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Measurement uncertainty of the mass fraction of total iron in iron ores, concentrates, agglomerates, and pellets

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Abstract

The paper considers the measurement of the mass fraction of total iron by the titrimetric method. A description of the measurement technique is given. It is shown that a special feature of the titrimetric method is the need to use a certified reference material with a known value of the mass fraction of total iron, which in this case acts as a reference measure with the value of which the corresponding value in the sample of the substance under consideration is compared. When implementing the measurement technique, two consistent input quantities are measured – the mass of the sample and the volume of the titrated solution; therefore, to determine both the titre and the mass fraction of total iron, the reduction method is used. In this case, it is necessary to separately evaluate the combined instrumental uncertainty of the measurements and the standard uncertainty of repeatability, based on which it is possible to calculate the standard and expanded uncertainty of the measurand. Procedures for the uncertainty evaluation of the titre and mass fraction of total iron measurements have been developed. Uncertainty budgets for these quantities have been evaluated. Examples of the uncertainty evaluation of the titre and mass fraction of total iron measurements based on real laboratory data and metrological characteristics of the measuring equipment used are considered.

Keywords: total iron; mass fraction; titrimetric method; measurement uncertainty; reduction method; uncertainty budget.

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Introduction

The mass fraction of total iron is the main component that meets the requirements of rational use of resources – state subsoil. For incoming control of raw materials, control of technological processes, and finished iron ore products, DSTU 8811.1:2018 [1] is used, or internal laboratory methods are used for determining the mass fraction of total iron by the titrimetric method, which are developed on its basis.

A special feature of the titrimetric method is the need to use a certified reference material (CRM) with a known value of the mass fraction of total iron, which in this case acts as a reference measure with the value of which the corresponding value in the sample of the substance being considered is compared. The CRM is reproduced at the beginning of a working shift and is the basis for further measurements of working samples of the corresponding content of total iron, so it is necessary to evaluate uncertainty budgets for both the titre and total iron.

When implementing method [1], two consistent input quantities are measured – the mass of the sample and the volume of the titrated solution. This leads to the emergence of a correlation between the results of observations of these quantities and, to be borne it in mind, to the need to use the reduction method (RM) [2–4] to determine both the titre and the mass fraction of total iron. The RM is not generally accepted in regulatory documents on measurement uncertainty (MU) [5, 6], therefore, there have been no attempts to develop corresponding procedures based on the method in metrological practice.

The aim of the paper is to develop a procedure for MU evaluation of the mass fraction of total iron in iron ores, concentrates, agglomerates, and pellets, taking into account the listed features of the titrometric method.

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Table 1

Measuring equipment (ME)

Equipment name	Metrological characteristics
Analytical balance	Measuring range up to 61 g, U_m = 0.00017 g, k_m=2
Graduated burette	Nominal capacity up to 50 ml, U_V = 0.026 ml, k_V=2
Certified reference material of total iron	Certified value of CRM, mass fraction, 62%, U_A = 0.1%, k_A=2

1. The essence of the measurement method

The method is based on the reduction of trivalent iron with a solution of tin dichloride to divalent iron and titration of the latter with a solution of potassium dichromate in the presence of an indicator – sodium diphenylamine sulfonate. The excess reducing agent is oxidized with mercury (II) chloride.

The measuring equipment used during the measurements, in accordance with the requirements of ISO/IEC 17025:2017 [7], is subject to calibration. The metrological characteristics are given in Table 1.

The mass fraction of total iron Y is measured in two stages:

1) First, the titre for CRM is determined using indirect measurements, as:

$$T = \frac{A \cdot m}{V \cdot 100}, \ \text{g/cm}^3, \tag{1}$$

where A is a certified value of CRM, mass fraction, %; m is the mass of CRM, g; V is the volume of the titrated solution for CRM, cm^3.

2) Using indirect measurements, the mass fraction of total iron Y in the sample of the test substance is determined as:

$$Y = T\frac{V_s \cdot 100}{M}, \ \%, \tag{2}$$

where V_s is the volume of the titrated solution for the sample, cm^3; M is the mass of the sample portion being analyzed, g.

For each stage, a procedure for MU evaluation shall be developed.

2. Procedure for MU evaluation of titre

The procedure consists of five main steps, outlined below.

1) Construction of a measurement model

The measurement model expresses the relationship between the output quantity (measurand) T and the input quantities, and is expressed by formula (1).

2) Evaluation of the input quantities values and the measurand

The estimate of a certified value of CRM $\hat{A}$ is taken from its calibration certificate.

The value of the CRM mass is estimated as the arithmetic mean of measurement values of $n=3$ individual values of the sample masses m_q:

$$\bar{m} = \frac{1}{n}\sum_{q=1}^{n} m_q. \tag{3}$$

The value of the titrated solution volume for CRM is estimated as the arithmetic mean of measurement values of $n=3$ individual values of the titrated solution volume V_q:

$$\bar{V} = \frac{1}{n}\sum_{q=1}^{n} V_q. \tag{4}$$

According to RM [2], the titre value is estimated as the arithmetic mean of individual titre values T_q using the following formula:

$$\bar{T} = \frac{1}{n}\sum_{q=1}^{n} T_q = \frac{\hat{A}}{100 \cdot n}\sum_{q=1}^{n}\frac{m_q}{V_q}. \tag{5}$$

3) Evaluation of standard uncertainties of input quantities and measurand

Instrumental standard uncertainties (SUs) of Type B of input quantities are evaluated through their expanded uncertainties U and coverage factors k, which are taken from calibration certificates accordingly:

$$u_B(\hat{A}) = \frac{U_A}{k_A}; \tag{6}$$

$$u_B(\hat{m}) = \frac{U_m}{k_m}; \tag{7}$$

$$u_B(\hat{V}) = \frac{U_V}{k_V}. \tag{8}$$

The combined instrumental SU of the titre measurement is calculated by the formula:

$$u_B(\hat{T}) = \sqrt{c_A^2 u_B^2(\hat{A}) + c_m^2 u_B^2(\hat{m}) + c_V^2 u_B^2(\hat{V})}, \tag{9}$$

where c_A, c_m, c_V are the corresponding sensitivity coefficients, which are equal to:

$$c_A = \left.\frac{\partial T}{\partial A}\right|_{\substack{m=\bar{m}\\V=\bar{V}}} = \frac{\bar{m}}{\bar{V} \cdot 100}; \tag{10}$$

$$c_{\hat{m}} = \left.\frac{\partial T}{\partial m}\right|_{\substack{A=\hat{A}\\V=\bar{V}}} = \frac{\hat{A}}{\bar{V} \cdot 100}; \tag{11}$$

$$c_V = \left.\frac{\partial T}{\partial V}\right|_{\substack{A=\hat{A}\\m=\bar{m}\\V=\bar{V}}} = -\frac{\hat{A} \cdot \bar{m}}{\bar{V}^2 \cdot 100}. \tag{12}$$

The SU of the repeatability of titre measurements, according to RM [2], is evaluated as:

$$u_r(\bar{T}) = \sqrt{\frac{1}{n(n-1)}\sum_{q=1}^{n}(T_q - \bar{T})^2} = \sqrt{\frac{1}{n(n-1)}\sum_{q=1}^{n}\left(\frac{\hat{A}}{100}\cdot\frac{m_q}{V_q} - \bar{T}\right)^2}. \tag{13}$$

Table 2

Uncertainty budget for the titre T measurement

Input quantities	Estimates of input quantities	SUs of input quantities	Degrees of freedom	Sensitivity coefficients	Uncertainty contributions
m	$\overline{m}$	$u_B(\hat{m})$	ν_m	c_m	$u_m(\hat{T})$
A	$\hat{A}$	$u_B(\hat{A})$	ν_A	c_A	$u_A(\hat{T})$
V	$\overline{V}$	$u_B(\hat{V})$	ν_V	c_V	$u_V(\hat{T})$
Measurand	Estimate of measurand	SU of measurand	EDF	Coverage factor	Expanded uncertainty
		$u_B(\hat{T})$	ν_B		
T_r	$\overline{T}$	$u_r(\overline{T})$	ν_r		
T	$\overline{T}$	$u(\hat{T})$	ν_{eff}	k	U

The SU of titre measurements is calculated using the formula:

$$u(\hat{T}) = \sqrt{u_B^2(\hat{T}) + u_r^2(\overline{T})}. \quad (14)$$

4) Evaluation the expanded uncertainty of the measurand

The expanded uncertainty of the titre measurement is evaluated as:

$$U_T = t_{p;\nu_{eff}} \cdot u(\hat{T}), \quad (15)$$

where $t_{p;\nu_{eff}}$ is the Student's coefficient for the confidence level p and effective degrees of freedom (EDF) ν_{eff}, which is calculated using the Welch–Satterthwaite equation:

$$\nu_{eff} = \frac{u^4(\hat{T})}{\frac{u_r^4(\overline{T})}{n-1} + \frac{u_B^4(\hat{T})}{\nu_B}}, \quad (16)$$

where ν_B is the EDF of Type B, which is attributed to the instrumental SU of the titre measurement and is calculated using the Welch–Satterthwaite equation:

$$\nu_B = \frac{u_B^4(\hat{T})}{\frac{c_A^4 u_B^4(\hat{A})}{\nu_A} + \frac{c_m^4 u_B^4(\hat{m})}{\nu_m} + \frac{c_V^4 u_B^4(\hat{V})}{\nu_V}}. \quad (17)$$

Here ν_A, ν_m, ν_V are the degrees of freedom of instrumental SUs of corresponding input quantities.

5) Evaluation of the uncertainty budget

The uncertainty budget for the measurement of the titre T is given in Table 2.

3. Example of MU evaluation of the titre

The values of repeated measurements of the quantities m and V for CRM at the titre T determination are given in Table 3.

The uncertainty budget for the measurement of the titre T is presented in Table 4.

The average values of the input quantities m and V were evaluated by formulas (3) and (4), respectively, for n=3.

The average value of the measurand T was evaluated by formula (5). The instrumental SUs of Type B of the input quantities A, m and V were evaluated by formulas (6), (7) and (8), using metrological characteristics of ME from Table 1, and the SU of repeatability of the measurand T was evaluated by formula (13).

4. Procedure for MU evaluation for the mass fraction of total iron

The procedure consists of five main steps, outlined below.

1) Construction of a measurement model

The measurement model expresses the relationship between the output quantity (measurand) Y and input quantities, and is expressed by the formula (2).

2) Evaluation of the values of input quantities and the measurand

The estimate of the titre value $\hat{T}$ is taken from the previous budget (Table 2).

Table 3

Laboratory values for the titre T determination

q	m (g)	V (cm^3)	T (g/cm^3)
1	0.5018	30.15	0.010319
2	0.5030	30.20	0.010326
3	0.5026	30.20	0.010318
Average values	0.50247	30.183	0.0103212
Instrumental SUs	0.000085	0.013	2.6341×10^{-6}

Table 4

The uncertainty budget for the measurement of the titre T

Input quantities	Estimates of input quantities	SUs of input quantities	Degrees of freedom	Sensitivity coefficients	Uncertainty contributions, g/cm^3
m	0.50247 g	0.000085 g	∞	0.02054 cm^{-3}	1.75×10^{-6}
A	62%	0.05%	∞	0.0001665 g/(cm^3·%)	8.32×10^{-6}
V	30.183 cm^3	0.013 cm^3	∞	–0.0003420 g/cm^6	-4.45×10^{-6}
Measurand	Estimate of measurand, g/cm^3	SU of measurand, g/cm^3	EDF	Coverage factor	Expanded uncertainty, g/cm^3
		9.596×10^{-06}	∞		
T_r	0.0103212	2.6341×10^{-6}	2		
T	0.0103212	9.9514×10^{-06}	407	2.006	1.996×10^{-05}

The value of the sample mass is estimated as the arithmetic mean $n_s=2$ of measurement values of the individual mass values M_q:

$$\bar{M} = \frac{1}{n_s}\sum_{q=1}^{n_s} M_q. \quad (18)$$

The value of the volume of the titrated solution for the sample is evaluated as the arithmetic mean $n_s=2$ of measurement values of individual values of the volume of the titrated solution V_{sq}:

$$\bar{V}_s = \frac{1}{n_s}\sum_{q=1}^{n_s} V_{sq}. \quad (19)$$

The mass fraction of total iron (Y) in percent is calculated by formula (2) in parallel in two samples. The results are considered acceptable if the absolute difference between the results of two measurements (Y_1, Y_2) does not exceed the value of the repeatability limit r. If the condition is met, the arithmetic mean of the results of two parallel measurements is taken as the measurement result:

$$\bar{Y} = \frac{1}{n_s}\sum_{q=1}^{n_s} Y_q = 100\frac{\bar{T}}{n_s}\sum_{q=1}^{n_s}\frac{V_{sq}}{M_q}. \quad (20)$$

3) Evaluation of standard uncertainties of input quantities and the measurand

The SU of the titre $u_c(\hat{T})$ is taken from Table 2 of the preliminary budget. Instrumental SUs of Type B of input quantities are evaluated through their expanded uncertainties U and coverage factors k, which are taken from calibration certificates accordingly:

$$u_B(\hat{V}_s) = \frac{U_{V_s}}{k_{V_s}}; \quad (21)$$

$$u_B(\hat{M}) = \frac{U_M}{k_M}. \quad (22)$$

The measurement instrumental SU of the mass fraction of total iron is calculated by the formula:

$$u_B(\hat{Y}) = \sqrt{c_T^2 u_B^2(\bar{T}) + c_M^2 u_B^2(\hat{M}) + c_{V_s}^2 u_B^2(\hat{V}_s)}, \quad (23)$$

where c_T, c_M, c_{V_s} are corresponding sensitivity coefficients, which are equal to:

$$c_T = \frac{\partial\hat{Y}}{\partial\hat{T}} = \frac{\hat{V}_s\cdot100}{\hat{M}}; \quad (24)$$

$$c_{V_s} = \frac{\partial\hat{Y}}{\partial\hat{V}_s} = \frac{\hat{T}}{\hat{M}}\cdot100; \quad (25)$$

$$c_M = \frac{\partial\hat{Y}}{\partial\hat{M}} = -\frac{\hat{T}\cdot\hat{V}_s}{\hat{M}^2}\cdot100. \quad (26)$$

The SU of repeatability of measurements of the mass fraction of total iron is calculated by the formula [8]:

$$u_r(\hat{Y}) = \frac{r}{2.77}. \quad (27)$$

The SU of measurements of the mass fraction of total iron is calculated by the formula:

$$u(\hat{Y}) = \sqrt{u_B^2(\hat{Y}) + u_r^2(\bar{Y})}. \quad (28)$$

4) Evaluation of the expanded uncertainty of the measurand

The expanded uncertainty of the measurement of the mass fraction of total iron is calculated as:

$$U_Y = t_{p;\nu_{eff}}\cdot u(\hat{Y}), \quad (29)$$

where $t_{p;\nu_{eff}}$ is the Student's coefficient for the confidence level p and EDF ν_{eff}, which is calculated using the Welch–Satterthwaite equation:

Table 5

Uncertainty budget for the measurement of the mass fraction of total iron

Input quantities	Estimates of input quantities	SUs of input quantities	Degrees of freedom	Sensitivity coefficients	Uncertainty contributions
T	$\hat{T}$	$u_B(\hat{T})$	ν_T	c_T	$u_T(y)$
V_s	$\overline{V_s}$	$u_B(\hat{V}_s)$	ν_{V_s}	c_{V_s}	$u_{V_s}(y)$
M	$\overline{M}$	$u_B(\hat{M})$	ν_M	c_M	$u_M(y)$
Measurand	Estimate of measurand	SU of measurand	EDF	Coverage factor	Expanded uncertainty
		$u_B(\hat{Y})$	ν_B		
Y_r	$\overline{Y}$	$u_r(\hat{Y})$	ν_r		
Y	$\overline{Y}$	$u(\hat{Y})$	ν_{eff}	k	U

$$\nu_{eff} = \frac{u^4(\hat{Y})}{\frac{u_r^4(\hat{Y})}{\infty} + \frac{u_B^4(\hat{Y})}{\nu_B}} = \nu_B \left[\frac{u(\hat{Y})}{u_B(\hat{Y})}\right]^4, \qquad (30)$$

where ν_B is the EDF of Type *B*, which is attributed to the instrumental SU of the measurement of the mass fraction of total iron and is calculated using the Welch–Satterthwaite equation:

$$\nu_{eff} = \frac{u_B^4(\hat{Y})}{\frac{c_T^4 u_B^4(\hat{T})}{\nu_T} + \frac{c_M^4 u_B^4(\hat{M})}{\nu_M} + \frac{c_{V_s}^4 u_B^4(\hat{V}_s)}{\nu_{V_s}}}, \qquad (31)$$

where ν_T, ν_M, ν_{V_s} are the degrees of freedom of the SU of the corresponding input quantities.

5) Evaluation of the uncertainty budget

The uncertainty budget for the measurement of the mass fraction of total iron Y is given in Table 5.

5. Example of the uncertainty evaluation of the mass fraction of iron in a sample

The values of M and V_s for determining the mass fraction of iron in the sample Y being analysed are given in Table 6.

The average values of the input quantities M and V_s were evaluated by formulas (18), and (19), respectively, for $n_s = 2$. The average value of the measurand Y was evaluated by formula (20). The SUs of Type *B* of the input quantities M and V_s were evaluated by

Table 6

Values of laboratory indicators when determining the mass fraction of iron in a sample

q	M (g)	V_s (cm^3)	Y(%)
1	0.5011	31.5	64.88
2	0.5012	31.4	64.66
Average values	0.50115	31.45	64.77
Instrumental SU	0.000085	0.005	0.144

Table 7

Uncertainty budget for the measurement of the mass fraction of total iron

Input quantities	Estimates of input quantities	SUs of input quantities	Degrees of freedom	Sensitivity coefficients	Uncertainty contributions, %
T	0.0103212 g/cm^3	9.951×10^{-6} g/cm^3	407	6275.57 %·cm^3/g	0.06245
V_s	31.45 cm^3	0.013 cm^3	∞	2.0595 %/cm^3	0.02677
M	0.50115 g	0.000085 g	∞	-129.29 %/g	-0.01099
Measurand	Estimate of measurand, %	SU of measurand, %	EDF	Coverage factor	Expanded uncertainty, %
Y_B		0.06883	600		
Y_r	64.7716	0.1444	∞		
Y	64.7716	0.1600	∞	2.0	0.3200

formulas (21) and (22), using metrological characteristics of the measuring equipment from Table 1, and the repeatability SU of the measurand Y was estimated by formula (27) in which the repeatability limit $r = 0.4$.

The uncertainty budget for the measurement of the mass fraction of total iron Y is presented in Table 7.

The complete result of measuring the mass fraction of total iron will look like as follows:

$$Y = (64.77 \pm 0.32)\%, \; p = 0.95.$$

Conclusions

The method for measuring the mass fraction of total iron in iron ores, concentrates, agglomerates, and pellets by the titrimetric method has been considered. Procedures for the evaluation of the uncertainty of the titre and mass fraction measurements of total iron based on RM have been developed. Uncertainty budgets have been evaluated, which can form the basis for building software tools based on MS Excel.

Examples of calculating the uncertainty for the titre and mass fraction of total iron have been considered.

Невизначеність вимірювання масової частки загального заліза в залізних рудах, концентратах, агломератах і окатках

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Анотація

Розглянуто методику вимірювання масової частки загального заліза титрометричним методом. Наведено опис методики вимірювань. Показано, що особливістю виконання титрометричного методу є необхідність використання стандартного зразка з відомим значенням масової частки загального заліза, який у цьому випадку виконує роль еталонної міри, зі значенням якої порівнюється відповідне значення в пробі речовини, що досліджується. Оскільки стандартний зразок відтворюється на початку робочої зміни і є основою для подальших вимірювань робочих проб відповідного вмісту загального заліза, потрібно скласти бюджети невизначеності окремо для титру та загального заліза. Під час реалізації методики вимірювання вимірюються дві узгоджені вхідні величини – маса наважки та об'єм титрованого розчину. Це приводить до виникнення кореляції між результатами спостережень цих величин та для її врахування – до необхідності використання методу редукції для визначення як титру, так і масової частки загального заліза. У цьому випадку потрібно окремо оцінити сумарну інструментальну невизначеність вимірювань і стандартну невизначеність повторюваності, на основі яких можна розрахувати сумарну стандартну та розширену невизначеності вимірювань. Розроблено процедури оцінки невизначеності вимірювань титру та масової частки загального заліза, які складаються з п'яти етапів: складання моделі вимірювання; оцінювання числових значень вхідних величин та вимірюваної величини; оцінювання стандартних невизначеностей вхідних величин та вимірюваної величини; оцінювання розширеної невизначеності вимірюваної величини; побудова бюджетів невизначеності, які можуть лягти в основу створення програмних засобів на основі MS Excel. Розглянуто приклади оцінювання невизначеності вимірювань титру та масової частки загального заліза на основі реальних лабораторних даних та метрологічних характеристик використаного вимірювального обладнання, в яких для обчислення значень вимірюваних величин та їх стандартних невизначеностей використовується метод редукції.

Ключові слова: загальне залізо; масова частка; титрометричний метод; невизначеність вимірювань; метод редукції; бюджет невизначеності.

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