

EVALUATION OF MEASUREMENT UNCERTAINTY FOR THE MOISTURE AND DRY MATTER MASS FRACTION IN INDUSTRIAL RESIDUES AND SLUDGES

Filomena C. Mouro¹, Sandra C. Calisto¹, Maria A. Trancoso¹

¹ LNEG – Laboratório Nacional de Energia e Geologia, IP., Lisbon, Portugal, maria.trancoso@ineti.pt

Abstract – Moisture mass fraction, w_{H_2O} , and dry matter mass fraction, w_{DM} , are analytical parameters required by environmental European regulations. The metrological quality, namely measurement uncertainty, comply the fitness for purpose and enhances the comparability of analytical results. In this work, the component by component approach for measurement uncertainty estimation of w_{H_2O} and w_{DM} is reported and the input quantities assessed. The measurement uncertainty of method's precision, under within-laboratory reproducibility conditions, $f(\text{precision})_{RW}$, was the only significant influence quantity when $w_{H_2O} > 0,10 \text{ g g}^{-1}$ for both ranges. In case of $w_{H_2O} \leq 0,10 \text{ g g}^{-1}$, the mass of the capsule containing sample after the drying step, $m_{(C+S)dry}$, has also a relevant contribution. Simplified models are proposed.

Keywords: uncertainty, moisture, dry matter, mass fraction.

1. INTRODUCTION

In environmental monitoring and chemical characterization of products and wastes the analytical results should be expressed in a dry basis, in order to improve comparability and to allow conformity evaluation. On the other hand, the compliance test for leaching of granular waste materials and sludges needs a liquid to solid ratio, being the solids reported to a dry basis, although the wet sample must be used. For example the ISO 12457-4:2002 [1] requires a liquid to solid ratio of 10 L kg⁻¹, for material with particle size below 10 mm, using a raw solid test portion containing 0,100 kg of dry mass per litre of leachant water, being the moisture mass fraction determined in parallel using a test portion different from the test portion for leaching.

The Portuguese Decree-law N. 152/2002 [2] defines some acceptance criteria for residues disposal in landfills, where the moisture mass fraction at 105 °C is one of them, allowing the residue classification as either inert or hazardous [3]. The Portuguese Decree-law N. 118/2006 [4] based on the European Directive 86/278/EC [3], describes

the juridical regime for agricultural use of sludges. Dry matter and moisture mass fractions are analytical parameters required. Therefore, the metrological quality of both moisture and dry matter mass fractions' results will have an effect on all analytical results converted to a dry basis.

Analytical results reported with measurement uncertainty are one of the best ways to show their metrological quality and fitness for purpose [5]. In this work, measurement uncertainties of both moisture and dry matter mass fractions were calculated using an intralaboratorial modelling approach that identifies, estimates and combines each individual input quantity uncertainty according to the law of propagation of uncertainties [5].

2. EXPERIMENTAL

2.1. Equipment

All weighings were performed using a calibrated Mettler AT 200 analytical balance (Mettler Toledo, Switzerland), with 200 g capacity and a digital resolution, $\delta m = 0,0001 \text{ g}$.

All drying operations were performed in thermostatically controlled and calibrated at $(105 \pm 5) \text{ °C}$ drying ovens (Heraeus, Hanau, Germany and Memmert, München, Germany).

2.2. Procedure

An in-house gravimetric method was used to determine the moisture and dry matter mass fractions based on the ISO 11465:1993 [6] for soil and EN 12880:2000 [7] for slags, inert ashes, industrial residues, domestic and industrial sludges. The quality control program used includes calibrated equipments, a constant mass criterion and duplicate analysis of the samples.

An amount of 2 to 5 g of sample was transferred to an empty porcelain capsule dried at $(105 \pm 5) \text{ °C}$ for 4 hours and then cooled in a desiccator, for at least 45 minutes. This procedure was repeated until fulfilling constant mass criterion, that is, the difference between two successive weighings of the sample doesn't exceed $\pm 0,005 \text{ g}$. Notice that the empty porcelain capsule was previously dried at $(105 \pm 5) \text{ °C}$.

3. RESULTS AND DISCUSSION

The moisture mass fraction, w_{H_2O} , expressed as $g\ g^{-1}$, is defined as the mass of water evaporated during the drying of the sample at (105 ± 5) °C to constant mass, in according to (1).

$$w_{H_2O} = \frac{m_{(C+S)} - m_{(C+S)dry}}{m_{(C+S)} - m_C} \quad (1)$$

where m_C is the mass of the empty capsule (g), $m_{(C+S)}$ the mass of the capsule containing sample (g) and $m_{(C+S)dry}$ the mass of the capsule containing sample after the drying step (g).

The dry matter mass fraction, w_{DM} , expressed as $g\ g^{-1}$, is defined as the dry residue content obtained after drying of the sample at (105 ± 5) °C to constant mass according to (2).

$$w_{DM} = \frac{m_{(C+S)dry} - m_C}{m_{(C+S)} - m_C} \quad (2)$$

The procedure used for estimation standard measurement uncertainty of w_{H_2O} , $u_c(w_{H_2O})$ is detailed. In this work, $u(x_i)$ is the standard measurement uncertainty of a quantity x_i .

Fig. 1 shows a cause and effect diagram identifying the uncertainty sources that influence both w_{H_2O} and w_{DM} . The main branches are the input quantities as described in (1), as well as in (2). An additional main branch related to the measurement uncertainty associated to method's precision, $f(\text{precision})_{Rw}$, was considered. Therefore, the measurands, w_{H_2O} and w_{DM} , were rewritten in (3) and (4).

$$w_{H_2O} = \frac{m_{(C+S)} - m_{(C+S)dry}}{m_{(C+S)} - m_C} f(\text{precision})_{Rw} \quad (3)$$

$$w_{DM} = \frac{m_{(C+S)dry} - m_C}{m_{(C+S)} - m_C} f(\text{precision})_{Rw} \quad (4)$$

with $f(\text{precision})_{Rw} = 1$.

Combined standard measurement uncertainty associated to w_{H_2O} , $u_c(w_{H_2O})$, was estimated by the application of the law of propagation of uncertainties, for independent input quantities [5] to (3) and is expressed by (5).

$$u_c(w_{H_2O}) = \sqrt{[c_1 u(m_{(C+S)})]^2 + [c_2 u(m_{(C+S)dry})]^2 + [c_3 u(m_C)]^2 + u[f(\text{precision})_{Rw}]^2} \quad (5)$$

with the sensitivity coefficients, c_1 , c_2 and c_3 expressed by (6), (7) and (8).

$$c_1 = \frac{1 - w_{H_2O}}{m_{(C+S)} - m_C} \quad (6)$$

$$c_2 = -\frac{1}{m_{(C+S)} - m_C} \quad (7)$$

$$c_3 = \frac{w_{H_2O}}{m_{(C+S)} - m_C} \quad (8)$$

Combined standard measurement uncertainty associated to w_{DM} , $u_c(w_{DM})$ can also be estimated by (5) to (8), although sensitivity coefficients values have opposite signs, since $w_{H_2O} = 1 - w_{DM}$.

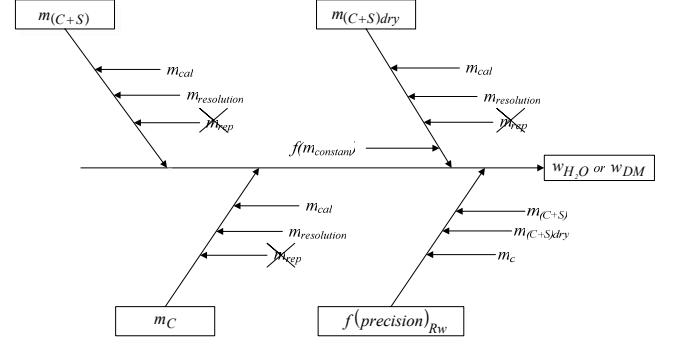


Fig. 1. Cause-effect diagram of measurement uncertainty sources associated to the determination of moisture and dry matter mass fractions in industrial residues and sludges (5). w_{H_2O} - moisture mass fraction ($g\ g^{-1}$) (1); w_{DM} - dry matter mass fraction ($g\ g^{-1}$) (2); $m_{(C+S)}$ - mass of the capsule containing sample (g); $m_{(C+S)dry}$ - mass of the capsule containing sample after the drying step (g); m_C - mass of the empty capsule (g); m_{cal} - calibration function of the scale; $m_{resolution}$ - analytical balance resolution; m_{rep} - repeatability contribution; $f(m_{constant})$ - constant mass criterion; $f(\text{precision})_{Rw}$ - precision under within-laboratory reproducibility conditions.

All standard uncertainties associated to weighing steps are influenced by the analytical balance resolution, $u(m_{resolution})$, and the calibration function of the scale, $u(m_{cal})$. Weighings repeatability contribution wasn't included because it has already been take into account in measurement uncertainty due to overall precision, $u[f(\text{precision})_{Rw}]$.

For the $m_{(C+S)dry}$ measurement uncertainty component, an additional contribution was considered due to the uncertainty of the constant mass criterion, $f(m_{constant})$, assuming a triangular distribution [5].

The $u[f(\text{precision})_{Rw}]$ (5) was estimated under within-laboratory reproducibility conditions from duplicate R-charts, which includes the scattering due different matrix and several concentration levels of measurand within long periods of time. The standard deviation, s , was calculated by the ratio between the mean value for each range, \bar{R} , and the tabled factor for duplicate sets, 1,128 [8]. Acceptance criteria were previously established: each relative range, R^{rel} , should be lower or equal than 0,10 when $w_{H_2O} > 0,10\ g\ g^{-1}$; for $w_{H_2O} \leq 0,10\ g\ g^{-1}$, $R^{rel} \leq 0,15$ was considered.

Table 1 shows the uncertainty budget, at different mass fraction levels for w_{H_2O} (3) and w_{DM} (4) of two sludges

Table 1. Uncertainty budget for moisture, w_{H_2O} , and dry matter w_{DM} , mass fraction, in two samples of sludges, one for each working range ($w_{H_2O} \leq 0,10 \text{ g g}^{-1}$ and $w_{H_2O} > 0,10 \text{ g g}^{-1}$).

Mass fractions $y / (\text{g g}^{-1})$	Input quantities				$u_c(y) / (\text{g g}^{-1})$	$U(y) / (\text{g g}^{-1})$	
	$m_{(C+S)}/\text{g}$	$m_{(C+S)dry}/\text{g}$	m_C/g	$f(\text{precision})_{Rw}$			
$w_{H_2O} = 0,086$ $w_{DM} = 0,914$	x_i	46,4741	46,2486	43,8445	1	0,0019	0,0039
	$ c_i $	0,35	0,38	0,033	1		
	$u(x_i)$	0,00010	0,0029	0,00015	0,0016		
	r_i	0,00034	0,32	0,0000060	0,68		
$w_{H_2O} = 0,628$ $w_{DM} = 0,372$	x_i	49,3992	46,0999	44,1434	1	0,0069	0,014
	$ c_i $	0,071	0,19	0,12	1		
	$u(x_i)$	0,00010	0,0029	0,00015	0,0069		
	r_i	0,0000011	0,0064	0,0000064	0,99		

y – measurand: w_{H_2O} - moisture mass fraction (g g^{-1}) (1), w_{DM} - dry matter mass fraction (g g^{-1}) (2); $m_{(C+S)}$ - mass of the capsule containing sample (g); $m_{(C+S)dry}$ - mass of the capsule containing sample after the drying step (g); m_C - mass of the empty capsule (g); $f(\text{precision})_{Rw}$ - precision under within-laboratory reproducibility conditions; $u(x_i)$; - standard measurement uncertainty associated to a quantity x_i ; $|c_i| = |\partial y / \partial x_i|$ - sensitivity coefficients in absolute value, c_1 (6), c_2 (7) and c_3 (8); r_i - relative variance of each input quantity, $r_i = [c_i u(x_i) / u_c(y)]^2$ [5]; $u_c(y)$ - combined standard measurement uncertainty of y (5); $U(y)$ - expanded measurement uncertainty of y : $U(y) = k u_c(y)$ ($k = 2$, $\alpha = 0,05$) [5]; k - coverage factor; α - significance level.

samples. It comprises the input quantities (5), sensitivity coefficients (absolute values), standard measurement uncertainties (absolute values), standard measurement uncertainties, relative variances and combined standard measurement uncertainties. In addition expanded measurement uncertainties are also shown in Table 1, for an approximate level of confidence of 95 % [5]. Relative expanded measurement uncertainty of w_{H_2O} , $U^{rel}(w_{H_2O})$, for both ranges is around 4 % and 2 %, respectively, which are quite acceptable values for gravimetric methods.

uncertainty of $f(\text{precision})_{Rw}$ and $m_{(C+S)dry}$ are the input quantities with major influence in $u_c(w_{H_2O})$, when $w_{H_2O} \leq 0,10 \text{ g g}^{-1}$.

In case of higher moisture mass fraction and dry matter values between 0,10 and 0,90 g g^{-1} , measurement uncertainty due to $f(\text{precision})_{Rw}$ is the dominant one.

Although the proposed modelling approach gives an extended equation to estimate $u_c(w_{H_2O})$ and $u_c(w_{DM})$ (5) the assessment of each input quantity contribution (Table 1) leads to a more simplified equation, as follows in Table 2.

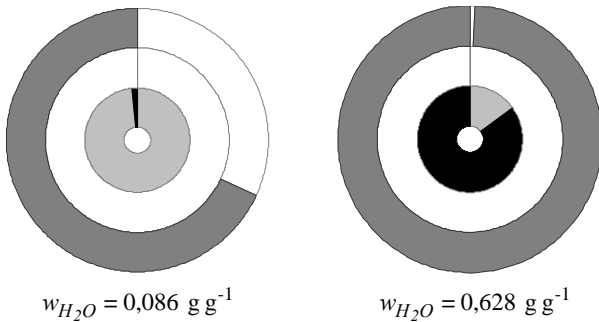


Fig. 2. Onion chart for uncertainty budget for moisture, w_{H_2O} , and dry matter w_{DM} , mass fraction, of two sludges samples.

w_{H_2O} - moisture mass fraction (g g^{-1}) (1); w_{DM} - dry matter mass fraction (g g^{-1}) (2); \blacksquare $m_{(C+S)}$ - mass of the capsule containing sample (g); \square $m_{(C+S)dry}$ - mass of the capsule containing sample after the drying step (g); \blacksquare m_C - mass of the empty capsule (g); \blacksquare $f(\text{precision})_{Rw}$ - precision under within-laboratory reproducibility conditions.

Fig. 2 shows the onion chart for the same data shown in Table 1, which depicts the outer three rings, improving visibility of smaller input quantities [9]. The measurement

Table 2. Combined standard measurement uncertainty functions

Range (g g^{-1})	$u_c(w_{H_2O})$ or $u_c(w_{DM}) (\text{g g}^{-1})$
$w_{H_2O} \leq 0,10$	$\sqrt{c_2^2 u(m_{(C+S)dry})^2 + u[f(\text{precision})_{Rw}]^2}$
$w_{H_2O} > 0,10$ $w_{DM} < 0,90$	$u[f(\text{precision})_{Rw}]$

In Fig. 3 a detailed behaviour of relative combined standard measurement uncertainty of moisture, $u_c^{rel}(w_{H_2O})$, and dry matter $u_c^{rel}(w_{DM})$ for both working ranges are shown. As can be seen, $u_c^{rel}(w_{H_2O})$ and $u_c^{rel}(w_{DM})$ decreases with the increasing of mass fraction, as expected.

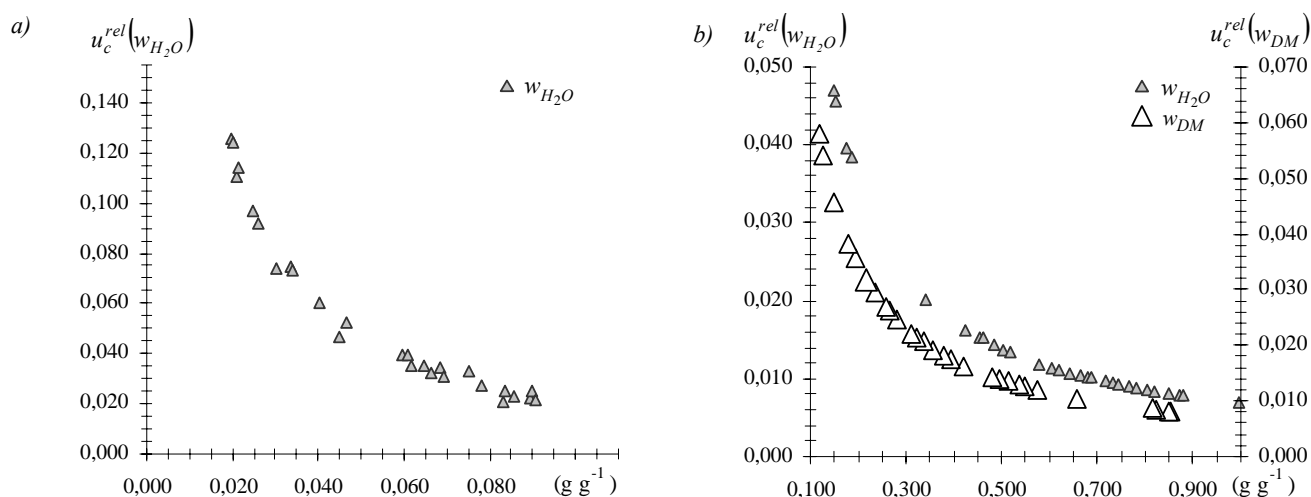


Fig. 3. Relative combined standard measurement uncertainty of moisture, w_{H_2O} , and dry matter w_{DM} , mass fraction versus mass fraction ranges. a) $w_{H_2O} \leq 0,10 \text{ g g}^{-1}$; b) $w_{H_2O} > 0,10 \text{ g g}^{-1}$ and $0,10 \leq w_{DM} \text{ (g g}^{-1}) < 0,90$.

A limit of quantification (L_Q) of $0,025 \text{ g g}^{-1}$ for moisture mass fraction can be estimated from Fig. 3 a), by applying the IUPAC recommendations [10], i.e., a w_{H_2O} content with a relative standard deviation (RSD) of 10 % as described by (9),

$$L_Q = K_d \sigma_Q \quad (9)$$

where K_d is the multiplier whose reciprocal equals the selected quantifying RSD: $K_d = 1/\text{RSD} = 10$ and σ_Q the standard deviation. This L_Q value corresponds to a relative expanded measurement uncertainty of $\pm 20 \%$ ($10\sigma \pm 2\sigma$) for a 95,45 % level of confidence.

The estimated L_Q corresponds to ten times the constant mass criterion ($\pm 0,005 \text{ g}$) for 2 g sample amount.

4. CONCLUSIONS

Simplified calculation models for measurement uncertainty of w_{H_2O} and w_{DM} were established after evaluation measurement uncertainties of the input quantities. For $w_{H_2O} > 0,10$ $f(\text{precision})_{Rw}$ component was the dominant one. For the lowest range, the $m_{(C+S)dry}$ contribution is also significant due to constant mass criterion, although decreases with increasing of w_{H_2O} .

For routine laboratory analysis, measurement uncertainty of analytical results should be a realistic, but also an expedite calculation model.

From $u_c^{rel}(w_{H_2O})$ and $u_c^{rel}(w_{DM})$ distribution of moisture and dry matter mass fraction, a limit of quantification can be estimated from IUPAC recommendations [10].

REFERENCES

- [1] EN 12457-4, "Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges – Part 4: One stage batch test at a liquid to solid ratio of 10 L kg^{-1} for materials with particle size below 10 mm (without or with size reduction)", *European Committee for Standardization*, Brussels, Belgium, Sept. 2002.
- [2] Decree-law N. 152/2002, 23rd May, in *Diário da República*, N.119/2002, Série I-A, Imprensa Nacional Casa da Moeda, 4680-4699, Lisbon, Portugal, 2002.
- [3] Council Decision, 19th December, in *Official Journal of the European Communities*, L 11, 27-49, Brussels, Belgium, 2002.
- [4] Decree-law N. 118/2006, 21st June, in *Diário da República*, N.118/2006, Série I-A, Imprensa Nacional Casa da Moeda, 4380-4388, Lisbon, Portugal, 2006.
- [5] GUM, "JGQM100:2008. GUM 1995 with minor corrections. Evaluation of measurement data - Guide to the expression of uncertainty in measurement", *Joint Committee for Guides in Metrology*, First edition, September 2008.
- [6] ISO 11465:1993, "Soil Quality – Determination of dry matter and water content on a mass basis – Gravimetric method", 1st Edition, *International Organization of Standardization*, Geneva, Switzerland, 1993.
- [7] EN 12880:2000, "Characterization of sludges. Determination of dry residue and water content", 1st Edition, *European Committee for Standardization*, Geneva, 2000.
- [8] W. Funk, V. Dammann and G. Donnevert, *Quality Assurance in Analytical Chemistry*, VCH Publishers, New York, USA, 1995.
- [9] K. W. Pratt, D. L. Duewer, "Visualization technique for uncertainty budgets: Onion charts", *Accreditation and Quality Assurance* n. ° 10, pp. 527–530, February 2006.
- [10] IUPAC Recommendations, "Nomenclature in evaluation of analytical methods including detection and quantification capabilities", *Pure & Appl. Chem.*, Vol. 67, N° 10, pp. 1699 – 1723, 1995.