UNCERTAINTY ESTIMATION FOR PHOSPHORUS DETERMINATION IN STANDARD AND WASTEWATER SLUDGE SAMPLES

Camelia DRAGHICI[1], Cristina JELESCU[2], Carmen DIMA[2], Mihaela SICA[1]

[1]Transilvania University of Brasov, Chemistry Department, Brasov, Romania, c.draghici@unitbv.ro

[2]Compania Apa Brasov (Water Company), Wastewater Laboratory, Brasov, Romania

"Analytical methods for non-wood raw materials and their products and processes", COST FP0901 meeting, Hamburg, August 19-21, 2010

Wastewater treated sludge

- is a non-wood waste materials
- contains valuable nutrients: N and P in inorganic and organic compounds
- possible valorisation as fertiliser for agricultural purpose

- consequently, the quality control of the wastewater sludge production is of great interest for any wastewater treatment plant laboratory

Study aim and objectives

- **Study aim**
  - **analytical methods validation and uncertainty estimation** for the measurement of total phosphorus (P_t)
- **Objectives**
  - **methods validation** for P_t determination in standard solutions
  - **uncertainty estimation** associated to the P_t in standard solutions
  - **uncertainty estimation** associated to the P_t in wastewaters treated sludge samples

NEW and not yet imposed by Romanian legislation

Why validation and uncertainty estimation?

- We need
  - trustful and reliable results
    - not only sensitive methods (equipment)
    - but transparent results (trust interval)
      - C = 11.002 ± 0.1655 (mg/L)
  - trustful and transparent laboratories
    - **R = C ± U**

Validation procedure

- Concentration domain (linearity)
- Limit of detection (LOD)
- Limita of quantitation (LOQ)
- Precision
  - repeatability
  - intermediate precision
- Accuracy – recovery test
- Robusness – against an influencing parameter

$$x_{LOQ} = \bar{x}_{blank} + 6 \cdot s_{blank}$$

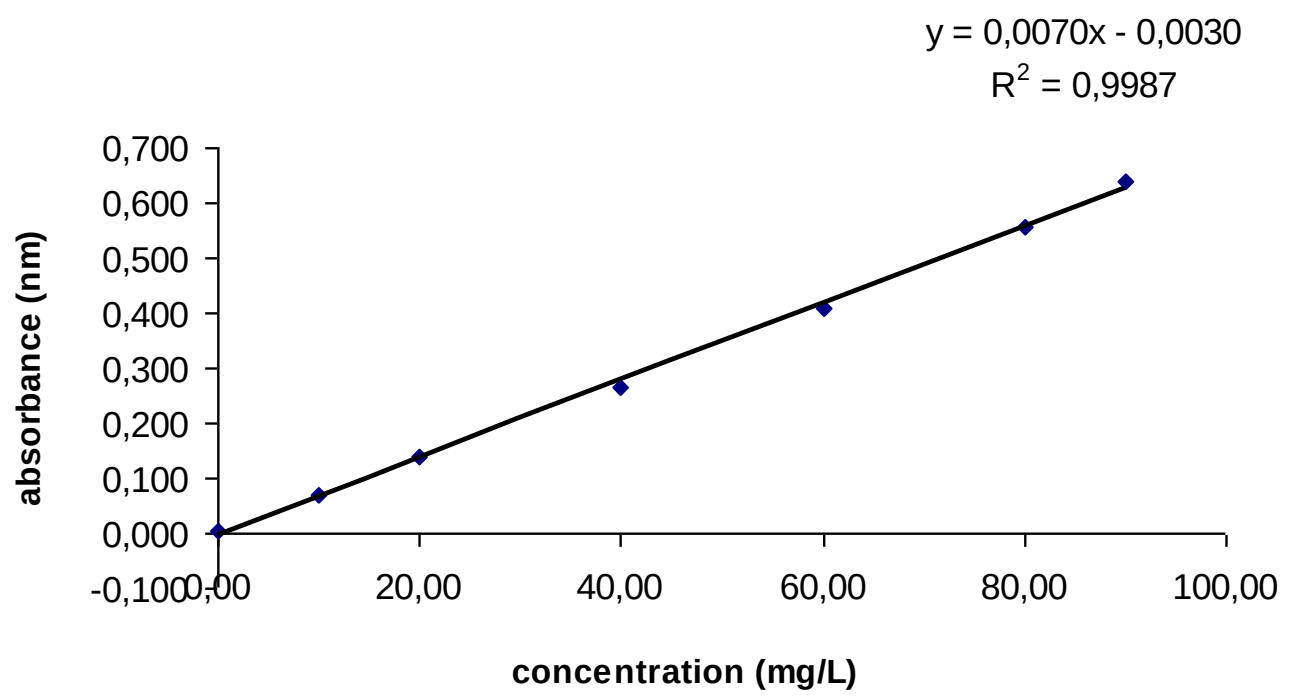
$$x_{LOD} = \bar{x}_{blank} + 3 \cdot s_{blank}$$

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}} \qquad s_x = \frac{s}{\sqrt{n}}$$

$$RSD\% = \frac{s}{\bar{x}} \cdot 100 \qquad \bar{x} \pm t \cdot s_x$$

$$R\% = \frac{CF - CU}{CA} 100$$

Concentration domain, LOD, LOQ



LOD	**1.05 mg/L**
LOQ	**1.74 mg/L**

The method is sensitive

The method is linear on the 10-90 mg/L concentration domain

Precision – by repeatability and intermediate precision

$[P_t]_{theor}$ (mg/L)	Precision	n	Average conc. (mg/L)	RSD (%)	S_x	Tolerance (t=2)	
						real conc.	trust interval
11	repeatability (RSD_r)	5	11.002	**2.3784**	0.0827	**11.002 ±**	**0.1655**
11	interim precision (RSD_{ip})	3x5	10.931	**2.6450**	0.0914	**10.931 ±**	**0.1829**

- $RSD_r < RSD_{ip}$
- The method is precise

Accuracy – by recovery test

Volume (mL)	Initial conc. (CU) (mg/L)	Added conc. (CA) (mg/L)	Final conc. (CF) (mg/L)	Recovery (R%)
2	10	10	20.50	**104.97**
4	10	20	30.34	**103.43**
8	10	40	50.35	**103.53**

- Requirements: 85% < R% < 105%
- The method is accurate

Robusness

$V_{ac\ 10\%}$ (mL)	$[Pt]_{theor}$ (mg/L)	$[Pt]_{real}$ (mg/L)	Colour
0	**11**	**12.58**	**blue-grey**
8	11	11.30	blue
16	**11**	**2.08**	**incolor**

- Robustness relative to the volume of the acidic solution (10%) used for the complex formation (8 mL is the volume required by the standard)
- The method is not robust against the volume of the acidic solution

Uncertainty estimation steps

1. Uncertainty sources identification

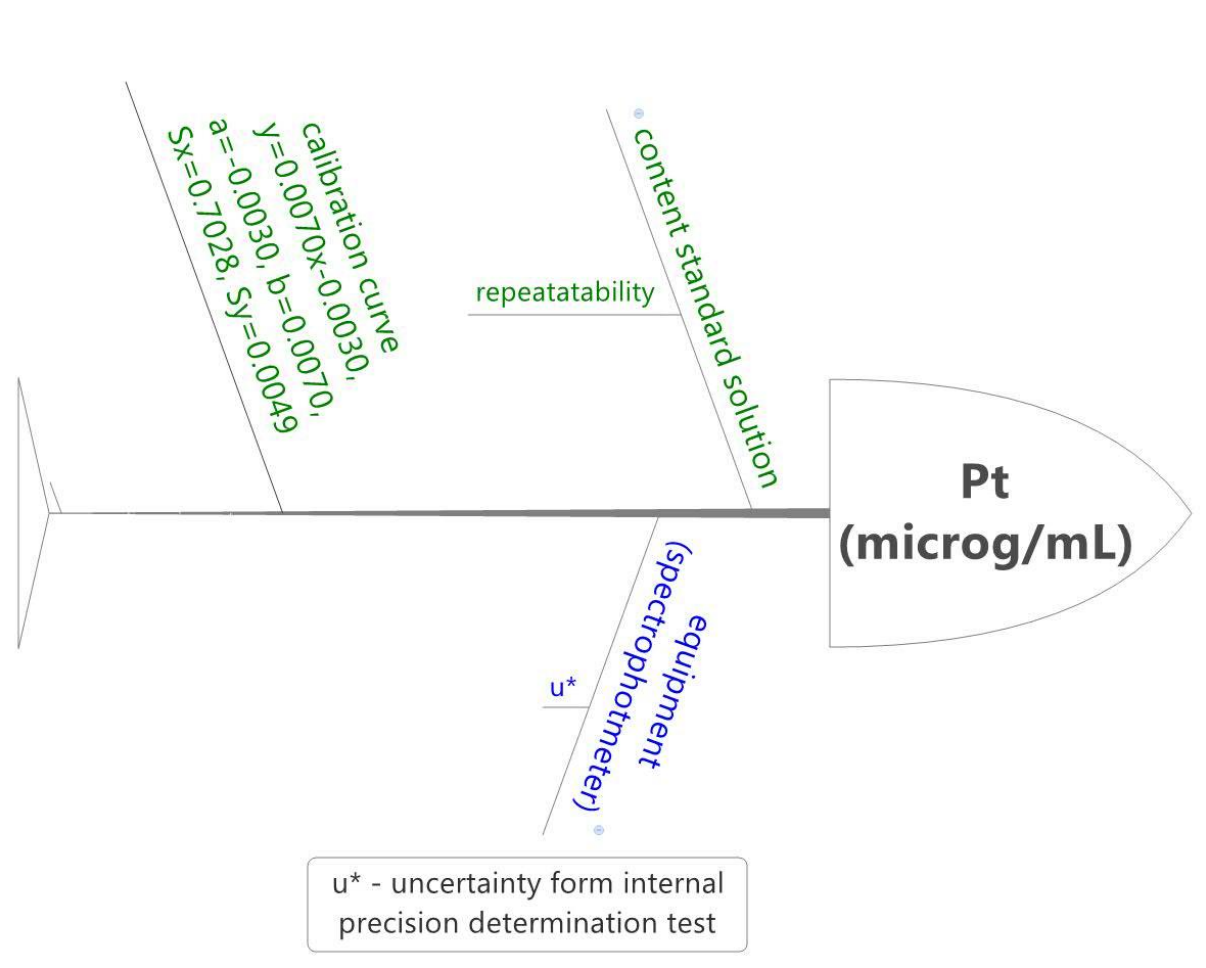
- Ishikawa diagrams

2. Different uncertainty types calculation

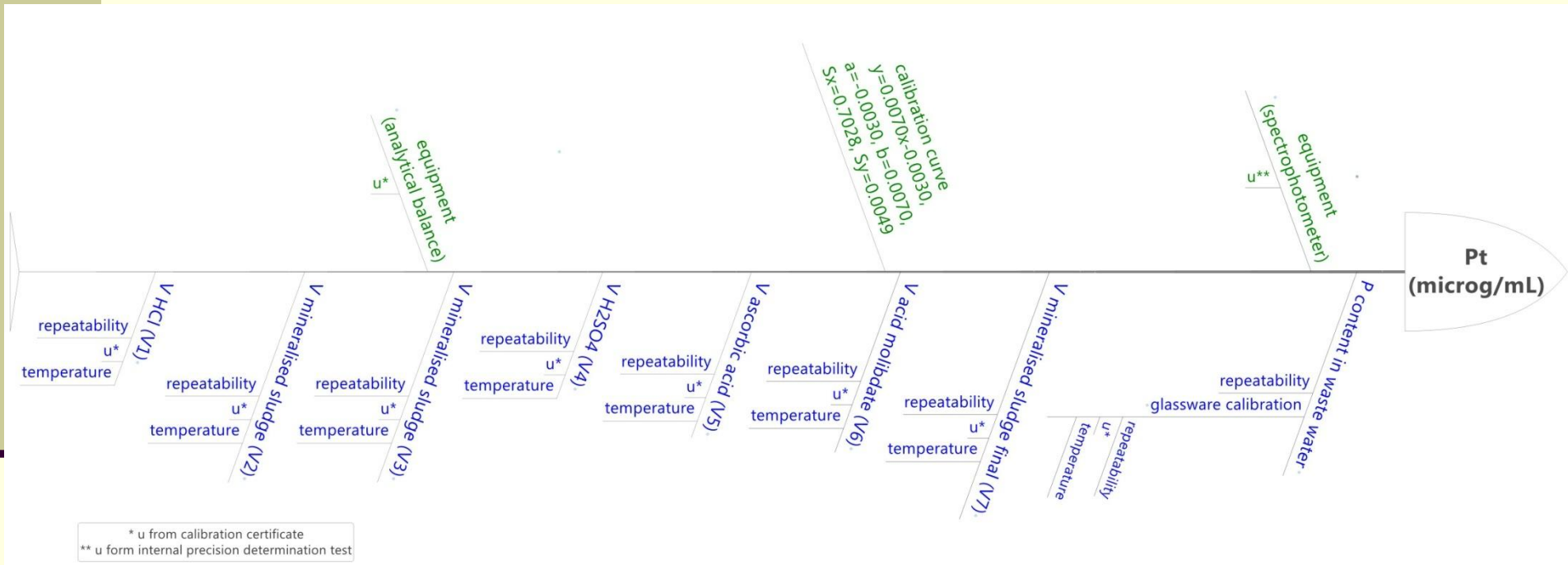
- standard uncertainty (u_x)
- relative standard uncertainty (u_r)
- combined relative standard uncertainty (u_c)
- extended standard uncertainty (U)

3. Result announcement: $R = C \pm U$

Ishikawa diagram for the standard solution



Ishikawa diagram for the wastewater treated sludge sample



"Analytical methods for non-wood raw materials and their products and processes", COST FP0901 meeting, Hamburg, August 19-21, 2010

Uncertainty types calculation

1. **standard uncertainty (u_x)**

$$u_x = \sqrt{\frac{\sum_{i=1}^{n}\left(x_i - \bar{x}\right)^2}{n-1}}$$

2. **relative standard uncertainty (u_r)**

$$u_r = \frac{u_x}{x}$$

3. **combined relative standard uncertainty (u_c)**

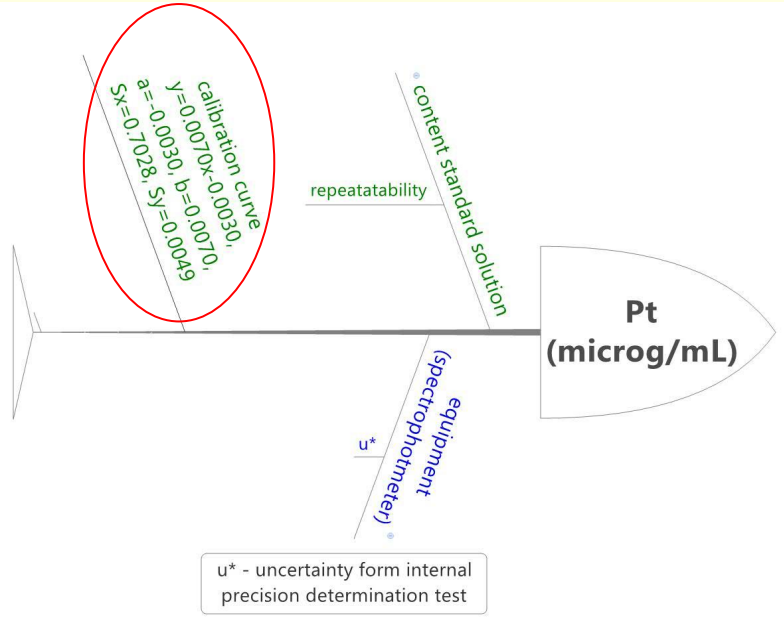
$$u_c = \sqrt{\sum u_r^2}$$

4. **extended standard uncertainty (U)**

(k=2, P=95%)

$$U = u_c \cdot k \cdot 100$$

U estimation of P_t determined in standard solution

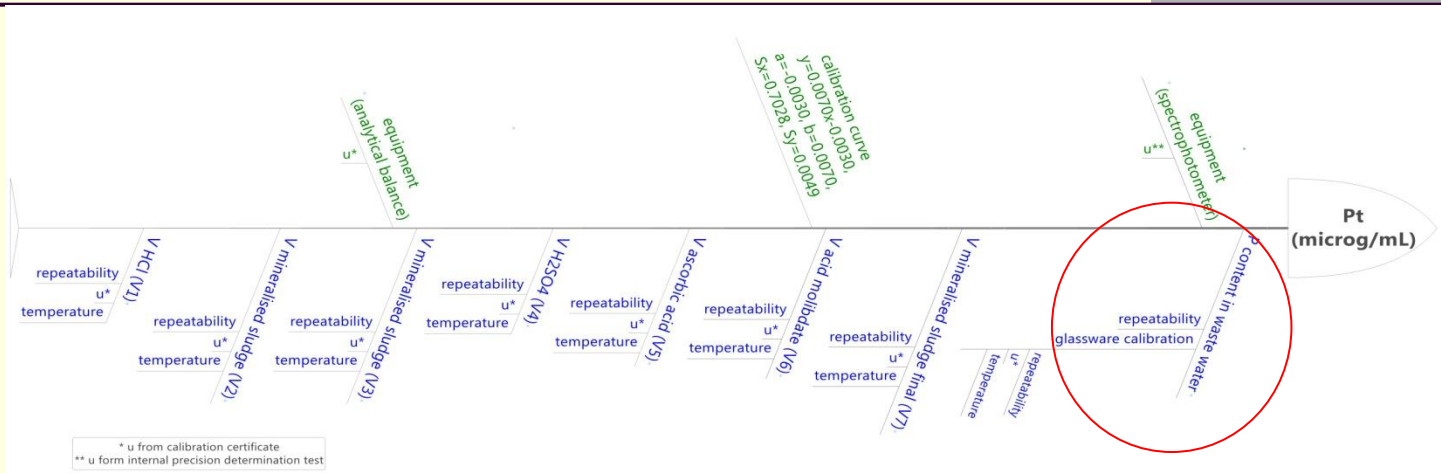


U source	x [P_t] (mg/L)	u_x	u_r
Repeatability (n=5)	11.00	0.26	0.02
Calibration curve	11.00	**0.70**	**0.06**
Equipment	11.00	0.04	0,0006

u_c	U (mg/L)	U (%)	Result
0.75	1.5	**13.6**	**11 ± 1.5 (mg/L)**

The higher contribution to the U is given by the calibration curve

U estimation of P_t determined in the wastewater treated sludge



U source	analytical balance	repeata-bility (n=3)	V1	V2	V3	V4	V5	V6	V7	Calib. curve	Specto-photom.
x	200 mg	65.85 mg/L	25 mL	100 mL	5 mL	8 mL	1 mL	2 mL	100 mL	65.85 mg/L	65.85 mg/L
u_x	0.2	**9.4373**	0.0437	0.1488	0.0074	0.0154	0.0074	0.0074	0.1488	0.7028	0.0409
u_r	0.0010	**0.1433**	0.0017	0.0015	0.0015	0.0019	0.0074	0.0037	0.0015	0.0107	0.0006

u_c	U (mg/L)	U (%)	Result
9.4824	18.96	**28.80**	**65.85 ± 18.96 (mg/L)**

1.5 < 18.96 (mg/L); **13.6 < 28.80 (%)**

$U_{standard} < U_{wastewater\ sludge}$

The higher contribution to the U is given by the repeatability

"Analytical methods for non-wood raw materials and their products and processes", COST FP0901 meeting, Hamburg, August 19-21, 2010

Conclusions

1. **The method was validated** for the concentration interval required by the Romanian standard
   - linear, sensitive, precise, accurate
   - not robust (relative to the acidic solution concentration)

2. **The uncertainty was estimated** for the P_t determination from standard solution and from wastewater treated sludge samples
   - $\mathbf{U_{standard} < U_{wastewater\ sludge}}$

3. **Further work** will be done for the U estimation
   - **calibration curve –** new equipment
   - **repeatability –** analize more samples, in order to control RSD%
   - **U estimation –** different wastewater sludge samples (untreated and treated)
   - **U estimation –** wastewater samples (untreated and treated)
     - **expected:** $\mathbf{U_{standard} < U_{wastewater} < U_{wastewater\ sludge}}$