Dunja Šeremešić, Dragica Grubić

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ODREĐIVANJE UKUPNE KISELOSTI U GORIVU ZA MLAZNE MOTORE: PROCJENA MJERNE NESIGURNOSTI

Sažetak

U radu je prikazan postupak procjene mjerne nesigurnosti rezultata ukupne kiselosti u uzorcima goriva za mlazne motore određene normiranom metodom. Analizirani su izvori nesigurnosti koji doprinose ukupnoj nesigurnosti određivanja ukupne kiselosti titracijskom metodom.

Pouzdani i usporedivi mjerni podaci važni su za donošenje odluke o kvaliteti goriva. Mjerni rezultat je nepotpun bez procjene njegove nesigurnosti koja je kvalitativni pokazatelj mjernog rezultata.

Procjena nesigurnosti može biti zbunjujuća jer ne postoji jedinstveni postupak za njezinu razradu. Koncept mjerne nesigurnosti ispitni laboratorij može upotrijebiti kao nadopunu tradicionalnom pristupu statističke kontrole mjernog postupka.

Sustavnim praćenjem literature, seminarima i međusobnim diskusijama uložili smo određeni napor u razumijevenje same problematike i primjene postupka procjene. U razradu smo uzeli standardnu metodu za koju imamo validacijske podatke kao i podatke iz međulaboratorijskih usporedbi (ASTM–Interlaboratory Crosschecking Program). Pri procjeni mjerne nesigurnosti rezultata kod određivanja ukupne kiselosti u mlaznom gorivu vodili smo se preporukama koje daje dokument EURACHEM/CITAC Guide: «Quantifying Uncertainty in Analytical Measurement» [3].

Ovim radom želimo pokazati da je podatak o mjernoj nesigurnosti još jedan od načina koji doprinosi kvaliteti mjernog rezultata i unapređenju sustava kontrole kvalitete u laboratoriju.

1. UVOD

Norma HRN EN ISO/IEC 17 025 [5] propisuje da ispitni laboratoriji moraju imati postupke za procjenu mjerne nesigurnosti i primjenjivati te postupke.

Mjerna nesigurnost je parametar pridružen mjernom rezultatu koji označava rasipanje vrijednosti i može se razumno pripisati mjerenoj veličini [8].

Svrha provođenja analize je utvrđivanje mjerne nesigurnosti normirane laboratorijske metode na osnovi dostupnih podataka. Općenito mjerna nesigurnost uključuje više sastavnica. Neke od njih mogu se procijeniti iz statističke razdiobe rezultata niza mjerenja i mogu se obilježiti eksperimentalnom standardnom devijacijom (vrsta A). Procjene ostalih sastavnica, koje se također mogu obilježavati standardnom devijacijom, procjenjuju se na osnovi pretpostavljenih razdioba vjerojatnosti, temelje se na iskustvu ili drugim informacijama (vrsta B).

U ovom radu koristili smo za izračunavanje pojedinih sastavnica mjerne nesigurnosti sljedeće jednadžbe koje smo u konačnici uvrstili u računalni program za izračunavanje sastavljene mjerne nesigurnosti:

a) Kada je sastavnica nesigurnosti određena iz serije ponovljenih mjerenja, tada je standardna devijacija srednje vrijednosti mjerenja korištena za izračun standardne nesigurnosti prema jednadžbi:

$$s_{\bar{x}} = \frac{s(x)}{\sqrt{n}} \quad (1)$$

b) Kod sastavnica nesigurnosti koje nisu određene nizom opažanja (eksperimentalno) pridružena nesigurnost procijenjena je na osnovi podataka iz umjernica, certifikata, tehničkih podataka, priručnika. Iz tih podataka i pretpostavljene razdiobe vjerojatnosti izračunali smo standardnu nesigurnost (npr. čistoća standardne tvari).

c) Sastavljena nesigurnost računata je prema jednadžbama:

$$u(y) = \sqrt{u(p)^2 + u(q)^2 + ...} \quad (2) \qquad u_c(y) = y\sqrt{\left[\frac{u(p)}{p}\right]^2 + \left[\frac{u(q)}{q}\right]^2} \quad (3)$$

gdje je y mjerena veličina, p i q su komponente nesigurnosti ili parametri modela mjerenja

d) Proširena nesigurnost (U) je posljednji korak u izračunu mjerne nesigurnosti. Ona daje interval koji obuhvaća najširu frakciju raspodjele vrijednosti koja se može pripisati mjerenoj veličini.

Dobiva se množenjem sastavljene nesigurnosti $u_c(y)$ s odabranim faktorom pokrivanja (k):

$$U = k^* u_c(y) \quad (4)$$

Uobičajeno, k iznosi od 2 do 3, ali može imati i druge vrijednosti. Kad je razdioba vjerojatnosti normalna, izbor k=2 obuhvatit će raspon uz razinu pouzdanosti od 95%.

Postupak procjene mjerne nesigurnosti obuhvaća sljedeće osnovne korake:

1. korak: definiranje mjerenja (što se mjeri)
2. korak: prepoznavanje izvora nesigurnosti
3. korak: kvantificiranje izvora nesigurnosti pojedinih sastavnica
4. korak: izračunavanje mjerne nesigurnosti (sastavljene i proširene)

2. Postupak procjene i analiza sastavnica mjerne nesigurnosti

2.1 korak 1: definiranje mjerenja

Opis mjernog postupka

Uzorak se otopi u smjesi toluena i izopropilnog alkohola koji sadrži malu količinu vode. U ovu bezbojnu otopinu uvodi se struja dušika i titrira sa standardnom otopinom KOH do krajnje točke titracije koja je indicirana promjenom boje (narančasta u kiselini i zelenosmeđa u lužini) uz dodatak indikatora p-naftolbenzena. KOH se standardizira s kalij-hidrogen ftalatom (KHP). Detaljan postupak opisan je u metodi ASTM D 3242.

Mjerena veličina je ukupna kiselost (UK) mlaznog goriva. Ona ovisi o masi KHP, njegovoj čistoći, molekularnoj masi KOH i KHP, volumenu KOH u točki ekvivalencije i masi uzorka.

Matematička ovisnost između navedenih veličina izračuna se iz jednadžbe:

$$\text{UK} = \frac{1000 \times m_{KHP} \times P_{KHP} \times V_{T2} \times M_{KOH}}{M_{KHP} \times V_{T1} \times m_{UZORKA}} \cdot [mgKOH / g] \cdots (5)$$

gdje je:

1000 - konverzijski faktor g $\rightarrow$ mg
m_{KHP} - odvagana masa kalijevog hidrogen ftalata (KHP), g
P_{KHP} - čistoća kalijevog hidrogen ftalata (KHP)
V_{T2} - volumen kalijeve lužine (KOH) za titraciju uzorka, ml
V_{T1} - volumen KOH za titraciju KHP, ml
M_{KHP} - molarna masa kalijevog hidrogen ftalata (KHP), gmol-1
M_{KOH} - molarna masa kalijeve lužine (KOH), gmol-1
m_{UZORKA} - odvagana masa goriva za mlazne motore (GM1), g
UK – ukupna kiselost, mgKOH/g

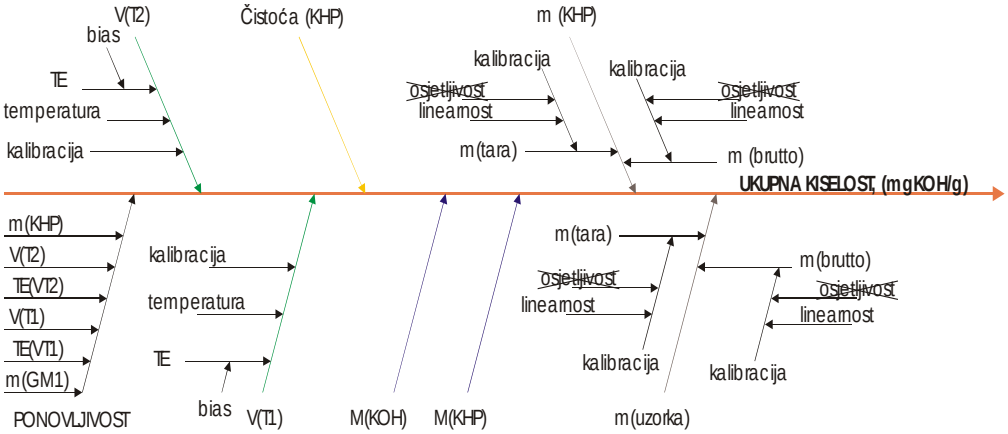
2.2 korak 2: prepoznavanje izvora nesigurnosti

Iz jednadžbe za izračunavanje mjerene veličine (5) proizlaze mjerne nesigurnosti, a njih je najbolje prikazati u dijagramu uzroka i posljedica (slika 1).

U proračun mjerne nesigurnosti rezultata dobivenih odabranom metodom ulaze sljedeći izvori nesigurnosti:

1. nesigurnosti mase standardne tvari-KHP i masa uzorka (vrsta B)
2. nesigurnosti molarnih masa (vrsta B)
3. nesigurnost čistoće standardne tvari kalijev hidrogen ftalat (vrsta B)
4. nesigurnost volumena za titraciju standardne tvari (vrsta B,B, A)
5. nesigurnost volumena za titraciju uzorka (vrsta B,B,A)
6. nesigurnost ponovljivosti mjerenja (vrsta A)

Slika 1



2.3 korak 3: kvantificiranje izvora nesigurnosti pojedinih sastavnica

2.3.1 Masa standardne tvari-kalijev hidrogenftalat (KHP) i masa uzorka (GM1)

Iz tehničkih podataka proizvođača vage uzet je doprinos linearnosti ± 0.15 mg. Ova vrijednost predstavlja maksimalnu razliku između stvarne mase na vagi i očitanja. Doprinos linearnosti uz pretpostavku pravokutne raspodjele pretvara se u standardnu nesigurnost:

$$\frac{0.15mg}{\sqrt{3}} = 0.087 \text{ mg}$$

Doprinos linearnosti treba uzeti u obzir dvaput, jednom za taru i jednom za bruto masu što daje nesigurnost.

$u(m_{KHP}) = u(m_{uzorka}) = \sqrt{2 \times (0.087)^2} = 0.12\text{mg} = 0.00012\text{ g}$

2.3.2 Molarna masa

Atomske mase i pripadajuće nesigurnosti uzete su iz IUPAC-ovih tablica.

$u(M_{KHP}) = \sqrt{(8 \times 0{,}00046)^2 + (5 \times 0{,}00004)^2 + (4 \times 0{,}00017)^2 + 0{,}000058^2} = 0.0038\ \text{gmol}^{-1}$

$u(M_{KOH}) = \sqrt{0{,}000058^2 + 0{,}00004^2 + 0{,}00017^2} = 0.00026\ \text{gmol}^{-1}$

2.3.3 Čistoća standardne tvari (K-hidrogen ftalat)

Čistoća (P) K-hidrogen ftalata prema certifikatu dobavljača dana je kao P = 1.0000 ± 0.0005.

Navedena nesigurnost uzeta je kao pravokutna razdioba te izračunata standardna nesigurnost:

$$u\,(P_{KHP}) = \frac{0.0005}{\sqrt{3}} = 0.00029$$

2.3.4 Volumen (V_{T1}) KOH za titraciju standardne tvari-kalijev hidrogen ftalat (tri doprinosa)

Titracija se izvodi automatskom biretom od 50mL. Doprinosi koji utječu na točnost dodanog volumena su: kalibracija birete, promjena volumena uzrokovana zbog razlike u temperaturi kalibracije birete i radne temperature, odstupanja kod dodavanja volumena.

a) kalibracija birete volumena 50 ml

Za standardnu nesigurnost kalibracije birete korišten je podatak koji navodi proizvođač za točnost dodavanja volumena: A = ± 0.2 % $\Rightarrow$ a = ± 0.1 ml

Podrazumijevajući trokutastu razdiobu standardna nesigurnost iznosi:

$$\frac{0.1ml}{\sqrt{6}} = 0.041\text{ml}$$

b) temperatura

Prema proizvođaču bireta je umjerena na 20°C, a radna temperatura se razlikuje prosječno za ±4°C. Koficijent ekspanzije volumena izopropilnog alkohola α = $1{,}016 * 10^{-3}$, a volumen alk. KOH utrošene za titraciju standarda pri određivanju normaliteta V_{T1} = 5,38 ml (uzorak 10, tablica 5). Standardna nesigurnost je izračunata na temelju pretpostavke pravokutne razdiobe za promjene temperature:

$$5{,}38 \times 1{,}016 * 10^{-3} \times 4 / \sqrt{3} = 0.013\text{ ml}$$

c) ponovljivost

Mjernu nesigurnost dodanog volumena KOH za titraciju standardne tvari utvrdili smo nizom odvaga istog volumena (tablica 1).

Iz dobivene standardne devijacije izračunali smo standardnu nesigurnost prema jednadžbi (1).

Tri gornja doprinosa sastavljena su u nesigurnost volumena (V_{T1}) prema jednadžbi (2).

$$u\,(V_{T1}) = \sqrt{u\,(\text{kalibracija})^2 + u\,(\text{temperatura})^2 + u\,(\text{ponovljivost})^2}$$

$$u\,(V_{T1}) = \sqrt{0.041^2 + 0.013^2 + 0.0069^2}$$

$$u\,(V_{T1}) = 0.0436$$

Tablica 1

Broj mjerenja	V_{KOH}, mL	m, g
1	5	3,881
2	5	3,916
3	5	3,898
4	5	3,883
5	5	3,900
6	5	3,853
7	5	3,929
8	5	3,873
9	5	3,902
10	5	3,899
	aritmetička sredina:	3,893
	standardna devijacija	0,022
	standardna nesigurnost	0,0069

2.3.5 Volumen (V_{T2}) za titraciju uzorka (tri doprinosa)

a) kalibracija birete volumena 50 ml

Za standardnu nesigurnost kalibracije birete korišten je podatak koji navodi proizvođač za točnost dodavanja volumena: A = ± 0.2 % $\Rightarrow$ a = ± 0.1 ml

Podrazumijevajući trokutastu razdiobu standardna nesigurnost iznosi:

$$\frac{0.1ml}{\sqrt{6}} = 0.041\text{ml}$$

b) temperatura

Prema proizvođaču bireta je umjerena na 20°C, a radna temperatura se razlikuje prosječno za ±4°C. Koficijent ekspanzije volumena izopropilnog alkohola α = $1{,}016 * 10^{-3}$, a volumen alk. KOH utrošene za titraciju uzorka V_{T2} = 0,087 ml (uzorak 10, tablica 5). Standardna nesigurnost je izračunata na temelju pretpostavke pravokutne razdiobe za promjene temperature:

$$0{,}087 \text{ x } 1{,}016 * 10^{-3} \text{ x } 4 / \sqrt{3} = 0.0002\text{ml}$$

c) ponovljivost

Za određivanje standardne nesigurnosti ponovljivosti mjerenja napravljen je pokus od 5 titracija istog uzorka.

Iz dobivene standardne devijacije izračunali smo standardnu nesigurnost prema jednadžbi (1).

Tablica 2

100 ml uzorka	
Broj mjerenja	V_{KOH}, ml
1	2.05
2	2.07
3	2.17
4	2.13
5	2.14
aritmetička sredina	2.112
standardna devijacija	0.05
standardna nesigurnost	0.022

Tri gornja doprinosa sastavljena su u nesigurnost volumena (V_{T1}) prema jednadžbi (2).

$$u(V_{T2}) = \sqrt{u(\text{kalibracija})^2 + u(\text{temperatura})^2 + u(\text{ponovljivost})^2}$$

$$u(V_{T2}) = \sqrt{0.041^2 + 0.0002^2 + 0.022^2}$$

$u(V_{T2})$ = 0.0465ml

Tablica 3

Broj mjerenja	m_{uzorka}, g	V_{KOH}, ml	UK mgKOH/g
1	79.08	0.11	0.00144
2	80.45	0.09	0.00116
3	79.60	0.08	0.00104
4	79.55	0.09	0.00117
5	80.80	0.11	0.00141
6	79.58	0.10	0.00131
7	81.30	0.15	0.00131
8	80.52	0.12	0.00145
9	79.55	0.13	0.00158
10	80.42	0.13	0.00157
srednja vrijednost			0.0013
standardna devijacija			0.00018
standardna nesigurnost			0.00006

2.3.6 Ponovljivost mjerenja ukupne kiselosti

Ponovljivost mjerenja odredili smo određivanjem ukupne kiselosti na istom uzorku 10 puta što je prikazano u tablici 3. Ova vrijednost može se direktno uzeti (prema preporukama EURACHEM-ovog vodiča) za računanje sastavljene standardne nesigurnosti jer ona sadržava različite segmente ponovljivosti odabranog mjerenja.

Prema podacima u tablici 3 standardna nesigurnost mjerenja iznosi:

$$\frac{0{,}00018}{\sqrt{10}} = 0{,}00006$$

2.4 korak 4: izračunavanje mjerne nesigurnosti (sastavljene i proširene)

Izračunate standardne nesigurnosti pridružili smo mjerenim veličinama dobivenim pri određivanju ukupne kiselosti 15 uzoraka goriva za mlazne motore i izračunali mjernu nesigurnost za svaki uzorak (tablica 5).

Za izračunavanje smo primijenili jednostavan računalni program opisan u EURACHEM-ovom vodiču koji je prikazan u prilogu 1, tablica 6. Unošenjem procijenjenih nesigurnosti i eksperimentalnih mjernih podataka dobili smo sastavljenu nesigurnost za pojedini uzorak .

U tablici 4 prikazane su vrijednosti mjerenih veličina dobivene određivanjem ukupne kiselosti u uzorku za čije je mjerenje izračunata najveća mjerna nesigurnost, njihove standardne nesigurnosti i njihove relativne standardne nesigurnosti.

Tablica 4

	opis	**vrijednost** x	standardna **nesigurnost** u(x)	relativna standardna nesigurnost u(x)/x
pon	ponovljivost	1	0,00006	0,00006
m_{KHP}	masa KHP	0,02017 g	0,00012 g	0,0059
P_{KHP}	čistoća KHP	1,0	0,00029	0,00029
M_{KHP}	molarna masa KHP	204,2212 g/mol	0,0038 g/mol	0,000019
V_{T2}	volumen KOH za tit. zorka	0,087 ml	0,0465ml	0,5344
V_{T1}	volumen KOH za tit. KHP	5,38 ml	0,0436 ml	0,0081
m(uz)	masa uzorka	79,71 g	0,00012 g	1,5E-6
M_{KOH}	molarna masa KOH	56,1094 g/mol	0,00026 g/mol	4,6E-6
UK	**ukupna kiselost**	0,00114 mgKOH/g	0,00061 mgKOH/g	0,5351

Proširenu nesigurnost U izračunali smo množenjem najveće sastavljene mjerne nesigurnosti s faktorom pokrivanja k=2:

$$U(UK) = 0{,}00122 \text{ mgKOH/g}$$

Tablica 5: Eksperimentalni podaci - ukupna kiselost

Br.uz	m_{KHP}, g	V_{T1}, ml	N_{KOH}	m_{uzorka}, g	V_{T2}, ml	u (UK)	UK mgKOH/g
1	0,02016	7,45	0,013	78,37	1,247	0,00045	0,0118
2	0,02016	7,45	0,013	78,23	1,247	0,00045	0,0118
3	0,02016	7,45	0,013	78,28	0,291	0,00044	0,0028
4	0,02011	10,17	0,009	79,10	1,111	0,00032	0,0076
5	0,02011	10,17	0,009	78,73	1,341	0,00033	0,0092
6	0,02010	9,22	0,011	77,70	1,581	0,00037	0,0122
7	0,02010	9,22	0,011	79,53	1,427	0,00036	0,0107
8	0,02086	8,69	0,012	77,28	1,367	0,00041	0,0117
9	0,02086	8,69	0,012	77,72	1,347	0,00040	0,0114
10	0,02050	5,38	0,018	79,71	0,087	0,00061	0,0011
11	0,02083	5,86	0,017	80,46	0,127	0,00056	0,0015
12	0,01977	11,72	0,008	79,87	1,181	0,00027	0,0068
13	0,01977	11,72	0,008	79,28	1,767	0,00028	0,0103
14	0,01903	13,90	0,007	80,18	2,001	0,00023	0,0094
15	0,01903	13,90	0,007	81,29	0,817	0,00022	0,0038

3. Međulaboratorijska određivanja ukupne kiselosti u uzorcima goriva za mlazne motore u organizaciji ASTM standardnom metodom

Odsjek za kontrolu kvalitete naftnih derivata dugi niz godina sudjeluje u međulaboratorijskom ispitivanju naftnih proizvoda te je navedena metoda konstantno praćena tim ispitivanjem.Pregled postignutih rezultata u tom razdoblju prikazali smo na grafikonu 2, prilog 2 gdje se iz z-vrijednosti može vidjeti pouzdanost naših rezultata.

Iz ASTM izvještaja [9] može se vidjeti da se naši rezultati nalaze unutar reproducibilnosti zadane metodom i u slučaju kada se iskažu proširenom mjernom nesigurnošću (grafikon 4, prilog 4).

ASTM UZORAK JF9807

Točna vrijednost: 0,0104 mgKOH/g (srednja vrijednost 86 laboratorija)

$R_{(ASTM\ metode)} = \pm 0{,}0041$, granice upozorenja (0,0063 – 0,0145)

$R_{(SVIH\ 86\ LAB\ )} = \pm 0{,}0075$, granice upozorenja (0,0029 – 0,0179)

Rezultat mjerenja u našem laboratoriju: 0,0100 mgKOH/g

Ako naš rezultat iskažemo uz proširenu mjernu nesigurnost $U_{(UK)}$ = 0.00122 mgKOH/g, dobivamo raspon mjernog rezultata od 0,00878 – 0.01122 mgKOH/g uz vjerojatnost od 95%.

ASTM UZORAK JF0007

Točna vrijednost: 0,0025 mgKOH/g (srednja vrijednost 106 laboratorija)

$R_{(ASTM\ metode)} = \pm 0{,}0020$, granice upozorenja (0,0005 – 0,0045)

$R_{(SVIH\ 106\ LAB\ )} = \pm 0{,}005$, granice upozorenja (0,0025 – 0,0075)

Rezultat mjerenja u našem laboratoriju: 0,0020 mgKOH/g

Ako naš rezultat iskažemo uz proširenu mjernu nesigurnost $U_{(UK)}$ = 0.00122 mgKOH/g, dobivamo raspon mjernog rezultata od 0,00078 – 0.00322 mgKOH/g uz vjerojatnost od 95%.

4. ZAKLJUČAK

4.1 Iz dobivenih podataka proizlazi da najveći doprinos ukupnoj mjernoj nesigurnosti potječe od volumena za titraciju uzorka V_{T2} .

4.2 Iz rezultata dobivenih eksperimentalnim određivanjem ukupne kiselosti goriva za mlazne motore i izračunatih mjernih nesigurnosti za svaki pojedini rezultat, može se vidjeti utjecaj volumena V_{T2} na mjernu nesigurnost. Najmanja utvrđena mjerna nesigurnost iznosi 0,0002mgKOH/g a najveća 0,0006mgKOH/g.

4.3 Pridruživanjem proširene mjerne nesigurnosti rezultatu dobivenom na ASTM uzorku u okviru međulaboratorijskog ispitivanja vidljivo je da su naši rezultati u granicama obnovljivosti definiranih metodom.

4.4 Mišljenja smo da je u analitičkoj kemiji gotovo nemoguće kvantificirati sve izvore (doprinose) nesigurnosti jer oni međusobno nisu nezavisni. Treba razmisliti o primjeni praktičnijih načina i korištenju podataka o reproducibilinosti za procjenu mjerne nesigurnosti.

Tablica 6: Program za računanje sastavljene mjerne nesigurnosti
Table 6: Program for calculating compounded measurement uncertainity

TOTAL ACIDITY DETERMINATION IN AVIATION TURBINE JET FUEL: MEASUREMENT UNCERTAINTY ESTIMATION

Abstract

The paper describes the procedure of measuring uncertainty evaluation in the results of total acidity in fuel samples for aviation turbine engines. An analysis has been performed of uncertainty sources contributing to total acidity determination by titration method.

Reliable and comparable measurement data are important for making decisions on fuel quality. Measurement results are incomplete without an evaluation of their uncertainty, which is a quantitative indicator of the results' reliability.

Uncertainty evaluation may be confusing, because there is no uniform procedure for its elaboration. Testing laboratories may use the concept of measurement uncertainty as an addition to the traditional approach to statistical control of the measurement procedure.

Through a systematic following of references, seminars and mutual discussions, we have made considerable efforts towards understanding the problem itself, as well as the application of the very procedure of evaluation. We have elaborated the standard method for which we have validation data and interlaboratory comparison data (ASTM-Interlaboratory Crosschecking Program). While evaluating the measurement uncertainty of results during the determination of total aciditiy in aviation turbine fuel, we have been guided by recommendations of EURACHEM/CITAC Guide: »Quantifying Uncertainty in Analytical Measurement».

The paper would like to show that the data on measurement uncertainty represent yet another way of statistical testing control, which - in combination with the measures of precision (repeatability and reproducibility) - deals with the accuracy of chemical analysis and improves the quality control system in laboratories.

1. INTRODUCTION

The HRN EN ISO/IEC 17 025 standard [5] prescribes that testing laboratories should have procedures for estimating the measurement uncertainty and apply them.

Measurement uncertainty is a parameter joined to the measurement result marking the dissipation of values and may be reasonably ascribed to the measured value [8].

The purpose of performing the analysis is to determine the measurement uncertainty of the standardized laboratory method on the basis of available data. Generally speaking, the measurement uncertainty includes several components. Some of

them may be estimated from the statistical distribution of results of a number of measurements and may be marked by experimental standard deviation (type A). Estimations of other components, which may also be marked by standard deviation, are estimated based on supposed probability distributions, experience, or other pieces of information (type B).

In the present paper, in order to calculate individual components of measurement uncertainty, we have used the following equations, eventually incorporated into the computer software for calculating measurement uncertainty:

a) When the uncertainty component is determined based on a series of repeated measurements, the standard deviation of medium measurement value is used for calculating standard uncertainty according to the following equation:

$$s_{\bar{x}} = \frac{s(x)}{\sqrt{n}} \quad (1)$$

b) In case of uncertainty components not determined by a series of observations (experimentally), the ascribed uncertainty has been estimated based on the data form gauges, certificates, technical data, manuals. From this data, and the assumed probability distribution, we have calculated the standard uncertainty (e.g. the purity of standard substance).

c) Thus incorporated uncertainty has been calculated according to the following equations:

$$u(y) = \sqrt{u(p)^2 + u(q)^2 + ...} \quad (2) \qquad u_c(y) = y\sqrt{\left[\frac{u(p)}{p}\right]^2 + \left[\frac{u(q)}{q}\right]^2} \quad (3)$$

where y is the measured value, p and q are the uncertainty components or measurement model parameters.

d) Widened uncertainty (U) is the last step in calculating the measurement uncertainty. It provides the interval encompassing the widest fraction of value distribution that may be ascribed to the measured value.

It is obtained by multiplying composed uncertainty $u_c(y)$ with the selected coverage factor (k):

$$U = k * u_c(y) \quad (4)$$

Usually, k amounts to 2 - 3, but may also have other values. When the probability distribution is normal, the k=2 choice shall encompass the range with the reliability level of 95%.

The measurement uncertainty estimation procedure encompasses the following basic steps:

Step 1: defining the measurement (what is being measured)

Step 2: recognizing the source of uncertainty

Step 3: quantifying the uncertainty source of individual components
Step 4: calculating the measurement uncertainty (composed and widened)

2. Estimation procedure and analysis of the measurement uncertainty components

2.1 Step 1: Defining the Measurement

Description of the Measurement Procedure
The sample is dissolved in a mixture of toluene and isopropyl alcohol containing a small volume of water. Into this colourless solution, a nitrogen flow is being introduced and titrated with a standard KOH solution up to the final titration point indicated by change of colour (orange in the acid and greenish-brown in the alkali), with the addition of indicator p-naphtolbenzene. KOH is standardized using potassium-hydrogen phtalate (KHP). Detailed procedure is described in the ASTM D 3242 method.

The measured value is the total acidity (TA) of jet fuel. It depends on KHP mass, its purity, molecular mass of KOH and KHP, KOH volume at the equivalence point and sample mass.

Mathematical dependence among the said values is calculated from the following equation:

$$\mathrm{TA} = \frac{1000 \times m_{KHP} \times P_{KHP} \times V_{T2} \times M_{KOH}}{M_{KHP} \times V_{T1} \times m_{SAMPLE}} \cdot [mgKOH / g] \cdots (5)$$

where:

1000 - conversion factor g $\rightarrow$ mg
m_{KHP} - weighted mass of potassium-hydrogen phtalate (KHP), g
P_{KHP} – purity of potassium-hydrogen phtalate (KHP)
V_{T2} - volume of potassium alkali (KOH) for sample titration, ml
V_{T1} - KOH volume for KHP titration, ml
M_{KHP} – molar mass of potassium-hydrogen phtalate (KHP), gmol-1
M_{KOH} - molar mass of potassium alkali (KOH), gmol-1
m_{SAMPLE} - weighted mass of jet engine fuel (JF1), g
TA – total acidity, mgKOH/g

2.2 Step 2: Recognizing Sources of Uncertainty

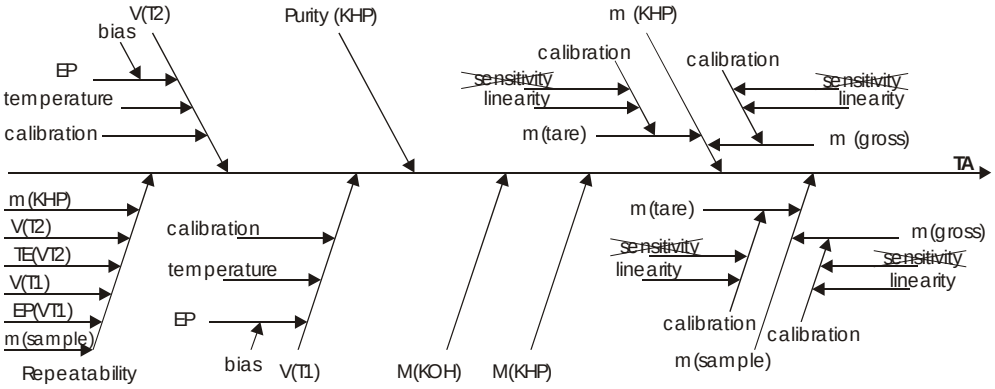
From the equation for calculating the measured value (5), result the measurement uncertainties, which are best shown in a diagram of causes and effects (Figure 1)

The calculation of the measurement uncertainty of data obtained through the selected method encompasses the following sources of uncertainty:

1. uncertainties of the standard substance mass -KHP and sample mass (type B)
2. uncertainties of molar masses (type B)

3. uncertainty of the standard substance purity - potassium-hydrogen phtalate (type B)
4. uncertainty of volume for the titration of standard substance (type B,B,A)
5. uncertainty of volume for the titration of sample (type B,B,A)
6. uncertainty of the measurement repeatability (type A)

Figure 1



2.3 Step 3: Quantification of the Given Components' Uncertainty Sources

2.3.1 Mass of the standard substance - potassium-hydrogen phtalate (KHP) and sample mass (GM1)

From the technical data supplied by the balance manufacturer, we have taken the linearity contribution of ± 0.15 mg. This value constitutes the maximal difference between the real mass on the balance and the one being read off. Linearity contribution assuming a rectangular distribution turns into standard uncertainty:

$$\frac{0.15mg}{\sqrt{3}} = 0.087 \text{ mg}$$

Linearity contribution has to be taken into account twice, once for tare and once for gross mass, which yields uncertainty

$u(m_{KHP}) = u(m_{SAMPLE}) = \sqrt{2 \times (0.087)^2} = 0.12\text{mg} = 0.00012 \text{ g}$

2.3.2 Molar Mass

Atomic masses and their pertaining uncertainties have been taken from IUPAC's tables.

$u(M_{KHP}) = \sqrt{(8\times 0{,}00046)^2 + (5\times 0{,}00004)^2 + (4\times 0{,}00017)^2 + 0{,}000058^2}$ =0.0038 gmol^{-1}

$u(M_{KOH}) = \sqrt{0{,}000058^2 + 0{,}00004^2 + 0{,}00017^2}$ = 0.00026 gmol^{-1}

2.3.3 Standard Substance (K-hydrogen phtalate) Purity

Purity (P) of the K-hydrogen phtalate according to supplier certificate is P = 1.0000 ± 0.0005.

The said uncertainty has been taken as rectangular distribution and the standard uncertainty calculated:

$$u(P_{KHP}) = \frac{0.0005}{\sqrt{3}} = 0.00029$$

2.3.4 Volume (V_{T1}) of KOH for the Titration of Standard Substance - potassium-hydrogen phtalate - (three contributions)

Titration is performed using automatic burette of 50ml. The contributions affecting the accuracy of added volume are: burette calibration, volume change caused by the difference between burette calibration temperature and operating temperature, aberrations in volume addition.

a) burette calibration - volume 50 ml

For standard uncertainty of burette calibration we have used the information stated by its manufacturer for the volume addition accuracy: A = ± 0.2 % ⇒ a = ± 0.1 ml

Implying a triagonal distribution, the standard uncertainty amounts to:

$$\frac{0.1ml}{\sqrt{6}} = 0.041\text{ml}$$

b) temperature

According to the manufacturer, the burette was gauged at 20^{o}C, while the operating temperature differs on the average by ±4 ^{o}C. The isopropyl alcohol volume expansion coefficient α = 1,016∗10^{-3}, and the volume of alk. KOH used for titration of the standard while determining normality V_{T1} = 5,38 ml (sample 10, table 5). Standard uncertainty has been calculated based on the assumption of a rectangular distribution for temperature change:

$$5{,}38 \text{ x } 1{,}016*10^{-3} \text{ x } 4 / \sqrt{3} = 0.013 \text{ ml}$$

c) repeatability

Measurement uncertainty of the added KOH volume for the titration of standard substance has been determined through a series of appraisals of the same volume (Table 1).

From the obtained standard deviation, we have calculated the standard uncertainty according to the following equation (1).

Table 1

N° of measurements	V_{KOH}, mL	m, g
1	5	3,881
2	5	3,916
3	5	3,898
4	5	3,883
5	5	3,900
6	5	3,853
7	5	3,929
8	5	3,873
9	5	3,902
10	5	3,899
	arithmetic mean:	3,893
	standard deviation	0,022
	standard uncertainty	0,0069

The above three contributions have been incorporated into volume uncertainty (V_{T1}) according to the equation (2).

$$u(V_{T1}) = \sqrt{u(\text{calibration})^2 + u(\text{temperature})^2 + u(\text{repeatability})^2}$$

$$u(V_{T1}) = \sqrt{0.041^2 + 0.013^2 + 0.0069^2}$$

$$u(V_{T1}) = 0.0436$$

2.3.5 Volume (V_{T2}) for Sample Titration (Three Contributions)

a) burette calibration - volume 50 ml

For standard uncertainty of burette calibration we have used the information stated by the manufacturer for volume addition accuracy: A = ± 0.2 % ⇒ a = ± 0.1 ml

Assuming a triangular distribution, the standard uncertainty is:

$$\frac{0.1ml}{\sqrt{6}} = 0.041\text{ml}$$

b) temperature

According to the manufacturer, the burette was gauged at 20°C, while the operating temperature differs on the average by ±4°C. The isopropyl alcohol volume expansion coefficient $\alpha = 1{,}016 * 10^{-3}$, and the volume of alk. KOH used for titration of the sample V_{T2} = 0,087 ml (sample 10, Table 5). Standard uncertainty was

calculated based on the assumption of rectangular distribution for temperature changes:

$$0{,}087 \times 1{,}016 * 10^{-3} \times 4 / \sqrt{3} = 0.0002\text{ml}$$

c) repeatability

In order to determine the standard uncertainty of the measurement repeatability, a test of 5 titrations of the same sample has been performed. From the standard deviation obtained, we have calculated the standard uncertainty according to the equation (1).

Table 2

100 ml of sample	
N° of measurements	V_{KOH}, ml
1	2.05
2	2.07
3	2.17
4	2.13
5	2.14
arithmetic mean	2.112
standard deviation	0.05
standard uncertainty	0.022

The above three contributions were incorporated into volume uncertainty (V_{T1}) according to equation (2).

$$u(V_{T1}) = \sqrt{u(\text{calibration})^2 + u(\text{temperature})^2 + u(\text{repeatability})^2}$$

$$u(V_{T2}) = \sqrt{0.041^2 + 0.0002^2 + 0.022^2}$$

$$u(V_{T2}) = 0.0465\text{ml}$$

2.3.6 Repeatability of the Total Acidity Measurement

The measurement repeatability was determined by identifying total acidity on the same sample 10 times, as shown in Table 3. The said value may be taken directly (according to the recommendations of EURACHEM's manual) for calculating composed standard uncertainty for it contains different segments of the chosen measurement's repeatability.

According to data in Table 3, the standard uncertainty of the measurement amounts to:

$$\frac{0{,}00018}{\sqrt{10}} = 0{,}00006$$

Table 3:

n° of measurement	m_{sample}, g	V_{KOH}, ml	TA mgKOH/g
1	79.08	0.11	0.00144
2	80.45	0.09	0.00116
3	79.60	0.08	0.00104
4	79.55	0.09	0.00117
5	80.80	0.11	0.00141
6	79.58	0.10	0.00131
7	81.30	0.15	0.00131
8	80.52	0.12	0.00145
9	79.55	0.13	0.00158
10	80.42	0.13	0.00157
mean value			0.0013
standard deviation			0.00018
standard uncertainty			0.00006

2.4 Step 4: Calculating measurement uncertainty (composed and widened)

The calculated standard uncertainties were joined to the measurement values obtained while determining the total acidity of 15 jet fuel samples, calculating the measurement uncertainty for each sample (Table 5).

Table 4

	description	**value** x	standard uncertainty u(x)	relative standard uncertainty u(x)/x
rep	repeatability	1	0,00006	0,00006
m_{KHP}	KHP mass	0,02017 g	0,00012 g	0,0059
p_{KHP}	KHP purity	1,0	0,00029	0,00029
m_{KHP}	KHP molar mass	204,2212 g/mol	0,0038 g/mol	0,000019
v_{t2}	KOH volume for sample titration	0,087 ml	0,0465ml	0,5344
v_{t1}	KOH volume for KHP tiation	5,38 ml	0,0436 ml	0,0081
m_{sample}	sample mass	79,71 g	0,00012 g	1,5E-6
m_{KOH}	KOH molar mass	56,1094 g/mol	0,00026 g/mol	4,6E-6
TA	**total acidity**	0,00114 mgKOH/g	0,00061 mgKOH/g	0,5351

For calculation, we have applied a simple computer software described in EURACHEM's manual, shown in Supplement 1, Table 6. By introducing the

estimated uncertainties and experimental measurement data, we came up with the composed uncertainty for the given sample .

Table 4 shows the measured values obtained by determining total acidity of the sample, taking into account the greatest measurement uncertainty, their standard uncertainties, and their relative standard uncertainties.

Widened uncertainty U was calculated by multyplying the greatest composed measurement uncertainty with coverage factor k=2:

U (TA) = 0,00122 mgKOH/g

Table 5: Experimental data – total acidity

Sample Nº	m_{KHP}, g	V_{T1}, ml	N_{KOH}	m_{sample}, g	V_{T2}, ml	u (TA)	TA mgKOH/g
1	0,02016	7,45	0,013	78,37	1,247	0,00045	0,0118
2	0,02016	7,45	0,013	78,23	1,247	0,00045	0,0118
3	0,02016	7,45	0,013	78,28	0,291	0,00044	0,0028
4	0,02011	10,17	0,009	79,10	1,111	0,00032	0,0076
5	0,02011	10,17	0,009	78,73	1,341	0,00033	0,0092
6	0,02010	9,22	0,011	77,70	1,581	0,00037	0,0122
7	0,02010	9,22	0,011	79,53	1,427	0,00036	0,0107
8	0,02086	8,69	0,012	77,28	1,367	0,00041	0,0117
9	0,02086	8,69	0,012	77,72	1,347	0,00040	0,0114
10	0,02050	5,38	0,018	79,71	0,087	0,00061	0,0011
11	0,02083	5,86	0,017	80,46	0,127	0,00056	0,0015
12	0,01977	11,72	0,008	79,87	1,181	0,00027	0,0068
13	0,01977	11,72	0,008	79,28	1,767	0,00028	0,0103
14	0,01903	13,90	0,007	80,18	2,001	0,00023	0,0094
15	0,01903	13,90	0,007	81,29	0,817	0,00022	0,0038

3. Interlaboratory determinations of total acidity in jet fuel samples organized by ASTM using standard method

Department for the Oil Products Quality Control has for a number of years been taking part in interlaboratory testing of oil products, and the said method has constantly been monitored by the said test. A review of results achieved in that

period was shown on Graph 2, Supplement 2, where the z-value reveals the reliability of our data.

The ASTM Report [9] shows that our results are within the reproducibility given by the method even in cases when they are indicated with widened measurement uncertainty (Graph 4, Supplement 4).

ASTM SAMPLE JF9807

Exact value: 0.0104 mgKOH/g (mean value of 86 laboratories)

$R_{(ASTM\ method)} = \pm 0{,}0041$, warning limits (0.0063 – 0.0145)

$R_{(ALL\ 86\ LABS)} = \pm 0{,}0075$, warning limits (0.0029 – 0.0179)

Measurement result at our laboratory: 0.0100 mgKOH/g

If our result is shown with a widened measurement uncertainty $U_{(TA)} = 0.00122$ mgKOH/g, we obtain the measurement result range of 0.00878 – 0.01122 mgKOH/g with a 95% probability.

ASTM SAMPLE JF0007

Exact value: 0.0025 mgKOH/g (mean value of 106 laboratories)

$R_{(ASTM\ method)} = \pm 0{,}0020$, warning limits (0.0005 – 0.0045)

$R_{(ALL\ 106\ LABS)} = \pm 0{,}0050$, warning limits (0.0025 – 0.0075)

Measurement result at our laboratory: 0,0020 mgKOH/g

If our result is shown with a widened measurement uncertainty $U_{(TA)} = 0.00122$ mgKOH/g we obtain the measurement result range of 0.00078 – 0.00322 mgKOH/g with a 95% probability.

4. CONCLUSION

4.1 From the data obtained it turns out that the greatest contribution to total measurement uncertainty comes from the volume for sample titration V_{T2}.

4.2 From the results obtained through experimental determination of the total acidity of jet fuels and the calculated measurement uncertainties for each individual result, we may observe the impact of volume V_{T2} on the measurement uncertainty. The lowest determined measurement uncertainty amounts to 0,0002 mgKOH/g and the highest to 0.0006mgKOH/g.

4.3 By joining the widened measurement uncertainty to the result obtained on the ASTM sample within interlaboratory testing, one may observe that our results are within repeatability limits defined by the method.

4.4 It is our opinion that, in analytical chemistry, it is almost impossible to quantify all the sources (contributions) to uncertainty, for they are not mutually independent. One should think about applying more practical ways and using reproducibility data for the measurement uncertainty estimation.

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389.63 normizacija mjeriteljstva	standardization of measuring
665.743.3 mlazno gorivo GM 1	jet fuel
543.852 : 665.743.3 sadržaj kiseline u mlaznom gorivu	acidity in aviation turbine fuel

Autori/Authors.

Dunja Šeremešić, Dragica Grubić

INA-industrija nafte, d.d. Zagreb, Sektor strateškog razvoja, istraživanja i investicija

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