TEST METHOD

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Supersedes: DOWM 101931-E02A

Percent Chlorine and Ash in Chlorinated Polyethylene Resins and Modified Polyolefin Elastomer

1. Scope

This method is applicable to determination of the following in chlorinated polyethylene (CPE) and modified polyolefin elastomer.

Analyte	Applicable Range
	% (wt/wt)
Chlorine	12 to 42
Ash	0 to 10

2. Principle

Two procedures are included in this method. Procedure A is used to measure the chlorine content of chlorinated polyethylene (CPE) and modified polyolefin elastomer. Procedure B is used to determine the ash content of chlorinated polyethylene (CPE) and modified polyolefin elastomer.

Procedure A - Percent Chlorine

The thermogravimetric analysis (TGA) of the sample determines the % wt/wt of hydrochloric acid (HCl) evolved and the total organic loss during heating. The % wt/wt chlorine in the sample is calculated from the % wt/wt HCl which evolved from the sample, the organic loss, the percent calcium stearate (Ca Stearate) and the percent calcium carbonate ($CaCO_3$) in the sample. The percent calcium stearate and calcium carbonate are determined independently from this method.

Procedure B - Percent Ash

A weighed sample is burned in a porcelain crucible over a gas flame then ignited in a muffle furnace and weighed again to determine the ash content.

3. Safety

3.1. Each analyst must be acquainted with the potential hazards of the equipment, reagents, products, solvents and procedures before beginning laboratory work. SOURCES OF INFORMATION INCLUDE: OPERATION MANUALS, MATERIAL SAFETY DATA SHEETS, LITERATURE AND OTHER RELATED DATA. Safety information should be requested from the supplier. Disposal of waste materials, reagents, reactants and solvents must be in compliance with laws and regulations from all applicable governmental agencies.

3.2. Ignition of chlorinated polyethylene (CPE) and modified polyolefin resin samples should be carried out in a fume hood.

4. Interferences (Note 16.1)

No direct interferences have been observed in the use of this method. If results are suspect based on the analytical history of the product, the data should be confirmed by an alternate method.

5. Apparatus

5.1. Thermogravimetric analyzer: Perkin-Elmer TGA-7 system, available from The Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859, or equivalent.

5.2. Platinum sample pan: Perkin-Elmer TGA High Temperature Platinum Sample Pan Kit, Part Number: N5190280, available from The Perkin-Elmer Corp., or equivalent.

5.3. Analytical Balance: capable of weighing to the nearest 0.0001-gram, Mettler model AL204, available from Mettler-Toledo Inc., PO Box 71, Hightstown, NJ 08520, www.mt.com, or equivalent (Note 16.2)

5.4. Porcelain crucible, 25-mL capacity, available from VWR International, 1310 Goshen Pkwy., West Chester, PA 19380-5985, www.vwr.com, or equivalent.

5.5. Crucible tongs, available from VWR International, or equivalent.

5.6. Meeker burner, available from VWR International, or equivalent.

5.7. Muffle Furnace, available from VWR International, or equivalent.

6. Reagents

6.1 Nitrogen: cylinder, less than 1% moisture, available from Fisher Scientific, 2000 Park Lane Dr., Pittsburgh, PA 15275-1126, or equivalent.

6.2 Air: cylinder, less than 1% moisture, available from Fisher Scientific, or equivalent.

6.3 Chlorinated Polyethylene: 25% (wt/wt) chlorine, available from Polysciences Inc., 400 Valley Road, Warrington, PA 18976, or equivalent.

7. Analysis Conditions - Procedure A – Percent Chlorine

Note: The parameters summarized below were used in the validation of the method and are provided as guidelines for setting up the method. The parameters will depend on each TGA system and may differ from those stated below.

Instrument: Perkin-Elmer TGA-7 thermogravimetric analyzer

Initial Conditions: (Note16.3)

Temperature:	50.00°C
Purge gas A:	Nitrogen
Head or Balance:	50 psi nitrogen
Furnace tube:	35 psi nitrogen
Purge gas B:	Air
Furnace tube:	35 psi air

Furnace Program Steps:

Step	Hold / Heat	Temperature	Detail / Rate	Data Points
	Purge furnace tube with Purge Gas A: (nitrogen)			
1	Hold	1.0 min at 50 °C	Isotherm	60
2	Heat	50.0 to 110.00 °C	40.00 °C/min	90
3	Hold	5 min at 110.00 °C	Isotherm	300
4	Heat	110.00 to 410.00 °C	20.00 °C/min	900
5	Hold	5 min at 410.00 °C	Isotherm	300
6	Heat	410.00 to 700.00 °C	80.00 °C/min	217
	1 minute into step 6, switch to Purge Gas B: (air)			
7	Heat	700.00 to 750.00 °C	40.00 °C/min	75
8	Hold	5 min at 750.0 °C	Isotherm	300
	4 minutes into step 8, switch back to Purge Gas A: (nitrogen)			

8. Calibration - Procedure A – Percent Chlorine

Calibrate the TGA according to the instrument manufacturer's operating instructions. (Reference 17.1). The instrument calibration status can be checked by analyzing a chlorinated polyethylene standard (Section 6.3).

9. Analysis Procedure - Procedure A – Percent Chlorine

Note: The instructions given below are specific for Perkin-Elmer TGA-7 system. Use of a different instrument may require modification of these instructions.

9.1. Press the **RAISE FURNACE TUBE** button to raise the furnace tube, if not already raised. Allow the weighing unit to stabilize before proceeding.

9.2. Press the **READ ZERO** button to zero the TGA. Observe the weight and weight % in the data windows. Repeat as needed until reading is stable at zero.

9.3. Press the **LOWER FURNACE** button to lower the furnace.

9.4. Carefully use the sample-pan lifting arm to lift the sample tray from the weighing unit. Carefully add 0.0004 to 0.0006 grams of sample to the sample pan (Section 5.2) and transfer the sample tray back onto the weighing unit.

9.5. Press the **RAISE FURNACE TUBE** button to raise the furnace. Allow the weight unit to stabilize before proceeding.

9.6. Press the **READ WEIGHT** button to weigh the sample. Observe the weight and weight % in the data windows. Repeat as needed until reading stabilizes.

9.7. Press the **INSTRUMENT VIEW** button to select the **INSTRUMENT VIEW** window.

9.8. Press the **START** button to begin the analysis sequence.

9.9. When the run is complete, the **INSTRUMENT VIEW** window will show the results.

9.10. The calculation of percent chlorine in chlorinated polyethylene and modified polyolefin elastomer requires data from other tests that are conducted on the resin samples. The test data required (for the percent chlorine calculation) and the methods used to obtain this data are shown in the following table.

Information needed for calculation	How obtained
% Calcium Stearate	DOWM 101457, most current version, (Reference 17.2) Percent calcium carbonate by FTIR (Note 16.4).
% Calcium Carbonate	DOWM 101382, most current version, (Reference 17.3) Percent calcium stearate by FTIR (Note 16.4).
% HCl loss or Delta Y	Section 9.10.3
% Total Organic Loss	Section 9.10.4

9.10.1. The first calculation for instrument "**DELTA Y**" determines the HCl loss during the analysis and is used to calculate the chlorine. With the **INSTRUMENT VIEW** window open, select "**CALC**" on the tool bar, in the "**CALC**" drop down menu select "**DELTA Y**".

9.10.2. Once the "**DELTA Y**" screen comes up, type in **8** for the "**Left Time Limit**" and **27.5** for the "**Right Time Limit**". These time limits typically cover a temperature range of 200-400 °C. (Note 16.5)

9.10.3. Press "**CALCULATE**" with the mouse pointer or hit "**ENTER**" on the keyboard. Record the resulting value as **HCl loss**. This value will be **A** in the calculation in Section 11.

9.10.4. The next calculation for instrument "**DELTA Y**" determines the **total organic loss** during the run. Calculate a second value using "**DELTA Y**" by setting the "**Left Time Limit**" at **8** and the "**Right Time Limit**" at **37.375.** This value will be **B** in the calculation in Section 11 (Note 16.5).

9.11. Calculate the percent chlorine using the equation in Section 11.

10. Analysis Procedure - Procedure B - Percent Ash

10.1. Weigh a clean, dry porcelain crucible on the analytical balance (Section 5.3) and record the weight to the nearest 0.0001-gram.

10.2. Add approximately 2.00 grams of resin sample to the crucible and record the weight to the nearest 0.0001-gram.

10.3. Using crucible tongs, hold the crucible over the flame of the Meeker burner located in a fume hood and burn off the sample.

10.4. Using crucible tongs, place the crucible containing the residue inside a muffle furnace at 760°C for 10 minutes.

10.5. Using crucible tongs, carefully remove the crucible from the muffle furnace and allow the crucible to cool.

10.6. Weigh the crucible containing ash and record the weight to the nearest 0.0001-gram.

10.7. Calculate the percent ash in the sample using the equation in Section 12.

11. Calculation (Note 16.1) - Procedure A - Percent Chlorine

If manual calculations are used, calculate the % wt/wt chlorine concentration in the original sample as follows:

$$\text{Wt/wt \%Chlorine} = \frac{A \times 0.9726 \times 0.9331}{B} - (0.4 \times C) + (0.253 \times D) - 1.851 \times 100\%$$

where:

A	=	HCl loss, in % (wt/wt) (Section 9.10.3)
B	=	Total organic loss, in % (wt/wt) (Section 9.10.4)
C	=	Calcium stearate (%) (Reference 17.2)
D	=	Calcium carbonate (%) (Reference 17.3)
0.9726	=	Weight ratio of chlorine in HCl (Atomic Wt. for Chlorine ÷ GMW of HCl)
0.9331	=	slope of the linear regression line for apparent TGA % (wt/wt) chlorine versus % (wt/wt) chlorine by neutron activation analysis (NAA). (See note immediately below for more detailed explanation)
1.851	=	Intercept of the linear regression line for apparent TGA % (wt/wt) chlorine versus % (wt/wt) chlorine by neutron activation analysis (NAA)
0.4	=	Linear Regression Factor for the effect of calcium stearate on % (wt/wt) chlorine results (Note 16.5)
0.253	=	Linear Regression Factor for the effect of calcium carbonate on % (wt/wt) chlorine results (Note 16.5)
100%	=	Conversion to % (wt/wt)

Note: During method development, samples of Chlorinated Polyethylene (CPE) were analyzed by both Neutron Activation Analysis (NAA) and Thermogravimetric analysis (TGA). A statistical software program (Note 16.6) was used to perform a linear regression analysis on the apparent (measured) weight percent chlorine (results from the TGA analysis) versus (the results of) the NAA analysis. The slope and intercept of the linear regression lines are included in the calculation for weight percent chlorine in chlorinated polyethylene (CPE). Similarly, the effects of calcium stearate and calcium carbonate were obtained by adding each of these components as an independent effect into the linear regression model (Note 16.5). The effects for these components are also included in the calculation for weight percent chlorine in chlorinated polyethylene (CPE).

12. Calculation - Procedure B - Percent Ash

Calculate the percent ash in the sample as follows:

$$\%\text{Ash} = \frac{\left(\text{Wt.}_{\text{Crucible + Ash}} - \text{Wt.}_{\text{Crucible}}\right)}{\left(\text{Wt.}_{\text{Crucible + Sample}} - \text{Wt.}_{\text{Crucible}}\right)} \times 100$$

where:

% Ash	=	% (wt./wt.) of ash in the resin sample
$\text{Wt.}_{\text{Crucible + Ash}}$	=	the weight, in grams, of the crucible and ash that remains after heating in the muffle furnace (Section 10.6)
$\text{Wt.}_{\text{Crucible + Sample}}$	=	the weight, in grams, of the crucible plus the resin sample used for the analysis (Section 10.2)
$\text{Wt.}_{\text{Crucible}}$	=	the weight, in grams, of the crucible (Section 10.1)
100	=	factor to convert results to % (wt/wt)

13. Precision (Note 16.7)

Precision data determined from multiple analyses [n] of two samples of chlorinated polyethylene and two samples of modified polyolefin elastomer over a two day period are given below. The estimated prediction intervals at the 95% confidence level [$\pm t_{(n-1)} \times s$; where $t_{(n-1)}$ = t-value at n-1 degrees of freedom, and s = standard deviation of the validation data] relate to future final results determined on similar samples. This assumes a normal distribution of results and equal variability between locations.

Percent Chlorine Analysis

Sample	**n**	**$t_{(n-1)}$**	**Average Chlorine Concentration $\bar{x}$**	**Standard Deviation** s	**Estimated Prediction Interval at the 95% Confidence Level for a future result**
			(% (wt/wt))	*(% (wt/wt))*	*(± % (wt/wt))*
Chlorinated polyethylene 1	10	2.262	25.68	0.199	0.450
Chlorinated polyethylene 2	10	2.262	41.92	0.470	1.060
Modified polyolefin elastomer 1	10	2.262	11.09	0.448	1.014
Modified polyolefin elastomer 2	10	2.093	27.41	0.233	0.527

The distribution of the percent chlorine results is assumed to be normal. The validity of this assumption has been verified using the Shapiro-Wilk test for normality. The test confirmed that the results for the percent chlorine analysis could originate from a normal distribution.

Percent Ash Analysis

Sample	**n**	**$t_{(n-1)}$**	**Average Ash Concentration** $\overline{X}$	**Standard Deviation** s	**Estimated Prediction Interval at the 95% Confidence Level for a future result**
			(% (wt/wt))	*(% (wt/wt))*	*(± % (wt/wt))*
Chlorinated polyethylene 1	10	2.262	1.58	0.042	0.10
Chlorinated polyethylene 2	10	2.262	3.41	0.032	0.07
Modified polyolefin elastomer 1	10	2.262	1.89	0.088	0.20
Modified polyolefin elastomer 2	10	2.262	3.41	0.074	0.17

The distribution of the Ash results is assumed to be normal. This assumption has not experimentally verified but is based on common experience in the field.

14. **Accuracy** (Note 16.7)

Analyses of four chlorinated polyethylene samples containing 25 to 42 % (wt/wt) of chlorine in polyethylene gave accuracies that averaged 98.0 % with a range of 95.6 to 99.6 % and a standard deviation of 1.73 %.

15. **Linearity** (Note 16.7)

The method was found to be linear over the range of 25 to 42 % (wt/wt) chlorine in chlorinated polyethylene.

16. **Notes**

16.1. If the additive package differs from the additive package used in this method validation the linear regression factors, precision, accuracy and linearity of the method will need to be evaluated and redetermined as necessary.

16.2. The accuracy of balances should be confirmed on a regular basis and documentation of the check should be kept.

16.3. Pressures can be converted into flow rates using an H-restrictor which is set at 1 psi = 1 mL/min.

16.4. The calcium stearate and calcium carbonate must be determined on a portion of the same chlorinated polyethylene lot as used for the TGA determination.

16.5. The time limits used in section 9.10.2 and 9.10.4 were established during earlier research done at The Dow Chemical Company. They were chosen based on the consistency of the method. These values are expected to be constant over the specified range of the method.

16.6. The factors for calcium stearate and calcium carbonate in Section 11 were obtained by adding each as an independent effect into the linear regression model. Those factors are applicable for the ranges of zero to 4 % (wt/wt) of calcium stearate and zero to 6 % (wt/wt) of calcium carbonate in chlorinated polyethylene.

16.7. The equation, displayed in Section 10, attempts to correct for additives (calcium stearate and calcium carbonate) present in the CPE sample, and to ensure that the TGA chlorine value correlates well to values obtained through neutron activation analysis (NAA). The samples used in the validation study had concentrations ranging from 25 to 42 % (wt/wt) chlorine, zero to 4 % (wt/wt) calcium stearate and zero to 6 % (wt/wt) calcium carbonate. A statistical software program was used to develop the linear regression model to correlate NAA chlorine levels against TGA measurements. The values obtained from the linear regression model that are used in Section 10 are not expected to change provided the same additive package is used.

16.8. In accordance with good laboratory practices, it is strongly suggested that the precision, accuracy and linearity of the method be re-determined if another set of equipment or additive package are to be used, or the method is to be used in another laboratory.

17. References

17.1. Perkin-Elmer TGA-7 operating manual, available from The Perkin-Elmer Corp., 761 Main Avenue, Norwalk, CT 06859.

17.2. DOWM 101457 (most recent version), "Calcium Stearate in Chlorinated Polyethylene Containing Calcium Carbonate Using Fourier Transform Infrared Spectroscopy", available from The Dow Chemical Company, Analytical Sciences, Midland MI 48667.

17.3. DOWM 101382 (most recent version), "Calcium Carbonate in Chlorinated Polyethylene Using Fourier Transform Infrared Spectroscopy" available from The Dow Chemical Company, Analytical Sciences.