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Comparison of Analytical Techniques for Measuring Hydrocarbon Emissions from the Manufacture of Fiberglass-Reinforced Plastics

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ABSTRACT

Research Triangle Institute and the U.S. Environmental Protection Agency conducted several projects to measure hydrocarbon emissions associated with the manufacture of fiberglass-reinforced plastics. The purpose of these projects was to evaluate pollution prevention techniques to reduce emissions by altering raw materials, application equipment, and operator technique. Analytical techniques were developed to reduce the cost of these emission measurements. Emissions from a small test mold in a temporary total enclosure (TTE) correlated with emissions from full-size production molds in a separate TTE. Gravimetric mass balance measurements inside the TTE generally agreed to within ± 30 % with total hydrocarbon (THC) measurements in the TTE exhaust duct. Pure styrene evaporation tests served as quality control checks for THC measurements and generally agreed to within ± 5 %.

INTRODUCTION

Hydrocarbon emissions from the manufacture of fiberglass-reinforced plastics (FRP) contribute to volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions in the workplace and the environment. In the FRP open molding process, a spray gun is used to apply a polyester resin gel coat to a mold, and then a spray gun or nonatomizing equipment is used to apply a polyester resin and fiberglass laminate to the cured gel coat. Styrene and methyl methacrylate are emitted as the gel coat and the laminate are sprayed onto the surface of the mold, as the laminate is rolled, and as the gel coat and the laminate cure. The open contact molding process usually is conducted in a well-ventilated facility to maintain the ambient styrene concentration at less than the current Occupational Safety and Health Administration (OSHA) standard of 100 parts per million by volume (ppmv). As a result of the dilution associated with this ventilation, styrene emissions are difficult to measure, capture, and control.

> **IMPLICATIONS**
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> Agreement between hydrocarbon emissions measurements using different analytical techniques enhances the credibility of the emissions measurements and the analytical techniques. The simplified test protocol and the gravimetric mass balance technique have potential utility for emissions measurement programs in other industries.

Southern Research Institute (SRI) conducted an evaluation of styrene emissions from a shower stall and bathtub manufacturing facility in Wilson, NC, during 1993.[1] The emissions were measured in the roof vents of spray booths and in building air exhaust vents using total hydrocarbon (THC) analyzers operated in accordance with U.S. Environmental Protection Agency (EPA) Method 25[2] and gas chromatographs in accordance with EPA Method 18.[3] SRI found that styrene is the only VOC emitted at this facility; that 48, 20, and 12% of styrene sprayed during gel coating, first lamination, and second lamination, respectively, were emitted to the atmosphere; and that 29% of the emissions occur during curing outside of the spray booths. SRI's data suggest that spray booth emissions are higher than values cited in EPA's *Compilation of Air Pollutant Emission Factors*, also known as AP-42.[4] Changes in raw materials, application equipment, operator techniques, or environmental conditions may change styrene emissions levels and may limit the applicability of these test results.

Research Triangle Institute (RTI), in cooperation with EPA's Air Pollution Prevention and Control Division, conducted five projects to study hydrocarbon emissions from the manufacture of FRP. The main purpose of these projects was to evaluate pollution prevention (P2) techniques to reduce emissions by altering raw materials, application equipment, and operator technique. A secondary purpose was to develop a simplified test protocol for such evaluations. As part of these projects, analytical techniques for measuring these emissions were developed. They have potential utility for measuring emissions in other industries. The five projects are summarized in Table 1.

TOTAL HYDROCARBON MEASUREMENTS AND CALIBRATIONS

Styrene was measured with a Ratfisch Model RS55-CA THC analyzer operated in accordance with EPA Method 25A. Specially formulated gel-coat and laminate resins containing only styrene were used to allow THC measurements to be correlated directly with styrene concentrations. The THC analyzer was calibrated with compressed propane in air mixtures to avoid concentration-pressure limitations associated with compressed styrene in air mixtures. Laboratory tests and field verifications between 1995 and 1997 repeatedly established that the propane-to-styrene correction factor for this specific THC analyzer is close (i.e., 0.362 to 0.391) to the theoretical carbon-number ratio of 0.375. Samples were delivered to the analyzer at atmospheric pressure to avoid slight pressure effects that had been observed in this analyzer.

TEMPORARY TOTAL ENCLOSURES

EPA Method 204 describes a protocol for capturing fugitive VOC emissions from surface coating and printing operations in a temporary or permanent total enclosure.[9] To ensure that all emissions are captured, natural draft openings (NDOs) may comprise no more than 5% of the enclosure's surface area, and the average face velocity through the NDOs must be at least 200 ft/min. NDOs must be at least four equivalent opening diameters from VOC sources and exhaust duct openings.

Figure 1 depicts a temporary total enclosure (TTE) that RTI/EPA used in the 1997 study of styrene emissions in the boat-building industry. This TTE was built from polyethylene sheeting over metal studs and was easily assembled and disassembled. It was constructed in a building where FRP application was not occurring. However, background air measurements were taken at the NDOs at the beginning and end of the tests to track styrene emissions from an adjacent mold shop. Mean background air concentrations for tests ranged between 0.4 and 4.5 ppmv as styrene, with an overall mean of 1.2 ppmv as styrene.

Gel coat or laminate was applied to a test mold, which remained in the enclosure until the resin was cured. All air left through a duct in which the air velocity was measured by EPA Methods 1 and 2.[10,11] THC concentrations in the duct were monitored until they returned to background levels. After correction for background levels, the styrene emission quantity for each test was calculated from the average THC concentration and average duct velocity. By recording the times that application, laminate rolling, and curing started and stopped, styrene emission quantities for each phase of the test can be determined. In the 1996 RTI/EPA study of filled resins conducted in a spray booth, on average, 58% of the styrene was emitted during application, 26% during rolling, and 16% during curing.

SIMPLIFIED TEST PROTOCOL

P2 research, which involves altering raw materials, application equipment, and operator technique for the FRP industry, will help to determine the effect of these alterations on styrene emissions. This research

Table 1. Summary of the five projects to study hydrocarbon emissions from the manufacture of FRP.

Year	Project Location	Purpose (Literature Reference)
1995	Research Triangle Park, NC	Evaluate pollution prevention techniques to reduce styrene emissions from FRP open molding process using neat (i.e., unfilled) resin.[5]
1995	Research Triangle Park, NC	Measure emissions from FRP pultrusion process in conjunction with the Society of the Plastics Industry Composites Institute (internal SPI report).
1996	Research Triangle Park, NC	Evaluate filler and resin variables affecting styrene emissions from FRP open molding process using filled resin.[6]
1996	Wilson, NC	Evaluate enclosures and other air flow management techniques to reduce size and cost of controls for FRP open molding process.[7]
1997	Arlington, WA	Develop and evaluate a simplified test protocol to determine emissions from the FRP open molding process (draft RTI report submitted to EPA) in conjunction with a National Marine Manufacturers Association (NMMA) baseline emissions characterization from fiberglass boat manufacturing.[8]

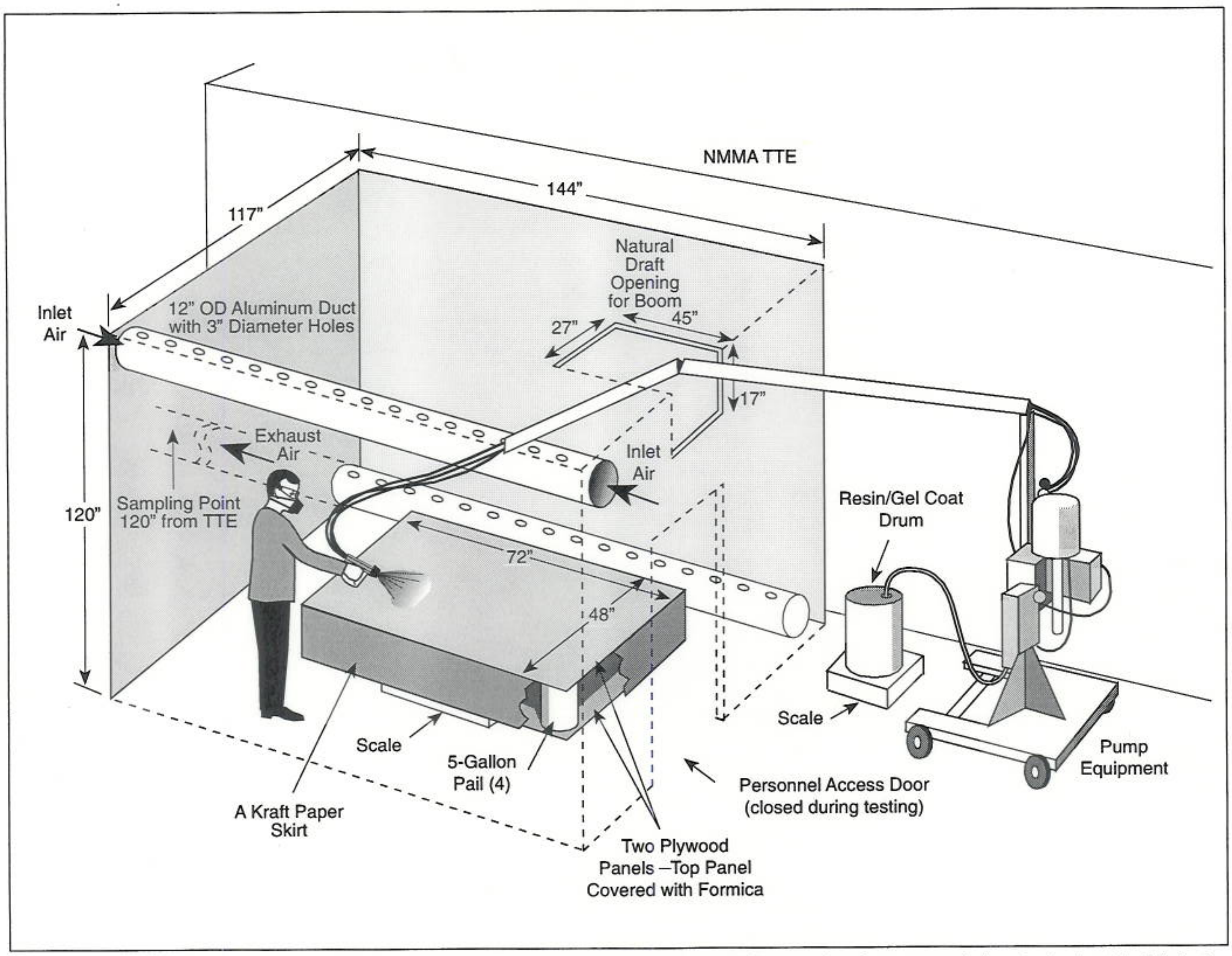

Figure 1. Temporary total enclosure (TTE) and experimental setup used in the 1997 RTI/EPA study of styrene emissions in the boat-building industry.

would be simplified if it could be done on a smaller scale than full-size production molds. RTI/EPA has used three-dimensional molds (0.6 m wide by 0.8 m long by 0.6 m high) and two-dimensional test panels (1.2 m wide by 1.8 m long) in its styrene emission studies. This approach has merit if there is a correlation between styrene emissions from these smaller molds and the corresponding emissions from full-size production molds. Such a correlation was observed during RTI/EPA's 1997 study, which was conducted simultaneously with the NMMA's baseline emissions characterization. Both studies used the same boat manufacturing facility, raw materials, application equipment, and operators to allow their results to be compared. Both studies used THC analyzers to measure the styrene emissions (although NMMA also measured individual hydrocarbons by gas chromatography). RTI/EPA and NMMA propane-in-air calibration standards agreed to within 1.5%.

The RTI/EPA TTE's dimensions were 3.0 m wide by 3.7 m long by 3.0 m high, with an exhaust flow rate of 54 m^3/min. The air turnover for the RTI/EPA TTE was 97 room changes per hour. The NMMA TTE's dimensions were 6.1 m wide by 13.7 m long by 4.3 m high, with an exhaust flow rate from 74 to 93 m^3/min. The air turnover rate for the NMMA TTE was 12 to 16 room changes per hour, which was comparable to that in the manufacturing areas on site. The effects of air velocity over the mold and other operational parameters on styrene emissions are addressed in a companion paper.[12] The RTI/EPA study used a 1.2 m-wide by 1.8 m-long test panel, and the NMMA study used 5.5- and 8.5-m-long boat hull molds and 5.5-m-long boat deck molds.

Figure 2 compares the THC measurements from the RTI/EPA and NMMA studies. Styrene emission quantities are normalized by the resin mass used in each application to allow the two sets of results to be compared. Nineteen of the 21 data pairs agreed to within ± 25%. The higher values in the figure are from six gel coat applications, and the lower values are from 15 lamination applications. Regression analysis of the lamination data yielded the following equation:

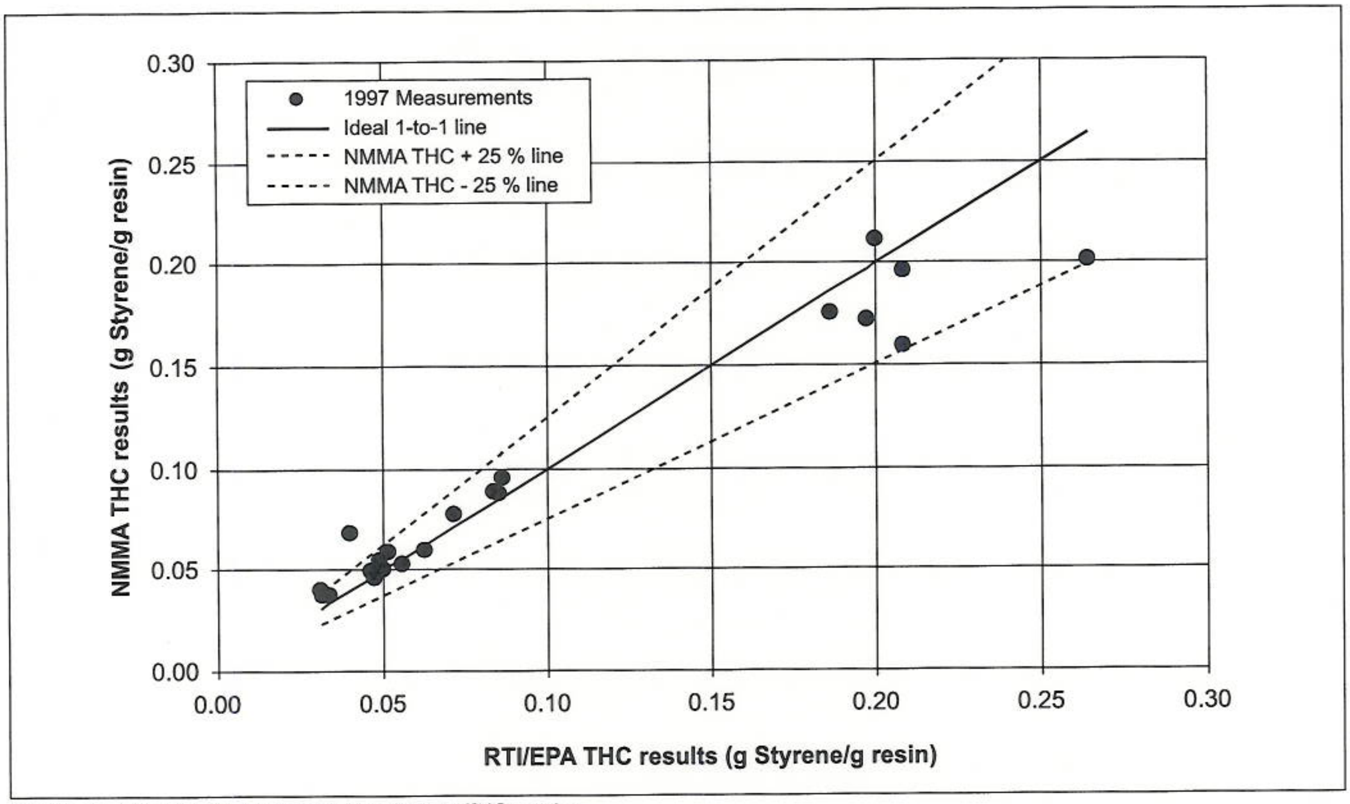

Figure 2. Comparison of RTI/EPA and NMMA THC results.

$$\text{NMMA THC} = 0.932(\text{RTI/EPA THC}) + 0.009 \quad (1)$$

with a coefficient of determination (r^2) of 0.859. Regression analysis of the gel coat data yielded much poorer results (i.e., r^2 = 0.363) because the same equipment and resin were used for all gel coat tests, which produced a relatively narrow range of values. The ratio of the mean NMMA value to the mean RTI/EPA value for the 15 lamination tests was 1.102. The corresponding ratio for the six gel coat tests was 0.894. These results suggest that emission factors obtained from the simplified test protocol have moderate accuracy. However, no quantitative data quality indicator (DQI) goal was established for the agreement between these two sets of measurements.

GRAVIMETRIC MASS BALANCE MEASUREMENTS

Hydrocarbon emission measurements would be further simplified if gravimetric mass balance (GMB) measurements could replace the more complex THC measurements. If one can measure the mass of all raw materials used in an application and the mass of the cured FRP product with sufficient accuracy and resolution, then the difference between these measurements is the mass of the styrene that was emitted during application and curing. Care is needed to account for all the mass involved in the application because the mass of styrene emitted is small relative to the masses that are being measured.

RTI/EPA conducted such GMB measurements during several projects. High-resolution (i.e., 1 g in 150 kg) floor scales were used to measure resin, catalyst, and fiberglass containers and test molds before applications and after THC concentrations had returned to background levels. These scales also measured the mass of ancillary equipment such as kraft paper and fiberglass veil put in the enclosure to capture overspray, protective garments for the operator, and laminate rollers.

During the 1995 study involving neat resin, approximately 0.4 kg of styrene was emitted during each of 25 lamination applications. Approximately 6.1 kg of resin, catalyst, and fiberglass were transferred from application equipment and raw materials containers weighing approximately 110 kg to a mold weighing approximately 50 kg and ancillary equipment weighing approximately 13 kg.

Figure 3 compares the GMB measurements with simultaneous THC measurements for 25 lamination tests in the 1995 study of neat resins and for 40 gel coat and lamination tests in the 1997 study. The ratios between individual GMB and THC values in the 1995 study ranged between 0.90 and 1.10, with a mean ratio of 0.96 and a standard deviation of 0.05. All 25 data pairs met the DQI goal of ± 30 % agreement. During the 1997 study, the GMB-to-THC ratios ranged between 0.70 and 1.70, with a mean ratio of 1.11 and a standard deviation of 0.21. Seven of the 40 data pairs did not meet the ±30% DQI goal.

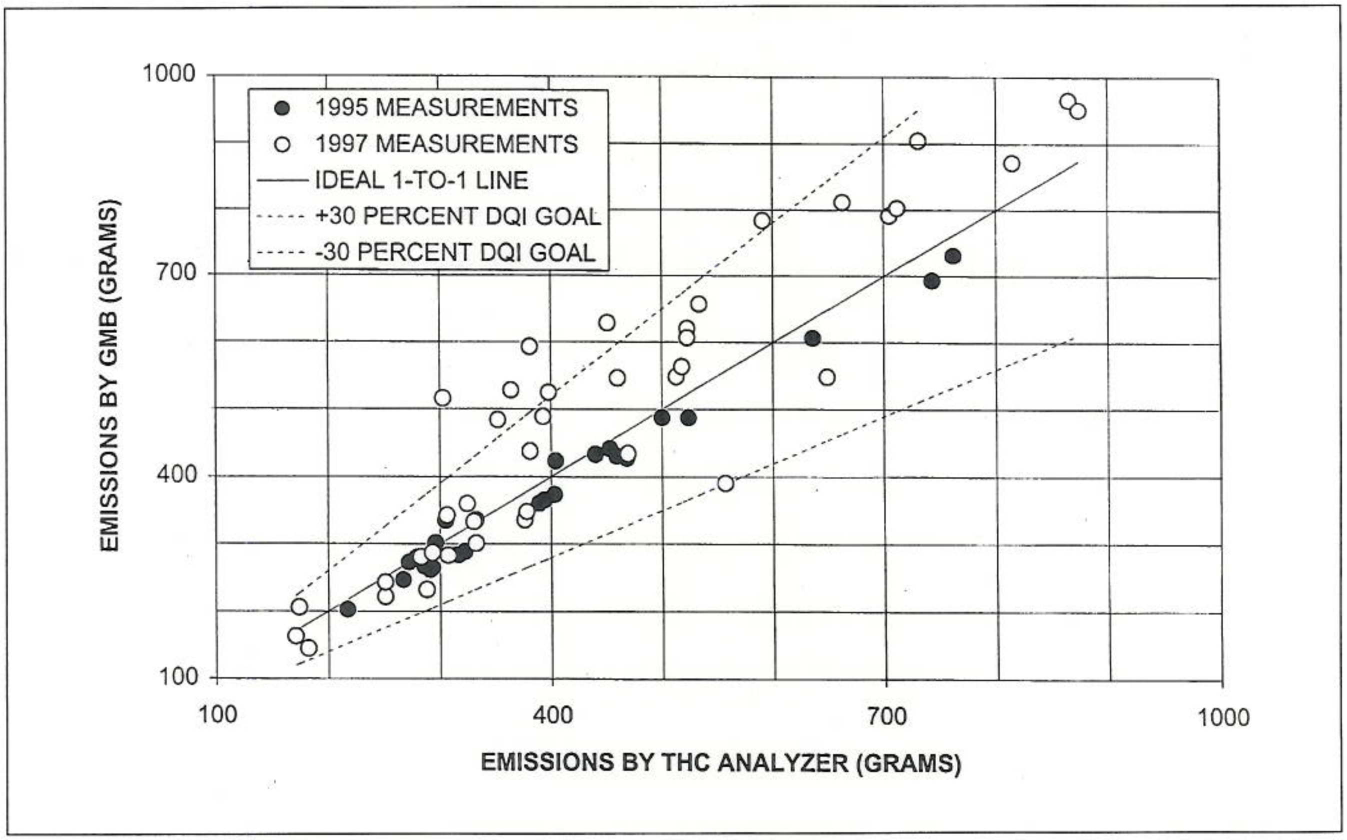

Figure 3. Comparison of RTI/EPA THC and GMB results.

A factor contributing to the less precise 1997 GMB measurements is the variable volume of resin contained in the piston pump of the lamination application equipment. The incorrect assumption was made that the volume was the same before and after the application. In contrast, the diaphragm pump of the gel-coat application equipment had a smaller internal volume, which had less effect on the GMB precision. Ideally, weighing both the application equipment and the resin container will reduce this imprecision. However, the application equipment was too heavy to be weighed by the floor scales.

PURE STYRENE EVAPORATION TESTS

The accuracy of the THC measurements was independently verified by gravimetric measurements during pure styrene evaporation tests. A pan containing liquid styrene and a wooden rack holding styrene-soaked towels were placed on a floor scale inside the enclosure. Electric fans increased the evaporation rate. As styrene evaporated inside the enclosure, the floor scale measured the styrene mass loss and the THC analyzer measured the styrene concentration in the enclosure's exhaust duct. If all measurements are accurate, the styrene emission quantity calculated from THC and duct velocity measurements should equal the gravimetric mass loss.

Figure 4 compares styrene emission quantities and gravimetric mass losses (GML) for nine pure styrene evaporation tests that RTI/EPA conducted between 1995 and 1997. Individual GML-to-THC ratios ranged between 0.947 and 1.034, with a mean ratio of 0.979 and a standard deviation of 0.041. Seven of nine data pairs met the DQI goal of ± 5 % agreement. NMMA performed two pure styrene evaporation tests during its baseline emission characterization. NMMA's GML-to-THC ratios were 0.998 and 0.940, which suggests that the NMMA and RTI/EPA results can be compared quantitatively.

SUMMARY

This paper has presented a number of analytical techniques that have been developed for measuring hydrocarbon emissions from the manufacture of FRP. TTEs are a useful means to capture fugitive emissions from sources that are difficult to sample. A simplified test protocol using smaller test molds can estimate emissions from full-size production molds. GMB measurements can generally estimate emissions within± 30 % accuracy provided care is taken to weigh all components of the process. Pure styrene evaporation tests provide an independent means to verify the accuracy (generally within ± 5 %) of THC measurements.

DISCLAIMER

This paper has been reviewed in accordance with EPA's peer review and administrative review policies and

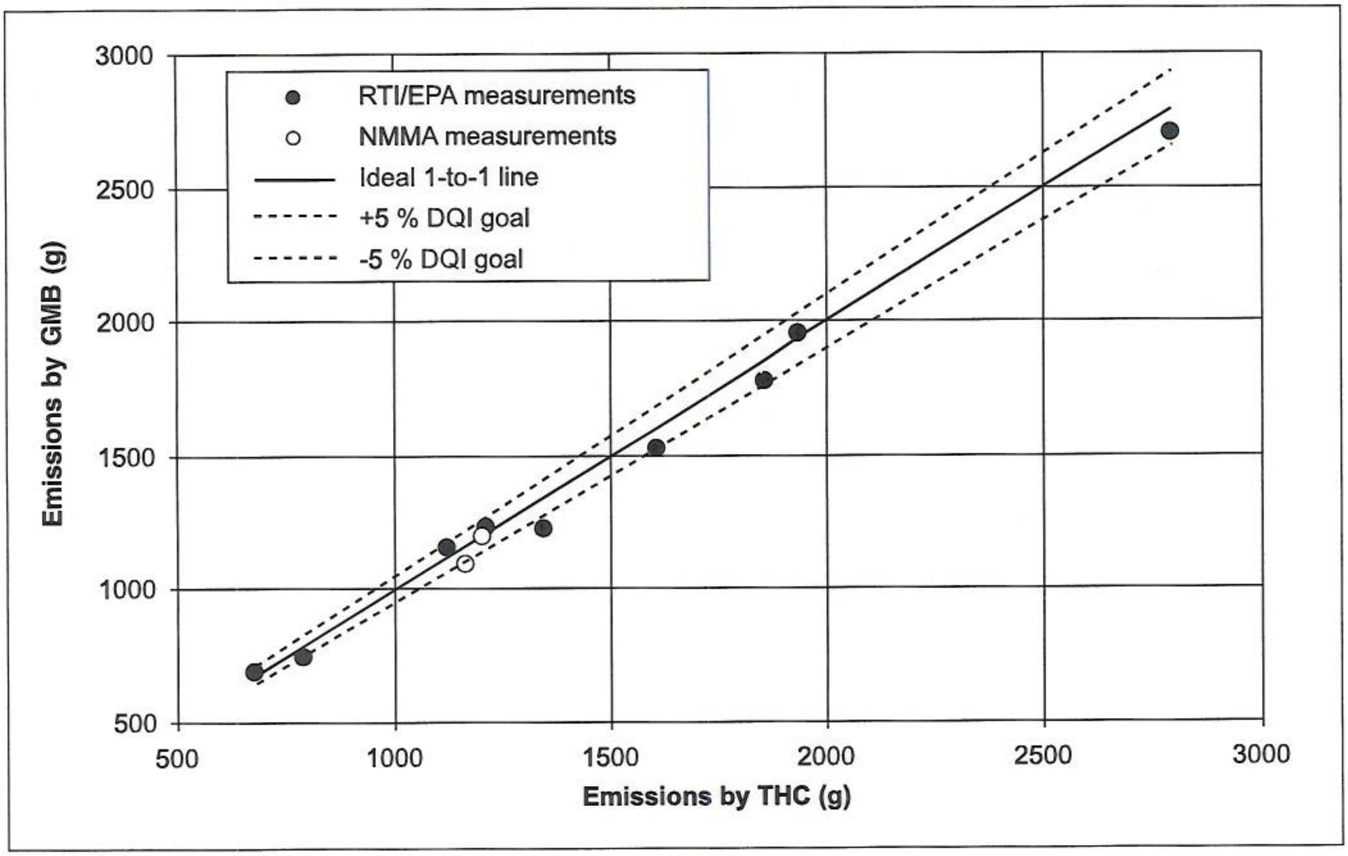

Figure 4. Summary of pure styrene evaporation tests.

approved for presentation and publication. Quality assurance and quality control (QA/QC) data are supported by QA/QC documentation as required by EPA's QA policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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