

**Acrolein Research Project – Contract 00-721
Draft Report**

Planning and Technical Support Division
Air Resource Board
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Summary

Because acrolein has been identified by OEHHA as a serious concern to human health as part of the Children's Environmental Health Protection Act (SB 25, Escutia, 1999), it is critical to be able to identify sources of acrolein so that public health can be protected.¹ Ambient levels of acrolein in many areas of California are well above exposure levels that can cause health problems, and efforts are being made to reduce these exposures.

Acrolein is emitted from many types of sources, including motor vehicles and wildfires. Acrolein is formed in the atmosphere, and also emitted from stationary sources as a byproduct of incomplete combustion. For stationary sources, it is very difficult to accurately measure acrolein from combustion processes, and there is currently no approved test method available. The test method (ARB M430) that has been used since 1991 has been brought into question, and attempts to develop a new method are ongoing. This report provides information on the ARB's most recent attempts to measure acrolein emissions from stationary sources and describes our test method development efforts.

In early 2001, ARB initiated a research project to compare seven test methods at four different facilities in Los Angeles that emit acrolein. The tests would allow ARB staff to determine if any of the test methods were able to accurately measure acrolein at each of the facilities. This would help ARB and OEHHA to evaluate the contribution of acrolein from stationary sources and determine if these emissions impact public health.

All four source tests took place in April, 2002, with mixed results. None of the test methods were conclusively shown to be able to consistently and accurately measure acrolein from these sources, especially at low emission rates. However, one of the experimental methods (Modified M430 with H₃PO₄/toluene) was identified as having potential promise, and subsequent source tests by Santa Barbara County and Monterey Bay Unified APCDs have provided additional data on several different acrolein sources.² This data has been reviewed and serves as a basis for additional testing.

The main conclusions of this project are as follows:

- Acrolein was difficult to quantify at low ppb levels from combustion sources using these test methods due to the degradation of the pollutant during testing and/or the inability of these test methods to measure acrolein at low levels
- Modified M430 with H₃PO₄/toluene is the method that shows the greatest potential
- The portable GC-MS also gave results that tend to appear in the center of the range of values measured from the other methods
- Despite variations in the results, there was enough consistency between the methods to suggest that acrolein emissions from three of the four sources tested were in the low ppb range
- The rotary kiln had acrolein emissions 100 to 1000 times higher than the other sources tested

Introduction

As a product of incomplete combustion, acrolein is present in gasoline and diesel exhaust, tobacco smoke, wood smoke and some industrial emissions, and is used as an herbicide and algaecide in irrigation canals, lakes and ponds. It can also be formed in the atmosphere from chemical reactions involving various hydrocarbons, including 1,3-butadiene. Acrolein is unstable in the atmosphere and breaks down within a few days of being emitted. As described in subsequent sections, this instability makes the measurement of acrolein very challenging.

Exposure to acrolein may cause respiratory effects, including coughing, nasal irritation, chest pain, and difficulty breathing. If inhaled in sufficient quantity, it can cause burning of the nose and throat, and can damage the lungs. Prolonged or repeated skin contact may result in skin burns and dermatitis.

OEHHA has adopted an acute noncancer reference exposure level (REL) of 0.19 $\mu\text{g}/\text{m}^3$ (0.09 ppb) and a chronic noncancer REL of 0.06 $\mu\text{g}/\text{m}^3$ (0.03 ppb).³ Because there is no cancer potency value established for acrolein, only acute and chronic noncancer health effects from the exposure to acrolein emissions are considered when evaluating health risks. Typical ambient levels of acrolein at all of the ARB's 17 air toxics monitors are between 0.4 and 1 ppb. These acrolein levels can cause serious adverse health effects.

As part of the SB 25 program, OEHHA has identified acrolein as one of the top 5 most important pollutants of concern, in part, because several studies in animals strongly suggest that acrolein may exacerbate asthma. This is of special concern for children, because asthma is more prevalent among children than adults, and because asthma episodes can be more severe in children than adults due to their smaller airways. This identification of acrolein as a threat to children's health further prompted ARB to measure sources of acrolein and work to identify a test method that could accurately measure acrolein.

Background on Test Method

ARB M430 is used to quantify formaldehyde and acetaldehyde emissions from combustion sources. The method contains a cautionary note against using the method for any other aldehydes, including acrolein. Since there has never been an approved method for acrolein, and acrolein is required to be reported from combustion sources, facilities reported acrolein in conjunction with their M430 results. ARB used the emissions data to calculate emission factors in the early 1990's because no other data existed for acrolein.

Other facilities that were required to quantify acrolein estimated their own emissions and health impacts using these emission factors. In the late 1990's, several research groups found that, as an unsaturated aldehyde, acrolein degrades rapidly during testing, and especially in the presence of NO_x. This meant that many facilities could have significantly underestimated their acrolein emissions and health risk. Although the mechanism for this degradation was unknown, ARB published an advisory in 2000 that stated that M430 could not be used for acrolein, and that the emission factors derived from the method were probably not accurate.⁴ Although facilities were left with no recommended method to measure acrolein, they were required to report their emissions to the local air district.

In late 2000, the ARB appropriated \$90,000 for a contract to study acrolein emissions. The contract stated that, "*a major source of acrolein emissions may be coming from natural gas-fired turbines, many of which are coming on-line as new power plants are being planned. This proposal would collect acrolein samples from various combustion sources to accurately determine emissions from the source types studied.*" Knowing a reliable method for accurately measuring acrolein had not been identified, ARB staff began searching for promising approaches.

After an extensive literature search, several experimental test methods were identified as having sufficient potential to merit research. However, instead of simply conducting a retention and comparison study to show that acrolein can be captured and quantified under laboratory conditions, it was necessary to prove that potential methods can measure acrolein under real world conditions where there is the potential for acrolein to degrade during testing. Simply showing that acrolein is stable in an impinger or a canister in the laboratory is not sufficient, because this would not prove whether the method could capture and stabilize the acrolein in a combustion matrix in the field without suffering degradation.

Testing Plan

The Air Resources Board (ARB) contracted with Ashland Chemical (Ohio) in 2001, based on a recommendation from James Loop (ARB), to conduct source testing in order to compare several test methods for the detection of acrolein from combustion sources. Mr. Loop thought at the time that Ashland's Aldechem tubes held the best chance for success as a test method for acrolein. This was later shown to be incorrect based on test results from this study.

A contract for \$90,000 was awarded to Gary Schoening at Ashland Chemical in Ohio, and testing began in April 2002. Mr. Schoening supervised a series of measurements of acrolein at four facilities in Los Angeles over the course of 5 days. Mr. Schoening was the lead engineer for this project and operated the Waters Sep-Pak Cartridges, the Modified M430 sampling train, and the Aldechem sampling tubes. Horizon Engineering (Oregon) conducted all of the initial field work using EPA Method 1 & 2 for flow rate, EPA Method 3A for CO₂ & O₂ and EPA Method 4 for moisture. Horizon helped the test team with logistics, but did not actually measure acrolein. Lehder Environmental Services Limited (Ontario, Canada) was chosen to perform the FTIR analysis for aldehydes given their expertise in using FTIR to measure challenging air pollution sources.

Two additional groups brought their own monitoring equipment to the test sites to measure acrolein in parallel with our original tests with the goal of having their method approved for testing. Bob Bertik of Air Quality Analytical (Los Angeles) operated a portable FTIR device and Dave Curtis of Field Portable Analytical (Sacramento) operated a portable GC-MS. Both systems were able to acquire real-time data within a few minutes of set-up at each test site. These two groups attended the testing at no cost to ARB and provided useful real-time data throughout testing, in addition to being candidates for the identification of a new test method for acrolein.

After a lengthy assessment, four facilities in Los Angeles were selected for testing, including a 128 mmBtu waste gas boiler at a refinery, a 22 Megawatt natural gas fired turbine at a power plant, a 290-Hp rich-burn natural gas stationary diesel engine with a 3-way catalyst, and a rotary kiln burning a complex fuel mixture. This provided the test group with a broad range of sources from which to challenge each of the test methods. A summary of the test results is included in Appendix A.

Test Methods

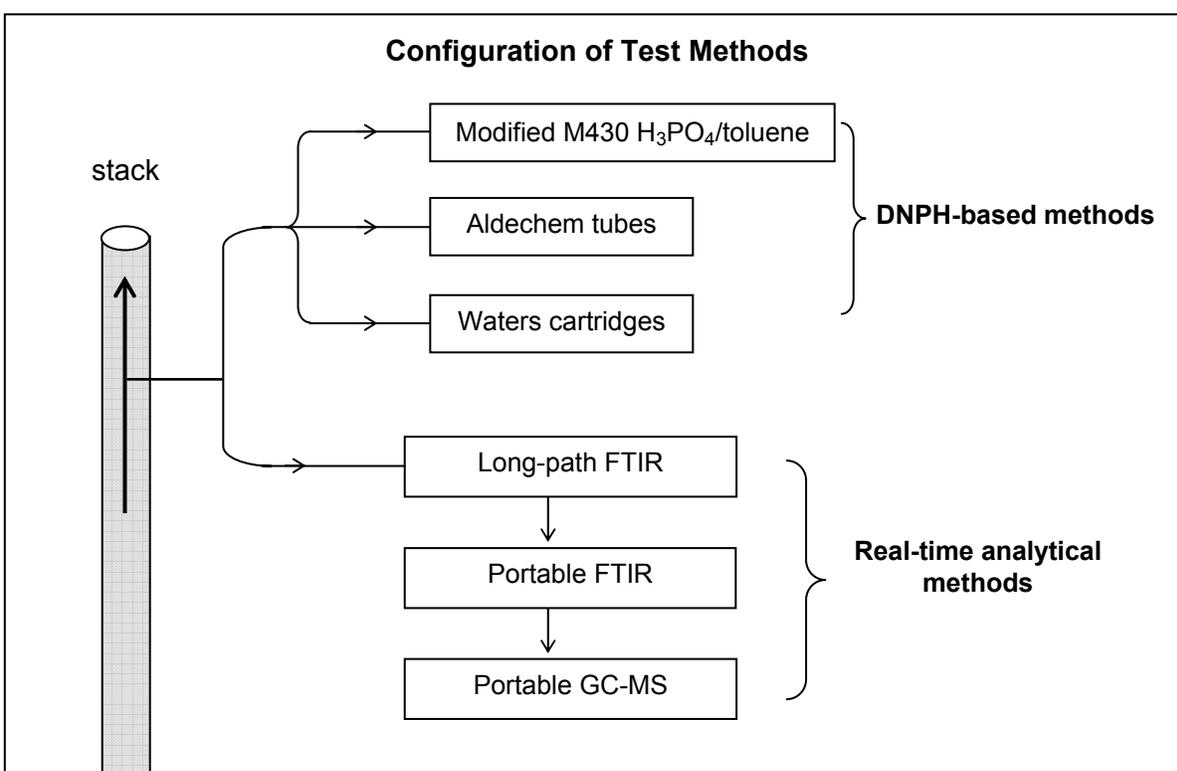
The following test methods were included in the research project. The name of the company that conducted each of the tests is listed in the table immediately following each test method description.

Test Method	Description
Modified M430 with post-extraction	The original M430 is used to measure formaldehyde and acetaldehyde from combustion sources. The sampling train requires the use of impingers containing dinitrophenyl hydrazine (DNPH), a derivatizing agent that reacts with carbonyls in the presence of hydrochloric acid, which catalyzes the nucleophilic addition and dehydration of the intermediate hydrazone adduct. This modification to M430 involving post-extraction was developed as a stopgap approach to decrease degradation of the hydrazone, using an organic extraction of the impinger solution immediately <u>after</u> a sample is collected. However, because acrolein often degrades by more than 75% during testing and before the extraction is able to halt degradation, only a small fraction of the total acrolein being emitted can be extracted and analyzed. ⁵ And because the degradation is inconsistent, it is impossible to calculate the original acrolein concentrations. Therefore, this method was never thought to be a reliable method for acrolein. (Almega conducted testing at the refinery only. The Modified M430 with extraction was not used at the other 3 sites.)
Modified M430 with H₃PO₄/toluene	This second modification requires the addition of phosphoric acid, a weaker acid than hydrochloric acid (a weaker acid is able to catalyze the reaction, and is less likely to degrade acrolein during testing). Toluene, an organic solvent, was also added to the impinger solution, which removes the newly formed acrolein hydrazone from the acidic aqueous layer into an organic layer where it is relatively stable. This continuous extraction was expected to reduce the decomposition of the hydrazone during testing by removing it from the acidic solution. (Ashland conducted testing at all 4 sites.)
Waters Sep-Pak Cartridges	DNPH-coated silica gel cartridges are used by ARB to estimate formaldehyde emissions from motor vehicles. Acrolein and several other aldehydes are also reported using this method, but it is uncertain if this technique is accurate for acrolein. The amount of acrolein recovered under ideal conditions during laboratory recovery studies is approximately 65%, making this method highly questionable for acrolein quantification. (Ashland conducted testing at 3 of the 4 sites.)
Aldechem tubes	Ashland has developed a sampling tube that utilizes DNPH-impregnated polystyrene beads in a glass sampling tube (rather than liquid impingers) with an acid adhered to the solid support to catalyze the conversion of acrolein into the acrolein hydrazone. This proprietary system has been used for formaldehyde but had not been verified for acrolein. (Ashland conducted testing at all 4 sites.)
FTIR (long-path and portable)	Fourier Transform Infrared Spectroscopy (FTIR) has the ability to measure several pollutants in real-time, which is essential when measuring sources of acrolein that are not at a steady state. The long-path FTIR was a state-of-the-art instrument with a high-end software package able to quantify pollutants under very challenging conditions. The portable FTIR was lightweight and easy to use, although it was a lower resolution instrument compared with the long-path FTIR (Lehder conducted testing at all 4 sites, and Air Quality Analytical conducted testing at the first 3 sites.)
GC-MS (portable)	Gas chromatography-mass spectrometry is extremely sensitive, but with serious technical limitations for smaller and/or more complex mixtures of pollutants. Real time measurements are possible for a wide range of pollutants. Results are improved when a single molecular ion (mass) corresponding to the analyte (pollutant) is targeted. (Field Portable Analytical conducted testing at only the first 3 sites.)

Details of Testing

Sampling Train Design

The day before testing began, all of the source test engineers and scientists met with ARB staff in Los Angeles to plan the week of testing. Because this project required so many methods to be tested simultaneously, and space around each of the stacks was limited, a few different configurations were discussed and the test team settled on the configuration in the following figure. It was determined that a single hot line could be brought down from the stack to all 3 real-time methods because the real-time analytical techniques are non-destructive. The sample line could continue through the long-path FTIR to the portable FTIR, and finally to the GC-MS, without any loss of sample. A "T" near the sampling port could be routed in parallel to the impinger, tube, and cartridge methods (see arrows for direction of flow). This allowed a single probe to be used for three DNPH-based methods and three real-time analytical methods. A second hot-line (not shown) was used at the refinery by Almega in order to allow for simultaneous testing of M430 (Modified M430 with post-extraction).



Refinery Boiler

After a short safety lesson at the refinery, the test team began sampling the waste gas boiler and successfully completed 4 runs before testing was halted late in the evening. At the same time, the refinery had their own source testers (Almega) run two different methods, M430 with post-extraction, and the Ashland tubes. The refinery wanted to make sure that the results from our testing matched their own tests, so two collocated probes were used during all testing. In total, 8 tests were performed in a series of 4 runs, including field blanks, field spikes, and lab blanks. For the first day of testing, more than 80 samples were taken with an additional 12 hours of real-time FTIR data and 7 hours of data points from the GC-MS. The laboratory analysis of this one day of testing took more than a week and, as described later in this report, almost all of the samples were below the limit of detection for the method (acrolein levels were quantified, but were not sufficiently higher than the field blanks in most cases to be able to be used for estimating acrolein concentrations).

This source was recommended for testing by Scott Wilson (SCAQMD) and was assumed to be a good candidate for acrolein testing. It was known that the relative amount of acrolein was small, compared with the other sources, but it was a surprise when none of the methods were able to measure acrolein. The only emission control system at the boiler was a selective catalytic reduction (SCR) system used for NO_x control. This had a negligible effect on acrolein emissions.

Power Plant Turbine

When testing was nearly complete at the refinery, two engineers drove to the power plant that would be tested the following day and identified sampling ports and worked out sampling collection logistics before the team arrived the next day for testing. On the day of testing, 4 runs were completed with no major problems.

Stationary Engine

The stationary engine was the most interesting source to be tested. Sampling ports had been built into the stack upstream and downstream of the 3-way catalyst and a tremendous amount of coordination was required to put all of the test methods together for this source, given the limited space around the sampling port, and the need to sample both the inlet and the outlet of the air pollution control device. During the second series of tests that afternoon, the real-time data operators noticed a large increase in VOCs during the 40 minute test. During this time, the engine owner was notified of the unusual jump in emissions and shortly after that time, the engine began to fail. The engine was stopped as an emergency precaution and sampling was halted after only 20 minutes. Eventually an engine part was replaced and the third sample was taken without incident.

Recycling Plant Rotary Kiln

After a long safety training session on the use of protective equipment at the recycling plant, the rotary kiln was tested and three samples were taken. Because the facility required such extensive training and the use of protective equipment, and the plant manager (incorrectly) predicted very low levels of acrolein from the kiln, part of the team decided not to take samples at the fourth site. This proved to be very unfortunate when real-time results started to come in from the FTIR during testing and measured levels were extremely high. Additional data on the two portable methods would have been very helpful at measuring the accuracy of all of the methods, given the high readings of formaldehyde, acetaldehyde, and acrolein at the rotary kiln. Due to the high plastic content in the fuel mixture, it was not totally unexpected to have such high acetaldehyde levels, but it was unusual to have acetaldehyde levels that were even higher than formaldehyde levels. In almost every other combustion source, formaldehyde levels are higher than other longer-chain aldehydes.

Test Results for each Source

The following table summarizes the results from all of the facilities that were tested. The complete results for each method are listed in Appendix A, including formaldehyde and acetaldehyde results. As can be seen in the following table, the range of acrolein concentrations measured was large, with very low acrolein levels at the refinery, power plant, and stationary engine outlet, medium levels at the stationary engine inlet, and very high levels at the rotary kiln. This provided an extremely challenging series of tests for each of the candidate test methods because each method would have to measure acrolein over a very wide range of concentrations and different testing environments (different fuels, temperatures, and combustion processes).

General Facility Comparison

Facility	Source	Acrolein (ppb)	Relative Acrolein Concentration
Refinery	Boiler	<0.2 - <50	Below Detection Limit
Power plant	Turbine	0.2 - 50	Low
Stationary engine	Outlet from catalyst	<0.2 - 28	Low
	Inlet to catalyst	10 - 700	Medium
Recycling Plant	Rotary kiln	100 - 5,000	Very High

As can be seen from the previous summary table, and in the detailed test results that follow, and in Appendix A, the concentrations measured from the boiler at the **refinery** were mostly below detection limits.

Run #	Acrolein Refinery Results (ppb)			
	1	2	3	4
Ashland (DNPH)	<0.2	<0.2	<0.2	1.4
M430 H ₃ PO ₄ toluene (DNPH)	1	2	<0.2	<0.2
Waters Sep-Pak (DNPH)	<0.3	<0.3	<0.3	<0.3
FTIR (Lehder)	<50	<50	<50	<50
FTIR (Portable)		<30	30	230
GC/MS (Portable)	<3.0	<3.0	<3.0	<3.0
M430 extraction (DNPH)	Non-detects reported between 59 and 121 ppb			

Even with fourteen source test engineers and scientists working to detect acrolein using the best available test methods, it was extremely difficult to detect acrolein. There is no explanation for why the portable FTIR measured higher acrolein levels than the other methods. Both formaldehyde and acetaldehyde were detected with most test methods, even though results were not consistent between methods. This matches data collected by Monterey Bay Unified APCD in 2004 that measured acrolein levels at a boiler of approximately 5 ppb using the modified M430 with H₃PO₄/toluene. It may be that these low (ppb) levels are very difficult to measure using any known test method, given the degradation problems identified in previous studies.

Acrolein results from the turbine at the **power plant** were low, although the levels of acrolein were above the detection limit in some cases.

Run #	Acrolein Power Plant Results (ppb)			
	1	2	3	4
Ashland (DNPH)	10.1	16.3	13.8	27.1
M430 H ₃ PO ₄ toluene (DNPH)	4.3	2	<0.2	2
FTIR (Lehder)	<50	<50	<50	<50
FTIR (Portable)	<30	<30	<30	50
GC/MS (Portable)	4.9	6.1	4.6	3.7

Interestingly, acrolein levels were expected to be lower than found during testing due to pollution control equipment in place to control VOCs that was at the end of its useful life. Even with these relatively higher overall levels of emissions, acrolein was very difficult to measure. This also correlates with data collected in Monterey in 2004 where natural gas turbine emissions were measured at approximately 7-10 ppb. This also suggests that future turbine testing for acrolein may prove to be even more difficult than first anticipated if acrolein levels continue to decline with increasingly stringent VOC limits for power plants.

Testing at the **stationary engine** included tests upstream (inlet) and downstream (outlet) of a 3-way catalyst, an air pollution control device installed to reduce VOC emissions. By comparing the two concentrations, ARB staff was able to determine that the 3-way

Run #	Acrolein Stationary Engine Results (ppb)					
	1-inlet	2-inlet	3-inlet	1-outlet	2-outlet	3-outlet
Ashland (DNPH)	46	13.7	8.2	28	<0.2	<0.2
M430 H ₃ PO ₄ toluene (DNPH)	28.3	32.3	21.8	<0.2	2.3	<0.2
Waters Sep-Pak (DNPH)	N/A			<0.3	<0.3	<0.3
FTIR (Lehder)	760	720	590	<50	<50	<50
FTIR (Portable)	1,400	780	1,510	30	530	160
GC/MS (Portable)	114	101	124	6.1	3.1	3.4

catalyst reduced relative acrolein concentrations by approximately 50-90%. The uncontrolled effluent (upstream at the inlet of the 3-way catalyst) provided acrolein concentrations that were high enough to be measured using most of the methods, while the controlled emissions (at the outlet) were reduced to low levels and were difficult for most methods to measure. In the future, this type of control equipment may be required for engines that have been found to impact public health. For comparison purposes, data collected in Monterey in 2004 on two natural gas engines without controls gave acrolein levels in the range of 50 ppb, which is similar to (inlet) levels measured in this study.

Measurements from the rotary kiln at the **recycling plant** had much higher concentrations of acrolein with levels in the 0.1 to 5 ppm range. At higher levels, most of the test methods measured similar acrolein levels, even though these higher levels are not at all common in other sources. It remains unproven whether any of these methods were accurate, although higher concentrations of acrolein seem to be easier to measure.

Run #	Acrolein Recycling Plant Results (ppb)		
	1	2	3
Ashland (DNPH)	555	108	99
430 toluene (DNPH)	3,690	1,776	1,716
Waters Sep-Pak (DNPH)	2,567	2,474	2,173
FTIR (Lehder)	5,000	4,000	4,300

Summary Conclusions for each Test Method

Modified M430 with post-extraction

The results from the extraction immediately after sampling were all very low and reported as non-detects when this method was used at the refinery. This method was not used at subsequent tests and no other side-by-side comparison studies are available. This method will not be investigated further because of expected degradation of the sample during testing.

Modified M430 with H₃PO₄/toluene

Spiked samples collected beside a non-spiked sampling train had an average recovery of 94% for acrolein (although formaldehyde levels were not consistent). However, the method seemed to fail during several tests, particularly during the stationary engine testing (inlet was same level as outlet), and the refinery test where formaldehyde levels were unreasonably high. This was more evidence that interferences and degradation during testing could still be a problem. Subsequent testing in Santa Barbara County and Monterey Bay Unified Air Pollution Control Districts revealed that the method did not have the sensitivity required to measure acrolein from all sources, but that it may be adequate for

measuring acrolein from sources with higher acrolein concentrations. Additional testing should continue.

Waters Sep-Pak Cartridges

ARB's motor vehicle testing laboratory in El Monte utilizes the Waters Sep-Pak DNPH cartridges for routine aldehyde testing, primarily for formaldehyde. Acrolein results derived from these DNPH-impregnated silica gel cartridges have not been completely validated and likely underestimate acrolein emissions. Because this method is used to estimate acrolein from motor vehicles in California, more testing should be completed to verify the existing measured acrolein levels.

Aldechem Tubes

This method was initially thought to be the best contender, but failed during much of the testing. Even though the DNPH and the acid are adsorbed onto the polystyrene solid-support in the tube, decomposition during testing was found despite contentions from Ashland that decomposition would be limited. The formaldehyde levels were also not acceptable, given the results from the refinery, which suggest that contamination must have been a factor.

FTIR

According to several US/EPA staff and other researchers, FTIR is not yet able to consistently and accurately measure acrolein in a combustion matrix at levels below 50 ppb. This was further confirmed during this project at both the refinery, the power plant, and the outlet from the stationary engine. Although FTIR remains an extremely useful real-time tool for other pollutants, and during testing helped to identify an engine that was beginning to break down, it will not be useful for acrolein unless the limit of detection can be reduced to levels approaching 10 ppb.

Formaldehyde and acetaldehyde were also measured at each source and FTIR results are provided in Appendix A. For the very high formaldehyde results from the rotary kiln, it was determined that those results were outside of the expected concentration range and did not fall in the range of the formaldehyde standard curves prepared for this project. It is estimated that the results are too high and the actual acrolein concentrations are lower (levels are estimated to be in the range of 3,000 ppb rather than 5,000 ppb).

Gas Chromatography Mass Spectrometry (GC-MS)

Acrolein can be detected using GC-MS, but the technique of real-time monitoring remains experimental for quantifying acrolein from a combustion matrix. Internal and surrogate standards were in the acceptable range before testing, and the line bias check was quantitative. An acrolein line spike was introduced after testing and the GC-MS showed good correlation with the expected concentrations. However, the lack of data on exact concentrations, and the potential degradation of acrolein in the presence of NO_x and high temperatures, does not allow for the quantification of acrolein. Due to this lack of data, the GC-MS results are not yet quantifiable. In order to consider GC-MS as a candidate test method for acrolein, more testing would have to be completed and a more accurate method for spiking the sample would have to be developed in order to account for any potential sample degradation during testing. The new method would then be reviewed by the ARB and adopted as a new ARB test method.

Other Laboratory Efforts

In 2004, US/EPA completed a method comparison study of three source test methods to investigate and measure acrolein from combustion sources, in part due to the research conducted by ARB and Ashland.⁶ Ashland's Aldechem tubes, Dansyl hydrazine (DNSH) sorbent tubes, and FTIR were used in side-by-side tests using a laboratory bench top source simulator. The simulator consisted of a glass manifold where NO_x, heat, and

moisture could be introduced to simulate conditions in a smoke stack. Results confirmed that the Aldechem tubes and DNSH sorbents are not adequate for measuring acrolein in those conditions. However, at very high levels of acrolein (1ppm), FTIR was able to accurately quantify acrolein. The researchers postulated that it may be possible to measure acrolein at low levels given the right test method.

Gary Schoening at Ashland has conducted additional testing of the Modified M430 with H_3PO_4 /toluene using a six horsepower, single-cylinder lawnmower engine.⁷ This source offered challenges to this method with aldehyde concentrations 100 to 500 times higher than were observed with a gas fired turbine during previous tests. Trip spikes were quantitative and acrolein recoveries were approximately 80% with no breakthrough to the 3rd impingers in the sample train. This suggests that the method may be robust if proper adjustments to the test method for lower concentrations can be made.

Sucha Parmar (Atmospheric Analysis, Ventura) has completed an acrolein retention study, which has helped us understand the stability of acrolein during testing using M430/toluene.⁸ For example, without acid, acrolein is stable in the presence of DNPH and toluene (although acid is normally required in the method, this shows that toluene can help the success of the reaction). Without toluene, acrolein recoveries drop to ~50% after degradation by the acid. This information confirms that the Modified M430 with H_3PO_4 /toluene should be considered for additional testing.

San Diego County APCD completed a series of source tests using a TO-14 (canister) method for a natural gas compressor and engines.⁹ The acrolein standards were developed in a hydrocarbon matrix rather than a combustion matrix, and so the results do not address potential degradation problems. This method should not be used to determine acrolein emission factors until a more thorough analysis can be completed.

Ken-Ichi Akiyama from the Japan Automobile Research Institute, is in the process of publishing results that suggest that O-(4-cyano-2-ethoxybenzyl) hydroxylamine (CNET) is able to accurately measure acrolein. ARB staff is very interested in these results and has requested reagents and samples in order to conduct our own testing to verify the results. Results from Japan indicate that CNET performed considerably better than the Waters cartridges, but may still degrade to 70% of the original concentration due to the instability of the reaction product over several hours, even at low holding temperatures.¹⁰

Conclusions

Understanding the sources of acrolein is extremely important. Current ambient acrolein levels pose a significant chronic risk to public health, and finding a test method that accurately measures acrolein from stationary combustion sources is a high priority.

This research project led to the development of the modified M430, which is still being investigated as a potential test method for acrolein. Several other methods were tested and it was confirmed that none of them in their present form were successful in measuring acrolein. However, at least two promising new methods have been identified in the past year, independent of this project, and more work will be needed to determine if they can meet the challenges that acrolein poses for source testers.

Some key findings of this project are:

- Acrolein was difficult to quantify at low ppb levels from combustion sources using these test methods due to the degradation of the pollutant during testing and/or the inability of these test methods to measure acrolein at low levels
- Modified M430 with H₃PO₄/toluene is the method that shows the greatest potential
- The portable GC-MS also gave results that tend to appear in the center of the range of values measured from the other methods
- Despite variations in the results, there was enough consistency between the methods to suggest that acrolein emissions from three of the four sources tested were in the low ppb range
- The rotary kiln had acrolein emissions 100 to 1000 times higher than the other sources tested

Next Steps

ARB staff has requested funds for additional testing as part of the ARB's FY 05-06 request for research proposals. Because the first opportunity to try the Modified M430 with H₃PO₄/toluene was during this testing, a more exhaustive series of tests should be conducted to verify previous laboratory data. A laboratory analysis would not be sufficient to determine if the method was accurate, but the results would help identify potential problems that could be anticipated during a source test.

Further testing is also needed to investigate San Diego's canister method using spiked samples and a more robust analysis. Additional testing in coordination with other local air districts, including Monterey Bay and Santa Barbara, should continue as soon as additional data can be generated as part of an ARB contract. CNET testing will begin shortly. Results will be made available and positive results will be investigated further.

Ambient acrolein tests are being planned in early 2006 by Dr. Tom Cahill from UC Davis as part of an ARB research project to measure acrolein near freeways. A mist chamber will be used in conjunction with sodium bisulfite and pentafluorobenzylhydroxylamine to capture and quantify acrolein using GC-MS. This method has been used several times to measure acrolein from combustion sources and may be able to be used as a source test after a more thorough investigation.

For questions regarding acrolein, please contact Mr. Chris Halm, (916) 323-4865, chalm@arb.ca.gov, Planning and Technical Support Division, or Mr. David Todd, (916) 322-8915, dtodd@arb.ca.gov, Monitoring and Laboratory Division.

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