Microwave Extraction Provides More Reliable Analysis of High Mass Unit Additives

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Shortly after the European Union (EU) adopted the RoHS (Restriction of Hazardous Substances) and WEEE (Waste from Electrical and Electronic Equipment) Directives, a major testing problem became apparent. These Directives are aimed at restricting the levels of certain materials in products being imported into the EU. The testing issue arises from the fact that there is no reliable, cost-effective way to test for the presence of high mass unit additives such as polybrominated flame retardants (PBB and PBDE).

These additives are used in a wide variety of material types, from rigid plastics to foams. Accurate extraction of PBB/PBDE from this range of materials depends in a large degree on the choice of solvent. In addition, for the testing to be cost-effective, sample size is a major limiting factor.

Initially, it was thought that EPA Method 1614 could be adapted for this analysis. However, efforts to do so showed that the method was limited in addressing the issues noted above. For example, Method 1614 specifies that samples be dissolved in several hundred milliliters of either toluene or methylene chloride solvent, which are expensive to dispose of. The method also requires a 10-gram sample and an extraction period of 16 to 24 hours. Further, a review of ASTM D5226-98, *Standard Practice for Dissolving Polymer Materials,* indicates that following EPA Method 1614 would not provide suitable extraction of copolymers, certain elastomers and various other materials.

A variety of methods were examined to overcome these problems, and extensive testing has shown that microwave-digestion is a suitable means of extracting polybrominated flame retardants from a wide range of materials. Advantages of this method are that it requires less than 50-ml of solvent and a sample size of 0.5 grams or less. Extraction time also can be cut to about four hours. The net result is considerable savings in both time and solvent costs. Tests on materials of known concentration produced results that were both precise and accurate.

Background

The RoHS Directive took effect in the EU in July 2006. The Directive severely restricts the concentration of lead, cadmium, mercury, hexavalent chromium and PBB/PBDE fire retardants in electronic equipment. RoHS specifies a maximum concentration value (MCV) of 0.01% by weight in homogeneous materials for cadmium and 0.1% by weight in homogeneous materials for lead, mercury, hexavalent chromium, polybrominated biphenyls (PBBs) and polybrominated diphenyl ethers (PBDEs).

MCVs define the maximum amount of the restricted substance that will be tolerated in each homogeneous material. The EU defines a homogeneous material as a unit that cannot be mechanically disjointed into single materials. Mechanical disjointed means that the materials can theoretically be separated mechanically by unscrewing, cutting, crushing, grinding or abrading. Therefore, a homogeneous material can be understood as being of uniform composition throughout; for example certain plastics, ceramics, glass, metal, alloys, paperboard, resins and coatings.

While reliable methods are available to test for cadmium, lead, mercury and hexavalent chromium, high mass unit materials such as PBB and PBDE are more difficult to extract. Presently, the only method that addresses such materials is EPA Method 1614, which describes a Soxhlet extraction method to remove PBDE from water, soil, sediment and tissue using High-Resolution Gas Chromatography (HRGC) and High-Resolution Mass Spectroscopy (HRMS).

However, while this method is accurate for extracting PBDE from the environment and biological matter, it has severe limitations for use with materials used in consumer electronics. First, the method calls for a 10-g sample. This sample size is significantly larger than the 0.5-g sample typically used for industrial materials and would require a great deal more time and effort to prepare.

Second, Method 1614 specifies that the sample be dissolved in several hundred milliliters of either toluene or methylene chloride. These solvents are not only expensive to purchase, they are also hazardous to handle and expensive to dispose of. As a result, tests using this method would be prohibitively expensive for the average supplier of consumer electronics.

The final problem is extraction time. Method 1614 typically requires 16 to 24 hours to run, which severely limits the number of tests a lab can perform in a day and increases the likelihood of errors that would invalidate the test. The long extraction time also increases test costs and would cause potential delays in getting a product to market.

All these problems pointed to the need for a less costly, less time-consuming method for extracting PBB and PBDE from consumer electronics products. A method based on microwave extraction shows promise, not only for polybrominated flame retardants but also for other high mass unit compounds.

Microwave Extraction

The new method is based on microwave digestion of polymers to extract PBB and PBDE. Basic steps in the process are:

Step 1 – Perform FTIR analysis on the sample to determine its polymer make-up. This is necessary to select the proper solvent later in the procedure.

Step 2 – Grind the polymer cryogenically and sieve to form a fine powder. This is a critical step because one concern in developing the method was the completeness of the extraction. Additives such as flame retardants are used at such low levels that efficient extraction is often a problem. To minimize this issue, the sample is ground under cryogenic conditions and sieved through fine mesh filters to produce an extremely small particle size.

Cryogenic grinding reduces polymer samples to a fine powder that provides a large surface area for the solvent to attack. Additives in samples ground this way are extracted more efficiently with more consistent results.

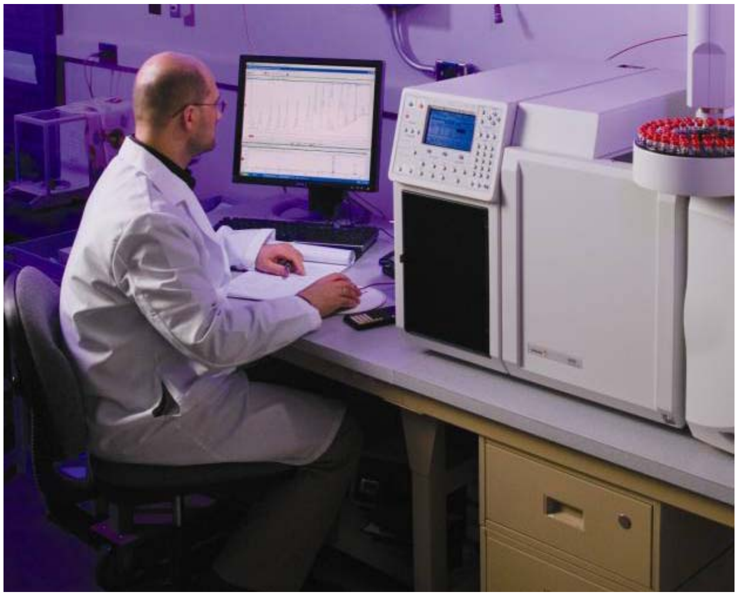
Cryogenic grinding ensures that samples are homogeneous and facilitates extraction by providing a large surface area for the solvent to attack. It was found that samples ground in this manner were extracted more efficiently with more consistent results.

Step 3 – Weigh the sample into a glass vial and add solvent. Determining the proper solvent was another challenge in developing the new method. Accurate quantification of PBB and PBDE flame-retardants depends not only on having the correct instrument, but also on the efficiency of extracting the compound from the material under test. Selecting the proper solvent is critical to ensure the complete removal of all PBB and PBDE for analytical testing. A related concern was to limit he amount of hazardous solvent to be handled.

A wide variety of solvents and solvent combinations were tested in the course of developing the new method. Results showed that a proprietary solvent mix, which is tweaked depending on the make-up of the polymer, provides excellent results in various matrixes. The solvent also reduced the amount of hazardous materials used as well as the total volume of solvents. In addition, it effectively dissolved a broader range of materials.

Step 4 – Insert the sample into a microwave vessel and run the digestion. Tests show that three successive digestions are required to extract 99.999% of the additive.

Step 5 – Combine the three extractions, and analyze with a GC/MS to determine the amount of additive present.



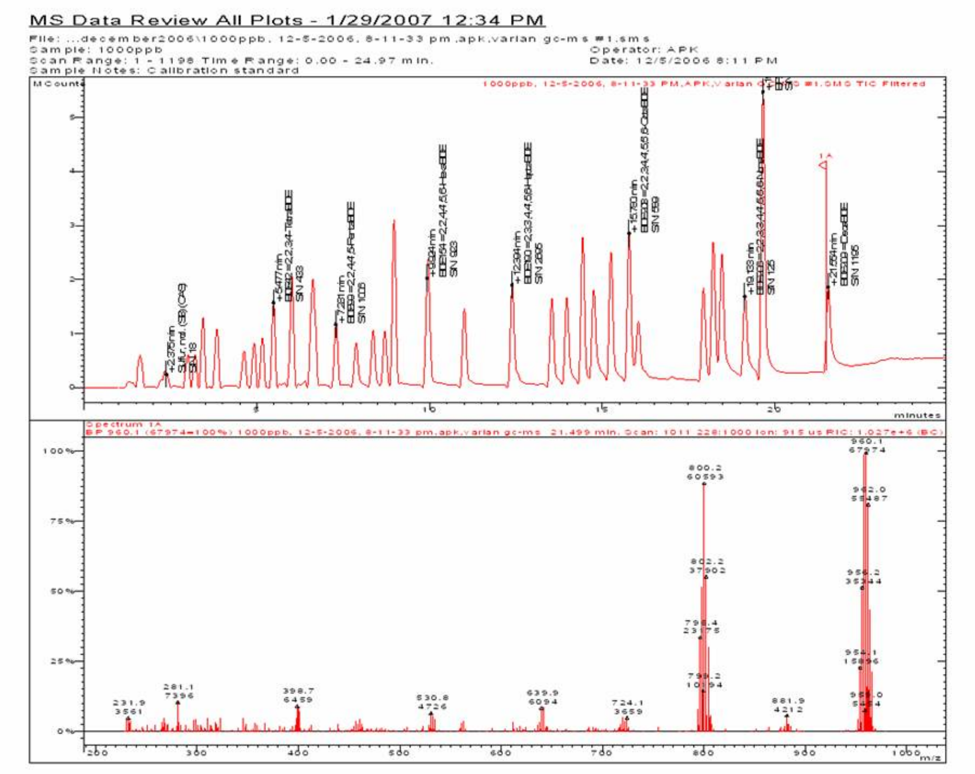
Gas Chromatography/Mass Spectrometer (GC/MS) provides a reliable indication of the presence of restricted materials; however, not all GC/MS equipment can detect the higher brominated forms of PBDE.

The main advantage of the microwave method is that it requires a sample size of 0.5 grams or less. In addition, it requires less than 50-ml of solvent. Finally, extraction time is only about four hours. The net result is considerable savings in both time and solvent disposal costs. Tests on materials of known concentration have produced results that are both precise and accurate.

Although the method has been fully tested only on polybrominated flame retardants, it is believed that it would be beneficial in the analysis of other high mass unit polymer additives.

Test Results

Due to the need to meet the requirements of the RoHS and WEEE Directives, the microwave extraction method was tested on components containing polybrominated flame retardants. However, before testing could begin, the lack of appropriate GC/MS standards had to be addressed. Theoretically, over 400 congeners of PBB and PBDE flame retardants are available, and each produces a specific profile in GC/MS analysis.

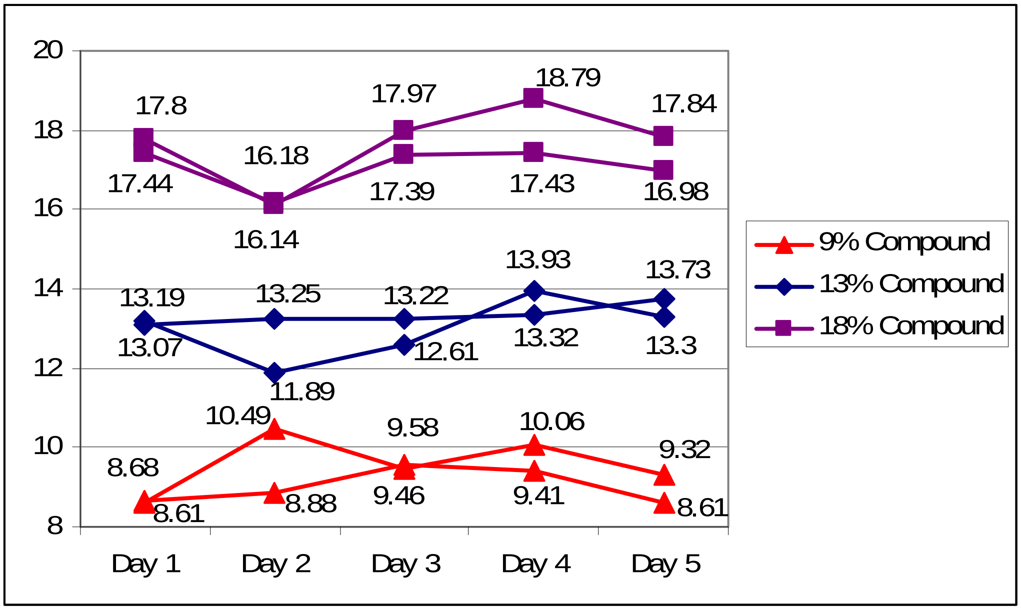


Two clusters of spikes on this GC/MS plot are characteristic of materials containing PBB and PBDE flame-retardants.

In reality, industry uses only about a handful of congeners of known concentration. Therefore, standards with known flame retardant concentrations of 9, 13 and 18% were examined to verify the test method. Samples were run in duplicate for 20 consecutive days.

To ensure maximum extraction, four digestions were done in sequence. Each extraction was run for 1 hour and recovered 99%, 0.9%, 0.099% and 10 ppm residual congener, respectively. These results indicate that three extractions are sufficient to recover the optimum amount of additive.

The graph below shows the extraction ranges for a deca-polybrominated di-phenyl ether congener. The data show an extraction efficiency of 99.999% with three successive extractions.



Other Applications

Tests have shown that the microwave-digestion method can be used to extract other materials besides flame retardants, including bisphenol, organotin, phthalates and PAH compounds. Future work will concentrate on proving applicability to other high mass unit additives used in plastics, such as UV absorbers, stabilizers, plasticizers, flow additives, etc.

One concern in applying this method to other high mass unit compounds is the potential for degradation of some additives by microwaves. This problem can be reduced by pressurizing the sample, thereby allowing the microwave apparatus to operate at a lower temperature.

Another issue that will be the subject of future development is the proper way to test a cured polymer system such as epoxy. These polymers present a challenge because the fire-retardant is bound into the chemical structure and is difficult to extract. Tests have shown that extremely fine grinding is required to extract the additive effectively.

In addition, future testing will be aimed at proving that the extraction technique works with a complex assembly of materials such as a circuit board. Typically, to obtain an accurate reading of additive content, a larger sample is required, and the percentage of polymer content in the assembly must be known.

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