

EVALUATION OF MEASUREMENT UNCERTAINTY FOR THE METHODS OF ANALYSIS USED TO ASSESS THE CHARACTERISTICS OF OLIVE OIL AND OLIVE-POMACE OIL FROM COMMISSION REGULATIONS EEC 2568/91 AND EC 1989/2003 – A CASE SAMPLE EVALUATING THE MEASUREMENT UNCERTAINTY FOR PEROXIDE VALUE

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ABSTRACT

Metrology has been present in our scientific knowledge for a long time, but mostly in physical measurements. Chemical measurement can be defined as a comparison of a quantity of measurand and relating it to a unit (e.g. mol/kg). When expressing a result of a measurement, the problem of traceability, validation and the measurement uncertainty (MU) evaluation must be challenged. It is well known that MU is a parameter associated with the result of a measurement that characterizes the dispersion of the values that could reasonably be attributed to the measurand. The EEC document 2568/91 with its annexes gives the methods of analysis to assess the characteristics of olive oils and olive-pomace oils with given limits. The EC document 1989/2003 gives the scheme, the algorithm, the pathway, the decision tree to differentiate between various types of olive oils using the particular determinations based on limits. The major lack of these EC methods is the non-existence of validation parameters, which are crucial in determining the MU (and in accreditation of a laboratory). There are several ways of evaluating (better term than calculating) the MU: with model equation, with use of a certified reference material (CRM) and with participation in a proficiency testing (PT) scheme. MU for a method of analysis is inherent to a laboratory and can serve as a tool for "measuring" the quality of a laboratory. Unfortunately, there are practically no CRM's in the olive oil testing field. The only way to achieve a usable MU is through participation in PT schemes.

Key words: CRM, EEC 2568/91, EC 1989/2003, metrology, olive oil, PT scheme, uncertainty

VALUTAZIONE DELL'INCERTEZZA DI MISURA DI METODI DI ANALISI USATI
PER ACCERTARE LE CARATTERISTICHE DEGLI OLI D'OLIVA E DEGLI OLI
DI SANSÀ D'OLIVA SECONDO I REGOLAMENTI CEE 2568/91 ED CE
1989/2003 – ESEMPIO DI VALUTAZIONE DELL'INCERTEZZA DI MISURA
PER DELL'INDICE DI PEROSSIDO

SINTESI

La metrologia è parte della nostra conoscenza scientifica ormai da lungo tempo, specialmente nelle misurazioni fisiche. Le misurazioni chimiche possono venir definite come confronto fra la quantità della sostanza misurata e la relativa unità di misura (per es. mol/kg). Quando viene espresso il risultato di una misurazione, i problemi di rintracciabilità, convalida e incertezza di misurazione (MU) devono venir posti in primo piano. È ben noto che MU sia un parametro associato al risultato della misurazione che caratterizza la dispersione dei valori, che possono venir ragionevolmente attribuiti alla sostanza misurata. Il documento CEE 2568/91, con i suoi allegati, fornisce i metodi di analisi usati per valutare le caratteristiche degli olii d'oliva e degli olii d'oliva residui in confronto ai limiti prestabiliti. Il documento CE 1989/2003 fornisce lo schema, l'algoritmo, il percorso da seguire nel processo di differenziazione dei vari tipi di olii d'oliva, usando particolari determinazioni basate sui limiti. La maggior lacuna di tali metodi EC consiste nella non-esistenza di parametri convalidati, cruciali nella determinazione di MU (e per l'accreditamento del laboratorio). Ci sono vari modi di valutare (ossia calcolare) MU: con un'equazione modello, con l'uso di materiali di riferimento certificati (CRM) e con la partecipazione allo schema di verifica empirica competente (PT). MU come metodo di analisi è inerente al laboratorio e può venir utilizzato come strumento per la "misurazione" della qualità del laboratorio. Purtroppo, praticamente non ci sono CRM nel campo di verifica empirica dell'olio d'oliva. L'unica via per raggiungere un MU utilizzabile è dunque partecipare allo schema di verifica empirica competente.

Parole chiave: CRM, CEE 2568/91, CE 1989/2003, metrologia, olio d'oliva, schema PT, incertezza

INTRODUCTION

"Nosotros (la indivisa divinidad que opera en nosotros) hemos soñado el mundo. Lo hemos soñado resistente, misterioso, visible, ubicuo en el espacio y firme en el tiempo; pero hemos consentido en su arquitectura, tenues y eternos intersticios de sinrazón para saber que es falso." We believe this quote by Argentinean writer, poet and critic J. L. Borges (Borges, 1932), can serve as a good starting point for the introduction of the topic of this article, dealing with the measurement uncertainties in the field of olive oil characteristics assessment.

The term measurement uncertainty must be introduced from the metrological point of view and that is why some basic terms and definitions will be presented. Metrology is simply the Science of measurement, measurement being the "set of operations having the object of determining a value of a quantity" (MIRS, 2001), and it is nowadays part of every scientific process in all spheres of science, including chemistry and its role in the sustainable development of our Earth (Meinrath & Kalin,

2005). Consequently, chemical measurement is a comparison, quantification of the measurand – "particular quantity subject to measurement" (EURACHEM, 1999) and its traceability to the unit. There are several important differences between physical and chemical measurement and they arise from the fact "that in physical measurement the issue is to compare quantities (e.g. lengths of different tables) traceable to a unit (e.g. metre) and in chemical measurement the issue is to compare an amount of analyte (e.g. content of DDT in meat) traceable to a unit (e.g. mol/kg)", thus giving the importance to the calibration of the instruments in the physical measurements and to the measurement procedure calibration in chemical measurements (Taylor *et al.*, 2003). A chemical measurement has many crucial steps, among them sample preparation and sampling, preparation and physical calibration of the instrument, measurement, data handling and reporting of the results. Another term that must be understood is traceability, which "is a property of the result of a measurement or the value of a standard whereby it can be related to stated references,

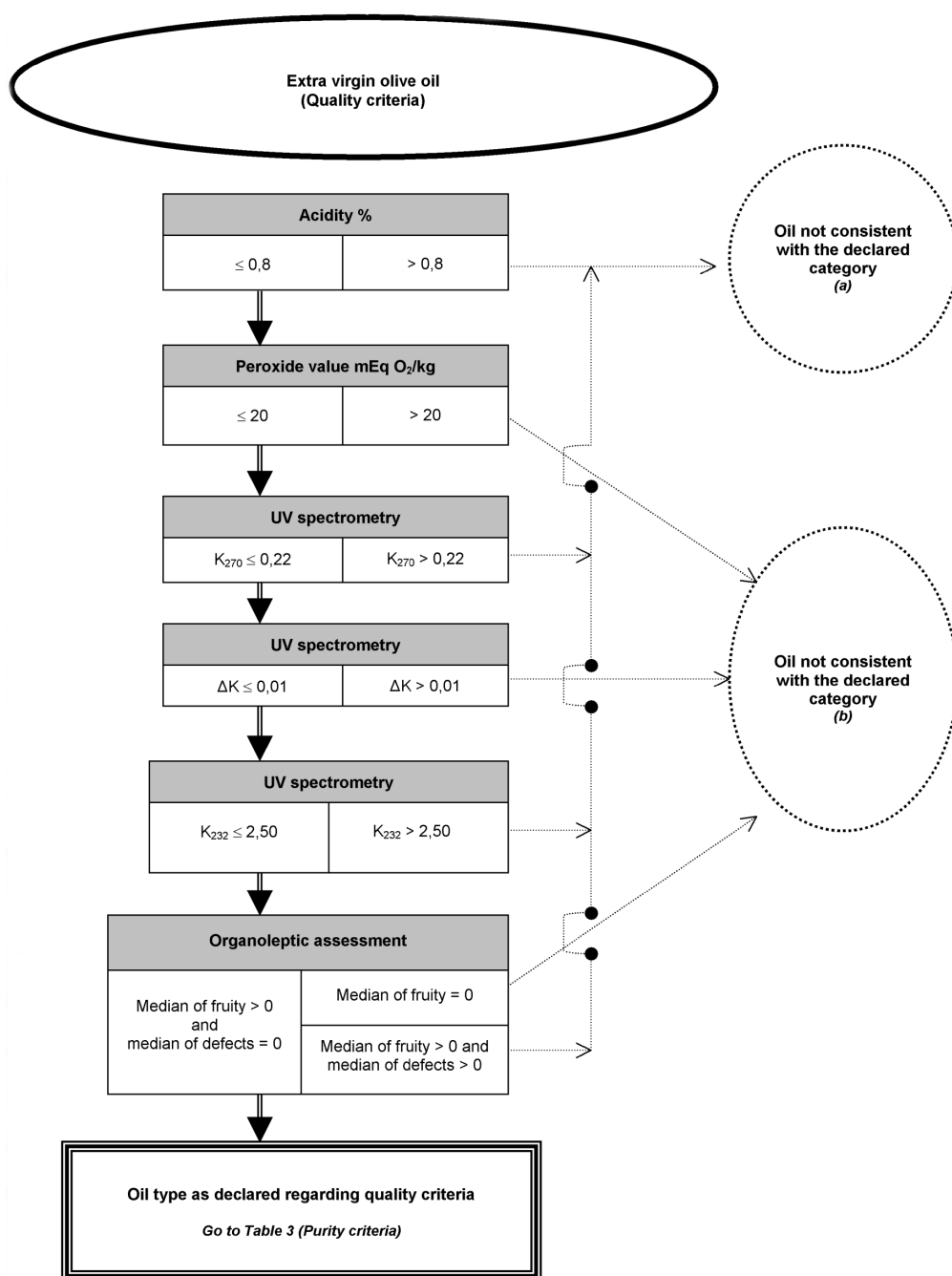


Fig. 1: Quality criteria for the extra virgin olive oil (EC 1989/2003, 2003).
Sl. 1: Kakovostni parametri za ekstra deviško oljčno olje (EC 1989/2003, 2003).

usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties." (ISO VIM, 1993). The next step in the proper understanding of the results of the chemical measurement is validation (of the method, of the instrument, of the software tools used ...), defined as "the confirmation by examination and provision of objective evidence that the particular requirements for a specific intended use

are fulfilled" (ISO/IEC 17025, 1999). Every (chemical) measurement result must be accompanied by "parameter associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand" – measurement uncertainty (ISO VIM, 1993).

Measuring uncertainty, which must accompany the result of a chemical measurement, is always connected

to the measurand, to the matrix characteristics, to the measuring – analytical method and concentration range as well. We deliberately did not want to enter into measuring uncertainty details like coverage factor, expanded uncertainty etc., but have instead tried to make the metrological concept of the measuring uncertainty as clear as possible.

The document "Regulation (EEC) No. 2568/91" (EEC 2568/91, 1991) and its amends give *inter alia* the methods of analysis and the limit values needed to assess the characteristics of olive and olive-pomace oil. The methods describe the way of performing chemical measurements in the quality field (*i.e.* the results show the quality of the oil in a declared category – e.g. extra virgin olive oil) and these are: acidity, peroxide value, UV spectrometry (K_{270} , ΔK , K_{232}) and in the purity field (the results show the consistency within declared category): 3,5-stigmastadienes, trans fatty acids (oleic, linoleic and linolenic), fatty acids content, $\Delta ECN42$, sterols composition and total sterols, erythrodiol + uvaol, waxes, saturated fatty acids in the 2-position, alcohols.

The document "Commission Regulation (EC) No. 1989/2003" (EC 1989/2003, 2003) gives the algorithm, the decision tree helping the assessor (analyst, laboratory manager, official inspector) in finding or judging the olive oil sample consistency with the declared category. There is another crucial value influencing the overall quality assessment – sensorial (organoleptic) assessment, but not being a chemical measurement it will not be discussed herewith. Figures 1 and 2 show the decision tree for the quality and purity criteria for extra virgin olive oil.

These methods of analysis have a big disadvantage in the light of the metrological point of view – they lack the validation parameters, which are the crucial point for many legal aspects of the testing laboratory comprising the accreditation documents. And here a sort of *circulus vitiosus* arises: how can a laboratory possibly come to these validation data? The only, although tedious way is to make the so called in-house methods and link them through traceable determinations and control samples to the mentioned methods of analysis from the document. And secondly, how to reach/determine all the needed (metrological and accreditation demand) uncertainty values for all methods of analysis?

It is well known that several approaches exist, some come from the uncertainty budget construction based on the model equations (Dehouck *et al.*, 2003; Tartacca *et al.*, 2003 (the only one dealing exclusively with olive

oils spectrophotometric determination); Clare, 2005; Populaire & Gimenez, 2006; Sooväli *et al.*, 2006), some use Certified Reference materials (CRM) (Gluschke *et al.*, 2005), some use data from the Inter Laboratory Comparisons (ILS) and/or Proficiency Testing (PT) schemes. A CRM is defined as "Reference material, accompanied by a certificate, one or more of whose property values are certified by a procedure, which establishes traceability to an accurate realization of the unit in which the property values are expressed, and for which each certified value is accompanied by an uncertainty at a stated level of confidence" (ISO VIM, 1993). Several definitions exist (Majcen, 2003) and lately there is a need for somehow more accurate definitions of CRM's (Emons *et al.*, 2006). In the olive oil field there are, unfortunately, practically no CRM's. There are ways, which a lab can take to solve this problem with the aid of control samples (Venelinov & Sahuquillo, 2006), but we cannot use this knowledge and experience at the beginning of the uncertainties evaluation – when the lab desperately needs it. All the approaches of uncertainty evaluation are to a minor or greater extent connected to the validation data (Hierro, 2003 (validation and uncertainty parameters for olive oils methods); Diaz *et al.*, 2004). It seems the only valid approach is the use of ILS/PT schemes. In the light of accreditation the PT schemes ("A periodic assessment of the performance of individual laboratories and groups of laboratories that is achieved by the distribution by an independent testing body of typical materials for unsupervised analysis by the participants." (EURACHEM, 1999) have somewhat "stronger" impact on the measurement uncertainty evaluation compared to the ILS ones. The "uncertainty" within the data used for the uncertainty evaluation arises from the possible inaccurate determination of the reference value, which is in the most cases assigned value (Wong, 2005; Patriarca *et al.*, 2006; Švegl *et al.*, 2006; Thompson & Wood, 2006; Thompson *et al.*, 2006), from the number and fitness of participants and from the quality of the organiser of the PT scheme. In the olive oil area there are, as far as we know, only 2 relevant organisers. One is the "International Olive Council" covering all the mentioned methods of analysis. It runs the PT scheme once a year and involves from 50-60 participants, which must be nationally approved labs within their respective countries. The other organiser is French "Bipea", which does not cover all the determinations and has somehow smaller number of participating labs and covers all types of fats on a monthly basis (10 samples per year).

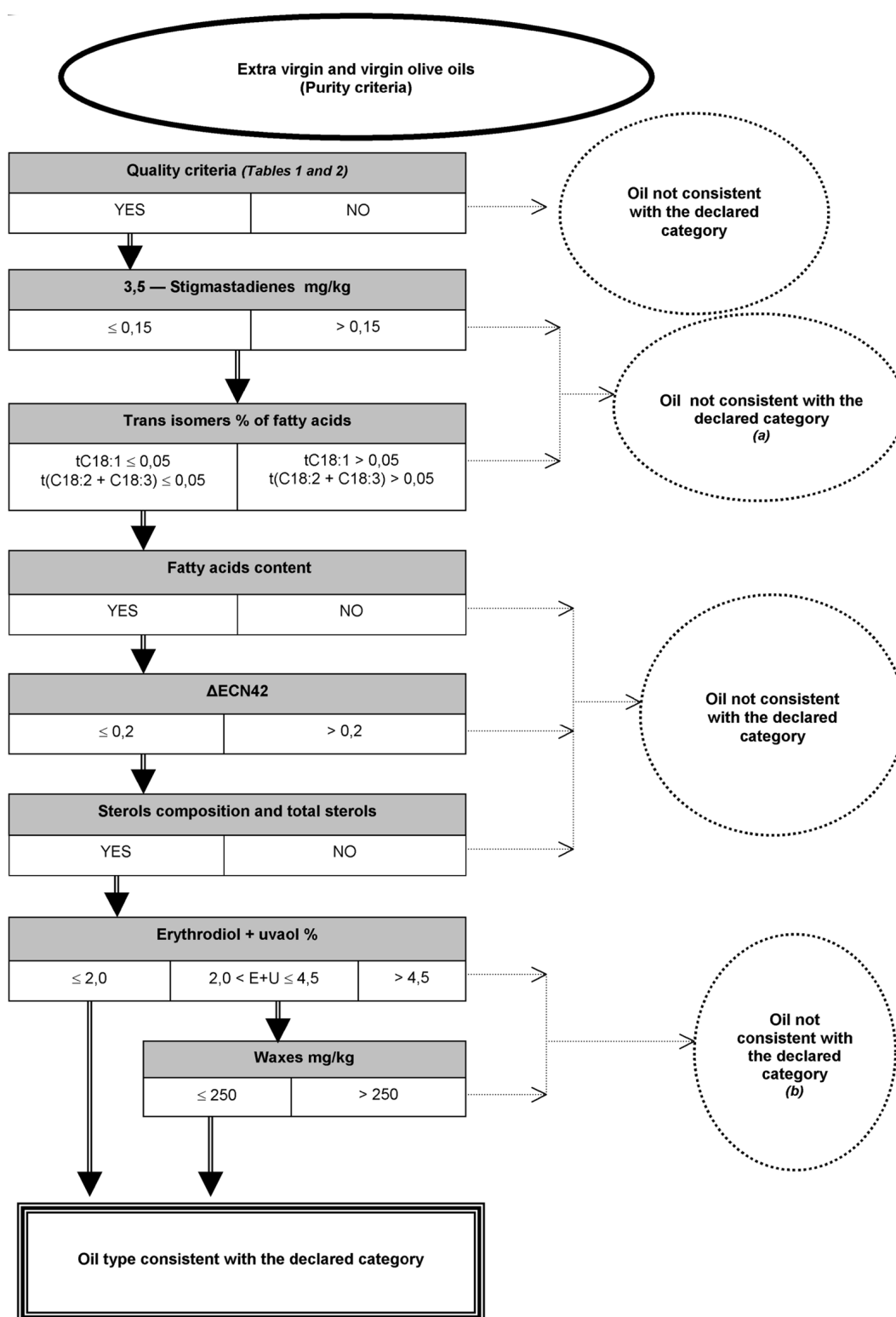


Fig. 2: Purity criteria for the extra virgin olive oil (EC 1989/2003, 2003).
Sl. 2: Parametri pristnosti za ekstra deviško oljčno olje (EC 1989/2003, 2003).

MATERIAL AND METHODS

For the purpose of this paper, only one method of analysis was chosen – determination of peroxide value – and the PT schemes' data for this method's results were used to evaluate the MU.

PT Schemes. The PT schemes our laboratory participated in were two:

- PT scheme organised by the International Olive Council (IOC), Príncipe de Vergara 154, 28002 Madrid (Spain);
- PT scheme organised by BIPEA, 6-14 avenue Louis Roche, F-92230 Gennevilliers, FRANCE; COFRAC accredited.

Samples. The determination of Peroxide value was performed in 9 oil samples in the years 2003, 2004 and 2005. The samples were as follows:

- IOC: sample 23-2003 (year 2003), 24-2004 (year 2004), 25-2004 (year 2004), 28-2005 & 29-2005 (year 2005);
- Bipea: sample B 21 358 (year 2004), B 21 359 (year 2004), B 21 360 (year 2004) & B 21 364 (year 2005).

Methods. The methods used were as follows:

- Method of Analysis – Determination of the peroxide value, EEC No. 2568/91, Annex III (EEC 2568/91, 1991);
- Statistical tools:
 - ISO 5725-2 (1994) Accuracy (trueness and precision) of measurement methods and results—Part 2: Basic method for the determination of repeatability and reproducibility of a standard measurement method. International Organization for Standardization (ISO), Geneva, Switzerland (ISO 5725-2, 1994);
 - ISO/DIS 13528 (2002) Statistical methods for use in proficiency testing by interlaboratory comparisons. International Organization for Standardization (ISO) Geneva, Switzerland (ISO/DIS 13528, 2002).
- Guides:
 - EURACHEM/CITAC Guide Quantifying Uncertainty in Analytical Measurement (EURACHEM, 2000);
 - Handbook for calculation of measurement uncertainty in environmental laboratories (Nordtest, 2004).

The method of analysis – determination of peroxide value is a redox titration where peroxides (hydro peroxides) present in the oil that is dissolved in acetic acid and chloroform react with potassium iodide oxidising it to free iodine. The iodine is titrated with standardized sodium thiosulfate solution and the peroxide value expressed in meq (mmol) of active oxygen/kg oil.

The method of analysis was used to measure – determine the Peroxide value in the samples. Guides (Eurachem, 2000; Nordtest, 2004) were used to construct the uncertainty budget for the Peroxide value determination. The statistical tools - 2 ISO standards (ISO 5725-

2, 1994; ISO/DIS 13528, 2002) helped us in calculating the robust means and robust standard deviations for each PT scheme and in calculating the intra-laboratory standard deviation.

RESULTS AND DISCUSSION

The measurement uncertainty evaluation of the measurand A is a property of the laboratory lab performing the chemical measurement based on the method M and is generally based on two relatively independent sources – the method M , under which the chemical measurement is made, and the laboratory lab that performs the chemical measurement. The combined uncertainty of the chemical measurement of measurand A - u_A is function of the uncertainty u_M arising from the method and uncertainty u_{lab} arising from the lab. u_A is calculated from the equation:

$$u_A = \sqrt{(u_M)^2 + (u_{lab})^2} .$$

There are several ways of calculating u_M :

- a) from the CRM
- b) from the model equation after constructing the uncertainty budget
- c) from method validation data
- d) from the method validation data combined with PT schemes' results – from the organisers side (Hierro, 2003)
- e) from the single or few PT schemes' results from the participants side and u_{lab} :
- f) from the CRM
- g) from the PT scheme
- h) from the recovery data

Two different measurement uncertainty evaluations (together with respective calculations and results) were used in our lab, and we show them briefly herewith.

First type of evaluation

At the beginning of our lab's activity we had the lack of validation data, we were not in possession of any CRM's and we participated in only one PT scheme (1 single determination). We were forced to use the combination of b) and g) calculation approach. We used the model equation

$$PV = 3000 \times \frac{(V - V_{bi}) \times V_p \times m_0 \times P}{m \times M_{KIO_3} \times V_0 \times V_b}$$

for the calculation of the peroxide value. Each variable's standard uncertainty was calculated according to EURACHEM guide's (EURACHEM, 2000) using the equation for the standard uncertainty of the sum. The value $(V - V_{bi})$ was expressed as DV and its uncertainty was calculated likewise. The repeatability element (REP) was calculated from the validation data (Tab. 1).

With the aid of the EURACHEM guide's (EURACHEM, 2000), basic equation

$$u_M(y) = y \sqrt{\left(\frac{u(DV)}{DV}\right)^2 + \left(\frac{u(V_p)}{V_p}\right)^2 + \left(\frac{u(m_0)}{m_0}\right)^2 + \left(\frac{u(P)}{P}\right)^2 + \left(\frac{u(m)}{m}\right)^2 + \left(\frac{u(M_{KIO_3})}{M_{KIO_3}}\right)^2 + \left(\frac{u(V_0)}{V_0}\right)^2 + \left(\frac{u(V_b)}{V_b}\right)^2 + \left(\frac{u(REP)}{REP}\right)^2} \dots$$

and spreadsheet calculation modification by Kragten (Ellison, 2005) for the calculation of the differentiation:

$$u_M(y, x_i) \approx y(x_1, x_2, \dots, (x_i + u(x_i)), \dots, x_n) - y(x_1, x_2, \dots, x_n)$$

the result for combined standard uncertainty was evaluated as $u_A = u_{PV} = 0,0617$ mmol/kg.

Tab. 1: The spreadsheet results for the calculation of the combined standard uncertainty for PV.

Tab. 1: Rezultati pregledničnega izračuna sestavljene standardne negotovosti za PŠ.

	DV (mL)	Vp (mL)	mo (mg)	P (mol/mol)	m (g)	M (g/mol)	V0 (mL)	Vb	REP	
Value	9,9756	10,0046	50,0000	1,0004	5,0000	214,0010	5,6000	250,0082	1,0000	
Uncertainty	0,0130	0,0102	0,0099	0,0011	0,0000	0,0005	0,0088	0,1517	0,0056	
DV (mL)	9,9756	9,9886	9,9756	9,9756	9,9756	9,9756	9,9756	9,9756	9,9756	
Vp (mL)	10,0046	10,0046	10,0148	10,0046	10,0046	10,0046	10,0046	10,0046	10,0046	
mo (mg)	50,0000	50,0000	50,0000	50,0099	50,0000	50,0000	50,0000	50,0000	50,0000	
P (mol/mol)	1,0004	1,0004	1,0004	1,0004	1,0015	1,0004	1,0004	1,0004	1,0004	
m (g)	5,0000	5,0000	5,0000	5,0000	5,0000	5,0000	5,0000	5,0000	5,0000	
M (g/mol)	214,0010	214,0010	214,0010	214,0010	214,0010	214,0015	214,0010	214,0010	214,0010	
V0 (mL)	5,6000	5,6000	5,6000	5,6000	5,6000	5,6000	5,6088	5,6000	5,6000	
Vb	250,0082	250,0082	250,0082	250,0082	250,0082	250,0082	250,0082	250,1599	250,0082	
REP	1,0000	1,0000	1,0000	1,0000	1,0000	1,0000	1,0000	1,0000	1,0056	
PV	9,9971	10,0102	10,0073	9,9991	10,0081	9,9971	9,9971	9,9814	9,9911	10,0530
u(y,xi)		0,0131	0,0102	0,0020	0,0110	0,0000	0,0000	-0,0158	-0,0061	0,0559
u(y)2, u(y,xi)2	0,0038	0,0002	0,0001	0,0000	0,0001	0,0000	0,0000	0,0002	0,0000	0,0031
index		0,0449	0,0271	0,0010	0,0317	0,0000	0,0000	0,0652	0,0097	0,8203
u(PV)	0,0617									
U(PV)	0,1234									

Figure 3 shows relative contribution of each uncertainty parameter from the model equation. It can be clearly seen that the biggest impact on $u_M = u_{PV}$ has the repeatability (data derived from method validation).

Combining these data for u_{M_i} : $u_{PV}/PV = 0.0617/9.9971 = 0.6172\%$ with the u_{lab} data from the IOC 2004 scheme – bias% = 2.919% and adopting the equation

$$u_A = \sqrt{(u_M)^2 + (u_{lab})^2}$$

we calculate the value = 3.045%. After converting the combined standard uncertainty to the expanded uncertainty, U, using coverage factor of k=2 and reporting 2 significant digits, the result becomes PV = 10.00 ± 0.61 mmol/kg.

Second type of evaluation

After the successful participation in different PT schemes and after gathering all the data from control charts and after calculating the intra-laboratory (=within laboratory) standard deviation, we were able to evaluate somehow more complex estimation of the expanded standard uncertainty for the determination of the peroxide value. We used the combination of e) and g). The

labs uncertainty changed as well. We used the bias data not only from a single, but from a few PT schemes we participated in – in all 9. The same goes for the e). Using the guide (Nordest, 2004), robust statistics for the calculation of the robust means and robust standard deviations for each PT scheme – algorithm A (ISO/DIS 13528, 2002), we were able to calculate all the values and set the following Table 2.

After calculating the intra-laboratory (=within laboratory) standard deviation S_{Rw} from control charts with the aid of (ISO 5725-2, 1994), which was 6.039451 %, we had all the necessary data for the uncertainty calculation. We had to calculate the "bias" uncertainty u_{bias} from laboratory bias

$$\left(RMS_{bias} = \sqrt{\frac{\sum bias_i^2}{n}} \right)$$

and the method bias (C_{ref}) using equation

$$u_{bias} = \sqrt{RMS_{bias}^2 + u(C_{ref})^2}$$

We calculated the method bias from the pooled robust relative standard deviations from the schemes and the laboratory bias from the Bias% data from Table 2.

Tab. 2: Robust statistics data for samples from different PT schemes. Legend: X_{ref} = assigned value; X_{lab} = our labs value; Bias% = relative percentage difference between X_{lab} and X_{ref} ; Szv% = relative robust standard deviation of the set; n labs = number of labs participating.

Tab. 2: Podatki robustne statistike za vzorce iz različnih shem PT. Legenda: X_{ref} = assignirana vrednost; X_{lab} = podatek našega laboratorija; Bias% = relativni odstotni odmik med X_{lab} in X_{ref} ; Szv% = relativni robustni standardni odmik niza; n labs = število sodelujočih laboratorijev.

Year	Sample	Xref	Xlab	Bias %	Szv %	No. labs
2003	coi 23-03	5.31	5.46	2.92	7.72	48
2004	coi 24-04	1.65	0.99	-40.30	28.06	48
2004	coi 25-04	4.68	4.01	-14.23	10.50	48
2005	coi 28-05	6.34	6.23	-1.74	7.45	49
2005	coi 29-05	4.54	4.21	-7.27	7.45	49
2004	B_21_360	2.05	2.15	4.88	24.39	8
2004	B_21_358	0.80	1.25	56.25	75.00	6
2004	B_21_359	3.65	4.15	13.70	52.06	5
2005	B_21_364	4.45	4.85	8.99	29.21	8

Finally we combined the bias uncertainty data with intra-laboratory standard deviation S_{RW} data using equation

$$u_{PV} = \sqrt{u_{bias}^2 + s_{RW}^2}.$$

In this way calculated combined uncertainty was quite elevated, so we had a detailed look at the data. After inspecting the PV ranges, we decided to split the data and uncertainty evaluation in two different concentration ranges: from 0–2 mmol/kg and from 2–10 mmol/kg. The 2 to 10 mmol/kg range has the calculated expanded uncertainty U with the coverage factor of k=2 for the value 9.9971 of 1.8 mmol/kg, so the result reads $PV = 10.0 \pm 1.8$ mmol/kg.

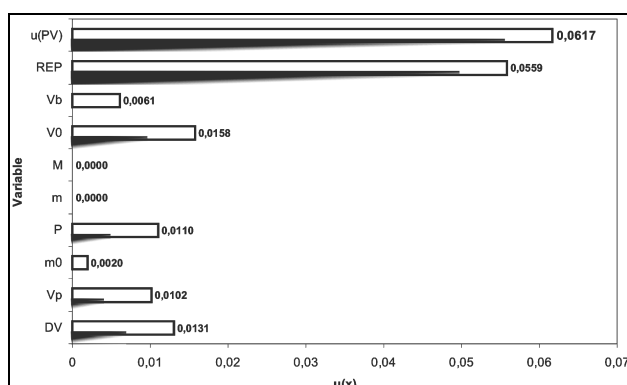


Fig. 3: Relative contribution of each uncertainty parameter from the model equation.

Sl. 3: Relativni prispevek posameznih segmentov negotovosti.

CONCLUSIONS

Considering both types of evaluation, it can easily be concluded that the first evaluation has much smaller U when compared to the second one. It is obvious that the partial components from the uncertainty budget have very limited influence compared to the repeatability influence, which is again relatively small compared to the laboratory (bias) influence from the PT scheme(s). On the other hand, of a real value are only repeatability (within-laboratory reproducibility) data from many years' control charts and results from PT schemes – in the lack of CRM's – giving us data for the method and laboratory uncertainty. So, if the lab wants to have relatively small U, it will have to emphasize its repeatability demands on their control charts, participate in good PT schemes and it will have to be able to afford itself to ignore certain schemes' results (the ones where the method uncertainties are relatively big compared to its own proficiencies). This is the only way to real, realistic and relatively small measurement uncertainties.

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OVREDNOTENJE MERILNE NEGOTOVOSTI ANALIZNIH METOD ZA UGOTAVLJANJE ZNAČILNOSTI OLJČNEGA OLJA IN OLJA IZ OLJČNIH TROPIN IZ UREDB EGS 2568/91 IN ES 1989/2003 – PRIMER OVREDNOTENJA MERILNE NEGOTOVOSTI PEROKSIDNEGA ŠTEVILA

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POVZETEK

Pred vsako meritvijo moramo biti prepričani, ali vemo, v kateri del stvarnosti, v katero področje fizičnega sveta, sodi. Zdaj postaja samoumevno, da tvori znanstveno disciplino, ki ji pravimo meroslovje. Meroslovje je v naši (znanstveni) zavesti že dlje časa, a ga kemiki nikoli nismo jemali dovolj resno, da bi se pri svojih rezultatih, kaj šele pri meritvah, z njim zares ukvarjali. Meroslovje je del znanstvenega procesa v vseh sferah znanosti in zatorej tudi kemije. Kemijsko merjenje je torej primerjava količine merjenca (npr. alfa-tokoferol v oljčnem olju) in njegova naveza na enoto (npr. mol/kg, mg/kg). Pri podajanju rezultata merjenja nastane problem sledljivosti – kako smo lahko zares prepričani, da je rezultat našega merjenja primerljiv z rezultati drugih, ki merijo isto veličino, in seveda obrnjeno. Na koncu uganke in po obdelavi drugega velikega vpliva na kakovost naše meritve (in rezultata) – validacije – leži ovrednotenje merilne negotovosti (OMN). MN je lastnost rezultata merjenja, ki določa, znotraj katerih meja okrog izmerjene veličine se skriva pravi rezultat (in s kakšno verjetnostjo). Dokument EGS 2568/91 s svojimi prilogami podaja analize metode za ugotavljanje značilnosti oljčnega olja in olja iz oljčnih tropin ter določa meje za posamezne kategorije le-tega. Dokument ES 1989/2003 pa podaja analitsko shemo, algoritem in pot za razlikovanje – kategoriranje posameznih kakovostnih razredov oljčnega olja glede na določene meje. Velik manko evropskih metod je dejstvo, da ni validacijskih parametrov, ki so ključni pri OMN (in pri postopku akreditiranja laboratorija za posamezno metodo).

Več načinov za OMN je: način z uporabo modelne enačbe, z uporabo CRM-jev in s sodelovanjem v shemah PT, ki pa so najbolj problematične – problem asignirane vrednosti. Prava pot navadno leži v trikotniku med vsemi tremi (samo dvema pri večini preskusov pri oljčnih oljih). OMN za posamezno metodo preskušanja je lastna laboratoriju in naj bi rabila za njegovo kakovostno umestitev "na trgu". A žal je v polju preskušanja oljčnih olj pomanjkanje ustreznih CRM-jev zelo pereče. Tako je edina pot, ki jo lahko uberemo do ovrednotenja MN, pot sodelovanja v shemah PT. Mednarodni svet za oljčno olje (IOC) je pomagal pripraviti dokument "Evaluation of the uncertainty of measurements and the critical difference: applications to analytical parameters", katerega avtor je Jose Ramon Garcia Hierro, ki s pomočjo izračunanih/določenih OMN laboratorijem olajša delo. Njihova »edina« skrb je tako zmanjšanje odstopanja od prave vrednosti oziroma povečanje točnosti. Večletne izkušnje našega laboratorija pri sodelovanju v shemah usposobljenosti – IOC, Madrid in Bipea, Francija, so nam pomagale pri postavitvi naših lastnih OMN, ki se nenehno izboljšujejo (problem najšibkejšega člana).

Ključne besede: CRM, EGS 2568/91, ES 1989/2003, metrologija, negotovost, oljčno olje, shema PT

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