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# Development of Green Digestion Methods of Soils for the Recovery of Cadmium, Arsenic, and Lead

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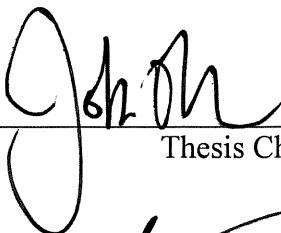
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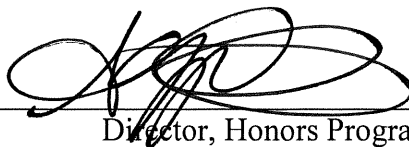
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Development of Green Digestion Methods of Soils for the Recovery of Cadmium, Arsenic, and  
Lead

Sid Patel

## Introduction

Recently, attention for chemistry research has been directed towards “Green Chemistry” which is the design of chemical “processes that reduce or eliminate the use or generation of hazardous substances”.<sup>1</sup> The Twelve Main Principles of Green Chemistry encompass this definition over a wider range. Specifically the 1<sup>st</sup> principle which states to prevent waste which needs to be specially treated or cleaned up.<sup>2</sup> Not only are these principles better for the environment, they are able to save money as well.<sup>3</sup> While the United States Environmental Protection Agency (EPA) has funded several projects under Green Chemistry, there are still processes which involve hazardous materials.<sup>4</sup> One of those is the method of soil dissolution for heavy metal analysis.<sup>5</sup> Before this is looked into; however, the causes and effects of soil pollution must be looked into, as soil digestion is part of a process used to determine qualitative and quantitative data about soil contamination.

Soil pollution is defined as the contamination of soils with hazardous chemicals via man-made or natural processes.<sup>6</sup> Man-made processes have generated large quantities of waste due to the wide-spread use of hazardous chemicals in various methods. There are a myriad of contaminants that contribute to soil pollution, such as polycyclic aromatic compounds (PAHs) as well as other forms of persistent organic pollutants (POPs) and heavy metals.<sup>7,8</sup> Each category of pollutants has unique and overlapping health risks to natural organisms and people. Polyaromatic hydrocarbons are quickly able to cause tumor formation, organohalides and other persistent organic pollutants can produce toxic byproducts or accumulate in the body, and heavy metals exhibit numerous symptoms of toxicity.<sup>9,10,11</sup> Therefore to protect the environment, work has been undertaken to identify, quantify, and determine the fate of various pollutants in the

environment, as pollutants frequently end up in incredibly far locations from their sources.<sup>12</sup> The scope of this review will be limited to methods of analyzing heavy metals in soil.

### **Current Heavy Metal Analysis in Soils**

Heavy metals can cause several different forms of what is generally classified as heavy metal poisoning. Therefore, research has been undertaken to quantify metal concentrations in soils as part of future works for soil remediation.<sup>13</sup> There are numerous methods involving various soil digestion techniques, but the ones which are the most relevant and generally accepted are the methods of soil dissolution created by the EPA, due to the EPA being a central organization in environmental protection and analysis. A representative example is the most recent EPA – created soil dissolution technique, Method 3052.<sup>5</sup> There are two main parts to analysis of heavy metals: 1) matrix destruction or isolation; and 2) spectroscopic techniques to analyze the presence of metals of interest. The isolation or destruction of the matrix is typically the most difficult step, due to the stability of silicates, which are a strong covalent network of silicon oxygen bonds.<sup>14</sup> The main method of destruction of these silicates which will lead to the overall dissolution of the soil sample is the use of hydrofluoric acid and nitric acid in a 1:3 ratio.

Hydrofluoric acid is an incredibly reactive acid that has the ability to break down silicates, and therefore dissolve the matrix for subsequent soil analysis.<sup>15</sup> While theoretically the use of this acid will lead to the best results, there are several disadvantages to the use of hydrofluoric acid. The primary reason is numerous health risks, such as internal organ damage and vision loss from fumes, and skin damage due to contact with hydrofluoric solution.<sup>16</sup> While hydrogen fluoride is not stable in the environment due to its reactivity, reactions of any kind will

generate corrosive substances. This leads into the second reason why hydrofluoric acid is non-ideal: hydrofluoric acid-containing residues require hazardous waste disposal.<sup>17</sup> Therefore, it is desired to create alternative methods of soil dissolution without employing the use of hydrofluoric acid, which is the main shortcoming of Method 3052. In addition, other EPA-approved digestion methods use various combinations of acids or single acids. All of these methods can result in the generation of hazardous waste. The rest of the method is highly applicable to further methods of instrumental analysis, which will be discussed later. It is necessary to look into alternative methods of soil dissolution for heavy metal analysis.

### **Alternative Methods of Soil Dissolution**

Research has been undertaken to compare various EPA soil dissolution techniques using recent EPA soil guidelines.<sup>18</sup> The interesting note about this publication is that no EPA prescribed method is perfect: there is variance between different methods of microwave digestion when analyzing recoveries of different metal species. For example, Method 3050, 3051A, and 3052 all had approximately the same recovery of arsenic, and Method 3051 had the worst recovery of arsenic in soil samples. Arsenic has several health risks associated with chronic exposure so there is more importance to find methods that will yield consistent results.<sup>10</sup> The EPA methods given would work, but only with a maximum recovery of 80%, so alternative methods are needed.

An alternative method of digestion employed aqua regia (3 parts concentrated hydrochloric acid to 1 part concentrated nitric acid) to digest soil samples, followed by analysis via ICP-OES.<sup>19</sup> This article demonstrated possibilities of using digestion methods which did not involve hydrofluoric acid, as the recoveries for cadmium were similar and those of lead were

greater using aqua regia compared to a mixture of hydrofluoric-hydrochloric-nitric acids, proving that hydrofluoric acid may not be as paramount to soil dissolution as previously thought.

Hydrogen peroxide has received little attention, but is worth mentioning as the highly reactive hydroxyl radicals produced are able to destroy complex matrixes such as organic wastewater.<sup>20</sup> Thirty percent hydrogen peroxide was used to destroy organic wastewater, which is a complex matrix similar to soil. Hydrogen peroxide may have applications to siliceous samples, but a long time was required for wastewater treatment, so alternative methods to hasten digestion times are needed.

Finally, chelating agents to extract metals from the soil matrix have also been studied. The specific chelating agents designed had multiple ligands such as tetradentate and hexadentate, as more ligands lead to higher formation constants in coordination chemistry.<sup>21</sup> A variety of biodegradable chelating agents have been used to chelate metals from the soil.<sup>22</sup> The greatest success rates overall were accomplished with S,S - Ethylenediamine-N,N'-disuccinic acid (EDDS) compared to Ethylenediaminetetraacetic acid (EDTA) as a control. While both did well, EDDS has the advantage of being biodegradable in the environment, unlike EDTA.<sup>23,24</sup> A variety of changes can be enacted on the sample to change metal recoveries such as pH adjustment, which is not mentioned frequently in other sources. With the major methods of soil digestion techniques covered, the next part of analysis is heavy metal detection.

### **Heavy Metal Detection**

According to Method 3052, there are numerous types of instrumental techniques that can be used to quantify heavy metals present in soil.<sup>24</sup> Atomic spectroscopy has been a popular and

dependable technique used for many years.<sup>25</sup> The next paragraphs will summarize the major advantages and disadvantages of numerous types of atomic spectroscopy.

Flame Atomic Absorption Spectroscopy (AAS) and Emission Atomic Absorption Spectroscopy (EAS) are grouped together as they use more outdated techniques which overlap. AAS measures the light that is absorbed by atomized samples, whereas EAS detects the light emitted by various atoms. The main advantages are low expense and ease of operation, as well as low maintenance. In addition, AAS and EAS can detect rare earth elements as well as a few common transition elements such as iron and molybdenum. However, AAS and AES have numerous drawbacks such as being mostly incapable of simultaneous multi-element analysis, moderate-high matrix effects, average limits of detection, and few orders of magnitude with respect to linear dynamic range. The latter three disadvantages are of utmost importance to analytical chemists, specifically matrix effects when analyzing soil samples. Therefore, the literature points to newer methods of atomic spectroscopy: inductively coupled plasmas (ICPs).<sup>26,27</sup>

ICP-Atomic Emission Spectroscopy (ICP-AES) and ICP-Mass Spectrometry (ICP-MS) both use plasmas to destroy all chemical bonds and leave only atomic species present, but use different types of detectors. ICP-AES once again measures the energy released of excited atomic species, whereas ICP-MS uses a mass spectrometer to analyze metal species. Both have plasma in common, which has numerous advantages compared to AAS and AES. The advantages of these are low matrix effects, multi-element analysis, good limits of detection, good precision, and six orders of linearity. The drawbacks such as high cost and maintenance, as well as difficulty of operation are to be expected. However, ICP-AES and ICP-MS are able to negate matrix effects and provide good limits of detection, which are relevant for trace metal



analysis.<sup>26,28</sup> However, Total X-Ray Fluorescence (TXRF) has also been shown to have relevance in this field, due to having a much lower cost than ICP instrumentation.

TXRF excites a sample with X-rays and measures the emitted secondary X-rays coming from the sample atoms. It has advantages regarding trace analysis, being able to detect down to the parts per billion (ppb) range, similar to ICP-AES and ICP-MS.<sup>29</sup> However, the X-ray source is much cheaper than the argon gas used for plasma generation. Therefore X-ray Fluorescence is able to operate at comparable levels of detection compared to ICP instrumentation at a lower cost, at a disadvantage of having to homogenize / dissolve the sample matrix, which ties into the first part of the review. TXRF technology can also be simplified down to hand-held use, which is convenient for rapid, on-site environmental analysis.<sup>30</sup> Even more significant advantages to this technique were demonstrated when a portable TXRF system was applied to environmental field work under limited conditions, which proved the robustness of this instrumentation compared to the numerous requirements of ICP-MS and ICP-AES.<sup>31</sup> It is due to these numerous advantages that TXRF will be used as the instrumental method for quantification of cadmium, arsenic, and lead.

With this initial overview on the parts of the research, now a hypothesis can be given. It is hypothesized that there are environmentally friendlier ways to digest soils for quantitative analysis of cadmium, arsenic, and lead. An overview of the methods used for analysis will be looked into next.

### **Methods**

Nitric acid and chelating agents (EDTA, EDDS, etc.) were purchased for this research. A standardized soil sample was purchased from the National Institute of Standards and Technology (NIST), which had precisely and accurately known metal concentrations. Internal standards,

which have precisely known concentrations, were used because a calibration curve was unnecessary. The internal standard served as a baseline, and the presence of internal standard scaled to relative concentrations of the analytes. Quartz planchettes were used for spotting the digested soil samples. The scan time for each planchette was 500 seconds. All soil samples were run in triplicate.

Since the standardized soil sample had accurate and precisely known concentrations of lead, cadmium, and arsenic, percent recoveries of these elements for the various experiments were able to be calculated. The concentrations of lead, cadmium, and arsenic as provided on the certificate of analysis served as the “true” concentration of these elements. Method 3052 was used, with some modifications. Obviously hydrofluoric acid was not be used, but was replaced with nitric acid or chelating agents. Digestion were assisted with soil ashing (heating in a muffle furnace) or microwave digestion, similar to Method 3052.

Muffling procedures used a muffle furnace to heat the soil sample to 400 °C for four hours at a time. The soil samples were placed in crucibles during the procedure. Microwave digestions involved dissolving the soil sample in 9 mL of the solution of interest (nitric acid, 70% or EDDS) and heating for 180 °C for 15 minutes.

#### *Nitric Acid Trials*

Trial 1 involved microwave digestion with 70% nitric acid. Trial 2 involved ashing the soil samples in crucibles, and then dissolving the ashed samples in 70% nitric acid, followed with shaking and centrifugation. All future samples were shaken at 600 RPM for 30 minutes and centrifuged for 5000 RPM for 15 minutes. Trial 3 dissolved the soil sample in 8M nitric acid, with shaking and centrifugation at the previously mentioned conditions. Trial 4 used the same conditions as Trial 3, but used a contact time of four hours.

### *EDDS Trials*

Trial 5 digested soil samples in 9 mL of 1:1000 EDDS, and used the same microwave conditions as used in Trial 1. Trial 6 dissolved the soil samples in 1:50 EDDS, followed with shaking. No centrifugation was used after this trial.

### *EDTA Trials*

All trials using EDTA did not involve the use of a microwave nor soil ashing, and all used a shaker and centrifuge. Trial 7 used a 0.05M EDTA solution, with shaking at 600 RPM for 30 minutes and centrifugation at 5000 RPM for 15 minutes. Trial 8 used the same centrifuge and shaking conditions as Trial 7, but the contact time was changed to four hours from 30 minutes. Trial 9 was the same as Trial 7, but used a 0.10M EDTA solution instead of 0.05M. In Trial 10, a 0.05M EDTA solution was mixed with 0.5M sodium carbonate and 0.5M sodium bicarbonate, with a 1:0.5:0.5 ratio of EDTA/carbonate/bicarbonate. The shaking and centrifugation conditions remained the same as in Trial 7. In Trial 11, a 1:1 mixture of 0.05M EDTA and 35% EDDS solution was used with the same conditions as Trial 7.

## **Theorized Results**

For runs involving concentrated acid, it is expected the recoveries of these soils will be the best. Acids other than hydrofluoric acid are involved in the EPA digestion process, and these are added in greater quantity than HF. The only drawback is that concentrated acid is still harmful to the environment and must go through neutralization at a minimum prior to disposal.

We are not sure of how successful the chelating agents will be. There were varied results in the paper regarding various metals.<sup>22</sup> Theoretically the chelating agents will be able to slip through the silicate network and coordinate to metals. EDTA will more than likely give higher metal recoveries due to its slightly higher formation constant to metals than EDDS, but will

likely be used as a baseline to compare EDDS. EDTA accumulates in the environment whereas EDDS quickly degrades, therefore being more in line for green dissolution techniques. Future works will continually aim to improve the metal recovery process using more environmentally friendly chemical processes.

## Results

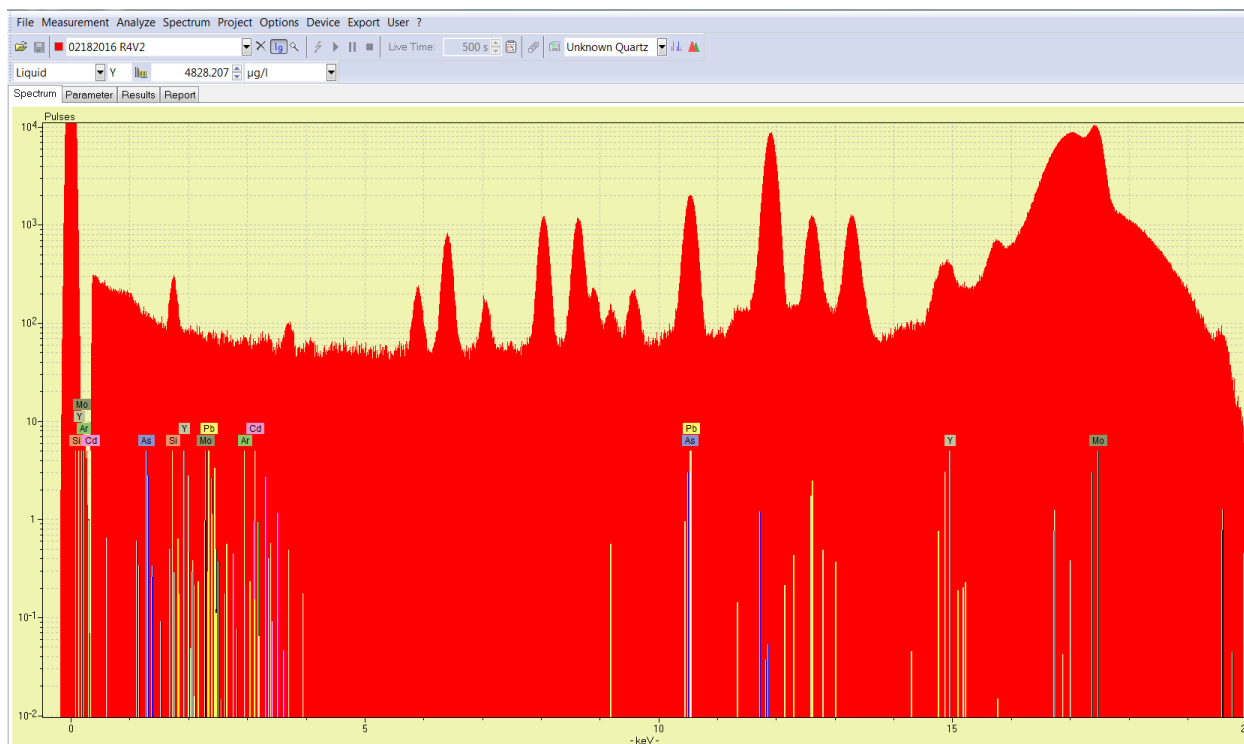


Figure 1: Sample T-XRF Spectra.

### *Nitric Acid Trials*

The first trial involved microwave digestion, using 9 mL of 70% nitric acid on a soil sample. The recoveries were impressive, as  $83.6 \pm 15.9$  % of lead and  $88.8 \pm 3.7$  % of arsenic in the soil samples was detected.

In Trial 2, the samples run had extracted  $70.5 \pm 9.7$  % of lead and  $72.4 \pm 9.5$  % of arsenic. Soil ashing can prove to be another useful method for soil analysis, provided the temperature

used in the furnace does not exceed 614 °C, where arsenic will sublime under atmospheric pressure.<sup>32</sup>

With Trial 3, the recoveries were determined to be  $89.0 \pm 4.8\%$  and  $78.6 \pm 2.5\%$  for lead and arsenic respectively, showing higher yields than those using the muffle furnace. Further trials would need to be pursued to ensure the yields were statistically different, as time can be saved by negating the furnace altogether.

The yields detected were  $70.4 \pm 5.8\%$  lead and  $67.4 \pm 5.1\%$  arsenic in Trial 4. No explanation can be given as to why the percent recoveries decreased with increased shaking time.

### *EDDS Trials*

A 1:1000 solution of EDDS was used in Trial 5, due to more concentrated samples creating uneven surfaces when the EDDS evaporated. Flat surfaces are required to ensure a representative surface of the sample.<sup>33</sup> The recovery of lead was  $43.8 \pm 10.8\%$  and the arsenic recovery was  $6.3 \pm 0.6\%$ . It's apparent that there was an immediate decrease in lead and arsenic recoveries attributed to using EDDS instead of nitric acid, but arsenic is especially of concern due to the steep drop in the amount detected. It is believed the solution was simply too diluted to chelate out the arsenic present.

In Trial 6 using a solution of 1:50 (EDDS: water), the recovery of arsenic significantly improved to  $22.3 \pm 1.8\%$ , but the lead recovery decreased to  $34.9 \pm 2.3\%$ . No explanation can be given as to why there was a significant drop in lead in addition.

### *EDTA Trials*

In Trial 7 using a 0.05M solution of EDTA, the recoveries were better than those of EDDS, giving  $45.9 \pm 0.7$  % arsenic recovery and  $63.9 \pm 0.9$ % lead recovery. In addition, worth mentioning is the low standard deviations reported as well, leading to the conclusion EDTA is better for reproducibility / precision of results.

Trial 8's method was the same as Trial 7, but increasing the contact time. Strangely enough, this again decreased the percent recoveries for lead ( $52.4 \pm 5.2$ %) and arsenic ( $45.9 \pm 0.7$ %). Similar to the nitric acid trial, no explanation can be given for the decreased percent recoveries with increased shaking time.

In Trial 9, the recovery for arsenic was  $14.0 \pm 0.2$ % and the recovery for lead was  $48.5 \pm 0.5$ %. Again, the values are lower than those of the 0.05M EDTA sample. Lo & Yang discovered, using EDTA for metal extraction from soils, that a more concentrated solution may not necessarily give better percent recoveries.<sup>34</sup>

With Trial 10, sodium carbonate and bicarbonate were added. Using this solution, the percent recovery of lead was  $59.5 \pm 1.6$ % and the recovery of arsenic was  $39.4 \pm 1.0$ %. While the addition of carbonate and bicarbonate did not improve the recoveries of lead or arsenic, the percent recoveries were similar to that of Trial 7. Due to little change in percent recoveries, sodium carbonate and bicarbonate are recommended due to their ability to chelate out other potential metals of interest such as uranium.<sup>35</sup>

Trial 11 produced the best results for arsenic and lead detection. With this solution, the recovery of arsenic was  $47.2 \pm 7.1$ % and the recovery of lead was  $75.0 \pm 10.9$ %. This is the best trial using green chemicals and no acids, so further trials should be run to ensure that the method is reproducible. A point to mention is the large standard deviations, which may be due to the

uneven surface of the quartz planchette. EDDS, when concentrated enough, spatters on the planchettes when heated. When using EDDS, a procedure allowing the solution to evaporate without heat should be investigated to potentially have a smoother surface on the planchette. The conditions and results for all trials are summarized in Table 1.

Trial #	Lead Recovery (%)	Arsenic Recovery (%)
Trial 1 – 70% nitric acid, microwave digestion	83.6 ± 15.9	88.8 ± 3.7
Trial 2 – Soil ashing, 70% nitric acid, shaking (30 minutes) and centrifugation	70.5 ± 9.7	72.4 ± 9.5
Trial 3 – 8M nitric acid, shaking (30 minutes) and centrifugation	89.0 ± 4.8	78.6 ± 2.5
Trial 4 – 8M nitric acid, shaking (4 hours) and centrifugation	70.4 ± 5.8	67.4 ± 5.1
Trial 5 – 1:1000 EDDS, microwave digestion	43.8 ± 10.7	6.3 ± 0.6
Trial 6 – 1:50 EDDS, shaking (30 minutes)	34.9 ± 2.3	22.3 ± 1.8
Trial 7 – 0.05M EDTA, shaking (30 minutes) and centrifugation	63.9 ± 0.9	45.9 ± 0.7
Trial 8 - 0.05M EDTA, shaking (four hours) and centrifugation	52.4 ± 5.2	44.6 ± 1.3
Trial 9 - 0.10M EDTA, shaking (30 minutes) and centrifugation	48.5 ± 0.5	14.0 ± 0.2
Trial 10 - 0.05M EDTA, 0.5M sodium carbonate, 0.5M sodium bicarbonate, shaking (30 minutes) and centrifugation	59.5 ± 1.6	39.4 ± 1.0

Trial 11 – 0.05M EDTA, 35% EDDS, shaking (30 minutes) and centrifugation	75.0 ± 10.9	47.2 ± 7.1
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Table 1: Summarized table of conditions and results for all soil procedures. Error bars are given as standard deviations.

### *Cadmium Recoveries*

While cadmium was a metal of interest to quantify, it proved more difficult than lead or arsenic. Cadmium recoveries were frequently implausible numbers (512% percent recovery) with large standard deviations, during the trials involving green chemicals. Even more frequently, cadmium was not detected at all throughout the nitric acid trials. It is believed that the cadmium recoveries were hampered due to the presence of elements interfering with cadmium's X-ray signal. Specifically, it is theorized that indium and silver from the soil and argon from the air are contributing to inaccurate percent recoveries.<sup>36</sup> Additional method development will have to be used to analyze soils for accurate cadmium concentrations.

### **Conclusion**

Soils are a complex matrix to study, due to their variable and complex compositions. Nevertheless, results have been provided here that illustrate how soils can be digested for analysis of heavy metal content using environmentally friendly reagents. Results are presented with the use of only nitric acid (instead of nitric and hydrofluoric), and with the use of green chemicals. Overall, the nitric acid trials were better for percent recoveries. However, the EDDS/EDTA mixture have shown the feasibility of green chemicals to replace nitric acid altogether for soil digestion, as the mixture had comparable results to nitric acid trials. In



addition, the EDTA/EDDS mixture had the advantage of being able to detect cadmium, which was not present in any nitric acid trial.

More research is obviously needed regarding numerous parts of this work. First off, more trials should be run to lower the standard deviations, and ensure reproducibility. In addition, method development needs to be used to find procedures for accurate cadmium detection. Potential methods include trying to precipitate silver using hydrochloric acid, as silver is almost as abundant as cadmium in the soil samples used.<sup>37</sup> Finally, more green chemicals need to be tested for cadmium, lead, and arsenic recovery. Some chemicals being looked into are lactic acid, oxalic acid, and citric acid due to their abilities to function as biodegradable chelating agents as well.<sup>38</sup>

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