

Digestion of Plastic Materials for the Determination of Toxic Metals with a Microwave Oven for Household Use

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A rapid sample-digestion method for the determination of toxic metals, cadmium, chromium, and lead, in polyethylene and polyvinyl chloride has been developed by using a microwave oven for household use. An appropriate amount of the sample taken in a PTFE decomposition vessel was mixed with nitric acid or nitric and sulfuric acids. The vessel was heated in a microwave oven by a predetermined operating program. The digested sample was diluted to a definite volume with water after evaporating most of the nitric acid. The precipitate, if formed, was filtered off by a membrane filter. The metals were determined by ICP-AES. The sample digestion required 5 min (for 20-mg sample) to 25 min (for 60-mg sample). The analytical results obtained for cadmium, chromium, and lead in a polyethylene certified reference material, BCR-680, digested with nitric acid, were in good agreement with the certified values.

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Introduction

Cadmium and lead are toxic elements, and are often mentioned in discussions about environmental protection. They are used in plastic materials as pigments or stabilizers. Plastic materials are widely used in a variety of daily products. Therefore, new regulations, such as Waste Electrical & Electronics Equipment (WEEE),¹ and Restriction of the use of certain Hazardous Substances in electrical & electronics equipment (RoHS)² have been passed. Hence, much attention is being given to the development of a fast, reliable, and inexpensive method for the determination of heavy metals in plastic materials.

The procedures found in the literature are mostly based either on plastic sample decomposition with sulfuric acid and hydrogen peroxide (conventional wet ashing)³⁻⁸ or on dissolving polymers in organic solvents⁹⁻¹² prior to analysis with flame atomic absorption spectrometry. Another approach is the direct analysis of solid samples assayed by graphite furnace atomic absorption spectrometry with a solid sampling device¹³⁻¹⁵ by X-ray fluorescence¹⁶ or by laser ablation ICP-MS.¹⁷ However, solid sampling presupposes the availability of solid standards for the construction of calibration graphs. The use of organic solvents to dissolve plastics is not applicable for sparingly soluble polymers.

When employing conventional wet ashing, difficulties may arise while determining lead, because the sulfuric acid required for dissolution leads to lead sulfate precipitations. Furthermore, the commonly used wet ashing with sulfuric acid in a Kjeldahl flask has the general disadvantage of open-vessel methods, such as loss of analytes, and the need for a longer digestion time and

more digestion reagents, resulting in undesirable contamination.

An alternative approach for dissolution of plastic samples is wet ashing utilizing microwave irradiation. The high pressure generated in a closed vessel, in which a sample in an acid solution is placed, and the rapid heating of the sample *via* direct microwave energization of the acid molecules, can result in a significantly reduced sample preparation time.¹⁸ Several studies have been reported using microwave energy for the digestion of plastic materials. However, most of those studies have been carried out using a commercially available microwave-assisted sample-preparation system,¹⁹⁻²¹ and the effect of sulfuric acid added for sample decomposition has not been examined in detail for the determination of lead and cadmium in plastics. Furthermore, this method is recommended only for routine analyses of a large number of samples with respect to the higher acquirement costs (more than fifty thousands US dollars) of commercially available microwave equipment. Therefore, the present work was undertaken to develop a simple and inexpensive microwave-assisted method for a relatively small number of plastic samples using a cheap microwave oven for household use.

In this work, nitric acid and a mixture of nitric and sulfuric acids were compared with each other from the standpoint of the effectiveness of sample dissolution using microwave energy for the determination of lead, cadmium, and chromium in plastics. For these metals, the trueness of the methods was proven by measuring certified reference materials, BCR-680 and BCR-681. The use of nitric acid alone gave better recoveries for lead in polyethylene even if the white residue of titanium was found, and had to be filtered off in advance of the ICP-AES measurement with yttrium as an internal standard.

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Experimental

Apparatus

A sealed PTFE decomposition vessel of 25 or 70-ml capacity with a polypropylene jacket (San'ai Kagaku, Nagoya, Japan) was used. A microwave oven for household use, National NE-A220 (power range: 100 – 500 W, Osaka, Japan) was employed for the digestion of samples. A sequential ICP-AES, SPS 1700 (Seiko Instruments, Chiba, Japan) was used to determine the metals of interest under the experimental conditions specified by the maker. A Shimadzu micro electronic balance AEM-5200 was used to weigh small amounts of samples. A scanning electron microscope (SEM) JSM-5310LV (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) and energy dispersive X-ray spectroscopy (EDS) JED-2140 (Japan Electron Optics Laboratory Co., Ltd., Tokyo, Japan) were employed for the qualitative analysis of insoluble substances encountered during sample decomposition. The SEM was operated in the backscattered electron image mode.

Reagents and samples

Certified reference materials for trace elements in polyethylene BCR-680 and BCR-681 were analyzed to test the accuracy of the proposed methods. Some polyvinyl chloride samples contaminated artificially with cadmium, chromium, and lead were also analyzed to extend the applicability of the proposed method.

Nitric acid for poisonous metal analysis and sulfuric acid of JIS special grade were used for sample digestion. The standard metal solutions (1000 mg/l) for AAS (Kanto Chemicals, Tokyo, Japan) were used to prepare calibration graphs for the metals of interest. Water prepared by passing deionized water through a Milli-Q water purification system (Nihon Millipore, Tokyo, Japan) was used throughout the work.

Glassware and PTFE vessels were soaked in 3% nitric acid and rinsed with purified water just before use.

Sample digestion

Method with nitric acid alone. A 20-mg portion of polyethylene or polyvinyl chloride was taken into a 25-ml PTFE vessel, and 2 ml of nitric acid was added to the sample. The vessel was placed in a polypropylene jacket, sealed tightly and heated in a microwave oven. The operating programs for the microwave oven are shown in Table 1. After cooling the PTFE vessel and polypropylene jacket in ice-cold water for 20 min, the digested sample was transferred to a 20-ml volumetric flask and diluted to the mark with water. The sample solution was filtered with an Omnipore membrane filter (pore size, 0.5 μm ; diameter, 25 mm, Nihon Millipore Ltd. Tokyo, Japan) and a 10-ml aliquot of the filtrate was used for the determination of the metals by ICP-AES using yttrium as an internal standard.

When the amount of the polyethylene sample taken was increased to 60 mg to obtain more precise analytical data for lead, 4 ml of nitric acid was added to the sample in a 70-ml PTFE vessel with a polypropylene jacket. The vessel was heated at 300 W for 4 min, cooled in ice-cold water for 15 min and released to expel the evolved gases, and then heated at 300 W for 4 min. The resulting sample solution was diluted to 20 ml in a volumetric flask and filtered as described above. A 10-ml aliquot of the filtrate was subjected to measurements of the metals by ICP-AES with yttrium as an internal standard.

Method with a mixture of nitric and sulfuric acids. A 10-mg portion of polyethylene or polyvinyl chloride was taken into the 25-ml PTFE vessel, and 1.5 ml of nitric acid and 0.5 ml of

Table 1 Operating programs for microwave digestion with nitric acid alone

Sample taken/mg	HNO ₃ /ml	Step	Time/min	Power/W
Polyethylene	20	1	1	150
		2	4	100
	60	1	4	300
		2	15	Cool and degas ^a
		3	4	300
Polyvinyl chloride	20	1	2	150
		2	2	300

a. Cool in ice-cold water for 15 min and then expel the gas evolved.

Table 2 Operating programs for microwave digestion with a mixture of nitric and sulfuric acids

Sample taken/mg	HNO ₃ /H ₂ SO ₄ /ml	Step	Time/min	Power/W
Polyethylene	10	1	1	150
		2	3	100
	60	3/1	1	4
Polyvinyl chloride	10	1	2	150
		2	1.5	300

sulfuric acid were added to the sample. The vessel was placed in the polypropylene jacket, sealed tightly and heated in a microwave oven. The operating programs for the microwave oven are given in Table 2. After cooling the PTFE vessel in ice-cold water for 20 min, the clear sample solution was transferred to a glass beaker with water and evaporated on a hot plate just to fumes of sulfuric acid. The sample solution was then transferred to a 10-ml volumetric flask and diluted to the mark with water, followed by the determination of the metals of interest by ICP-AES. In this case, the internal standard method was not used for the ICP-AES measurement because the concentration of sulfuric acid in the final sample solution to be subjected to ICP-AES could be adjusted to a constant value.

Results and Discussion

Microwave-assisted digestion

Polyethylene. Ritter *et al.*²² represented in their report related to interlaboratory tests on polymers that the addition of hydrogen peroxide was not mandatory when microwave digestions were used for the determination of heavy metals in polymer matrices. Therefore, nitric acid was used singly as a digestion reagent in our preliminary experiments. First 10 mg of polyethylene certified reference material BCR-680 was digested with 2 ml of nitric acid by heating at 150 W for 1 min, and then at 100 W for 3 min. The resulting digest was diluted to 10 ml with water, and a white precipitate was observed. Therefore, the precipitate was filtered off with a membrane filter (0.45 μm) and the filtrate was subjected to ICP-AES. The precipitate collected on a membrane filter was analyzed qualitatively by EDX; the obtained chart is shown in Fig. 1. The peaks at 4.5 and 4.9 keV indicate the existence of titanium, which might be used as a catalyst for the production of

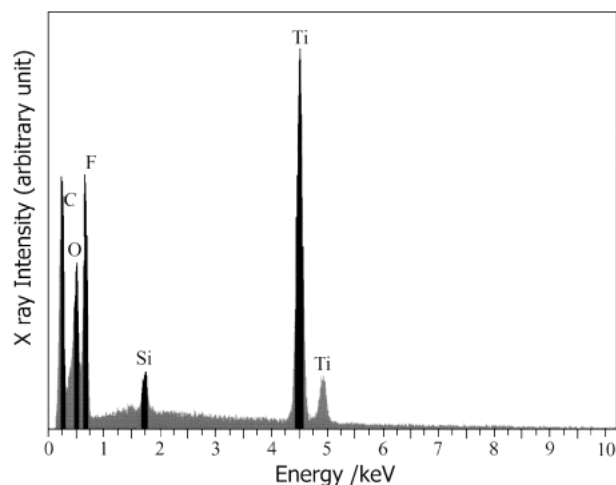


Fig. 1 X-ray spectrum of the precipitate found in the microwave digestion of BCR-680 with nitric acid.

polyethylene. The peak at 1.7 keV suggests the existence of silicon, which might be introduced in the manufacturing process of polyethylene as an impurity.

Differing acid concentrations in nitric acid digested samples caused by uncontrolled nitric acid losses during digestion made a close matrix matching of standards impossible. Therefore, the internal standard method was preferred, just as Ernst *et al.*²⁰ reported.

Consequently, the amount of a polyethylene sample to be analyzed was increased from 10 mg to 20 mg for convenience, and the sample digestion and ICP-AES measurement were conducted as described in Experimental.

Next, nitric acid was used as a digestion reagent along with sulfuric acid. About 1.5 ml of nitric acid and 0.5 ml of sulfuric acid were added to 10 mg of polyethylene BCR-680 or BCR-681 and heated in a microwave oven for 1 min at 150 W, and then for 3 min at 100 W. The digested sample was evaporated on a hot plate to fumes of sulfuric acid and diluted to 10 ml with water, yielding a clear solution without any detectable formation of a precipitate. Consequently, the resulting sample solution was subjected to ICP-AES without filtration. However, when 60 mg of BCR-680 was taken and digested with a mixture of nitric and sulfuric acids, a white precipitate was observed and filtered off before the ICP-AES measurement of the metals,

Polyvinyl chloride. Polyvinyl chloride was hardly decomposed by the nitric acid method applied to polyethylene, and hence the power of the microwave oven for the second step was increased from 100 W to 300 W. Polyvinyl chloride samples gave no residues, even if nitric acid alone was used as a digestion reagent, and hence did not require filtration of the digested sample solution before the ICP-AES measurement of the metals. This means that polyvinyl chloride used as samples did not contain substances such as titanium, which is insoluble in nitric acid.

Polyvinyl chloride samples were also decomposed with a mixture of nitric and sulfuric acids. As is the case for polyethylene samples, the amount of residual sulfuric acid could be adjusted at a constant value, and 10 mg of polyvinyl chloride sample was prepared as a 10 ml solution to be subjected to the ICP-AES measurement of the metals.

Digestion time and power

Commercially available microwave-assisted sample digestion

Table 3 Analytical results (mg/kg)^a for cadmium, chromium, and lead in plastics digested with nitric acid

Sample taken/mg	Cd	Cr	Pb
Polyethylene BCR-680			
20	135.0 ± 1.6	116 ± 2	107 ± 5
60	137.1 ± 0.7 [140.8 ± 2.5] ^b	113 ± 1 [114.6 ± 2.6] ^b	107 ± 1 [107.6 ± 2.8] ^b
Polyvinyl chloride A			
20	83.1 ± 0.8	143 ± 3	155 ± 3
Polyvinyl chloride B			
20	109.0 ± 0.5	n.d. ^c	190 ± 3

a. Average ± s.d. ($n = 4$).

b. Certified values.

c. Less than detection limit. See Table 1 for the operating programs for a microwave oven.

Table 4 Analytical results (mg/kg)^a for cadmium, chromium, and lead in plastics decomposed with a mixture of nitric and sulfuric acids

Sample taken/mg	Cd	Cr	Pb
Polyethylene BCR-680			
60	133.5 ± 2.9 ^b	112 ± 1 ^b	n.d. ^c
10	136.6 ± 5.3 [140.8 ± 2.5] ^e	114 ± 4 [114.6 ± 2.6] ^e	(35 ± 12) ^d [107.6 ± 2.8] ^e
Polyethylene BCR-681			
10	21.4 ± 0.5 [21.73 ± 0.78] ^e	18.3 ± 0.2 [17.67 ± 1.08] ^e	n.d. ^c [13.78 ± 0.50] ^e
Polyvinyl chloride A			
10	79.8 ± 1.7	149.6 ± 3.0	112 ± 2
Polyvinyl chloride B			
10	112.4 ± 2.4	n.d. ^c	157 ± 2

a. Average ± s.d. ($n = 10$).

b. $n = 3$.

c. Less than detection limit.

d. Less than determination limit.

e. Certified values.

See Table 2 for the operating programs for a microwave oven.

systems are generally equipped with PTFE vessels of at least 100-ml capacity. The use of digestion vessels of larger capacity requires a higher microwave power and a longer cooling time (40 min or more). On the other hand, the compact digestion vessels used in the present work could be heated by a lower microwave power and cooled in a shorter time, leading to a considerable reduction in the experimental time.

Determination of cadmium, chromium, and lead in polyethylene and polyvinyl chloride

The proposed method was applied to the determination of cadmium, chromium, and lead in polyethylene and polyvinyl chloride samples. The analytical results obtained by decomposing the samples with nitric acid are listed in Table 3. The analytical values obtained for the polyethylene certified reference material BCR-680 are in good agreement with the certified values. The more polyethylene sample that we used for each analysis, the better was the repeatability. Certified reference materials of polyvinyl chloride are not available, and the accuracy is unknown concerning the results for polyvinyl chloride. The repeatability for both polyethylene and polyvinyl chloride samples is fairly excellent, because the relative

standard deviations of four repeated determinations are 0.5 to 2%.

The analytical results obtained by decomposing the samples with nitric and sulfuric acids are summarized in Table 4. The values obtained for cadmium and chromium in BCR-680 and BCR-681 are in good agreement with the certified values. For BCR-680, the effect of the sample size was examined, and it was found that the sample size had no effect on the determinations of cadmium and chromium. However, the value for lead was depressed to less than the detection limit when the sample size was increased from 10 to 60 mg. This might be ascribed to the formation of a precipitate of lead sulfate, which was filtered off in advance of the ICP-AES measurement of the metals. When 10 mg of BCR-680 was analyzed, the value obtained for lead varied widely from run to run. In this case, complicating features induced by slightly soluble lead sulfate and some other substances involved in the sample solution might have caused the lowering and scattering of analytical values for lead, even though no precipitate was found with the naked eye. Therefore, if we want to determine lead in a polyethylene sample, the use of nitric acid as a digestion reagent must be recommended.

The analytical values of cadmium and chromium in polyvinyl chloride decomposed with nitric and sulfuric acids are in fairly good agreement with those for the corresponding samples decomposed with nitric acid alone. On the other hand, the analytical values for lead in the polyvinyl chloride samples are extremely lower than those for the corresponding samples decomposed with nitric acid alone. This discrepancy in the analytical values might be attributable to the formation of the lead sulfate precipitate, of which a clear mechanism could not be given.

Therefore, the use of sulfuric acid as a decomposition reagent should also be avoided in the determination of lead in polyvinyl chloride.

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