Water determination in various plastics

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Karl Fischer

Summary

The presence of excessive water in plastics adversely affects the performance of polymeric goods which is why water determination is of crucial importance. This article describes the accurate and straightforward determination of the water content using the Karl Fischer Oven Method in ten different plastic types that are not amenable to direct Karl Fischer titration.

The plastic sample being tested is heated in a hermetically sealed vial. The moisture liberated from the sample is transferred via a dry carrier gas stream into the titration cell where it is coulometrically titrated. For every plastic type, the optimum oven temperature was determined in a water release curve. This procedure ensures fast and quantitative water extraction in a reasonable time while excluding interfering decomposition reactions. Thermally stable polycarbonates, fiber-reinforced polyesters and acrylonitrile-butadiene-styrene (ABS) resins were heated up to 230 °C to extract water. Thermally less stable resins such as polyamides and PVC were only heated to 150 and 100 °C, respectively.

The ten plastic samples investigated showed water contents between 360 and 2120 µg/g. The PVC powder had the lowest water content. However, after three weeks, water re-determination demonstrated a water uptake of 46%. When dealing with hygroscopic plastic samples, special attention should be given to the sample preparation procedure.

Introduction

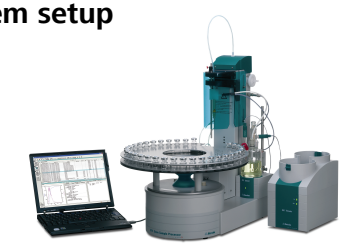
The determination of the water content in plastic pellets is crucial, because it has a significant influence on the characteristics of the final product. Loss on drying (LOD) is a method commonly used to determine the water content. However, when using LOD, not only the water, but the total amount of volatile components released at higher temperatures is determined.

Water determination according to Karl Fischer is an invaluable alternative to specifically determine the water content. Most plastics, as for example PET, are not soluble in solvents commonly used in Karl Fischer titration. Therefore, a direct titration is out of the question. With the 874 Oven Sample Processor, the sample does not need to be dissolved. In a sealed sample vial it is simply heated up to a previously determined temperature and the evaporated water transported to the Karl Fischer titration cell using a stream of dry carrier gas.

This poster deals with the determination of the optimal oven temperature and the water content of different kinds of plastics. The experiments revealed that besides the determination of the oven temperature, sample preparation is one of the most important steps of the analysis, especially in case of hygroscopic plastic samples.

System setup

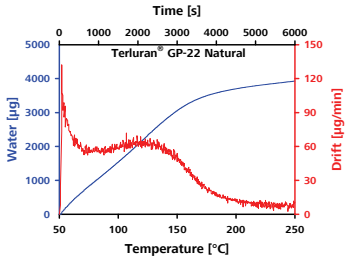
- 874 Oven Sample Processor
- 851 KF Coulometer
- 801 Stirrer



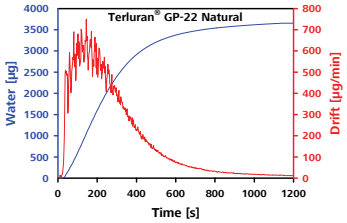
Procedure

- The optimum oven temperature has to be determined:
  The optimum oven temperature for driving off the water ensures complete water extraction in a reasonable time excluding decomposition of the polymer sample. For unknown samples, water release curves are recorded in the temperature range of 50 to 250 °C using a heating rate of 2 °C/min. The red curves show the actual titration rate corresponding to the reacted water amount (drift in µg/min) and the blue curves indicate the absolute amount of determined water in µg.
- Three «blank determinations» (three empty vials with septa) are carried out under measuring conditions.
- Approx. 2 g of sample were weighed in a vial and tightly closed with a septum.
- Samples are placed on the sample processor rack and all relevant data (sample weight, sample identification, T_{oven}, etc.) is entered into the ***tiamo***™ software.
- The system is periodically checked with a Hydranal®-Water Standard KF-Oven with known water content.

Water content in different plastic types



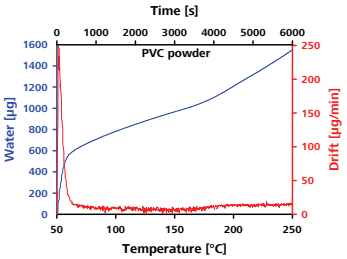
Terluran® GP-22 Natural releases surface water below 70 and bound water below 90 °C. The stable drift below 20 µg/min points to the fact that below 250 °C no decomposition occurred. In contrast, polyamid samples (with the exception of Grilamid TR 55 Natural) showed no stable drift below 20 µg/min. Therefore, in these samples, water was driven off at 150 °C.



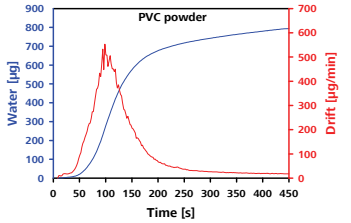
Polymer type	ABS[1]	PA[2]				PPA[3]	PC[4]	PET[5]		Standard
Trade name	Terluran® GP-22 Natural	Grilamid® TR 55 Natural	Ultramid® A3K Natural	Ultramid® A3K Black	Ultramid® A3H-G5 Black	Grivory HTV-3H1 Natural	Makrolon® 1243 (color code 550111)	PET regrind (recyled)	PET regrind (new)	HYDRANAL®-Water Standard KF-Oven, 220...230 °C, 5.57 ± 0.05%
Oven temperature	230 °C	230 °C	150 °C	150 °C	150 °C	150 °C	230 °C	230 °C	230 °C	230 °C
1	1371.0	1078.2	1059.7	907.8	1006.3	695.7	1180.4	2196.2	1661.2	*1 & 2* 5.63 5.56
2	1382.9	1103.0	1057.0	925.0	1028.4	755.9	1167.4	2146.2	1644.3	*3 & 4* 5.52 5.54
3	1384.3	1116.2	1078.4	940.8	1042.6	741.2	1186.0	2144.1	1632.5	*5 & 6* 5.59 5.54
4	1398.1	1183.4	1120.7	993.9	1049.7	773.4	1185.9	2176.1	1635.2	*7 & 8* 5.48 5.50
5	1401.1	1199.2	1114.2	972.0	1065.7	786.6	1174.1	2203.8	1648.5	*9 & 10* 5.58 5.48
Mean value [µg/g]	**1387.5**	**1136.0**	**1086.0**	**947.9**	**1038.5**	**750.6**	**1178.8**	**2173.3**	**1644.3**	**5.54%**
Uncertainty[a] [µg/g]	**15.2**	**65.4**	**37.0**	**43.4**	**27.9**	**43.7**	**10**	**34.3**	**14.2**	**0.034%**

[1]ABS = acrylonitrile-butadiene-styrene-copolymer, [2]PA = polyamide, [3]PPA = poly(phthalamide), [4]PC = polycarbonate, [5]PET: poly(ethylene terephthalate)
[a]Uncertainty = student t-factor × standard deviation × (number of single determinations)$^{0.5}$

Water content in PVC powder



After the initial water release, the drift slightly decreases and remains stable up to 160 °C. At this temperature the drift starts to rise again and the PVC discolors. To avoid interferences from decomposition water, moisture content of the PVC powder was determined at 100 °C. At the time of a three-week re-determination, water content of the PVC powder increased from 365 to 533 µg/g pointing to a significant water uptake during sample preparation.



Polymer type	PVC		Standard
Trade name	Poly(vinyl chloride) sample		HYDRANAL®-Water Standard KF-Oven, 220...230 °C, 5.57 ± 0.05%
Oven temperature, t	100 °C	100 °C, three weeks later	230 °C
1	360	532	*1 & 2* 5.63 5.56
2	375	528	*3 & 4* 5.52 5.54
3	356	531	*5 & 6* 5.59 5.54
4	365	538	*7 & 8* 5.48 5.50
5	370	537	*9 & 10* 5.56 5.48
Mean value [µg/g]	**365**	**533**	**5.54%**
Uncertainty[a] [µg/g]	**9**	**5**	**0.034%**

[a]Uncertainty = student t-factor × standard deviation × (number of single determinations)$^{0.5}$

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