Analysis of metals content in Thermo Scientific[™] Nalgene[™] HDPE bottles and competitors

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Key Words

Bottles, HDPE, metal content

Goal

Highlighting the extremely low content of metals in Thermo Scientific™ Nalgene™ plastic bottles.

Abstract

In many systems plastic bottles are used to contain reagents, intermediates, and products in solution. In such systems, it is critical to ensure that the bottle remains strictly a container and does not interact with the contents to change them in any way. Low levels of certain metals are often found in plastic resins, and due to the nature of plastic these can be extracted from the resin by many solvents. Here, we examine the metal content of high density polyethylene (HDPE) bottles from several different brands, and find that Thermo Scientific Nalgene HDPE bottles contain lower levels of metals than competitors. These bottles have a clear advantage for use in containing reagents that are sensitive to contamination from metals.



Introduction

Containers made of plastic resins are used to contain a wide variety of materials in many different settings. Especially in the biological and chemical fields, these materials can include high-value reagents, intermediates, or products; or critical components in sensitive assays. Some of these types of materials can be extremely sensitive to reactive compounds that may be found in the plastic, even at low concentrations. In such cases, the value of the container goes beyond the ability to maintain the closure seal and includes any manner in which the plastic container itself alters the contents. While plastic containers are a generally inexpensive solution for storage of reagents or products, low-quality containers may result in higher costs in the long run through the contamination and subsequent loss of high-value contents. Part of the quality offering on these types of containers is the verification that they do not leach detrimental substances into the solutions contained within. Metal contamination is of particular interest in plastic containers, since they are often present at some levels in the plastic base resin and

can react readily with many solutions that are normally stored in them. Here, we examined the metal content, as well as limited other contaminants, of several different bottles made with a high-density polyethylene (HDPE) base resin, and compared bottles from Thermo Scientific Nalgene to several competitors.



Experimental details:

Metals were evaluated by High Resolution Inductively Coupled Plasma Mass Spectrometery (ICP-MS).

Sample Preparation

Three bottles of each brand were tested. A portion (approx. 200-250 mg) of plastic was cut from the body of each bottle using a zirconium ceramic-blade knife that was cleaned between each sample. Each plastic piece was deposited directly into a polypropylene centrifuge tube for cleaning. The goal of cleaning was to remove any surface contamination resulting from the cutting process. Approximately 2 mL of a 2% solution of nitric acid (HNO $_3$, Fisher brand Optima grade) in ultrapure (18.2 M Ω -cm) water was added to each tube. The tube was shaken for about one minute, and then the 2% HNO $_3$ was poured off of the sample. Ultrapure water was used to rinse the sample and tube twice, and the sample was allowed to dry at room temperature inside the tube.

Sample Digestion

Cleaned, dried samples were weighed into Teflon digestion vessels and nitric acid (3.5 mL) and Fluka brand TraceSelect Ultra grade 30% hydrogen peroxide solution (H_2O_2 , 1.5 mL) were added to each vessel. The vessels were sealed and heated to 190°C in a microwave digester.

After the vessels cooled, they were opened and the contents rinsed into a pre-cleaned, pre-weighed 2 oz.

Nalgene LDPE bottle. The digested samples ("digestates") were diluted to approximately 50 g total with ultrapure water. Two samples of Nalgene LDPE bottles were also digested for comparison. Spike recovery tests were performed for additional portions of three plastic bottles. A known amount of each element of interest (except Hg) in the form of a liquid standard was added to the sample prior to digestion. Results for unspiked and spiked replicates were compared in order to calculate percent recoveries. These recoveries are listed in the results table.

Vessel blanks (empty vessels microwaved with digestion reagents) were prepared and analyzed alongside the samples in order to check for vessel and/or reagent backgrounds. These backgrounds were found to be insignificant.

Preparation of standards: Instrument calibration standards were prepared from commercially purchased (High Purity Standards) single- and multi- elemental solutions. Standards were prepared gravimetrically, with weighing at every step, in order to accurately calculate exact concentration values. 2% HNO, was used as a diluent. The standards consisted of four series, each with five different concentrations, which encompassed all elements of interest (except for Hg). Digested polymer samples were diluted for analysis by a factor of 2 using ultrapure water. For those samples that contained very high levels of certain elements, further dilutions and re-analyses were performed. Internal standards Sc, In, and Tl were added to all samples and standards. Internal standards are used to correct for matrix effects in the instrument.

Instrumental Analysis: All samples were analyzed using a VG Axiom high-resolution ICP-MS. A total of four instrumental runs were required to analyze all samples. For each run, the necessary standards were analyzed to calibrate the ICP-MS. Blanks and QC standards were analyzed throughout each run in order to monitor backgrounds and ensure continuous and correct instrument response. The calibration for Hg was calculated based on the response of Tl and a measured historical response factor. Thus the Hg limits of detection should be regarded as semi-quantitative. No Hg was detected in any of the samples. For the polymer samples, results are reported in units of ppb, or parts per billion by weight (ng/g), relative to the solid plastic.

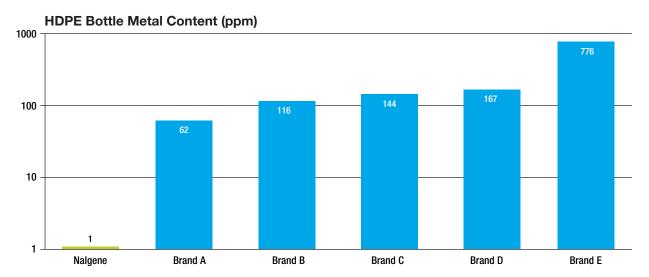


Figure 1. Total metal content (plus silicon and phosphorous) in various brands of HDPE bottle, in parts per million (ppm). Y-axis is logarithmic.

250 and 500 mL plastic bottles were analyzed for content of selected metals as well as silicon, phosphorous, and antimony. Nalgene bottles were found to contain far less total metal contamination than nearest tested competitor. With silicon and phosphorous included, the nearest competitor was more than an order of magnitude higher in contamination than Nalgene bottles (Figure 1). On examination of individual contaminants (Table 1), Nalgene bottles were found to have the lowest levels (or below the limit of detection) in 12 out of the 17 substances tested for, and were very near the lowest levels in 4 of the remaining substances. Nalgene bottles were also below the limit of detection for biologically toxic lead and mercury. In comparison, several competitors had contamination levels several orders of magnitude higher than Nalgene with some or many of the substances tested. In some cases, these measurements ranged into the tens (or hundreds) of parts per million, whereas contamination in Nalgene bottles was found only in parts per billion.

It is important to note that due to the digestion process used for this study, the levels found are higher than those likely to be found in the bottle contents. This test represents the worst-case scenario of all metals that could possibly be extracted from the plastic. However, knowing the levels of contaminants is important, especially since containers for diagnostics and specialty packaging often are used for intermediate storage of reagents used in highly sensitive analytical chemistry and critical assays. In such applications, even small concentrations of specific metals can alter results. For example calcium, magnesium, and zinc can cause protein precipitation and/or enzyme

inactivation. Bottles used for packaging peroxidase reaction reagents are very sensitive to iron and manganese as these can degrade hydrogen peroxide, reducing assay sensitivity. Reagents used for testing blood levels of calcium or magnesium are also sensitive to contamination from these metals which may alter test results. The high quality of both the virgin plastic resin and the process and tooling used to mold these bottles allows Nalgene to produce bottles with very low metal content. In such highly sensitive systems, using Nalgene bottles would be very beneficial in maintaining the integrity of any assays using reagents stored in plastic bottles.

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Conclusion

The extremely low quantity of detectable metals is indicative of the high quality of both the resin and the process used to manufacture Nalgene HDPE bottles.

	Nalgene, 500 mL HDPE	Brand A, 500 mL HDPE	Brand B, 500 mL HDPE	Brand C, 500 mL HDPE	Brand D, 250 mL HDPE	Brand E, 500 mL HDPE
Na	<lod< td=""><td><lod< td=""><td>393</td><td>218</td><td><lod< td=""><td>167</td></lod<></td></lod<></td></lod<>	<lod< td=""><td>393</td><td>218</td><td><lod< td=""><td>167</td></lod<></td></lod<>	393	218	<lod< td=""><td>167</td></lod<>	167
Mg	<lod< td=""><td>26</td><td>37</td><td>8,454</td><td>740</td><td>109</td></lod<>	26	37	8,454	740	109
Al	383	311	2,702	9,457	12,949	392
Si	147	46,136	96,050	10,050	267	137,981
Р	152	13,285	15,377	20,251	88	142
Ca	<lod< td=""><td>164</td><td>85</td><td>93,308</td><td>122,537</td><td>423</td></lod<>	164	85	93,308	122,537	423
Ti	466	1,177	15	1,544	29,447	198
Cr	<lod< td=""><td>770</td><td>1,229</td><td>3</td><td>117</td><td>1,991</td></lod<>	770	1,229	3	117	1,991
Fe	68	55	45	258	513	235
Ni	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>70</td><td>111</td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>70</td><td>111</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>70</td><td>111</td></lod<></td></lod<>	<lod< td=""><td>70</td><td>111</td></lod<>	70	111
Zn	<lod< td=""><td>22</td><td>163</td><td>110</td><td>249</td><td>634,080</td></lod<>	22	163	110	249	634,080
Мо	<lod< td=""><td><lod< td=""><td>6</td><td><lod< td=""><td>9</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td>6</td><td><lod< td=""><td>9</td><td><lod< td=""></lod<></td></lod<></td></lod<>	6	<lod< td=""><td>9</td><td><lod< td=""></lod<></td></lod<>	9	<lod< td=""></lod<>
Cd	3	<lod< td=""><td>4</td><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	4	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Sn	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Sb	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td>7</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td>7</td><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>7</td><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td>7</td><td><lod< td=""></lod<></td></lod<>	7	<lod< td=""></lod<>
Hg	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td><lod< td=""></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""></lod<></td></lod<>	<lod< td=""></lod<>
Pb	<lod< td=""><td><lod< td=""><td><lod< td=""><td>1</td><td>6</td><td>8</td></lod<></td></lod<></td></lod<>	<lod< td=""><td><lod< td=""><td>1</td><td>6</td><td>8</td></lod<></td></lod<>	<lod< td=""><td>1</td><td>6</td><td>8</td></lod<>	1	6	8
Total	1,220	61,946	116,107	143,652	167,000	775,836

Table 1. Levels in parts per billion (ppb) of substances extracted from samples taken from several HDPE bottles. COD indicates the sample contained below the level of detection for the indicated substance.">COD indicates the sample contained below the level of detection for the indicated substance.

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