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CEN/TC 264/WG 5

Total dust at low concentrations

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Subject :	**Additional test** **Evaluation of a procedure for the recovery of dust deposits upstream of the filter** **February 1997**
Comments	***For information***

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For Info./~~meeting~~/~~comment~~ R. Pearce

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Air Quality

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CEN/TC 264/WG 5

Total Dust at low Concentrations

Evaluation of a Procedure for the Recovery of Dust Deposits upstream of the Filter (Laboratory Experiments)

January/February, 1997

This test was performed as part of a mandat for the European Commission (DG IX) and the EFTA-Secretariat to CEN concerning: A standard for a manual refernce method allowing the calibration of automated meausrement systems for total dust emissions into the air.

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1. Summary

In the laboratory experiments were performed to reduce the uncertainty of the rinsing procedure to recover dust deposits upstream of the filter. For the improved rinsing and evaporation/drying procedure an uncertainty of about 0.7 mg or 0.18 mg/m^3 were found (for 4 samples together as in the 4th ring test). A mechanical cleaning is not recommended because contamination of the brush and rod occurred.

2. Aim of the Measurement

As the results of the 4th ring test indicated, there might be up to 50% of the total dust found as deposits in front of the filter, which cannot be neglected. The ring test also showed that the results of blank rinsing deviate significantly from zero and are therefore a major source for the large uncertainty of this method. Until now unfortunately no validation data has been presented to the working group and therefore additional experiments were necessary to improve the existing procedure. Only by reducing the uncertainty in the rinsing procedure can an acceptable overall uncertainty of the dust measurement be achieved.

The aim of this study is to check and if necessary to improve, step by step, the cleaning, rinsing, evaporation, drying and weighing procedures. A validated method has been presented separately, which is already included in the standard. Also a description of "internal" validation tests for laboratories which intend to use this method is necessary.

According the resolution no 42 (CEN TC 264 WG 5) and the corresponding letter from the secretary (December 12, 1996) EMPA was asked to carry out the experiments proposed in the offer dated December 10, 1996.

3. Measuring Procedure and Equipment

The procedure for these experiments will follow as closely as possible the method specified in the present version of the standard (revision 5, from May 1996). A more detailed description is included in the measuring program of the 4th ring test (document CEN TC 264 WG 5 N 100). If changes or additional steps became necessary they are described in this report.

3.1 Weighing Procedure

In the first step the weighing procedure and the conditioning of the containers were investigate The balance (Mettler AT 201 with a resolution of 0.01 mg) was located in a temperature (22 °C ± 1.0 °C) and humidity controlled room (relative humidity 50 % ± 1 %). A "wind screen" was used to reduce the open space of the balance. The results from the balance were transferred after 1, 2, and 3 minutes to the computer and saved automatically. The automatic calibration mode of the balance was activated at the beginning of each weighing sequence and during the weighing every time the balance demanded. The automatic self calibration of the balance was controlled using an external reference weight of 20 g. The samples were dried in an oven (Salvis; TSW 120 ED) at 160 °C and cooled in desiccator over silica gel for 20 hours instead of the proposed 4h. For larger containers more time is necessary to reach thermal equilibrium. This duration for cooling in the desiccator was kept constant for all experiments.

Experiments:

Five individual containers made of three different materials (PTFE, glass, ceramic) were use The procedure (drying, cooling and weighing) was repeated five times.

3.2 Evaporation and Drying Procedure

Containers:

Material	Manufacturer		Volume	Mass (empty)
PTFE	Teflon® BIOBLOCK			
	NALGENE	(with lid)	250 ml	60 g or 90 g
Glass	PYREX			
	France	(without lid)	250 ml	154 g
Ceramic	Haldenwanger			
	Berlin		200 ml	82 g

Solvents:

Water: NANOPURE (conductivity of ≈ 18 MΩ/cm); filter 0.2 µm pore size

Acetone: Merck p. A. with a certified residue of < 0.001 %
(= 0.008 mg/ml; in 50 ml is < 0.4 mg)

During the evaporation of the solvent mixture NO BOILING is permitted to occur because of the danger of losses. To recover the vapour, especially the acetone, the containers were placed in a desiccator in the oven. The initial temperature was set to 90 °C and the pressure was 400 mbar (absolute). From time to time the temperature and the low pressure were increased. For the last period they were kept at 140°C and 200 mbar (absolute). After the evaporation, which took about 20 h, the containers were placed in the drying oven directly (at ambient pressure) for 2 hours at 160 °C before they were carefully transferred to the desiccator located in the weighing room.

Experiments:

Solvent blank: 10 samples of 100 ml water and 50 ml acetone were evaporated in ceramic containers, dried, cooled and weighed (see paragr 3.1).

Dust recovery: 10 empty containers were dried, cooled and weighed, then a certain amount of dust from an electro static precipitator of a municipal waste incinerator were added. To determine the dust weight exactly, the containers, including dust, were dried, cooled and weighed. After the addition of the solvent the samples were evaporated in ceramic containers, dried, cooled and weighed again (see paragr 3.1).

3.3 Rinsing Procedure

Five identical suction tubes made from titanium were used (length: 2 m; inner diameter 10 mm). The tubes were cleaned before the first experiment following the normal procedure (mechanical cleaning with a brush, water, HNO_3, water, clean air).

For rinsing, one end of the tube was closed and 50 ml cleaning solution pored in. Then the other side was also closed and the tube turned several times.

Without mechanical cleaning:

Rinsing
- washing twice with 50 ml purified water
- washing once with 50 ml acetone (quality p.a.)

Experiments
- Five clean tubes were each rinsed three times and the three samples evaporated in ceramic containers, dried, cooled and weighed (see paragr 3.1).

With mechanical cleaning:

Brushing
- twice
  - washing with 40 ml purified water
  - cleaning with a nylon brush on a titanium rod or with a PTFE patch on a PTFE tube the dust collected on the brush/patch was washed into the container with approx. 10 ml water.
- once
  - washing with 50 ml acetone (quality p.a.)

Experiments
- Five clean tubes were each rinsed and mechanically cleaned three times and the three samples evaporated in ceramic containers, dried, cooled and weighed (see paragr 3.1).

In case of the PTFE tube and patches the sharp edges of the titanium suction tube caused visibl PTFE pieces in the rinsing solution. Therefore only the titanium rod was used for the subsequent experiments.

4. Results

4.1 Empty Containers

Mean difference in mass of empty PTFE containers of five successive weightings

PTFE experiment no.	**mean difference** [mg]	**lowest value** [mg]	**highest value** [mg]	**standard deviation** [mg]
1	-16.41	-29.94	-0.96	11.83
2	2.31	-2.95	8.01	4.47
3	-4.28	-9.90	-0.98	3.56
4	-0.54	-2.16	0.71	1.04
5	0.14	-1.57	1.92	1.48
mean difference	**-3.76**			**5.93**
lowest value		**-29.94**		
highest value			**8.01**	

Comments to PTFE containers:

The weighing of the PTFE containers was very difficult because the results changed several mg per minute even when lids were used. The use of PTFE containers is therefore r recommended.

Mean difference in mass of empty glass containers of five successive weighings

Glass experiment no.	**mean difference** [mg]	**lowest value** [mg]	**highest value** [mg]	**standard deviation** [mg]
1	-0.17	-1.02	0.99	0.75
2	0.23	-0.06	0.45	0.22
3	0.49	0.26	0.72	0.17
4	0.47	0.34	0.70	0.15
5	-0.07	-0.15	0.04	0.08
mean difference	**0.19**			**0.36**
lowest value		**-1.02**		
highest value			**0.99**	

Glass with 1 reference sample no.	**mean difference** [mg]	**lowest value** [mg]	**highest value** [mg]	**standard deviation** [mg]
1	-1.06	0.48	2.01	0.67
2	-0.19	-0.43	0.07	0.23
3	-0.03	-0.25	0.20	0.19
4	0.16	0.04	0.36	0.15
5	-0.15	-0.20	-0.09	0.05
mean difference	**0.17**			**0.34**
lowest value		**-0.43**		
highest value			**2.01**	

Comments to glass containers:

The absolute mass of the glass containers was approx. 154 g. The difference between the lowest and the highest mass was 0.8 g. The correction using a reference container did not improve the deviation from zero. Perhaps better results could be obtained using smaller and therefore lighter containers.

4.3 RINSING PROCEDURE

The blank rinsing was carried out using five clean suction tubes made of titanium, each tube was rinsed three times:

tube no.	rinsing					
	no. 1 [mg]	no. 2 [mg]	no. 3 [mg]			
1	0.03	-0.31	-0.17			
2	-0.30	-0.29	-0.15			
3	-0.21	-0.11	-0.41			
4	-0.27	-0.35	-0.05			
5	-0.05	-0.05	-0.41	**overall mean [mg]**	overall lowest v. [mg]	overall highest v. [mg]
mean	-0.16	-0.22	-0.24	**-0.21**		
lowest value	-0.30	-0.35	-0.41		-0.41	
highest value	0.03	-0.05	-0.05			0.03
standard dev.	0.14	0.13	0.16	**0.15**		

The blank rinsing including mechanical cleaning was carried out using five clean suction tubes made of titanium, each tube was rinsed three times:

tube no.	rinsing incl. mechanical cleaning					
	no. 1 [mg]	no. 2 [mg]	no. 3 [mg]			
1	0.84	0.77	0.53			
2	0.54	0.40	0.62			
3	-	0.34	0.23			
4	0.81	0.89	0.50			
5	0.72	0.86	0.70	**overall mean [mg]**	overall lowest v. [mg]	overall highest v. [mg]
mean	0.73	0.65	0.52	**0.63**		
lowest value	0.54	0.34	0.23		0.23	
highest value	0.84	0.89	0.70			0.89
standard dev.	0.13	0.26	0.18	**0.19**		

In the second table of the glass and ceramic containers the results were corrected by the difference of one container (reference). The result (mean difference) in case of ceramic is much closer to zero.

This procedure improved the weighing because long term changes were corrected (e.g. change of the air density due to variations of ambient pressure). To introduce this correction of the results it seemed advisable to use the average difference of three reference containers.

4.2 Evaporation and Drying Procedure

10 samples of solvent and 10 samples of solvent / dust were evaporated and weighed

sample no.	solvent blank	recovery of dust in the rinsing solutions			
		dust before	dust after evap.	difference	recovery relative
	[mg]	[mg]	[mg]	[mg]	[%]
1	-0.08	12.21	12.20	-0.01	99.9
2	-0.04	13.54	13.76	0.22	101.6
3	-0.01	16.05	15.97	-0.08	99.5
4	-0.09	13.17	13.23	0.07	100.5
5	0.04	13.15	13.36	0.21	101.6
6	-0.30	12.43	12.38	-0.05	99.6
7	0.02	14.45	14.46	0.01	100.0
8	0.02	12.74	12.71	-0.03	99.8
9	-0.01	12.70	12.46	-0.24	98.1
10	-0.17	12.91	12.78	-0.13	99.0
mean	**-0.06**	13.33	13.33	**0.00**	100.0
lowest value	**-0.30**			**-0.24**	98.1
highest value	**0.04**			**0.22**	101.6
standard dev.	**0.11**			**0.14**	1.1

Comments:

The mean values of the solvent blank as well as the difference (before and after the addition/evaporation of solvent) were very close to zero. However, the standard deviation increased from the dry container to the samples including dust.

Mean difference in mass of empty ceramic containers of five successive weighings

Ceramic sample no.	**mean difference** [mg]	**lowest value** [mg]	**highest value** [mg]	**standard deviation** [mg]
1	0.18	0.13	0.24	0.05
2	0.12	0.04	0.22	0.07
3	0.27	0.22	0.30	0.03
4	0.10	0.05	0.16	0.04
5	0.02	-0.04	0.10	0.07
mean difference	**0.14**			**0.06**
lowest value		**-0.04**		
highest value			**0.30**	

Ceramic with 1 reference sample no.	**mean difference** [mg]	**lowest value** [mg]	**highest value** [mg]	**standard deviation** [mg]
1	0.05	-0.11	0.10	0.06
2	-0.03	-0.10	0.08	0.08
3	0.07	0.04	0.08	0.02
4	-0.08	-0.12	-0.05	0.03
5	0.08	0.00	0.14	0.07
mean difference	**0.02**			**0.05**
lowest value		**-0.12**		
highest value			**0.14**	

Comments to ceramic containers:

The absolute mass of the ceramic containers was approx. 82 g. The difference between the lowest and the highest mass was 4.1 g. The correction using a reference container brought the mean very close to zero. The standard deviations of the mass differences were the lowest of the three materials tested.

Comments to the different materials of the containers:

The use of PTFE containers is not recommended. In case of glass and ceramic containers (without reference) the mean differences between two weighings were about the same. Because of the lower standard deviation in the case of ceramic, this material was used for the subsequent experiments.

Comments:

Standard deviations are a little higher than in the case of the evaporation experiments. Taking the negative mean value of the rinsing into account, the mechanical cleaning seems to produce some residue. Because the values do not decrease from the first to the third cleaning the only explanation is that, also in the case of the nylon brush and the titanium rod, some material gets into the solution either from the tube or the cleaning equipment. The rinsing blank under this condition is much lower than the values found during the 4th ring test. Obviously it is much easier to work in the laboratory than at the stack of a plant. As long as a major part of the deposit of real samples is not lost by rinsing only, in our opinion no mechanical cleaning should be used.

5. Conclusions

Ceramic containers showed the smallest standard deviation from one weighing to the next but also smaller glass containers seemed appropriate for the evaporation and drying of rinsing solutions. However, no PTFE containers are recommended.

During the evaporation of the solvent mixture NO BOILING is permitted to occur because of the danger of losses. This step takes a long period of time. During the whole process care has to be taken that no contamination of the samples occurs.

The duration of the cooling phase in the desiccator should be kept constant. The proper calibration of the balance and especially the use of the balance with the containers chosen has to be optimised. Slight air movements or small differences in temperature between e.g. container and balance can disturb the weighing.

Using reference containers of the same size and material long term changes can be corrected (e.g. change of the air density due to variations of ambient pressure). It seems advisable to use the average difference of three reference containers.

The acetone as well as the water used caused no problems with residues. It seems that the batch of acetone had much less dry residue than specified in the certificate.

Each step increases the standard deviation of the weighings slightly but no major increase was found.

The residues found in the rinsing solutions of the tubes showed no decrease, the results were scattered around zero and the overall mean was slightly negative. The problem of the negative mean might be solved by using a reference container to correct the weighings for long term changes (e.g. air density)

The uncertainty (95% confidence level) is calculated from the mean value the standard deviation and the t_{95} factor: $u = \overline{x} + s \cdot t_{95,n-1} \cdot \sqrt{2}$

	mean (absolute) [mg]	standard deviation [mg]	number of results n	$t_{95,\ n-1}$	uncertainty [mg]
dry container	0.14	0.05	25	2.064	0.286
solvent blank	0.06	0.11	10	2.262	0.412
evaporation incl. dust	0.00	0.14	10	2.262	0.448
rinsing	0.21	0.15	15	2.145	0.665
mechanical cleaning	0.63	0.19	15	2.145	1.206

In the 4th ring test after four samples the parts upstream of the filter were rinsed. Assuming that 1 m^3 is the volume per sample then the uncertainty estimated for the rinsing procedure (without mecanically cleaning) is about 0.7 mg or 0.18 mg/m^3 which is much lower than the incerase of the uncetainty from the dust on the filter (repeatability r = 0.48 mg/m^3) to the total dust including rinsing (repeatability r = 1.23 mg/m^3). This indicates that the procedure has been improved or an unknown source of error has been neglected.

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