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MEASUREMENT UNCERTAINTY OF SPECTROPHOTOMETRIC DETERMINATION OF HEXAVALENT CHROMIUM IN WATER

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Hexavalent chromium, +6 oxidation state of chromium, is known to be human carcinogen besides damaging respiratory system, kidney, liver, skin and eyes and it can be discharged to surface waters through industrial processes such as welding on stainless steel, painting and electroplating. For the determination of this carcinogen hexavalent chromium in water, one of the most common analytical methods is the colorimetric diphenylcarbazide method. But, in order to report an analysis accurately, the measurement uncertainty of the parameter must be accompanied to the result of the analysis. The aim of this study is to present the measurement uncertainty of hexavalent chromium in water that is determined by the colorimetric method. The sources of uncertainty are specified by a cause-effect diagram and enlarged by using the calculations, thus giving the budget of uncertainty. At the end of the calculations, it was found that the measurement uncertainty was dominantly affected by the calibration curve whereas the precision had no significant effect on the measurement uncertainty. The expanded relative uncertainty was determined as ±0.05 with 95% confidence level.

Keywords: Hexavalent chromium, measurement uncertainty, UV-visible spectrophotometry.

1. Introduction

Increased level of industry unfortunately leads contamination of water sources with heavy metals including mercury, zinc and chromium, which is becoming one of the main health problems for living organisms, not only for human being but also for animals and plants [1,2]. Chromium (Cr), the sixth most abundant element in the earth, may bind to iron and oxygen in the form of chromite [3]. The main states of Cr are the trivalent (CrIII) and hexavalent (CrVI) forms which are widely used in industry including steel works, metal finishing, petroleum refining, Cr electroplating and leather tanning as well as in pharmacy as body-mass–reducing and muscle development agent.

Cr(III) is necessary for biological function of living organism whereas the studies have also proved that Cr(VI) is 1000 times more toxic and carcinogenic than Cr(III) in case of inhalation [4-7]. In a trace amount, Cr(III) is essential to

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the metabolism of carbohydrates, proteins and lipids [6]. Due to its structure and charge similarity with sulfate, Cr(VI) is easily transported into cells via the sulfate transport channels while Cr (III) cannot be transported into the cell. Inside the cell, Cr(VI) is first reduced to Cr(V), afterwards to Cr(III) and then the final compound binds to vitamin C and other reducing agents. On the other hand, Cr(V) may be deoxidized by H_2O_2 and increase human hemoglobin peroxidation [8]. During the production and usage of Cr, a part of it is unfortunately released into the soil and causes long term hazardous effects on ground and surface water, soil ecology, food chain and finally on human health [9,10]. In leather industry, after tanning process, approximately 1.0%–4.0% of Cr(III) remains in the dry tannery sludge and when it is thought that annual production is in high amounts (million tons), it is classified as a hazardous waste product worldwide. In surface waters in which Cr(III) is dominant, the maximum allowable Cr concentration has been settled as 100µg/L while the average concentration of chromium is determined in the range of 0.2–1 µg/L in rainwater, 0.04–0.5 µg/L in seawater [11].

There are many methods to determine the concentration of Cr in water samples including, atomic absorption and ICP-MS while Cr(VI) concentration is determined via ion chromatography and spectrophotometer [12-14]. In order to detect lower concentrations down to 0.06 µg/L, ion chromatographic method should be preferred whereas spectrophotometric method is superior to the chromatographic method due to its simplicity, fastness and economy. Hexavalent chromium can be determined by the colorimetric method in the range from 100 to 1000µg/L. In the colorimetric method, hexavalent chromium is determined by reaction with diphenylcarbazide in acid solution. The red-violet color of the unknown composition is measured at 540nm [15]. On the other hand, analysis results are affected by random errors whose magnitudes depend on the measurement conditions. In order to determine these error sizes, measurement uncertainty of the analysis must be expressed together with the measured value, thus providing the result as a range of values with an accepted level of confidence [16-18]. Measurement uncertainty is defined as a non-negative parameter characterizing the dispersion of the quantity values being attributed to a measurand, based on the information used [17]. Amanatidou et al (2011) examined the combined standard uncertainty of the spectrophotometric determination of nitrite and nitrate and found that the contribution of the calibration curve to the uncertainty was very significant while the contribution of the method and laboratory bias to the uncertainty was insignificant [19]. The studies related with the measurement uncertainty of the spectrophotometric determination of total phosphorus showed that the major uncertainties are associated with proof volume, calibration curve and reproducibility within laboratory [20]. In another study analyst, stock solution preparation, the measurement volumes and the linear fitting least squares method are linked with the measurement uncertainty of the spectrophotometric determination of total phosphorus [21]. Ulrich and coworkers (2006) also studied the measurement uncertainty of the methylmercury determination in fish samples by cold vapor atomic absorption spectrometry and found that the major contributions to the uncertainty were associated with recovery and calibration curve [22]. Furthermore, Diaconu et al (2015) studied the measurement uncertainty of the spectrophotometric determination of acetaminophen after its transport through bulk liquid membrane and found that the major contribution to the uncertainty was associated with discharge of volume [23].

The aim of this study is to determine the measurement uncertainty of spectrophotometric determination of Cr(6+) in water. In order to express the analysis results of Cr(6+), the measurement uncertainty of the analyses must be given together with the numerical results. In this study, we detailed the subparameters of expanded uncertainty. Calibration standards were prepared by using a traceable certified reference material of 1000 mg/L hexavalent chromium solution and thus the uncertainty associated with the preparation of standard solution was calculated considering this situation. Uncertainty associated with precision was calculated by using one-way ANOVA. Following the detailing of the subparameters of expanded uncertainty, the contributions of each to the total were analyzed. Since spectrophotometric method is a universal method for many other water analyses, the uncertainty evaluation model should be a guide to the other similar spectrophotometric analysis.

2. Materials and Methods

2.1 Chemicals

Sulfuric acid, phosphoric acid, 1,5-Diphenylcarbazide and acetone were purchased from Sigma-Aldrich. Hexavalent chromium stock solution of 1000 mg/L is a certified reference material (CRM) purchased from Ultra Scientific Analytical Solutions. All reagents used were of analytical purity grade and all solutions were prepared by using ultra-pure water.

2.2 Analysis procedure

0.25 mL concentrated H_3PO_4 was added to 100 mL of sample at room temperature. By using 0.2N H_2SO_4 and a pH-meter, pH of the sample was brought to 2.0±0.5 and then 2 mL diphenylcarbazide solution was added and the sample was hold for 5-10 minutes for the color development. Then the absorbance of the sample was measured at 540nm in 5cm cell of the UV-visible spectrophotometer. Calibration standards were treated the same as the samples which leads to the preparation of calibration curve. The samples were quantified as µg/L by using the relevant calibration curve.

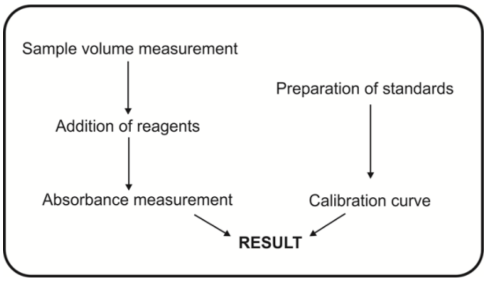

Fig. 1. Diagram of the spectrophotometric determination of hexavalent chromium

3. Results and Discussion

Measurement uncertainty of an analysis must be calculated and be given together with the experimental result in order to make it helpful. The sources of uncertainty for spectrophotometric determination of Cr(VI) are identified by using the cause and effect diagram as shown in Fig. 2. and the formulas used in the calculations are based on the Eurachem/CITAC Guides.

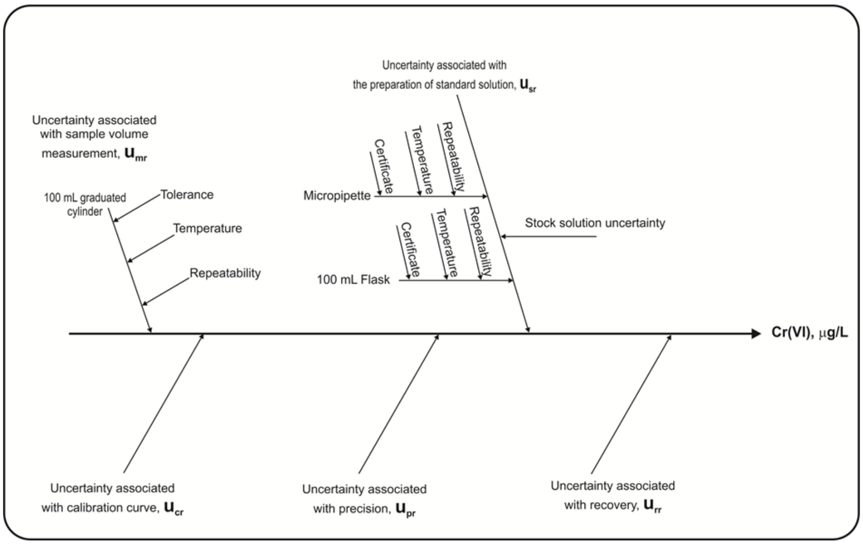

Fig. 2. Cause-and-effect diagram for the spectrophotometric determination of Cr(VI)

3.1 Uncertainty associated with sample volume measurement, u_{mr}

Sample volume is measured by a 100mL class-A graduated cylinder (tolerance :±0.5) which brings three sources of uncertainty: calibration (expressed as measurement tolerance), temperature and repeatability.

3.1.1 Measurement tolerance uncertainty, u_{m1}

$$u_{m1} = \frac{0.5}{\sqrt{6}} = 0.2041\ mL \tag{1}$$

where 0.5 is the tolerance of the graduated cylinder at a temperature of 20°C and √6 comes with the assumption of triangular distribution.

3.1.2 Temperature uncertainty, u_{m2}

The graduated cylinder has been calibrated at 20°C but the laboratory temperature varies in the range of ±3°C. By the assumption of rectangular distribution for the temperature, the uncertainty is found as:

$$u_{m2} = \frac{V*\Delta T*\alpha}{\sqrt{3}} = \frac{100*3*2.1\ 10^{-4}}{\sqrt{3}} = 0.0364\ mL \tag{2}$$

where V=volume of the graduated cylinder,

ΔT= temperature change,
α= volumetric coefficient of expansion for water, $2.1*10^{-4}\ {}^{o}C^{-1}$

3.1.3 Repeatability uncertainty, u_{m3}

By using the results of a series of ten fill and weigh experiments of 100mL graduated cylinder and by using both the mass and the density at the measured temperature, the volumes are calculated which gives a standard deviation of

$$u_{m3} = 0.1143\ mL$$

Thus,

$$u_m = \sqrt{u_{m1}^2 + u_{m2}^2 + u_{m3}^2} \tag{3}$$

$$u_m = \sqrt{0.2041^2 + 0.0364^2 + 0.1143^2} = 0.2368\ mL$$

And the relative uncertainty is calculated by division by the volume as:

$$u_{mr} = \frac{0.2368}{100} = 0.0024$$

3.2 Uncertainty associated with the preparation of standard solution, u_{sr}:

In order to obtain a 10 mg Cr(VI)/L solution, 1mL stock solution of 1000mgCr(VI)/L was diluted to 100mL with ultra-pure water. The uncertainty associated with the preparation of standard solutions brings three sources of uncertainty: stock solution uncertainty, volume of micropipette uncertainty and volume of 100 mL flask uncertainty.

3.2.1 Stock solution uncertainty, u_{sr1}: 1000 mgCr(VI)/L stock solution is a traceable certified reference material (CRM) with an uncertainty of 2 mg/L at k=2 confidence interval. Thus, the stock solution uncertainty is given as follows:

$$u_{sr1,1} = \frac{2}{1000 * 2} = 0{,}001$$

3.2.2 Volume of micropipette uncertainty, u_{sr2}

a) Measurement tolerance uncertainty, $u_{sr2,1}$

$$u_{sr2,1} = \frac{0.00395}{2} = 0.00198\ mL$$

where 0.00395 is the uncertainty and k=2 is the coverage factor given in the calibration certificate of the micropipette.

b) Temperature uncertainty, $u_{sr2,2}$

$$u_{sr2,2} = \frac{V * \Delta T * \alpha}{\sqrt{3}} = \frac{1 * 3 * 2.1\ 10^{-4}}{\sqrt{3}} = 0.00036\ mL \qquad (4)$$

where V=volume of the micropipette,

ΔT= temperature change,

α= volumetric coefficient of expansion for water, $2.1*10^{-4}$°C^{-1}

c) Repeatability uncertainty, $u_{sr2,3}$

By using the results of a ten series of fill and weigh experiments of 1mL micropipette and by using both the mass and the density at the measured temperature, the volumes are calculated which gives a standard deviation of $u_{sr2,3} = 0.00297\ mL$

Thus, the relative uncertainty is calculated by division by the volume as,

$$u_{sr2} = \frac{\sqrt{u_{sr2,1}{}^{2} + u_{sr2,2}{}^{2} + u_{sr2,3}{}^{2}}}{1\ mL} = \frac{\sqrt{0.00198^{2} + 0.00036^{2} + 0.00297^{2}}}{1\ mL} = 0.00358 \quad (5)$$

3.2.3 Volume of 100mL volumetric flask uncertainty, u_{sr3}

a) Measurement tolerance uncertainty, $u_{sr3,1}$

$$u_{sr3,1} = \frac{0.1}{\sqrt{6}} = 0.04082\ mL$$

where 0.1 is the tolerance of the volumetric flask and √6 comes with the assumption of triangular distribution.

b) Temperature uncertainty, $u_{sr3,2}$

$$u_{sr3,2} = \frac{V*\Delta T*\alpha}{\sqrt{3}} = \frac{100*3*2.1\ 10^{-4}}{\sqrt{3}} = 0.03637\ mL \quad (6)$$

where V=volume of the volumetric flask,
ΔT= temperature change,
α= volumetric coefficient of expansion for water, $2.1*10^{-4}\,^{o}C^{-1}$

c) Repeatability uncertainty, $u_{sr3,3}$

By using the results of a ten series of fill and weigh experiments of 100mL volumetric flask and by using both the mass and the density at the measured temperature, the volumes are calculated which gives a standard deviation of

$$u_{sr3,3} = 0.16554\ mL$$

Thus the relative uncertainty is calculated by division by the volume as:

$$u_{sr3} = \frac{\sqrt{u_{sr3,1}{}^{2} + u_{sr3,2}{}^{2} + u_{sr3,3}{}^{2}}}{100\ mL} = \frac{\sqrt{0.04082^{2} + 0.03637^{2} + 0.16554^{2}}}{100\ mL} = 0.00174 \quad (7)$$

Then standard solution preparation uncertainty is:

$$u_{sr} = \sqrt{u_{sr1}{}^{2} + u_{sr2}{}^{2} + u_{sr3}{}^{2}} = \sqrt{0.001^{2} + 0.00358^{2} + 0.00174^{2}} = 0.0041 \quad (8)$$

3.3 Uncertainty associated with the calibration curve, u_{cr}

Calibration curve is defined as the expression of the relation between indication and corresponding measured quantity value [17]. The calibration solutions were measured three times by using UV-visible spectrophotometer and the calibration curve prepared by the calibration solutions are given in Fig.3. The calibration solutions were prepared by diluting the standard solution at different rates and the uncertainties associated with these dilutions are however included in the uncertainty associated with the calibration curve.

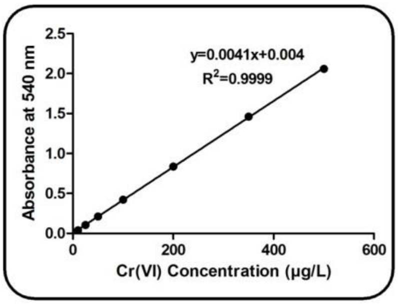

Fig.3. The calibration curve of spectrophotometric determination of Cr(VI) in water.

The calculation of uncertainty associated with the calibration curve is done by the following equations:

$$u_{(c_0)} = \frac{s_r}{b}\sqrt{\frac{1}{p}+\frac{1}{n}+\frac{(c_0 - c_{avg})^2}{S_{xx}}} \tag{9}$$

$$S_{xx} = \sum_{i=1}^{n}(c_i - c_{avg})^2 \tag{10}$$

$$s_r = \sqrt{\frac{\sum_{j=1}^{n}[y_j - (a + b * c_j)]^2}{n-2}} \tag{11}$$

Where s_r= residual standard deviation

b= slope of the calibration curve

a= intercept of the calibration curve

p= number of measurements made for the determination of concentration of sample

n= number of measurements made for calibration curve

c_0= concentration of the sample

c_{avg}= average concentration of calibration standards
y_j= absorbance of the j^{th} calibration standard
$c_{i/j}$= concentration of the i^{th}/j^{th} calibration standard

By using the above equations and measurement of the sample in three replicates with an average of 75.467µg/L, it was found that

$s_{r=}$ 0.0133
S_{xx}= 1870521.43and
$u_{(c0)}$= 2.0089µg/L

In order to find the relative standard certainty associated with the calibration curve, $u_{(c0)}$ is divided by the average concentration:

u_{cr}=2.0089/75.467= 0.02662

3.4 Uncertainty associated with precision, u_{pr}

Precision which consists of the concepts of repeatability and reproducibility is a factor that should be taken into consideration in the calculation of measurement uncertainty. Repeatability test is made with the same operator, same material in a narrow time period while reproducibility is made by varying the factors affecting the result like different operators, different equipment and in a long-time period, thus giving the largest variation in results [18,24,25].

Table1.

Results of the three analysts who studied for precision uncertainty

Measurement number, n	Results of 1^{st} analyst, µg/L	Results of 2^{nd} analyst, µg/L	Results of 3^{rd} analyst, µg/L
1	80.321	81.982	80.920
2	82.118	81.038	81.148
3	80.303	80.333	80.053
4	80.503	80.904	80.512
5	78.875	79.753	79.947
6	79.476	79.559	80.752
7	79.683	80.875	80.466
8	79.263	80.187	80.388
9	80.857	80.650	80.680
10	79.071	80.685	80.421

Uncertainty associated with precision is calculated by using the reproducibility data that are obtained from the measurement results of three analysts in different days.

Measurement results of three analysts in different days are used for the evaluation of the closeness of the results. The individual random effects in the measurement are identified and quantified by one-way ANOVA test whose results have to be taken into account for the evaluation of uncertainty associated with precision [26].

Table 2.

One-way ANOVA results of three analyst who studied precision uncertainty

ANOVA

Variance source	*SS*	*df*	*MS*	*F*	*P-value*	*F criteria*
Between groups	1,795685	2	0,897842	1,704155	0,200916	3,354131
Within groups	14,22508	27	0,526855			
Total	16,02077	29				

Since F<F criteria, closeness of the results of the analysts to each other is proven.

The uncertainty associated with precision is calculated as follows:

$$u_{pr} = \frac{s}{\bar{x}\sqrt{n}} = \frac{0.983}{80.047 * \sqrt{10}} = 0.00388 \tag{12}$$

where s= maximum standard deviation of the analysts
$\bar{x}$= average result of the analyst with the maximum deviation
n= number of measurements of the analysts

3.5 Uncertainty associated with recovery, u_{rr}

Recovery (or bias) is a measure of the losses or interferences that arise from the difference between the amount of analyze measured in the sample relative to that expected in the sample which gives an uncertainty that needs to be calculated [24,25].

In order to find the uncertainty associated with recovery, 10 samples at known concentration of Cr(VI) were studied. Recoveries were calculated by dividing the measured concentration by the expected concentration of spiked sample.

$$u_{rr} = \frac{(s / R_{avg})}{\sqrt{n}} \tag{13}$$

where s= standard deviation of the recoveries
R_{avg}= average of the recoveries
n= number of measurements

Table 3.

Recovery results of spectrophotometric determination of Cr(VI)

Sample no	Measured concentration of Cr(VI), µg/L	Expected concentration of Cr(VI), µg/L	Recovery
1	152.84	150.00	1.019
2	152.13	150.00	1.014
3	150.75	150.00	1.005
4	150.88	150.00	1.006
5	149.78	150.00	0.999
6	149.37	150.00	0.996
7	149.57	150.00	0.997
8	149.05	150.00	0.994
9	149.17	150.00	0.994
10	150.38	150.00	1.003
Standard deviation			0.009
Average			1.003
u_{rr}			**0.00269**

The maximum u_{rr} is taken as the uncertainty associated with the recovery.
u_{rr}= 0.00269

Calculation of the relative combined standard uncertainty, u_r

$$u_r = \sqrt{u_{mr}^2 + u_{sr}^2 + u_{cr}^2 + u_{pr}^2 + u_{rr}^2} \tag{14}$$

$$u_r = \sqrt{0.00237^2 + 0.0041^2 + 0.02662^2 + 0.00388^2 + 0.00269^2} = 0.027$$

Calculation of the relative expanded uncertainty, u_{re}

Expanded uncertainty is defined as the quantity defining an interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of values that could reasonably be attributed to the measurand. Coverage factor is defined as the numerical factor used as a multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty [26].

In our study, the expanded uncertainty is calculated by multiplying the combined standard uncertainty by the coverage factor k=2 at a confidence level of 95%:

$$u_{re} = u_r * k = 0.027 * 2 = 0.054 \approx 0.05$$

In order to give a 500µg/L hexavalent chromium result, it should be reported as:
Result = 500µg/L±(500µg/L*0.05) = 500±25µg/L

4. Conclusion

Uncertainty budget is defined as the statement of a measurement uncertainty, of the components of that measurement uncertainty and of their calculation and combination [17]. In this study, the budget of uncertainty for the spectrophotometric determination of Cr(VI) was studied as in Fig. 4.

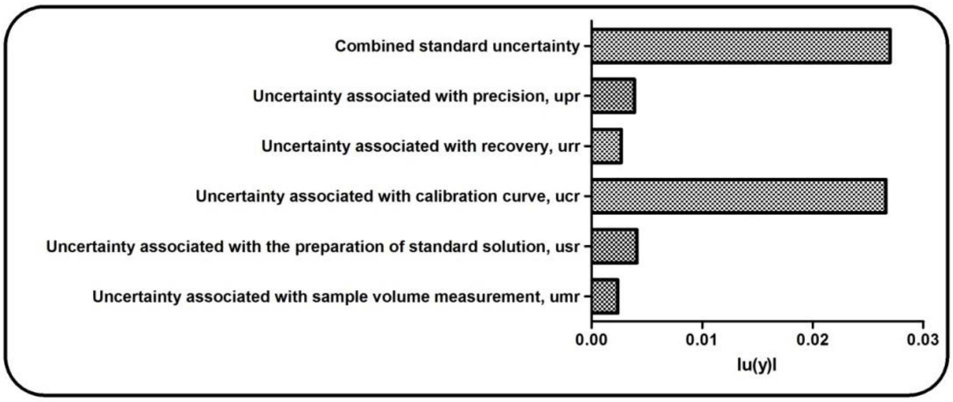

Fig. 4. Uncertainties contributions in spectrophotometric determination of Cr(VI)

The major contribution to the combined standard uncertainty was found to be the uncertainty associated with the calibration curve while the uncertainty associated with the precision was found to be insignificant when compared with the other uncertainty sources that are schematized in our cause and effect diagram.

R E F E R E N C E S

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