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Comparison of three methods to determine the active content of aqueous silane or siloxane based hydrophobic impregnation agents

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SUMMARY: Determining the active content (via the dry content) of hydrophobic impregnating agents is often required for quality control. Most standard laboratory methods for determining the dry content are carried out at elevated temperature. When using these methods, the active content is often underestimated considerably as a large part of the active ingredient(s) can evaporate during testing. A method using a microwave oven was proposed by a raw material supplier. The study compares this method with two other methods. They clearly show that the microwave oven method is the most accurate of the investigated methods to measure the active (dry) content of these volatile compounds.

KEY-WORDS: silane, siloxane, hydrophobic impregnating agent, aqueous, dry content

INTRODUCTION

The determination of the active content of hydrophobic impregnating agents on the basis of the dry content is often carried out for quality control of raw materials or as a means of product characterisation. Most standard laboratory methods for determining the water content are carried out at elevated temperatures (105 to 120°C) in order to achieve a fast evaporation of water. Silanes contained in hydrophobic impregnating agents for building materials show a considerable volatility at these temperatures and even siloxanes can be volatile under such conditions.

TRADITIONAL METHODS

Oven method (EN 480-8)

Determination of dry material content according to the European Standard EN 480-8:2012.

A small sample of the hydrophobic impregnating agent (2.0 ± 0.2 g) is dried in an electrical oven at 105 ± 3°C (Fig. 1) until it reaches constant weight.

Figure 1. Laboratory oven, such as as Ehret TK/L 4061 (Ehret Labor- und Pharmatechnik)

Automatic infrared method

The automatic infrared method uses a Mettler Toledo HR 83 Halogen Moisture Analyser (Fig. 2) with the following parameters:

- Drying temperature: 120°C,
- Switch-off criterion No. 3 (Δ weight 1 mg / 50 s).

Note: This switch-off criterion is factory-set. It is suitable for most sample types (standard quality control setting).

A small quantity of the sample (1.0 ± 0.1 g) is dispersed onto a sample pan filled with quartz sand (0.1 - 0.4 mm) and placed in the analyser for the test.

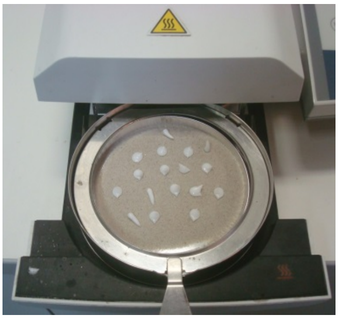

Figure 2. Infrared measurement

PROPOSED NEW METHOD

The proposed method uses a household microwave oven available in any supermarket such as Primotecq MV 1766 Easy Wave (Fig. 3).

Figure 3. Household microwave oven

Required devices and materials

- Microwave oven, such as Primotecq MV 1766 Easy Wave (or similar oven with a maximum power output of 700 W).
- Analytical or semi-analytical balance, such as Mettler Toledo PM 480 Delta Range (readability 0.1mg or 1 mg).
- Laboratory balance (3-6 kg maximum), such as Mettler Toledo XS 6002 S.
- Glass fibre filters Whatman GF 10, diameter 100 mm, GE Healthcare Life Sciences, Cat. No. 10370320 (Note: This test method works only on glass filter paper, such as Whatman GF 10 Glass Fibre Filters, CAT No. 10 370 320. Ordinary cellulose-based filter papers are not suitable).
- Supporting device for glass filters such as a plastic (coated) test tube rack.
- Disposable Pasteur pipets, capacity 2-3 ml or similar pipets.
- Stopwatch.
- Petri dish showing the following dimensions: approximately 190 mm diameter, 90 mm height, 3mm glass thickness.
- Tap water.

Calibration

Prior to using the microwave oven for the measurement of the active content, it is necessary to calibrate it using the method described below:

- 1000 g ± 5 g deionized water of 10-22°C is poured into a 190 mm diameter / 90 mm height petri dish.

- Determine and record the starting temperature of the water portion in the petri dish. All temperatures are measured twice with a thermometer having an accuracy of 0.1°C.
- Place the petri dish in the microwave oven and start the microwave device. Run the microwave device for exactly 60 seconds, measured by a stopwatch.
- Thereafter, mix the water in the petri dish well by stirring and determine the increase in water temperature.
- Repeat twice the microwave irradiation for another 60 s, then measure again the increase in water temperature
- Calculation of power output of the microwave device:
  - Total difference in temperature in °C x 70 = power output in Watts
  - Target power output: 650 ± 32 Watts (618-682 Watts)

The results from a calibration run are presented in Table 1.

Table 1. Results of the calibration measurements for the microwave oven.

Power output setting	Net weight [g]	Temp. 0’ **[°C]**	Temp. 1’ [°C]	Temp. 2’ [°C]	Temp. 3’ [°C]	ΔTemp 0-3’ [°C]	Con-version factor	Power output [Watt]
M-High	1000.0	21.3	26.4	31.2	35.7	14.4	70	1008
Medium	1000.0	21.6	26.3	30.1	33.9	12.3	70	861
M-Low to Medium	1000.2	21.6	24.6	27.8	30.6	9.0	70	630
	1000.1	20.0	23.5	26.6	29.4	0.4	70	658

Methodology

- Weigh 0.5 ± 0.02 g (with an accuracy of ± 0.001 g) of the impregnating agent by placing small, evenly distributed droplets of it on the whole surface of a 100 mm diameter glass filter paper.
- The filter paper is placed on a plastic rack and air dried for 5 minutes. Air must be able to circulate freely.
- Put the rack with the glass fibre filter into the microwave oven, see Fig. 4.
- Irradiation time: 180 seconds or 3.00 minutes at 650 ± 32 Watts power output (using the calibration data obtained previously).
- Weigh the glass fibre filter immediately after irradiation and record the result.
- Quadruple measurements are taken. A maximum standard deviation of 0.7% is tolerated.

Figure 4. Glass filter placed on rack in the microwave oven

TESTED PRODUCTS AND RESULTS

The following commonly used products, listed in Table 2, were used for this study:

Table 2. Product description. Please note that Active Content corresponds to that reported by the manufacturer.

Product type		Chemical base	Active content
A	Silane emulsion	Alkoxy silane	≈40%
B	Silane/siloxane emulsion	Alkoxy silane + siloxane + water	≈60%
C	Silane/siloxane emulsion diluted	Alkoxy silane + siloxane + water	≈7%
D	Silane/siloxane cream	Alkoxy silane + siloxane + water	≈80%

Products A and D are used for concrete protection and are generally applied undiluted. Product B is a concentrated emulsion for brick and natural stone protection. In practice, this product is diluted with water in a ratio ranging from 1:5 to 1:11 by the manufacturer depending on the requirements of the job. Product C is the diluted product B (approx. 1:9), the ready to use emulsion for bricks and stone protection.

The same lot of each material was used for all the test series. Tables 3 to 6 present the experimental data obtained with the three methods.

Table 3. Determination of solid content of product A with the three methods.

Sample No.	Initial sample weight [g]	Final sample weight [g]	Total solid content **[%]**	Average % (Std. Dev.)
Microwave method				
1	0.501	0.199	39.72	40.13 (0.33)
2	0.502	0.203	40.44	
3	0.500	0.200	40.00	
4	0.503	0.203	40.36	
Oven method (EN 480-8:2012)				
1	0.014	0.144	7.15	7.12 (0.07)
2	2.003	0.143	7.14	
3	2.011	0.142	7.06	
4	2.010	0.145	7.21	
5	2.020	0.142	7.03	
6	2.003	0.143	7.14	
Infrared method:				
1	1.004	0.048	4.78	4.64 (0.15)
2	1.033	0.048	4.65	
3	1.024	0.046	4.49	

Table 4. Determination of solid content of product B using different methods

Sample No.	Initial sample weight [g]	Final sample weight [g]	Total solid content %	Average % (Std. Dev.)
Microwave method				
1	0.504	0.298	59.13	59.87 0.55
2	0.503	0.302	60.04	
3	0.506	0.303	59.88	
4	0.498	0.301	60.44	

Table 4 (continued)

Oven method (EN 480-8:2012)				
1	2.046	0.496	24.24	24.21 (0.04)
2	2.033	0.492	24.20	
3	2.000	0.484	24.20	
4	2.013	0.488	24.24	
5	2.007	0.486	24.22	
6	2.001	0.483	24.14	
Infrared method:				
1	1.032	0.241	23.35	23.50 0.44
2	1.028	0.238	23.15	
3	1.067	0.256	23.99	

Table 5. Determination of solid content of product C (Product B diluted 1:9) using different methods

Sample No.	Initial sample weight [g]	Final sample weight [g]	Total solid content %	Average % (Std. Dev.)
Microwave method				
1	0.504	0.036	7.14	7.09 (0.62)
2	0.499	0.036	7.21	
3	0.510	0.032	6.27	
4	0.506	0.033	6.52	
5	0.503	0.037	7.36	
6	0.499	0.040	8.02	
Oven method (EN 480-8:2012)				
1	2.005	0.062	3.09	3.03 (0.09)
2	2.004	0.061	3.04	
3	2.008	0.062	3.09	
4	2.017	0.063	3.12	
5	2.016	0.058	2.88	
6	2.010	0.061	3.03	
Infrared method:				
1	1.011	0.021	2.08	2.04 (0.04)
2	1.028	0.021	2.04	
3	1.043	0.021	2.01	

Table 6. Determination of solid content of product D using the three methods.

Sample No.	Initial sample weight [g]	Final sample weight [g]	Total solid content %	Average % (Std. Dev.)
Microwave method				
1	0.500	0.399	79.80	79.70 (0.54)
2	0.504	0.405	80.36	
3	0.503	0.400	79.52	
4	0.511	0.410	80.23	
5	0.509	0.402	78.97	
6	0.498	0.395	79.32	
Oven method (EN 480-8:2012)				
1	2.023	0.115	5.68	5.60 (0.17)
2	2.026	0.111	5.48	
3	2.004	0.109	5.44	
4	2.005	0.116	5.79	
Infrared method				
1	1.005	0.046	4.58	4.67 (0.13)
2	1.099	0.053	4.82	
3	1.044	0.048	4.60	

The summarized experimental data for each of the four products tested by means of the three methods is given in Table 7.

Table 7. Measurement of dry content using the three methods: EN 408-8.2012 with an electrical oven, the automatic IR method via a Mettler Toledo Moisture Analyser HR83, and the proposed microwave oven

Product type		Specified active content	Measured active content		
			Electrical oven	Moisture Analyser	Microwave method
A	Silane emulsion	≈40%	7.12 ± 0.07	4.64 ± 0.15	40.13 ± 0.33
B	Silane/siloxane emulsion	≈60%	24.21 ± 0.04	23.50 ± 0.43	59.87 ± 0.55
C	Product B, diluted 1:10	≈7%	3.0 ± 0.09	2.04 ± 0.04	7.09 ± 0.63
D	Silane/siloxane cream	≈80%	5.60 ± 0.17	4.67 ± 0.14	79.70 ± 0.54

DISCUSSION AND CONCLUSIONS

Using the traditional evaporation methods such as EN 480-8 or the infrared method to determine the active content (via the dry content) of silane/siloxane emulsions and creams, the values of dry content obtained are grossly underestimated. The cream product is the one having the worst variation compared to the specified active content:

- Product A (refer to Table 7): 7.1 and 4.7% compared to the specified active content of 40% given by the manufacture and confirmed by the microwave method.
- Product D (refer to Table 7): 5.6 and 4.7% compared to the specified active content of 80% given by the manufacture and confirmed by the microwave method.
- Products B and C (refer to Table 7), which contain higher content of siloxanes, seem to be less volatile. However these values are still significantly lower compared to specified values: 2-3% versus 7% and ~24% versus 60% respectively, that were also confirmed by the microwave method.

All solid contents determined by the microwave method match the active contents specified by the manufacturer. The accuracy of these values is good as the standard deviation obtained is very low (below 1%).

Obviously, standard evaporation methods cannot be used for quality control of incoming goods or raw materials or as a mean of product characterisation.

We believe that the observed large variations compared to the theoretical values are due to a dragging effect. The much higher boiling points of silane and siloxane compared to water does not prevent their evaporation when exposed to excessive heat. The water evaporates and pulls silane & siloxane molecules with it thereby simulating much lower solid contents when the equilibrium has been reached. Such methods are completely unsuitable to determine solid content of silane and silane / siloxane emulsions and creams.

The new proposed microwave method is more specific as it selectively activates water molecules.

Therefore, we recommended to use this method for the determination of the dry content (or active content) of all types of aqueous silane and silane/siloxane emulsions. In our opinion this method should be used for product characterisation (especially when required for technical standards or evaluation) or incoming good or raw material quality control.