

Text for talk on Acrolein analysis
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1. I'm going to talk about some of the analytical issues associated with the measurement of acrolein in air-sampling canisters. The health-risk assessment community has come to recognize it as a particularly harmful compound, and as such, the EPA has recently developed a large interest in measuring its concentration in the air.
2. Our lab has instrumentation, similar to most other labs that do VOCs air-toxics measurements. A few items to note: there is a splitter downstream of the GC column, leading to both an FID and a mass spectrometer. So, we have two signals to look at. Acrolein can easily be seen on both detectors, and in Rhode Island ambient air, it has no co-eluters. Also, the GC column has a 2 micron film thickness. For nonpolar species it gives slightly wider peak-widths than the more conventional 1-micron column, but polar species such as the oxygenates have less peak tailing.
3. This is what a series of acrolein standards look like on the FID. Typical for a polar compound, the retention time moves forward as the amount of the compound increases.
4. The Mass Spectrometer has a similar appearance. We use the mass 56 ion. The mass 55 ion gives a fairly similar response, but not quite as sensitive. Also, the compound 3-methyl-1-butene comes through just before acrolein, and it produces a mass 55 ion.
5. The calibration curve is usually pretty nearly linear. The y-axis is simple peak-area of the 56 ion. The x-axis is in ml of a 22 ppb tank. Since the top value is 250 ml and our normal sample size for an ambient air sample is 500 ml, the top of the calibration range is about 11 ppb. The bottom is at 10 ml of the standard tank, which corresponds to an air sample concentration of about .4 ppb.
6. The FID is usually more nearly linear than the MS.
7. This piece of an FID chromatogram shows the area around acrolein. We see isobutane and acetaldehyde, methanol, 1-butene and its isomer 2-methylpropene, 1,3-butadiene and butane; trans and cis-2-butenes, with some ethylene oxide alongside the trans isomer; then ethanol, a small acetonitrile peak, then acrolein just in front of this large peak that contains acetone, isopentane and propanal. Then we see 1-pentene, isopropanol, and pentane, then isoprene and some pentenes.

| compound | RT |
|-----------------|-----------|
| isobutane | 10.57 |
| acetaldehyde | 10.74 |

| | |
|--------------------|-------|
| methanol | 11.59 |
| 1-butene | 11.88 |
| 1,3-butadiene | 12.10 |
| butane | 12.37 |
| ethylene oxide | 12.91 |
| trans-2-butene | 12.93 |
| cis-2-butene | 13.67 |
| ethanol | 15.08 |
| acetonitrile | 15.45 |
| acrolein | 15.82 |
| isopentane | 16.16 |
| acetone | 16.17 |
| 1-pentene | 16.93 |
| isopropanol | 17.27 |
| pentane | 17.48 |
| isoprene | 17.69 |
| trans-2-pentene | 17.87 |
| cis-2-pentene | 18.24 |
| dichloromethane | 18.34 |
| 2,2-dimethylbutane | 19.18 |

8. Here's the same region of the chromatogram with some of the significant ions for that region plotted. Note that in this air sample, which is fairly typical, the acrolein peak is quite small. We operate the mass spectrometer in full-scan mode. If we were to go to SIM mode, the peak could be a good deal larger.
9. Here's a close-up look at the acrolein peak on the FID.
10. And here it is on the mass spectrometer. Note the small peaks of 3-methyl-1-butene and acetonitrile under the ethanol peak, just ahead of acrolein.
11. We've done several canister-testing experiments, in which we open up a group of canisters simultaneously and fill them with ambient air, then analyze a couple of them immediately, then let them all sit for a week or two, and then analyze all of them. We try to do this at a time when the air is fairly dirty, so there's more stuff to look at. The chromatogram we just looked at was a reference for a set of canisters we opened on the morning of October 3rd. Here we see an overlay with the run done 8 days later on the same can. Note that virtually all the peaks are unchanged.
12. Here's another of the canisters of that group. The butanes and butenes are all unchanged. But acetaldehyde is a lot bigger, as is acrolein. Herein lies the problem with trying to measure acrolein or any of the oxygenates from canister samples. I don't know how these compounds are being created or what they're coming from. The amount of production seems to vary from one canister to another – some cans are pretty good, and others clearly are not.

13. The sampler may play a role as well. These two samples were pumped by two co-located Xontech 910s, and we can see that they agree well for most of the well-behaved compounds, but one of them has a bit more acetaldehyde. This could easily be due to the canister producing more of it, but we've noticed that one of these two samplers consistently produces samples with higher aldehydes, than the other sampler. So, samplers can play a role as well.
14. Here's a pair where one sampler produced more of the odd-carbon alcohols, methanol and isopropanol.
15. Here we have the results of our most recent can-testing experiment (Oct 3rd), for the compound isobutane. The bar on the left represents the concentration at the time when the cans were first filled. It comes from an average of the two initial runs and represents what the air had in it when the sample was first collected. Then we have two groups of bars, in which each bar represents an individual canister. Most of the cans in the first group were analyzed at 8 days; and this second group represents the same cans at 22 days. Note this bar represents can 102 at 8 days, and this one represents it at 22 days. Repeat for can 12655. Generally, we see that isobutane is stable in all of these cans.
16. Butane is stable also.
17. Benzene is pretty good too.
18. Looks like there might be a problem for toluene, in a couple of the cans.
19. The same cans have a real problem with propene. Lets look at some other light alkenes.
20. 1-butene is the same; those two cans seem to be "eating" it.
21. isoprene's even worse; those two cans have "eaten" nearly all of it, and it looks like another can may be producing the stuff.
22. now here's acetaldehyde, with the opposite problem; a lot of production. 5 of the 11 look pretty good at 8 days, and marginal at 22 days. The other 6 are all bad.
23. and acrolein's about the same, maybe a little better.
24. We did a lot of this work in 2002, and here's an acrolein chart for one of the sets then. All of the cans produced a lot.
25. Here's another set from 2002, with more mixed results. Both of the sets from 2002 were taken at mid-day when we had hot, dirty air with lots of ozone. The recent (Oct 3rd) set that I showed were filled early in the morning in Providence, while we were still under an inversion, so the air was dirty, but there was no ozone.

26. Now, I'll show some co-located data from our East Providence PAMS site. There are two Xontech 910a samplers on two different manifolds. The 2005 benzene numbers look like this. Perfect agreement.
27. butane looks great also.
28. Butadiene looks pretty good, considering that the levels are mostly pretty low.
29. Acrolein, however is mostly chaos. The two measurements are barely correlated.
30. Acetaldehyde has the same problem.
31. So does acetone.
32. So does benzaldehyde. You can see that there is some correlation, but it's not a reliable measurement.
33. Ethylene Oxide too.
34. Here's isoprene. Note that there's a lot of it around during the summer.
35. This is a summary of our precision data for 2005. The numbers in the table represent % diff values. Looking at ethylene, for example, of 58 pairs of numbers, half of them were within 4% of each other and $\frac{3}{4}$ of them were within 8% of each other. For butadiene, half of the 58 data pairs were within 15% of each other, and $\frac{3}{4}$ were within 25%. Most of these measurements were at low concentrations. Over here we see that only 5 of them were at or above 5 times the MDL, and of those, $\frac{3}{4}$ were within 10%. Note that most of the tox compounds have pretty good agreement, even though the concentrations are quite low. The oxygenates aren't so good, though. Our acrolein median value is 33%. All of the acrolein measurements are low in concentration, but notice that for the other aldehydes, high concentrations are still problematic.
36. During the PAMs season, we collect 3-hour samples in near-real time at the same East Providence site where we take the co-located 24-hour cans. Our "ambient canister" fills passively for 3 hours, gets analyzed immediately at the end of the 3-hour period, then gets pumped out and starts re-filling. Of all the acrolein numbers that we've produced, these are the only ones that I think are likely to be reliable. Here we see acrolein and isoprene plotted together for this past July. Isoprene has a strong diurnal cycle which is driven by temperature. Acrolein tends to follow it somewhat. On these days in mid-July, acrolein has an morning rush-hour peak, followed by a second peak in late afternoon, that is probably following isoprene. I suspect that the afternoon acrolein is coming from the destruction of isoprene.
37. Here's acrolein plotted with 1-butene, which is mostly from local traffic. There's a pretty good correlation here too. These are mostly morning rush-hour peaks.

38. In 2002, our 3-hour and 24-hour samples were on the same clock. (They aren't any more). The 3-hour samples, when consolidated into 24-hour averages, should match up with the 24-hour samples. For benzene and MTBE, they do, but for acrolein, they don't.
39. To conclude: if we want good data, we need to be sure that our canisters aren't producing the compounds that we're trying to measure. At least some of the cans that we have been using, do have this problem. We retired quite a few of them in 2002, and will retire at least one more (can 102) after this small round of testing. Whether we'll ever identify a group of cans that are completely trustworthy or not, I don't know. I think that anyone trying to measure acrolein or any of the other oxygenates, will have to pay a great deal of attention to their canister collection. Unfortunately, I don't know how or why the oxygenates are being produced, so I can't predict what it will take to solve the problem. I suspect that acrolein production may be the result of several different phenomena, and that both the atmospheric conditions at the time of sampling, and the sampling equipment (cans and sampler) may be significant factors.