COMPARING THE CO CONTENT OF CIGARETTE SMOKE AND AUTO EXHAUST USING GAS CHROMATOGRAPHY

by Dan Jaffe and Laurie Chavasse

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Abstract

We have found that measurements of environmentally relevant parameters generate some of the greatest student enthusiasm in our freshmen chemistry laboratories. In this regard we have developed a lab exercise to investigate and compare the carbon monoxide content of automobile exhaust and cigarette smoke using equipment available in most undergraduate labs. This experiment uses gas chromatography with thermal conductivity detection to analyze for the % by volume concentrations typically found in cigarette smoke and auto exhaust. Students are usually surprised to discover that cigarette smoke has a much higher CO concentration than does the exhaust from a clean, well maintained vehicle.

Introduction

Undergraduates often view science classes as boring and unrelated to their world. In this regard, environmentally relevant labs which examine familiar pollution sources (e.g. cars and cigarettes) provide an important connection between science and the students' own experiences. In addition because the students are already familiar with these objects they are curious and ready to develop interesting and testable hypotheses. In this paper we report on a lab to compare the CO concentration of car exhaust with cigarette smoke. It has been our experience that students are especially fascinated by working on environmental problems involving cars and/or cigarettes. This lab is currently being used in the general chemistry course for freshmen at the University of Alaska where it was developed.

In an earlier report [Jaffe and Herndon, 1995] we described a method using gas chromatography with a thermal conductivity detector (GC/TCD) to measure the CO content in auto exhaust. The GC/TCD method for CO has a detection limit of ~0.05 % v/v. This is near the level of CO found in the exhaust of a clean, warmed up, well maintained vehicle. In contrast, the CO mixing ratio from a poorly maintained vehicle can be as high as 15% v/v, and are thus easily detectable by GC/TCD (Air pollutants are commonly reported as a volumetric "mixing ratio" which is identical to a mole fraction. Thus, 1% v/v refers to a gas mixture whereby 1 out of every 100 molecules is CO.)

Cigarette smoke contains an amazing array of gaseous and particulate compounds. This includes (in approximate order by mass): carbon dioxide, water, carbon monoxide, particulate matter (mostly tar), nicotine, nitrogen oxides, hydrogen cyanide, ammonia, formaldehyde, phenol and dozens of other well known toxic compounds. Some of these components are present in extremely high concentrations. For example cigarette smoke contains much higher concentrations of carbon monoxide (0.5-5% v/v) than the auto exhaust from a well maintained vehicle. This concentration of CO would be lethal if inhaled continuously for ~30 minutes. Because of the relatively high concentrations of CO in cigarette smoke it is possible to conduct quantitative measurements using a basic gas chromatograph with thermal conductivity detection.

Standard methods for collection of cigarette smoke have been developed by the Federal Trade Commission (FTC). The FTC method is intended to approximate a typical smoking pattern and consists of one 35 cm^3 "puff" of 2 seconds duration once per minute. Mainstream (MS) smoke is the smoke which is directly inhaled by the smoker whereas sidestream (SS) or secondhand smoke is the smoke which is released to the environment from the burning cigarette. Measurements on both SS and MS smoke have been made for many of the toxic constituents in cigarettes [e.g. Guerin 1991; Guerin et al, 1987; Rickert et al., 1984]. The ratio of the mass released in SS vs MS smoke is ~1-10 for a typical smoking pattern. This means that total emissions are greatest in the SS smoke, although this depends on the compound and the type of cigarette. Many cigarette brands have ventilation slits in or near the filter which will dilute the concentration of tar, CO and other compounds in the MS smoke. For particulate matter and CO the SS/MS mass ratios are typically in the range of 0.4-2 and 2-8, respectively, however there is a large amount of variation.

Because the quantities and concentrations of the toxic constituents in cigarette smoke are quite high we concluded that it should be possible to quantify these using methods available to undergraduate science students. In developing this laboratory exercise, our goal was to minimize the complexities as much as possible, while still maintaining a scientifically valid approach. In this light we chose to ignore the differentiation between MS and SS smoke and to focus instead on a total smoke sample obtained by continuously "smoking" the cigarette. Certainly many of the same methods described in this paper could be applied to the MS and SS smoke separately, however to date we have not done so. In a separate report [Jaffe et al., 1997], we have described a series of experiments on cigarette smoke which do not require the use of a gas chromatograph, and are thus useable in secondary science classrooms. By utilizing a gas chromatograph, undergraduate science students are able to conduct an experiment which brings to light the remarkable finding that cigarette smoke has higher CO concentrations than the exhaust from most cars.

Experimental

The smoking apparatus is shown in Figure 1 and Photo A. In earlier experiments the cigarette was inserted directly into a one hole rubber stopper in the top of the flasks, but due to leaks this has been changed. A more leak free connection can be made by inserting a piece of glass tubing into the stopper, attaching this to Tygon™ tubing and putting the cigarette into the Tygon™ tubing.

To start the experiment, the cigarette is inserted into the tubing, the vacuum turned on and flow rate adjusted to 0.5-1.0 liter per minute. The cigarette is then lit and after waiting at least 1 minute a syringe is inserted directly into the tubing and a gas sample withdrawn. It is important that the Erlenmeyer flask be the smallest size available, as a large Erlenmeyer will result in lower CO concentrations due to dilution until the cigarette smoke has completely flushed the flask (about 2 flushing times). For the data reported in this paper, Lucky Strike brand cigarettes were used as the unfiltered type and Camel Filter 100's were chosen as the filtered type.

Car exhaust was obtained by collecting the exhaust directly into sandwich sized "zipper-type" bags. In our earlier versions of this lab we used a small vacuum pump but later found that this was unnecessary. The plastic bag should be flushed with exhaust, filled and then quickly sealed. Based on our earlier work [Jaffe and Herndon, 1995] it is best if the GC-TCD analysis is conducted on the same day as the samples are collected, although this is not absolutely essential. A sample of the exhaust for injection into the GC-TCD is obtained by inserting a syringe needle through the plastic bag. A resealable sample port can be made on the plastic bags with 2 pieces of transparent tape, one on top of the other.

For the experiments described here, we used a GOW MAC 150 Series gas chromatograph with thermal conductivity detector. The column was a 1/4" o.d. by 6' molecular sieve (5Å) column and the oven temperature was set to 70-75^o C. The detector current was 200 mA, the carrier gas was He and the column flow rate was set to 60 ml/min. The column should be baked out at elevated temperature prior to each class use. A 1.0 ml aliquot of the standard, car exhaust and cigarette smoke samples are injected identically into the gas chromatogram. For our freshmen chemistry classes we use inexpensive plastic syringes to inject the samples into the GC.

The standard used is a small compressed gas cylinder containing 1% v/v CO in N_2. This is the only item needed for this lab which is not commonly available in most undergraduate labs and can be bought for under $100 (Scott Specialty Gases, Freemont, CA). A convenient way to provide the standard to the students is by filling 1 or 2 of the "zipper type" bags with the standard. The students can then sample the standard in the exact same manner as the exhaust. This also guards against an accidental release of the lecture bottle standard. Our previous work [Jaffe and Herndon, 1995] has shown that the CO response on the TCD is linear. Thus for simplicity and economy we use only a single point calibration with the standard, however it would be a straight forward exercise to produce multiple concentration standards by appropriate dilution of the standard with clean air.

Results

Figure 2 shows a chromatogram of the CO standard. Since the TCD has a relatively low sensitivity, compared with other GC detectors, only the major components in each sample will be detected. This includes N_2, O_2 and CO. Since air contains both N_2 and O_2 as the main components and the standard contains little or no O_2 it is relatively straightforward to identify which peak is which. A small O_2 peak is sometimes present in the standard chromatogram (see Figure 2) which is probably due to our imperfect transfer of the standard to the plastic bags. Water and CO_2 are apparently retained by the column and do not appear in the chromatogram as identifiable peaks. For these conditions, the retention times for O_2, N_2, and CO are 0.74, 1.0, and 1.8 minutes, respectively. By comparing the height of the O_2 peak in the standard with the O_2 peak in air (20% v/v) it is possible to estimate the amount of contamination in the calibration standard. For the chromatogram shown in Figure 2, we estimate that the O_2 content is less than 0.5 % v/v which represents an insignificant dilution of the calibration standard by ambient air.

Figure 3 shows a chromatogram of the cigarette smoke sample. It shows O_2, N_2, CO, and a 4th unidentified peak which appears as a small peak on the tail of the N_2 peak. Other compounds which might be detectable in the exhaust and cigarette smoke samples are H_2 (exhaust), NO (exhaust or cigarettes), HCN (cigarette), acetaldehyde, benzene, or other hydrocarbons (exhaust or cigarettes). It should be pointed out that even in an extremely polluted urban environment where CO mixing ratios often exceed 10 parts per million by volume (ppmv), this is many orders of magnitude less than the exhaust mixing ratios (%) and is well below what is possible to detect with the TCD. In general, chromatograms obtained from the exhaust samples appear essentially identical to the cigarette smoke samples, but with varying amounts of CO.

The CO peak height for the 1% standard varies from day to day, but typically has a height of 4-5 cm on the chart recorder at an attenuation of 2. The CO peak height for a well-performing, warmed up vehicle will be much less than the standard under these conditions, although for a cold vehicle much greater exhaust CO mixing ratios are observed (Jaffe and Herndon, 1995). It is a simple matter to convert these peak heights to CO mixing ratios using:

$$\text{CO(unknown)} = \text{CO (standard)} * \text{Peak height(unknown)}/\text{Peak height(standard)}$$

Table 1 reports on some cigarette and car exhaust data obtained by students at the University of Alaska.

Table 1. CO mixing ratios in % v/v

	Exhaust from warm car	**Non-filter cigarette**	**Filter Cigarette**
Mean	0.24	2.4	2.8
S.D.	0.26	0.4	0.6
Range	bdl[*]-0.82	1.8-2.9	1.6-3.7
N	16	4	10

[*]below detection limit

Discussion

The range of cigarette smoke concentrations we have found, 1.6-3.7 % (v/v) is comparable to the range of 1.5-5.5% (v/v) reported from other studies [Godish 1985].

Cigarettes clearly put out much higher concentrations of CO than most cars. In fact all of the cigarette measurements we made gave CO mixing ratios of greater than 1.0%, which is interesting in that this level is the usual “passing” value for cars which must have annual emission tests. Of the cars we tested in this experiment none exceeded the 1.0% level, although we have seen higher values from other vehicles we have tested.

The filtered and unfiltered cigarettes yielded similar CO data. At a 95% confidence level the data from the two types of cigarettes cannot be distinguished. This is in contrast to the data on tar and other particulates where we found that the filtered cigarettes yield much lower amounts of tar.

This relatively simple experiment lends itself to inquiry and hypothesis testing. This is because students are already familiar with the basic principles behind the internal combustion engine and certainly many of them will know quite a bit about real smoking patterns. In our Chem 106 course (second semester of general chemistry with mostly freshmen) this lab generates the most enthusiasm of any of the labs the students do during the semester.

The visual nature of this experiment also provides strong evidence to a population most at risk of becoming smokers. In collecting the CO samples, a beautiful pattern of dense smoke appears in the Erlenmeyer flask. In addition, the tar which accumulates in the flask, tubing and glass wool trap are powerful visual and olfactory clues as to the true nature of inhaled cigarette smoke. (Because of the tar it is recommended that the equipment used in this lab be dedicated to this experiment.) Since it can be shown that inhaled smoke contains similar or more carbon monoxide than in car exhaust, there is an immediate "real-world" significance attached to the measured levels of this well known toxin. In addition this leads to the obvious question: why isn't smoking immediately lethal? The answer must lie in the fact that smokers do not inhale continuously on the cigarette. However nonetheless, there are serious health implications of this high level of CO in cigarette smoke due to the very tight bonding of CO to hemoglobin. Smokers have between 2-5% of their hemoglobin tied up with CO and therefore unavailable for O_2 transport.

Regarding hypothesis development, this basic experiment can be broadened to test a wide range of interesting and relevant hypotheses. For example a partial list might include:

1) Is more CO released in mainstream or sidestream smoke?

2) What factors increase the production of CO in cigarette smoke? (e.g. flow rate, humidity, combustion at reduced pressure/high altitude)?

3)Why do cold or poorly tuned vehicles generate much more CO during combustion, as compared to a warm, well tuned vehicle?

4) Why do cigarettes produce a greater CO concentration, as compared to a well tuned car?

5) Do laboratory animals die if exposed continuously to undiluted, mainstream cigarette smoke for 60 minutes?

Finally, it is possible to combine the GC measurements of CO in cigarette smoke with mass measurements of the tar content using a filtration technique we have developed. It is also possible to use less accurate, but simpler, colorometric indicator tubes to measure the CO mixing ratios in cigarette smoke or exhaust. Both of these projects are suitable for secondary science classes and are described in a separate report. [Jaffe et al., 1997].

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Internet resources:

FDA home page on Children and Tobacco:

http://www.fda.gov/opacom/campaigns/tobacco.html

CDC's Tobacco Information and Prevention home page (TIPS):

http://www.cdc.gov/nccdphp/osh/

EPA home page on Indoor Air Quality and Secondhand Smoke:

http://www.epa.gov/docs/iedweb00/index.html

Pictures

Setup used to “smoke” cigarette and obtain smoke sample

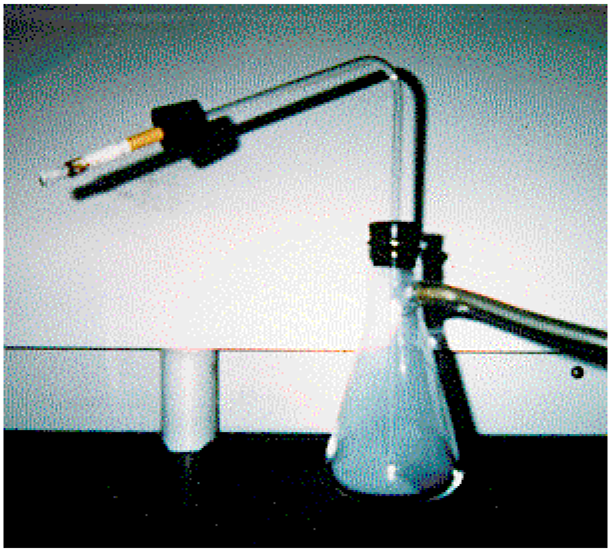

Figure 1: Experimental apparatus for obtaining cigarette smoke sample.

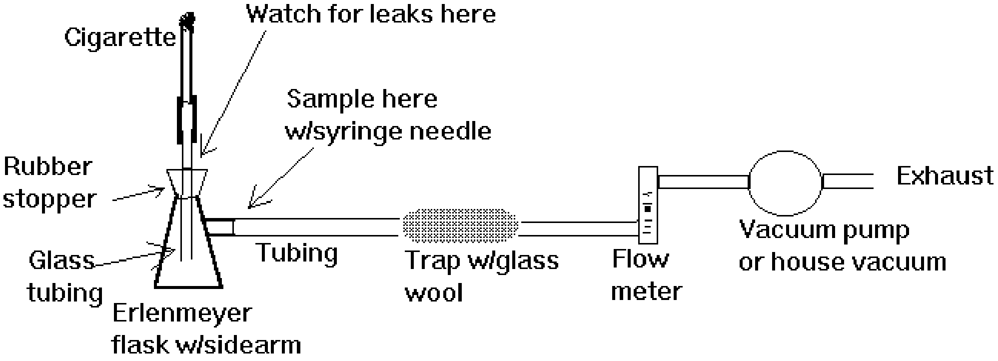

Figure 2. Digitized chromatogram of the 1.0% v/v CO in N_2 calibration standard. The chromatogram was collected at an attenuation of 4, oven temperature of 75°C, He flow rate of 60 ml/minute, detector current of 200 milliamps, an injection volume of 1.0 ml and using a 5 Å molecular sieve column 6' x 1/4" o.d. For these conditions the O_2, N_2 and CO elute at 0.6, 0.9 and 1.8 minutes, respectively. The small amount of O_2 present in this sample was determined to be 0.5% v/v and is due to contamination of the standard during handling (see text).

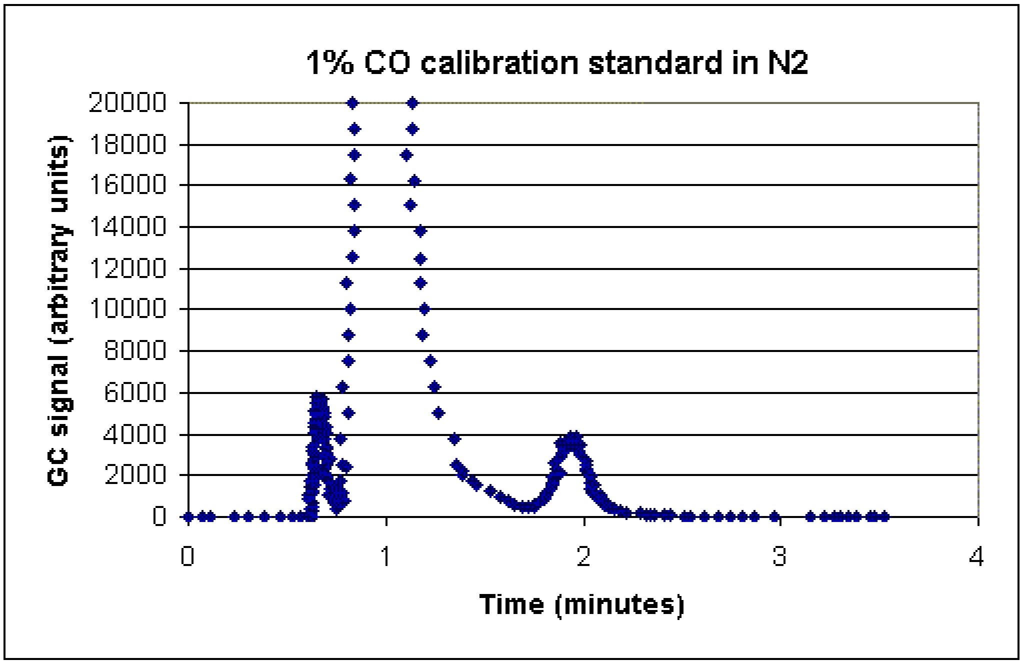

Figure 3. Chromatogram of a sample of cigarette smoke. Conditions are identical to those used for the calibration standard shown in Figure 1. The CO content of this sample was determined to be 2.3% v/v.