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DEVELOPMENT OF AN ANALYZER FOR EXHAUST
FROM METHANOL/HYDROCARBON-FUELED MOTOR VEHICLES

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Prepared for California Air Resources Board

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DEVELOPMENT OF AN ANALYZER FOR EXHAUST
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by

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ABSTRACT

In order to obtain accurate data for the content of unburned methanol in exhaust gases of vehicles fuelled on methanol mixtures during emissions testing, the California Air Resources Board initiated a study to develop an analyzer that would determine methanol and hydrocarbons separately. Global Geochemistry Corporation has designed and built an instrument for this, based on a "modulator" which preferentially pulses the concentration levels of methanol in the test gas and allows it to be differentiated from hydrocarbons, which are not modulated. It is also responsive to ethanol. The modulator is based on adsorption and desorption of methanol in a packed microtube, controlled by temperature pulses. The unit is a modification of a flame ionization analyzer (FIA) already in use for hydrocarbon analysis. It consists of the modulator and an electronics module that uses a microprocessor for modulator control and for processing of the output signal of the FIA. The unit is simple and compact, has a response time of 10 seconds, precision of $\pm 2\%$ of full-scale (which is set on the FIA and has the same range options), accuracy of ± 2 mv, and gives two separate simultaneous outputs, either analog or digital, for hydrocarbons and methanol. The unit was tested at the ARB Haagen-Smit Test Facility with good results and is installed there as the contract deliverable.

Acknowledgements -- Professor John B. Phillips, consultant on this project, is a member of the Department of Chemistry and Biochemistry at the University of Southern Illinois, Carbondale, Illinois. He also wrote the computer programs that control the instrument operations. Duc H. Banh translated these computer programs into microprocessor chip elements and built the electronics unit. The assistance of the staff of the Emissions Testing Facility at the Haagensmit Laboratory of the Air Resources Board in testing the instrument is gratefully acknowledged.

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The statements and conclusions in this report are those of the contractor and not necessarily those of the California Air Resources Board. The mention of commercial products, their source or their use in connection with material reported herein is not to be construed as either an actual or implied endorsement of such products.

SUMMARY AND CONCLUSIONS

In this project an instrument was designed and built that gives simultaneous measurements of methanol and hydrocarbons in diluted vehicle exhaust. The objective was to allow the ARB to obtain accurate readings of unburned methanol emitted from vehicles fueled with methanol mixtures, during testing on the dynamometer emissions test facility at the ARB Haagen-Smit Laboratory. (Methanol gives an erroneously low response when measured with the conventional hydrocarbon analyzers in use).

The new methanol analyzer is based on a device called a "modulator", which is controlled by an electronic microprocessor. It contains a material that absorbs methanol preferentially over hydrocarbons from a gas stream of diluted exhaust, and then desorbs the methanol when heated. This sorption-desorption cycle takes less than one second, and each heat pulse results in a sharp pulse of methanol vapor into the sample gas stream. The magnitude of each pulse is proportional to the methanol concentration in the sample gas. The modulator is controlled by an electronic microprocessor that actuates pulses of electric heating power to a conductive coating on the modulator. The sample gas then flows into the ordinary flame ionization hydrocarbon analyzer (FIA). The signal from the FIA is routed back to the microprocessor, where the pulsed signals from the modulated methanol and the non-pulsed continuous signals due to hydrocarbons plus methanol are separated electronically and provided as two outputs to a readout device (one channel for hydrocarbons and one for methanol). The output can be either analog or digital. The response time is less than ten seconds and readout may be obtained at all times during operation. Calibration is carried out with a gaseous methanol standard and is done automatically by flipping a switch.

The instrument is compact, light weight, and has very few and simple controls. It has been adapted to a Horiba FIA of the type in use at the Haagen-Smit Laboratory, but could probably be used with almost any conventional FIA. It has also been tested with ethanol instead of methanol and responds equally well. The precision as tested to date is better than $\pm 2\%$, and the accuracy $\pm 2\%$ of full scale. Ranges are set on the FIA, and will be the same as for hydrocarbons on that instrument. The instrument was provided at the request of ARB with an output range of 100 mv full-scale analog, but could be adjusted in manufacture to any value up to 5 v, or could be provided with digital rather than analog output.

RECOMMENDATIONS

We recommend that after sufficient use on the experimental dynamometer to show the long term stability and ease of operation of the instrument, it replace the hydrocarbon analyzer now in use there. Additional units can also be provided as add-ons to the FIAs in use on other dynamometers at Haagen-Smit, if the use of methanol or ethanol fuels becomes widespread enough to warrant it.

It would also be useful to test its response to other alcohols often used as co-solvents in alcohol-gasoline fuels, because it is not certain at present whether these higher alcohols will respond like methanol and ethanol, or like hydrocarbons.

The principle used in this analyzer may be adaptable to other specific pollutants or chemical classes of pollutants of interest to ARB. It is also probable that a comparable analyzer could be made for analysis of ambient air for alcohols or perhaps other compounds, using a more sensitive ambient air monitor version of the FIA.

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1.0 INTRODUCTION

An important responsibility of the California Air Resources Board (CARB) is to determine emissions from mobile sources. One such emission is hydrocarbons, and the CARB tests many gasoline-powered motor vehicles each year for their exhaust hydrocarbon emissions, because these are important precursors in the generation of photochemical smog. The use of methanol as an alternate fuel or fuel extender has been proposed because it can be synthesized from many different materials and readily purified. In anticipation of the possibility that the use of methanol as a fuel or fuel extender may become more widespread, the CARB foresaw the need for a vehicle exhaust analyzer capable of differentiating between methanol and hydrocarbons. Among the analyses carried out on vehicles tested on the dynamometers at the Haagen-Smit Laboratory is the monitoring of hydrocarbons collected during the standard driving cycle. Currently this is measured either with a flame ionization detector (FID) or a non-dispersive infrared (NDIR) detector. Both of these are customarily calibrated with hydrocarbons. Because both types of instruments respond in a predictable way to hydrocarbons of all types, one compound (such as propane for the FID) is a convenient representative of the whole class and has been shown to provide good calibration for it. By contrast, methanol is known to give reduced responses, compared to the same amount of carbon in a hydrocarbon, with both instrument types. Obviously a vehicle running on a fuel containing methanol could show an erroneously low value for "hydrocarbon" content of its exhaust, if part of the emissions were unburned methanol.

The project reported here was therefore initiated. The analyzer was expected to have a fast response and be compatible with existing calibration and computer interfacing features at the CARB Haagensmit vehicle-testing facility. The desired performance characteristics of the instrument are shown in Table 1. GGC contracted to develop such an instrument.

Table 1. DESIRED PERFORMANCE CHARACTERISTICS FOR ANALYZER

- 1) Accuracy: Two percent of full scale
- 2) Response time: Ten seconds for 90% of full scale
- 3) Output: 0-5 Volts to full output signal
- 4) Repeatability: Two percent from regression curve
- 5) Ranges: 0-30, 0-100, 0-300, 0-1000, 0-3000 ppm
- 6) Calibration: Provisions compatible with existing procedures
for FID and NDIR instruments

Other desired characteristics:

Compactness

Compatibility with existing ARB trains, computer, and other
equipment: suitable for mounting in ARB instrument racks

Easy calibration and repair

Spare parts availability at least equal to the same features of
current GC systems

Market retail price with accessories not over \$15,000

2.0 NARRATIVE HISTORY OF INSTRUMENT DEVELOPMENT

2.1 Background

In a previous study funded by the US Department of Energy, GGC demonstrated a laboratory prototype analyzer for species of hydrocarbons in mixtures from C₄ to C₇. This was based on the concept of multiplex gas chromatography with thermal adsorptive modulation. It was reasoned that the problem of differentiating between only two such dissimilar materials as methanol and hydrocarbons should be simpler than this multi-component analysis. It was also hoped that with a selective modulator, no gas chromatographic separation would be necessary. Consequently the first efforts were directed towards finding a modulator that would be selective for methanol over hydrocarbons. Three possible ways of modulating methanol were identified.

1) Thermal desorption -- This requires a substance to which methanol is preferentially adsorbed. A short segment of column or tube (preferentially capillary, for the reduced heat capacity) is packed or internally coated with the adsorbent. The outside of the tube is coated with an electrically conductive paint or wound with wire, with leads attached. Modulation is achieved by periodically pulsing the conductor with an electric current to cause a chemical signal, i.e. a pulse of increased analyte concentration in the sample stream passing through the tube, due to the thermal desorption.

2) Selective oxidation -- This requires a substance that will selectively catalyze the oxidation of methanol (possibly to CO₂). Modulation is achieved by periodic thermal pulsing (as in mode 1 above) to the oxidation temperature, or by valve switching that exposes the sample stream to the oxidant.

3) Selective Reduction -- This method would involve the use of zeolites to catalyze the reduction of methanol to methane in the presence of hydrogen gas (easily routed from the FID supply). Modulation is achieved as in 2) above. This is a less attractive mode than 1) or 2) because the analyzer responses to methanol and methane are not as dissimilar as they would be for the removal of methanol.

Method 1) was investigated first, because of its greater familiarity and the fact that it appeared to be a more promising approach. The salts CaCl_2 and CoCl_2 were both known to form associations or complexes with alcohols. Modulators packed with these two were tested in various ways and showed modulation, albeit weak, that under some conditions was greater than the effect on hydrocarbons. There also appeared to be irreversible effects that might have been due to catalytic oxidation. While these first trials were underway a more detailed literature search was made for more strongly adsorbing modulator materials with greater selectivity.

2.2 Alcohol-Specific Modulation

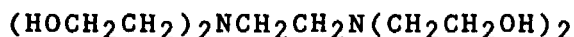
Boric acid modulation -- A concurrent literature search by the project consultant, Professor Phillips of Southern Illinois University, suggested possibly more effective modulators. The first to be examined was boric acid. This was tested in various concentrations on Chromosorb W and did modulate methanol; however n-octane (as test hydrocarbon) also appeared to be modulated. The methanol signal peaks were followed by broad negative peaks, but the octane peaks had no negative peaks. Although this difference could perhaps be utilized to quantify the methanol, the precision did not look to be as good as desired. These tests were run in the presence of water vapor, which appeared not to have any effect. This was a useful finding.

It was also discovered in the boric acid studies that a

column segment of boric acid on Chromosorb W could remove a methanol modulation signal generated ahead (upstream) of it, but had no such effect on hydrocarbon signals. The boric acid apparently acted analogously to an electronic filter in removing high frequency methanol pulses. It was possible to apply this by first thermally modulating both methanol and hydrocarbons with a short segment of a DB-5 capillary quartz gas chromatographic column, filtering out the methanol modulation with a boric acid filter, and modulating again with a second DB-5 segment. A simple fixed time offset between the two pulses was used, so that alternate pulses represented 1) hydrocarbon/methanol, and 2) hydrocarbon only. The difference between the responses to the two modulations corresponded to the methanol concentration.

This device was usable and effective, but had these drawbacks: the modulator is difficult to construct and somewhat fragile: it limits the gas flow more than is desirable, causing a slowed time response; optimization of the staggered timing of the two modulation pulses is time consuming; and the complex of modulators and filter is clumsy and bulky to mount inside the flame ionization detector.

THEED modulator -- Another possibility found in the literature search was tetrahydroxyethylethylenediamine (THEED):



This material is a good complexing agent for methanol. It was tested in a device in which a short column segment packed with THEED as a nearly methanol-specific thermal modulator is followed by a hydrocarbon filter consisting of a coating of a low volatility hydrocarbon, squalane, on Chromosorb W. (Squalane does not adsorb methanol to a measurable extent). In this system methanol is modulated by the THEED modulator and the resultant methanol signal pulse passes through the squalane filter unchanged. Meanwhile the hydrocarbon is modulated weakly or not at all on the THEED segment, and any weak hydrocarbon modulation signals are removed by passage through the squalane filter. Thus the pulsed (AC) signals are a direct measure of the methanol

concentration. The magnitude of the absolute DC voltage signal generated in the detector, on the other hand, is a direct measure of the sum of hydrocarbon and methanol, and the pulsed (AC) methanol value may be subtracted from this sum to derive the hydrocarbon concentration.

2.3 Laboratory prototype construction

Initial tests were made on a gas chromatograph with an FID for detection, and an available Apple 2e computer for modulation pulse control and data manipulation. An IBM PC was later substituted for the Apple, and a Horiba FIA-23A total hydrocarbon analyzer as detector. With this latter combination the modulator (described below) was placed in the FIA just before the detector. In addition to these components, a microswitch was actuated from the computer to switch a 24 v DC power supply in and out of the modulator heater circuit, providing the modulation heat pulses. The analog output of the FIA was converted to the digital form with an A/D converter board in the IBM. Output from the computer data manipulation was displayed on the monitor screen. The computer program, written in FORTH, controlled the modulator, accepted calibration signals from the FIA, converted FIA sample signals into concentrations for hydrocarbons and methanol, and displayed them in real time on the IBM monitor.

The final version of the modulator assembly is shown in Figure 1. It is constructed of 0.5 mm i.d. quartz capillary tube. The 1.5 cm modulator segment is packed with 100/120 mesh THEED-coated Chromosorb W, and the 3 to 5 cm filter segment is packed with Carbosieve coated with 5% w/w squalane. The unit is dimensioned and shaped to make it possible to replace the final sample flow controller capillary part in the Horiba FIA directly. The sample flow controllers in the FIA are stainless steel capillaries mounted inside a small oven whose temperature is controlled to 53°C. Mounting the modulator in place of the last one of these capillaries (just ahead of the detector) protects it from damage. The heater leads are brought out through a small

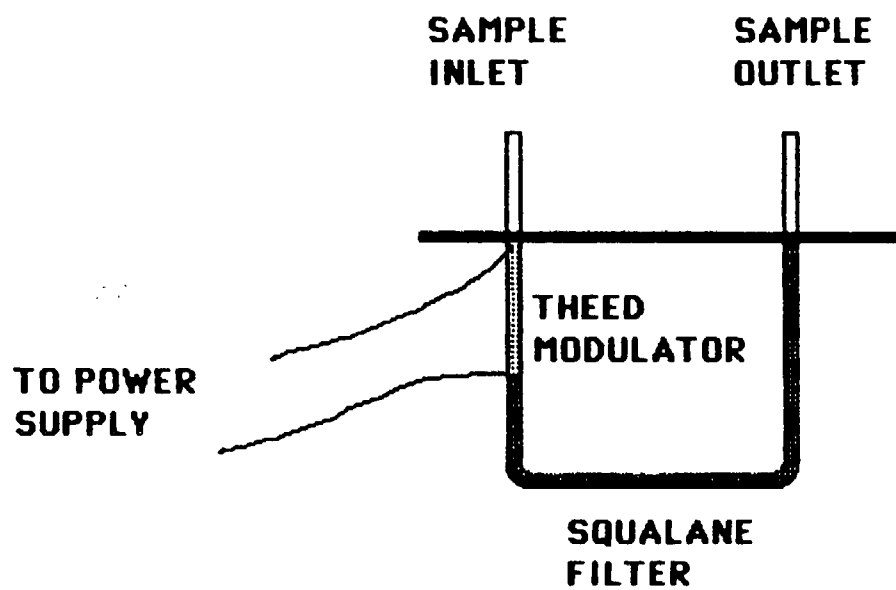


FIGURE 1- METHANOL MODULATOR

hole in the top of the oven. The modulator restricts the sample flow to a degree closely similar to the original FIA capillary, and no great adjustment of the pressure or the detector amplification is required.

This prototype instrument was given preliminary testing at the CARB Haagensmit Laboratory in March of 1986. It performed well, and comparison of the results with gas chromatographic bag sample analyses, as shown in Table 2, were good, considering that the calibrations were not made with the same materials, and the samples were not taken exactly simultaneously nor at the same part of the test stand.

2.4 Construction of Final Prototype

The FORTH computer program for the laboratory prototype was translated and encoded into a Z-80 microprocessor. This and other components, such as the power supply, switching circuitry, and input and output features were assembled into an electronics module having the following functions:

1. Acceptance of detector signal and amplification and digitization of it.
2. Modulation control (thermal pulse duration, frequency and power).
3. Signal processing (separating the AC and DC components of the signal and applying calibration factors to it for output in terms of concentrations).
4. Signal conversion, digital to analog. (This was necessary because the CARB computer at the Haagensmit laboratory accepts only analog input data. With a different computer system the digital form might be used).
5. Calibration operations.
6. Signal output.

2.5 Laboratory Tests

Repeatability tests run with different ranges of methanol

content were made using blends of methanol in nitrogen made by Scott Specialty Gases, and certified by them to contain 3 ppm, 286 ppm, and 3000 ppm, each $\pm 2\%$. Repetitive runs were made while continuously flowing the reference gas into the analyzer. The 3 ppm blend is below the minimum of the five specified ranges of 0-30, 0-100, 0-300, 0-1000, and 0-3000 ppm, but assuming that the same absolute standard deviation would apply for the 0-30 range, we find the following midrange results:

<u>Range, ppm</u>	<u>Rel. Std. Dev.</u>	<u>N</u>
0-30	0.70 %	23
0-286	0.30 %	17
0-3000	1.13 %	13

The value for the 3000 ppm range was greatly increased by one outlier value, whose removal reduced the R.S.D. from 1.13 % to 0.35 %. The values for intermediate ranges 0-100 and 0-1000 (not available) would be expected to fall within the same general limits. One set of four repetitive runs taken from a dilute vehicle exhaust bag at the dynamometer on April 2, 1987, averaged 50.8 ± 0.80 ppm methanol, e.g. 1.57 % RSD. (See Table 3 below).

2.6 Dynamometer Tests

The first attempts to test this had to be discontinued because although the ARB specifications in the RFP called for an output signal of 0-5 v DC, the computer on the research dynamometer where this is to be used requires an input of 0-100mv DC. GGC provided this change in output range by a hardware alteration in the circuitry of the instrument. Although this allowed interfacing, all the available input ports on the CARB computer are in use already for other instrument measurements. This means that one of them would have to be omitted in order to put in data from the methanol analyzer. This was not desirable because the need for the methanol analyzer was intermittent, and the other measurements were always needed. The alternative used was to take manual readings with a digital voltmeter (DVM) and

convert them to concentrations by means of a calibration table.

In calibrating the instrument it should be noted that there is no NBS standard for methanol. Calibration mixtures were purchased as custom blends in nitrogen gas from Scott Specialty Gases.

The instrument was demonstrated to the CARB research dynamometer staff and, along with an instruction manual, was left for testing over a period of several months. During this period there were a number of occasions on which cross checks were made with bag samples analyzed by the CARB analytical laboratory, using gas chromatography. The results of these tests, listed in Table 3, show good agreement for methanol between the two methods in most cases; the ARB method for methanol is probably less precise than the analyzer, because it is working with more dilute samples. Another factor limiting the accuracy of comparison is the fact that the GGC methanol analyzer readings were taken in the course of the vehicle testing, whereas the ARB laboratory determinations of methanol were obtained some time later from the Tedlar bags; during this time interval, condensation and dissolution of methanol could occur. The ARB methanol results are higher than those of the GGC analyzer in only two cases, and then only by one and two ppm, respectively; usually they are somewhat lower, suggesting the possibility of slight losses.

Total hydrocarbons are given for both the Beckman FIA analyzer (calibrated on propane) and by the ARB GC method. The latter are summed from determinations of three separate groups of individual hydrocarbon components: C₁, C₂-C₅, and C₆-C₁₀, whereas the GGC analyzer is calibrated with propane (similar to the routine hydrocarbon values taken by the Beckman FIA). This is the probable reason that in most cases, including those in Table 2, the ARB values for total hydrocarbons are higher than those by the GGC analyzer. The Beckman FIA gives a total for both hydrocarbons and methanol, but the response for methanol is only about 70% of that for hydrocarbons with the same carbon content. An additional column in Table 3 is given in which this low FIA

Table 2. Tests of GGC Methanol Analyzer on Vehicle Exhaust
(Haagensmit Laboratory 3/20/86)

<u>Bag</u>	<u>Sample</u>	<u>Range</u>	<u>Analyzer Results*</u>			<u>ARB Bag Results*</u>	
			<u>mv (HC)</u>	<u>THC</u>	<u>MeOH</u>	<u>THC</u>	<u>MeOH</u>
Gasoline-fuelled vehicle (83 Dodge Omni):							
	bkgd	2	8-9	6	0	9	1
1	sample	4	150	123	1	129	1
	bkgd	2	8-9	6	0		
2	sample	3	25	19	0.6-0.7	29	1
Methanol fuelled vehicle (85 Toyota Camry):							
	bkgd	2	7	6	0.2	10	1
1	sample	4	22	19	80	28	60
	bkgd	2	6	4	0.5		
2	sample	2	6	4	1.3	14	1

Note: Bag no. 1 contains the exhaust from the cold-start cycle,
bag no. 2 contains exhaust from the second cycle started
soon after the first cycle is complete.

* All values are in ppmV, except for mv (HC).

Table 3. Extended Time Tests on GGC Methanol Analyzer

<u>Bag</u>	<u>Analyzer Results^a</u>		<u>Beckman FIA^a</u>		<u>ARB Bag Results^a</u>	
	<u>THC^b</u>	<u>MeOH</u>	<u>THC^c</u>	<u>THC+MeOH^d</u>	<u>THC^e</u>	<u>MeOH</u>
Test # 18-C-15, 8/12/86						
1	f	49	72	87	28.6	50
2	f	3	6	6	5.9	< 1
3	f	6	7	7	4.9	< 1
Test # 18-C-16, 8/13/86						
1	f	50	85	100	42.2	50
2	f	0.5	6	6	8.8	< 1
3	f	6	25	25	22.3	1
Test # 18-C-21 9/24/86						
1	22	43	67	79	30.42	40
2	4	0	5	5	8.58	0
3	5	0	6	6	9.10	0
Test # 10-C-13 3/31/87						
1	26.4	91.8	103	121	42.5	60
2	6.0	0	7	8	5.9	2
3	21.6	12.8	23	25	19.09	8

Multiple Readings (from one bag)

4/2/87						
1	17.0	51.2			29.6	40
2	15.1	51.2			30.2	40
3	16.6	49.6			28.9	40
4	g	51.2			28.5	40

-
- ^a All values are in ppm by volume
^b Calibrated with propane
^c Beckman FIA readings uncorrected, calibrated on propane
^d Beckman FIA readings corrected for low methanol response by adding 30% of ARB bag value for methanol
^e ARB analyses calibrated by individual species, not on propane
^f Readings unavailable due to lack of DVM
^g Sample gas exhausted after 3rd reading

response is corrected by adding 30% of the ARB laboratory GC methanol value. Comparing the six tests where both analyzer and corrected Beckman FIA values are available, the ratios of analyzer to corrected Beckman totals are 65/79, 4/5, 5/6; 118.2/121, 6/8, and 34.4/25. We believe the agreement of these comparisons is limited mainly by the differences in the calibration procedures for the various methods.

During use at the ARB dynamometer stand it was observed that after some months the calibration voltage drifted downward. (This does not affect the precision or accuracy of measurement unless downward drift is great enough to cause the signal output to become too low for good measurement, or so rapid that calibration must be made too often). The drift was traced to a sample gas leak and corrected. Subsequent to this, drift occurred very slowly, such that weekly calibrations were sufficient to maintain good measurements. The rate of drift suggests that the probable useful lifetime of the modulator is at least several months, requiring replacement no more often. No other operating problems were encountered.

3.0 INSTRUMENT DESCRIPTION

3.1 General Description

The Methanol/Hydrocarbon Analyzer was made by modifying the Horiba FIA-23A Hydrocarbon Analyzer. The general features of the original Horiba instrument remain the same except that the sample introduction and signal processing are different. The original Horiba FIA-23A Hydrocarbon Analyzer utilizes the principle of Flame Ionization Detection and the sample input stream directly passes through the detector without any treatment. The detector output is a DC signal which corresponds to the total hydrocarbons concentration level. To analyze methanol and hydrocarbons in a gaseous sample stream, some means of separation is necessary.

In the Methanol/Hydrocarbon Analyzer, one of the original sample capillary flow restrictors (CAP2) in the oven compartment is replaced by the methanol modulator. The purpose of this methanol modulator is to modulate the incoming gaseous sample and generate a methanol modulation signal in a pulse form. It has no effect on hydrocarbons. The subsequent detection of methanol and hydrocarbons is then based on the measurement of these two forms of signals; a DC signal for hydrocarbons and a pulsed AC signal for methanol. Besides the original capabilities provided by the Horiba FIA-23A Total Hydrocarbon Analyzer, this Methanol/Hydrocarbon Analyzer provides the additional information of methanol content in the gas sample.

The Methanol/Hydrocarbon Analyzer consists of two additional components: the Modulator and the Electronics Module. These two units are connected through a pair of electric leads. The Electronics Module is also electrically connected to the Horiba Electronic Module (OPE-415).

3.2 Methanol Modulator

The Methanol Modulator is a 7 cm long, 0.53 mm ID, fused silica capillary tube packed with a 1.5 cm section of 100/120 mesh THEED (tetraethylethylenediamine)-coated packing material followed by a 3 to 5 cm section of Carbosieve packing material

containing 5% (wt/wt) Squalane. Conductive paint is coated on the outside capillary surface of the section containing THEED packing only. A pair of 22 gauge wires are used to connect this electrically conductive region to the Power Supply Unit. The Methanol Modulator is mounted in the oven in the place of an original sample capillary flow restrictor (CAP2), which is removed. The oven temperature is kept at a constant 53°C so that fluctuations in ambient temperature will not affect the modulator performance.

3.3 Modulator Functions

A modulator is a sample introduction device. A general thermal modulator is a short piece of fused silica capillary chromatographic column coated with a thin film of conductive material on its outside surface. In the quiescent state, sample components in the gas stream entering the modulator are partially retained by the stationary phase, the extent of retention depending on the sample capacity factor. On command from a signal source (for example, a microprocessor), an electrical current is allowed to pass through the conductive coating, thereby raising the temperature of the modulator. When the modulator temperature is raised, the sample components are depleted from the stationary phase, resulting in an increase of sample concentration in the sample gas stream. When this electrical current is turned off, the modulator cools down and the fresh sample gas components entering the modulator are again retained by the modulator stationary phase. This cooling process briefly decreases the sample concentration in the flowing sample stream. Alternation of the heating and cooling cycles results in alternate increases and decreases in sample concentration. The detector responds to such periodic concentration changes by putting out an AC signal superimposed on the unmodulated DC signal. If there is no change in sample concentration, the detector output remains as the DC signal.

The Methanol Modulator as illustrated in Figure 1 is a selective sample introduction device. Each thermal modulation of

this modulator generates two different forms of signal (AC and DC). The methanol modulation signal is in AC form and the hydrocarbon signal is in DC form. The principle of generating these two different forms of signal is based on the sample capacity factors of the materials packed inside the Methanol Modulator. The first section of the modulator contains THEED packing material which retains methanol very strongly and hydrocarbons very weakly. The second section packed with Carbosieve containing 5% Squalane, by contrast, retains hydrocarbon strongly and methanol weakly. Therefore the second section of the Methanol Modulator tube, to which no heat pulses are applied, acts like a hydrocarbon filter. As the gaseous sample containing both methanol and hydrocarbons enters the first section of the Methanol Modulator, methanol is retained but most of the hydrocarbons are allowed to pass through freely. A heat pulse applied to this first section of the Methanol Modulator desorbs methanol and (at most) a small amount of hydrocarbons from this section, generating an AC signal (a pulse). The pulse of desorbed material enters the second section of the Methanol Modulator. The small AC signal of hydrocarbons generated by the thermal modulation is "damped" by the second section of the Methanol Modulator because of the filtering effect due to its retention of hydrocarbons. However, the AC signal of methanol is not affected because of the lack of retention by Carbosieve-Squalane and is subsequently detected by the flame ionization detector. In the meantime, the damped hydrocarbons signal continues as a DC signal and is also detected by the detector. The result of this modulation event is two signals. The methanol signal is an AC signal and is superimposed on a DC methanol plus hydrocarbons signal. These two signals are processed further and separated electronically. The Z80 microprocessor in the Electronics Module controls the pulse event and does the signal processing.

3.4 Electronics Module

The Electronics Module is housed in a separate module package containing ± 12 VDC and 5 VDC power supplies, the Z80 microprocessor, the electronic relay, the amplifier circuitry and output circuitry. It uses the same AC power as the Horiba Electronics Module. The Electronics Module receives the 0-5 volts standard signal output from the Horiba Electronics Module. All controls necessary to operate the Methanol Modulator are located in the same Electronics Module. The two standard outputs from the Analyzer Electronics Module are each 0-100 millivolts, separately labeled as MEOH and CH. The output labeled as MEOH carries the methanol signal and CH carries the hydrocarbon signal.

The module is 12"w x 7"d x 4"h. Signal leads connect it to the FIA, and modulator leads connect it to the modulator heater. Two output leads carry the output signal for methanol and hydrocarbon, respectively. The unit is powered by 115 VAC. Specifications are given in Table 4. Controls and indicators are as follows:

1. POWER lamp -- indicates when power is on.
2. PULSE lamp -- indicates when a modulation pulse is made.
3. POWER switch -- controls power to the module.
4. MODULATOR switch -- prevents modulator pulsing when turned off, to lengthen its life when not in use or to obtain total methanol plus hydrocarbon readout.
5. RESET pushbutton -- resets the module, stops the modulation pulse.
6. KCORR pushbutton -- initiates the computation of the factor for calculating the methanol fraction of the total DC signal from the FIA. This is calibrated with methanol span gas.
7. NORMAL pushbutton -- initiates sample analysis, starting the modulation pulses and calculations. The results are output continuously to the data acquisition system, with updates every 5 seconds.

Table 4. Instrument Specifications

Measuring Principle.....	Selective modulation and flame ionization detection
Accuracy.....	$\pm 2\%$ of full scale, i.e. $\pm 2\text{mv}$
Repeatability.....	$\pm 2\%$ from daily calibration of span gas
Response Speed.....	10 seconds
Outputs (both channels).....	0-100 millivolts
Power Requirement.....	115 VAC $\pm 10\%$, 60 Hz
Sample Gas Pressure Requirement...	8 psi at the sample inlet of the instrument
Burner Gas Requirement.....	According to the Horiba FIA Specifications
Ranges.....	0-30, 0-100, 0-300, 0-1000, 0-3000 ppm for both methanol and hydrocarbons

The Electronics Module provides the following functions:

1. Detector signal amplification and digitization.
2. Modulation control (thermal pulse duration, frequency, and power).
3. Signal processing (separating AC and DC signal).
4. Signal conversion (digital-to-analogue).
5. Calibration operations.
6. Signal output.

The Electronics Module also contains the Power Supply Unit and the Microprocessor Motherboard.

3.5 Power Supply Unit

The Power Supply Unit is the power supply for the thermal pulsing of the Methanol Modulator and for the Microprocessor Motherboard. The power requirement for this Power Supply Unit is 115 VAC, 60 Hz.

3.6 Microprocessor Motherboard

The Microprocessor Motherboard contains a Z80 microprocessor whose function is to control each electronic component through a specific electronic instruction. The instructions are electronically encoded in this microprocessor and are non-removable. The Power Supply Unit provides the necessary electrical protection to prevent the Z80 microprocessor chip from being damaged by a sudden voltage surge or a static shock. The other main electronic parts include a 10 bit A/D converter and two 8 bit D/A converters. The function of the A/D converter is to digitize the 0-5 V detector signal from the Horiba Electronics Module into a 10 bit number for further processing. The function of the D/A converters are to convert the processed digital signals into 0-5 V analog signals. A voltage divider scales this output voltage down to 0-100 millivolts.

3.7 Operation

The FIA analyzer is operated in an entirely normal fashion,

as it is for ordinary hydrocarbon measurements, and according to the Horiba instrument manual instructions. The ranging and other settings are also the same as usual.

After the methanol analyzer power and modulator switches are switched on, it is put in standby condition by pushing RESET. Zeroing is carried out with zero gas on the FIA, and then the KCORR button is pushed once to indicate the microprocessor that this is the background value. This starts the pulsing sequence (the PULSE lamp flashes once every 5 seconds). Methanol calibration gas is introduced and the NORMAL button is pushed once after readings are steady. This causes the calculation of the KCORR and starts signal processing, with outputs sent to the two channels. The desired output reading on the methanol channel is achieved by adjustment of the SPAN control on the FIA. The same procedure is followed on the FIA with propane as hydrocarbon span gas, but no changes are made in the methanol analyzer settings. The SPAN setting on the FIA is adjusted to give the desired output on the hydrocarbon channel. When sample gas is introduced, the analyzer will now give output on both channels corresponding to the methanol and hydrocarbon levels in the sample. To obtain combined readings for both methanol and hydrocarbons, the modulator switch is turned off. This prevents modulation pulses from occurring, and also prolongs the life of the pulse heating circuit. It is advisable to switch this off when methanol analysis is not needed, to keep the instrument warm and to retain the calibration setting without continuously pulsing the modulator.

4.0 CONCLUSIONS

The GGC Methanol Analyzer is an effective device for measurement of methanol in the presence of hydrocarbons over the range of at least one to 3,000 ppm. It makes use of a commercial flame ionization analyzer (the Horiba FIA-23A, but almost any flame analyzer instrument could be adapted for the purpose). The output voltage range is fixed during the construction, but could be set at other voltage ranges and provided in either analog or digital form by straightforward changes in circuitry. As it stands, it meets the specifications of the contract except where changes have been mandated by CARB itself, namely the change in output voltage range, and the lack of an input port on the CARB computer to accept the analyzer output.

If methanol becomes an important fuel component in the future, to the degree that more vehicle testing for it is called for, this design offers an excellent instrument to provide the good measurements needed.

The instrument is equally adaptable to ethanol measurements. Although not in the contract requirements, GGC has tested the analyzer with ethanol and found that the modulator response appears to be closely similar to that for methanol. With appropriate calibration this would make it useful for exhaust tests with gasohol or other ethanol fuel blends, and with other emission problems associated with either of the two alcohols.

With a more sensitive version of the FIA intended for ambient air monitoring, the instrument could be used for monitoring of these two alcohols in ambient air.

It may also be possible to extend the principle used here to other pollutant compounds or classes of compounds of interest to the ARB.