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Design of a Large-Scale Soxhlet Extraction System for Conventional High Explosives

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Abstract

A method for purification of bench- to pilot-scale quantities of conventional high explosives (CHE) was required. A commercial off the shelf Soxhlet extraction apparatus was redesigned and procured for high-quality, high throughput batches of materials.

Introduction

Explosives are chemicals with unusual characteristics for which traditional chemical purification methods are widely applicable. A few unique properties of explosives related to hazards (*e.g.*, critical temperature) constrain these purification methods. Chromatographic analysis (*e.g.*, HPLC) and traditional recrystallization are of little consequence on small scale, but many, such as HPLC or column chromatography, are not amenable to scale up. Those that are, such as recrystallization, can be time consuming and solvent intensive, particularly when removal of impurities (and not other property engineering, such as particle size distribution) is the only goal. One of the few methods that allowed sufficient throughput for bench- and pilot-scale purification without excessive solvent consumption was solid-liquid Soxhlet extraction. The quality of such an extraction was a tradeoff for the CHE safety hazard (friction) when comparing disposable and reusable thimbles, so a modified design was required to retain the quality of a reusable thimble and the low hazard of a disposable thimble. This particular apparatus was designed around the extraction of octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) with acetone.

Results and Discussion

Traditional Soxhlet extraction relies on material dissolved in freshly distilled solvent to be filtered (Figure 1).[1]

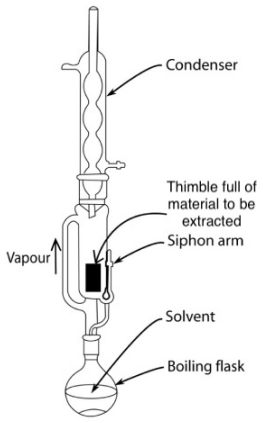

Figure 1. Typical Soxhlet extraction apparatus.

The filter containing this material, the thimble, is typically either a disposable cellulose material with a porosity of approximately 10 µm or a reusable glass thimble fitted with a fritted glass disc with a porosity as small as 0.9 µm.[2,3] Safety must be taken into consideration when extracting explosives, and cellulose thimbles have the advantage of being disposable and avoiding cleaning requirements. Despite having a finer porosity and thus yielding more pure material, reusable glass thimbles usually require mechanical action on the glass frit to be cleaned, which is a friction initiation hazard for any remaining energetic materials.

To reduce friction hazard to the same level as that found on the cellulose thimble while retaining the fine porosity, a new reusable glass thimble was designed (Figure 2). This new design had the added advantage of transparency, allowing the progress of the extraction to be monitored by simple viewing (something untenable in an opaque cellulose thimble).

Figure 2. New reusable Soxhlet thimble.

This thimble, made entirely of borosilicate glass, was fashioned from a tube 85 mm in outer diameter, approximately 273 mm in overall length, with a bead at the top and a borosilicate window ring sealed into the tube. This window had holes drilled in it at regular intervals that were fire polished to achieve a smooth surface to minimize potential sources of friction compared to rough glass or a fritted material (Figure 3). The feet of the thimble were approximately 80 mm in length and 12 mm in height. The top of the thimble sported two holes approximately 30 mm in diameter facing opposite one another with an inward flare to facilitate removal of the thimble from the Soxhlet extractor.

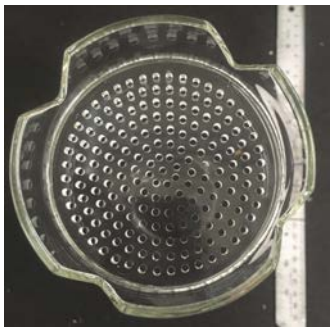

Figure 3. The bottom of the new glass thimble with fire polished perforations.

The dimensions of this thimble were intended to fit two commercial off the shelf products: the largest ground glass joint available at the time (a standard taper 103/60 joint),[4] and one of the standard sizes for Whatman glass fiberboard filters.[2] A 70 mm filter was found to be the largest filter that would fit the interior of a thimble designed to fit in the 103/60 joint and was chosen to maximize volume. The Whatman glass fiberboard filters were available in a variety of porosities, as listed in Table 1 below.

Table 1. Whatman glass fiberboard filter grades, porosities, and drain times.[2]

Filter Grade	Porosity (µm)	Drain Time (s)
GF/A	1.6	13.0
GF/B	1	5.5
GF/C	1.2	10.5
GF/D	2.7	2.6
GF/F	0.7	19.0
934-AH	1.5	3.7

One of these filters would be placed on top of the porous window, and then the material to be extracted on top of the filter. In this way, the filter always had pressure from the extracted material and/or the solvent, preventing the filter from floating. No buoyancy of the filter was observed.

A variety of these filters were investigated to determine their suitability for use in a Soxhlet extraction. It was originally postulated that filters with longer drain times (such as the GF/F filter) would not allow for the extract to drain in a timely manner to facilitate a Soxhlet extraction, since this apparatus drains quickly by siphon. However, after testing the GF/A, GF/B, GF/C, GF/F, and 934-AH papers with acetone (the GF/D was not tested due to its larger porosity), no extract latency issues were observed. Therefore, the two smallest porosity filters were chosen (the GF/B and GF/F) for extraction with this solvent. Higher viscosity solvents, if used, may pose a problem for some or all of these filters, although none were tested to validate this hypothesis.

Glass fiberboard filters are soft, pliable, chemically inert and provide low friction compared to the hard glass fritted discs typically employed in filtration. This allows for the advantage of finer porosity of the fritted glass filter while still maintaining a low friction environment to reduce explosion hazard. Cleanup of the new thimble consists of removing the thimble from the Soxhlet device, wetting with solvent if necessary, and then removing of the filter by hand or with large tweezers. The thimble can then be easily and quickly cleaned with a solvent wash or in a soap bath. Any removal of insoluble material can be accomplished through simple fluid washes or wet scrubbing with a soft bristled brush, as opposed to fritted discs, which often require significant effort scrubbing with stiff bristled brushes or metal spatulas followed by harsh chemical washes (*e.g.*, concentrated acids, oxidizers, and/or hot solvents).

The largest Whatman cellulose thimble available (60 mm Ø × 180 mm long) allowed between 350–450 g of HMX to be extracted over the course of seven days, but had to be trimmed by hand to length and did not maximize space inside the extractor due to a small diameter. The newly designed reusable thimble with glass fiberboard filters increased this throughput to 700–850 g in three days because of larger capacity and less solvent holdup. Although the new thimbles could physically hold as much as 1 kg of HMX, this led to excessive run times and sometimes browning of the extracted HMX, so the load was decreased to approximately 700–850 g to maximize throughput of material.

Comparison of the efficiency of the cellulose and new glass thimbles was performed by first extracting HMX in the cellulose thimble and then extracting it again with the new reusable thimble. The resultant 1 µm GF/B filter from the glass thimble is viewed in Figure 4.

Figure 4. Impurities passing the cellulose thimble but caught on the 1 µm GF/B filter in the new glass thimble.

When HMX as received from Holston Army Ammunition Plant was extracted through the 1 µm GF/B filter without the cellulose pre-filter, the impurities were even more evident (Figure 5), although totaled only 104 mg for over 850 g of HMX extracted.

Figure 5. Impurities from commercial HMX as received not passing the 1 µm GF/B filter in the new glass thimble.

For greater purity, this HMX was further extracted through a 0.7 µm GF/F filter. The impurities left behind on this filter were insubstantial (Figure 6), totaling only a further 60 mg for the same ~850 g batch of HMX.

Figure 6. Impurities resulting from the 0.7 µm GF/F filter extraction of material previously extracted through a 1 µm GF/B filter.

In addition to a redesign of the thimble, the Soxhlet extractor itself had to be redesigned. The original Soxhlet extractor purchased was the largest commercial off the shelf product available from Wilmad Lab Glass. This piece of glassware had a 103/60 joint at the top and a 34/45 joint at the bottom. While functional, the smaller joint at the bottom was prone to seizing after heating and required a flask with a 34/45 joint or an adapter to make a larger necked flask fit the condenser. For an extractor of this size, a minimum 3 L flask is required to provide adequate volume of solvent to allow for a full Soxhlet extractor of solvent without allowing the boiling flask to go dry and without overfilling the boiling flask initially. A 34/45 joint on a 3 L boiling flask is inadequate in size to allow entry of large brushes for cleaning or for removal of large crystals in the case of their formation in the boiling flask during extraction. Ordinarily, such crystals would be broken through mechanical insult, but with explosives this procedure would constitute a safety hazard, so a new design was required. The largest standard taper ground glass joint size that had an available heavy, knurled poly(tetrafluoroethylene) (PTFE) sleeve (55/50) was used on the bottom of the new extractor to facilitate

both cleaning and removal of large crystals should they form, reducing explosion hazard. The PTFE sleeve was placed between the joint on the flask and that of the extractor to avoid glass-on-glass friction that could present an explosion hazard, and this was further sealed by a PTFE rope.

The siphon arm on the new Soxhlet extractor was initially increased in overall diameter from 6 mm to 10 mm with the intent that the new siphon arm would allow faster draining of the extract. In practice with acetone, however, the larger diameter failed to siphon the extract, which instead slowly trickled down the siphon arm back into the flask. This failure was surmised to be due to the low surface tension of acetone. Although this may have been successful with a higher surface tension solvent, the glassware was modified to return the siphon arm to its original diameter whereafter it performed as designed with acetone. The final design of the Soxhlet extractor is shown in Figure 7.

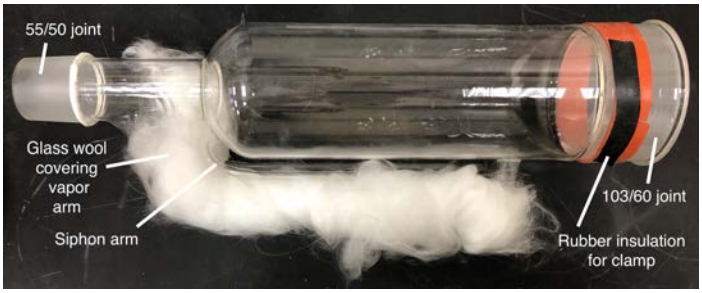

Figure 7. Soxhlet extractor design, with glass wool wrapped around vapor arm, PTFE rope around 55/50 joint, and rubber sleeve for clamp connection.

The condenser atop the Soxhlet extractor, the silicon oil heating bath, and temperature controllers[5] for the entire apparatus remained unchanged. All ground glass joints were fitted with PTFE sleeves or wrapped in PTFE tape and sealed with PTFE rope if sleeves were unavailable in the correct size (such as in the case of the 103/60 joint). The condenser was plugged with glass wool at the outlet to prevent particulate from entering the system and reduce the evaporation rate of the solvent while still retaining flow for an open system.

This apparatus is applicable to any CHEs with appreciable solubility in a high- or moderate-volatility solvent and provides advantages in both safety and monitoring over traditional methods (glass fritted and cellulose thimbles). Care should be taken to understand the safety precautions associated with given explosives, including but not limited to the friction, impact, and spark sensitivities, any reactivity with solvent, and critical temperatures. In particular, a solvent with a boiling point at least 20 °C below the critical temperature of the explosive to be extracted should be chosen (preferably lower).

Experimental

General

HPLC grade acetone (Fisher), Grade B Class III HMX (Eurenco), Grade B Class I HMX (Holston Army Ammunition Plant), and silicon oil (Alfa) were used as received. Large scale weights were measured on an OHaus Ranger 3000 balance while analytical measurements were performed on a Mettler Toledo AG285 balance.

Example Soxhlet Extraction of 852 grams of HMX with Acetone

A 3 L flask with a 55/50 female joint was charged with a PTFE coated magnetic stir bar and 2.5 L of acetone. This was clamped in an Ace 3 L Instatherm bath charged with silicon oil and controlled by an Ace 12116 temperature controller with an independent GlasCol Therm-O-Watch TOW-TCM12 controller redundant backup temperature cutoff. Beneath this was placed a Corning magnetic stir plate. The flask was fitted with a PTFE sleeve on the joint and on top of this was placed a 1.6 L 103/60 by 55/50 Soxhlet extractor. This was clamped to a scaffold and clamps on this and the flask were checked to ensure undue torque was not being applied to the apparatus. An 85 mm diameter custom glass thimble with fire polished perforations was fitted with a 70 mm diameter Whatman GF/B filter and charged with 852 g of HMX. This was carefully lowered into the Soxhlet extractor. A large 103/60 Allihn condenser was wrapped with PTFE tape around the ground glass joint and lowered onto the Soxhlet extractor. The condenser was clamped and again all clamps were adjusted to relieve torque. The condenser was plugged at the top outlet with glass wool and the jacket connected to a chilled fluid unit maintained at 5 °C. The top of the 103/60 and 55/50 joints were wrapped with PTFE rope. The silicon oil bath was covered with aluminum foil and topped with glass wool insulation. The vapor arm of the Soxhlet extractor was wrapped with glass wool. The stirring was commenced and heating was initiated. The silicon oil bath was maintained at 70 °C and reflux was obtained.

Reflux and thus extraction were maintained until the glass thimble was empty of white material, approximately 72 h. Heating was then discontinued and the apparatus allowed to cool to RT. Once cool, the apparatus was checked to ensure no HMX contaminated any joints, and was then disassembled. The extracted material was vacuum filtered, air dried, and then oven dried at 60 ° C overnight. The apparatus was washed with acetone and allowed to air dry for subsequent use. Typical yield was quantitative, and impurities totaled less than 0.02 % $^{w}/_{w}$.

Acknowledgements

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References

(1) Mayo, D.W.; Pike, R.M.; Butcher, S.S.; Trumper, P.K. "Microscale Techniques for the Organic Laboratory," **1991**, Wiley: New York, pp.110–112.
(2) Product specification, www.cytivalifesciences.com, accessed 9/28/2020.
(3) "Frit Porosity and Sizes", Adams and Chittenden Scientific Glass Co-op, https://adamschittenden.com/technical/frits/frit-size, accessed 9/28/2020.
(4) "Ground joints, outer, full length", Chemglass Life Sciences, https://chemglass.com/ground-joints-outer-full-length, accessed 9/28/2020.
(5) Saavedra, R.A.; Golder, A.C.; Hartline, E.L.; Armenta, C.E.; Ramos, K.J.; Windler, G.K. *Temperature Control of a Soxhlet Extraction Process for Purification of Explosives*, **2019**, Government Report LA-CP-19-20663, Los Alamos National Laboratory, Los Alamos, NM, USA.