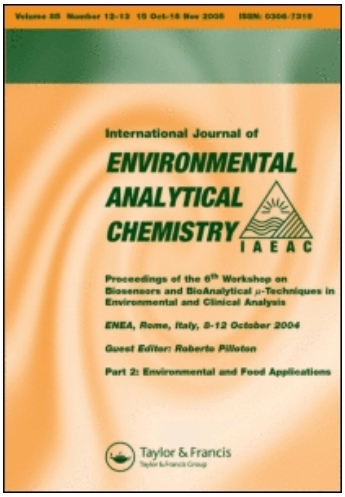

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THE VARIABILITY OF DRY-MASS CORRECTION FOR CERTIFIED REFERENCE MATERIALS

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A realistic or an acceptable level of variability that can be expected between laboratories when reporting dry-mass corrections for candidate reference materials is not known. The proper use of solid certified reference materials (CRMs) necessitates a dry mass correction so the elemental composition can be reported as a mass of analyte per unit dry mass of sample.

The water content of seven, biological and environmental, certified reference materials (Measurements and Testing Programme, formerly the BCR) was studied as a function of time, each in seven micro-environments ranging from 15 to 94-percent relative humidity. For the determination of water in these different relative humidity environments, one CRM was observed to have a reproducibility as high as 23-percent ($\alpha = 0.05$). This degree of variability suggests reproducibility consistently less than 10-percent ($\alpha = 0.05$), as observed in interlaboratory campaigns to certify candidate reference materials, represents acceptable between laboratory variability.

KEY WORDS: Dry-mass correction, humidity, reference material, variability, water.

INTRODUCTION

Solid Certified Reference Materials (CRMs) are homogenized and dried materials that have been characterized for their elemental composition. They are used to control analytical quality, to validate new methods of analysis, and to assure the world wide comparability of data. The amount of water a reference material contains is determined so the analyte concentration can be reported as the mass of analyte per unit dry mass of sample. This measure removes error from between bottle/sample variability of moisture. If a bottle is left open for a significant amount of time, the humidity of the environment will affect the amount of water determined. In recent projects by Measurements and Testing Programme, (formerly the Community Bureau of Reference, BCR, a Commission of the European Communities) the variability of dry mass correction results for several reference materials was questioned.

A water determination for the purpose of dry-mass correction is usually performed by a gravimetric method. In the most common gravimetric method, a precisely weighed 0.1 to 1-g portion of the CRM is oven dried at 102 ± 1°C for 3–4 hours before cooling in a dessicator for reweighing (successive weighings should not differ by more than 0.2-mg)[1]. With some alternative gravimetric methods, organic samples may be dried at ambient or subambient temperatures using: reduced pressure drying (approximately 1.3×10^4 Pa) in

a vacuum dessicator over $Mg(ClO_4)_2$ for 48-hours; vacuum drying at room temperature for 24-hours at a pressure of approximately 30-Pa using a cold-trap; or by freeze drying for 20-hours at a pressure of approximately 3-Pa[2]. Although other methods[3] exist for the determination of water including: chemical (Karl Fischer titration); thermal; separation; infrared spectrophotometric; radiochemical; and physical methods, oven drying is the simplest and by far the most widely used method for determining water in reference materials for the purpose of dry-mass correction.

Most work in the literature on the topic of determining water is on the measurement of water in food substances. One study evaluates the repeatability and reproducibility of the determination of moisture in cheese using a microwave technique[4]. Such a study applied to certified reference materials, which contain significantly smaller amounts of water, has not been performed. A treatise by Mitchell and Smith[3] gives a comprehensive review of methods available for the determination of water.

The following qualitative and quantitative definitions[5] for **reproducibility** were applied in this study:

Qualitative definition. The closeness of agreement between individual results obtained with the same method on identical test material but under different conditions (different operators, different apparatus, different laboratories and/or different times).

Quantitative definition. The value below which the absolute difference between two single test results on an identical material obtained in the above conditions, using a standardized test method, may be expected to lie with 95-percent confidence, and is represented by the symbol, R, where

$$R = t\sqrt{2}\sqrt{(\text{estimate of } \sigma_w^2) + (\text{estimate of } \sigma_b^2)} \quad (1)$$

and where

σ_w^2 is an estimate of the within lab variance (analysis of variance within lab mean square),

σ_b^2 is an estimate of the between lab variance,

$$\sigma_b^2 = \frac{\text{BLMS} - \text{WLMS}}{\text{\# determinations per lab'}}$$

WLMS is the analysis of variance within laboratory mean square, BLMS is the analysis of variance between laboratory mean square, and

t is the two-sided critical value for the t-test (at 5% level of significance unless otherwise indicated) using n degrees of freedom where:

$$n = (\text{no. of labs} - 1)\left[1 + (\text{no. of determinations per lab} - 1)\frac{\text{WLMS}}{\text{BLMS}}\right]^2$$

A second statistic presented is the repeatability and the following quantitative definitions[6] for **repeatability** were applied in this study:

Qualitative definition. The closeness of agreement between successive results obtained from the same method on identical test material under the same conditions (operator, same apparatus, same laboratory, and short intervals of time).

Quantitative definition. The value below which the absolute difference between two single test results obtained in the above conditions may be expected to lie with a specified probability, usually 95-percent, and is represented by the symbol, r, where

$$r = t\sqrt{2}\,s, \tag{2}$$

where s is the sample standard deviation of the successive determinations made under repeatability conditions or, in the case of an analysis of variance evaluation of repeatability

$$r = t\sqrt{2}\sqrt{\text{estimate of } \sigma_w^2}, \tag{3}$$

where the estimate of σ_w^2 is the analysis of variance within-samples mean square, and t is the two-sided critical value for the t-test (at 5% level of significance unless otherwise indicated) using n degrees of freedom where

n = (no. determinations per laboratory-1) (no. laboratories).

As with all analytical measurements, including the determination of water for dry-mass correction, there is between laboratory variability. Equation (4) identifies the main sources of total, between laboratory variability, σ_{tot}, for this determination:

$$\sigma_{tot}^2 = \sigma_w^2 + \sigma_b^2, \tag{4}$$

where σ_w is the within laboratory variability, and σ_b is the between laboratory variability.

Variability between laboratory may be expressed as:

$$\sigma_b^2 = \sigma_{meth}^2 + \sigma_{analyst}^2 + \sigma_{rh}^2, \tag{5}$$

where σ_{meth} is the random error associated with the type of drying method used, $\sigma_{analyst}$ is the random error owing to differences between analysts, and σ_{rh} is the random error due to variation in the relative humidity between laboratories. Owing to identical methods ($\sigma_{meth} = 0$), and assumed competent analysts ($\sigma_{analyst} \approx 0$), equation (4) simplifies to:

$$\sigma_{tot}^2 = \sigma_w^2 + \sigma_{rh}^2 \tag{6}$$

If σ_{rh} could be found by simulating laboratories with different relative humidities (part II of this study), and if it was approximately equal to or larger than the interlaboratory σ_{tot} values (part I of this study), then σ_{tot} may be considered to be realistic and not dominated by between laboratory fluctuations in the relative humidity. If on the other hand σ_{rh} is found to be much less than σ_{tot}, then an analysis of within laboratory variability would be necessary to determine the acceptability of σ_{tot}.

The objective of this work is to determine whether the variability of water determinations in certification projects is realistic based on a study to determine the maximum between laboratory variability that could occur for the determination of water in a variety of reference materials. This will be measured in a simulation type study by determining the water content of a selection of organic and inorganic CRMs stored in a variety of humidity environments. A comparison will be made with the interlaboratory results to see if the total, between laboratory reproducibility of the dry-mass correction data is realistic, i.e. lower than the reproducibility measured in the simulation.

EXPERIMENTAL

Laboratories participating in the certification studies were requested to submit only three water determinations. In cases where more than three were submitted, only the first three determinations were used. Laboratories were instructed to oven dry their samples at 102 ± 1°C for 3–4 hours before cooling in a dessicator for reweighing. An analysis of variance was performed on this interlaboratory data to determine the reproducibility of the dry-mass correction.

Owing to the nature of measurements for this study, measurements of mass changes in an analytical balance over long periods of time (8-hours), the temporal, mass stability of the balance was monitored for over 68-hours both as a function of temperature and relative humidity.

Seven certified reference materials were evaluated for their moisture content in seven humidity environments (Table 1) as described below:

1) A solution trough with a salt solution (Table 1) was placed in a Metler AE163 analytical balance (Figure 1). The humidity was monitored using an electronic hygrometer (Omega model RH-201C). The time for this microenvironment to reach constant humidity was shortened by fixing an Archer cooling fan (Cat. No. 273–244) to the inside rear wall of the analytical balance.
2) Approximately 750-mg of a desicator dried ($CaSO_4$) CRM (Table 2) was placed on the analytical balance.
3) The mass was observed until constant mass, i.e. defined as a change of not more than 0.2-mg in 10-minutes.
4) Steps 2 and 3 were repeated with all CRMs.
5) Steps 1 through 4 were repeated with all saturated salt solutions.

Table 1 Salt solutions used to create specific relative humidity environments in the analytical balance.

Salt solution of other environment	*Mass salt/g/100-mL H_2O*	*Observed relative humidity/%*
$CaSO_4$ (s)	n/a	14–20
$LiCl{\bullet}H_2O$ (aq)	69.7	27–39
$KC_2H_3O_2$ (aq)	135.1	40–50
$NaNO_2$ (aq)	88.7	64–69
$NaC_2H_3O_2$ (aq)	82.8	70–74
$NaCO_3{\bullet}10H_2O$(aq)	30.2	81–87
H_2O (l)	n/a	86–94

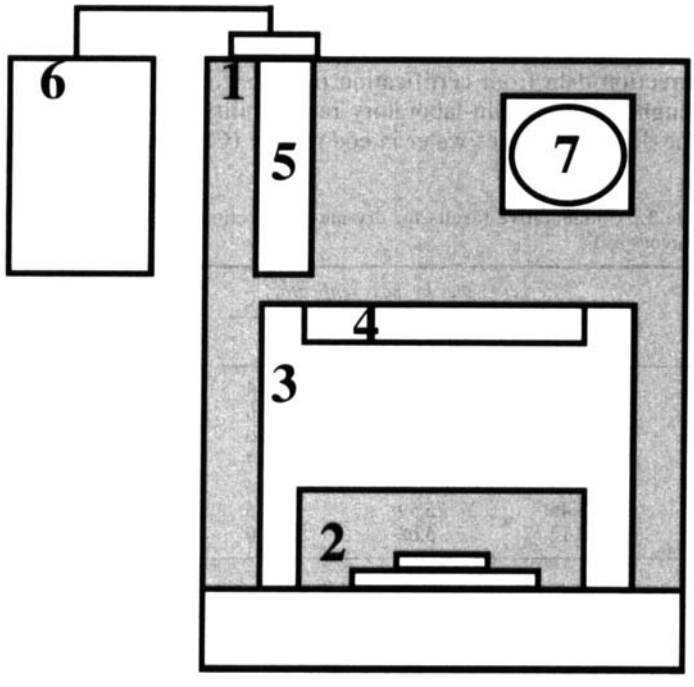

Figure 1 Apparatus used to determine water content of CRMs at various relative humidities: 1) analytical balance; 2) balance pan; 3) solution trough; 4) solution trough reservoir; 5) electronic hygrometer; 6) hygrometer digital readout; 7) air circulating fan.

Table 2 Certified reference materials (Measurements and testing programme, formerly the BCR).

	Certified reference material	*Description*
1	141	Calcareous loam soil
2	142R	Light and sandy soil
3	143R	Sewage sludge amended soil
4	277	Estuarine sediment
5	402	White clover
6	414	Plankton
7	482	Lichen
8	422	Cod muscle
9	141R	Calcareous soil
10	144R	Domestic origin sewage sludge
11	146R	Industrial origin sewage sludge

RESULTS AND DISCUSSION

The data collected is presented in two parts: I) dry-mass correction data from the Measurements and Testing Programme certification exercises; and II) data from experimental simulation studies. Materials for this study were selected to include a variety of both inorganic and organic type materials.

Measurements and testing programme certification data

Dry-mass correction data from certification projects for seven CRMs is presented in Tables 3 through 9. The within-laboratory repeatability($\alpha = 0.05$) is shown for each laboratory. The determination of water in cod muscle (CRM 422) was the most difficult

Table 3 Collaborative results for dry-mass correction applied to CRM 141R, calcareous soil[7].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	4.16	4.20	5.84	5.83
2	5.34	5.51	5.86	1.61
3	4.70	5.00	4.80	0.93
4	6.09	6.09	5.27	2.88
5	5.25	5.10	5.14	0.40
6	5.46	5.59	5.45	0.47
7	5.12	5.08	5.20	0.37
		Mean		1.8

Table 4 Collaborative results for dry-mass correction applied to CRM 144R, domestic origin sewage sludge[7].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	4.29	4.29	3.67	2.18
2	4.71	4.01	4.72	2.48
3	2.8	3.2	2.8	1.40
4	4.47	4.53	4.61	0.43
5	3.979	3.791	3.749	0.74
6	4.41	4.35	4.25	0.49
7	4.23	4.35	4.28	0.37
		Mean		1.2

Table 5 Collaborative results for dry-mass correction applied to CRM 146R, industrial origin sewage sludge[7].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	3.73	3.93	3.56	1.13
2	4.54	4.37	4.24	0.91
3	3.7	3.4	3.4	1.05
4	4.76	4.84	4.33	1.67
5	4.34	4.313	4.2897	0.15
6	4.61	4.44	4.54	0.52
7	4.29	4.41	4.35	0.36
		Mean		0.8

Table 6 Collaborative results for dry-mass correction applied to CRM 422, cod muscle[8].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	3.46	1.74	2.25	2.25
2	3.8	3.8	3.7	0.35
3	1.04	4.79	2.08	11.7
4	5.7	5.2	6.4	3.67
5	1.84	1.68	1.95	0.83
6	2.79	2.87	2.67	0.61
7	3.47	3.9	3.53	1.42
8	5.0	4.1	1.5	11.05
9	4.722	5.15	4.35	2.43
10	3.54	3.35	1.5	6.85
11	2.55	4.47	5.62	9.43
12	0.68	0.6	2.4	6.18
		Mean		4.7

Table 7 Collaborative results for dry-mass correction applied to CRM 402, white clover[9].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	5.0000	4.8500	4.93	0.46
2	4.08	4.15	4.28	0.62
3	4.1824	4.059	4.0039	0.56
4	5.91	5.81	4.73	3.98
5	5.27	5.33	5.42	0.46
6	4.6	4.5	4.4	0.61
7	8.97	8.8	9.23	1.32
8	5.19	5.23	5.15	0.27
9	9.4	8.87	9.21	1.63
10	3.3	3.34	3.26	0.24
11	4.09	4.06	4.15	0.28
12	4.25	4.23	4.18	0.22
13	6.15	6.11	6.28	0.54
14	3.05	3.05	2.94	0.39
15	4.57	4.62	4.48	0.43
16	7.63	7.54	6.12	5.15
17	4.48	4.33	4.75	1.29
		Mean		1.1

and the mean repeatability of that determination, 4.7-percent, was more than twice as imprecise as the nearest mean repeatability, 1.8-percent for calcareous soil (CRM 141R). The cod muscle differed from all other materials in this study by being the only material that was freeze-dried. Owing to the hygroscopic nature of this freeze-dried material, and to its water content naturally changing during the time of sampling from the bottle for weighing, poor repeatability for the determination of water in this material is expected. Although this freeze dried material had the lowest mean water determination

Table 8 Collaborative results for dry-mass correction applied to CRM 414, plankton[1].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	9.2300	9.0800	9.09	0.51
2	7.88	7.85	7.85	0.11
3	7.58	7.71	7.55	0.53
4	7.9	8.2	8.3	1.27
5	7.66	7.49	7.76	0.83
6	8.7	8.82	8.73	0.38
7	8.06	8.33	7.55	2.4
8	8.01	7.1	8.04	3.25
9	6.92	7	7.09	0.52
		Mean		1.1

Table 9 Collaborative results for dry-mass correction applied to CRM 482, lichen[10].

Lab	*Percent water by mass replicates*			*Repeatability*
	1	*2*	*3*	
1	5.06	5.09	5.11	0.15
2	5.63	5.55	5.36	0.84
3	5.5	5.5	5.5	0.00
4	5.8	5.9	5.7	0.61
5	5.64	5.61	5.62	0.09
6	6.19	6.17	6.15	0.12
7	5.37	5.42	5.21	0.67
8	5.92	6.6	6.49	2.22
		Mean		0.6

for the six materials evaluated from BCR certification exercises, there is no significant correlation between the water content of a CRM and the repeatability of the determination.

Table 10 summarizes the between laboratory, analysis of variance reproducibility (Equation 1) and the repeatability (Equation 4) of this determination for the seven participating laboratories and the seven CRMs. The poorest ***reproducibility***, 9.1-percent, was observed for the dry-mass correction applied to white clover(CRM 402). The 9.1-percent reproducibility implies that there is a 95-percent chance that two determinations, selected at random, from different laboratories will have an absolute difference less than 9.1-percent. With the exception of lichen at 0.55-percent, the least reproducible determinations were for organic materials. The reproducibility of dry-mass correction for the three soils was consistently less than l-percent.

The analysis of variance ***repeatability*** was the poorest for cod muscle, 3.1-percent. This result implies that, within any particular laboratory, the absolute difference between any two determinations can be expected, with 95-percent confidence, to be less than 3.1-percent.

Table 10 Between laboratory (n = 7) analysis of variance reproducibility and analysis of variance repeatability for the determination of water in Measurements and Testing (BCR) certified reference materials.

Certified reference material	*Material description*	*Reproducibility ($\alpha = 0.05$)*	*Repeatability ($\alpha = 0.05$)*
141R	Calcareous soil	0.61	0.34
144R	Domestic origin sewage sludge	0.99	0.16
146R	Industrial origin sewage sludge	0.58	0.08
422	Cod muscle	4.95	3.10
402	White clover	9.12	0.23
414	Plankton	1.24	0.17
482	Lichen	0.55	0.07

Experimental humidity simulation studies

Figure 2 shows the uptake of water over time by dried CRMs when placed in a high (86–94%) relative humidity environment. Owing to the lack of availability of soil CRMs 141R, 144R and 146R reported in PART I, soil/sludge CRMs 141, 142R, and 143R were substituted and estuarine sediment CRM 277 was added to this list. The soils and sediment were the least hygroscopic while an organic reference material

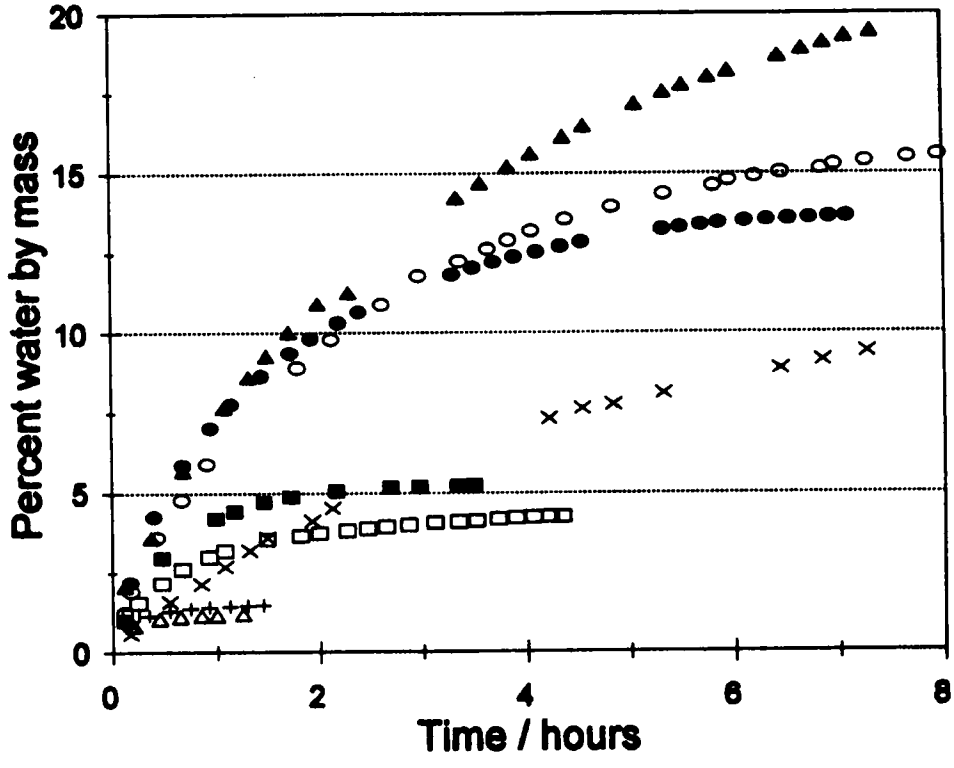

Figure 2 Uptake of water by dried CRMs exposed to 86–94% relative humidity: (●) CRM 482; (○) CRM 402; (▲) CRM 414; (■) CRM 141, (□) CRM 277; (+) CRM 143R; (△) CRM 142R; and (×) CRM 422.

Table 11 Experimental simulation summary of maximum water absorbed by BCR CRMs in different relative humidity environments and comparison with the reproducibility of the interlaboratory BCR certification studies.

BCR CRM	*Percent water by mass in CRMs at different relative humidity environments*							*Reproducibility*	
	14–20%	*27–39%*	*40–50%*	*64–69%*	*70–74%*	*81–87%*	*86–94%*	*Simulation* $\sqrt{2}\,ts$	*Inter-laboratory*
141/141R	0.18	1.45	2.22	3.95	3.88	4.20	5.20	5.5	0.61
142R/144R	0.13	0.74	0.48	0.52	0.93	0.90	1.16	1.1	0.99
143R/146R	0.2	0.34	0.64	1.05	1.22	1.17	1.47	1.5	0.58
277	0.06	0.35	0.79	2.48	3.06	3.56	4.24	5.2	–
402	0.77	2.88	3.03	9.19	10.76	12.81	15.81	17.7	9.12
414	0.30	2.07	2.84	10.48	11.53	12.39	20.98	22.7	1.24
482	1.63	3.32	4.53	10.16	9.88	12.20	13.61	14.5	0.55
422	–	–	–	–	–	–	14.7	–	4.95

material, CRM 414 plankton, absorbed as much as 19-percent water in 7-hours. The CRMs were measured for their water content as a function of time in six other humidity environments. These results are summarized in Table 11 with a comparison to the reproducibility of the interlaboratory BCR certification studies presented in part I.

For the determination of water in each CRM, the reproducibility of the experimental simulation was larger than the interlaboratory reproducibility. Had the experimental simulation reproducibility included the within laboratory variability, which it did not, then the interlaboratory reproducibility measures would still have been less than the experimental simulation reproducibility. Therefore, a within-laboratory experimental simulation study was not necessary, and the reproducibility observed in the interlaboratory BCR certification studies represents an acceptable level of variability.

Acknowledgments

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