UNCERTAINTY ESTIMATION OF PHENOLIC COMPOUNDS DETERMINATION IN STANDARD SOLUTIONS

Camelia Draghici[1], Carmen Dima[2], Cristina Jelescu[2], Gheorghe Coman[1], Lucia Dumitrescu[1], Mihaela Sica[1], Ileana Manciulea[1]

[1]Transilvania University of Brasov, Romania

[2]Apa Company, Brasov, Romania

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Analytical techniques for phenolic compounds determination

Technique	Compounds	Matrix	LOD (µg/L)	Ref.
UV-VIS Spectrometry	substituted phenols	tap water , suface water, wastewater	> 1	[1]
LC	chlorinated and nitro- fenols	tap water	0.01 – 0.1	[2]
		suface water	0.1 – 1.0	
GS-FID	chlorinated phenols	suface and waste waters	0.14 – 16	[2] [3]
		soil, sludge	0.15 – 0.71	
CE	chlorinated phenols	wastewater	0.1 – 1.0	[4] [5]
HPLC-UV	phenols, aliphatic and aromatic acids, aldehides	degradation products in biomass hydrolisates	0.002 – 17	[6]

Study aim and objectives

- **Study aim**
  - **performances evaluation** of a wastewater treatment laboratory, for the phenols content control
- **Objectives**
  1. **method validation** procedure development
  2. **uncertainty estimation** associated to the phenolic compounds determination in standard solutions

NEW and not yet imposed by Romanian legislation

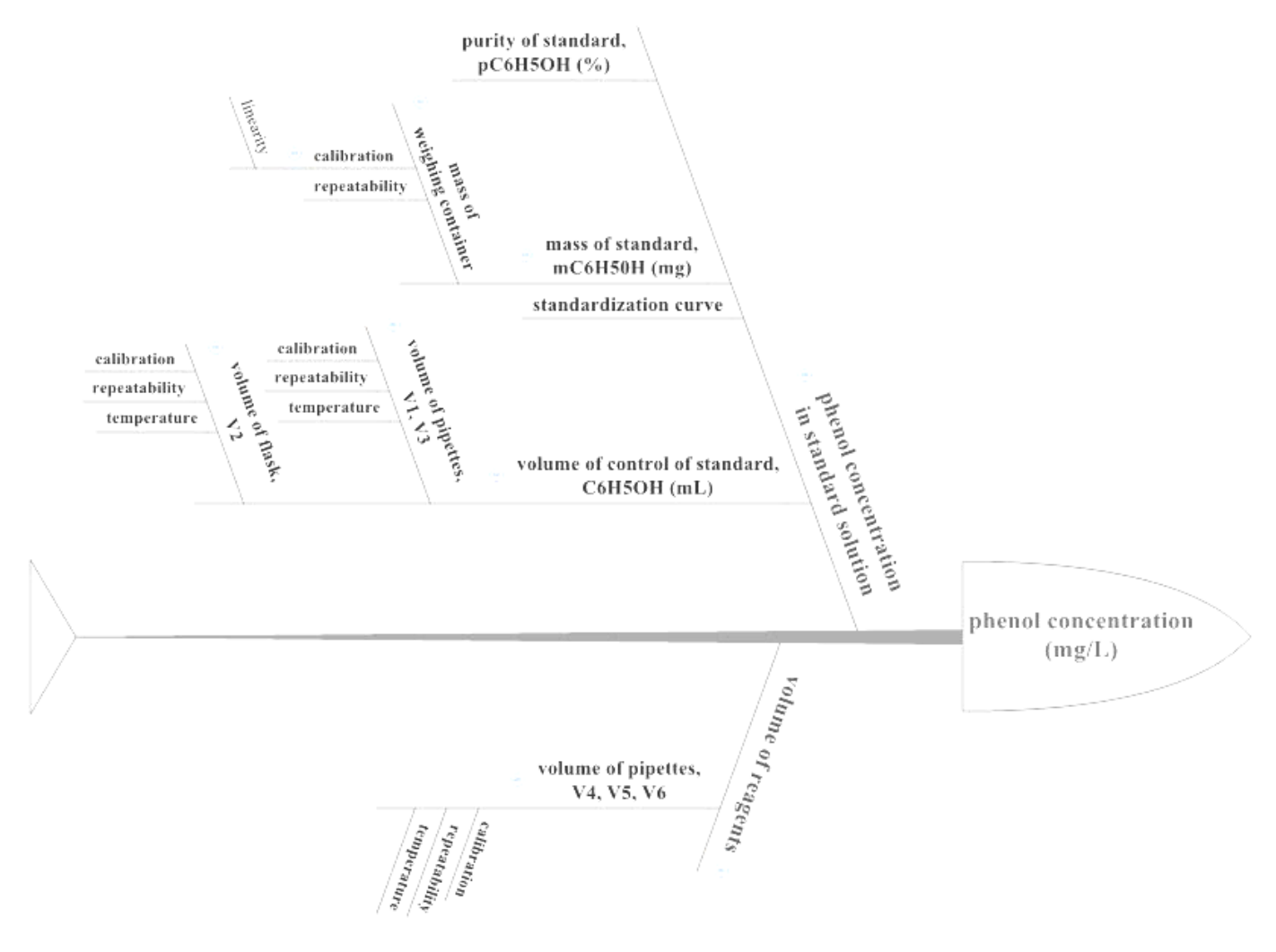
Validation procedure

- Selectivity – different interfering compounds
- Concentration domain
- Precision
  - repeatability
  - intermediate precision
- Accuracy – recovery test
- Limit of detection (LOD)
- Limita of quantitation (LOQ)
- Robusness – different influecing parametres

Uncertainty estimation working steps

- **Uncertainty sources identification**
  - Ishikawa diagram
- **Different uncertainty types calculation**
  - standard uncertainty (u_x)
  - relative standard uncertainty (u_x/x)
  - combined relative standard uncertainty (u_c)
  - extended standard uncertainty (U)
- Result announcement as: $R = C \pm U$

Uncertainty sources identification Ishikawa diagram



Uncertainty types calculation

1. standard uncertainty (u_x)

$$u_{(y(x1,x2,...))} = \sqrt{\sum_{i=1,n} u(y,x_i)^2}$$

2. combined relative standard uncertainty (u_c)

$$\frac{u_{C_{fenol}}}{C_{fenol}} = \sqrt{\left(\frac{u_{P_{fenol}}}{P_{fenol}}\right)^2 + \left(\frac{u_{m_{fenol}}}{m_{fenol}}\right)^2 + s^2 + \left(\frac{u_{V_1}}{V_1}\right)^2 + \left(\frac{u_{V_2}}{V_2}\right)^2 + \left(\frac{u_{V_3}}{V_3}\right)^2 + \left(\frac{u_{V_4}}{V_4}\right)^2 + \left(\frac{u_{V_5}}{V_5}\right)^2 + \left(\frac{u_{V_6}}{V_6}\right)}$$

3. extended standard uncertainty (U) (k=2, P=95 %)

$$U_{(y(x1,x2...))} = u_c \cdot k$$

Uncertainty estimation for standard solution

Symbol	Uncertainty sourse	Value (x)	Standard uncertainty (u_x)	Relative standard uncertainty (u_x/x)
P_{phenol}	phenol purity (%)	99	0.0058	0.00006
m_{phenol}	phenol mass (g)	1	0.008	0.008
y=bx+a	calibration curve	-	0.002	-
V_1	standard volume (control) – pipette (mL)	5	0.006	0.0012
V_2	standard volume (control) – flask (mL)	250	0.136	0.00054
V_3	standard volume (control) – flask (mL)	100	0.06	0.0006
V_4	buffer solution volume – pipette (mL)	5	0.006	0.0012
V_5	volume of colouring agent – pipette (mL)	2	0.004	0.002
V_6	volum de hexacianoferat – pipette (mL)	2	0.004	0.002
Statistic parametre		**Calculated value**		
Combined relative standard uncertainty, $\mathbf{u_c}$ (mg/L)		0,.018		
Extended standard uncertainty, **U** pt k=2, P=95 %) (mg/L)		0.0036		

Phenol concentration in standard solution is: 0.2 ± 0.0036 mg/L

Conclusions

- **The method was validated for the concentration interval required by the Romanian standard**
  - **it is selective, linear, precise, accurate, sensiteive robust (relative to pH)**
- **The uncertainty was estimated for the phenol and phenolic compounds determination from phenol standard solution**
- **The laboratory can deliver reliable results and ensures quality for the phenolic compounds determination in the municipal wastewaters**

References

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Possible contribution to COST PF0901 project

- HPLC-DAD determination of biomass secondary products – WG1
  - aliphatic and aromatic acids
  - aldehides
  - phenols

- Metrological approach
  - method validation
  - uncertainty estimation
  - comparative methods and/or laboratory testing
    - PT – proficiency testing
    - ILC – interlaboratory comparisons

Certainty we wait for you to Brasov!