Standard Operating Procedure

Task: Sending Compounds for Elemental Analysis
Date: 12/19/2014
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Background

- Elemental analysis (EA) is a process by which the elemental composition of a sample is analyzed. Generally, EA is used by synthetic chemists to determine the mass fractions of carbon, hydrogen, and nitrogen (CHN) in a given sample. This information can then be used to corroborate a known structure and gauge purity of a sample.
- In CHN combustion analysis, a sample of a known mass is burned in the presence of an excess of oxygen. The combustion products, CO_2, H_2O, and N_2 or N_xO_y, are then captured by various traps and analyzed spectroscopically or by thermal conductivity to give CHN percentages.

Training Requirements:

- Lab safety training
- Ampule sealing training

Potential Hazards:

- Hazards associated with chemicals being sent
- Lacerations from glass of exploding or imploding ampules
- Burns

Special PPE Requirements:

- Flame resistant lab coat
- Kevlar gloves (optional)
- Face shield (optional)

Materials Needed:

- Product for analysis (see below for phase, quantity, and purity requirements)
- Oven-dried 2 mL and 20 mL vials and caps for air-stable sample
- Oven-dried ampule for air- and moisture-sensitive sample
- Bulb or Modified 24/40 cajon adapter for air- and moisture-sensitive sample
- Butane torch for ampule sealing
- Mailing tube
- Small box
- Analysis request form for each sample
- FedEx mailing label

Procedure:
Preparing Sample

1. Prepare a clean sample of your analyte. **Note**: Only high purity material should be sent for elemental analysis. Perform purification by crystallization or chromatography if needed.

- Amount of sample needed. **Note:** Sending enough sample for duplicate analysis is recommended. Check with your analytical contractor to confirm mass requirements.
  - Single analysis → 3-5 mg
  - Duplicate analyses → 6-10 mg

2. Thoroughly dry your sample.
   - If sample is crystalline, crush into a fine powder to ensure complete solvent removal.
   - Use a Schlenk flask or "vac shack" to dry sample on high-vac line for 24-48 hours.

3. Pack your sample in a vial or ampule in accordance with compound stability/sensitivity.
   - Air-stable compounds
     - Place pure, dry oil or powder into an oven-dried 2 mL vial then cap tightly and tape shut.
     - Wrap the 2 mL vial in a Kimwipe. **Note:** This prevents rattling/jostling during shipping.
     - Place sealed 2 mL vial into a 20 mL vial and tape shut.
   - Air- and moisture-sensitive compounds should be sent in the flame-sealed ampule. The ampule can be prepared using the Cajon adapter or pipet bulbs (see below).
   - Using the Cajon adapter
     - Place pure, dry oil or powder into an oven-dried ampule in a glovebox. **Note:** Avoid leaving compound inside the neck of the ampule. Flame sealing will likely decompose the sample near the seal, which could cause problems in the analysis.
     - Attach the modified 24/40-Cajon adapter (see image) to ampule containing your sample. **Note:** Make sure to loosen the threaded Cajon adapters to allow the rubber O-ring to slide onto the glass tubing easily, then tighten and pull gently on the ends to ensure a good seal.
     - Close the Kontes valve to isolate your sample.
     - Remove assembly from glovebox and attach to Schlenk line. **Note:** A direct glass-to-glass connection with the main manifold is recommended for best vacuum.
     - Complete three evacuate/refill cycles to place the system under vacuum up to the Kontes valve on the adapter. **Note:** Your sample is still under glovebox atmosphere.

     - Open Kontes valve on adapter assembly to completely evacuate the ampule
     - Backfill the ampule with N_2 or Ar to ~800 microns according to the procedure below. **Note:** A partial vacuum will make sealing the ampule easier and reduce the likelihood of glass pieces being pulled into your sample upon opening.
       - Start by closing the Kontes valve between the solvent traps and the main manifold to place vacuum line under static vacuum. ***Never leave the traps under static vacuum when they are being cooled with liquid N_2***!
       - Use crossover valve to slowly refill vacuum manifold and ampule to ~800 microns (~0.8 torr or ~0.001 atm) with inert gas. **Note:** Be sure that ampule is still open to the line during this step.

        - Close crossover valve.
    - Close Kontes valve on adapter assembly.
    - Flame-seal the ampule using a butane torch to heat evenly around the neck of the ampule at the narrowest point. ***Seek in-person training from an experienced lab member before attempting this procedure.***
    - Remove adapter assembly from Schlenk line. ***Caution: glassware and Cajon adapter may be very hot!***
    - Use the butane torch to clean up the seal, for example by melting any long filaments back to the tip of the seal.
    - Return vacuum line to dynamic vacuum.
  - Using a bulb
    - Place pure, dry oil or powder into an oven-dried ampule in a glovebox. **Note:** Avoid leaving compound inside the neck of the ampule. Flame sealing will likely decompose the sample near the seal, which could cause problems in the analysis.
    - Cap the ampule with the *squeezed* bulb to make partial vacuum (see image). *Partial vacuum makes flame-sealing easier and better.*
    - Bring the capped ampule out from the glovebox.
    - Flame-seal the ampule using a butane torch. Slowly rotate the ampule to heat evenly around the neck of the ampule. ***Seek in-person training from an experienced lab member before attempting this procedure.***
    - Use the butane torch to clean up the seal, for example by melting any long filaments back to the tip of the seal (see image of a good example).

4. Pack sample(s) into a mailing tube using appropriate packing materials to ensure samples will not break in transit.

Interpreting elemental analysis data

- Analysis data will be returned by e-mail within a few days.
- Based on the expected molecular formula, calculate the weight percentage by atom for %C, %H, %N. ChemDraw has a tool to do this automatically, but triple check that the molecular formula is correct.
- Values within ±0.4% are considered to be within variance and “passing” elemental analysis. This is typically the threshold for publication-quality materials. Note that ±0.4% is not a percentage of the reported value, but an additive/subtractive range. For example, if you expect C 22.92% and the analysis reports C 22.72%, that is a 0.3% difference and within range.
- If you have strong evidence for co-solvation, such as the presence of a solvent molecule in the unit cell of the crystalline material, you may consider including the solvent in the weight percent calculation. This practice should be limited to cases where it is highly probably that solvent would remain in the material. For example, if you crushed a crystal and pumped on it overnight, most solvents of co-crystallization will

have evaporated. ***Do not add fractional solvent molecules or try adding various organic solvents until a satisfactory fit is obtained***.

- Note that some impure mixtures can have pristine-looking elemental analysis results. Most commonly this includes geometric isomers, which all have the same molecular formula. ***Beware not to over-interpret purity based on consistent elemental analysis data***.
- Hopefully all of your elemental analyses will hit. If not, consider further purifying your sample. Or consider re-sending the same material if you fear that sample handling errors (in preparation, shipping, or analysis) could have occurred. When reporting elemental analysis results, if you ship the same material multiple times, usually we will report all of the obtained values unless there is a reason to discard some of the results. For example, if the material is purified further, only the results using pure material should be reported. However, if most of the chemistry was carried out with less pure material, and the purification was only performed in order to pass elemental, that should be noted in the Experimental Section or Supporting Information.
- *Organometallics* has recently adopted a new position on EA as follows for compounds that have been exhaustively characterized by other methods but do not hit for EA: "… elemental analysis is no longer an inflexible requirement, but rather very strongly encouraged … The journal strongly encourages characterization of all new compounds by EA. Where EA is collected and reported, the chemical yield must be reported for the specific batch for which EA is actually obtained." and "In all cases, [we] now require that manuscripts describing synthetic work contain a statement explaining how the purity of the new compounds has been established."

References and Related SOPs:

- Crystallization
- Vacuum Traps
- http://www.robertson-microlit.com/services/CHN-elemental-analysis
- *An Editorial About Elemental Analysis.* DOI: 10.1021/acs.organomet.6b00720