

# Determination of As, Pb and Se in fish tissue by ICP-MS: method validation and uncertainty statements

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APAT - IUPAC International Workshop

Roma 6-8 March 2006

# Digestion procedure selection

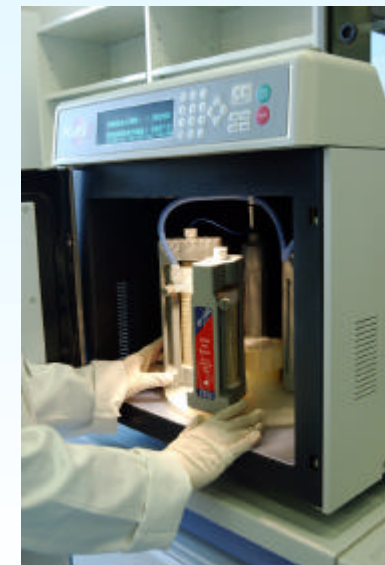
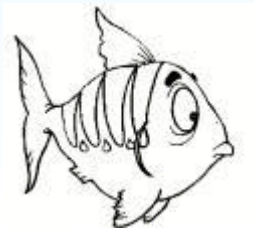
Different acid mixtures and different microwave digestion programmes have been tested on samples of 0.5 g NRCC-Dorm 2- Dogfish muscle CRM



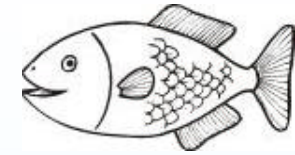
Choice guided by the best recovery (R%)  
obtained with



Acid Mixture: 6 ml  $\text{HNO}_3$  + 1 ml  $\text{H}_2\text{O}_2$   
MO Programme: 5 step, Power Max 650 W;  
time 17 min



# Method validation



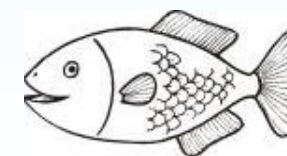
1. **Repeatability and Recovery** evaluated by repeated independent analyses (including digestion) on CRM NRCC-DORM2 dogfish muscle and BCR422 cod muscle, by only one operator in the same day
2. **Reproducibility** evaluated by repeated independent analyses on BCR422 and ENEA tuna RM (higher concentration range) by three different operators working in different days with respect to the others.
3. **LOD & LOQ**
4. **Robustness** evaluated applying different dilution factor

# 1. Repeatability & Recovery

	DORM-2			BCR 422		
Element	As	Se	Pb	As	Se	Pb
Mean value (mg kg <sup>-1</sup> )	18.35	1.41	0.072	21.49	1.68	0.086
Standard deviation (mg kg <sup>-1</sup> )	0.495	0.053	0.005	0.298	0.03	0.005
Mean Recovery (%)	102	101	110	102	103	101
CV(%)	2.7	3.7	6.5	1.4	1.7	6.0
n of measurements	13	13	11	9	9	8

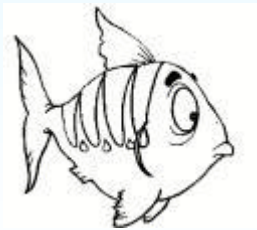
## 2. Coefficient of variation CV% for each operator

	BCR422				TUNA RM	
Operator	As		Se		Pb	
	CV%	n	CV%	n	CV%	n
<b>A</b>	1.4	9	1.7	9	3.5	10
<b>B</b>	1.4	7	3.1	7	1.8	7
<b>C</b>	1.6	11	2.0	11	3.0	7



### 3. Detection Limit & quantification limit

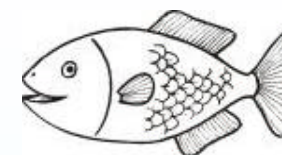
element	LOD ( $\mu\text{g L}^{-1}$ )	LOQ ( $\mu\text{g L}^{-1}$ )
As	0.0136	0.0450
Se	0.0146	0.0487
Pb	0.0170	0.0560



$$\text{LOD} = \frac{3s * [C]}{S - B}$$

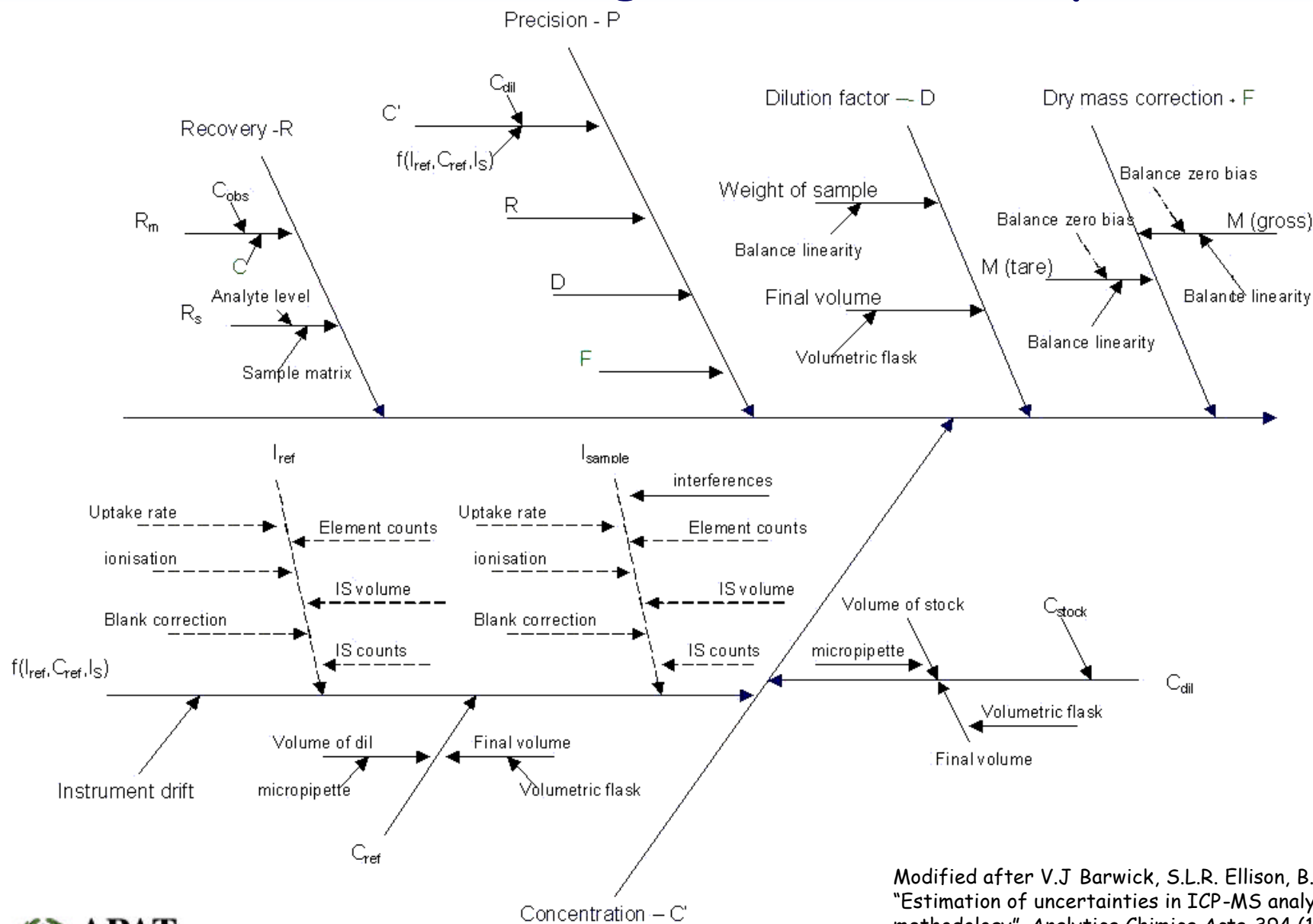


# 4. Robustness



	As		Se		Pb	
Dilution factor	1:100	1:300	1:100	1:300	1:100	1:300
Concentration CRM (mg kg <sup>-1</sup> )	21.1	21.1	1.63	1.63	0.085	0.085
mean value (mg kg <sup>-1</sup> )	19.83	21.35	1.526	1.673	0.069	0.072
Standard deviation (mg kg <sup>-1</sup> )	0.326	0.384	0.030	0.036	0.006	0.008
CV %	1.64	1.80	1.98	2.17	8.99	10.57
n measurements	11	11	11	11	8	7

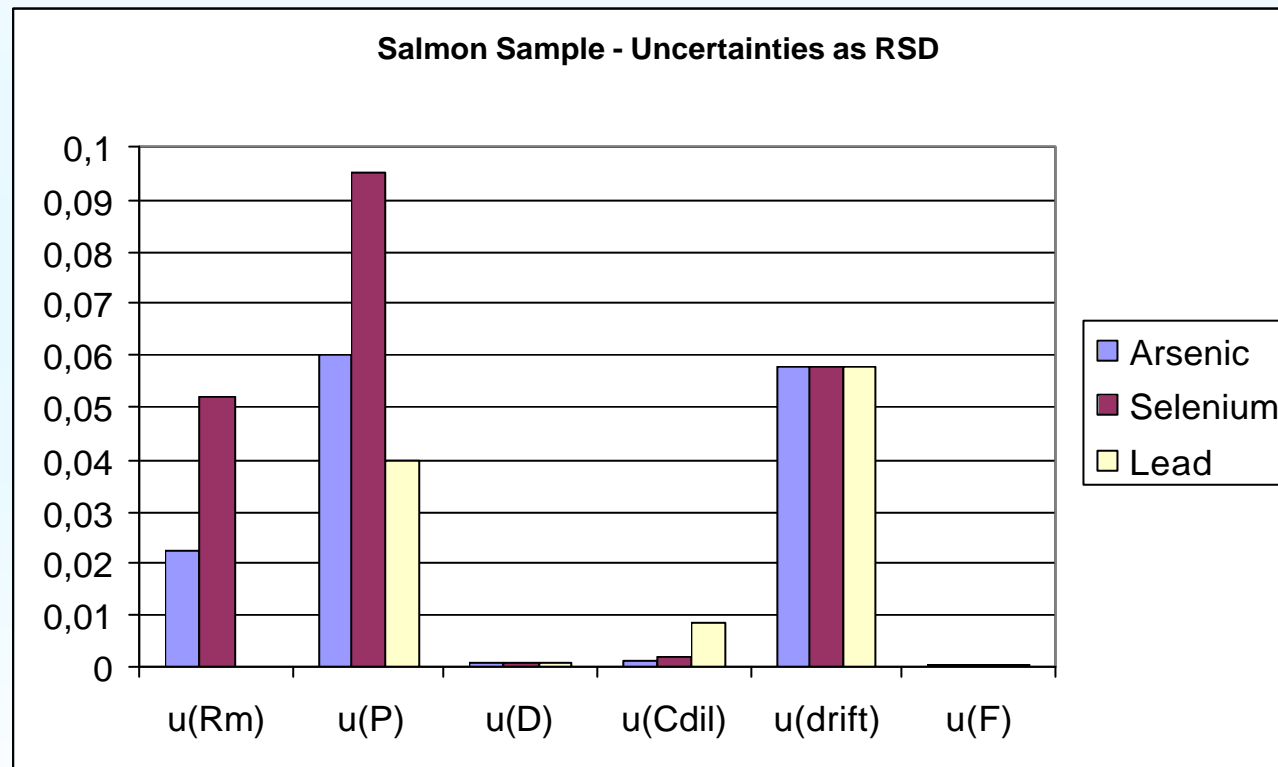
# cause-effect diagram - uncertainty sources



C

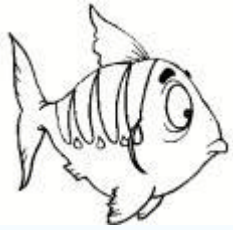
Modified after V.J Barwick, S.L.R. Ellison, B. Fairmain, "Estimation of uncertainties in ICP-MS analysis: practical methodology". Analytica Chimica Acta 394 (1999) 281-291.

# Contribution to the overall uncertainty



# As associated uncertainty

Parameter		Uncertainty as RSD
Method recovery	$u(R_m)$	0.0227
Precision	$u(P)$	0.06
Dilution factor	$u(D)$	0.0012
Concentration of dilute working standard	$u(C_{dil})$	0.001536
Instrument drift	$u(drift)$	0.0577
Dry mass correction	$u(F)$	0.00058



# Expanded uncertainty for a salmon sample

element	C (mg/kg)	U (mg/kg)
As	3.99	0.69
Se	0.47	0.11
Pb	0.85	0.12