-ray picture



Section 6.2.1.1. - EU Reg. 2015/1998

K. Osterloh, N. Wrobel, U. Ewert

Process approach | staged detection process

BAM

Airfreight → **X-ray $E \leq 300$ keV** → **ETD by IMS** → **Transport ✈**

x-ray of palletised airfreight ($E \leq 300$ keV)

Content: ???

Picture provided by C. Weißkopf, Smith Heimann, 2016.

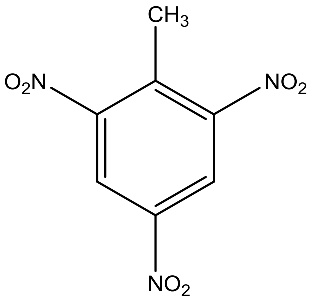
Method

www.bam.de

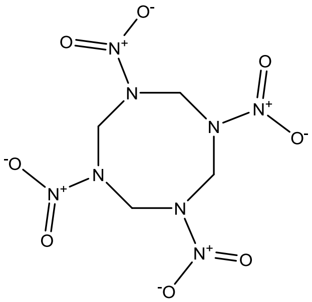
Explosives

- Substances or mixtures of substances which, after energetic activation, react within a few seconds, releasing a high amount of energy

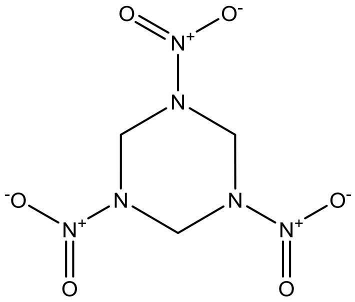
- Tests referring to **ASTM E2520 - 15**, Standard Practice for Measuring and Scoring Performance of Trace Explosive Chemical Detectors



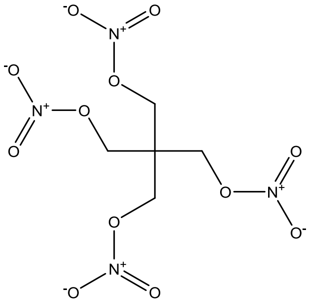
TNT



HMX



RDX



PETN

ECAC certified devices

Bruker Daltonik
DE-tector

Safran
Itemiser 4DX

Smiths Detection
Ionscan 600

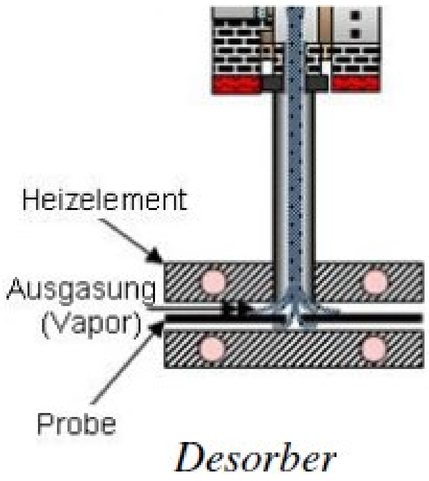
L3 Security & Det. Sys.
QS-B220

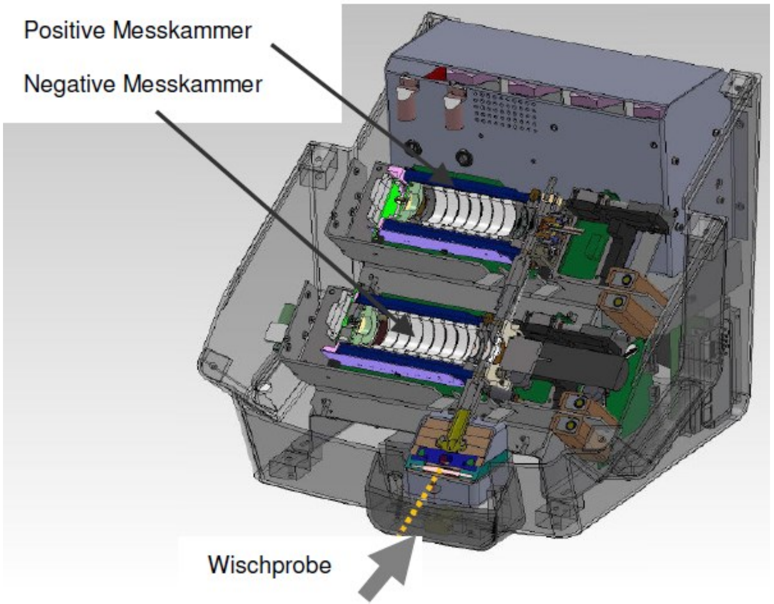
Nuctech | TR2000DB

1st Detect
Tracer 1000
Linear Ion Trap Mass Spectrometer

European Civil Aviation Conference (ECAC), https://www.ecac-ceac.org/, Certified ETD devices https://www.ecac-ceac.org/documents/10189/62763/ECAC-CEP-ETD-Web-Update-20-February-2019.pdf/771e9026-a606-4a30-b8cf-6316e165b2d1, all pictures from the producers‛ homepage or data sheets.

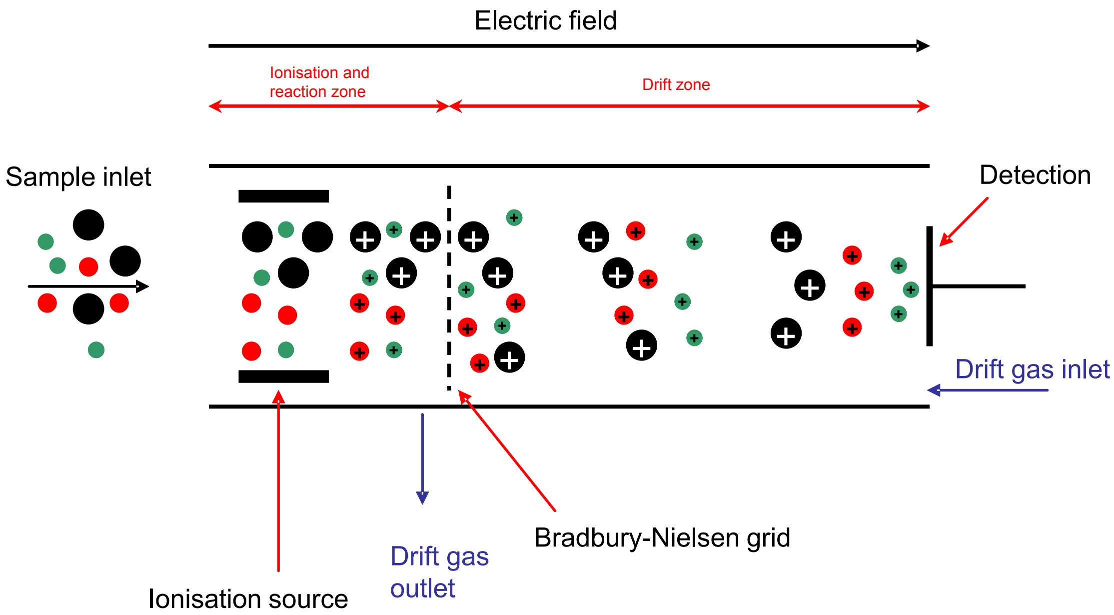
General set-up





Figures: D-TeC System Consulting GmbH, Systeminformation QS-B220 (in German), **2014,** http://www.d-tec-system.de/m/pdf_dl_QS-B220%20mit%20Drucker.pdf

Ion mobility spectrometry (IMS)



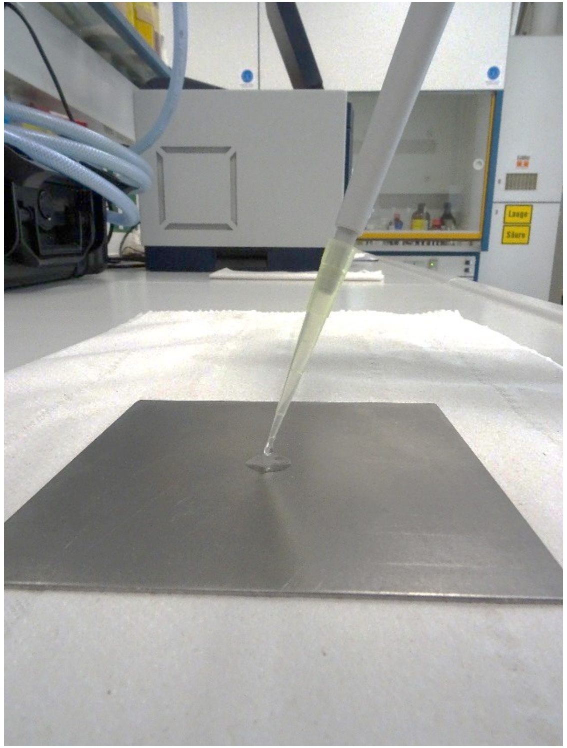
$$K_0 = K \cdot \left(\frac{T_0}{T}\right) \cdot \left(\frac{p}{p_0}\right)$$

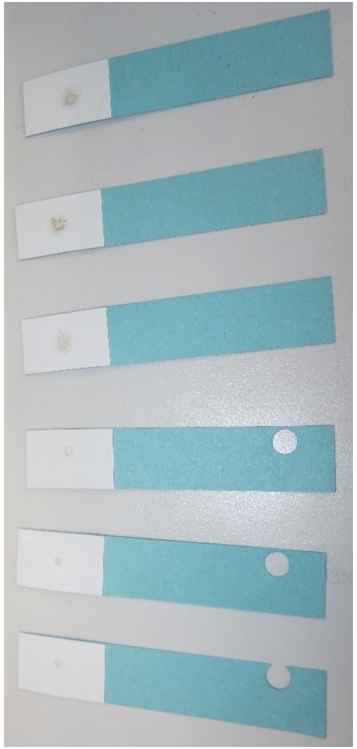
$$= \frac{s}{t_d \cdot E} \cdot \left(\frac{T_0}{T}\right) \cdot \left(\frac{p}{p_0}\right)$$

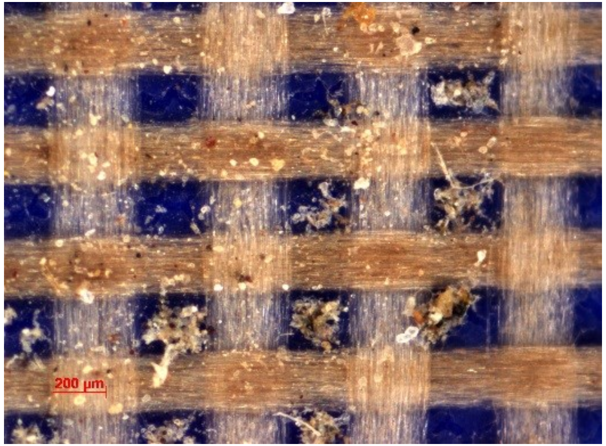
K_0 = reduced mobility in $cm^2/(V \cdot s)$
K = mobility in $cm^2/(V \cdot s)$
T_0 = 273.15 K
T = drift tube temperature in K
p = gas pressure in hPa
p_0 = 1013.25 hPa
s = drift tube length in cm
t_d = drift time in s
E = electric field in V/cm

More information about IMS: G. A. Eiceman, Z. Karpas, H. H. Hill, *Ion Mobility Spectrometry, 3rd edition*, CRC Press Taylor & Francis Group, Boca Raton, https://doi.org/10.1201/b16109, **2015**.

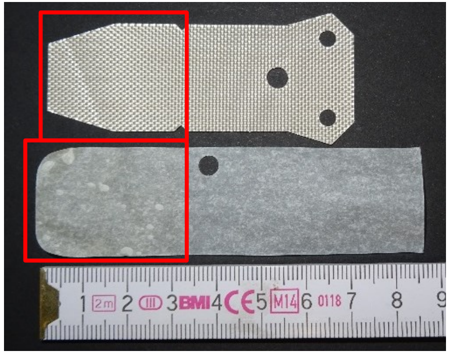
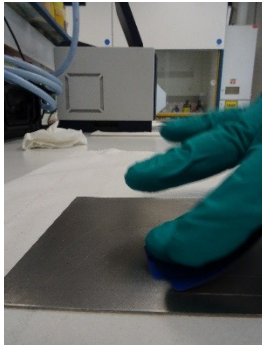
Application on surfaces – two methods





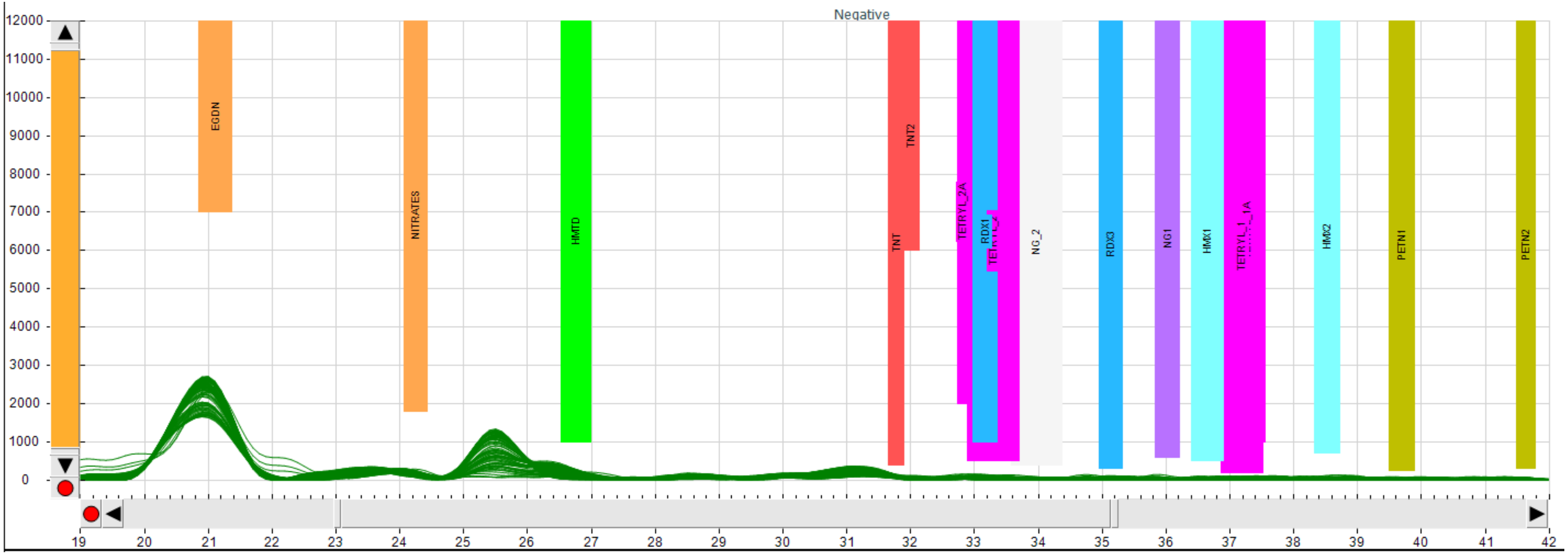


Swab sampling

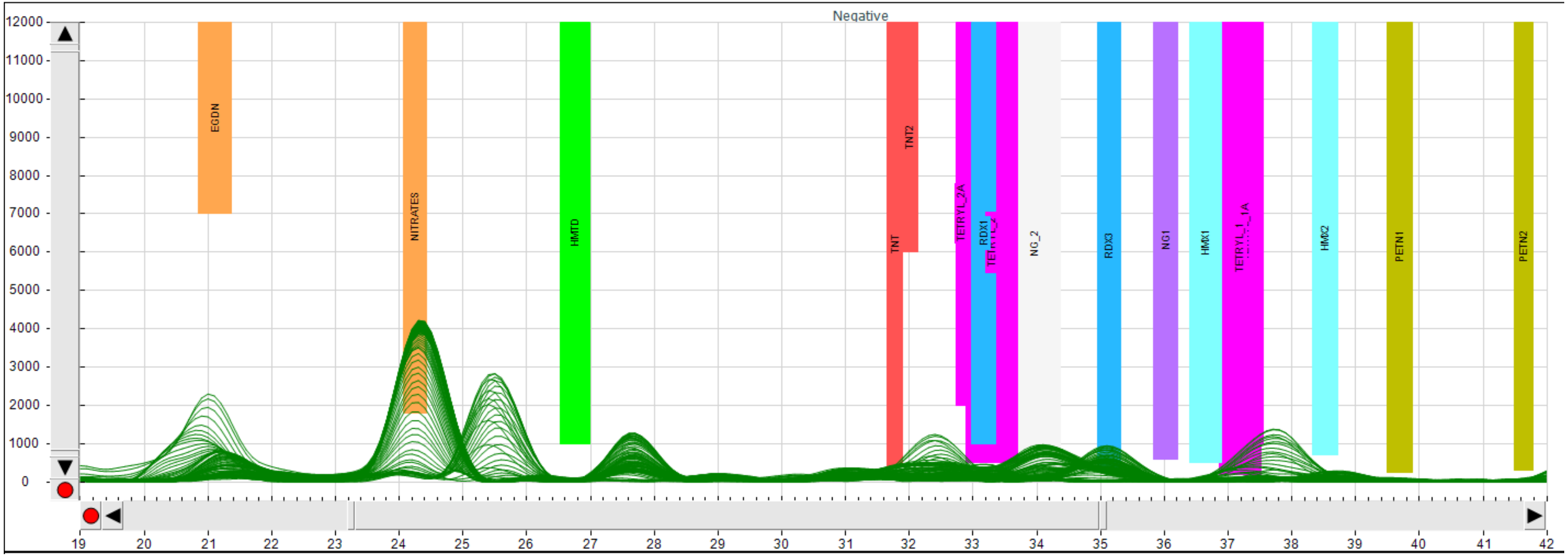

Example: Blank

Blank sample trap → no alarm → true negative (TN)



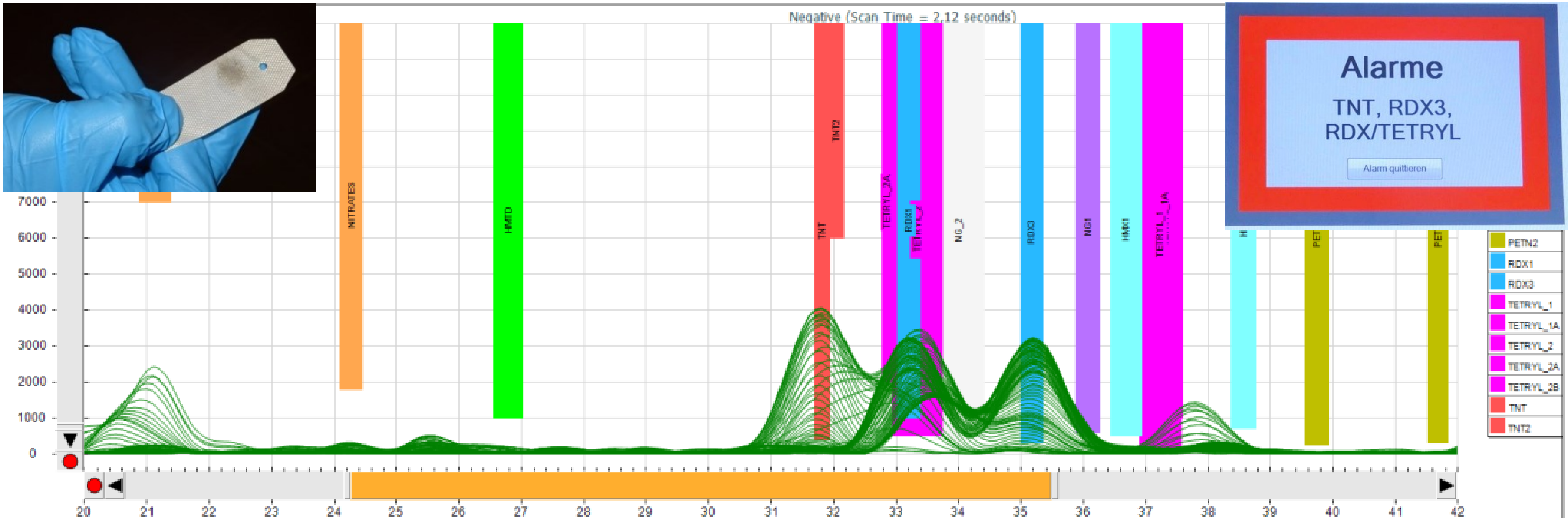
Example: Swab sample

Swab sample from a laboratory table surface → alarm → false positive (FP)



Example: Swab sample of a suspicous surface

- Alarm indication when a detected amount of substance exceeded a threshold → true positive (TP)

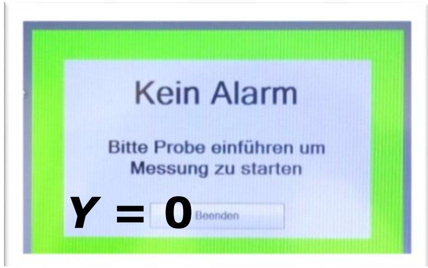


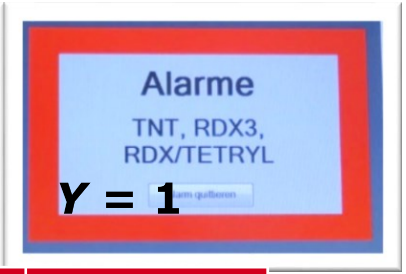
Results

www.bam.de

Boolean screening results

- Yes/No-indications $Y_i \in \{1,0\}$
- True-positive rate (sensitivity, probability of detection (POD))





Measurement

ETD device		Explosive		
		Presence (1)	**Absence (0)**	Total
	Alarm (A)	**TP**	**FP**	TP+FP
	No Alarm (A*)	**FN**	**TN**	FN+TN
	Total	TP + FN	FP + TN	N

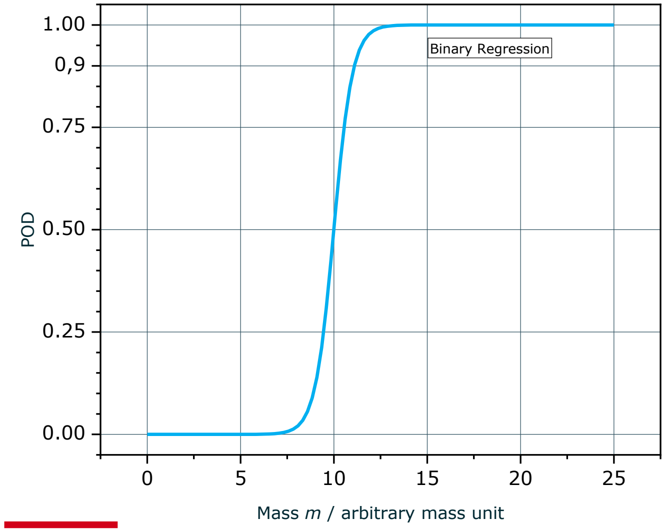
Decision

Performance characterisation for binary classification via performance function

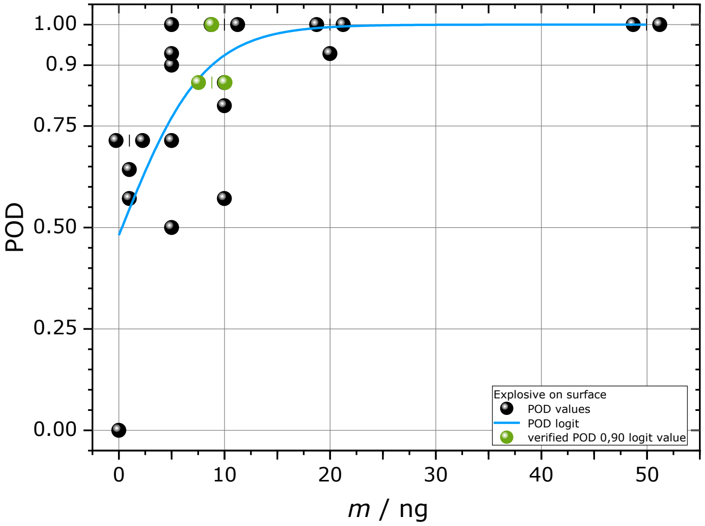
- POD = Positive test results (TP) over applicated explosive mass

$$POD = \frac{L}{1 + e^{-A(m-B)}}$$

L = 1
A = logistic growth rate
B = mass value of $POD_{0.5}$
m = independent variable



Logit function of a real example



Deposition of a defined mass

Description	Process equations
Weighed portion	$m_E = m_{nom} \cdot PUR$
Stock solution	$\beta_s = \frac{m_E}{V}$
Dilution	$\beta_i = \frac{V_{s-eq} \cdot \beta_s}{V_i}$
Mass deposit	$m_{dep} = \beta_i \cdot V_{Pip}$

Preparation of a calibration standard, GUM Workbench example “example A1.smu”,
S. L. R. Ellison, A. Williams (eds.), Quantifying Uncertainty in Analytical Measurement
EURACHEM / CITAC Guide **2012**.

Influence quantities

Weighed portion: Resolution of balance

- 0.00001 g
- Calibration certificate 0.00011 g
- Repeatability 0.0001 g
- Purity: substance depending

Stock solution – acetone/methanol (10/90 and 500 mL):

- Flask label (class B) 0.3 mL
- Temperature 0.1 mL/K
- Repeatability 0.001 L

Test solution (100 mL)

- Flask label (class A): ± 0.1 mL
- Temperature: 0.1 mL/K
- Repeatability ± 0.2 mL
- Pipetted volume of stock ± 2 %

Deposition:

- Pipetted volume of the test solution

Further unquantified causes:
Dust and solvent effects

Budget for mass deposit

Description	X_i	x_i	$u(x_i)$	$c_i(y_j)$	$u_i(y_j)$	$h_i(y_j)$
Weighed portion	m_E	0.4995 g	1.040E-03 g			
Weighed portion on balance display	m_{nom}	0.5 g				
Resolution of balance	δA	0 g	5.770E-06 g	40	2.300E-04 ng	0.0 %
Calibration certificate	δCAL	0 g	6.350E-05 g	40	2.500E-03 ng	0.0 %
Repeatability	δR	0 g	1.000E-03 g	40	4.000E-02 ng	4.9 %
Purity	PUR	0.999	5.770E-04	20	1.200E-02 ng	0.4 %
Mass concentration stock solution	b_s	0.999 g/L	4.380E-03 g/L			
Nominal stock solution volume	$V_{s\text{-}nominal}$	0.5 L				
Calibrated Volume (flask label)	$f_{V\text{-}s\text{-}calibration}$	1	1.730E-03	-20	-3.500E-02 ng	3.7 %
Temperature influence	$f_{V\text{-}s\text{-}temperature}$	1	3.290E-03	-20	-6.600E-02 ng	13.4 %
Repeatability	$f_{V\text{-}s\text{-}repeatability}$	1	1.000E-03	-20	-2.000E-02 ng	1.2 %
Mass concentration of test solution	b_i	0.01998 g/L	8.890E-05 g/L			
Aliquote volume of stock solution	$V_{s\text{-}eq}$	0.002 L				
Nominal test solution volume	$V_{i\text{-}nominal}$	0.1 L				
Calibrated Volume (flask label)	$f_{V\text{-}i\text{-}calibration}$	1	5.770E-04	-20	-1.200E-02 ng	0.4 %
Temperature influence	$f_{V\text{-}i\text{-}temperature}$	1	4.850E-04	-20	-9.700E-03 ng	0.3 %
Repeatability	$f_{V\text{-}i\text{-}repeatability}$	1	2.000E-04	-20	-4.000E-03 ng	0.0 %
Conversion factor 1E+3	$k_{Volumen}$	1000 ng·L/(g·µL)				
Pipetted volume	V_{pip}	1 µL				
Repeatability	δImp	1	7.690E-03	20	1.500E-01 ng	73.0 %
Systematic error (data sheet)	δSE	1	1.440E-03	20	2.900E-02 ng	2.6 %

	Y_j	y_j	$u(y_j)$
Mass of the explosive (k = 1)	m_{dep}	19.98 ng	0.9 %

Measurement uncertainty of POD

$$POD = \frac{L}{1 + e^{-A(m-B)}}$$

Inverse POD-function

$$m_{0.9} = \frac{A \cdot B - \ln\left(\frac{L}{POD} - 1\right)}{A} = \frac{A \cdot B - \ln\left(\frac{1}{0.9} - 1\right)}{A}$$

Sensitivity coefficients of parameters *A* and *B*

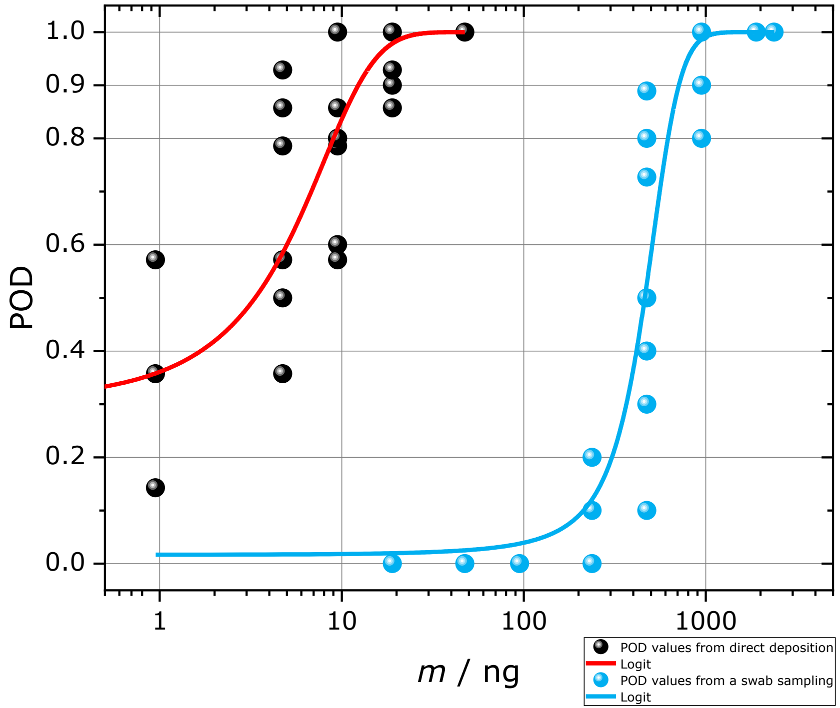
$$\frac{dm_{0.9}}{dA} = \frac{\ln\left(\frac{1}{0.9} - 1\right)}{A^2}$$

$$\frac{dm_{0.9}}{dB} = 1$$

Budget equation

$$m_{0.9} = \frac{A \cdot B - \ln\left(\frac{1}{0.9} - 1\right)}{A} \cdot \delta m_{\text{dep}}$$

Measurement uncertainty of *POD* = 0.9
Direct deposit and swab sampling from a surface



Direct

$m_{0.9}$ = 12.3 ng

Swab sampling

$m_{0.9}$ = 711.4 ng

Coefficient

$$C = \frac{m_{0.9-\mathrm{swab}}}{m_{0.9-\mathrm{direct}}} = 57.8$$

Measurement uncertainty of POD
Direct deposit and swab sampling from a surface

Direct	Description	X_i	x_i		$u(x_i)$	$c_i(y_j)$	$u_i(y_j)$
	POD with 0.9 TP-rate	$POD_{0.9}$	0.9				
	Parameter A	A	0.244 ng^{-1}		0.064 ng^{-1}	-36.770	-2.361 ng
	Parameter B	B	3.339 ng		0.904 ng	1	0.904 ng
	Limited POD	L	1		0	-40.908	0.000
	Mass deposit	δm_{dep}	1		0.90 %	12.327	0.111 ng
		Y_j	y_j		$u(y_j)$		
	Mass of the explosive (k = 1)	m_{dep}	12.3	ng	2.5 ng	20.5 %	
	Mass of the explosive (k = 2)				5.1 ng	41.1 %	

Swab sampling, solvent transfer	Description	X_i	x_i		$u(x_i)$	$c_i(y_j)$	$u_i(y_j)$
	POD with 0.9 TP-rate	$POD_{0.9}$	0.9				
	Parameter A	A	0.009 ng^{-1}		0.003 ng^{-1}	-28244.720	-83.322 ng
	Parameter B	B	462.235 ng		27.219 ng	1	27.219 ng
	Limited POD	L	1		0	-1133.787	0.000
	Mass deposit	δm_{dep}	1		0.90 %	711.353	6.402 ng
		Y_j	y_j		$u(y_j)$		
	Mass of the explosive (k = 1)	m_{dep}	711.4	ng	87.9 ng	12.4 %	
	Mass of the explosive (k = 2)				175.8 ng	24.7 %	

Summary

- IMS is a useful method for explosive trace detection as well as narcotics detection and supports primary screening results of suspicious objects / potential threats within the staged detection process before an air plane takes off
- Method to determine measurement uncertainty for ETD on the basis of Boolean results
- $POD_{0.9}$: direct deposit $<$ swab sampling
- Expression of measurement uncertainty on binary results (up to 48 h after deposition at ambient conditions)
- Not all alarms mark a threat (*FP*-results, plausibility check of the air waybill content and x-ray pictures)