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CEN/TC 264/WG 5

Total dust at low concentrations

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Determination of the uncertainty of the procedure for the determination of the mass of dust contained in rinsing solutions from dust measurements

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REPORT

Determination of the uncertainty of the procedure for the determination of the mass of dust contained in rinsing solutions from dust measurements

CEN/TC 264/WG 5

February 13, 1997

CONTENTS

SUMMARY

This report describes the results of tests for the determination of the uncertainty in the procedure for the weighing of dry extracts from rinsings.

As the determination of the amount of dust in rinsings has a substantial contribution to the determination of the total dust concentration in flue gases, a procedure with a known uncertainty is needed. Therefore it was agreed upon during the meeting of the CEN/TC 264/WG 5 in Dübendorf (21 - 22 november 1996) that tests should be performed.

The report describes a study into the influence of various sources of errors on the uncertainty in the determination of the amount of dust in rinsings as well as practical tests in which the uncertainty was determined.

From the study and the tests a practical procedure for the determination of dust in rinsings is proposed.

Using this procedure it showed from the tests that the uncertainty in the determination of dust in rinsings is ± 0.6 mg (95% confidence level) in the range of 2 - 8 mg of dust.

1 INTRODUCTION

1.1 Background

During the preparation of a draft standard for low dust concentrations it became clear that dust deposits in the equipment could not be neglected. Therefore the dust sampling equipment have to be rinsed and the amount of dust in the rinsings have to be determined. As the determination of the amount of dust in rinsings has a substantial contribution to the determination of the total dust concentration in flue gases, a procedure with a known uncertainty is needed. Therefore it was agreed upon during the meeting of the CEN/TC 264/WG 5 in Dübendorf (21 - 22 november 1996) that tests should be performed (resolution 42).

1.2 Description of the working program

The uncertainty has been determined in the following steps:

1. Determination of the optimal volume and weight of the weighing container.
   Calculation of the buoyancy effect due to different temperature and pressure conditions during pre-weighings and after-weighings and how a correction can be made for this effect.
   Estimation of the optimal volume and weight in respect to the balance resolution.
   Also the effect of specified residues in the acetone by the manufacturer is be checked.
   By means of a calculation with the relevant parameters the effect on the uncertainty in the end result has been determined.

2. Check on optimal evaporation temperature.
   The present evaporation temperature of 120 °C might be to high. Dust may be lost during boiling of the acetone/water mixture. A visual inspection on boiling has been made at 95, 105 and 120 °C.

3. Determination of the uncertainty of the whole procedure (without dust).
   The evaporation and weighing procedure has been followed completely with acetone (of one and the same chemical lot) and water. This has been done three times with six different weighing containers. From these data the uncertainty has been determined.

4. Determination of the uncertainty of the complete procedure with known amounts of dust.
   Known amounts of dust (in the order of 2 - 5 mg of fly-ash from the ESP of a coal-fired power plant) were added to storage containers. Thereafter the whole procedure was followed in order to determine the uncertainty. This has been done 3 times (using six different weighing containers). From the differences between the added amount of dust and the determined weight the uncertainty of the total procedure has been calculated.

The procedure as described for the field test in "La Chaux de Fonds" has been used as a basis for the determinations (CEN/TC 264/WG5 N113).

1.3 Necessity for buoyancy correction

Due to the fact that very low amounts of dust (about 2 mg or less) are weighed in relative large containers the effect of the difference in air density cannot be neglected. On average the measuring containers (liquid volume about 25 ml) with the dust from the rinsings have an air displacement of about 8 cm^3. Under practical conditions an air density difference of about 0.06 kg/m^3 (equal to 0.06 mg/cm^3) between pre-weighing and after-weighing can be encountered (as explained in annex A). From this the difference in buoyancy is 8 x 0.06 = 0.48 mg. This shows that a correction for buoyancy is nessecary.

2 DETERMINATION OF THE OPTIMAL VOLUME AND WEIGHT OF THE WEIGHING CONTAINERS

2.1 Volume and weight of the containers

The uncertainty in the weighing result of dust deposits is depending among others on the resolution of the balance used. The amount of dust expected in the rinsings is estimated as follows. At dust concentrations of 5 mg/m^3 and a sampled gasvolume of 1 m^3, the amount of dust is 5 mg. When assuming a deposit of 50% then an amount of 2.5 mg has to weighed. The uncertainty in the weighing result on a balance is (on average) 2 times the resolution. Using a balance with a resolution of 0.1 mg, will give an uncertainty of 0.2 mg, with a weighing result of 2.5 mg this is equal to 8%. This is an uncertainty in the reading of the weighing result only, which is rather high. For a balance with resolution of 0.01 mg the uncertainty is 0.8%. So for accurate weighings at least a balance with a resolution of 0.01 mg is needed.

Several modern balances are capable to weigh with a resolution of 0.01 mg with relatively heavy weights (depending upon the type and manufacturer of the balance up to 30 g or higher). As an amount of at least 150 ml of rinsing liquid has to be evaporated a container of about 200 ml is needed.

When using glass containers (beakers) it shows that only containers with a volume of about 25 ml can be used with respect to their weight. In table 2.1 the weights of different glass containers are given.

Table 2.1 Weight of glass containers with different volumes

Volume (ml)	Weight (g)
25	20
50	35
100	95
250	115

When using small containers the evaporation has to be performed in several steps. Another method is to use light-weight containers. Plastic containers made of polymethylpentene (PMP) are commercially available and are resistant to temperatures up to 180 °C. A 100 ml container of PMP only weighs 18 g. Therefore some weighing tests were carried out with these containers. However it showed that these containers could not be weighed to constant weight when heated several times to the temperature of 160 °C. Therefore the use of these containers was rejected and tests were carried out with glass containers only.

2.2 Correction for buoyancy

2.2.1 INTRODUCTION

As already stated in the introduction a correction for the difference in buoyancy during the pre-weighing and after-weighing is needed. This correction can be performed in two ways:

I correction by means of a reference weight (reference container) which is also weighed during the pre-weighing and after-weighing;
II correction by means of calculation of the difference in air density during the pre-weighing and after-weighing.

2.2.2 CORRECTION BY MEANS OF A REFERENCE CONTAINER (METHOD I)

In this procedure the weight difference of a reference container of the after-weighing and pre-weighing is subtracted from the difference in weight of the measuring container (see annex B).

As the air exerts a buoyancy force to the measuring container as well as the reference container, the volume of these two containers should be the same in order to avoid systematic differences. The influence of the difference in volume of the two containers has been calculated (annex B) and it shows that under practical conditions the difference in weight between the measuring container and reference container should be less than 2 g, so that the systematic difference will be less than 0.05 mg when a difference in air density occurs of 0.06 kg/m^3.

2.2.3 CORRECTION BY MEANS OF THE CALCULATION OF THE AIR DENSITY (METHOD II)

The correction can also be performed on basis of a calculation of the air density during the pre-weighing and after-weighing. This has been worked out in annex C in detail.

The air density is calculated by means of a formula from the measured ambient air pressure, the temperature in the weighing room and the relative humidity (see annex D). It shows that stated uncertainty for the pressure and temperature measurement in the draft standard (3) cannot be used for the weighings as this gives a too high uncertainty in the calculation of the air density. For an appropiate air density calculation the uncertainties should be <± 1 mbar, <± 0.5 °C and <± 20% relative humidity, or <± 1 mbar, <± 0.75 °C and <± 10% relative humidity.

3 RESIDUES IN ACETONE

Acetone contains a certain amount of residue which influences the results of the weighings. Any residues will result in too high dust contents.

In table 3 the residues in several grades of acetone are given derived from analysis specifications of different manufacturers of acetone.

Table 3 Residues in acetone

Manufacturer	Analysis specification	Equivalent amount in mg/l
A	< 0.001%	< 8
B	< 2 ppm	< 1.5
	< 0.001%	< 8
	< 0.005%	< 40
C	< 0.001%	< 8
	< 0.0005%	< 4
D	< 0.001%	< 8
	< 10 mg/l	< 10
	< 3 mg/l	< 3
	< 0.0005%	< 4
	< 5 mg/l	< 5
	< 0.0002%	< 1.6
E	< 0.002%	< 16
	< 0.0005%	< 4
	5 ppm	< 4
	< 0.001%	< 8

From table 3 it shows that the residues are in the range between 1.5 and 40 mg/l of acetone. During the rinsings an amount of 50 - 100 ml acetone is used. This equals to a residue of 0.08 - 4 mg, which gives a systematic error in the determination of the dust.

4 CHECK ON THE OPTIMAL EVAPORATION TEMPERATURE

A check on the optimal evaporation temperature was made as the present evaporation of 120 °C might be to high. Dust could be lost during boiling of the acetone or water .

During this check it showed that the acetone/water mixture (50 ml of acetone and 100 ml of water) evaporates very slowly even at temperatures of 95 °C, 105 °C and 120 °C. At these temperatures no "bubbles" were seen. However at a temperature of 160 °C the evaporation of the acetone is too rapid as bubbles are formed. Therefore a maximum temperature of 120 °C is recommended for the evaporation of an actone/water mixture. During evaporation also the liquid temperature was measured by means of a thermometer (see table 4.1).

Table 4.1 Liquid temperatures during evaporation

Oven temperature °C	Liquid temperature °C
95	65
105	75-80
120	85-90
160	95

It showed that if the 150 ml of liquid has to be evaporated in aliquotes of about 25 ml the evaporation procedure would take a long time, including a number of handlings. At least 6 times the rinsing liquid from the storage container had to be pourred into the 25 ml container. Therefore it was chosen to evaporate the bulk of the liquid in a 250 ml container until only about 5 - 10 ml of liquid was remaining. Then this amount of liquid was rinsed out from the 250 ml container into a weighed container of 25 ml. Thereafter the remaining liquid was evaporated.

The evaporation of the 150 ml of liquid occurred for 2 hours at a temperature of 120 °C to evaporate the acetone. Next the liquid was evaporated during about 4 hours at a temperature of 160 °C. After about 4 hours the remaining 5 - 10 ml of liquid was transferred to a weighed 25 ml container and the remaining liquid was evaporated at the same temperature of 160 °C, which took about another 4 hours.

5 DETERMINATION OF THE UNCERTAINTY OF THE PROCEDURE

5.1 Introduction

For the determination of the uncertainty of the total procedure measurements were carried out with six measuring containers and one reference container. The evaporation and weighing procedure is laid down in annex E with adaption to the results of the previous chapter. The procedure was carried out using an amount of 50 ml of acetone and 100 ml of water.

First two series of weighings were carried out without the use of a rinsing liquid and the evaporation step. Then three series of weighings were carried out with the following sequence: weighing of the empty container, weighing of the container after evaporation of the rinsing liquid, and weighing of the container after addition of a known amount of fly-ash and an amount of rinsing liquid and evaporation.

The reference container has been treated the same way (heating in oven and drying in desiccator) but without addition of rinsing liquid and without addition of fly-ash.

The weighings were carried out on a balance with a resolution of 0.01 mg (Mettler AE 163). Before each series of measurements an automatic calibration of the balance was performed with an internal calibration weight.

From all these weighings the uncertainty in the procedure has been determined in the next paragraphs.

5.2 Empty container weighings

The detailed results of the weighings are given in annex F. In table 5.1 only the differences in the after-weighings and pre-weighings are given. The containers were heated in an oven at 160 °C and cooled down in an desiccator and weighed.

Table 5.1 Results of the empty container weighings

Container	Differences between the after-weighings and pre-weighings (mg)					
	No correction		Correction with reference container		Correction with air density	
	Series		Series		Series	
	S2-S1	S3-S2	S2-S1	S3-S2	S2-S1	S3-S2
Reference	-0.24	0.13	0.00	0.00	-0.19	0.14
M1	-0.29	0.27	-0.05	0.14	-0.25	0.28
M2	-0.26	0.20	-0.02	0.07	-0.22	0.21
M3	-0.27	0.24	-0.03	0.11	-0.23	0.25
M4	-0.25	0.13	-0.01	0.00	-0.20	0.14
M5	-0.19	0.14	0.05	0.01	-0.15	0.15
M6	-0.22	0.09	0.02	-0.04	-0.17	0.10
Average (M1-M6)	-0.25	0.18	-0.01	0.05	-0.20	0.19
Standard deviation (M1-M6)	0.04	0.07	0.04	0.07	0.04	0.07

5.3 Results of weighings after the evaporation procedure

The detailed results of the weighings are given in annex F. In table 5.2 only the differences in the after-weighings and pre-weighings are given.

Table 5.2 Results of the weighings after evaporation of the rinsing liquid

	Differences between the after-weighings and pre-weighings (mg)								
	No correction			Correction with reference container			Correction with air density		
	Series			Series			Series		
Container	S4-S3	S6-S7	S10-S9	S4-S3	S6-S7	S10-S9	S4-S3	S6-S7	S10-S9
Reference	-0.15	0.13	-0.05	0.00	0.00	0.00	-0.08	0.09	-0.16
M1	-0.25	0.13	0.21	-0.10	0.00	0.26	-0.19	0.09	0.11
M2	-0.29	0.18	0.20	-0.14	0.05	0.25	-0.22	0.14	0.10
M3	-0.31	0.22	0.11	-0.16	0.09	0.16	-0.25	0.18	0.01
M4	-0.18	0.11	0.66	-0.03	-0.02	0.11	-0.11	0.07	-0.04
M5	-0.22	0.07	0.10	-0.07	-0.06	0.15	-0.16	0.03	0.00
M6	-0.11	0.06	0.04	0.04	-0.07	0.09	-0.04	0.02	-0.07
Average (M1-M6)	-0.23	0.13	0.12	-0.08	0.00	0.17	-0.16	0.09	0.02
Standard deviation (M1-M6)	0.07	0.06	0.07	0.07	0.06	0.07	0.08	0.06	0.07

5.4 Results of weighings with a known amount of fly-ash

The fly-ash was weighed in a storage container, whereafter the fly-ash was rinsed and transferred to an evaporation container of 250 ml filled with 150 ml of an acetone/water mixture. The fly-ash originated from an electrostatic precipitator from a coal-fired power plant of 600 MW fired with Australian coal.

The detailed results of the weighings are given in annex F. In table 5.3 only the differences in the pre-weighings and after-weighings after subtraction of the added amount of fly-ash are given.

Table 5.3 Results of the weighings with fly-ash

Container	Differences between after-weighings and pre-weighings after subtraction of the added amount of fly-ash (mg)								
	No correction			Correction with reference container			Correction with air density		
	Series			Series			Series		
	S5-S4	S8-S7	S12-S11	S5-S4	S8-S7	S12-S11	S5-S4	S8-S7	S12-S11
M1	0.66	0.12	0.20	0.44	0.07	0.27	0.63	0.07	0.31
M2	0.05	0.18	0.32	-0.17	0.13	0.39	0.02	0.13	0.43
M3	0.69	0.09	0.01	0.47	0.04	0.08	0.66	0.04	0.12
M4	0.63	0.13	0.10	0.41	0.08	0.17	0.60	0.08	0.22
M5	0.70	0.07	0.30	0.48	0.02	0.37	0.67	0.02	0.41
M6	0.63	0.15	broken	0.41	0.10	-	0.60	0.10	-
Average (M1-M6)	0.56	0.12	0.19	0.34	0.07	0.26	0.53	0.07	0.30
Standard deviation (M1-M6)	0.25	0.04	0.13	0.25	0.04	0.13	0.25	0.04	0.13

6 DISCUSSION

For the comparison of the results the average and standard deviation are combined in table 6.1.

Table 6.1 Combined weighing results

		Differences in after-weighings and pre-weighings (mg)					
		No correction		Correction with reference container		Correction with air density	
	Series	Average	Standard deviation	Average	Standard deviation	Average	Standard deviation
Empty containers	S2-S1	-0.25	0.04	-0.01	0.04	-0.20	0.04
	S3-S2	0.18	0.07	0.05	0.07	0.19	0.07
Weighings after evaporation	S4-S3	-0.23	0.07	-0.08	0.07	-0.16	0.08
	S7-S6	0.13	0.06	0.00	0.06	0.09	0.06
	S10-S9	0.12	0.07	0.17	0.07	0.02	0.07
Weighings with fly-ash	S5-S4	0.56	0.25	0.34	0.25	0.53	0.25
	S8-S7	0.12	0.04	0.07	0.04	0.05	0.04
	S12-S11	0.19	0.13	0.26	0.13	0.30	0.13
Empty containers	S2-S1 and S3-S2	-0.03	0.23	0.02	0.06	-0.01	0.21
Weighings after evaporation	S4-S3, S7-S6 and S10-S9	0.01	0.18	0.03	0.12	-0.02	0.13
Empty containers and weighings after evaporation	S2-S1, S3-S2, S4-S3, S7-S6 and S10-S9	-0.01	0.20	0.03	0.10	-0.01	0.16
Weighings with fly-ash	S5-S4, S8-S7 and S12-S11	0.30	0.26	0.22	0.20	0.29	0.26

From these results it shows that no increase in weight could be detected due to residues in the acetone. The acetone used had a stated residue of < 0.001%, which equals to < 8 mg/l. With an amount of 50 ml this gives 0.4 mg of residue (maximum). From the measurements it shows that the residue in the acetone is far below this 0.4 mg.

Some of the averages within one series (which should be zero) are systematic positive or negative. However this seems to be random between the series. If the values of each series of weighings of the empty containers and the weighings of the evaporation are combined (see table 6.1), then it shows that the average values are close to zero. By combining the values the systematic differences within the series are transferred to the standard deviation.

There are no systematic differences in the combined series of the weighings with the empty containers nor in the combined series of the weighings after evaporation. As the standard deviations for the weighing results of the empty containers and the weighings after evaporation are more or less the same, the results of both series are combined (see table 6.1 second last line).

For the fly-ash weighings it shows that a systematic difference is present. The reason for this systematic difference is not known. The standard deviation for the weighings with fly-ash are systematic higher than for the other weighings. This shows that an extra uncertainty is introduced during the procedure (rinsing of storage containers with fly-ash).

From the table it can be deduced that the standard deviations for the correction with air density and without correction are significant higher than the standard deviation using a reference container. It seems that solely a correction for the difference in air density is not sufficient to compensate for unknown errors (such as non-lineairity or hysteresis of the balance). Therefore it is recommended to correct the weighing results by means of a reference container which is treated in the same way as the measuring container.

The total uncertainty in the weighing (using the correction with the reference container and taking into account the systematic difference) is calculated as:

$$\text{Uncertainty (95\% confidence level)} = \text{systematic difference} + t_{n-1} \times \text{standard deviation} \qquad (1)$$

For the "fly-ash" weighings this is:

$$U_{\text{fly-ash}} = 0.22 + 2.12 \times 0.20$$

$$U_{\text{fly-ash}} = 0.644 \text{ mg}$$

$$U_{\text{fly-ash}} \approx 0.6 \text{ mg}$$

For the "evaporation" weighings this is:

$$U_{\text{evaporation}} = 0 + 2.05 \times 0.10$$

$$U_{\text{evaporation}} \approx 0.2 \text{ mg}$$

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ANNEX A.1

Estimation of maximum air density differences

In this annex the maximum air density difference during after-weighing and pre-weighing is estimated on basis of the natural fluctuations in barometric pressure and temperature. The air density itself is calculated with a formula which is given in annex D.

The maximum difference in air density is estimated as follows.

The relative humidity can vary between almost zero (in winter time) and to almost 100% during a wet summer. The temperature in a laboratory could vary between about 15 °C (winter) and to about 35 °C (summer). The barometric pressure on earth varies on average between 950 mbar (storm) and 1050 mbar (anticyclone). These values are combined to get extreme values of the air density. For a winter period (1050 mbar, 15 °C and 0% relative humidity) the air density is 1.26971 kg/m^3 (or mg/cm^3) and for a summer period (950 mbar, 35 °C and 100% relative humidity) 1.05228 kg/m^3. The difference between these two values is 0.21743 kg/m^3. However it will be very seldom that these two extreme values will be encountered in practice when performing measurements. By calculating the air density (using the formula in annex D) for several situations it shows that the difference in air density is about half of the extreme value and is $0.21743/2 = 0.10872 \approx 0.11$ kg/m^3.

This value can be used when the time-period between pre-weighings and after-weighings is rather long (about 7 days or more). If the weighings are performed for instance within 36 hours the natural variations are usually smaller. For the determination of the dust content in the rinsings this would be more or less practical as the evaporation takes about one working day. In that case the maximum difference in air density is estimated as half of the previous value and then equals to $0.11/2 = 0.06$ kg/m^3.

ANNEX B.1

Correction for buoyancy (method I)

USE OF A REFERENCE OBJECT

Derivation of the correction formula

It is assumed that the reference object is an empty measuring container.

The apparent weights of the reference container at the pre-weighing and after weighing are given by:

$$G_{r1}^{a} = G_r - V_r \cdot \rho_{a1} \qquad \text{(B1)}$$

$$G_{r2}^{a} = G_r - V_r \cdot \rho_{a2} \qquad \text{(B2)}$$

in which:

G^a_{r1}	- the apparent weight (reading of the balance) of the reference container during the pre-weighing
G^a_{r2}	- the apparent weight (reading of the balance) of the reference container during the after-weighing
G_r	- the true weight of the reference container
V_r	- the volume of the reference container
ρ_{a1}	- the density of air during the pre-weighing
ρ_{a2}	- the density of air during the after-weighing

The difference in the two apparents weights is obtained by subtracting (2) and (1), which gives:

$$G_{r2}^{a} - G_{r1}^{a} = - V_r \cdot (\rho_{a2} - \rho_{a1}) = k_b \qquad \text{(B3)}$$

in which:

k_b - the correction for buoyancy

Formula (B3) gives the difference in apparent weight of one and the same reference container due to the difference in air density during the two weighings.

Correction for buoyancy (method I, continued)

For the measuring container to be weighted the following formula's are applied:

$$G^a_{m1} = G_{m1} - V_m \cdot \rho_{a1} \qquad \text{(B4)}$$

$$G^a_{m2} = G_{m2} - V_m \cdot \rho_{a2} \qquad \text{(B5)}$$

in which:

G^a_{m1}	- the apparent weight (reading of the balance) of the measuring container during the pre-weighing
G^a_{m2}	- the apparent weight (reading of the balance) of the measuring container during the after-weighing
G_{m1}	- the true weight of the measuring container during the pre-weighing
G_{m2}	- the true weight of the measuring container during the after-weighing
V_m	- the volume of the measuring container

The weight of the dust is calculated by subtracting the apparent weights of the measuring containers:

$$G^a_{m2} - G^a_{m1} = (G_{m2} - G_{m1}) - V_m \cdot (\rho_{a2} - \rho_{a1}) \qquad \text{(B6)}$$

In order to make the apparent differences equal to true differences the last term in formula (B6) should be compensated exactly. This is done by using the differences in buoyancy determined with the reference container:

$$G^a_{m2} - G^a_{m1} = (G_{m2} - G_{m1}) - V_m \cdot (\rho_{a2} - \rho_{a1}) + V_r \cdot (\rho_{a2} - \rho_{a1}) \quad \text{or} \qquad \text{(B7)}$$

$$G^a_{m2} - G^a_{m1} = (G_{m2} - G_{m1}) - V_m \cdot (\rho_{a2} - \rho_{a1}) - k_b \qquad \text{(B8)}$$

The true dust content is calculated from the difference in the apparent weights of the measuring containers with subtraction of the correction k_b (k_b can be positive as well as negative!). The correction k_b is calculated from the weighings with the reference container (see formula B3).

ANNEX B.3

Correction for buoyancy (method I, continued)

Determination of the restrictions

However the use of a reference container is restricted. After rearranging formula (B7):

$$G^{a}_{m2} - G^{a}_{m1} = (G_{m2} - G_{m1}) - (V_m - V_r) \cdot (\rho_{a2} - \rho_{a1}) \qquad \textbf{(B9)}$$

it shows that, when the volumes of the measuring container (V_m) and the reference container (V_r) are not exactly the same, a systematic error occurs. When limits are set for this systematic error the maximum tolerable difference in volumes can be calculated.

This systematic error is also dependent on the difference in air density encountered during the after-weighing and pre-weighing. In annex A a difference of 0.06 kg/m^3 has been estimated.
If a maximum systematic error of 0.05 mg in the weighing result is accepted then the maximum allowed difference in volume can be calculated from:

$$(V_m - V_r) \times (\rho_{a2} - \rho_{a1}) \leq 0.05 \text{ mg} \qquad \textbf{(B10)}$$

$$(V_m - V_r) \times 0.06 \leq 0.05 \text{ mg} \qquad \textbf{(B11)}$$

$$(V_m - V_r) \leq 0.833 \text{ cm}^3 \qquad \textbf{(B12)}$$

When it is assumed that the density of the glass of the containers is the same then the maximum allowable difference in weight is calculated from:

$$\Delta G = (V_m - V_r) \times \rho \qquad \textbf{(B13)}$$

$$\Delta G = 0.833 \text{ cm}^3 \times 2.23 \text{ g/cm}^3 = 1.85 \text{ g} \qquad \textbf{(B14)}$$

Thus a set of glass containers should be selected which do not differ more than about 2 g in weight from the reference container in order to have a maximum systematic error in the weighing of 0.05 mg due to differences in the air density.

In formula (B13) it is assumed that the density of the reference container and the measuring container are exactly the same. This assumption could be wrong in practice if containers of different manufacturers are used.

Correction for buoyancy (method I, continued)

The difference in volume of the containers is calculated with:

$$(V_m - V_r) = \left(\frac{G_m}{\rho_m} - \frac{G_r}{\rho_r}\right) \qquad \textbf{(B15)}$$

By applying the law of propagation of errors, the variation in volume solely due to the variation in density is determined:

$$\Delta V = \sqrt{\left(\frac{G_m^2 \times \Delta\rho_m^2}{\rho_m^4} + \frac{G_r^2 \times \Delta\rho_r^2}{\rho_r^4}\right)} \qquad \textbf{(B16)}$$

Assuming equal weights for the reference container and measuring container the influence of the density can be calculated (under assumption that the density belongs to one and the same population).

$$\Delta V = \sqrt{\left(\frac{G^2 \times \Delta\rho^2}{\rho^4} + \frac{G^2 \times \Delta\rho^2}{\rho^4}\right)} = G \times \frac{\Delta\rho}{\rho^2} \times \sqrt{2} \qquad \textbf{(B17)}$$

The containers weigh about 20 g, while the density of normal borosilicate glass is 2.23 g/cm^3 (variation in density less than 1%). Using these values the variation in volume is calculated:

$$\Delta V = 20 \times \frac{0.02}{2.23^2} \times \sqrt{2} = 0.114 \text{ cm}^3 \qquad \textbf{(B18)}$$

So the difference in volume can be 0.114 cm^3 higher or lower due to a variation in density than the previous calculated 0.833 cm^3 with equal density. In the case that the difference in volume is higher the systematic error in the weighing of the dust will be (0.114 + 0.833)/0.833 x 0.05 = 0.056 mg.

As normally the density of the glass is not known exactly it is strongly recommended to use glass containers of the same size, the same type of glass and obtained from the same manufacturer, to assure a minimal influence on the systematic error due to a variation in the density.

ANNEX C.1

Correction for buoyancy (method II)

CORRECTION BY MEANS OF THE CALCULATION OF THE AIR DENSITY

Derivation of the correction formula

For the measuring container to be weighted the following formula's are applied:

$$G^{a}_{m1} = G_{m1} - V_m \cdot \rho_{a1} \tag{C1}$$

$$G^{a}_{m2} = G_{m2} - V_m \cdot \rho_{a2} \tag{C2}$$

in which:

G^{a}_{m1} - the apparent weight (reading of the balance) of the measuring container during the pre-weighing

G^{a}_{m2} - the apparent weight (reading of the balance) of the measuring container during the after-weighing

G_{m1} - the true weight of the measuring container during the pre-weighing

G_{m2} - the true weight of the measuring container during the after-weighing

V_m - the volume of the measuring container

ρ_{a1} - the density of air during the pre-weighing

ρ_{a2} - the density of air during the after-weighing

The weight of the dust is calculated by subtracting the true weights of the measuring containers:

$$G_{m2} - G_{m1} = (G^{a}_{m2} - G^{a}_{m1}) + V_m \cdot (\rho_{a2} - \rho_{a1}) \tag{C3}$$

It is assumed that the increase in volume due to the dust is negligible, so that the volume at the after-weighing and pre-weighing are equal. In formula (C3) only the (glass) volume (V_m) of the measuring container is not known. The volume is calculated by combining two formula's:

$$V_m = \frac{G_{m1}}{\rho_c} \tag{C4}$$

$$G_{m1} = G^{a}_{m1} + V_m \cdot \rho_{a1} \tag{C5}$$

in which:

ρ_c - the density of container

Correction for buoyancy (method II, continued)

After rearranging the formula's:

$$V_m = \frac{G^a_{m1}}{(\rho_c - \rho_{a1})} \qquad \textbf{(C6)}$$

In the denumerator of this formula the density of the (ρ_{a1}) can be neglected with respect to the density of the container ρ_c. The density of the air is about 1.25 mg/cm^3 and the density of the container is 2.23 g/cm^3.

Combination of the formula's (C6) and (C3) gives the correction formula with the calculation of the air density:

$$G_{m2} - G_{m1} = (G^a_{m2} - G^a_{m1}) + G^a_{m1} \times \frac{(\rho_{a2} - \rho_{a1})}{\rho_c} \qquad \textbf{(C7)}$$

Determination of the restrictions

The last term in formula (C7) is the correction for the difference in air density. In this correction however also measuring errors are present. Any errors in this correction will add to a systematic error in the result. By applying the law of propagation of errors this error can be estimated.

$$E = G^a_{m1} \times \frac{(\rho_{a2} - \rho_{a1})}{\rho_c} \qquad \textbf{(C8)}$$

$$\Delta E^2 = \left(\frac{G^a_{m1}}{\rho_c}\right)^2 \times \left(\Delta\rho^2_{a1} + \Delta\rho^2_{a2} + \left(\frac{\Delta\rho_c}{\rho_c}\right)^2 \times (\rho_{a2} - \rho_{a1})^2\right) \qquad \textbf{(C9)}$$

The error in both air density determinations is the same, so $\Delta\rho_{a1} = \Delta\rho_{a2} = \Delta\rho_a$.

Formula (C9) is rearranged to:

$$\Delta E^2 = \left(\frac{G^a_{m1}}{\rho_c}\right)^2 \times \left(2 \times \Delta\rho^2_a + \left(\frac{\Delta\rho_c}{\rho_c}\right)^2 \times (\rho_{a2} - \rho_{a1})^2\right) \qquad \textbf{(C10)}$$

ANNEX C.3

Correction for buoyancy (method II, continued)

By setting the same restriction of a systematic error of 0.05 mg as in annex B and assuming an uncertainty of 1% in the density of the container, the maximum allowable error for the determination of the density of the air can be determined. For this estimation the weight of container (G_{m1}^{a}) is taken 20 g, the density of the container (ρ_c) 2.23 g/cm^3, for uncertainty in the density of the container ($\Delta\rho_c/\rho_c$) 1% and the difference in the density of the air ($\rho_{a2} - \rho_{a1}$) a value of 0.06 mg/cm^3 (see annex A).

$$\sqrt{\left(\frac{G_{m1}^{a}}{\rho_c}\right)^2 \times \left(2 \times \Delta\rho_a^2 + \left(\frac{\Delta\rho_c}{\rho_c}\right)^2 \times (\rho_{a2} - \rho_{a1})^2\right)} \leq 0.05 \text{ mg} \qquad \text{(C11)}$$

$$2 \times \Delta\rho_a^2 \leq 0.05^2 \times \left(\frac{\rho_c}{G_{m1}^{a}}\right)^2 - \left(\frac{\Delta\rho_c}{\rho_c}\right)^2 \times (\rho_{a2} - \rho_{a1})^2 \qquad \text{(C12)}$$

$$2 \times \Delta\rho_a^2 \leq 0.05^2 \times \left(\frac{2.23}{20}\right)^2 - 0.01^2 \times 0.06^2. \qquad \text{(C13)}$$

$$\Delta\rho_a \leq 0.004 \text{ mg/cm}^3 \text{ (or kg/m}^3\text{)} \qquad \text{(C14)}$$

In annex D it is shown what the uncertainty in the determination of the ambient pressure, the temperature and the relative humidity should be in order to obtain this uncertainty in air density.

ANNEX D.1

Calculation of the air density

The air density can be calculated in several ways or can be found in handbooks.

In this annex a formula from the Mettler company (1) is used. This formula has been checked against values from the "Handbook of Chemistry and Physics" (2). It was found that the deviations were less than 0.03% for the extreme values mentioned in annex A.

$$\rho_a = \frac{0.348444 \times p_b - \phi \times (0.00252 \times t - 0.020582)}{(273.15 + t)} \qquad \text{(D1)}$$

in which:

ρ_a - actual air density (kg/m^3)

p_b - barometric pressure (mbar)

ϕ - relative humidity (%)

t - temperature (°C)

The error in the air density depends upon the errors in the measurement of the barometric pressure, the relative humidity and the temperature.

In annex C it has been shown that the maximum allowable uncertainty in the air density is 0.004 mg/cm^3. If the uncertainty for the barometric pressure and temperature is taken from the draft standard, then the maximum uncertainty in the measurement of the relative humidity can be determined.

For the both the barometric pressure and absolute temperatue a value of 1% is used in the draft standard (3). This equals to 10 mbar (± 5 mbar) and 2.7 °C (± 1.4 °C).

As the derivation for the propagation of errors is quite complex for formula (D1) an alternative method is used to calculate the maximum allowable error for the relative humidity. This is done by the so-called "spread-sheet"-method (4).

The results of these calculations are shown in table D1.

ANNEX D.2

Calculation of the air density (continued)

Table D1. Uncertainty in air density for different uncertainties in ambient air pressure, temperature and relative humidity

Parameter	Uncertainty					
Pressure (mbar)	± 5	± 1	± 1	± 1	± 1	± 1
Temperature (°C)	± 1	± 1	± 0.5	± 0.5	± 0.5	± 0.75
Relative humidity (% RH)	0	0	0	± 10	± 20	± 10
Air density (kg/m^3)	± 0.0082	± 0.0044	± 0.0024	± 0.0030	± 0.0043	± 0.0038

From these calculations it shows that the stated uncertainties in the draft standard (3) are too high for an accurate air density determination during the weighing. The uncertainty for the pressure should be < ± 1 mbar, the temperature < ± 0.5 °C and the relative humidity < ± 20%, or the temperature < ± 0.75 °C and the relative humidity < ± 10%.

ANNEX E.1

Procedure for evaporation and weighing

This procedure is based on the procedure described in the measuring plan for the field test in "La Chaux de Fonds" (document CEN/TC 264/WG 5 N113) and adapted to the results from the described tests in this report.

1. Clean the measuring containers and one reference container and dry in an oven at 160 °C for at least 1 hour.

2. Cool down in an desiccator (about 2 hours) and weigh the containers.

3. Evaporate the rinsing liquid in an evaporation container at 120 °C for at least 2 hours (to evaporate the acetone). In the test described in this report a mixture of 50 ml acetone and 100 ml of water was used.

4. Then evaporate the water at 160 °C until about 5 - 10 ml of liquid remains (this takes about 4 hours).

5. Transfer this liquid to a weighed measuring container and rinse the evaporation container by adding the liquid to the measuring container.

6. Evaporate at 160 °C until dry (this takes about 4 hours).

7. Cool down in an desiccator (about 2 hours) and weigh the containers.

8. Correct the weighings with the weight difference of the reference container (see annex B).

ANNEX F.1

Weighing results

On the next pages of this annex the weighing results are given.

Used equipment

Balance - Resolution of 0.01 mg at a weighing range of 0 -30 g (Mettler AE 163).

Ambient pressure - Absolute pressure sensor (Druck DPI 261).
Uncertainty < ± 0.3 mbar.

Relative humidity - Relative humidity Sensor (Endress & Hauser RH 2250).
Uncertainty < ± 0.5% RH

Temperature - Measured with the relative humidity sensor (Endress & Hauser RH 2250).
Uncertainty < ± 0.5 °C

ANNEX F.2

Weighing results (continued)

Empty containers

P mbar	1023.2	1025.9	1026.6	1011.5	1009.9	Differences in mg								
RV %	33.9	23.5	25.2	27.7	28.5									
T °C	19.7	19.4	19.2	20.0	19.9									
Air-den.	1.21408	1.21963	1.22118	1.19947	1.19792									
	Weight in g					No correction			Correction with reference			Correction with air density		
Series	**S1**	**S2**	**S3**	**S10**	**S11**	**S2-S1**	**S3-S2**	**S11-S10**	**S2-S1**	**S3-S2**	**S11-S10**	**S2-S1**	**S3-S2**	**S11-S10**
Refer.	19.49059	19.49035	19.49048	19.49070	19.49074	-0.24	0.13	0.04	0.00	0.00	0.00	-0.19	0.14	0.04
M1	16.94966	16.94937	16.94964	16.95045	16.95035	-0.29	0.27	-0.10	-0.05	0.14	-0.14	-0.25	0.28	-0.10
M2	17.96083	17.96057	17.96077	17.96157	17.96148	-0.26	0.20	-0.09	-0.02	0.07	-0.13	-0.22	0.21	-0.09
M3	17.36322	17.36295	17.36319	17.36387	17.36378	-0.27	0.24	-0.09	-0.03	0.11	-0.13	-0.23	0.25	-0.09
M4	18.38327	18.38302	18.38315	18.38390	18.38383	-0.25	0.13	-0.07	-0.01	0.00	-0.11	-0.20	0.14	-0.07
M5	17.22077	17.22058	17.22072	17.22164	17.22159	-0.19	0.14	-0.05	0.05	0.01	-0.09	-0.15	0.15	-0.05
M6	18.50591	18.50569	18.50578	18.50648	broken	-0.22	0.09		0.02	-0.04		-0.17	0.10	
Average (M1-M6)						**-0.25**	**0.18**	**-0.08**	**-0.01**	**0.05**	**-0.12**	**-0.20**	**0.19**	**-0.08**
Standard deviation (M1-M6)						**0.04**	**0.07**	**0.02**	**0.04**	**0.07**	**0.02**	**0.04**	**0.07**	**0.02**

Series 11 : Repeated weighing of measurement number 10

ANNEX F.3

Weighing results (continued)

After evaporation of the rinsing liquid

P mbar	1026.6	1034.5	Differences in mg		
RV %	25.2	29.0			
T °C	19.2	19.4			
Air-dens	1.22118	1.229344			
	Weight in g		No correction	Correction with reference	Correction with air density
	Empty	Rinsing			
Series	**S3**	**S4**	**S4-S3**	**S4-S3**	**S4-S3**
Reference	19.49048	19.49033	-0.15	0.00	-0.08
M1	16.94964	16.94939	-0.25	-0.10	-0.19
M2	17.96077	17.96048	-0.29	-0.14	-0.22
M3	17.36319	17.36288	-0.31	-0.16	-0.25
M4	18.38315	18.38297	-0.18	-0.03	-0.11
M5	17.22072	17.22050	-0.22	-0.07	-0.16
M6	18.50578	18.50567	-0.11	0.04	-0.04
Average (M1-M6)			**-0.23**	**-0.08**	**-0.16**
Standard deviation (M1-M6)			**0.07**	**0.07**	**0.08**

P mbar	1033.0	1030.2	Differences in mg		
RV %	31.5	28.2			
T °C	19.4	19.8			
Air-dens	1.227315	1.222531			
	Weight in g		No correction	Correction with reference	Correction with air density
	Empty	Rinsing			
Series	**S6**	**S7**	**S7-S6**	**S7-S6**	**S7-S6**
Reference	19.49052	19.49065	0.13	0.00	0.09
M1	16.95008	16.95021	0.13	0.00	0.09
M2	17.96107	17.96125	0.18	0.05	0.14
M3	17.36367	17.36389	0.22	0.09	0.18
M4	18.38345	18.38356	0.11	-0.02	0.07
M5	17.22105	17.22112	0.07	-0.06	0.03
M6	18.50624	18.50630	0.06	-0.07	0.02
Average (M1-M6)			**0.13**	**0.00**	**0.09**
Standard deviation (M1-M6)			**0.06**	**0.06**	**0.06**

ANNEX F.4

Weighing results (continued)

After evaporation of the rinsing liquid (continued)

P mbar	1022.6	1011.5	Differences in mg		
RV %	28.2	27.7			
T °C	20.1	20.0			
Air-dens	1.212177	1.199472			
	Weight in g		No correction	Correction with reference	Correction with air density
	Empty	Rinsing			
Series	**S9**	**S10**	**S10-S9**	**S10-S9**	**S10-S9**
Reference	19.49075	19.49070	-0.05	0.00	-0.16
M1	16.95024	16.95045	0.21	0.26	0.11
M2	17.96137	17.96157	0.20	0.25	0.10
M3	17.36376	17.36387	0.11	0.16	0.01
M4	18.38384	18.38390	0.06	0.11	-0.04
M5	17.22154	17.22164	0.10	0.15	0.00
M6	18.50644	18.50648	0.04	0.09	-0.07
Average (M1-M6)			**0.12**	**0.17**	**0.02**
Standard deviation (M1-M6)			**0.07**	**0.07**	**0.07**

ANNEX F.5

Weighing results (continued)

With fly-ash

P mbar	1034.5	1036.3	Differences in mg			Added amount of fly-ash	Differences after subtraction of the added amount of fly-ash (mg)		
RV %	29.0	28.8							
T °C	19.4	20.8							
Air-dens	1.229344	1.225296							
	Weight in g		No	Correction with			No	Correction with	
	Acetone	Fly-ash	correction	reference	air density	mg	correction	reference	air density
Series	**S4**	**S5**	**S5-S4**	**S5-S4**	**S5-S4**	**f**	**S5-S4-f**	**S5-S4-f**	**S5-S4-f**
Refer.	19.49033	19.49055	0.22	0.00	0.18				
M1	16.94939	16.95572	6.33	6.11	6.30	5.67	0.66	0.44	0.63
M2	17.96048	17.96340	2.92	2.70	2.89	2.87	0.05	-0.17	0.02
M3	17.36288	17.37093	8.05	7.83	8.02	7.36	0.69	0.47	0.66
M4	18.38297	18.38669	3.72	3.50	3.69	3.09	0.63	0.41	0.60
M5	17.22050	17.22393	3.43	3.21	3.40	2.73	0.70	0.48	0.67
M6	18.50567	18.51037	4.70	4.48	4.67	4.07	0.63	0.41	0.60
Average (M1-M6)							**0.56**	**0.34**	**0.53**
Standard deviation (M1-M6)							**0.25**	**0.25**	**0.25**

P mbar	1030.2	1023.6	Differences in mg			Added amount of fly-ash	Differences after subtraction of the added amount of fly-ash (mg)		
RV %	28.2	27.5							
T °C	19.8	20.1							
Air-dens	1.222531	1.213437							
	Weight in g		No	Correction with			No	Correction with	
	Acetone	Fly-ash	correction	reference	air density	mg	correction	reference	air density
Series	S7	**S8**	**S8-S7**	**S8-S7**	**S8-S7**	**f**	**S8-S7-f**	**S8-S7-f**	**S8-S7-f**
Refer.	19.49065	19.49070	0.05	0.00	-0.03				
M1	16.95021	16.95265	2.44	2.39	2.37	2.32	0.12	0.07	0.05
M2	17.96125	17.96546	4.21	4.16	4.14	4.03	0.18	0.13	0.11
M3	17.36389	17.36589	2.00	1.95	1.93	1.91	0.09	0.04	0.02
M4	18.38356	18.38691	3.35	3.30	3.28	3.22	0.13	0.08	0.06
M5	17.22112	17.22895	7.83	7.78	7.76	7.76	0.07	0.02	0.00
M6	18.50630	18.51009	3.79	3.74	3.71	3.64	0.15	0.10	0.07
Average (M1-M6)							**0.12**	**0.07**	**0.05**
Standard deviation (M1-M6)							**0.04**	**0.04**	**0.04**

Weighing results (continued)

With fly-ash (continued)

P mbar	1011.5	1023.6	Differences in mg			Added amount of fly-ash	Differences after subtraction of the added amount of fly-ash (mg)		
RV %	27.7	27.5							
T °C	20.0	20.1							
Air-dens	1.199472	1.213437							
	Weight in g		No correction	Correction with		mg	No correction	Correction with	
	Acetone	Fly-ash		reference	air density			reference	air density
Series	**S11**	**S12**	**S12-S11**	**S12-S11**	**S12-S11**	**f**	**S12-S11-f**	**S12-S11-f**	**S12-S11-f**
Refer.	19.49074	19.49067	-0.07	0.00	0.05				
M1	16.95035	16.95321	2.86	2.93	2.97	2.66	0.20	0.27	0.31
M2	17.96148	17.96725	5.77	5.84	5.88	5.45	0.32	0.39	0.43
M3	17.36378	17.36627	2.49	2.56	2.60	2.48	0.01	0.08	0.12
M4	18.38383	18.38864	4.81	4.88	4.93	4.71	0.10	0.17	0.22
M5	17.22159	17.22458	2.99	3.06	3.10	2.69	0.30	0.37	0.41
M6	broken	-				4.30			
Average (M1-M6)							**0.19**	**0.26**	**0.30**
Standard deviation (M1-M6)							**0.13**	**0.13**	**0.13**