Measurement Uncertainty forDetermination of Hexavalent Chromium in Seawater and Other Matrices by Colorimetric Method

Procedure:

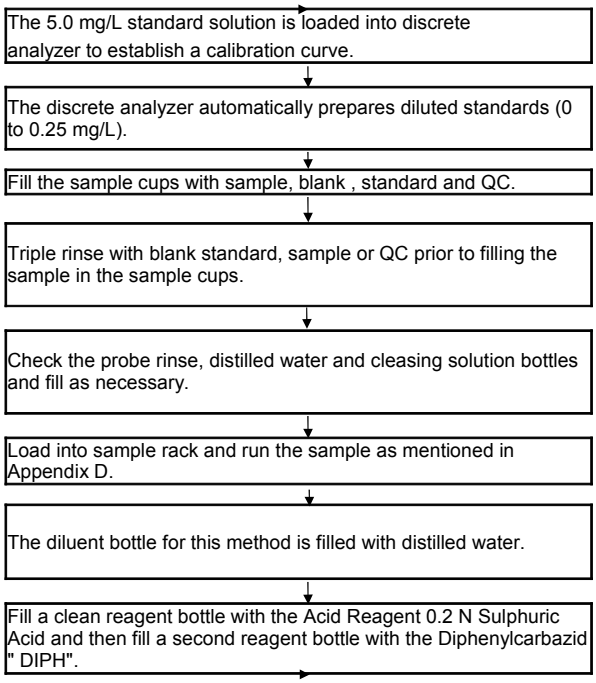
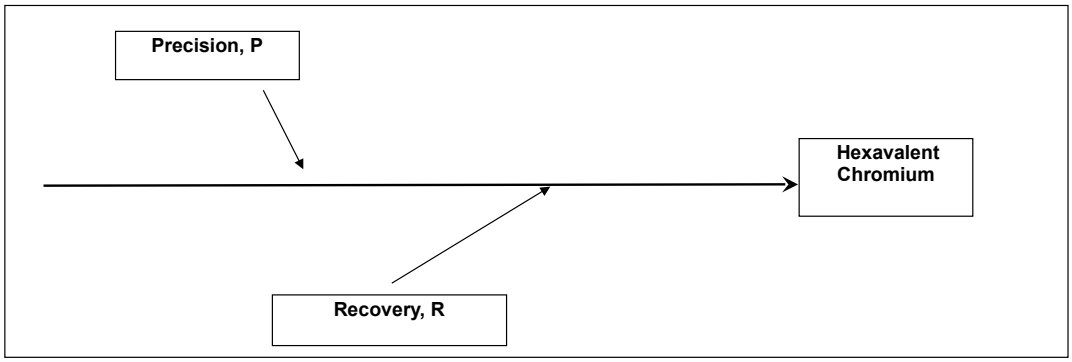


Figure 1: Cause and effect diagram for determination of Hexavalent Chromium



1) Precision Data

Precision Data for spiking samples of 0.005, 0.05 and 0.25 Hexavalent Chromium in distilled water.
Data was collected over a period of time. Rsd value is taken as standard uncertainty for μ(Precision).

Table 1

No	Spiked at 0.005 mg/L	Spiked at 0.05 mg/L	Spiked at 0.25 mg/L
1	0.0049	0.0501	0.2497
2	0.0053	0.0509	0.2491
3	0.0049	0.0501	0.2495
4	0.0041	0.0503	0.2493
5	0.0053	0.0503	0.2491
6	0.0047	0.0499	0.2493
7	0.0053	0.0501	0.2491
Mean	**0.0049**	**0.0502**	**0.2493**
SD	**0.0004**	**0.0003**	**0.0002**
RSD	**0.0890**	**0.0064**	**0.0009**

$$RSD_{pooled} = \sqrt{\left(\frac{(n_1 - 1) \times RSD_1^2 + (n_2 - 1) \times RSD_2^2 + \ldots}{(n_1 - 1) + (n_2 - 1) + \ldots} \right)}$$ **= 0.0515**

2) Recovery

Determination of Method Recovery, Rm

Concentration of spiked sample, mg/l = 0.05

Table 2

Replicate	Observed Conc, 0.05 mg/L
1	0.0501
2	0.0509
3	0.0501
4	0.0503
5	0.0503
6	0.0499
7	0.0501
Mean	0.0502
Std Deviation	0.0003
RSD	0.0064

Uncertainty due to spike solution = 0.0029 (refer Appendix I)
Rm = Mean conc./ Conc. of spike solution = 1.004

$$\mu R_m = R_m x \sqrt{\left(\frac{sd}{C_{obs}} \right)^2 \frac{1}{n} + \left(\frac{\mu C_{spike}}{C_{spike}} \right)^2}$$ = 0.0583

Significant testing, t-test is calculated as below

$$tc = \frac{|1 - Rm|}{\mu Rm}$$ = 0.0730

Determination of Sample Recovery, Rs

Table 3

No	Repeatability at 0.05 mg/l		
	Sea Water	Industrial Effluent	River Water
1	0.0502	0.0446	0.0496
2	0.0500	0.0448	0.0493
3	0.0496	0.0453	0.0488
4	0.0498	0.0446	0.0490
5	0.0496	0.0448	0.0490
6	0.0496	0.0451	0.0493
7	0.0514	0.0443	0.0493
Mean,	0.0500	0.0448	0.0492
Std Deviation	0.0006	0.0003	0.0003
RSD	0.0129	0.0075	0.0054

SD of the mean recovery, μR_s = **0.0028**

Combine standard Uncertainty for Recovery = $\sqrt{(\mu R_m)^2 + (\mu R_s)^2}$

= 0.0584

Uncertainty Budget:

Parameter	Description	Value,x	Standard uncertainty $\mu(x)$	$\left(\frac{\mu x}{x}\right)$	$\left(\frac{\mu x}{x}\right)^2$
P	**Precision**	1	0.0515	0.0515	0.002654
Rec	**Recovery**	1	0.0584	0.0584	0.000014
Combined Relative Std Uncertainties					**0.051652**

CALCULATION OF OVERALL MEASUREMENT UNCERTAINTY FOR THE METHOD

$$\mu_x(x) = \sqrt{\left(\frac{\mu\ \mathrm{Re}\ c}{\mathrm{Re}\ c}\right)^2 + \left(\frac{\mu P}{P}\right)^2}$$

= 0.0517

Expanded Uncertainty at 95% confidence level, K = 2 will be 0.1034

At any Hexavalent Chromium concentration, the uncertainty of Hexavalent Chromium will be:

m (Hexavalent Chromium concentration) = Conc x 0.1034

Therefore, Uncertainty at 0.05 Hexavalent Chromium Concentration will be calculated as;

m (x) = 0.05 x 0.1034
= 0.005

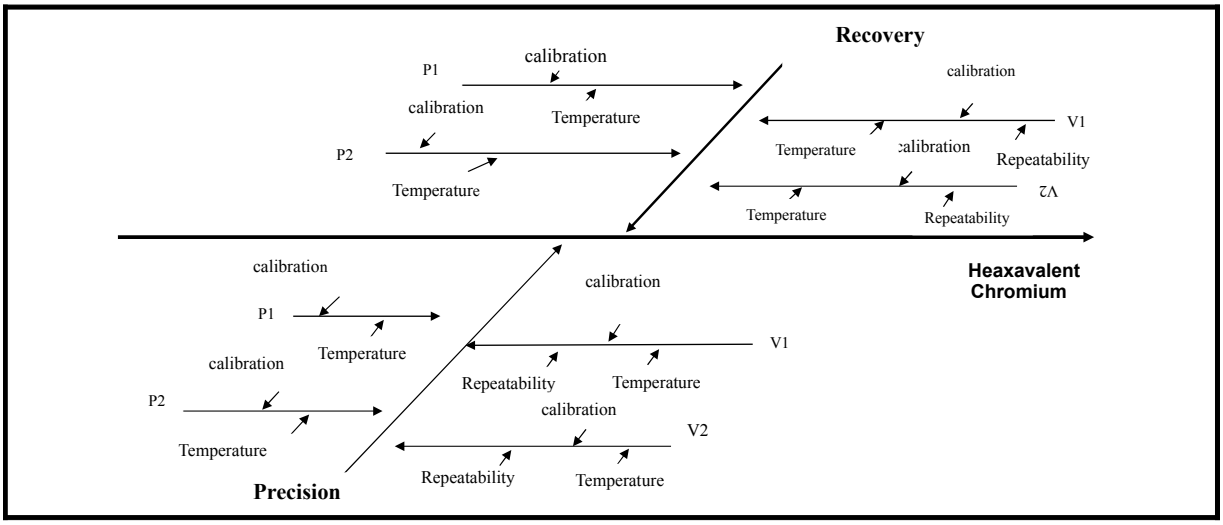
And will be written as **0.050 ± 0.005 mg/L Hexavalent Chromium.**

Appendix D

Measurement Uncertainty for concentration of spiked solution (Hexavalent Chromium)

* The uncertainty for spike solution was calculated using bottom-up approach and tabulated as below:

Figure 1: Cause and Effect Diagram for Chromium Hexavalent



Uncertainty contributions

P1= Uncertainty from micropipette 5 ml
P2= Uncertainty from micropipette 5 ml
V1= Uncertainty from 100 ml volumetric Flask
V2= Uncertainty from 100 ml volumetric Flask

Appendix D

Desciption of sources of uncertainty	Value	Data/Information	Distribution	Standard uncertainty	Relative Standard uncertainty
Volume of solution (ml)					
Pipette (P1)	**5**				
certified volume	0.02	Manufacturer's quote ± 0.015	triangular, √6	0.0061	
variation in filing	0.0058	From repeatability experiment, std deviation	normal	0.0058	
temperature variation (±)	4	From lab temp variation of ± 4°C and taking coeficient of expansion of water is 2.1×10^{-4}	rectangular, √3	0.0024	
Combined				0.0088	0.0018
Pipette (P2)	**5**				
certified volume	0.02	Manufacturer's quote ± 0.015	triangular, √6	0.0061	
variation in filing	0.01	From repeatability experiment, std deviation	normal	0.0058	
temperature variation (±)	4	From lab temp variation of ± 4°C and taking coeficient of expansion of water is 2.1×10^{-4}	rectangular, √3	0.0024	
Combined				0.0088	0.0018
Flask (V1)	**100**				
certified volume	0.1	Manufacturer's quote ± 0.1 at 20°C	triangular, √6	0.0408	
variation in filing	0.09	From repeatability experiment, std deviation	normal	0.0889	
temperature variation (±)	4	From lab temp variation of ± 4°C and taking coeficient of expansion of water is 2.1×10^{-4}	rectangular, √3	0.0485	
Combined				0.1092	0.0011
Flask (V2)	**100**				
certified volume	0.1	Manufacturer's quote ± 0.1 at 20°C	triangular, √6	0.0408	
variation in filing	0.09	From repeatability experiment, std deviation	normal	0.0889	
temperature variation (±)	4	From lab temp variation of ± 4°C and taking coeficient of expansion of water is 2.1×10^{-4}	rectangular, √3	0.0485	
Combined				0.1092	0.0011
Combined uncertainties					**0.0029**