

Using a Flame Ionization Detector (FID) to Continuously  
Measure Toxic Organic Vapors in a Paint Spray Booth

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## INTRODUCTION

U.S. Air Force (AF) industrial operations procuring and maintaining equipment and facilities are the greatest sources of volatile organic compound (VOC) and hazardous air pollutant (HAP) emissions at AF installations. These emissions are subject to stringent environmental regulations that have been evolving for two decades, and are expected to continue their evolution for decades to come. The USAF has stated its commitment to complying with the new environmental standards, but two considerations prevail: (1) maintaining the current standard of workplace safety, and (2) keeping the cost of the emission control as low as possible.

### Program History

The AF Civil Engineering Laboratory (CEL) and Environmental Protection Agency's (EPA's) Air and Energy Engineering Research Laboratory (AEERL) began a study of AF air compliance issues in 1986. The initial study showed that paint spray booths at several sites tested would not comply with potentially more stringent emission regulations unless emissions levels were lowered.<sup>1</sup> To combat this problem, the report suggested that exhaust recirculation be considered as a means of decreasing the volume of exhaust air requiring treatment and, therefore, lowering the pollutant emissions. Unfortunately, this innovative recommendation met opposition in the AF industrial hygiene (IH) community.

The primary objection raised by AF IH personnel references 29 Code of Federal Regulations (CFR) 1910.107 (d) (9),<sup>2</sup> which explicitly states that recirculation of emissions from paint spray booths is prohibited. Upon further consideration, Occupational Safety and Health Administration (OSHA) issued a letter<sup>3</sup> to EPA stating that the regulation in question pertains to fire safety and not to personnel toxic exposures. Instead, OSHA referenced 29 CFR 1910.1000<sup>4</sup> for toxic exposures, which does not prohibit recirculation. 29 CFR 1910.107 (d) (9) was not intended to prohibit recirculation or institution of innovative technologies. Rather, it ensures that booth operations remain within safe levels. Thus, under the OSHA de minimus rule, a booth may use recirculation if the booth irrefutably complies with 29 CFR 1910.1000. Based on this compromise, a demonstration study was developed at Travis Air Force Base (AFB), California.

The CEL/AEERL team conducted two site studies of spray booths, and will conduct more studies at Travis AFB in June 1992. The first study was conducted at McClellan AFB, CA. It determined that fluidized-bed incineration and an adsorption/desorption preconcentration process will effectively remove VOCs

from exhaust gas. The disadvantage of both systems is that the estimated cost of treating the full circulating stream may be exorbitant<sup>5</sup> depending on the volumetric flow to be treated.

A second study was conducted at Hill AFB, Utah. The spatial distribution of volatile, metal, and isocyanate species was measured in a horizontal-flow, waterfall booth. The results show that the toxics concentrate near the bottom of the booth and in the painter's breathing zone.<sup>6</sup> The concentration in the painter's breathing zone appears to result from localized eddy currents in the air stream, which are caused by the presence of the painter's body as an obstacle. Armstrong Laboratory's IH newsletter has cited excessive exposures to toxic metals, under just such conditions, in a context that implicitly recommends wearing a respirator while painting in a horizontal-flow booth.<sup>7</sup>

Travis AFB serves as the test site for two studies to be conducted. Both studies are designed such that workplace safety standards are not sacrificed and comply with OSHA regulations and directives. For example, during the study, an informed volunteer painter will be equipped with a supplied air respirator and skin protection. This gear is commonly required by AF shops conducting spray painting operations. Also, air toxic measurements will be taken inside and outside the respirator and, as an added safety measure, the painter will be medically evaluated before and after painting tests.

Also incorporated into the Travis AFB study is the design of a fail-safe diversion system for converting the recirculating flow pattern back to "straight-through" ventilation. This relies upon the use of a flame ionization detector (FID) to monitor the concentration levels within the booth. The information obtained from using this instrument for measurement gives a total hydrocarbon analysis, as opposed to a speciated compound analysis. However, the compound of interest can be identified by calculating its percent composition of the total, assuming complete volatilization of the paint system's components.

The Travis AFB study will provide an experimental basis for evaluating the impacts of exhaust modifications on air toxic emission rates and on attainment of IH standards.

### Project Objective

This project, which is a component of the justification process for the experimental evaluation of flow-splitting and exhaust recirculation, is the final step in preparation for evaluation of these techniques. Although the immediate purpose is to establish that the Travis AFB test does not present an extraordinary health risk to the volunteer painter and other

personnel participating on the testing team in the booth, the study will also apply to any other volatile mixture of defined composition in a paint spray booth.

Specifically, the objective is to demonstrate experimentally that the response of a FID is adequate for determining, reliably, that the concentration of toxic compounds will remain, at all times, less than 25% of the short term exposure limit (STEL). This FID system must activate when: (1) the instantaneous concentration exceeds 25% of the STEL<sup>8a</sup> for the coating and catalyst, NSN 8010-01-336-3036, used exclusively during the demonstration, (2) a concentration of 23% of the STEL is maintained for 15 consecutive minutes, or (3) a concentration of 20% of the STEL has been measured during a total of 180 nonconsecutive minutes during a single painter's shift. This mechanism ensures that the exposure standards specified in 29 CFR 1910.1000 are not exceeded at 15-minute or 8-hour time-weighted levels during the test.

The purpose of generating these data is to confirm that, when accurately set and properly maintained and calibrated, the FID can reliably detect any excursions above an arbitrarily selected threshold, sound an alarm to alert site personnel, and trigger devices that reconfigure the ventilation system and/or disable the spray gun and intercede before harmful exposure develops during the spray booth operation.

## **EXPERIMENTAL DESIGN**

### **Continuous Analyzer**

A total hydrocarbon FID from Ratfisch Instruments, model RS-55CA, was used for the project. The analyzer is configured with four measuring ranges: 0-100, 0-1000, 0-10,000, and 0-100,000 parts per million as carbon (ppmC). Sample gas was introduced into the hydrogen flame through a sample capillary at a low flow rate. The FID response was based on the concentration of the VOCs in the sample gas and the type of compounds present. The analyzer output consisted of both a 0 to 1 V analog recorder signal and a front panel display.

### **Test Mixture Composition**

This project specifically addresses the health risks attending the use of the polyurethane coating and aliphatic isocyanate catalyst, NSN 8010-01-336-3036. Lists of the hazardous components for the specified coating and catalyst were identified in the manufacturer's Material Safety Data Sheets (MSDSs). The weight percentage of each component was used to calculate a combined weight in the mixture (3:1 ratio by weight of coating to

catalyst), from which the weight percentage was calculated based on the VOC content only. The calculated composition of the mixture is shown in Table 1.

TABLE 1. COMBINED COATING/CATALYST SOLVENT COMPOSITION<sup>a</sup>

Compound	Wt. % (NSN <sup>c</sup> 8010-01-336-3036)			Wt. % of VOC content
	Coating	Catalyst	Combined	
n-Butyl acetate	5	5	5	13.4
Ethyl-3-ethoxypropionate	5	20	8.75	23.4
Toluene	1	0	0.75	2
Xylene <sup>b</sup>	1	5	2	5.4
Methyl isobutyl ketone	5	35	12.5	33.5
Methyl ethyl ketone	5	0	3.75	10
Ethylbenzene	0.1	0	0.075	0.2
PGME acetate <sup>d</sup>	1	0	5	2
2,4-Pentanedione	5	0	0.75	10
			3.75	

<sup>a</sup>3:1 mixture (by weight)

<sup>b</sup>Substituted xylene for "C8 & C10 aromatic hydrocarbon" from MSDS for 03GN240CAT.

<sup>c</sup>National Stock Number

<sup>d</sup>Propylene glycol monomethyl ether (PGME) acetate is the common name for 1-Methoxy isopropyl acetate.

#### Calculation of Exposure Limit

The STEL for each component is shown in Table 2. Where available, the STEL given corresponds to the OSHA permissible exposure limit (PEL). For compounds not having an OSHA PEL-STEL, the STEL is assumed to be 1.5 times the manufacturer-recommended Threshold Limit Value (TLV)-time weighted average (TWA).

Application of the ACGIH rule<sup>bb</sup> for additive effects to the data in Table 2 resulted in a calculated STEL for the coating and catalyst, NSN 8010-01-336-3036, of 350 mg/m<sup>3</sup>. This value is based on the assumption that volatilization is complete and uniform; although this is not strictly correct, toxicity of the less-volatile constituents is greater, so the calculated value underestimates the "true" exposure limit. (Comparable STELs were calculated for several other polyurethane coatings presently in AF inventory, but a significantly lower value was calculated for MIL-P-23377 primer.)

TABLE 2. COMBINED COATING/CATALYST STEL CALCULATION

Compound	Wt. % (of VOC)	STEL, mg/m <sup>3</sup>	Source of STEL
n-Butyl acetate	13.4	950	OSHA PEL
Ethyl-3 ethoxypropionate	23.4	447	Manufacturer
Toluene	2.0	560	OSHA PEL
Xylene	5.4	655	OSHA PEL
Methyl isobutyl ketone	33.5	300	OSHA PEL
Methyl ethyl ketone	10.0	885	OSHA PEL
Ethylbenzene <sup>a</sup>	0.2	545	OSHA PEL
PGME acetate <sup>b</sup>	2.0	810	Manufacturer
2,4-Pentanedione	10.0	123	Manufacturer

Mixture STEL =  $1 / (0.134/950 + 0.234/447 + 0.02/560 + 0.054/655 + 0.335/300 + 0.1/885 + 0.002/545 + 0.02/810 + 0.1/123) = 350 \text{ mg/m}^3$

<sup>a</sup>Omitted from mixture since weight % is insignificant.

<sup>b</sup>Propylene glycol monomethyl ether (PGME) acetate is the common name for 1-Methoxy isopropyl acetate.

#### Test Mixture Preparation

Nine mixtures were prepared for characterizing the analyzer response in the 0-1000 ppmC range and three mixtures were prepared for the 0-100 ppmC range. The highest concentration mixture was prepared by vaporizing a known mass of a liquid mixture and flushing it into an evacuated aluminum cylinder with a known volume of dry air. The liquid mixture was prepared by adding a given mass of each compound to a glass vial, based on the weight percentages shown in Table 1.

Subsequent mixtures were prepared by withdrawing a portion of the gaseous mixture and refilling the cylinder with dry air. A bourdon tube vacuum/pressure gauge was used to measure accurately cylinder pressures for determining test mixture concentrations.

#### Test Mixture Analysis

During normal field operation, the Ratfisch RS-55CA analyzer uses an internal pump to draw a high volumetric flow rate of sample through a sample port, past a tee at the FID, and then through a back-pressure regulator before exhausting through the bypass port. The back-pressure regulator is used to adjust the sample gas pressure, which controls the flow rate of sample gas through a capillary and into the FID. The normal pressure is 2 psig (13.8 kPa).

Since the sample gas mixture in this study was contained in an aluminum cylinder at approximately 40 psig (275.8 kPa), operation of the analyzer was modified. The internal sample pump was not operated, but was left in the sample flow path. To conserve sample test mixture,

the bypass port was fitted with a shutoff valve. When this valve was closed, the sample back-pressure regulator was not functional. The sample gas pressure was regulated with an in-line single-stage pressure regulator installed at the outlet of the test mixture cylinder. Similar regulators were used to set the gas pressures for the propane calibration gases and the zero air.

The FID was operated with normal settings for hydrogen fuel (6 psig or 41.4 kPa) and combustion air (11 psig or 75.8 kPa).

Each of the test mixtures and calibration gas mixtures was sampled in the analyzer, and the FID response was recorded on a strip chart recorder. The in-line pressure regulator was adjusted so that the same sample pressure was used in all analyses.

## RESULTS

### Propane Calibration and VOC Mixture Analysis Results

The analyzer was first calibrated for the 0-1000 ppmC range. With zero air passing into the sample inlet port, the zero potentiometer was adjusted to produce a zero output from the FID. Then, with a standard containing 525 ppmC propane in air passing into the sample inlet port, the span potentiometer was adjusted to produce an analyzer output reading corresponding to 525 ppmC. Three additional concentrations of the standard containing propane in air were also analyzed.

After changing the analyzer range setting to 0-100 ppmC, the zero and span were adjusted while sampling zero air and a standard containing 46 ppmC propane in air standard, respectively. Two additional concentrations of the standard containing propane in air were also analyzed in this range.

To illustrate the response of characteristics of the analyzer to both propane and the VOC test mixture, plots of analyzer response versus concentration for both the 1000 and the 100 ppmC ranges are shown in Figures 1 and 2. The concentrations for the propane and the solvent mixture are expressed in milligrams per cubic meter. Linear regression analysis was performed for each set of data, and the results are shown in each figure, respectively.

Both of these figures display straight-line fits to data generated by passing the solvent mixture, representative of the volatile fraction of the coating and catalyst, and the calibration gas, propane, through the RS-55CA FID. The results of the linear regression analyses of the two figures further support the statement that FID response to the organic analytes was linear over the entire range measured and well below the STEL calculated for the coating and catalyst, NSN 8010-01-336-3036, or any other paints for which the STEL was estimated.

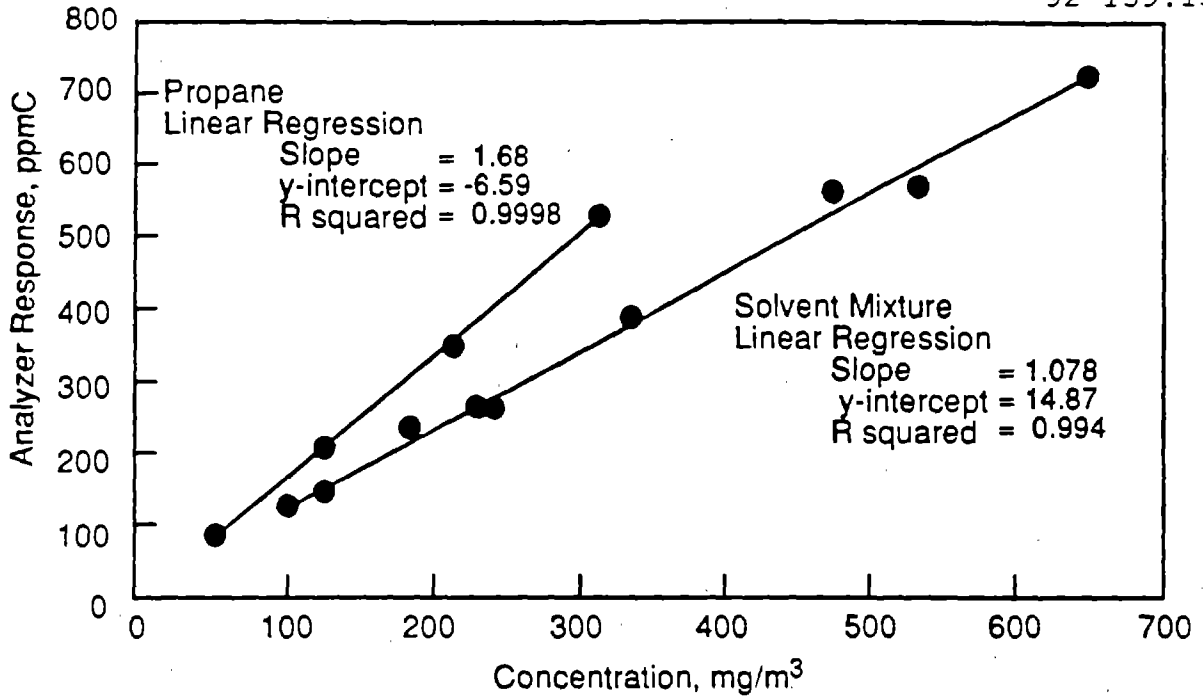


Figure 1. Ratflsch RS-55CA Calibration 0-1000 ppmC Range.

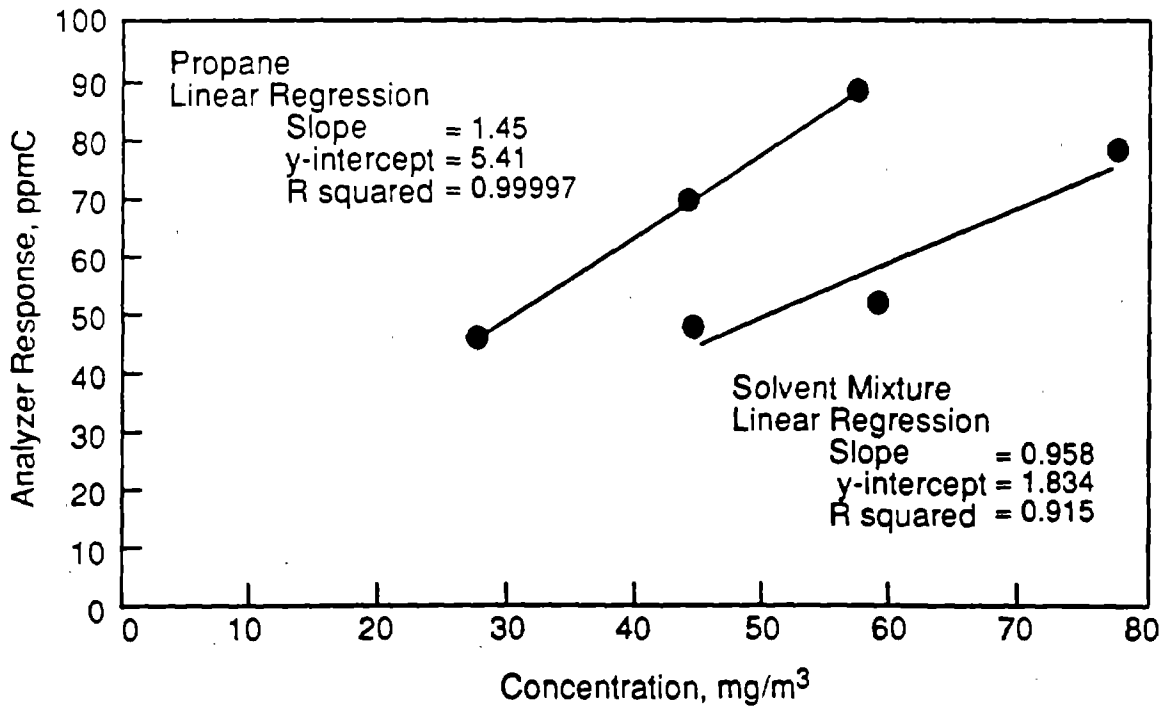


Figure 2. Ratflsch RS-55CA Calibration 0-100 ppmC Range



## DISCUSSION

The test at Travis AFB will use a servo-actuated set of flap valves to convert a horizontal-flow spray booth from straight-through (single-pass) circulation into a partially recirculating system. During recirculation, a portion of the exhaust stream will be filtered, mixed with an equal volume of fresh air, and returned via an intake filter to the circulating air stream. For the test, the exhaust stream will be released without treatment. However, the concentrations of air toxic materials will be measured and the acquired data will be used to estimate the cost and effect of application of available technologies for purification of the reduced exhaust stream prior to releases.

Similar measurements will also be made on the recirculated stream to evaluate the impact on IH safety standards. Calculations indicate that, as long as the particulate control system (dry filters) is maintained and operated properly, the increase in toxic exposure will be negligible in comparison to ambient spray booth concentrations. However, no calculation can exclude all potential risk of overexposure to personnel in the spray booth. A prudently conservative attitude dictates that the experiment be conducted under circumstances that minimize both the risk of exposure and the extent to which overexposure could occur. Risk minimization is the purpose of incorporating the FID into the study.

As designed, the recirculating booth will include the FID immediately behind the intake filters. The FID will continuously measure the concentration of combustible airborne volatile substances and report to two triggering devices. As in the case of the solvent mixture, no other sources of toxic substances exist, so any additional contributions by non-halogenated combustibles will overestimate the exposure.

The first triggering device will respond immediately to any instantaneous excursion above  $350 \text{ mg/m}^3$ , the calculated STEL. Overexposure would then be limited to the air volume passing into and through the intake plenum and booth during the fraction of a second required for the servos to switch the flap valves to a fresh air intake.

The second triggering device, a computer, will store a record of the FID outputs at a fixed sampling rate, and convert to straight-through ventilation if either of the following two criteria is met: 1) a period of 30 consecutive seconds is maintained at  $87.5 \text{ mg/m}^3$  (25% of the STEL), or 2) a total of 180 nonconsecutive minutes at  $87.5 \text{ mg/m}^3$  (25% of the STEL) is accumulated during a single painter's shift.

The results in Figure 1 include, as the lowest point in the range,  $105 \text{ mg/m}^3$ , and the results in Figure 2 include, as the highest point in the range,  $77 \text{ mg/m}^3$ . Thus, an extrapolation is made to cover the range from  $77$  to  $105 \text{ mg/m}^3$  that includes the point  $87.5 \text{ mg/m}^3$ , or 25% of the STEL. The results in Figures 1 and 2 demonstrate that the FID exhibits sensitivity and linearity of response adequate to discriminate organics accurately below  $87.5 \text{ mg/m}^3$ .

## CONCLUSIONS

This study has demonstrated linear and similar responses of a Ratfisch RS-55CA FID to a solvent mixture identical to the volatile organics in the coating and catalyst, NSN 8010-01-336-3036, and to the calibration gas, propane, used in field calibrations of the FID. Sensitivity and linearity have been shown to extend from 715 to 45 mg/m<sup>3</sup>, which brackets the calculated STEL and lower action thresholds. Monitoring is maintained constantly, and, under field conditions, equilibration occurs rapidly and analysis and output transpire in milliseconds. As a trigger for fail-safe conversion from recirculation mode into a straight-through booth configuration, the FID may confidently be expected to initiate a corrective response before a transient elevation of VOC concentrations overexposes area personnel.

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