SF_6 by Gas Chromotography Version 1.0

I. Overview

Gas Chromotography separates component gases that are selected by a detector. These components are then quantified using a standard curve. The ECD detector emits electrons that ionize the make-up gas molecules creating a stable electron cloud. The ECD maintains a constant current equal to the cloud by applying periodic pulses. When a gas is injected, electronegative compounds enter the ECD cell and combine with free electrons in the cloud. In response, the ECD increases it's pulse rate to maintain a constant current. The detector measures this pulse rate and PeakSimple software observes the data as peaks. The peaks are then integrated to find the area under the curve.

Standard injections of known concentration and volume and their peak areas can be used to determine the concentration of unknown gases by measuring the area by gas chromatography of the unknown and then relating these areas to a regression obtained from the standard injections.

This protocol explains how to use the SRI Gas Chromatograph ECD detector, how to obtain a regression from standard injections, and how to use that regression to determine the concentration of SF_6 in unknown samples.

II. Equipment

A. SRI 8610C Gas Chromatograph. The Electron Capture Detector (ECD) is used. This corresponds to PeakSimple channel 3.
B. PeakSimple 2000 Chromatography Integration Software connected to the SRI GC.
C. Syringe – 1 ml Gastight® by Hamilton Co. Needle – PrecisionGlide® 25 gauge, 1 ½ inch length.
D. Make-up gas – N_2 20psi
E. Carrier gas – argon-methane 35psi
F. Septa – Supelco Thermogreen™ LB-2
G. Column – Porapak Q 80/100. 6' x 1/8". Stainless steel.
H. Gas standard – SF_6 (10 or 20 ppm) in N_2 .

III. Safety

A. Make sure all the connections are leak free. To check for leaks, squirt soapy water on each connection. There will be bubbles formed if the connection leaks. Tighten connections as needed.
B. The ECD oven and column oven are hot. Do not touch these when the red oven cover is raised.
C. Make sure the carrier gas and the make-up gas containers are secured to the wall so they don't fall.

IV. Gas Standard Dilutions

A. Dilutions are made by injecting different volumes of the same concentration of standard. For example, if 1mL of 1ppm is injected the concentration is 1ppm, but if 0.5 mL of 1ppm gas is injected, the concentration is 0.5ppm.
B. You can also create dilutions in a separate vial. Inject more gas than what the vial holds to make it pressurized. Use the equation $C_1V_1=C_2V_2$. .
   a. Example: making a 10ppm dilution with nitrogen gas and SF_6 in nitrogen:

(1000ppm standard) x V_1 = (10ppm dilution)x (100mL nitrogen)

V_1= 1mL

V. Instrument Conditions

Record the instrument conditions in the lab book. For SF_6, the below conditions are usually optimal.

A. Column Temperature – 70ºC
B. ECD Heat – 150ºC
C. ECD Current – 300mV
D. Carrier #1 – 15psi

VI. Getting Ready

A. Connect carrier and make-up gas into the inlets on the left side of the GC. See SRI operation and service manual for diagram.
B. Connect the column to the ECD.
C. Turning on the GC -- Turn on the flow of the carrier and make-up gases FIRST, then switch on the GC by the switch on left side of GC.
D. Turn on PeakSimple
   a) Start menu – programs – PeakSimple NT – PeakSimple
   b) Go to File – open control file – ECD – Open
E. Check the baseline. Usually the baseline will not stabilize unless the GC has been on for a couple of hours. It is a good idea to keep the machine on overnight if it is used frequently. Check the baseline by allowing the program to run (press the space bar). There will be some noise (small peaks) but overall the line should be straight.
F. Check to see if there are no leaks (see safety section).

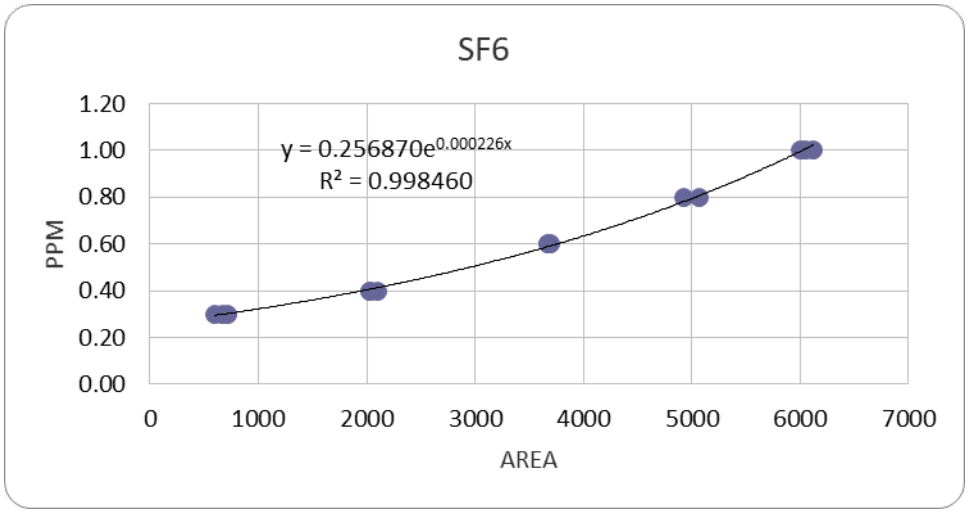
G. Check all instrument conditions.
H. Check needle septum. This will need to be changed periodically (about every 50 injections). If it looks hashed, change it. To get to the septum, unscrew the device that the needle is inserted in. The green septum will be inside that.
I. Inject a standard concentration of SF_6 with a specific volume repeatedly to check accuracy. The SF_6 peak should occur at between 1.4 and 1.5 minutes retention time (RT). The retention time will vary depending on how you inject the gas, but if you inject the gas the same each time, this RT should vary little. The peak should have the similar integration area with each injection since the concentration and volume of each injection are the same.
J. Integrating the peaks
    a) The first injection – right click on the SF_6 peak. Click on "add component".
    b) Go to 'edit' and 'manual integration'. Create the best base-line under the peak.
    c) Go to 'view' and 'results'. This will give you the retention time and area. Make sure that the results are on channel 3. The default is channel 1, so you will have to change it for your first injection.
    d) Create a chart similar to the following example to record data.

Date	Retention time	Area	Volume (mL)	Conc. (ppm)
5/8/02	1.450	2756.6610	0.5	500
5/8/02	1.450	2799.5580	0.5	500
5/8/02	1.433	2730.0620	0.5	500

J. Make a regression from the standard (see VII below).
K. Start injecting samples. Inject the same volume of sample each time.
L. Shut down – Turn off GC before turning off carrier and make-up gas.

VII. Making a Regression with Standard SF_6
A. Once the machine has recorded consistent data using the methods above, you can begin instrument calibration. This will be a graph with concentration on the y-axis and area on the x-axis (see example below). This will be used to find the unknown concentration of samples of SF_6 collected from the field.
B. First – inject known concentrations of standard, varying the concentration. Do each concentration at least 3 times. For NEON SF_6 samples, field values typically range between 0.3-1.5 ppm. Record data.
C. Enter concentration and area data into spread sheet (Excel). Do an exponential regression analysis with concentration as the y-variable and area as the x-variable. Check the R-squared. It should be at least .99 or better. Record slope.

D. The following is an example of regression data and graph:



1PPM=25UL		
Volume	ppm	Area
25	1.00	6116
25	1.00	6003
25	1.00	6051
20	0.80	4930
20	0.80	5066
15	0.60	3677
15	0.60	3699
15	0.60	3670
10	0.40	2031
10	0.40	2029
10	0.40	2095
7.5	0.30	715
7.5	0.30	596
7.5	0.30	670

VIII. Injecting Unknown Samples
- A. Inject a method blank (ambient or compressed air, free of SF_6) at the beginning of each sample set, after 10 unknowns, and at the end of the set.
- B. When injecting samples, use the same volume injection each time.
- C. Inject a check standard at the beginning, of each sample set, after every 10 unknown samples, and at the end of the set. If check standard value exceeds 5% of known value, the set must be re-run.
- D. Record sample identification #, date, retention time, peak area, and volume injected. Concentration will be determined later.

IX. Determining Concentration of Unknowns – Calculations
- A. It is easiest to do these calculations on an Excel spread-sheet
- B. Exponential Equation

ppm SF_6 = (intercept)exp(slope)x(area)	This is in the equation for exponential regression y-ab^x

Note that this equation will give the SF_6 concentration in the sample, and should be sufficient for estimating reaeration if each sample was processed with the same water and headspace volumes at the same temperature. If not, the actual SF_6 dissolved in the original water sample will need to be calculated from these data and the Ideal Gas Law.

X. Trouble-Shooting
- A. The peaks are inconsistent with different areas and retention times.
  1. Wait for a while before making another injection. There may be residual gases in the column from the previous injection.
  2. If the above does not work, bake the column. Increasing the column temperature to about 170ºC for about 4 hours or overnight does this.
- B. Injections are inconsistent - some result in peak data and some result in no data.
  1. Check the needle. The needle may be clogged. Test the needle by trying to bubble air into a puddle of EtOH (this will dry faster than water). If clogged, clean it out or try using a beveled tip needle.
- C. For specific questions, contact the website: www.srigc.com