ICAC Proposed Conditional Test Method (CTM-042)*

Use of Flame Ionization Detector-Methane Cutter Analysis Systems for VOC Compliance Testing of Bakeries

1.0 Background

Performance testing of volatile organic compounds (VOC) destruction devices such as thermal oxidizers and catalytic oxidizers require simultaneous measurements of non-methane hydrocarbons (NMHC) in the gas streams entering and exiting the destruction device. In the past, continuous total hydrocarbon measurements employing testing protocol in accordance with U.S. EPA Test Method 25A (Gaseous Organic Concentration - Flame Ionization) has been combined with laboratory analysis of grab samples taken hourly. This approach has been demonstrated to be labor intensive, costly and does not provide real-time measurements necessary to evaluate the performance of the thermal or catalytic oxidizer.

2.0 Purpose

Use of this method is limited to measuring VOC emissions from bakeries. The purpose of this Conditional Test Method (CTM) is to provide an alternate method for making real-time non-methane hydrocarbon measurements for providing immediate information regarding performance of the VOC destruction device. This method describes the use of a hot flame ionization detector (FID) based instrument equipped with a catalytic methane cutter in conjunction with U.S. EPA Test Method 25A to provide real-time differential measurement of total hydrocarbons, methane and by difference non-methane hydrocarbons.

This CTM is directly applicable to large commercial bakeries. The measurement of VOC's in bakeries is required to verify air pollution control equipment destruction efficiency as required by various state regulations. The large majority of these state regulations are State Implementation Plan (SIP) driven. A minority of states have "State Only" legislation requiring oxidizes, and testing of them, on bakeries.

Extensive commercial data has been gathered from large commercial bakeries, where exhaust gases from ovens baking bread, crackers and other yeast products are tested. These exhaust streams typically contain ethanol in concentrations of 1,000 to 5,000 ppm, methane in concentrations of 50 to 1000 ppm and moisture at 2 to 15%. A catalytic oxidizer on this application will destroy 95-99% of the non-methane hydrocarbons, reducing the ethanol to concentrations of 10 ppm to 250 ppm in the oxidizer exhaust. The other compounds will virtually maintain their concentrations. Due to the large amounts of moisture and the water solubility of the non-methane hydrocarbon, condensation must be avoided. The relatively large amount of methane to non-methane hydrocarbon, especially in the oxidizer exhaust, makes it more important to make this measurement by one technique.

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3.0 Technical Approach

A heated flame ionization analyzer (HFIA) when equipped with a catalytic methane cutter upstream of the detector accepts a continuous flow of sample delivered by a heat traced sample line maintained above 375°F. A catalytic methane cutter is a catalytic device consisting of catalyst in a reactor designed by type of catalyst and operating temperature to combust all non-methane hydrocarbons and leave only methane. Instrument suppliers provide different approaches to this technology. There are “single detector/single amplifier” instruments and “dual detector/dual amplifier” instruments. Both types of instruments give measurements of total hydrocarbons and measurements of methane in the stream and by difference they measure non-methane hydrocarbons.

With “single detector/single amplifier’ instruments, the sample stream is alternately either passed through or around a selective catalytic combustion reactor (methane cutter) before entering the detector, which alternately measures either methane or total hydrocarbons. Instrument software controls the switching times (usually 1-minute cycles) and continuously displays the THC, CH4 and non-methane results.

With “dual detector/dual amplifier” instruments, the sample stream is continuously split. Part of the sample goes to a direct measuring detector measuring total hydrocarbons. The other part of the sample goes to a selective catalytic combustion reactor (methane cutter) followed by a detector, which continuously measures methane.

From either of these instruments, the measurements of total hydrocarbons and measurements of methane are subtracted to give the non-methane hydrocarbon result.

FID Theory of Operation

The technique of flame ionization detection (FID) relies on the ionization of molecules during high temperature combustion in the reaction zone of the FID-flame to determine the total hydrocarbon concentration within a gaseous sample. The analyzer has an adjustable heated oven (60 to 200°C) which contains a heated sample pump and burner in which a small flame is elevated and sustained by regulated flows of air and 100% hydrogen or a 40/60% mixture of hydrogen and helium. The burner jet is used as an electrode and is connected to the negative side of a precision power supply. An additional electrode, known as the "collector", is connected to a high impedance, low noise electronic amplifier. The two electrodes establish an electrostatic field. When a gaseous sample is introduced to the burner, it is ionized in the flame and the electrostatic field causes the charged particles (ions) to migrate to their respective electrodes. The migration creates a small current flow between the electrodes. This current is measured by the precision electrometer amplifier and is directly proportional to the hydrocarbon concentration of the sample.

Methane Cutter Theory of Operation

Operation of a methane cutter is based upon different combustion temperatures of methane compared to other non-methane hydrocarbon compounds. The methane cutter uses an oxidizing catalyst that is maintained at a temperature specific for the catalyst used, to selectively combust 95% of the non-methane hydrocarbons in the sample stream, while not reacting the methane content of the sample. As the sample stream is passed through the cutter, non-methane hydrocarbons oxidize to CO_2 and H_2O, which are not detected by the FID. The FID only measures the unreacted methane in the sample stream. By taking the difference between the methane-only measurement and the total hydrocarbon measurement, the non-methane hydrocarbon content is determined.

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4.0 Equipment Specifications

Equipment specifications will vary among manufacturers. The table below lists the minimum specifications required for equipment to apply this procedure for continuously measuring methane, non-methane and total hydrocarbons.

Flame Ionization Detector	
Method of Operation:	Flame ionization
Ranges:	Minimum of 2 user selectable ranges between 0-10 and 50,000 ppm full scale
Repeatability:	±5.0% F.S.
Zero Drift:	≤ ±3%F.S. per 24 hours
Span Drift:	≤ ±3%F.S. per 24 hours
Linearity:	≤ ±3%F.S.
Oven Temperature:	Between 165°C and 190°C
Response Time (T_{90}), measured at sample inlet:	≤10 seconds
Sample Flow Rate:	0.5 to 3.0 SLPM
Fuel:	100% H_2 or 40% H_2 / 60% He mixture
Ambient Operating Temp.:	0° to 40° C at ≤90% R.H.
Display:	Direct digital LED display
Output Signal:	Current: 4-20 mA linear, isolated resistive load of 750Ω Voltage: 0 to 100 mV; 0 to 5 V DC; 0 to 10 VDC
Power Requirements:	120 VAC ± 10% at 50/60 Hz
Configuration:	19-inch rack mountable
Selective Catalytic Cutter	
Accuracy:	≤3.0%
Repeatability:	≤3.0%
Oxidizing Efficiency:	≥95% of Ethanol/Methane in air to be oxidized in the 100ppm range
Sample Flow Rate:	0.50 to 3.0 SLPM
Catalyst Temperature:	Based on catalytic material
Catalyst Life Cycle:	12 months at concentrations of 500 ppm carbon
Power Requirements:	115 VAC at 50/60 Hz
Ambient Operating Temp.:	0° to 40° C at ≤90% R.H.

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5.0 Test Method

Calibrate the FID THC analyzer using the manufacturers recommended procedure.

1. Zero all three channels, (THC, CH_4 and NMHC) of the analyzer using an inert zero calibration gas such as N_2 or zero air having a hydrocarbon concentration $\leq$0.10 ppm.
2. Following the manufacturer's procedure, calibrate of all three channels, (THC, CH_4 and NMHC) of the analyzer with a known methane span gas and a known non-methane (ethanol) span gas.

   Note1: The methane concentration and non-methane (ethanol) concentration of the span gases should approximate 80-90% of the measurement range at which the FID will be used to make measurements. Follow Method 25A for guidance on gas concentrations for calibration.

   ***Note2*:** Calibration gases should comply with US EPA Protocol 1 (±1%) or RATA Class gas specifications.
3. Verify analyzer calibration on the methane channel with a known methane in air concentration. The analyzer should give a measurement equal to the certified span gas methane concentration of the cylinder (±3%).
4. Verify analyzer calibration on the non-methane channel with a known non-methane hydrocarbon (ethanol) in air concentration. The analyzer should give a NMHC measurement equal to the certified span gas concentration for the cylinder (±3%).
5. Following system calibration, calculate the efficiency of the methane cutter. If the efficiency of the methane cutter is $\leq$95%, replace and re-calibrate the analyzer prior to proceeding. The methane cutter efficiency should be periodically tested using a gas mixture of methane and non-methane hydrocarbon (ethanol).
6. Initiate sample flow from the VOC destruction device and begin making measurements and recording results.

6.0 Calculations

The methodology, equations and performance specifications follow Method 25A very closely. Calculate the concentrations of methane, non-methane and total hydrocarbons as follows:

$$Cc = K\, C_{meas} / \varepsilon$$

Where:

Cc = NMHC (ethanol) concentration

C_{meas} = THC_{meas} - M_{meas}

K = Response Factor for the NMHC (ethanol)

ε = determined efficiency fraction of the methane cutter. This value is 1.0 if no methane is present, as in a calibrated gas cylinder containing only ethanol in air.

M_{meas} = methane (CH_4) concentration as directly measured on the methane channel.

THC_{meas}= Measurement on the total hydrocarbon channel, calibrated to methane.

Methane cutter efficiency can be determined by testing a certified mixture of methane and the NMHC of interest (ethanol). The equation for the methane cutter efficiency is as follows:

$$\varepsilon = K\, C_{meas\ NMHC} / C_{cert\ NMHC}$$

Note: the cutter is cutting NMHC, not methane. Therefore the efficiency is calculated by the non-methane components.

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Where:

ε = *efficiency of the methane cutter*

$C_{cert\ NMHC}$ = certified concentration of NMHC (ethanol) in a mixture of methane and NMHC (ethanol)
or
certified concentration of NMHC (ethanol) with a balance of nitrogen

$C_{meas\ NMHC}$ = measured NMHC (ethanol) concentration on the methane channel

Note: The presence of CH4 in certified NMHC can lead to errors in determining absolute efficiency measurement.

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Appendices of Supporting Data

Appendix A – Test Data Source

The data supporting this submittal is taken from a stack test report on a commercial bakery owned and operated by Stroehmann Bakeries L.C. in West Hazleton, Pennsylvania tested on July 12, 2003. The test was conducted by AirRECON, an independent testing company and report submitted to the state for the purpose of verifying air pollution control compliance of a CSM Worldwide catalytic oxidizer on the bakery. The test utilized a flame ionization detector (FID) with a methane cutter as described in the subject submittal. The full report was filed and accepted by the state after submittal on August 16, 2001. Because of its size, the full report is not included in this submittal, but can be supplied upon request or directly from the state.

Subsequently, several other similar tests were conducted at other commercial bakeries. The results were similar to those reported here.

Appendix B – Certificates of Analysis for Calibration Gases

The gases used in this test have the attached certificates of analysis. The standard is NIST traceable. The gases were certified according to the EPA protocol procedures. Calibration and Bias gas samples consisted of methane in air. Ethane in nitrogen was used for determining response factor. Mixtures of ethanol and methane in air wee used for measuring cutter efficiency. Spectra Gases prepared all samples.

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Appendix C – Pre-Test Calibration of FID Channels to Methane

The FID used in this test was a JUM 109A with two channels, one measuring Total Hydrocarbons (THC) and one measuring Methane (M). By difference in measurement signals the Non-Methane Hydrocarbon (NMHC) was calculated. Because there are two FID's in one instrument, both had to be calibrated. Method 25A was followed regarding protocol for sampling, measurements, and calibration and bias checks on the FID. Table 1 shows a summary of the calibration data taken on the THC and M channels using the calibration gases. The table refers to the raw data in strip charts taken continuously during the calibration period.

In reviewing strip chart data please note that the data runs up the page from one page to the next. The date and time print first and the data follow. Also, the printed dates on the charts are off by one day (i.e. the date printed on the chart of July 13, 2001 is really July 12, 2001).

TABLE 1

Pre-Test Calibration Of FID Channels to Methane

Strip Chart Ref. Page #	Time/Date	Gas Cylinder Concentration	MEASUREMENTS (ppm) THC	M	NMHC
149	7:46AM; 7/12/01	260ppm CH_4	262.9	255	6.9
149	7:44 AM; 7/12/01	552ppm CH_4	558.6	548.7	7
149	7:39A; 7/12/01	858ppm CH_4	859.1	867	-4.6
156	9:22AM; 7/12/01	858ppm CH_4	859.1	863.5	1.6
156	9:26AM; 7/12/01	552ppm CH_4	564.7	566.6	-4
157	9:29AM; 7/12/01	260ppm CH_4	268.1	268	-0.7
157	9:31AM; 7/12/01	Zero CH_4	1.2	0.9	0.1

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Appendix D – Ethanol Response Factor and Ethanol/Methane Cutter Efficiency

The response factor for the FID was determined using gas samples of ethanol in air. Summary data is shown in Table 2. The response factor is calculated using the formulas in section 6.0 above. Note that since the sample has no methane in it, the efficiency fraction of the methane cutter is 1.00. The table refers to the raw data in the strip chart.

TABLE 2

Response Factor for Ethanol

Strip Chart Ref. Page #	Time/Date	Gas Cylinder Concentration	MEASUREMENTS (ppm) THC	M	NMHC	Response Factor K
152	8:10AM; 7/12/01	798ppm Ethanol	935.3	1.7	932.3	0.85
153	8:18AM; 7/12/01	81.4ppm Ethanol	94.4	0.4	93.8	0.86

Methane cutter efficiency was determined by analysis of gas mixtures of ethanol and methane. The data was taken on July 3, 2001, about 10 days before the bakery performance test in West Hazleton, PA. A summary of data results is provided in Table 3 and the raw strip chart data is presented in table format in Table 4. The raw FID Strip Chart Data is also enclosed. Since the instrument was calibrated at a different time and location from the data taken above, the response factors for ethanol have changed slightly. This is not significant, since the response factors are determined each time the method is run. Cutter efficiency does not change much once determined, although it should be checked periodically as explained above.

It is the opinion of the ICAC, based on available data that the best way to determine instrument precision is to use single component gas standards. Errors can be introduced in preparing and maintaining mixtures of gases as chemically different as ethanol (a water-soluble di-polar molecule) and methane (a saturated non-polar alkane). Also, the difficulty in assuring that the certified gas mixture composition is being delivered to the instrument can be avoided by using single gas components of known composition to calibrate and challenge the instrument.

TABLE 3

Ethanol and Methane Mixed Gas Analysis

Strip Chart Ref. Page #	Time/Date	Gas Cylinder Concentration	MEASUREMENTS (ppm) THC	M	NMHC	NMHC Response Factor K	Methane Cutter Efficiency E

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460	12:08 PM; 7/3/01	798ppm Ethanol	912.4	0.7	911.7	0.88	
462	12:20PM; 7/3/01	1010ppm CH_4/509ppm Ethanol	1558	1026	532		98%
463	12:27PM; 7/3/01	97.9ppm CH_4/ 52.1ppm Ethanol	151.4	97.8	53.6		99%

TABLE 4

Raw Data on Ethanol and Ethanol/Methane Gas Mixtures

Date	Time	Outlet O2	Outlet CO2	Outlet THC as CH4	Outlet CH4	Outlet NMHC	FID Analyzer Strip-Chart Page #
Challenge With 798ppm Ethanol in N_2		**%**	**%**	**ppm**	**ppm**	**ppm**	**ppm**
7/3/2001	12:05:47	0.2	0.0	891.8	2.5	889.3	460
7/3/2001	12:06:17	0.1	0.0	899.2	1.9	897.3	460
7/3/2001	12:06:47	0.1	0.0	904.1	1.6	902.5	460
7/3/2001	12:07:17	0.1	0.0	906.4	1.1	905.3	460
7/3/2001	12:07:47	0.1	0.0	907.2	1.0	906.2	460
7/3/2001	12:08:17	0.1	0.0	910.4	0.8	909.6	460
7/3/2001	12:08:47	0.1	0.0	912.4	0.8	911.6	460
7/3/2001	12:09:17	0.1	0.0	905.8	1.5	904.3	461
Challenge With 1010ppm Methane and 509ppm Ethanol in Air							
7/3/2001	12:15:05	20.8	0.0	1405.0	1426.9	-21.9	461
7/3/2001	12:15:35	20.8	0.0	1552	1026	526	461
7/3/2001	12:16:05	20.8	0.0	1555	1025	530	461
7/3/2001	12:16:35	20.8	0.0	1557	1022	535	461
7/3/2001	12:17:05	20.8	0.0	1562	1028	534	461
7/3/2001	12:17:35	20.8	0.0	1559	1026	533	461
7/3/2001	12:18:05	20.8	0.0	1560	1025	535	461
7/3/2001	12:18:35	20.8	0.0	1561	1029	532	461
7/3/2001	12:19:05	20.8	0.0	1561	1027	534	461
7/3/2001	12:19:35	20.8	0.0	1559	1029	530	462
7/3/2001	12:20:05	20.8	0.0	1560	1024	536	462
7/3/2001	12:20:35	20.8	0.0	1558	1026	532	462
Challenge With 97.9ppm Methane and 52.1ppm Ethanol in Air							
7/3/2001	12:23:34	20.9	0.0	150.5	98.6	51.9	462
7/3/2001	12:24:04	20.9	0.0	150.5	98.6	51.9	462
7/3/2001	12:24:34	20.9	0.0	150.9	98.9	52.0	462
7/3/2001	12:25:04	20.9	0.0	151.0	98.3	52.7	462
7/3/2001	12:25:34	20.9	0.0	151.3	98.2	53.1	462
7/3/2001	12:26:04	20.9	0.0	150.7	98.1	52.6	462
7/3/2001	12:27:04	20.9	0.0	151.4	98.0	53.4	463
7/3/2001	12:27:34	20.9	0.0	151.4	97.8	53.6	463

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Appendix E – Test Data and Post Test Bias/Drift Check Data

Three one-hour tests were conducted. After each test a zero and bias/drift check was made using the mid point gas sample concentration. Table 5 summarizes data and raw data is provided on Strip Chart Page Numbers 171, 184, 200-203 and 216. The data shows good repeatability and accuracy within required constraints. There was a problem with test # 3 that was detected during the after-test bias check. This lead to the decision to recalibrate the FID and rerun the last test numbered #4. This is a good example of the flexibility of this method in that instrument problems can be detected during the course of the test and the test can be salvaged, rather than incurring costly and time delayed retesting.

Test run data is supplied to show the value of real time NMHC data in conducting these tests. Current test methods 25A and 18 do not provide real time information of this kind. Figures 1 through 6 are graphs of test data from each test run and the resulting instantaneous and average destruction efficiency measurements. Without this method, the best we can get is real time THC In and Out which dose not provide useful information on system NMHC destruction performance. The data behind these figures are contained in Attachments 10 through 18.

ICAC believe this conditional test method provides accurate, timely and reliable data. It is based on well-established flame ionization technology. It basically follows established Method 25A protocol. There is a definite need especially in bakery applications for this method

TABLE 5

Post Test Run FID Bias/Drift Check Data

Strip Chart Ref. Page #	Time/Date	Gas Cylinder Concentration	MEASUREMENTS (ppm) THC	M	NMHC
AFTER TEST RUN # 1					
170	11:25AM; 7/12/01	Zero CH_4	1.2	0.6	0.5
171	11:33AM; 7/12/01	552ppm CH_4	572.8	568.1	2.5
AFTER TEST RUN # 2					
185	13:18; 7/12/01	Zero CH_4	0.7	0.2	0.4
185	13:25 ; 7/12/01	552ppm CH_4	563.9	542.3	19.7
AFTER TEST RUN # 3					
200	14:55 ; 7/12/01	Zero CH_4	0.5	-0.1	0.5
201	14:59; 7/12/01	552ppm CH_4	538.8	509.4	26.3
				Failed Drift	

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RECALIBRATE					
202	15:13 ; 7/12/01	858ppm CH_4	857.6	852.2	10.4
202	15:13 ; 7/12/01	552ppm CH_4	559.4	561.2	-3.5
202	15:14 ; 7/12/01	260ppm CH_4	261.1	258.3	1.9
AFTER TEST RUN # 4					
216	16:49; 7/12/01	Zero CH_4	5	0.8	3.8
		552ppm CH_4	575.2	573.1	-0.8

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