**Laboratory #5**

**Chem 6614 Instrumental Methods of Chemistry**

**SUNY Alfred State College**

**Due Thursday 22 March (post break)**

**Mixture Component Identification Using IR and GC methods in combination**

**5.1. Background**

Environmental laboratories, forensic laboratories and industrial manufacturing facilities (e.g. refineries, chemical plants, food processing facilities) commonly need to ascertain the identity of unknown organic mixtures. In these settings it is usually the case that some a priori experience as to the range of possibilities for the mixture is available. For example, if the mixture brought to a forensic lab is one taken from a crystal meth lab, ether and alcohol are likely candidates for the mixture components. If, however, you find a clear , volatile liquid spill on the floor of a refinery, you might logically assume it to be comprised of alkane or alkene hydrocarbons.

As you have already discovered, IR spectroscopy, particularly when supplemented with an ATR attachment, provides a quick and easy check on whether such functional groups are indeed present. However, IR is not a good way to decide if more than one kind of a particular compound class is present since both the diagnostic and fingerprint regions of compounds in a given class are often quite similar and individual compounds in a class can mask each other.

However, given a hint from the IR as to the functional group class, a modern, automated GC like the HP Agilent 6890N can easily and quickly provide an analyst with the number of components in the mixture, and, if the most likely components are a priori known, standard mixtures of these can be run and compared against the unknown under identical chromatographic conditions. A match in retention times between known peaks and unknown peaks thus serves as strong evidence for the latter’s identity.

**5.2. Purpose**

Identify the mixture components in an unknown organic mixture through a combination of IR and GC analysis.

**5.3. Procedure**

The laboratory instructor will demonstrate how to start and program the Agilent 6890 FID GC using the Chemstation software.

Student teams will then be assigned unknown mixtures for which brief histories are attached. Standard mixtures (alkanes, alcohols, ketones) will be provided wherein the components are equal in volume % and neat.

Each team will be tasked with running one standard mixture through the ATR-FTIR and the Agilent GC (using wet needle injection) as well as recording similar data for their unknown. Copies of the annotated standard runs will be made available to the entire class.

A single, common protocol for the thermal ramp schedule, split ratio , purge flow and column flow rates supplied by the instructor will be applied for all three standards.

Based on the collected GC and FTIR standard and unknown results as well as unknown histories, students will propose compound identities for all components in their unknown mixture and estimate relative v/v% based on GC peak areas.

A brief, written description of methods is required in your notebook, with emphasis on instrument settings connected to IR and GC, as well as any sampling protocols (e.g. volume of injection, use of ATR head).

**5.4. Observations**

Include:

1. Copies of pertinent standard IR and GC, as well as your unknown IR and GC runs with relevant tabulations of conditions on each document.
2. Table of observed retention times and peak identities for relevant knowns and your unknown . Your table should have an appearance similar to the sample below where you should note that the exact source of the data (the GC trace #) is indicated
3. If known volumes of sample are used rather than wet needle, include that volume in μL.

**Table 1:**

**Observed GC Peak tr and Peak Area, A, for Unknown A and Selected Reference MixturesObtained with Agilent 6890N GC with FID1,2**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Reference 1  tr (min) | A(ref #1)  pA\*s | Reference 2  tr(min) | A(ref #2)  pA\*s | Unknown A  tr(min) | A(unk. A)  pA\*s |
| 1.0 | 4.3 | 0.6 | 6.7 | 1.0 | 2.1 |
| 2.5 | 5.0 | 4.0 | 5.8 | 4.0 | 10.0 |
| 3.7 | 5.0 | 6.0 | 4.9 | 6.0 | 4.8 |
| GC trace 1 |  | GC trace 2 |  | GC trace 3 |  |

1Reference #1 = ethanol,1- butanol, 3 pentanol 1:1:1 by volume

2Reference #1= acetone, methyl ethyl ketone, 2-hexanone 1:1:1 by volume

1. Table of main diagnostic bands observed from your FTIR spectra for relevant standard mixtures run, and from your unknown, (See sample on next page)

**Table 2:**

**Main Observed Diagnostic IR bands for Unknown A and Selected Reference1,2 Mixtures Obtained with Perkin Elmer Spectrum 1 and ATR head in from 4000-500 cm-1**

|  |  |  |
| --- | --- | --- |
| Reference 1 | Reference 2 | Unknown A |
| 3500 br, vvs |  | 3500 br, vs |
| 2950 multiplet, s | 2900 multiplet s | 2930 multiplet s |
| - | 1700 sh, s | 1700,s s |
| Etc | Etc | etc |

1Reference #1 = ethanol,1- butanol, 3 pentanol

2Reference #1= acetone, methyl ethyl ketone, 2-hexanone

**5.5. Calculations**

1. **Provide comparison tables similar to that below for GC and IR data**

**Table 3:**

**Assigned GC peaks for reference mixtures 1 and 2 vs Unknown A peaks1**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reference 1  tr (min) | Assignment | Reference #2 | Assigment | Unknown A  tr(min) |
| 1.0 | Ethanol | 0.6 | Acetone | 1.0 |
| 2.5 | 1-butanol | 4.0 | Methyl ethyl ketone | 4.0 |
| 3.7 | 3-pentanol | 6.0 | 2-hexanone | 6.0 |
| GC trace 1 | Follows bp | GC trace 2 | Follows bp | GC trace 3 |

See table 1 for relevant data source

**Table 4:**

**IR mode/group motion assignment for reference mixtures 1 and 2 vs Unknown A bands1**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Reference 1 | Assignment | Reference 2 | Assignment | Unknown A |
| 3500 br, vvs | Alcohol O-H stretch |  |  | 3500 br, vs |
| 2950 multiplet, s | Alkyl C-H stretch | 2900 multiplet s | Alkyl C-H stretch | 2930 multiplet s |
| - |  | 1700 sh, s | C=O ketone stretch | 1700,s s |
| Etc |  | Etc |  | Etc |

1See table 2 for relevant data source

1. **State your conclusions as to your unknown mixture’s identity and in a paragraph or two explain your reasoning using Table 3,4 and information provided about the sample source.**
2. **Show your calculations using table 1 data to estimate volume % of the identified unknowns you claim are present above**

**5.6. Results**

a) Unknown label and source (e.g. unknown A from ChemicalsSuck solvent factory)

b) Unknown component ID and their estimated volume %

**Unknown A narrative:**

**Unknown A** is a sample provided by Maggot OxyChemical Inc., a local manufacturer of oxygenated solvents, including several low to mid-weight alcohols. The sample was collected from the desk used by CEO Maggot’s special assistant, Ms. Bambi “Fancy Nails” Vavoom . It is suspected that one of the plant’s aging chemical transfer lines has released vapors that somehow managed to condense and drip directly onto Ms Vavoom capacious person and onto her even more capacious workspace. Ms. Vavoom’s large desk sports a massive collection of hair brushes, nail care products, makeup and many similar objects devoted to personal care but little else. CEO Maggot has been unusually forceful in demanding an analysis. “I don’t want nothing bad to touch my go-to gal,” he notes.

**Unknown B narrative** :

Dirk’s Fly-By-Night auto body shop uses large quantities of ketonic (C=O bearing) paint stripper solvents . Dirk is being sued by the Green Weenies Defense Organization, a collection of aging ex-Sierra Club fanatics who rent office space next to Dirk’s shop. The Green Weenies suspect Dirk is surreptitiously dumping stripper into their dumpster to save the cost of having to dispose of his used chemicals. With great difficulty the Green Weenies have emptied the dumpster, sponged out and filtered the fragrant and slightly oily liquid found on the dumpster’s floor and submitted it as **Unknown B.** Dirk, for his part, is not taking the suit very seriously. Says Dirk:

“It’s booze they found. That bunch of aging, tree-hugging, ex-hippies spend all day drinking cheap vodka and all night smoking bad dope in there. Why can’t they go out and get a real job?” .

**Unknown C narrative:**

While vigorously attempting to use solvents to remove grease and old paint from the side of a rusty storage tank that he has salvaged from the abandoned OilSux refinery , Norbert Scrounge, a hard scrabble farmer in the Texas Panhandle manages to poke a hole right through a weakened section of the tank. The liquid inside has drenched him head to toe and he has breathed in a lot of the vapors.

As Norbert breathlessly reports to the OSHA spill team: “Danged, it was probably the durned trip haulin’ it from the refinery over that dadburned piece of crap Texas road that caused the problem . I shoulda never moved the dadburned tank. Shiiiit fire I hope I don’t die. I still ain’t been to Disney World !”

The remaining liquid in the tank is the source of **Unknown C.**