



Laboratoire national de métrologie et d'essais





EURAMET 924

Part 2

Fortified surface water

Guillaume Labarraque
Paola Fiscaro

guillaume.labarraque@lne.fr
paola.fiscaro@lne.fr

Preliminary tests (1)

Surface water sample treatment:

- ❖ 2 l provided by Bipea* filtered at 0,45 μm , acidified with 2 % HNO_3 then divided 2 x 1 l for Cd, Ni, Pb and for Hg (stabilized with BrCl)
- ❖ Semi quantitative analysis to estimate the “natural” contents
- ❖ Fortifying to reach the required levels
Cd # 0,6 $\mu\text{g/l}$ – Hg # 0,5 $\mu\text{g/l}$ – Ni # 40 $\mu\text{g/l}$ – Pb # 20 $\mu\text{g/l}$
- ❖ Bottling

* Bipea a French PT provider

Preliminary tests (2)

LNE followed the same protocol than BAM:

Bottle cleaning protocol:

- **PFA Bottles (for Cd, Ni, Pb)** - rinsed 3 times with high pure water, filled with 2 % HNO_3 during 24 h, and dried
- **Translucent glass (for Hg)** - same protocol but filled with 2 % HNO_3 + 0,5 % BrCl during 24 h

Preliminary tests (3)

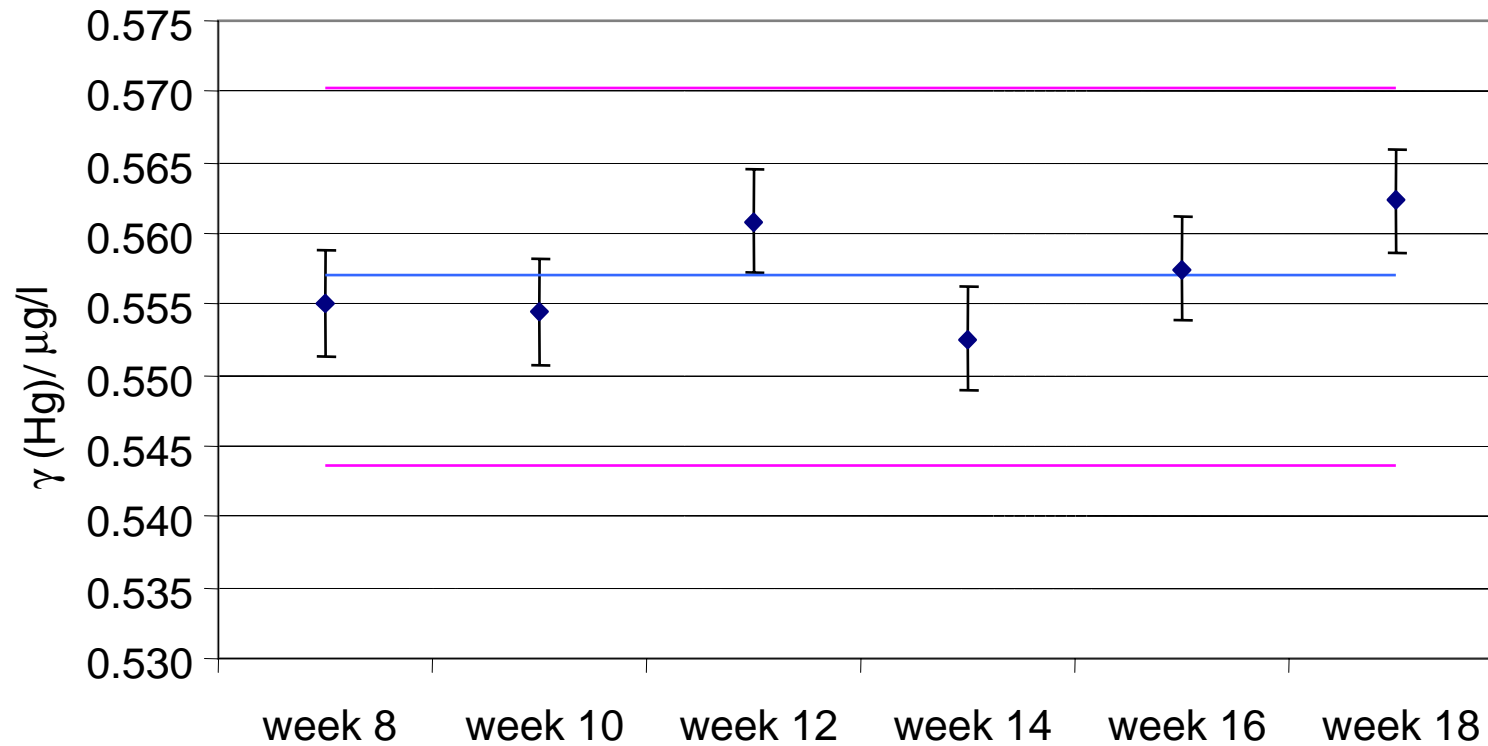
Stability test:

- Performed during 3 months on 10 PFA and 10 glass bottles filled with the fortified surface water
- One ID-ICP/MS analysis is performed every 15 days on each element and each bottle (direct analysis of Hg without cold vapour)
- Results of ANOVA : no bottle effect and stability during time
- Reproducibility on means $UR = 2SR$

UR = 2 % for Hg, Ni, Pb and 5 % for Cd

Preliminary tests (4)

Stability test for Hg



Preliminary tests (5)

Releasing test :

- 5 PFA and 5 glass bottles filled with blank reagents analysed during 3 months for Cd, Hg, Ni, Pb and compared each time to fresh blanks :
- No real effect detected
- Hg analysis done directly without cold vapour (LQ # 30 ng/l)

Surface water sample

- Bipea provided 20 l of surface water.
- The protocol is the same than the one followed for preliminary test sample.
- Two secondary batches of 10 l were prepared: one for Cd, Ni and Pb and the other for Hg

Unfortified surface water (Cd, Ni, Pb)

As decided at the launch of the project, no gravimetric reference values will be provided for Cd, Ni and Pb. So their “natural” contents in the water sample had been only estimated:

Cd: 0,3 – 0,4 µg/l,

Pb: 4 – 5 µg/l,

Ni: 1 – 2 µg/l

Fortified surface water (Cd, Ni, Pb)

Amounts added in the surface water :

Cd 0,405 µg/l – Ni 38,319 µg/l – Pb 19,754 µg/l

- ✓ The deadline for the comparison part 2 was postponed
→ LNE had studied the stability over an additional period of 2 months (2 ID analysis for each element on 2 bottles every 15 days)
- ✓ The results lie within the stability observed during the preliminary tests (target value = value provided by LNE for the comparison part 2)

Unfortified surface water (Hg)

For Hg a gravimetric reference value is attempted

- From the secondary batch of 10 l stabilized with BrCl, the residual content of Hg is analysed by ID-ICP/MS (cold vapour)

Hg = 12 ng/l and 8 ng/l (06/2007)

- 10 glass bottles are filled with the surface water before fortifying. 3 bottles were sent to BAM, 1 to PTB and 1 to NRC and analysed by AFS (BAM) and CVAAS (NRC)

Unfortified surface water (Hg)/2

Results BAM : bottle n° 3 Hg = 12 ng/l (n=6) (10/2007)

bottle n° 4 Hg = 34 ng/l (n=7)

bottle n° 5 Hg = 12 ng/l (n=3)

Results NRC : bottle n° 1 Hg = 39 ng/l (11/ 2007)

Results PTB : bottle n°2 Hg = ?

Unfortified surface water (Hg)/3

LNE analysed the last 5 bottles by ID-ICP/MS (cold vapour)

bottle n°6 Hg = 13 ng/l (n=1) (02/2008)

bottle n°7 Hg = 5 ng/l (n=1)

bottle n°8 Hg = 11 ng/l (n=1)

bottle n° 9 Hg = 8 ng/l (n=1)

bottle n° 10 Hg = 5 ng/l (n=1)

Bottle n°7 has been sent to BAM → 10 ng/l

Unfortified surface water (Hg)

LNE has tested possible contamination from the bottle and/or cap:

One bottle has been agitated overnight upside-down

→ bottle n° 9 Hg = 11 ng/l (n=1)

Fortified surface water (Hg)

Quantity added in the natural sample:

$$\text{Hg}_{\text{grav}} = 0,554 \mu\text{g}$$

$$\text{Hg}_{\text{tot}} = \text{Hg}_{\text{grav}} + \text{Hg}_{\text{res}}$$

$$u(\text{Hg}_{\text{tot}}) = \sqrt{u_{\text{grav}}^2 + u_{\text{stab}}^2 + u_{\text{res}}^2}$$

$$u_{\text{grav}} = 0,0058 \mu\text{g/l}$$

$$u_{\text{stab}} = 0,0067 \mu\text{g/l}$$

$$u_{\text{res}} = ?$$

Fortified surface water (Hg)

- ✓ The deadline for the comparison part 2 was postponed
→ LNE had studied the stability over an additional period of 2 months (2 ID analysis without cold vapour on 2 bottles every 15 days)
- ✓ The results stay within the 2 % stability observed during the preliminary tests (target value = value provided by LNE for the comparison part 2)