

Incorporating Gas Chromatography and CHN Elemental Analysis into the Undergraduate Science Laboratory Curricula

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Project Summary

The final charge of this grant was to improve Arizona Western College's (AWC) Chemistry (General and Organic) and 2+2 Environmental Science AWC/NAU (Northern Arizona University-Yuma) programs by developing and then incorporating new capillary gas chromatography (GC) and elemental analysis activities into the aforementioned laboratory curricula. Elemental analysis is carried out using a Carbon Hydrogen Nitrogen (CHN) elemental analyzer. Students in General Chemistry 1 & 2, Organic Chemistry 1 & 2, and the Environmental Science program gained valuable exposure to and constant use of these modern analytical instruments.

CHN Instrument

Overall, the CHN analyzer was reliable. Some problems though arose that resulted in instrument downtime. Of course, this usually happened at the most crucial stages. The biggest problem centered around the CHN detector, which at times gave negative mass percent nitrogen for nitrogen-based standards. Typically, the simplest solution was to turn the instrument off and let it cool (from 945^oC to room temperature!!) before restarting. As one would expect sufficient cooling of the heavily insulated high-temperature combustion and reduction columns typically took more than a three-hour lab session to accomplish. Overall, the problems associated with the CHN though were minor and did not result in significant and crippling instrument downtime.

CHN Lab Activities

Organic Chemistry students used the CHN elemental analyzer to determine the purity of compounds made in multi-step synthesis reactions or extracted from consumer products such as coffee or tea. General Chemistry students used the elemental analyzer to determine: 1) the basic chemical composition of anthracite and bituminous coals used in electrical power production, and 2) the theoretical volume of ethanol produced from one acre of post-harvest biomass. Environmental Science students conducted a carbon and nitrogen analysis of the biomass in a compost pile as a function of depth and in research projects also compared the mass percent of nitrogen (mass % N) in: 1) plant leaf tissue versus stems, 2) soil adjacent trees native to the Sonoran Desert, 3) the seed coat and cotyledon of legume seeds, 4) protein shake powder, and 5) the ash of burned seed pods. A complete list of CHN elemental analyzer activities is found below.

Activities marked with a spade symbol (♠) serve as an introductory activity to CHN analysis.

<u>CHN Activity</u>	<u>CHM 151/154</u>	<u>CHM 235</u>	<u>CHM 236</u>	<u>ENV 101/280</u>
♠How Much Is Three Milligrams of Sample?	X			
♠Anthracite or Bituminous Coal?	X			X
♠Pine or Oak: Which Is Best as a Fuel for Heating?	X			
Ethanol from Post-Harvest Cellulosic Biomass	X			
Elemental Analysis of Recrystallized Acetanilide		X		
Elemental Analysis of Caffeine Extracted from Tea		X		
Elemental Analysis of Mononitrated Isomeric Products Derived from Methylbenzoate and Bromobenzene			X	
C:N Profiles in an Aged Compost Pile				X
Student Research Projects				X

Summary Description of CHN Activities

All CHN analyses were performed on a Perkin Elmer Carbon Hydrogen Nitrogen (CHN) 2400 Series II Elemental Analyzer. Operating conditions included the following:

Temperature of:

combustion column = 925°C

reduction column = 641°C

detector oven = 82°C

Gases:

carrier: UHP Helium (99.99%) at ~20psi regulator outlet pressure

oxidant: UHP Oxygen at ~20psi regulator outlet pressure

♦ ***An Introduction to CHN Analysis: How much is three milligrams of sample?***

The CHN analyzer requires between 1.5-3.0mg sample for analysis. Do students really know how much (or little) 3mg is? Before using the CHN and to assess student understanding of 3mg of sample size, students are given a small beaker of sand, a spatula, and small white piece of paper. They are asked to place ~3mg of sand on the paper. The photos below are a representative sampling of student responses. A penny, which weighs 2.5g, is used for size reference. The photos clearly show students really haven't a good idea how small 3mg sample is. The PI did this activity for each class that used the CHN analyzer.



♦ ***Anthracite or Bituminous Coal?***

In this activity first students carry out the sample mass estimation activity described above (*An Introduction to CHN Analysis: How much is three milligrams of sample?*) and then are given two large pieces of coal- one being anthracite and the other bituminous (see photos below). Students don't know that the two are different coal types. They are then asked how could one determine if the two physically identical pieces are the same or different types of coal?



Anthracite

Bituminous

After a brainstorming session addressing this question and the potential analysis methods, students are introduced to the CHN analyzer and its ability to determine chemical composition (the mass percent of carbon, hydrogen, and nitrogen in a sample). Though the two pieces of coal are indistinguishable in physical appearance, a CHN analyzer can determine that the two identical looking samples are indeed different types of coal since anthracite and bituminous coals have different chemical compositions, namely with respect to mass percent carbon (~70-80% C bituminous vs. >90% C anthracite). After the brainstorming session, students are given a brief overview of how the CHN analyzer works. They are shown spent combustion and reduction tubes and the "insides" of the CHN analyzer and the parts therein described. Samples are prepared for analysis and an analysis is carried out. Analysis of CHN data of the two coal types follows.

This same type of activity is done with wood (*^Pine or Oak: Which Is Best as a Fuel for Heating?*). The procedure is identical to that of coal but instead students are asked to determine if two pieces of wood come from the same or different tree.

Ethanol from Post-Harvest Cellulosic Biomass

Students use CHN data to compute the theoretical volume of liquid ethanol (C_2H_5OH) that could be produced from the post-harvest cellulosic biomass of an acre of Durham wheat, a perishable foodstuff grown in the numerous agricultural fields bordering the AWC campus. The PI developed this relevant fieldwork-based lab because liquid ethanol is a viable alternative bio-based fuel that could substitute for street-grade gasoline. Local investors have aggressively proposed building an ethanol plant 45 miles east of the AWC campus.

In this activity students first map out the perimeter of an acre (geometrical shape = square, 209' x 209') using 300' tape measures, estimate the weight of the biomass found in the acre just measured, and then determine the wheat stalk density (~80 stalks/ft²). In order to determine the dry weight of cellulosic biomass found in an acre of Durham wheat, heads are removed from five stalks, the stalks are allowed to air dry for a week, and then weighed collectively to give ~2.65g/stalk. Students then calculate the total dry cellulosic biomass found in an acre of Durham wheat (~20,000 pounds, lbs.). Dried stalks are cut into small pieces, ground in a mortar, and prepared for CHN analysis (mass percent carbon = 45.7% C). From the mass percent carbon (mass % C) data, students calculate the mass of carbon available (~9,150 pounds) for potential conversion to

ethanol (~52% C by mass, 24g C/46g C₂H₅OH). From the mass of carbon available students then compute the theoretical mass (~17,500 lbs) and then volume of ethanol (~2,675 gallons when $d = \sim 6.5$ lbs/gal at 25^oC) that could be obtained from an acre of post-harvest cellulosic biomass, assuming for simplicity of calculations that conversion of available carbon to ethanol is 100%. Of course, the efficiency is woefully lower.

The photos on the next page show students gathering samples and data in the field for the *Ethanol from Post-Harvest Cellulosic Biomass* activity.



Elemental Analysis of Recrystallized Acetanilide

Using the CHN analyzer Organic Chemistry students determine the mass percent of solid product (acetanilide) recrystallized from a crude mixture of acetanilide (71.09% C, 6.71% H, 10.36% N) and other substances. Students determine if the CHN data supports conclusions drawn from mixed melting point observations.

Elemental Analysis of Caffeine Extracted from Tea

The CHN analyzer is used to determine the mass percent of solid product extracted and isolated from tea. Mass percent data obtained is then compared to pure caffeine (49.48% C, 5.15% H, 28.87% N). Organic Chemistry students determine if the CHN data supports conclusions drawn from mixed melting point observations.

Elemental Analysis of Mononitrated Isomeric Products Derived from Methylbenzoate and Bromobenzene

Organic Chemistry students perform a CHN elemental analysis on products synthesized and isolated from the nitration of methylbenzoate and bromobenzene.

C:N Profiles in an Aged Compost Pile

In this activity Environmental Science students use the CHN analyzer to determine the C:N ratio as a function of depth in a compost heap (~4'w x ~8'l x ~3'h). Students first estimate both the heap's volume and weight of biomass and then insert at different depths long-stem metallic soil temperature probes into the heap to gauge the temperature vs. depth profile. Biomass is collected at varying depths and the larger particles removed in succession via soil sieves of successively finer mesh. The finest biomass collected is allowed to air dry for a week and then subjected to CHN analysis, which unfortunately revealed no noticeable trend in C:N as a function of depth.

Environmental Science Student Research Projects

- Is Nitrogen a Significant Factor in the Growth of the Palo Verde?
- Nitrogen Content in Honey Mesquite (*Prosopis glandulosa*): Leafs in Contrast to Stems
- Comparison of Nitrogen Levels in *Populus fremontii* and *Prosopis pubescens* Leaves
- Nitrogen Levels in Soils Around a Desert Legume