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Uncertainty Calculation for the Determination of Chromium Oxide in Leather

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Abstract

This work describes the uncertainty calculation for the determination of chromium oxide in leather. Following the various steps for the calculation of uncertainty which includes assembling a list of sources of uncertainty, with the help of basic formula used to calculate the measure and as all parameters cause an influence on the result because of the uncertainty value associated with it then the basic cause and effect diagram is made which shows the correlation between these and indicates their effect on the uncertainty of the result.

All individual sources of uncertainty are evaluated by quantification. Mass, purity, and molecular mass of potassium dichromate are calculated against the volume of sodium thiosulphate following the first step in the test method is the standardization of sodium thiosulphate with the primary standard, potassium dichromate. So the overall uncertainty value depends on the uncertainties associated with the mass, purity, and molecular mass of potassium dichromate.

Keywords: *Leather, chromium oxide, uncertainty, quality assurance, ISO/IEC 17025*

Deride Krom Oksit Tayini için Belirsizlik Hesaplaması

Öz

Bu çalışma, deride krom oksit tayini için belirsizlik hesaplamasını açıklamaktadır. Ölçümü hesaplamak için kullanılan temel formül yardımıyla ve tüm parametreler kendisiyle ilişkili belirsizlik değeri nedeniyle sonuç üzerinde bir etkiye neden olduğundan, belirsizlik kaynaklarının bir listesinin bir araya getirilmesini içeren belirsizliğin hesaplanması için çeşitli adımların ardından bunlar arasındaki korelasyonu gösteren ve sonucun belirsizliği üzerindeki etkisini gösteren temel neden-sonuç diyagramı yapılmaktadır.

Tüm bireysel belirsizlik kaynakları niceleme ile değerlendirilir. Potasyum dikromatın kütlesi, saflığı ve moleküler kütlesi, sodyum tiyosülfatın hacmine göre hesaplanır ve test yöntemindeki ilk adım, sodyum tiyosülfatın birincil standart olan potasyum dikromat ile standardizasyonudur. Dolayısıyla genel belirsizlik değeri, potasyum dikromatın kütlesi, saflığı ve moleküler kütlesi ile ilişkili belirsizliklere bağlıdır.

Anahtar Kelimeler: *Deri, krom oksit, belirsizlik, kalite güvencesi, ISO/IEC 17025*

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1. Introduction

This work describes the uncertainty calculation for the test method of determination of Chromium oxide in leather. Measurement of uncertainty for the test methods carried out in labs is a parameter given with the result of an analyte, the measurand, i. e., the range of values attributed to the measurand, with some determined level of confidence. It characterizes the dispersion of values that could reasonably be attributed to the measurand. The concentration of Cr_2O_3 in leather is the measurand. The result is reported with the calculated uncertainty.

($C_{measurand}$ ± uncertainty value)

Here the measurand is the concentration of Chromium oxide in leather.

(C_{Cr2O3} ± uncertainty value)

It is the range of values where the true value is present in between this range, also a known and determined level of confidence, as every measurement method has an uncertainty accompanying it. The statement of the uncertainty reported with the result provided to the customer the 'quality' of the result. Therefore, reporting the uncertainty with the result is designed for the labs for testing the quality parameter requested by the customers (*EURACHEM/CITAC Guide, Quantifying uncertainty in analytical measurement*, 2012). In every lab performing under the scope of ("General requirements for the competence of testing and calibration laboratories," 2017), Quality Management System is responsible for quoting the value of uncertainty with the results of Measurements. This applies to the labs working under the Quality System Management of ISO/IEC 17025:2071 ("General requirements for the competence of testing and calibration laboratories," 2017), under the section of 'Evaluation of Measurement Uncertainty', Clause no. 7.6.

The measurement uncertainty for the determination of Chromium Oxide in leather (Meyer, 2007; Rowley, 2001) is described in this study in detail.

1.1. There is a procedure to calculate the uncertainty as given below.

1.1.1. A list of all sources of uncertainty is assembled, which includes all the parameters in the basic expression, used to calculate the measurand from their specific values. All the sources of uncertainty in this expression may influence the result of the measurand, so, considered as the potential uncertainty sources. The all-inclusive list of total sources of uncertainty is built, which, usually has the parameters causing produce an uncertainty associated with their value and are therefore considered as possible uncertainty sources.

1.1.2. After studying the basic expression cause and effect diagram is made which shows the sources of uncertainty and indicates their influence on the measurement of the result. For example, the following diagram the so-called cause and effect diagram is useful for this Measurement uncertainty to break up for the test. It also helps to eliminate the double counting of sources. For example, the following diagram is applied for this test in the study.

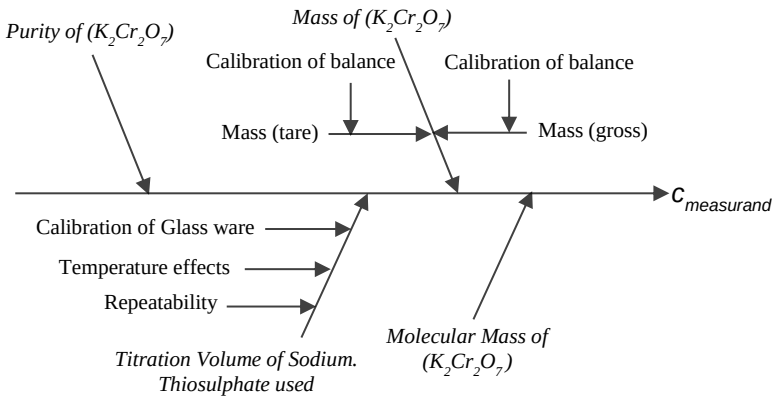

Figure 1. Cause and effect diagram

1.1.3. After identifying all the uncertainty sources, the uncertainty attributed to these sources is quantified. The uncertainty is evaluated from each source and then combined. Here Mass, the Purity and Molecular mass of ($K_2Cr_2O_7$) is counted against the Volume of Sodium thiosulphate.

1.1.4. Uncertainty sources in the available data set were then examined and checked to include all the pertinent contributions to uncertainty. The square root of the total standard uncertainty sources, by combining all the uncertainty components according to the law of propagation of uncertainty was obtained and the combined standard uncertainty, U_C was then calculated.

1.1.5. The value of Expanded Uncertainty, U_E obtained if the combined standard uncertainty is multiplied by the coverage factor 2. Expanded uncertainty is a quantity that covers a large portion of the spreading of values that could practically be ascribed with the measurand, i.e., the confidence level is increased up to 95%. So the result of the measurand is reported with the value of uncertainty, U_E (expanded).

2. Materials and Methods

All chemicals were of analytical grades, (Merck). The leather sample was a finished one and cut into small pieces.

The method employed is the standard test which covers the determination of chromium oxide in leather. The amount of chromium in leather, determined by the wet oxidation of leather, is reported as chromium oxide ("Determination of chromium oxide in leather," 2018).

A 0.1 N solution of secondary standard, Sodium thiosulfate, $Na_2S_2O_3.5H_2O$ was prepared and standardized against the solution of primary standard Potassium dichromate, $K_2Cr_2O_7$. Later the same burette containing Sodium thiosulfate was again used in the titration of chromium contents in an oxidization reaction flask to determine the endpoint to calculate the measurand, i. e., concentration of chromium oxide (Vogel, Jeffery, Bassett, & Mendham, 1989).

So, the first uncertainty is calculated by combining all the parameters associated with the measurement sequence. Standardization of Sodium thiosulfate is used for the calculation of uncertainty of the measurand concentration of chromium oxide and for the reason the same burette (same solution) is used for the titration of Sodium thiosulfate with the reaction flask containing the sample content (Dewani et al., 2012).

According to the test procedure, there are various steps for the determination of chromium oxide in leather, given as under.

2.1. Standardization of Sodium Thiosulfate with Potassium Dichromate

To standardize the Sodium thiosulfate solution, a 0.1 N solution of Potassium dichromate was prepared. Important parameters of Potassium dichromate are the molecular weight, purity, weight of Potassium dichromate, and the volume of $Na_2S_2O_3$ used at the endpoint of the titration.

$$\text{Amount} = \frac{\text{N x Eq.wt. x 100}}{1000}$$

Potassium dichromate (0.1 N) was prepared by dissolving 0.4903 g in 100 ml distilled water. 10 ml (0.04903 g) of this Potassium dichromate (0.1 N) solution was consumed in titration and the endpoint of the titration, i. e., the volume of Sodium thiosulfate was calculated as per the formula given below,

$N_1V_1 = N_2V_2$ (Vogel et al., 1989)

2.1.1. Method calculation

1 ml 0.1 N Sodium thiosulphate = 0.00253 g of Cr_2O_3

$$C_{Na_2S_2O_3}\ (\text{mol/L}) = \frac{1000 \cdot m_{K_2Cr_2O_7} \cdot P_{K_2Cr_2O_7}}{M_{K_2Cr_2O_7} \cdot V_T}$$

Where,

m = mass of $K_2Cr_2O_7$

P = purity

M = molar mass
V_T = titration Volume of $Na_2S_2O_3$
1000 = conversion factor (ml) to (L)

The formula for the determination of chromium oxide in leather,

$$\% \text{ of } Cr_2O_3 = \left(\frac{\text{ml of 0.1 N sodium thiosulphate x 0.00253}}{\text{Weight of sample}}\right) \text{x } 100$$

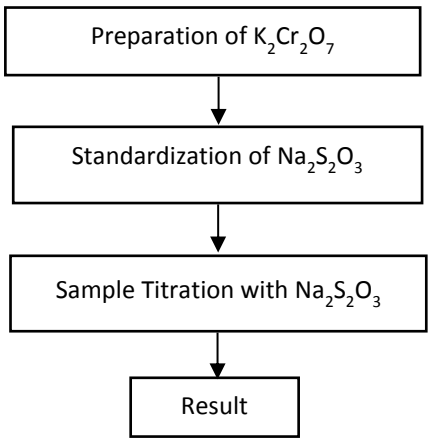

Figure 2. Determination of chromium oxide in leather

3. Research Findings and Discussion

We carried out the calculation of uncertainty as per guidelines found in the literature. The calibration uncertainty values were obtained from calibration certificates from the manufacturers or calibration agencies.

3.1. Sources of Uncertainty

The uncertainty sources are displayed in the Cause & Effect diagram as given in Figure 1.

3.2. Quantification of Uncertainty Components

3.2.1. Mass, $m_{K2Cr2O7}$

The calibration certificate of analytical balance quoted the combined standard uncertainty, $u_c \pm 0.092$ mg. This value was accounted for twice, i. e, once for the tare step and second for the gross mass.

$U_m = \pm \sqrt{2 \text{ x } (0.0.092)^2}$
$= \pm$ 0.13 mg

The total uncertainty in mass was calculated to include repeatability and read-out errors with uncertainty acquired from balance calibration.

$$U_m = \pm \sqrt{(\mu_{\text{cal}})^2 + (\mu_{\text{ro}})^2 + (\mu_{\text{rep}})^2}$$

3.2.2. Purity, $P_{K2Cr2O7}$

The purity of potassium dichromate was given as 99.99 % by the supplier.
Uncertainty in P was, therefore, 99.99 $\pm$ 0.01%
The quoted uncertainty on the bottle of potassium dichromate was taken and divided by a rectangular distribution,

$$u(P_{K_2Cr_2O_7}) = \pm \frac{0.01}{\sqrt{3}} = \pm 0.0058$$

(Kadis, 1998)

3.2.3. Molar mass, $M_{K2Cr2O7}$

The molecular formula of Potassium dichromate $K_2Cr_2O_7$ as given in the periodic table of elements with standard uncertainties of individual elements (Wieser et al., 2013) was employed, quoted here in Table 1.

Table 1. Standard uncertainties of individual elements of potassium dichromate

Element	Atomic Weight	Quoted Uncertainty	Standard Uncertainty
Cr	51.9961	± 0.0006	0.000346
K	39.0983	± 0.0001	0.000058
O	15.9994	± 0.0003	0.00017

The uncertainties in the atomic weights of its elements also given in the IUPAC table were then combined, and divided by $\sqrt{3}$ yielding the corresponding standard uncertainties, quoted in Table 2.

Table 2. Total standard uncertainties of individual elements of potassium dichromate

Element	Atomic Weight	Total Atomic Weight	Standard Uncertainty
K_2	2 x 39.0983	78.1966	± 0.000116
Cr_2	2 x 51.9961	103.9922	± 0.000692
O_7	7 x 15.9994	111.9958	± 0.00119

This gave a molar mass for $K_2Cr_2O_7$ is stated below.

$M_{K2Cr2O7}$ = 78.1966 + 103.9922 + 111.9958

= 294.1136 g.mol^{-1}

The overall uncertainty contribution for $M_{K2Cr2O7}$ was then calculated as:

$u(M_{K2Cr2O7}) = \pm\sqrt{(0.00016)^2 + (0.000692)^2 + (0.00119)^2}$

$u(M_{K2Cr2O7}) = \pm$ 0.00138 gmol^{-1}

3.2.4. Volume, V_T

The titration was accomplished using a volumetric flask (100 ml), a burette (25 ml), and a pipette (10 ml). The volume of sodium thiosulphate discharged from the burette was noted at the end point of titration and the same three uncertainty sources in each of the volumetric glassware, i.e. flask, pipette & burette are involved. These include repeatability, calibration of the glassware and temperature effect on glassware, volume variation, and the readout error of the burette at the point of detecting the endpoint. So these are also combined to calculate the total uncertainty in volume, u(V_T).

Burette (25 ml)

Calibration

The calibration certificate quoted combined standard uncertainty as

± 0.00603 ml.

Repeatability

A standard deviation value was obtained through ten fill and weight experiments are ± 0.02 ml

Temperature Effects

The coefficient of expansion of water is 2.1x10^{-4} ^{o}C^{-1}. The calibration certificate showed the temperature of 25 ^{o}C at which its burette is calibrated, while the temperature in the laboratory is 30 ^{o}C while performing the test. 9.7 ml is consumed in titration.

Volume Variation = ± (9.7 x 5 x 2.1x10^{-4})

= ± 0.0102 ml

Assuming a rectangular distribution for the temperature variation i.e.,

$$\frac{0.0102}{\sqrt{3}} = \pm 0.00588 \text{ ml}$$

Combine all three contributions.

$U(V) = \pm\sqrt{(0.00603)^2 + (0.02)^2 + (0.00588)^2}$

$U(V) = \pm 0.022$ ml

Volumetric Flask, (100 ml)

Calibration quoted combined standard uncertainty as $\pm$ 0.00858 ml.

Repeatability value is $\pm$ 0.015 ml

Volume Variation = $\pm$ (100 x 5 x 2.1×10^{-4})

$u(V)$ = $\pm$ 0.105 ml, then again divided by $\sqrt{3}$ gives:

Standard Uncertainty $u(V)$ = $\pm$ 0.060 ml

Combining all three contributions,

$u(V) = \pm \sqrt{(0.00858)^2 + (0.015)^2 + (0.06)^2}$

= $\pm$ 0.0624 ml

Pipette, (10 ml)

The calibration certificate quoted combined standard uncertainty as $\pm$ 0.132 ml.

Repeatability value is $\pm$ 0.02 ml while the volume variation was $\pm$ 0.0105

Standard Uncertainty $u(V) = \pm$ 0.0060 ml

Combine all three contributions.

$u(V) = \pm\sqrt{(0.0132)^2 + (0.02)^2 + (0.0060)^2}$

= $\pm$ 0.024 ml

3.3. Calculation of u_c, The Combined Standard Uncertainty

Standard uncertainties involved in the standardization of Sodium thiosulfate with potassium dichromate were combined in a mathematical expression as follows,

$$\frac{U_C(C_{Na2S2O3})}{cNa2S2O3} = \pm \sqrt{\left[\frac{um K2Cr2O7}{m K2Cr2O7}\right]^2 + \left[\frac{uP K2Cr2O7}{P K2Cr2O7}\right]^2 + \left[\frac{uM K2Cr2O7}{M K2Cr2O7}\right]^2 + \left[\frac{uV_{TNa2S2O3}}{V_{TNa2S2O3}}\right]^2}$$

The same uncertainty contributions during the standardization procedure with potassium dichromate are applied in the determination of chromium oxide, as the same burette was used in the titration of the sample flask. So,

$$\frac{U_C(C_{Cr_2O_3})}{cCr_2O_3} = \pm \sqrt{\left[\frac{um K2Cr2O7}{m K2Cr2O7}\right]^2 + \left[\frac{uP K2Cr2O7}{P K2Cr2O7}\right]^2 + \left[\frac{uM K2Cr2O7}{M K2Cr2O7}\right]^2 + \left[\frac{uV_{TNa2S2O3}}{V_{TNa2S2O3}}\right]^2}$$

V_T = titrant volume of Sodium thiosulphate from the burette.

$$U_C(C_{Cr_2O_3}) = \pm \sqrt{\left[\frac{um K2Cr2O7}{m K2Cr2O7}\right]^2 + \left[\frac{uP K2Cr2O7}{P K2Cr2O7}\right]^2 + \left[\frac{uM K2Cr2O7}{M K2Cr2O7}\right]^2 + \left[\frac{uV_{TNa2S2O3}}{V_{TNa2S2O3}}\right]^2} \times C_{Cr_2O_3}$$

By putting all the values in the above expression the uncertainty value for the determination of chromium oxide is calculated and denoted as **X** %, as shown below

$$u_C(C_{Cr_2O_3}) = \mathbf{X}\ \%$$

3.4. Calculation of the Expanded Uncertaint

The combined standard uncertainty was multiplied by a coverage factor of 2, i.e., (95% confidence level) to obtain the expanded uncertainty $U(C_{Cr_2O_3})$.

$U(C_{Cr_2O_3})$ = $u_c(C_{Cr_2O_3})$ x 2
= **Y** %

The concentration of chromium oxide is written as;

$(C_{Cr_2O_3} \pm Y)$ % k = 2 $C_{Cr_2O_3}$ = concentration of chromium oxide

4. Conclusion and Recommendations

Uncertainty calculation for the determination of chromium oxide in leather is developed for the first time at a lab scale according to the standard test method, ("Determination of chromium oxide in leather," 2018). The same uncertainty contributions during the standardization procedure with potassium dichromate are applied while calculating the concentration of chromium oxide because the same burette containing secondary standard, Sodium Thiosulfate, is then used in titrating the reaction flask in which chromium content of the leather sample is in the oxidized state. The overall procedure addresses the individual budgets for the major and important contributors to measurement uncertainty and the parameters associated with them. A similar approach can be used to carry out uncertainty estimations in other similar experiments. It is highly recommended to apply for the present work in accredited laboratories for the calculation of uncertainty associated with the determination of chromium oxide in leather.

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Author Contribution and Conflict of Interest Declaration Information

All authors contributed equally to the article. There is no conflict of interest.

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