INSTITUT CARNOT Icéel

Botanickel
By Aperam & Econick

GDR Promethée

Routine use of HDXRF spectrometry for hydrometallurgy

Baptiste LAUBIE[1,2], Thomas MONOT[1], Clémence PINCHAUX[1,2], Marie-Odile SIMONNOT[1]
[1]Université de Lorraine, CNRS, LRGP, Nancy
[2]Econick, Lunéville

June 5 2025

econick

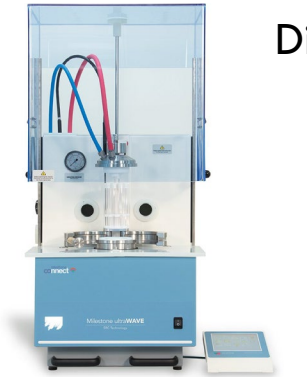
LRGP LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

UNIVERSITÉ DE LORRAINE

cnrs

Context

Analytical procedure for elemental analysis



Digestion

→ ICP

ICP disadvantages

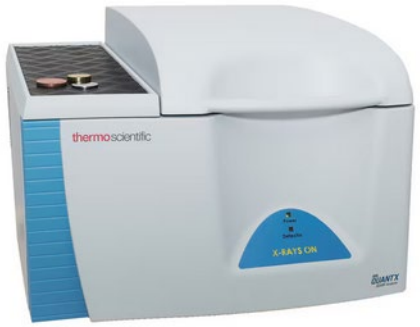
- *Related to the investment*
- *Related to the operation and to the maintenance*: Ar, torch *etc.*
- *Related to the method*: sample destruction, calibration, nebulization (matrix effect, solid, speciation, elemental ratios *etc.*)

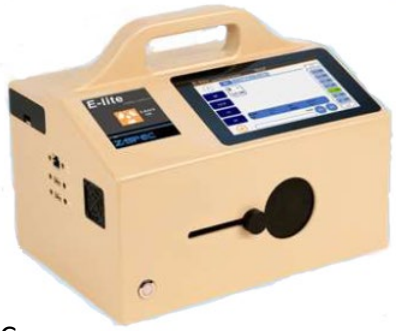
⇨ Money and time consuming

Is there any alternative without losing analysis quality?

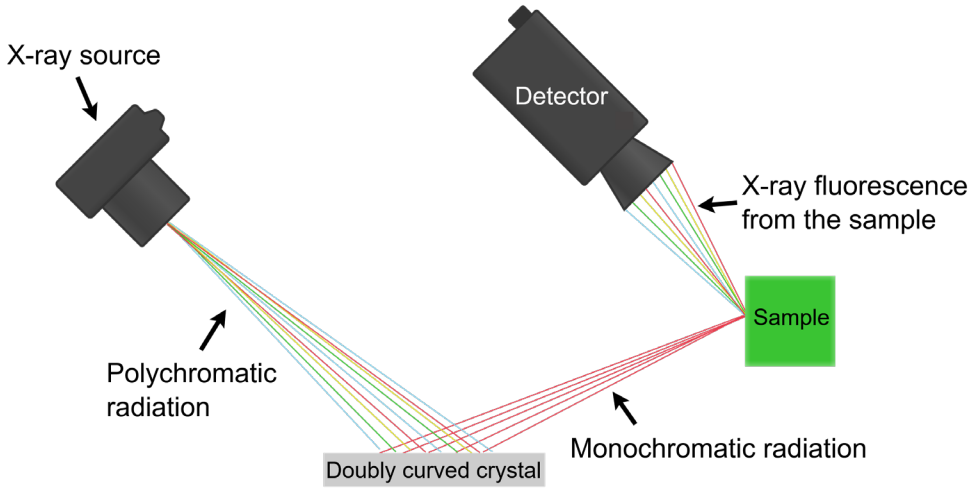
Context

Development of benchtop ED-XRF
HD-XRF
M-XRF





Z-SPEC



HDXRF avantages

- *Related to the investment*
- *Related to the operation and to the maintenance*: portable, few consumables, no need of protection officer
- *Related to the method*: for solids and liquids, no sample destruction, no calibration, no dilution, response in less than one minute

⇨ Can this type of device be used routinely in the case of hydrometallurgical solutions?

Methodology

Study of the device's response for an ICP multi-element standard (0.1 to 1000 ppm)

↓

Assessment of limits of detection and of quantification

↓

Study of the device's response for Ni up to 10 000 ppm

↓

Study of the effect of several ratios Ni/other elements

↓

Study of the effect of an organic matter rich matrix

Real sample

ICP standard

Element	Concentration (ppm)
Al	1000
Ca	1000
Cd	1000
Co	1000
Cr	1000
Cu	1000
Fe	1000
K	1000
Mg	1001
Mn	1000
Na	1000
Ni	1001
P	1000
Pb	1000
S	1000
Zn	1000

- Triplicates
- Calibration method: Water
- Time: 30 s

LRGP LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

Agromining

Metal-farming - Nickel

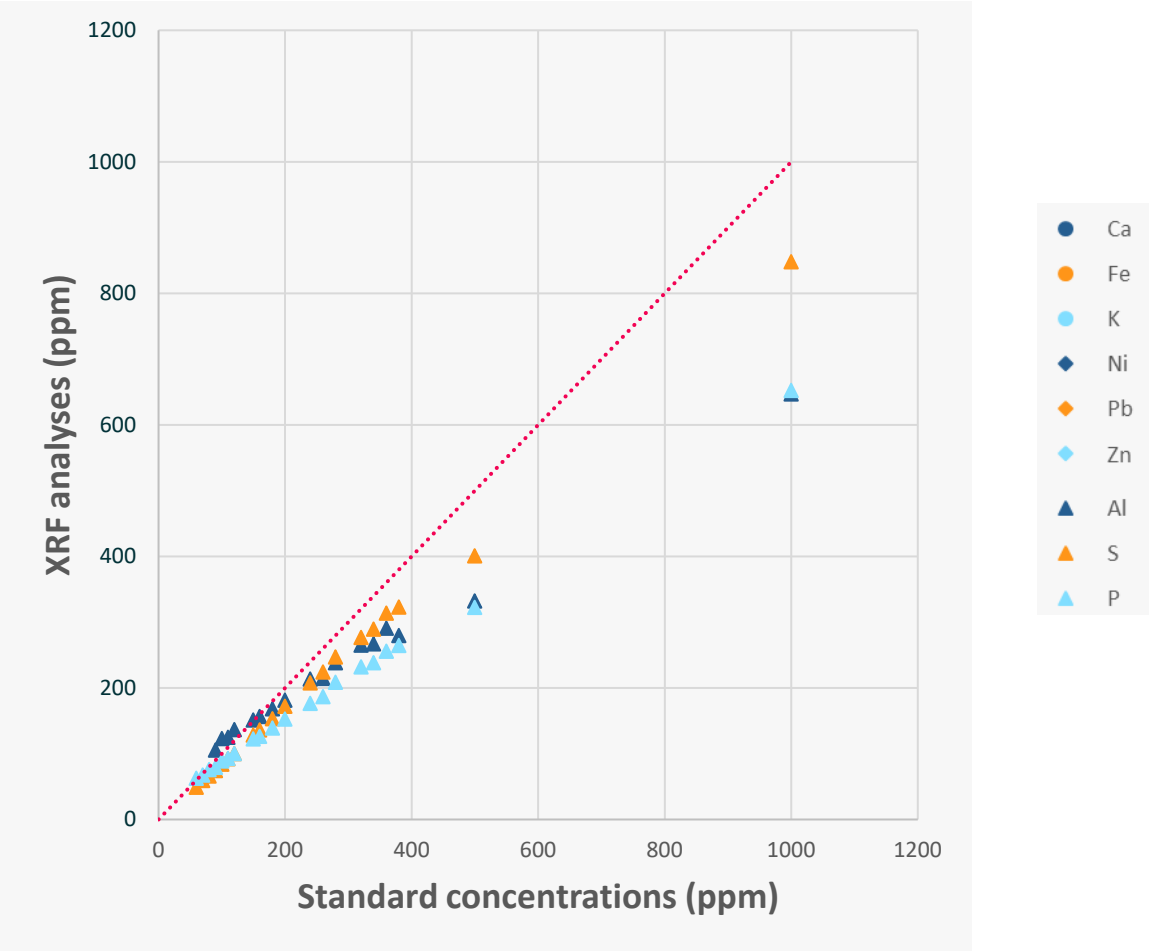
In Europe

In subtropical areas

In practice

Results

ICP multi-element standard

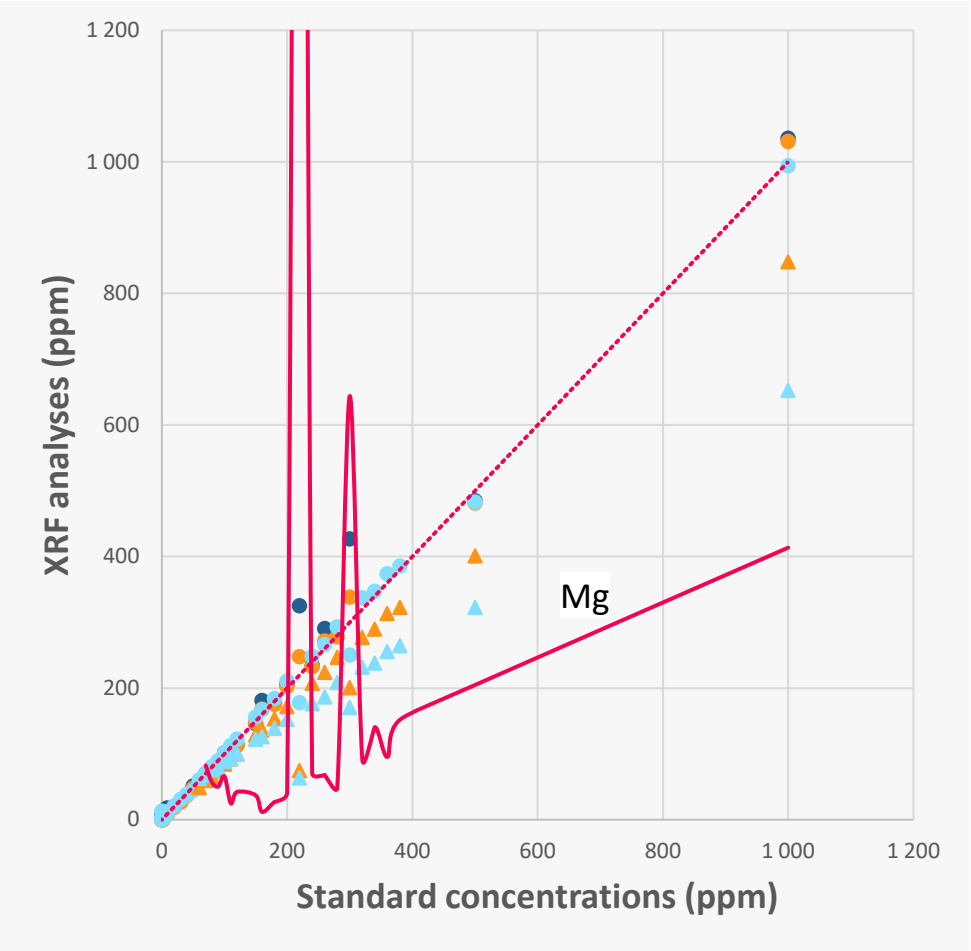


⇨ Ca, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, Zn
linear response and slope ~ 1

⇨ Al, S, P
linear response, but slope << 1
Al: 42%, S: 16%, P: 38%

Results

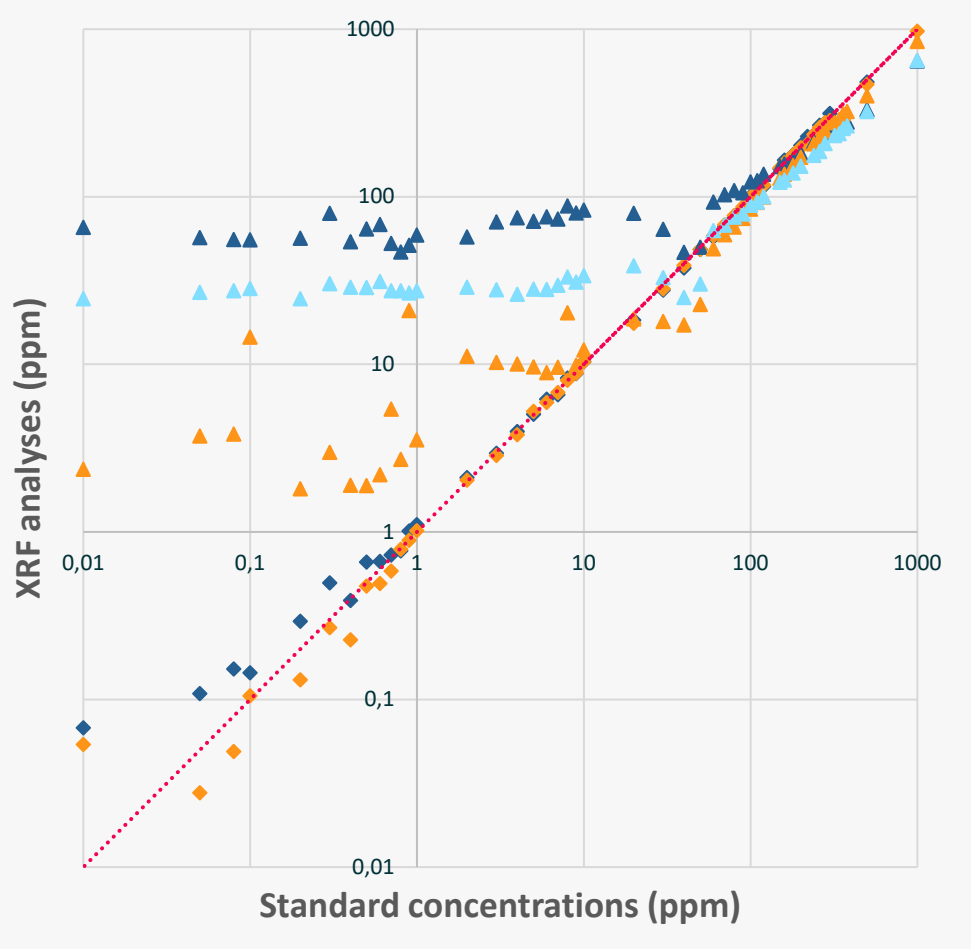
ICP multi-element standard



⇨ Aberrant responses
⇨ Linked to Mg

Results

Limits of detection/quantification



$$LOD^* = \frac{3.3\sigma}{S} \qquad LOQ^* = \frac{10\sigma}{S}$$

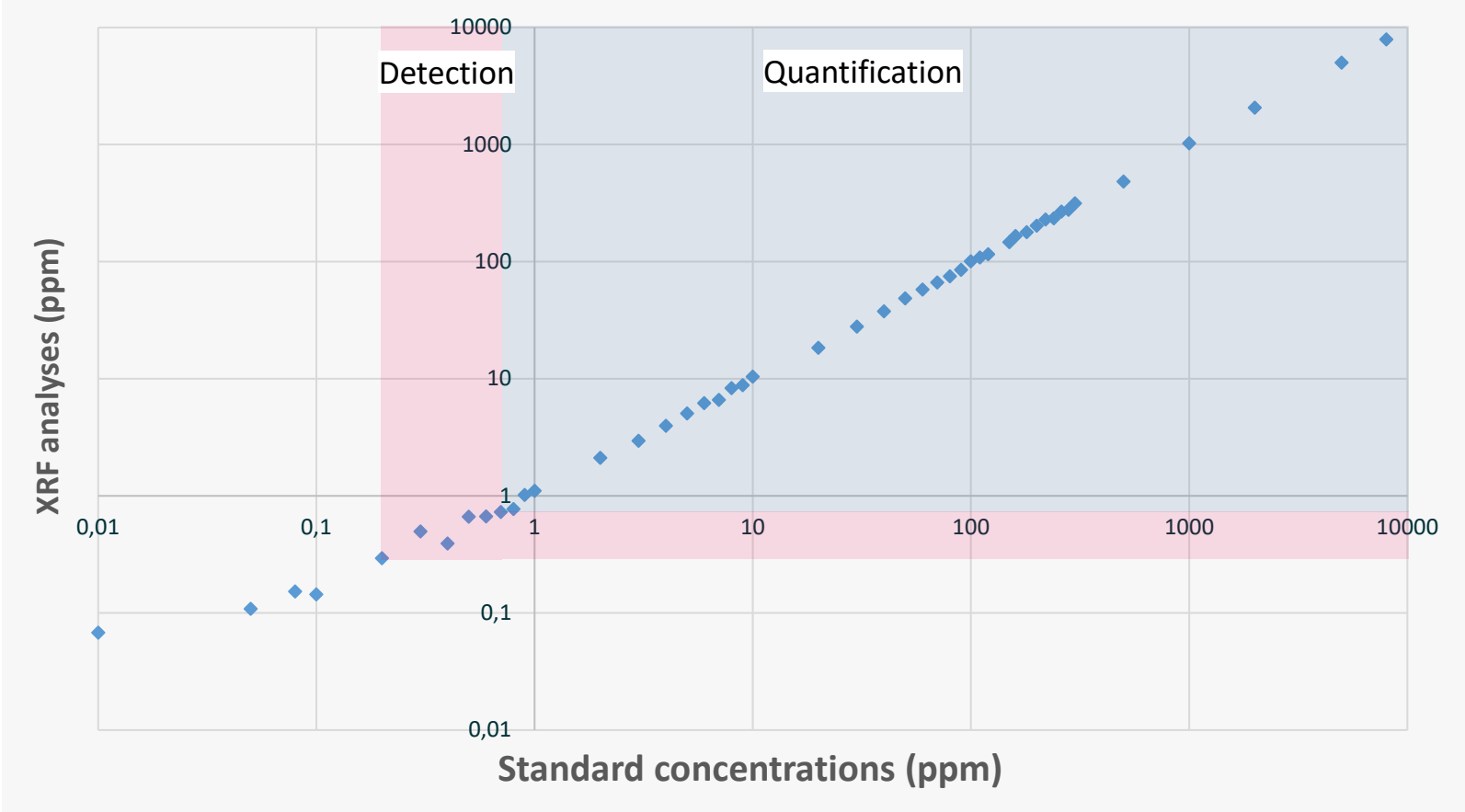
S: slope; σ: linear regression residues

**ICH Harmonised tripartite guideline - Validation of analytical procedures: test and methodology Q2(R1), 2005*

JP500		
Pb	LOD	~0.2 ppm
	LOQ	~1 ppm
Mn	LOD	~0.5 ppm
	LOQ	~1 ppm
Cr	LOD	~1 ppm
	LOQ	~3 ppm
Cu	LOD	~0.1 ppm
	LOQ	~0.3 ppm
Co	LOD	~0.3 ppm
	LOQ	~0.7 ppm
Fe	LOD	~1 ppm
	LOQ	~3 ppm
Ca	LOD	~7 ppm
	LOQ	~21 ppm
Ni	LOD	~0.2 ppm
	LOQ	~0.7 ppm
Zn	LOD	~0.3 ppm
	LOQ	~1 ppm

Elite		
Al	LOD	~70 ppm
	LOQ	~210 ppm
K	LOD	~1 ppm
	LOQ	~3 ppm
S	LOD	~40 ppm
	LOQ	~115 ppm
P	LOD	~50 ppm
	LOQ	~150ppm

Specific case: Ni



⇨ Quantification

0.7 to 10 000 ppm

⇨ Effect on Ni/other elements

No effect

Agromining samples

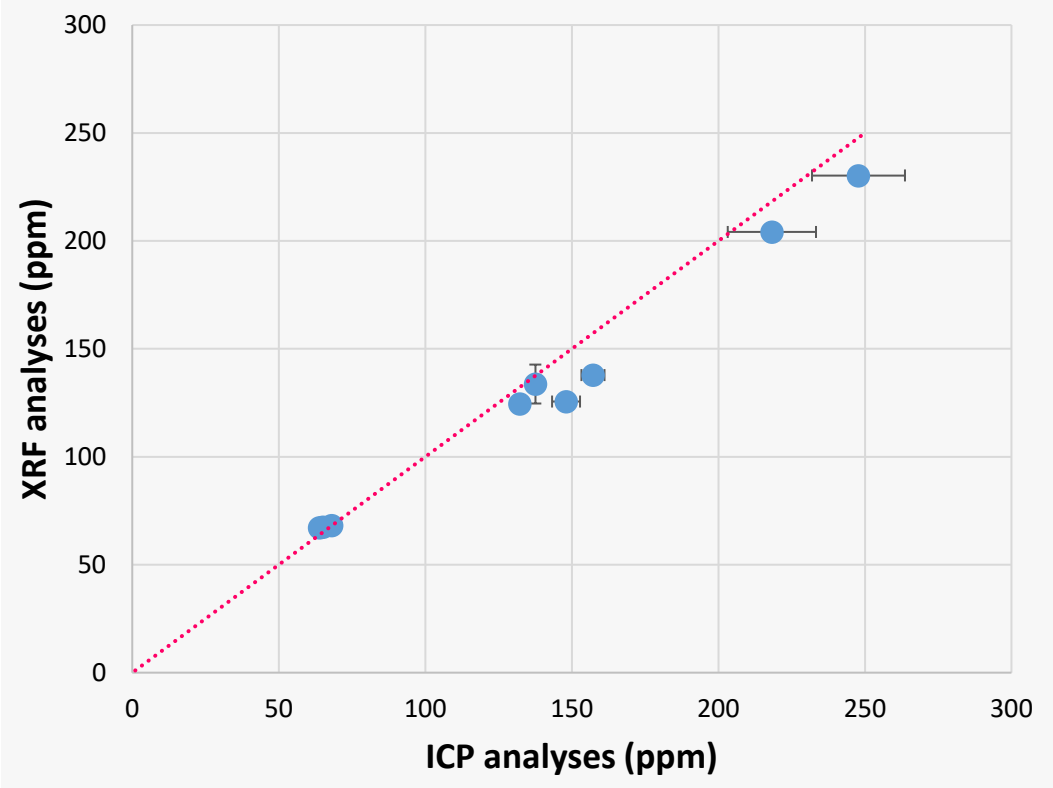
Characteristics

- Tropical hyperaccumulator ([Ni] ~ 2.5%)
- Water
- C_{org} ~ 5 g/L

- ICP-OES analyses: HNO_3 digestion + dilution
- XRF anlayses: direct measurement

⇨ **Validated method** for routine monitoring

Ni concentrations



Conclusions

⇨ Elemental analysis is a key point in hydrometallurgy

⇨ Importance of the quantification algorithm

Fixed values at low concentrations (impossibility to make blanks)

Sometimes, aberrant values

⇨ Excellent analytical responses for a lot of elements in solutions

Wide linearity range without calibration

No matrix effect detected

Real saving in time and money but need preliminary validation

LRGP LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

econick

LRGP LABORATOIRE RÉACTIONS ET GÉNIE DES PROCÉDÉS

UNIVERSITÉ DE LORRAINE

cnrs

GDR Groupement de recherche
Prométhée Prodécés hydrométallurgiques pour la gestion intégrée des ressources primaires et secondaires

Routine use of HDXRF spectrometry for hydrometallurgy

ChEAP : CHemical Elemental Analysis without Preparation

Thank you for your attention

baptiste.laubie@univ-lorraine.fr

INSTITUT CARNOT Icéel

Botanickel By Aperam & Econick