Study of accuracy profiles for different elements by ICP-AES and ICP-MS

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Context and purpose

The accuracy profile is a graphical representation of accuracy depending on the concentration, that is to say the variation of both the trueness (bias) and precision. This profile reflects the ability of the instrument to work with an accuracy tolerance in a concentration range given.

Accuracy profiles represent a possible statistical tool for the interpretation of validation studies.

The objective of this work was to examine the accuracy profile of different elements by ICP-AES and ICP-MS. This study is based on the use of reference materials and takes into account the internal repeatability and the inter-day reproducibility.

Theory of accuracy profile

Accuracy is the sum of the trueness expressed by a bias or a recovery yield and the precision expressed by a standard deviation modified by a coverage factor (or Mee factor). In our case of intralaboratory testing, precision correspond to the intermediate precision.

In practice : $\boxed{\text{accuracy} = \text{bias}^* \pm k_s.S_R}$ * or recovery yield % (= experimental value / reference value)

with k_s : coverage factor or Mee factor and S_R : standard deviation of intermediate precision

It is necessary to calculate S_R and k_s

- ❖ intraday repeatability : serie of determinations in the same day ⇨ standard deviation S_r
- ❖ interday reproducibility : day by day independent series ⇨ standard deviation S_L (1 serie = 1 day)

$$S_r^2 = \frac{SCE_{intraday}}{p(n-1)} \qquad S_L^2 = \frac{1}{n}\left(\frac{SCE_{interday}}{p-1} - S_r^2\right) \qquad S_R^2 = S_r^2 + S_L^2$$

☞ SCE : Sum of squares of deviations from an average,

☞ p : number of series (or days) and n : number of determinations by serie (or day).

$\boxed{k_s = t.C}$ t is the Student factor for a degree of freedom (ddl).

It is necessary to calculate C : $H = \frac{S_L^2}{S_r^2}$ $G^2 = \frac{H+1}{nH+1}$ $C = \left(1+\frac{1}{npG^2}\right)^{1/2}$

You have to know the degree of freedom, ddl = $\frac{(H+1)^2}{\frac{\left(H+\frac{1}{n}\right)^2}{p-1}+\frac{1-\frac{1}{n}}{np}}$

As ddl is not an integer, it is necessary to interpolate linearly t (in relation to Student's t distribution table)

Analysis by ICP-AES

Varian Vista Pro apparatus

Seaspray nebulizer, cyclonic chamber, axial view, CCD detector

Operating conditions :

Conditions d'utilisation pour: Toutes les raies	
Puissance (kW)	1,30
Débit Plasmagène (L/mn)	15,0
Débit auxiliaire (L/mn)	1,50
Pression Nébuliseur (kPa):	200
Temps lecture par réplique (s):	10,00
Délai Stabilisation Instr (s):	30
Paramètres d' introduction de l'échantillon	
Délai de prélèvement (s)	60
Vitesse de pompe (t/mn)	20
Temps de rinçage (s):	10
Pompage rapide (Introduction/rinçage)	
Rinçage optimisé	Rinçage optimisé
Paramètres généraux	
Répliques:	5

Analysis by ICP-MS

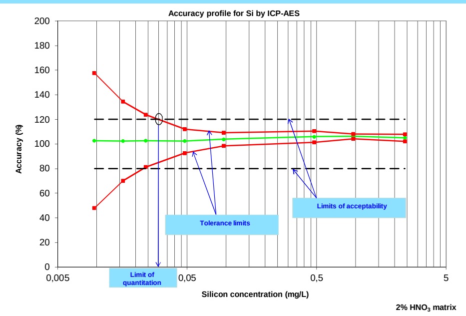
Varian 820 MS apparatus

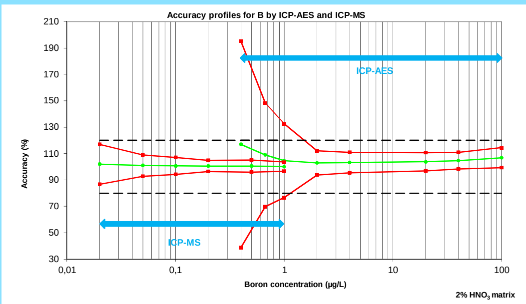
Micro-concentric nebulizer, scott spray chamber cooled to 3°C with Peltier effect , DDEM detector

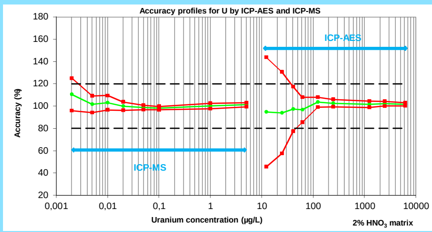
Operating conditions :

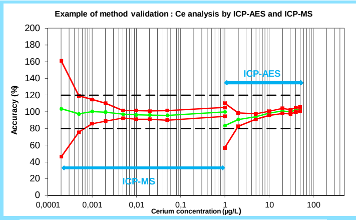
Parameter	Value
Flow Parameters (L/min)	
Plasma Flow	15,0
Auxiliary Flow	1,50
Sheath Gas	0,24
Nebulizer Flow	1,00
Torch Alignment (mm)	
Sampling Depth	6,5
Other	
RF Power (kW)	1,40
Pump Rate (rpm)	6
Stabilization delay (s)	60
Ion Optics (volts)	
First Extraction Lens	-1
Second Extraction Lens	-207
Third Extraction Lens	-252
Corner Lens	-205
Mirror Lens Left	48
Mirror Lens Right	38
Mirror Lens Bottom	32
Entrance Lens	0
Fringe Bias	-2,6
Entrance Plate	-35
Pole bias	0,0

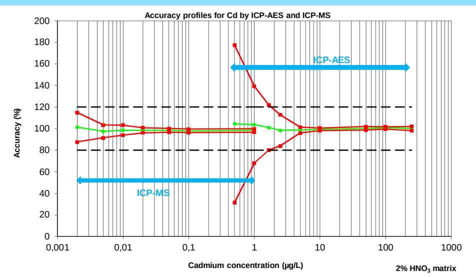
Results

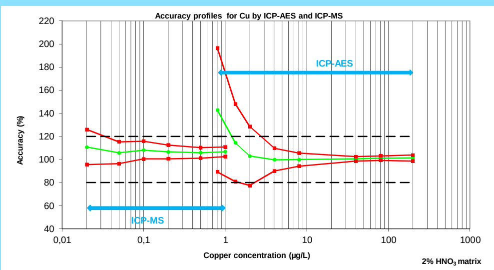


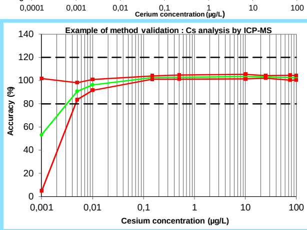












Conclusions

✓ This work enabled access to the limits of quantitation of various elements analysed and permited to evaluate the measurement uncertainties in the concentration range studied : important parameters within the context of method validation.

✓ A comparison of the results obtained by the two techniques has allowed to highlight the performance of each device, since the method of the accuracy profile enables to observe actually the capabilities of the instrument and of the method.

✓ Examples of results obtained in the method validation framework for different analytical programs were used to illustrate the theme of the accuracy profile.