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Application of Extractive Cryogenic Preconcentration with Fourier Transform Infrared Spectroscopy: Preliminary Laboratory Results

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Abstract

In collaboration with the Jefferson County Department of Health (JCDH) and the Environmental Protection Agency (EPA) Region IV, the University of Alabama in Huntsville (UAHuntsville) developed a near-real-time trace gas monitor using extractive cryocooled inert preconcentration combined with Fourier transform infrared spectroscopy (ECIP-FTIR). The ECIP-FTIR uses a commercial FTIR spectrometer, a commercial long-path IR gas cell, a commercial acoustic Stirling cyrocooler, and two custom parallel cryogen-free cryotraps to autonomously monitor an evolving multi-pollutant suite of volatile organic compounds (VOCs). Every 15 minutes, the system records a trace gas absorption spectrum and the derived trace gas mixing ratios, using continuous non-preconcentrated sample flow through the gas cell, to achieve detection limits of ~10 parts per billion by volume (ppbv). Every 4 hours, the FTIR and gas cell obtain similar data on preconcentrated batch samples that have been thermally desorbed from the cryotrap, to improve detection limits to ~50 parts per trillion by volume (pptv). We present initial laboratory data to demonstrate the ECIP-FTIR methodology, which is well suited for a wide range of trace gas research and monitoring applications, including EPA National Air Toxics Trends Stations (NATTS) and National Core monitoring network (NCore).

1. Introduction

Both anthropogenic and natural pollution sources emit measurable amounts of volatile organic compounds (VOCs) into the troposphere. Nitrite radicals (NO_x) at night and hydroxyl radicals (HO_x) during the day oxidize these VOCs resulting in increased formation of reactive organic peroxy molecules. Increased peroxy molecules result in greater chemical ozone (O_3) production (Atkinson, 2000). Quantitative measurements of VOCs in highly-polluted urban environments would enhance the understanding of reactive organic peroxy compounds and their roles in increased O_3 production. Also, differences between nocturnal and diurnal mechanisms lead to variations in both VOC type and concentration. Real-time quantitative measurements would improve the understanding of these different processes with higher temporal sensitivity than is historically available.

In addition to their role in O_3 production, VOCs have adverse affects on human health. Various health studies have associated asthma (Dales and Raizenne, 2004; Weisel, 2002), respiratory diseases (Diez et al., 2000; Kriebel et al., 2001), and various forms of cancer to direct inhalation of VOCs. Secondary products, like O_3, have also been associated with adverse health conditions (Devlin et al., 1997; Samet et al., 2000). With this in mind, it is important to note how different atmospheric

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environments have unique emission sources, and thus unique atmospheric mixing ratios of VOCs and their secondary products (i.e. Batterman et al., 2002; Russo et al., 2009; White et al., 2008).

In Title III of the 1990 Clean Air Act Amendments, the United States Environmental Protection Agency (EPA) listed 188 VOCs as hazardous air pollutants (HAPs) because of the adverse affects these compounds have on human health. At present, the EPA uses chemically-active adsorbent cartridges with post-collection multi-pollutant analysis to monitor VOCs, the primary of which is Compendium Method TO-15 (U.S. EPA 1997). However, difficulties arise in this method, because some VOCs degrade during the storage process causing significant analysis errors (Kelly and Holdren, 1995).

2. Instrumentation

In order to meet the emerging needs of the EPA and other federal agencies, UAHunstville, in collaboration with JCDH and EPA Region IV has developed an ambient air quality sensor to make improvements on current EPA standard technologies, while avoiding some of the major deficiencies of these standard methods. This experimental air quality monitor uses extractive FTIR spectroscopy with cryogen-free low-temperature preconcentration, here in referred to as ECIP-FTIR. Figure 1 shows the instrumentation layout of the ECIP-FTIR, which measures a multi-pollutant suite of VOCs using FTIR spectroscopy in two separate sampling modes.

The first mode is continuous flow through the gas cell. In continuous flow mode, the ambient sample travels through the gas cell inlet pump, then splits into either the gas cell flow path or the gas cell bypass. The gas cell bypass directs the partially diluted ambient flow through a back-pressure controller to maintain the gas cell at a pressure of 1 atm. Temperature and relative humidity sensors monitor the bypass flow to verify the pre-set dilution. The gas cell flow path channels the same partially diluted ambient air through a multi-port inlet valve and into the long-path gas cell, where the FTIR continuously analyzes the sample. The volumetric flow rate through the gas cell is controlled at 2 liters per minute (LPM) by a critical orifice with a downstream exhaust pump. This flow rate ensures adequate residence time in the gas cell. The gas cell bypass and gas cell flow path rejoin downstream of the gas cell and upstream of a mass flow meter, which monitors the combined flow through the two gas cell branches. This mode provides measurements of high-concentration VOCs with a detection threshold of ~10 ppbv at a temporal resolution of 15 minutes.

The second mode is batch sample collection in a cryogenic trap followed by rapid thermal desorption into the same gas cell. In this flow path, ambient air samples split into one or both of two parallel three-stage traps. The first stage collects water vapor at 253 K. The second stage traps CO_2 at 213 K. The ECIP-FTIR removes these two minor gases from the sample to avoid plugging of the downstream traps, to prevent liquid water from flooding the gas cell, and to minimize spectral interference from these two dominant infrared-active constituents. After the water and CO_2 traps remove both minor gases, the cryotrap preconcentrates the remaining analytes at 100 K. Following the completion of the four-hour collection process, the ECIP-FTIR thermally desorbs the contents of the cryotrap at 373 K and deposits the desorbed concentrate into the gas cell for FTIR analysis. The three-stage trap preconcentrates ambient trace gases every 4 hours to increase the signal-to-noise ratio (SNR) of the instrument by a factor of 240, which decreases the detection threshold to less than 50 pptv.

After the ECIP-FTIR collects spectral samples of either continuous flow or batch samples, quantitative software analyzes the measured spectra, performs a partial least squares (PLS) linear regression against deresolved high-quality library spectra (Sharpe et al., 2004), and calculates the ambient mixing ratios of the analytes targeted by this research. Table 1 lists the target analytes, with the possibility of expanding depending upon the research focus, including traffic (i.e. Batterman et al., 2002) or anthropogenic (i.e. Hagerman et al., 1997) emissions.

In addition to routine ambient measurements, the ECIP-FTIR performs daily quality-assurance and quality-control (QA/QC) measurements to ensure the accuracy of the measurements collected. The QA/QC manifold performs internal system validation cycles on a daily basis. The spike flow can either flow directly into the gas cell or mix with incoming ambient air to quantify analyte losses and relate artifacts, and identify the flow channels where those artifacts might be occurring. Also, the FTIR performs internal QA/QC measurements to ensure optical alignment and removal of external interferents.

Custom-built process control software performs each system process in a carefully designed, completely automated sequence. The automation software gives the user the capability to deploy the ECIP-FTIR into the field without continuous intervention, saving time and money while maintaining, and in some cases improving, measurement quality. Also, with the instrument fully automated, the user can deploy the system in high-interest areas (i.e. near an industrial factory or local school) to collect source-specific data during extended runs without repetitive manual initialization and control.

All the subsystems that make up the ECIP-FTIR combine to compose an instrument that will markedly improve the understanding of high temporal resolution processes that affect mixing ratios of air toxics in an industrialized urban setting.

3. Analysis

The ECIP-FTIR uses a quantitative analysis method based on the linear nature of Beer's Law, which states

$$T_i(\lambda) = \frac{I_i(\lambda)}{I_0(\lambda)} = \exp\left(-\sum_{i=1}^{N} \sigma_i(\lambda) C_i L\right)$$
$$A_i(\lambda) = \log_{10}\frac{1}{T_i(\lambda)} = \sum_{i=1}^{N} \sigma_i(\lambda) C_i L \qquad (1)$$

where $\sigma_i(\lambda)$ is the cross section of the ith molecule (cm^2), L is cell path length (cm), and C is the concentration of the ith molecule (cm^{-3}). Solving the above linear equation for concentration yields

$$C_i = \frac{A_i(\lambda)}{\sigma_i(\lambda) L} \qquad (2)$$

Appling this result to the continuous flow mode, yields an expression for the concentration of the ith compound in ambient air

$$C_i^{amb} = \left(\frac{1+\frac{F_{VOC}}{F_{amb}}}{1-\frac{F_{dil}}{F_{cell\_tot}}}\right)\left(\frac{1}{L_{cell}}\right)\left(\frac{A(\lambda)}{\sigma(\lambda)}\right) - \left(\frac{F_{VOC}}{F_{amb}}\right) C_{VOC} \qquad (3)$$

where F represents specific flow rates measured by the mass flow meters (liters per minute; LPM), and C_{VOC} is the concentration of the calibration gas when spike sample is introduced (cm^{-3}). When operating in batch sampling mode, the cryogenic preconcentration process increases measurement sensitivity. Mathematically, a preconcentration term represents this increase in sensitivity

$$C_i^{amb} = \left(1+\frac{F_{VOC}}{F_{amb}}\right)\left(\frac{1}{L_{cell}}\right)\left(\frac{A(\lambda)}{\sigma(\lambda)}\right)\left(\frac{Vcell}{F_{trap}\cdot\Delta t_{trap}}\right) - \left(\frac{F_{VOC}}{F_{amb}}\right) C_{VOC} \qquad (4)$$

Term 4 in Equation 4 is the preconcentration term, which is a function of gas cell volume

(L), trap flow rate (LPM), and trap residence time (min). The PLS algorithm programmed into the ECIP-FTIR determines Term 3 in Equations 3 and 4 by using compound-specific absorption peaks and all other values are either measured by the system.

4. Current Status and Preliminary Data

Currently, the ECIP-FTIR is in laboratory ready test condition. We have collected numerous system measurements, including signal-to-noise ratio (SNR) evolution, subsystem tests, health and safety monitors, cell purging and cryotrap efficiency, and calibration gas spectra.

Ideally, SNR increases as a function of the square root of the number of sample scans. In a real-world scenario, we must account for sources of noise (vibration, electromagnetic interference, radio frequency interference, pressure and temperature fluctuations, etc.) when designing a field instrument. Initial testing focused on characterizing how well the ECIP-FTIR performed when compared to ideal conditions. Figure 2 shows the results of this test. The black trace is the actual SNR measured by the FTIR using a geometric scan sequence (1, 2, 4, 8, 16…1024) at 4cm^{-1} resolution. The red trace represents the square root of the number of sample scans, with the green envelope representing the Poisson statistics of this set up. This test indicates the FTIR has excellent stability after scanning for 1 hour. During field sampling, the FTIR will not scan more than 15 minutes.

During preparation of the fluid subsystem, a trace amount of methanol in lab air illustrated the sensitivity of the ECIP-FTIR analysis system. Figure 3 shows the methanol spectrum (blue trace) measured with 15 minute co-addition overlaid with a deresolved library spectrum (green trace) at 1cm^{-1} resolution. It is clear the instrument is able to sample the trace amount of methanol in air even with low resolution. Operationally, the ECIP-FTIR will operate at 0.5 cm^{-1} resolution, which will improve peak identification and separation of coincident peaks for quantification.

Finally, a synthetic spectrum using Birmingham concentrations of a few selected VOCs demonstrated the complex nature of the real atmosphere. Figure 4 illustrates this complexity with key absorption peaks following a simulated 4-hour preconcentration. It is clear that in complex mixtures, such as the real atmosphere, spectral overlap will occur if the ECIP-FTIR collects the sample at low spectral resolution. At 0.5 cm^{-1} resolution, more of the spectral complexity will become evident, and the ECIP-FTIR will use the unique absorption features of each compound to calculate ambient concentrations, as described above.

5. Future Work

Following field retrofitting, a rigorous field study will commence. Initial deployment takes place at an EPA sampling site in Huntsville, AL (Figure 5). The Huntsville EPA has built a space for the instrument to operate, with adequate air handling and separation from high volume aerosol samplers. The Huntsville EPA equips this site with EPA standard samplers for NO_x, CO_2, and O_3, as well as meteorological monitors (temperature, pressure, wind speed direction.). On the campus of UAHuntsville, we will have access to multiple meteorological sensors, like a 915 MHz vertical wind profiler, ceilometer, and sun photometer, which will provide information about the vertical structure of the sample regime. This suite of measurements along with near-real-time VOC data will provide insight into the processes affecting the air quality of a small urban setting, including nocturnal/diurnal cycling, photolysis, and vertical and horizontal transport. This sample regime will provide an opportunity to test the overall operations of the device as well as the measurement sensitivity before placing it in a highly-polluted environment.

Once the Huntsville tests are complete, we will coordinate a field study with JCDH to monitor VOC concentrations in North Birmingham, one of the most polluted locations in the United States (American Lung Association, 2009). At present, JCDH is operating ambient air quality sensors as well as VOC sample canisters at a number of sites in Birmingham, including four local schools as part of the EPA School Monitoring Initiative. The JCDH sampling heritage provided guidance to identify the target analytes listed in Table 1 as well as the most ideal location for the ECIP-FTIR to operate. Numerous industrial facilities surround emitting a wide range of organics, inorganics, and aerosol near the North Birmingham site (Figure 6). With such high ambient concentrations, the ECIP-FTIR can monitor high temporal resolution data which can identify sources of primary and secondary pollutants, which affect the health of the surrounding population, including North Birmingham Elementary School.

In North Birmingham, the ECIP-FTIR will operate along side other EPA standard monitors such as 24-hour particulate matter particle counters and speciation, NH_4, O_3, NO, NO_2, HNO_3, CO_2, and SO_2, and wind speed and direction, temperature, pressure, humidity, and solar radiation. This suite of instrumentation along with climatological records of VOCs and other trace constituents will provide ample support for an extensive 6-month field study.

6. Conclusions

This paper presents the on-going research performed at UAHuntsville to design, develop, and implement an autonomous air quality sensors using FTIR spectroscopy in concert with inert cryogenic preconcentration. This instrument seeks to present a new solution for the EPA VOC monitoring initiative, which currently uses 24 hour canister samples collected every 6 days. The ECIP-FTIR will improve data latency by collecting continuous flows samples of high-concentration constituents at 15 minute temporal resolution, and batch samples of low-concentration compounds at 2-4 hour resolution. Laboratory testing indicates the analysis system will provide adequate sensitivity and measurement stability to perform autonomous VOC measurements in situ with minimal user intervention. This method will avoid many of the difficulties encountered by EPA Compendium Methods by removing physical sample handling and post-processing, providing a cost effective and efficient method for obtaining concentrations of a number of VOCs listed by the Clean Air Act as hazardous to human health.

Following the completion of field retrofitting, we will deploy the ECIP-FTIR at two unique locations in Alabama to demonstrate the utility of this method for monitoring VOCs in both a small, low-pollution environment (Huntsville) and a large, highly-polluted urban environment (Birmingham). Along with complementary measurements of inorganics and meteorology, we can identify key components to the chemical mechanisms affecting the air quality in both locations, with the capability to capture high temporal resolution processes which form secondary pollutants, such as formaldehyde and ozone. This information will provide a greater understanding of the chemical processes in both Huntsville and Birmingham, and how these processes are affecting local and regional air quality.

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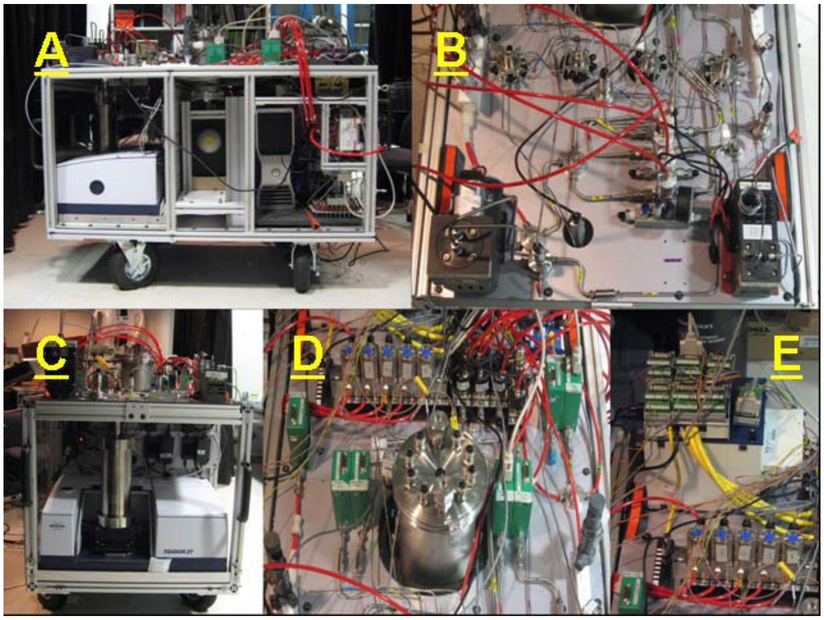

Figure 1. The ECIP-FTIR Instrument Layout. Panel A shows the entire instrument layout. From left to right, the FTIR, cryocooler, and electronics compartment with operations PC can be seen. Panel B shows the fluid subsystem including flow passages, inlet pumps, and shut off and flow selection valves. Panel C shows the optical subsystem with emphasis on the FTIR and gas cell. Panel D show the cryogenic subsystem and QA/QC manifold along with mass flow controllers (green boxes). Panel E shows the data acquisition system and mass flow junction boxes.

Table 1. ECIP-FTIR quantitative analysis algorithm target analytes. Compounds are in order of increasing molecular weight. The average mixing ratios are from 2005 Birmingham data collected by JCDH.

Target Analyte	Molecular Weight (g/mol)	Average (ppbv)	EPA MDL (ppbv)
Formaldehyde	30.03	3.100	0.020
Acetaldehyde	44.05	1.035	0.010
1,3-butadiene	54.09	0.100	0.070
Acrolein	56.06	0.725	N/A
Carbonyl sulfide	60.07	N/D	N/A
Vinyl chloride	62.50	N/D	0.060
Benzene	78.11	0.850	0.040
Methylene chloride	84.93	0.092	0.060
Chloroform	119.38	0.035	0.050
Trichloroethylene	131.39	N/D	0.070
Carbon tetrachloride	153.82	0.114	0.080
Tetrachloroethylene	165.80	0.052	0.052

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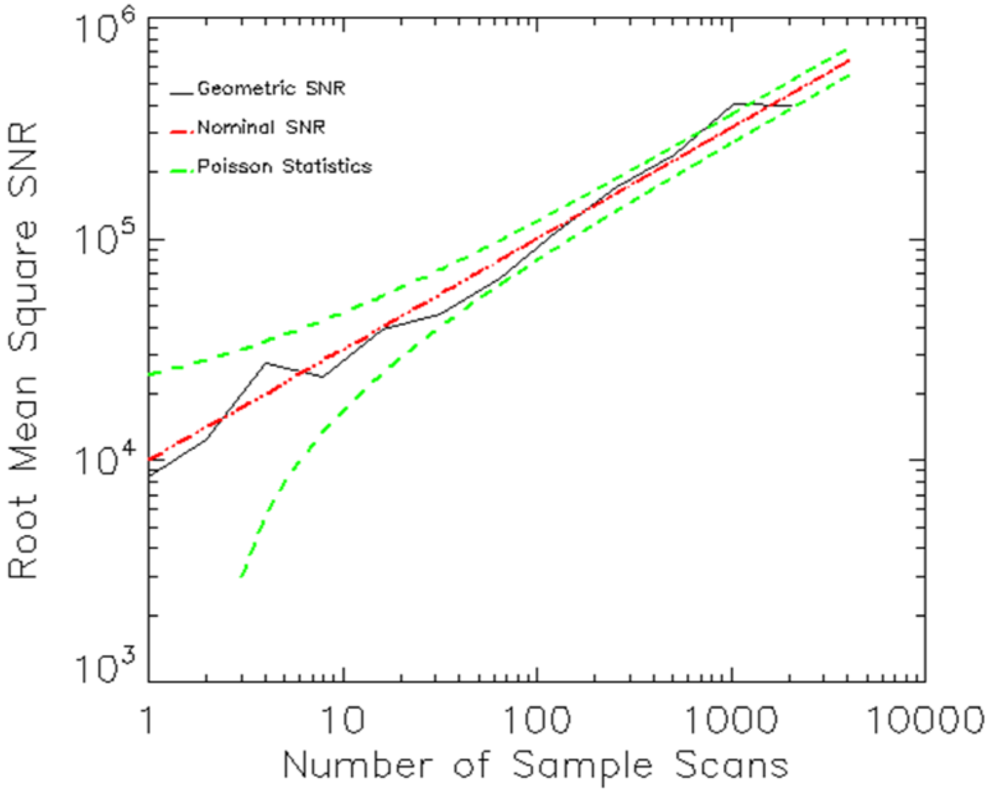

Figure 2. SNR of the ECIP-FTIR as a function of sample scans. The black trace represents the measured SNR using a geometric scan sequence (1, 2, 4, 8… 1024). The red trace is the nominal SNR which increases as the square root of the number of sample scans. The green traces form the envelope described by Poisson statistics.

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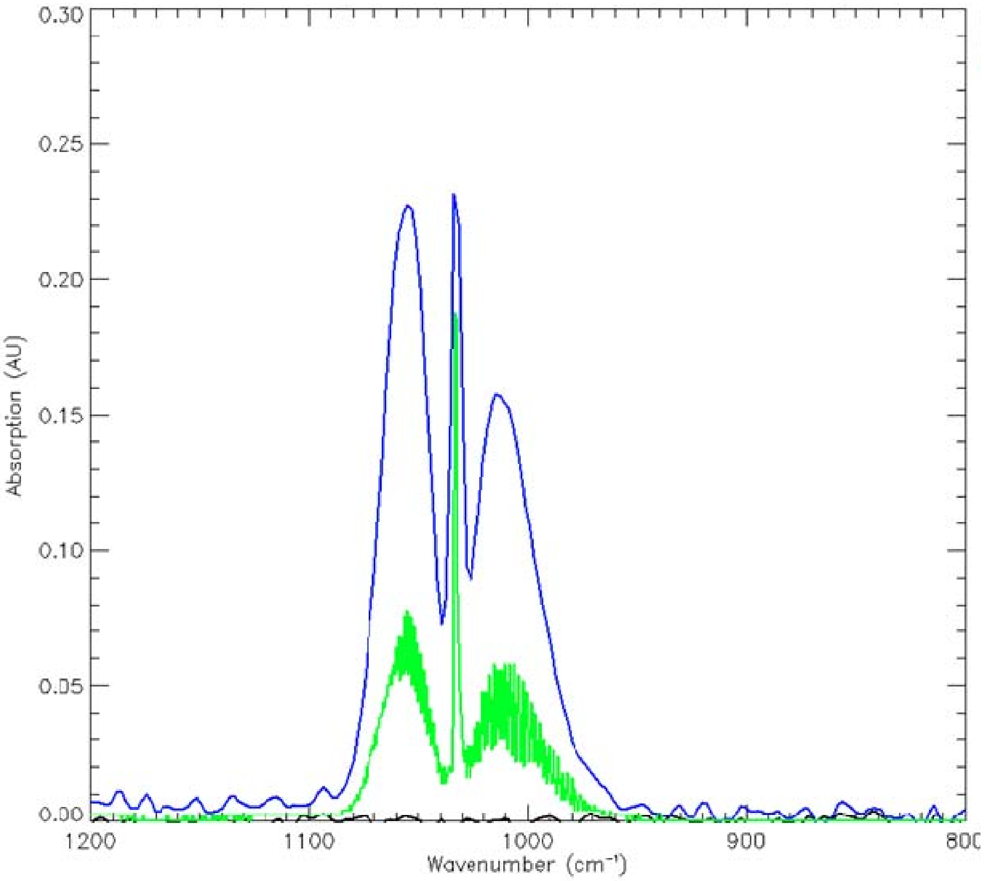

Figure 3. IR Spectrum of trace methanol in air taken at 1cm^{-1} resolution and 15 minute co-addition. The blue trace is the measured methanol spectrum. The green trace is the deresolved library spectrum.

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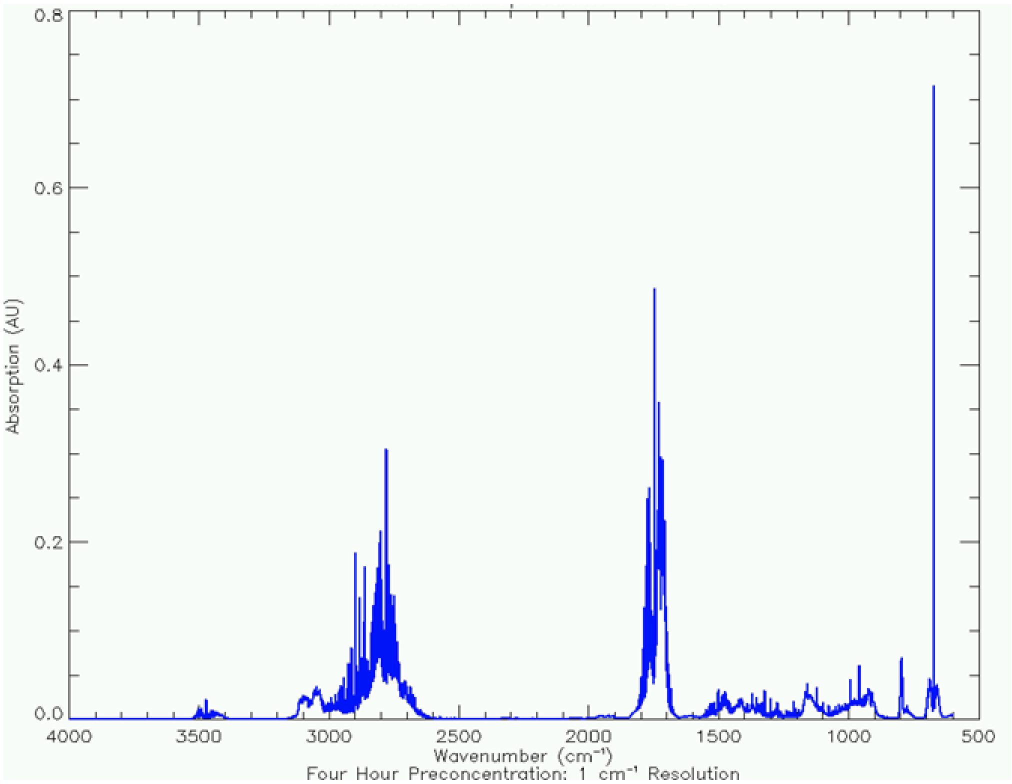

Figure 4. Synthetic IR spectrum of VOCs using concentrations in Birmingham after 4 hour cryogenic concentration.

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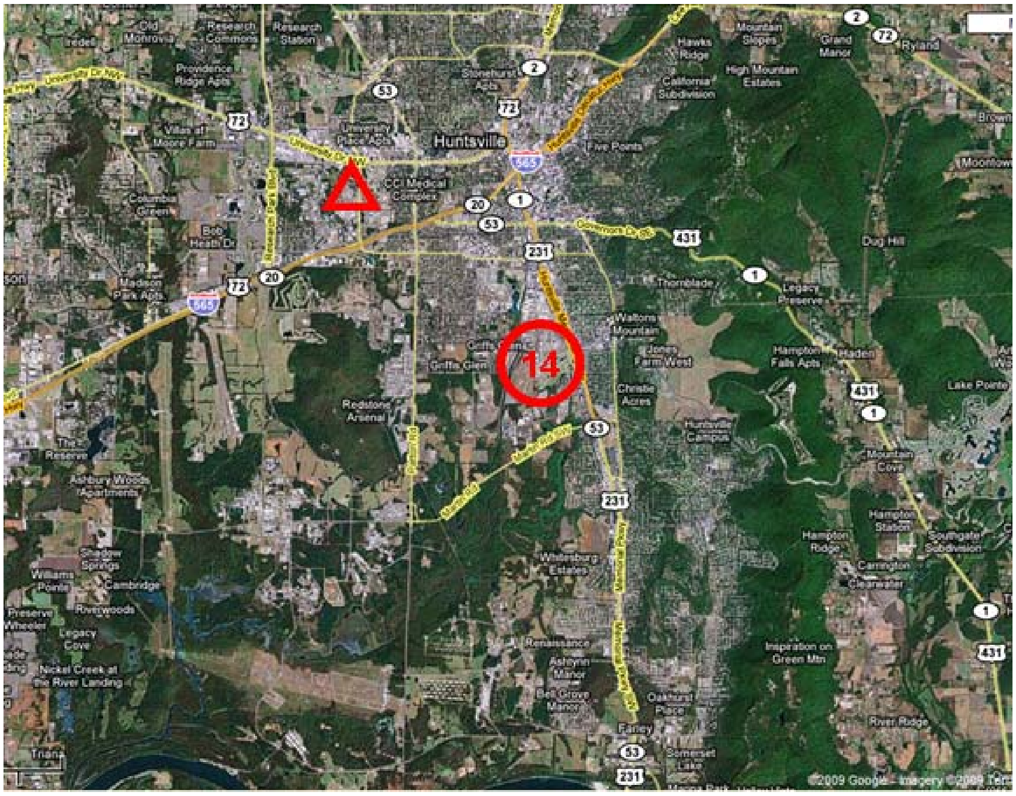

Figure 5. Locations of Huntsville EPA Site 014 (circle) and UAHuntsville Atmospheric Science Department (triangle)

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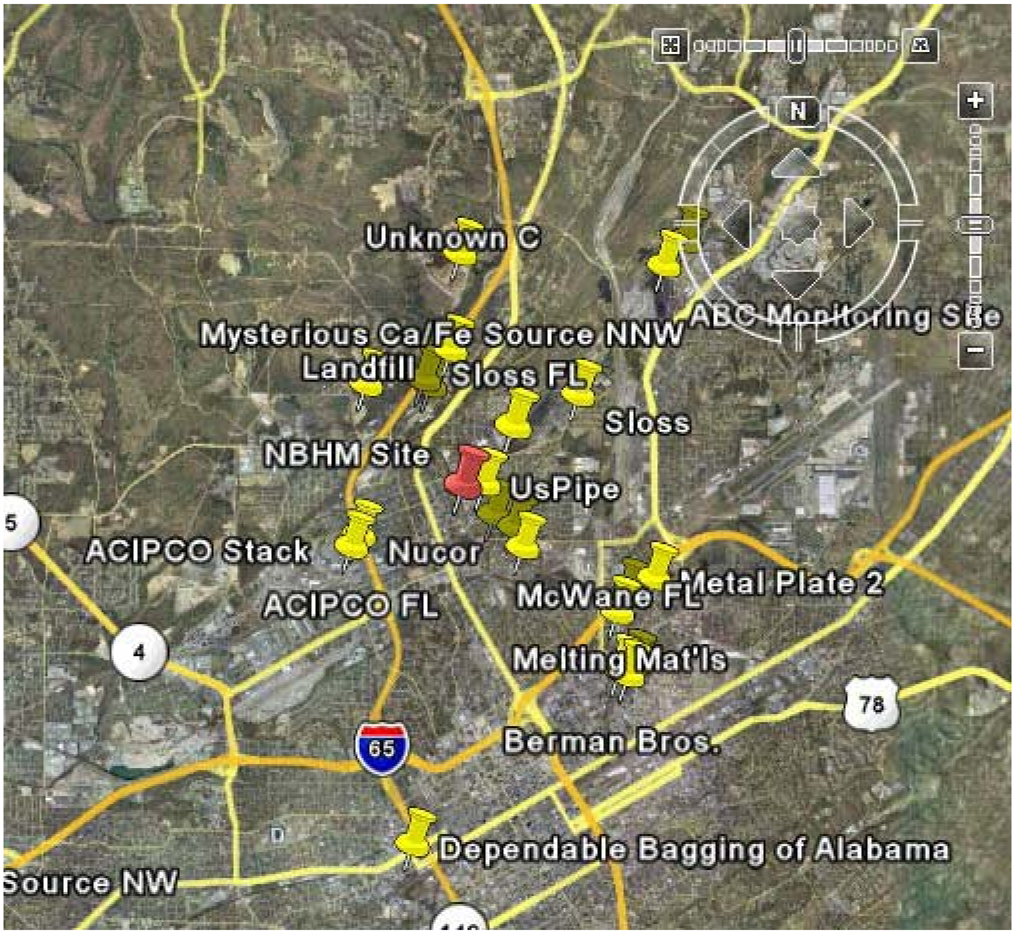

Figure 6. Locations of JCDH North Birmingham monitoring station (red pin) and the surrounding industrial locations (yellow pins).