BASELINE DATA ON THE QUALITY OF GASOLINES IN HAWAII AND THEIR IMPLICATION IN PREPARING ALCOHOL BLENDS

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Mahalo nui loa!

PREFACE

Perhaps no single item is purchased by more people around the world, and in such massive amounts, as is gasoline. While this is no earth-shaking fact, the absence of rudimentary knowledge about the product, by the user, may well be. Aside from the fact that it is a means of providing transportation, the average purchaser knows little to nothing about its composition, its effect upon the environment, its pharmacological or toxicological impact upon man and, equally as important in the long run, its finite availability.

Efforts to minimize the impact of each of these areas have sporadically surfaced and, in certain instances, reforms have been initiated. Notable among those with lasting effect are the efforts of the Environmental Protection Agency to eliminate the use of organometallic lead as an octane enhancer. Not all the side effects of this reduction have been positive.

Substantial changes in the composition of gasoline blends have mandated upstream changes to the basic automobile engine, its compression ratio, the cleanliness or completeness of the burn, and the inclusion of exhaust gas modifiers (catalytic converters). Most changes were occasioned by the increase in volatility or vapor pressure, the doubling of the amount of aromatics, the increased use of oxygenates (alcohols and ethers) and the increase in olefins and diolefins.

The efforts of Dr. William Scheller, University of Nebraska at Lincoln, in taking the lead in the modern development of alcohol blended fuels, will probably have a longer lasting beneficial effect upon our environment, due to the elimination of environmentally degrading components from the base stock and the inclusion of ethanol with its resultant octane enhancement, than will any other single activity. The inclusion of a renewable extender to our finite fuel supply, even as little as 10%, will have long term dramatic effects upon the environment, mankind and the future availability of reasonably priced fuel.

This project, entitled "Expansion of Petroleum Products Quality Assurance Testing to Include Biomass Derived Fuel Additives and Blends," has identified the need for the constant monitoring of such a complex blend as contemporary gasoline. Money was provided by Exxon overcharge funds, which were disbursed by the Department of Business and Economic Development. The mandatory inclusion of oxygenates, with upper and lower limits, must be considered essential.

We should get on with it!

George E. Mattimoe

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INTRODUCTION

Nearly all of the motor vehicle fuel used in Hawaii is gasoline, which is used in most of the passenger cars and other light vehicles, or diesel, which is used to operate buses, trucks and other heavy vehicles. The high consumption of these petroleum fuels in the United States has been the most important factor contributing to dependence on imported crude oil. Among the alternative non-petroleum motor vehicle fuels which could be considered include gasohol (a blend of 10% ethanol and 90% gasoline), blends of methanol and gasoline, neat ethanol and methanol. Any carbonaceous material (e.g. coal, lignite, wood, wastes, and agricultural and municipal residues) can be used to produce methanol. Ethanol production through the fermentation of grains, sugar and fruits has been practiced for centuries[1,2,3,4,5]. Hawaii has been conducting studies on the utilization of alternate sources of energy for a number of years. This office has received a financial grant from the Energy Division, Hawaii State Department of Business and Economic Development, to conduct studies on gasoline as a part of alternate energy planning.

The alcohol blends (a mixture of methanol or ethanol and gasoline) can be utilized for motor vehicles designed to operate on gasoline without any engine modifications, although adjustments in carburetor and ignition timing may be required for some engines. Only specialized vehicles with high compression ratio engines can utilize neat alcohol (ethanol or methanol) fuels. Until engines suitable for utilizing neat alcohol fuels are mass produced, the use of alcohol blends as alternative motor vehicle fuel is more practical. Alcohol blends are subject to several problems: (1) phase separation (separation into water-alcohol and gasoline-alcohol layers in fuel tanks) if they are exposed to a certain amount of water. This can occur when a vehicle is not used for a long time and the fuel absorbs atmospheric water vapor. This is especially applicable to our island state; (2) compatibility of alcohols to different gasoline components; (3) vapor lock; and (4) cold starting. Even in tropical Hawaii during some December and January mornings, the temperature drops to the low sixty degrees Fahrenheit.

Gasoline is the mixture of a large number of organic solvents. Its boiling point range is approximately 90°F to 220°F. Depending on feedstock and refining processes, each of two gasolines produced at two different refineries may be of unique composition. Hawaii has two petroleum refineries. The objective of this project has been to compile baseline data on the quality of gasoline at different service stations and to determine how storage, location and change in temperature affect its quality. Both microscopic and macroscopic data should be part of this study. For example, ASTM D86 and D3710 explicitly give volatility and implicitly a probable composition of gasoline. In routine monitoring, this type of testing is useful. However, the identity and relative percent composition of a gasoline need to be known in alcohol blend studies in order to obtain information, such as latent heat of vaporization, polarity and azeotropic properties of different components. Knowledge of gross properties of gasoline, such as Reid vapor pressure, water, and API gravity, are helpful also in preparing a proper alcohol gasoline blend.

A gas chromatograph-mass spectrophotometer (GC-MS) was utilized to identify all the major components of gasoline. Later, a GC equipped with flame ionization detector (FID) was used to quantitate these compounds. Polar additives, such as anti-oxidants and anti-corrosion agents, were identified also by GC-MS. Samples were analyzed for water by the Karl Fischer method, Reid vapor pressure by the bomb method, and API gravity by the hydrometer method. An unleaded, regular, 87 octane gasoline was chosen for this study. Initially, four service stations were selected for sample collection studies. Later, 16 other service stations were added to this list. Samples were collected from April through August, 1989.

EXPERIMENTAL SECTION

Collection of Sample. Four different service stations were selected to study for any difference in gasoline composition between the bottom and top portions of the gasoline tank. Later, the gasoline was sampled from a pump, which had just previously pumped five gallons to remove any residual gasoline which might have been trapped in the pumping system. The collected sample was filled to the top of a one-litre Nalge bottle and screw capped immediately. This was placed in an ice chest and transported to the laboratory, where it was stored in a refrigerator until analysis. When it was learned that the gasoline composition of samples taken from the top and bottom of a gasoline tank and from the pump were identical, all samples for this study were obtained from the gasoline pump. The sampling site was selected on the basis of accessibility.

Temperature of Sample. The temperature of gasoline samples taken from top and bottom portions of a gasoline tank were comparable to a sample obtained from a pump which had previously delivered five gallons. Thus, the temperature of the gasoline sample was recorded from the sample obtained from a pump which previously had pumped five gallons.

Storage of GC-MS and GC Sample. A one-litre Nalge bottle containing gasoline was transferred from the refrigerator to an ice chest and cooled to approximately 0°C. After vigorously shaking the bottle, approximately one mL of the sample was transferred into a one mL Hyperseal vial, which was immediately capped with Dura-Bond seal. No head space was apparent in the sample. This was stored in a freezer. Approximately 100 mL were later transferred into a flask to be used for the Karl Fischer determination of dissolved water in gasoline. The remaining portion of the sample was returned to the ice chest.

Reid Vapor Pressure. ASTM method D323[6] was used to measure the Reid vapor pressure. A mercury manometer was constructed in the laboratory. This was used to check the calibration of the meter which is attached to the Reid vapor pressure bomb. A Reid vapor pressure bomb, meeting the specification of ASTM D323, was purchased from Hawaii Chemical and Scientific Company. A one-litre Nalge bottle containing approximately 800 mL was removed from the ice chest, where it had been cooling, shaken vigorously 40-50 times and returned to the ice chest. This procedure was repeated three times. The open gasoline chamber of the bomb was immersed in an ice-water bath for 15-20 minutes. The air chamber and the gauge were purged with a stream of air. Later, the air chamber, together with the gauge, was immersed in 100°F water bath for approximately 15-20 minutes. Then, the gasoline chamber was removed from the water-ice bath and, as much as possible, the water removed. A chilled gasoline sample was transferred from the Nalge bottle into the gasoline chamber and was immediately screw-connected to the air chamber and shaken 40-50 times. Later, the bomb was placed in a 100°F water bath. The bomb was shaken three additional times, each consisting of 50 shakes. The Reid vapor pressure was then measured.

Determination of Dissolved Water. Before starting the analysis for dissolved water, each sample was checked for the presence of free water or any appearance of cloudiness. Following the ASTM D1744 method[7], a 50 mL portion of the gasoline sample at 60°F was transferred into a Karl Fischer (KF) titrating apparatus. After noting that the sample was being mixed adequately by a magnetic stirrer, it was titrated with the KF titrant. The endpoint of the titration was observed by reading the coulometric meter, which was connected to a pair of platinum electrodes. Before analyzing a sample, the water equivalent of KF reagent was determined. The weight of gasoline analyte was calculated from specific gravity and volume of the sample.

API Gravity. This measurement was based on the ASTM method D1298[8]. A gasoline sample was placed in a glass cylinder and its temperature was brought to 60°F in a water bath. A glass hydrometer graduated to cover the API range of the sample was used to determine the API values.

GC-MS and GC Analyses. A Hewlett-Packard (HP) model 5890 GC was interfaced to another HP model 5970 MSD mass spectrometer. This MS had an electron-impact (EI) source and a quadrupole mass analyzer. The HP model 5860 GC was equipped with FID. An HP model 300, chem-station computer, which was accessed to HP models 7946 and 9133 disc drives, controlled both the MS and the GC, respectively. High resolution PONA capillary columns, 50 m x 0.2 mm x 0.5 μm, which had been coated with crosslinked methyl silicone, were each connected to a separate injection port and connected to either the MS or the GC-FID. The head pressure was set at 135 psi and the flow rate was set at 33 mL/min. The GC was set at 1:50 split-mode. Both injection port temperatures were set at 250°C and the FID was set at 250°C, also. The oven temperature of the GC was initially set at 35°C and was ramped at 10°C/min. The final temperature of the oven was set at 250°C and was maintained for 15 minutes. The GC-MS interface temperature was maintained at 260°C. The MS was tuned with perfluorotributylamine prior to the beginning of each analysis. A 0.2 μL gasoline sample, contained in a sealed hypovial, was injected into the GC for both GC-MS and GC analysis. Both qualitative and quantitative calibration mixtures referred in ASTM method D3710[9], a simulated distillation technique were periodically injected into the GC to check the performance of the capillary columns. These mixtures were obtained from Supelco. It was found that as the PONA column deteriorates, the resolution of 2,3-dimethylbutane/2-methylpentane, methylcyclopentane/benzene, and toluene/2-methylheptane peaks in the chromatogram fails. Monitoring of these peaks was used as part of the quality assurance aspect of this study.

Mass Spectral Interpretation. Most unknown mass spectra were identified either through comparison of the analyte spectra with NBS mass spectral library stored in the MS computer or mass spectra of injected standard compound. However, the identification of all the major components of a gasoline sample by a unit resolution EI MS, which is interfaced to a GC, is not feasible. Many early eluting components do not have sufficiently distinguishing mass spectral characteristics for unequivocal identification. A double bond in number of olefins are known to shift in a GC-MS analysis. Depending on the analyte, sometimes it is difficult to differentiate a double bond from a cyclic structure. Many isomers of aromatic compounds have identical or similar mass spectra. Therefore, other characteristics, such as boiling points, relative retention data and chromatographic properties, also were used in the identification of some components.

GC Quantitation. The integration of chromatographic peaks and their relative percentage compositions were performed by the GC computer. Based on Ettre's article[10], the relative responses of gasoline components in GC-FID were considered to be approximately equal. Components were divided and added into aliphatics, olefin+cyclics, and aromatic groups.

Isolation and Preconcentration of Gasoline Additives. A method developed by Youngless et al[11] was used to isolate and preconcentrate the gasoline additives. Three grams of Kieselgel 60G were packed into a chromatographic glass column, which had been packed previously with a small portion of glass wool. Approximately two grams of sodium sulfate were added on the Kieselgel 60G. A 100 mL gasoline sample was transferred into this column. After all the gasoline portion had passed through this column, two 50 mL portions of hexane were used to wash the column. Then, two 25 mL portions of methanol were used to elute the sample from the column. This eluate was transferred into a 125 mL separatory funnel, which had 10 mL of hexane. After liquid-liquid partitioning, the methanol portion was centrifuged and concentrated in boiling water. This extract was injected into the GC-MS for identification.

g. 1 Map of Oahu

Fig. 1.
Locations of Service Stations

Table I. Dissolved Water in Gasoline (ppm)

Service	Sample Collection Date												
Stations	5/1/89	5/12/89	5/19/89	5/26/89	6/2/89	6/9/89	6/16/89	6/23/89	7/7/89	7/14/89	7/19/89	7/28/89	8/4/89
A		230				240				120			
B		410				280				270			
C				280				380				210	
D				580				320				140	
E				390				450				310	
F				560				280				140	
G		390				160				150			
H		460				520				270			
I	390		160		490		130	180			230		
J		460				320				250			
K	410		280		380		300		300				
L	320		100		240		160		220		200		120
M		460				530		560		260			
N	460		610		320		520		120		350		340
0	360		430		390		350		390		320		240
P	430		570				570		150		210		260
Q		170		540	280								
R		240				350				220			
S				520				530				160	
T				540				320		270			

Table II. Reid Vapor Pressure (psi)

Service Stations	Sample Collection Date 5/1/89	5/12/89	5/19/89	5/26/89	6/2/89	6/9/89	6/16/89	6/23/89	7/7/89	7/14/89	7/19/89	7/28/89	8/4/89
A		11.2				10.6				10.8			
B		11.4				10.2				10.4			
C				11.1				10.9				10.4	
D				10.0				9.8				10.2	
E				10.0				9.8				9.7	
F				10.0				11.1				9.9	
G		10.4				10.6				10.2			
H		10.8				10.6				9.8			
I	10.8		11.0		10.6		11.2	10.8			9.8		
J		10.4				10.4				10.6			
K	10.6		10.8		11.2		10.8		11.0				
L	10.8		10.4		10.2		10.4		10.6		10.8		9.8
M		10.4				10.8		11.3		10.4			
N	11.4		10.8		10.4		10.2		10.2		9.8		9.7
O	10.8		11.2		11.4		11.0		11.4		10.9		10.6
P	10.2		10.6				10.8		10.4		9.8		9.8
Q		11.4		10.9	11.2								
R		11.4				10.4				10.2			
S				11.4				11.0				10.8	
T				10.9				11.2		11.0			

Table III. API Gravity

Service Stations	Sample Collection Date												
	5/1/89	5/12/89	5/19/89	5/26/89	6/2/89	6/9/89	6/16/89	6/23/89	7/7/89	7/14/89	7/19/89	7/28/89	8/4/89
A		57.20				57.55				57.35			
B		57.20				57.60				58.25			
C				56.85				56.25				57.85	
D				62.80				62.55				64.35	
E				63.75				62.75				63.75	
F				63.45				62.85				63.55	
G		63.00				63.10				63.65			
H		62.55				62.95				63.15			
I	62.85		62.90		63.45		63.35	63.85			63.95		
J		62.90				63.35				63.95			
K	56.20		56.50		57.75		57.25		56.25				
L	62.10		63.10		60.75		60.30		63.15		63.50		64.90
M		57.95				57.65		55.95		54.35			
N	62.80		62.50		63.35		63.50		64.20		63.20		63.95
O	55.60		56.60		56.85		56.75		56.75		56.65		57.30
P	63.40		63.40				63.20		63.95		63.20		63.95
Q		57.15		57.85	57.90								
R		63.00				63.45				63.45			
S				57.95				55.95				58.45	
T				57.85				55.75		57.90			

Table IV. The Effect of Sampling on the Aliphatics, Olefin+Cyclics, and Aromatics Ratio of Gasoline*

Service Stations	TOP			BOTTOM			PUMP		
	A	B	C	A	B	C	A	B	C
L	37.6	23.1	25.0	37.6	23.8	25.8	37.0	23.8	25.6
O	40.7	21.2	25.5	40.7	20.8	25.9	41.1	21.6	24.8
P	39.5	4.7	49.4	39.8	4.9	50.3	39.8	4.9	48.8
Q	41.3	21.2	22.1	40.7	21.7	23.6	41.4	22.5	20.8

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*A=aliphatics; B=Olefins+Cyclics; C=Aromaticas. These are total composition in percent (%). All values less than .5 % were not included in this calculation. Top and bottom refer to the top and bottom portion of the gasoline tank respectively. Pump refers to the gasoline pump .

Table V-1. General and Composition Data

Service Station:	"A"
Location:	Kaimuki
Material of the Tank:	Steel
Age of the Tank:	14 years
Total Capacity:	5000 gal.
Frequency of Delivery:	10 days

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	3 days	3 days	3 days
Volume of Gasoline Remaining in Tank:	3600 gal.	3200 gal.	3500 gal.
Temperature of Gasoline:	84° F	86° F	88° F
Aliphatics:	35.3 %	37.9 %	36.6 %
Olefins+Cyclics	8.2 %	6.4 %	7.0 %
Aromatics:	50.7 %	49.3 %	50.3 %
Other Components below .5 percent:	5.8 %	6.4 %	6.4 %

Table V-2. General and Composition Data

Service Station	"B"		
Location:	Kailua		
Material of the Tank:	Steel		
Age of the Tank:	10 years		
Total Capacity:	6500 gal.		
Frequency of Delivery:	3 days		

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	3 days	3 days	3 days
Volume of Gasoline Remaining in Tank:	6350 gal.	1000 gal.	4800 gal.
Temperature of Gasoline:	80° F	84° F	86° F
Aliphatics:	36.6 %	38.8 %	38.5 %
Olefins+Cyclics:	7.5 %	6.5 %	7.0 %
Aromatics:	50.5 %	49.2 %	48.2 %
Other Componenets below .5 percent	5.4 %	5.5 %	6.3 %

Table V-3 General and Composition Data

Service Station:	"C"
Location:	Ewa
Material of the Tank:	Steel
Age of the Tank:	25 years
Total Capacity:	7000 gal.
Frequency of Delivery:	3-4 days

	Sampling Date		
	5/26/89	6/23/89	7/28/89
Interval between Delivery and Sample Collection:	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank	5500 gal.	6200 gal.	4000 gal.
Temperature of Gasoline	86° F	89° F	87° F
Aliphatics:	--	38.7 %	45.8 %
Olefins+Cyclics:	--	6.4 %	6.7 %
Aromatics:	--	48.8 %	41.8 %
Other Components below .5 percent:	--	6.1 %	6.4 %

Table V-4. General and Composition Data

Service Station:	"D"		
Location:	Mililani		
Material of the Tank:	Fiberglass		
Age of the Tank:	3 years		
Total Capacity:	10000 gal.		
Frequency of Delivery:	5 x per week		
		Sampling Date	
Interval between Delivery	5/6/89	6/23/89	7/28/89
and Sample Collection:	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank:	6400 gal.	5300 gal.	7000 gal.
Temperature of Gasoline:	85° F	86° F	89° F
Aliphatics:	34.1 %	38.5 %	41.0 %
Olefins+Cyclics:	26.5 %	25.2 %	22.5 %
Aromatics:	25.7 %	27.8 %	26.5 %
Other Components below .5 percent:	13.7 %	8.5 %	10.0 %

Table V-5. General and Composition Data

Service Station:	"E"
Location:	Ewa
Material of the Tank:	Fiberglass
Age of the Tank:	7 years
Total Capacity:	10000 gal.
Frequency of Delivery:	3 days

	Sampling Date		
	5/26/89	6/23/89	7/28/89
Interval between Delivery and Sample Collection:	1 day	2 days	1 day
Volume of Gasoline Remaining in Tank:	6900 gal.	6500 gal.	7700 gal.
Temperature of Gasoline:	89° F	91° F	90° F
Aliphatics:	32.3 %	34.3 %	33.8 %
Olefins + Cyclics:	20.2 %	24.6 %	29.2 %
Aromatics:	36.3 %	28.7 %	26.2 %
Other Components below .5 percent:	11.4 %	12.4 %	10.8 %

Table V-6. General and Composition Data

Service Station:	"F"
Location:	Aiea
Material of the Tank:	Steel
Age of the Tank:	30 years
Total Capacity:	4000 gal.
Frequency of Delivery:	4 days

	Sampling Date		
	5/26/89	6/23/89	7/28/89
Interval between Delivery and Sample collection:	2 days	2 days	1 day
Volume of Gasoline Remaining in Tank:	2300 gal.	2600 gal.	3500 gal.
Temperature of Gasoline:	86° F	87° F	87° F
Aliphatics:	36.2	34.6	37.2
Olefins+Cyclics:	28.9	24.4	23.0
Aromatics:	23.3	30.2	26.1
Other Components below .5 percent:	11.5	10.8	13.9

Table V-7. General and Composition Data

Service Station:	"G"
Location:	Kailua
Material of the Tank:	Fiberglass
Age of the Tank:	3 years
Total Capacity:	10000 gal.
Frequency of Delivery:	3 days

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	3 days	1 day	2 days
Volume of Gasoline Remaining in Tank:	5100 gal.	8500 gal.	7800 gal.
Temperature of Gasoline:	83° F	87° F	86° F
Aliphatics:	34.7 %	35.4 %	37.1 %
Olefins+Cyclics:	25.3 %	24.3 %	27.9 %
Aromatics:	28.7 %	27.4 %	26.4 %
Other Components below .5 percent:	11.3 %	12.9 %	8.6 %

Table V-8. General and Composition Data

Service Station:	"H"		
Location:	Kaimuki		
Material of the Tank:	Fiberglass		
Age of the Tank:	5 years		
Total Capacity:	10000 gal.		
Frequency of Delivery:	2-3 days		
		Sampling Date	
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	2 days	1 day	2 days
Volume of Gasoline Remaining in Tank:	3300 gal.	3400 gal.	1600 gal.
Temperature of Gasoline:	85° F	87° F	89° F
Aliphatics:	36.1 %	32.6 %	37.2 %
Olefins+Cyclics:	23.1 %	21.0 %	24.2 %
Aromatics:	29.1 %	34.0 %	28.3 %
Other Components below .5 percent	11.7 %	12.4 %	10.3 %

Table V-9. General and Composition Data

Service Station: "I"
Location: Manoa
Material of the Tank: Fiberglass
Age of the Tank: 7 years
Total Capacity: 10000 gal.
Frequency of Delivery 3-4 days.

	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/16/89
Interval between Delivery and Sample Collection:	4 days	3 days	0 day	3 days	2 days	4 days
Volume of Gasoline Remaining in Tank:	--	5300 gal.	6800 gal.	5000 gal.	7000 gal.	5000 gal.
Temperature of Gasoline:	81° F	82° F	85° F	85° F	87° F	87° F
Aliphatics:	33.9 %	35.4 %	33.9 %	37.6 %	34.7 %	37.8 %
Olefins+Cyclics:	21.6 %	23.4 %	21.2 %	26.7 %	22.7 %	22.4 %
Aromatics:	30.7 %	29.1 %	35.2 %	23.8 %	25.8 %	26.8 %
Other Components below .5 percent	13.8 %	12.1 %	9.7 %	12.9 %	16.3 %	13.0 %

Table V-10. General and Composition Data

Service Station: "J"
Location: Kaneohe
Material of the Tank: Fiberglass
Age of the Tank: 5 years
Total Capacity: 10000 gal.
Frequency of Delivery: 3-4 days

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	1 day	3 days	1 day
Volume of Gasoline Remaining in Tank:	3200 gal.	3400 gal.	6800 gal.
Temperature of Gasoline:	84° F	85° F	86° F
Aliphatics:	34.3 %	36.3 %	35.1 %
Olefins+Cyclics:	27.4 %	23.1 %	27.2 %
Aromatics:	24.1 %	30.7 %	30.5 %
Other Components below .5 percent:	14.2 %	9.9 %	7.2 %

Table V-11. General and Composition Data

Service Station: "K"
Location: Manoa
Material of the Tank: Steel
Age of the Tank: 14 years
Total Capacity: 5000 gal.
Frequency of Delivery: 10 days

	Sampling Date					
	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/19/89
Interval between Delivery and Sample Collection:	4 days	5 days	21 days	17 days	5 days	--
Volume of Gasoline Remaining in Tank:	--	2400 gal.	--	2800 gal.	3900 gal.	--
Temprature of Gasoline:	79° F	83° F	84° F	82° F	84° F	
Aliphatics:	39.9 %	38.8 %	41.6 %	44.5 %	41.6 %	40.1 %
Olefins+Cyclics:	1.5 %	2.9 %	3.7 %	3.5 %	2.5 %	2.8 %
Aromatics:	54.6 %	53.6 %	49.4 %	46.4 %	48.5 %	51.0 %
Other components below .5 percent:	4.0 %	4.7 %	5.3 %	5.6 %	7.4 %	6.1 %

Table V-12. General and Composition Data

Service Station: "L"
Location: Kalihi
Material of the Tank: Steel
Age of the Tank: 10 years
Total Capacity 10000 gal.
Frequency of Delivery: 2 days

	Sampling Data						
	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/19/89	8/4/89
Interval between Delivery and Sample Collection:	0 day	0 day	1 day	0 day	0 day	2 days	0 day
Volume of Gasoline Remaining in Tank:	--	5000 gal.	500 gal.	6500 gal.	4800 gal.	6000 gal.	5700 gal.
Temperature of Gasoline:	83°F	83° F	86° F	86° F	89° F	88° F	87°F
Aliphatics:	38.1 %	37.3 %	37.2 %	41.2 %	36.1 %	36.6 %	34.2 %
Olefins+Cyclics:	23.4 %	23.8 %	18.6 %	9.2 %	18.6 %	25.1 %	8.8 %
Aromatics:	26.7 %	26.8 %	37.6 %	37.5 %	24.3 %	35.9 %	44.6 %
Other Components below .5 percent:	11.8 %	12.1 %	11.1 %	12.1 %	21.0 %	12.4 %	12.4 %

Table V-13. General and Composition Data

Service Station: "M"
Location: Hawaii Kai (Koko Head)
Tank Material: Fiberglass
Age of Tank: 5 years
Total Capacity: 8000 gal.
Frequency of Delivery: 2 days

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank:	3200 gal.	4200 gal.	4000 gal.
Temperature of Gasoline:	---	84° F	86° F
Aliphatics:	41.2 %	40.7 %	41.3 %
Olefins+Cyclics	5.4 %	3.5 %	4.7 %
Aromatics:	49.5 %	47.8 %	50.8 %
Other Components below .5 percent:	3.9 %	8.0 %	8.0 %

Table V-14. General and Composition Data

Service Station: "N"
Location: Punahou/Kaimuki
Material of the Tank: --
Age of the Tank: --
Total Capacity: --
Frequency of Delivery: --

	Sampling Date						
	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/19/89	8/4/89
Interval between Delivery and Sample Collection:	3 days	2 days	2 days	2 days	3 days	1 day	2 days
Volume of Gasoline	--	6700 gal.	4900 gal.	3900 gal.	2600 gal.	6000 gal.	5200 gal.
Remaining in Tank:	--	6700 gal.	4900 gal.	3900 gal.	2600 gal.	6000 gal.	5200 gal.
Temperature of Gasoline:	82° F	86° F	89° F	90° F	90° F	89° F	89° F
Aliphatics:	30.6 %	32.0 %	30.0 %	36.3 %	37.9 %	36.8 %	36.4 %
Olefins+Cyclics:	33.7 %	23.0 %	26.7 %	27.3 %	26.8 %	28.0 %	29.4 %
Aromatics:	28.3 %	31.7 %	29.8 %	25.2 %	25.1 %	24.5 %	23.9 %
Other Components below .5 percent:	7.4 %	13.3 %	13.5 %	11.2 %	10.2 %	10.7 %	10.3 %

Table V-15. General and Composition Data

Service Station: "O"

Location: Kalihi

Material of the Tank: Steel

Age of the Tank: 21 years

Total Capacity: 10000 gal.

Frequency of Delivery: 3 days

	Sampling Date						
	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/19/89	8/4/89
Interval between Delivery and Sample Collection:	3 days	2 days	1 day	2 days	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank:	—	2600 gal.	6600 gal.	4800 gal.	6800 gal.	6000 gal.	5900 gal.
Temperature of Gasoline:	83° F	85° F	85° F	86° F	86° F	86° F	85° F
Aliphatics:	37.8 %	39.0 %	38.4 %	40.0 %	40.3 %	40.6 %	40.8 %
Olefins+Cyclics:	7.8 %	4.8 %	10.9 %	4.3 %	3.8 %	4.8 %	3.6 %
Aromatics:	49.5 %	49.0 %	47.9 %	49.5 %	49.4 %	50.3 %	49.5 %
Other Components below .5 percent:	4.9 %	7.2 %	2.8 %	6.2 %	6.5 %	4.3 %	6.1 %

Table V-16. General and Composition Data

Service Station:	"P"
Location:	Alakea/Punahou
Material of the Tank:	--
Age of the Tank:	--
Total Capacity:	--
Frequency of Delivery:	5 days

	Sampling Date						
	5/1/89	5/19/89	6/2/89	6/16/89	7/7/89	7/19/89	8/4/89
Interval between Delivery and Sample Collection:	3 days	2 days	1 day	2 days	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank:	--	2500 gal.	3300 gal.	3000 gal.	--	2100 gal.	3400 gal.
Temperature of Gasoline:	81° F	85° F	84° F	84° F	--	86° F	86° F
Aliphatics:	29.3 %	35.4 %	35.5 %	34.2 %	36.6 %	35.3 %	34.8 %
Olefins+Cyclics:	35.8 %	25.0 %	25.2 %	25.9 %	25.3 %	25.8 %	29.2 %
Aromatics:	20.4 %	25.4 %	25.7 %	25.6 %	25.6 %	24.8 %	22.6 %
Other Components below .5 percent:	14.5 %	14.2 %	13.6 %	14.2 %	12.5 %	14.1 %	13.4 %

Table V-17. General and Composition Data

Service Station: "Q"
Location: Kaneohe
Material of the Tank: Fiberglass
Age of the Tank: 3 years
Total Capacity: 10000 gal.
Frequency of Delivery: 5 days

		Sampling Date	
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	1 day	1 day	1 day
Volume of Gasoline Remaining in Tank:	7600 gal.	7600 gal.	7600 gal
Temperature of Gasoline:	82° F	84° F	86° F
Aliphatics:	37.3 %	37.3 %	37.0 %
Olefins+Cyclics:	8.0 %	7.0 %	7.3 %
Aromatics:	49.0 %	50.6 %	49.4 %
Other Components below .5 percent	5.7 %	5.4 %	6.3 %

Table V-18. General and Composition Data

Service Station:	"R"
Location:	Kokohead(Hawaii Kai)
Material of the Tank:	--
Age of the Tank:	7 years
Total Capacity:	10000 gal.
Frequency of Delivery:	--

	Sampling Date		
	5/12/89	6/9/89	7/14/89
Interval between Delivery and Sample Collection:	--	--	--
Volume of Gasoline Remaining in Tank:	5000 gal.	7000 gal.	4600 gal.
Temperature of Gasoline:	83° F	--	--
Aliphatics:	35.2 %	37.7 %	35.3 %
Olefins+Cyclics:	26.2 %	24.9 %	24.9 %
Aromatics:	24.7 %	24.7 %	27.2 %
Other Components below .5 percent:	13.9 %	12.7 %	12.6 %

Table V-19. General and Composition Data

Service Station: "S"
Location: Pearl City
Material of the Tank: Fiberglass
Age of the Tank: 3 years
Total Capacity: 10000 gal.
Frequency of Delivery: Daily

	Sampling Date		
	5/26/89	6/23/89	7/28/89
Interval between Delivery and Sample Collection:	0 day	0 day	0 day
Volume of Gasoline Remaining in Tank:	7300 gal.	8000 gal.	7700 gal.
Temperature of Gasoline:	84°F	85°F	84°F
Aliphatics:	40.0 %	38.9 %	44.1 %
Olefins+Cyclics:	3.8 %	4.3 %	3.2 %
Aromatics:	48.2 %	51.8 %	48.2 %
Other Components below .5 percent:	8.0 %	5.0 %	4.5 %

Table V-20. General and Composition Data

Service Station: "T"
Location: Mililani
Material of the Tank: Steel
Age of the Tank: 15 years
Total Capacity: 10000 gal.
Frequency of Delivery: Daily

	Sampling Date		
Interval between Delivery	5/26/89	6/23/89	7/28/89
and Sample Collection:	0 day	0 day	0 day
Volume of Gasoline Remaining in Tank:	7800 gal.	6500 gal.	5000 gal.
Temperature of Gasoline:	85° F	87° F	86° F
Aliphatics:	33.3 %	36.2 %	41.1 %
Olefins+Cyclics:	9.3 %	7.0 %	6.4 %
Aromatics:	52.9 %	51.8 %	51.7 %
Other Components below .5 percent:	4.5 %	5.0 %	.8 %

Table VI-1. Major Components of Shell Gasoline

Component	Composition (%)
2-methylpropane	.54
butane	2.80
2-methylbutane	13.53
pentane	8.17
2-methylpentane	.70
3-methylpentane	3.69
hexane	2.04
methylcyclobutane	2.72
methylcyclopentane	2.00
benzene	4.14
cyclohexane	.86
2-methylhexane	1.34
3-methylhexane	1.48
heptane	1.34
methylcyclohexane	1.37
toluene	21.08
2-methylheptane	.64
3-methylheptane	.50
1,3-dimethylcyclohexane	.51
octane	.64
ethylbenzene	2.65
1,3-dimethylbenzene	12.80
1,2-dimethylbenzene	4.21
1-ethyl-2-methylbenzene	1.71
1-ethyl-4-methylbenzene	.76
1,3,5-trimethylbenzene	2.09

Table VI-2. Major Components of Union 76 Gasoline

Components	Composition (%)
butane	1.84
2-methylbutane	10.14
1-pentene or ethylcyclopropane	.65
pentane	4.43
2-pentene (cis/trans) or 1,2-dimethylcyclopropane	.64
2-methyl-2-butene (cis/trans)	1.27
cyclopentene	1.38
2-methylpentane	4.07
hexane	2.37
3-methylpentane	2.61
methylcyclopentane	1.63
4-methylcyclopentene	.52
benzene	2.56
cyclohexane	.72
2-methylhexane	1.65
2,3-dimethylpentane	.65
3-methylhexane	1.68
1,3-dimethylcyclopentane	.51
1,2-dimethylcyclopentane	1.09
heptane	1.80
methylcyclohexane	1.48
2,4-dimethylhexane	.53
2,3,4-trimethylpentane	.57
toluene	13.56
2-methylheptane	.89
3-methylheptane	.72
octane	.72
ethylbenzene	2.44
1,3-dimethylbenzene	11.77
1,2-dimethylbenzene	4.11
1-ethyl-3-methylbenzene	2.61
1,3,5-trimethylbenzene	1.28
1,2,3-trimethylbenzene	.58
1,2,4-trimethylbenzene	3.37
1-methyl-3-propylbenzene	.71
2-ethyl-1,4-dimethylbenzene	.54
1,2,3,5-tetramethylbenezene	.50
naphthalene	.61

Table VI-3. Major Components of Union 76 Gasoline

Components	Composition (%)
n-butane	2.07
2-methylbutane	12.38
1-pentene or ethyl cyclopropane	.76
3-methyl-1-butene	2.22
pentane	2.25
2-methyl-1-butene	2.17
2-pentene(cis/trans)	1.20
2-methyl-2-butene(cis/trans)	4.44
2,3-dimethylbutane	1.98
2-methylpentane	5.69
hexane	3.31
2-methyl-1-pentene	.92
3-methylpentane	2.16
3-hexene(cis/trans)	.82
4-methyl-2-pentene(cis/trans)	1.10
3-methyl-2-pentene(cis/trans)	.80
2-hexene(cis/trans)	1.06
methylcyclopentane	2.36
4-methylcyclopentene	.57
benzene	.81
2-methylhexane	2.19
2,3-dimethylpentane	.76
3-methylhexane	1.82
1,3-dimethylcyclopentane	.68
1,2-dimethylcyclopentane	.64
heptane	1.05
2-methylhexane	1.23
3-methylhexane	.92
2-methylhexene	1.31
2,4-dimethylhexane	.63
2,3,4-trimethylpentane	.88
toluene	4.93
2-methylheptane	1.15
3-metkylheptane	.93
octane	.53
ethylbenzene	.99
1,3-dimethylbenzene	5.98
1,2-dimethylbenzene	1.95
1-ethyl-2-methylbenzene	1.59
1,3,5-trimethylbenzene	.98
1,2,4-trimethylbenzene	3.01
1-ethyl-3-methylbenzene	.68
1-methyl-3-(1-methyl-ethyl)benzene	.82
1-methyl-2-(1-methyl-ethyl)benzene	.57
1,2,3,5-tetramethylbenzene	.54
1,2,3,4-tetramethylbenzene	.89
2,3-dihydro-4-methyl-1 H Indene	.86
naphthalene	.96

Table VI-4 Major Components of Chevron Gasoline

Components	Composition (%)
isopropane	1.12
n-butane	.56
2-butene (cis/trans)	.60
2-methylbutane	12.05
1-pentene or ethylcyclopropane	2.26
pentane	2.43
2-pentene (cis/trans) or 1,2-dimethylcyclopropane	2.29
2-methyl-2-butene (cis/trans)	1.25
2-methyl-2-butene (cis/trans)	4.60
cyclopentene	1.50
3-methyl-1-pentene	6.22
hexane	3.32
2-methylpentane	.97
3-methylpentane	2.10
2-methyl-1-pentene	.88
3-methyl-1-pentene	1.15
3-hexene (cis/trans)	.85
4-methyl-2-pentene	.51
2-hexene (cis/trans)	1.10
3-methyl-2-pentene (cis/trans)	2.48
methyl cyclopentane	.68
benzene	.89
cyclohexane	2.21
2-methylhexane	.65
2,3-dimethylpentane	1.87
3-methylhexane	.69
1,3-dimethylcyclopentane	.71
1,2-dimethylcyclopentane	.69
heptane	1.01
methylcyclohexane	1.06
2,3,4-trimethylpentane	1.36
toluene	4.90
2-methylheptane	1.25
3-methylheptane	.90
1,2-dimethylcyclohexane	.50
octane	.61
ethylbenzene	.93
1,3-dimethylbenzene	5.68
1,2-dimethylbenzene	1.90
1-ethyl-3-methylbenzene	2.07
1,3,5-trimethylbenzene	.89
1,2,3-trimethylbenzene	2.87
1,2,4-trimethylbenzene	.63
1-methyl-3-propylbenzene	.54
2-ethyl-1,4-dimethylbenzene	.84
1,2,3,5-tetramethylbenzene	.57
2,3-dihydro-5-methyl-1H-Indene	.56
naphthalene	1.19
2-methylnapthalene	.52

Table VI-5. Major Components of 7-11 Gasoline

Components	Composition (%)
n-butane	2.36
2-methylbutane	10.80
pentane	6.62
2-methylpentane	.63
3-methylpentane	4.21
hexane	2.09
methylcyclobutane	2.72
methylcyclopentane	2.12
benzene	3.83
2-methylhexane	.93
2,3-dimethylpentane	1.80
3-methylhexane	2.08
heptane	1.75
toluene	21.60
2-methylheptane	.87
3-methylheptane	.70
octane	.53
ethylbenzene	2.83
1,3-dimethylbenzene	14.10
1,2-dimethylbenzene	4.60
1-ethyl-4-methylbenzene	1.25
1-ethyl-2-methylbenzene	.83
1,3,5-trimethylbenzene	2.31

Table VI-6. Major Components of Aloha Petroleum Gasoline

Components	Composition (%)
n-butane	1.23
butene	2.35
2-methylbutane	11.86
pentane	6.86
methylcyclobutane	.52
2-methylpentane	4.06
hexane	2.23
2-methylpentane	2.88
methylcyclopentane	2.01
benzene	3.76
cyclohexane	.78
2-methylhexane	1.78
2,3-dimethylpentane	.56
3-methylhexane	2.07
heptane	1.87
methylcyclohexane	1.35
toluene	20.93
2-methylheptane	.79
3-methylheptane	.69
octane	.73
ethylbenzene	2.81
1,3-dimethylbenzene	13.99
1,2-dimethylbenzene	4.79
1-ethyl-4-methylbenzene	1.46
1-ethyl-2-methylbenzene	.68
1,3,5-trimethylbenzene	2.08

Table VI-7. Major Components of Circle-K Gasoline

Components	Composition (%)
n-butane	.85
butene	1.96
2-methylbutane	10.21
pentane	4.89
2-methylpentane	3.96
hexane	1.85
3-methylpentane	2.46
methylcyclopentane	1.77
benzene	3.25
2-methylhexane	2.35
2,3-dimethylpentane	.53
3-methylhexane	1.88
heptane	.50
methylcyclobutane	1.84
toluene	20.84
2-methylheptane	.67
3-methylheptane	.54
1,3-dimethylcyclohexane	1.01
ethylbenzene	3.37
1,3-dimethylbenzene	15.86
1,2-dimethylbenzene	5.52
1-ethyl-2-methylbenzene	2.58
1-ethyl-3-methylbenzene	1.03
1,3,5-trimethylbenzene	1.08

Table VI-8. Major Components of Gas Express Gasoline

Components	Composition (%)
isopropane	1.28
butane	3.20
2-methylbutane	13.68
pentane	6.71
2-methylpentane	4.63
hexane	2.11
3-methylpentane	2.91
methylcyclopentane	1.98
benzene	3.81
2-methylhexane	2.44
2,3-dimethylpentane	.52
3-methylhexane	1.87
heptane	1.77
methylcyclohexane	1.53
toluene	19.68
2-methylheptane	.54
3-methylheptane	.79
octane	1.35
ethylbenzene	2.78
1,3-dimethylbenzene	12.73
1,2-dimethylbenzene	4.42
1-ethyl-4-methylbenzene	1.89
1-ethyl-2-methylbenzene	.74
1,3,5-trimethylbenzene	2.17

Table VI-9. Major Components of Texaco Gasoline

Components	Composition (%)
n-butane	2.69
2-butene(cis/trans)	.59
2-methylbutane	11.63
1-pentene or ethylcyclopropane	.63
2-methylbutene	1.86
pentane	2.00
2-pentene(cis/trans) or 1,2-dimethylcyclopropane	1.85
2-methyl-2-butene(cis/trans)	.99
2-methyl-2-butene(cis/trans)	3.75
2,3-dimethylbutane	.91
2-methylpentane	6.62
hexane	2.90
2-methylpentane	.74
3-methylpentane	2.08
2-methyl-1-pentene	1.64
3-methyl-1-pentene	.63
3-hexene(cis/trans)	.92
4-methyl-2-pentene	2.28
2-hexene(cis/trans)	.57
3-methyl-2-pentene(cis/trans)	.97
methylcyclopentane	2.47
benzene	.64
2-methylhexane	1.78
2,3-dimethylpentane	.87
3-methylhexane	1.57
1,4-dimethylcyclopentane	.87
1,3-dimethylcyclopentane	1.57
1,2,-dimethylcyclopentane	1.78
heptane	1.28
methylcyclohexane	1.81
2,3,4-trimethylpentane	.89
toluene	5.81
2-methylheptane	1.05
3-methylheptane	.75
octane	1.33
ethylbenzene	.95
1,3-dimethylbenzene	5.42
1,2-dimethylbenzene	1.80
1-ethyl-3-methylbenzene	2.23
1,3,5-trimethylbenzene	.88
1,2,3-trimethylbenzene	2.65
1,2,4-trimethylbenzene	.60
2-ethyl-1,4-dimethylbenzene	.72
1,3-diethylbenzene	.68
naphthalene	.79
methylnaphthalene	.94

Table VI-10. Major Components of Fastop Gasoline

Component	Composition(%)
n-butane	1.13
butene	2.81
2-methylbutane	12.12
pentane	5.82
2-methylpentane	4.31
hexane	1.98
3-methylpentane	1.80
methylcyclopentane	1.88
benzene	3.47
2-methylhexane	1.98
2,3-dimethylhexane	2.39
3-methylhexane	1.80
4-methyl-1-hexene	1.71
heptane	1.53
toluene	18.50
2-methylheptane	.57
3-methylheptane	.83
ethylbenzene	2.77
1,3-dimethylbenzene	12.46
1,2-dimethylbenzene	4.31
1-ethyl-4-methylbenzene	1.95
1-ethyl-2-methylbenzene	.76
1,3,5-trimethylbenzene	2.24
1,2,4-trimethylbenzene	1.39

Table VII-1. Polar Additives of Shell Gasoline

3-nitro-1,2-benzenedicarboxylic acid
1-fluoro-2-methyl-4-nitrobenzene
2-fluoro-1-methyl-4-nitrobenzene
1,2-benzenedicarboxylic acid diisooctyl ester
bis(2-ethylhexyl)phthalate

Table VII-2. Polar Additives of Chevron Gasoline

phenol
2-methylphenol
3-methylphenol
2,3-dimethylphenol
3,5-dimethylphenol
2-ethylphenol
3,4-dimethylphenol
2-ethyl-5-methylphenol
2,3,6-trimethylphenol
2-methynaphthalene
3-ethyl-5-methylphenol
3-ethyl-2,6-dimethylpyridine
1-methylnaphthalene
3,5-bis(1-methylethyl)phenol
1-ethylnaphthalene
2,6-dimethylnaphthalene
1,8-dimethylnaphthalene
bis(2-methoxyethyl)-1,2-benzene dicarboxylic acid ester
2,6-piperazinedione
N,N-dimethyl-2-butene-1,4-diamine
3-nitro-1,2-benzenedicarboxylic acid

Table VII-3. Polar Additives of Union 76 Gasoline

3,5-heptadien-2-one
4-methylphenol
4-methylbenzenamine
3,5-dimethylphenol
2,3-dimethylphenol
3,5-dimethylbenzenamine
2,5-dimethylbenzenamine
3,4-dimethylphenol
3,4-dimethylbenzamine
2-ethyl-6-methylphenol
3-ethyl-5-methylphenol
2,3,6-trimethylphenol
4-(1H-pyrrol-2yl)-3-buten-2-one
4-ethoxybenzaldehyde
2-methylquinoline
3-methylquinoline
2,3,5,6-tetramethylphenol
2,7-dimethylquinoline
1,4-benzenedicarboxylic acid
4-(2-phenylethyl)-phenol

Table VII-4. Polar Additives of Texaco Gasoline

2-cyclopenten-1-one
2-ethyl-1-hexanal
4-methylphenol
2,3-dimethylphenol
2-ethylphenol
3,4-dimethylphenol
4-ethyl-3-methylphenol
3-ethyl-5-methylphenol
2,3,6-trimethylphenol
3,5-bis(1-methylethy)phenol
2-ethylnaphthalene
1,8-dimethylnaphthalene
1,3-dimethylnaphthalene
1,2-dimethylnaphthalene
1,4,6-trimethylnaphthalene
1,6,7-trimethylnapthalene
9-methoxyanthracene
1-octanol
butyl-2-methoxypropyl-1,2-benzenedicarboxylic acid
1,2,4,5,6-heptafluoro-3-methoxybicyclo(2.2.2.)octa-2-ene

Table VIII. The Effect of Sampling on the Composition of Gasoline*

	(1)			(2)			(3)			(4)		
Components	T	B	P	T	B	P	T	B	P	T	B	P
Aliphatics:	37.6	37.8	37.0	40.9	40.7	41.1	39.5	39.8	39.8	41.3	40.7	41.4
Olefins + Cyclics:	23.1	23.8	23.8	21.2	20.8	21.6	4.7	4.9	4.9	21.2	21.7	22.5
Aromatics:	25.0	25.8	25.6	25.5	25.5	24.8	49.4	50.3	48.8	22.1	23.6	20.8
Others below .5 percent:	14.8	12.6	13.6	12.5	12.0	12.5	6.4	5.0	6.5	15.4	14.0	15.3

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* Letters "T", "B", and "P" refer to top, bottom and pump portions of the gasoline samples. Numbers "1", "2", "3", and "4" refer to service stations "L", "N", "O", and "P" respectively. All numerical values are in percent (%).

Table IX. Statistical Data on Water, API Gravity and Reid Vapor Pressure of Gasoline[*]

Service Stations	(I)		(II)		(III)	
	SD	Mean	SD	Mean	SD	Mean
A	54	196	.2	10.8	.1	57.4
B	63	320	.5	10.6	.4	57.7
C	68	305	.3	10.8	.6	59.9
D	119	318	.2	10.0	.9	63.3
E	57	383	.1	9.8	.5	63.4
F	174	326	.5	10.3	.3	63.3
G	110	233	.2	10.4	.3	63.2
H	106	416	.2	10.4	.2	62.9
I	131	263	.4	10.7	.4	63.4
J	87	343	.1	10.4	.4	63.4
K	51	334	.2	10.9	.6	56.8
L	69	194	.3	10.4	1.5	62.5
M	116	452	.4	10.7	1.4	56.5
N	147	388	.5	10.3	.5	63.3
O	56	354	.3	11.0	.5	56.6
P	168	365	.4	10.3	.3	63.5
Q	155	330	.2	11.2	.3	57.5
R	57	270	.5	10.7	.2	63.3
S	172	403	.2	11.1	1.1	57.5
T	117	376	.1	11.0	1.0	57.2

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[*] (I), (II), and (III) designate water, Reid vapor pressure, and API gravity respectively.

Table X. Boiling Point Data of Some Binary Azeotropes[*]

Compound	b.p. (°C)	Binary Azeotrope	b.p. (°C)
		Benzene/Methanol	58.3
Benzene	80.1		
		Benzene/Ethanol	67.8
Ethanol	78.3		
		Hexane/Methanol	50.0
Hexane	69		
		Hexane/Ethanol	--
Heptane	98.4		
		Heptane/Methanol	59.1
		Heptane/Ethanol	--
Methanol	64		
Methylcyclopentane	71.8	Methylcyclopentane/ Methanol	64.6
		Methylcyclopentane/ Ethanol	78.3
Toluene	110.6		
		Toluene/Methanol	63.8
Octane	125.4	Toluene/Ethanol	76.6
		Octane/Methanol	63.0
		Octane/Ethanol	76.3

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[*] b.p.= boiling point. This data is listed in G. Claxton. "Physical and Azeotropic Data", The National Benzole and Allied Products Association, Cambridge, 1958.

RESULTS AND DISCUSSION

Methods of Sample Collection. Table IV lists the relative proportion of aliphatics: olefin+cyclics: aromatics of the samples taken from the top and bottom portions of the gasoline tank and a pump which had just previously discharged five gallons of gasoline. These data confirm our hypothesis that there is no change in the composition of gasoline samples taken by any of these methods.

Major Components of Gasoline. Based on differences in their major components, the gasoline samples studied in this project can be divided into three groups. For the purpose of discussion, gasolines from different service stations were grouped as: (1) Chevron and Texaco; (2) Shell, Aloha Petroleum, Fastop, Gas Express, 7-11, and Circle K; and (3) Union 76. A gasoline belonging to the first group is characterized by its large proportion of olefin+cyclics, such as 1-pentene, 2-methylbutene, 2-pentene (cis/trans), 2-methylpentene (cis/trans), 3-methylpentene (cis/trans), 1,4-, 1,3-, and 1,2-dimethylcyclopentane, and 2-hexene (cis/trans). There are also aromatics, such as benzene, toluene, xylenes and other aromatic compounds. Note that, unlike those gasolines belonging to the second group, the first group does not have as much benzene and toluene. The aliphatics, such as 2-methylbutane, 2-methylheptane, 3-methylheptane, 2-methylpentane, and 3-methylpentane are also present. Aliphatics were present in all three groups of gasoline samples investigated in this project. The relative proportion of aliphatics: olefin±cyclics: aromatics is 50:35:40. The second group of gasoline contains a very high proportion of aromatics. Note the high concentrations of benzene and toluene. It has almost all the aliphatic components found in the first group; however, there is a very small portion of olefin+cyclics. The proportion of aliphatics: olefin+cyclics: aromatics is 50:.05:60. The third group had different components, depending on when a sample had been collected. These samples appeared to be a blend of gasoline from the first and second group of gasolines (refer to Tables VI-1 through VI-10).

Tables V-1 through V-20 contain data on a relative proportion of aliphatics: olefin+cyclics: aromatics of those samples which had been collected from May through August, 1989. Table IV contains similar information for samples which were collected in April. The individual components were identified by GC-MS and quantitated by GC. These were summed according to structure. With few exceptions, there was no significant change in the compositional data of the first and second groups of samples. The first group has a greater number of different components than the second group. It was observed during this study that a number of components, greater than or equal to .5%, changed for some samples, especially those belonging to the first group. A major component was defined in this study as one which is greater than or equal to .5% composition. A few samples, whose relative proportions had deviated, also had a greater number of slightly less than .5% components in their chromatograms. Further, most of these less than .5% components were not early eluting, volatile chemicals, such as butane and 2-methylbutane which could be rationalized by evaporation. Also, the presence of a sufficient quantity of different anti-oxidants and the absence of gum-like material in the gasoline samples which is usually formed as a result of oxidation would rule out the possibility of oxidative degradation occurring during storage of gasoline at a service station. There was difficulty in collecting gasoline samples at the refineries. However, based on the reasons stated above, we can reasonably conclude that the few minor differences in the compositional data are probably related to either small changes in the composition of the feedstock petroleum or slight changes in the refining processes. The changes in the composition of the third group were caused by blending of the first and second types of gasolines.

Effects of Storage and Temperature on Changes in Calculated Research Octane Number of Gasoline. Interest in the calculated octane number of gasoline has intensified in recent years, probably as a result of mini- and microcomputer applications to chemical instrumentation[12,13,14]. The near infrared (NIR), nuclear magnetic resonance (NMR), and GC techniques were applied to this area of the studies. In all of these methods, either the gross or individual composition data of a gasoline sample is obtained by any one of these instrumental methods; NMR can determine a relative proportion of aliphatics: olefin: cyclics: aromatics by integrating a proton NMR spectrum of gasoline; in NIR, overtones of fundamental vibrational frequencies of different chemical bonds occurring in the medium infrared frequency region are measured in the NIR region which yield cumulative information on the nature of gasoline components; and in the GC method, individual components are determined when these are partitioned between the liquid and gaseous phases in the GC column. Then, an algorithm is written which correlates the compositional data of a gasoline sample to the octane number of the same sample which was determined by the classical octane engine. Once this is established, a calculated octane number of similar gasoline can be determined. When there is major compositional change in the gasoline sample, then few constants in the algorithm have to be modified.

In this study, all the major components of gasoline samples were identified by GC-MS and these components were later quantitated by GC. An algorithm which had been developed by Walsh[12] was used to calculate the research octane number (RON). In reviewing the GC-MS and GC data on three types of gasolines, cited earlier in this study, it was determined that the algorithm developed by Walsh should be more applicable to the second type of gasoline. Samples from Service Stations "O" and "K" were collected for this study.

To study the effect of storage in a service station tank on changes to the RON, Service Station "K" was selected. This station is located in cool Manoa Valley and the change in gasoline temperature was minimal during this study. Even in July, the temperature of a gasoline sample was only 84°F. A sample, which had been collected five days after a delivery, was selected as the reference RON data. The temperature of this sample was 83°F and the highest temperature in the ground tank during the study was 84°F. Therefore, it is reasonable to assume that the temperature was nearly constant during this study (see Table V-11). A change in calculated RON was +1 after 17 days of storage. Even after 21 days, calculated RON was identical to the reference value (see Figure 2).

Service Station "O" was selected for studying the effect of temperature on any changes in calculated RON while keeping the storage time constant. All samples from this station were collected no later than three days after a gasoline delivery. In fact, most samples were collected one day after a delivery. A sample which had been delivered just two days before collection was selected as the reference. Its temperature, measured at the service station, was 82°F. Changes in calculated RON vs. changes in temperature is plotted in Figure 3. Even when the gasoline temperature was 86°F, there was either no change or +2 in the values of calculated RON. According to reference 12, the accuracy of this method is ±2 at the 95% confidence limit. Also, note that the proportion of aliphatics: olefin+cyclics: aromatics of the first group of gasoline samples did not change significantly between the temperatures of 82°F and 89°F. As stated earlier, a slight difference in the proportion of some samples is probably due to changes at the refinery. Also note that any component which was below .5% was not included in these calculations.

Possible Explanation for Constant Gasoline Composition During Storage at Service Stations. The data on the effects of temperature and storage on gasoline composition under actual service station conditions have indicated that there is no significant change even at a ground gasoline temperature of 89°F and after having been stored for 21 days. However, all

Fig. 2. Effect of Storage on the Change in Calculated RON

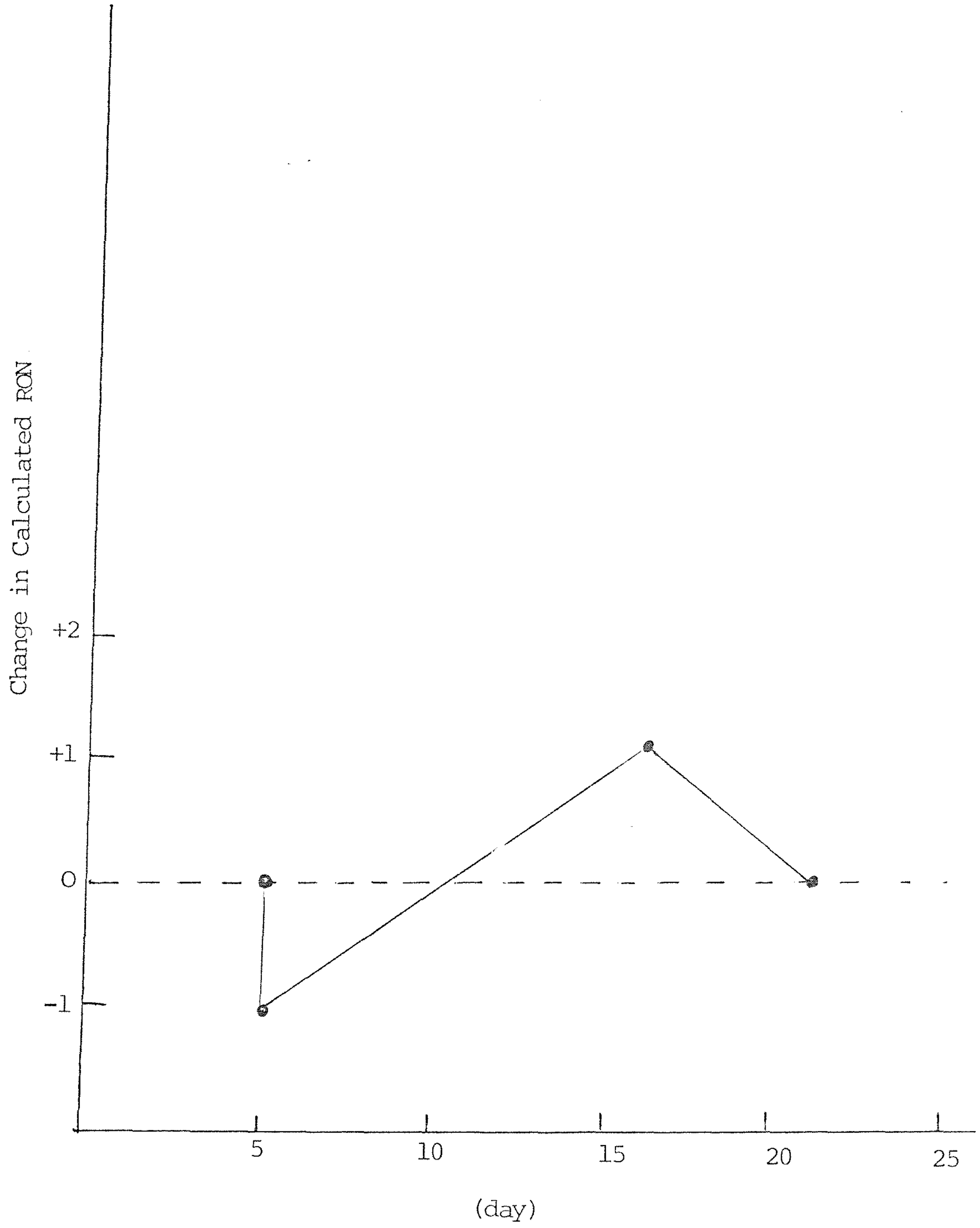
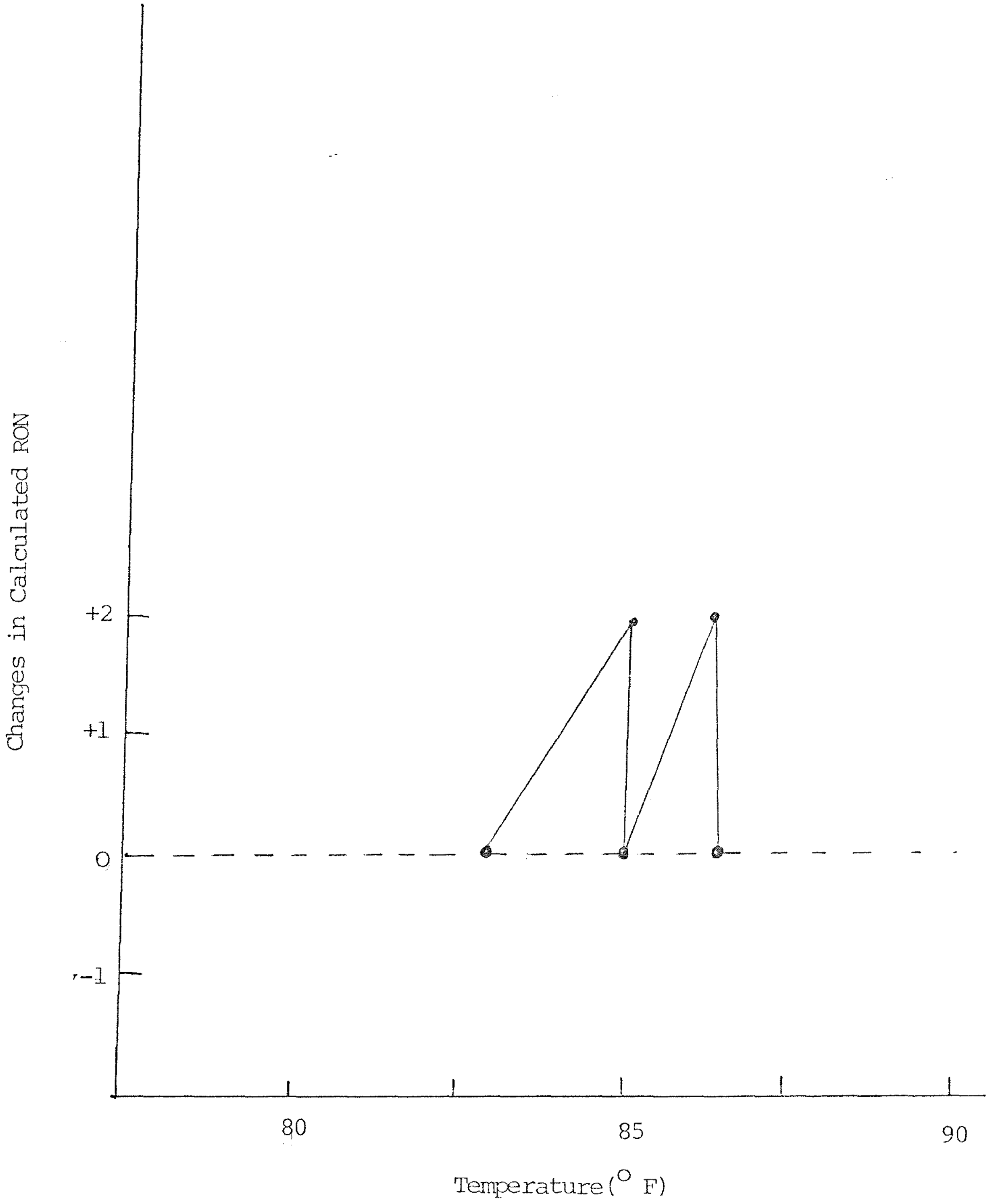


Fig. 3. Effect of Temperature on the Change in Calculated RON



gasoline tanks at service stations have vents which consist of a pipe, the diameter of which is about two inches and extends approximately 15-20 feet above the ground. Also, there are a number of components, the boiling points of which are below 89°F. Here are some boiling point data: boiling points of n-butane, 2-methylbutane, 2,2-dimethylpropane, 2-methyl-1-butene and 3-methyl-1-butene are 31.1°F, 82.1°F, 49.1°F, 88.0°F and 68.1°F, respectively[15].

There are factors which help to maintain the composition of a gasoline constant. These are the physical mixing of gasoline whenever it is pumped for usage and another is the physical chemistry of gasoline. In the liquid state, molecules of different gasoline components are held together by dispersion or van der Waal's forces. Also, a small amount of polar and polarizable forces are also acting among alcohols, amines, some aromatics, carboxylic acids and ketones. The dispersion force increases with an increase in molecular mass. Therefore, for example, n-butane is liquid while long chain hydrocarbons, such as waxes, are solid at standard, temperature and pressure. It was discussed earlier that there was no compositional difference in the gasoline samples which were collected from the bottom and top portions of the gasoline tank. Probably stronger van der Waal's forces, exerted by the higher molecular mass components, help to bind the lower mass molecules in keeping them in solution.

A sample of gasoline placed in a container open to the atmosphere will eventually evaporate leaving a waxy residue. However, no significant evaporation of gasoline stored in an underground tank was observed. The effect of greater van der Waal's forces exerted by higher molecular mass components and the mixing of gasoline which occurs when it is being pumped have been stated as helping to keep the components of gasoline at the service station constant.

However, even if an average potential energy which binds the gasoline molecules to the liquid state is substantial, there are always some molecules which have enough kinetic energy to overcome the binding forces and enter into the vapor state. According to Maxwell-Boltzmann distribution law, a fraction of molecules which have kinetic energies greater than some minimum value E, the value required for the molecules to leave the liquid is proportional to the Boltzmann factor, $e^{-E/kT}$, where E is the energy, k is the Boltzmann constant and T is the temperature in absolute scale. Thus, even if the temperature remains constant, a fraction of liquid molecules, with enough kinetic energy to evaporate, remain the same and will continue. Also, the evaporation increases with increase in temperature. If a container is adequately opened to atmosphere, vapor molecules are swept away and evaporation continues until all the liquid is converted into the vapor state. A gasoline tank, with its connecting venting pipe, can be compared analogously to a small reflux condenser which is attached to an infinitely large distilling flask. Here, an ensemble of gasoline molecules, with kinetic energies greater than the Boltzmann factor, escape into the head space above the liquid and, soon, vapor-liquid equilibrium is established in the tank and its venting pipe. However, since the diameter of a venting pipe is about two inches, only a very small fraction of the vapor comes in contact with the atmosphere. Therefore, there is minimum change in the original vapor-liquid equilibrium. Evaporation-condensation equilibrium is constantly occurring in the narrow venting pipe and in the head space in the gasoline tank. A physio-chemical process may be thermodynamically favorable; however, kinetically may not be significant. These reasons, stated here, may account for the lack of any significant change in gasoline composition which had been stored in its tank at a service station for 21 days.

<u>Anti-Oxidants and Anti-Corrosive Agents</u>. Autoxidation is a radical chain reaction between molecular oxygen and organic compounds at low or moderate temperature. This reaction results in the formation of hydroperoxides.

(1) $RH + O_2 \rightarrow ROOH$

These hydroperoxides then undergo further decomposition either through thermolysis or photolysis to produce radicals to initiate radical chain reactions.

$$(2)\quad ROOH \rightarrow ROO^{\bullet} + H^{\bullet}$$

The effects of autoxidation are very undesirable in many ways; for example in the rancidification of edible oils, the perishing of rubber, and gum formation in petroleum products. Gum is the end product of oxidation and polymerization reactions involving mainly the olefinic constituents of gasolines. The essential feature of an antioxidant in gasoline is that it interrupts the autoxidation radical chain, thereby retarding the autoxidation process. It is therefore necessary that compounds used as antioxidants must have a readily abstractable hydrogen and electron delocalization. This condition is satisfied by aromatic amines and phenols, both of which are extensively used as anti-oxidants because of their ability to act as efficient chain-transfer agents.

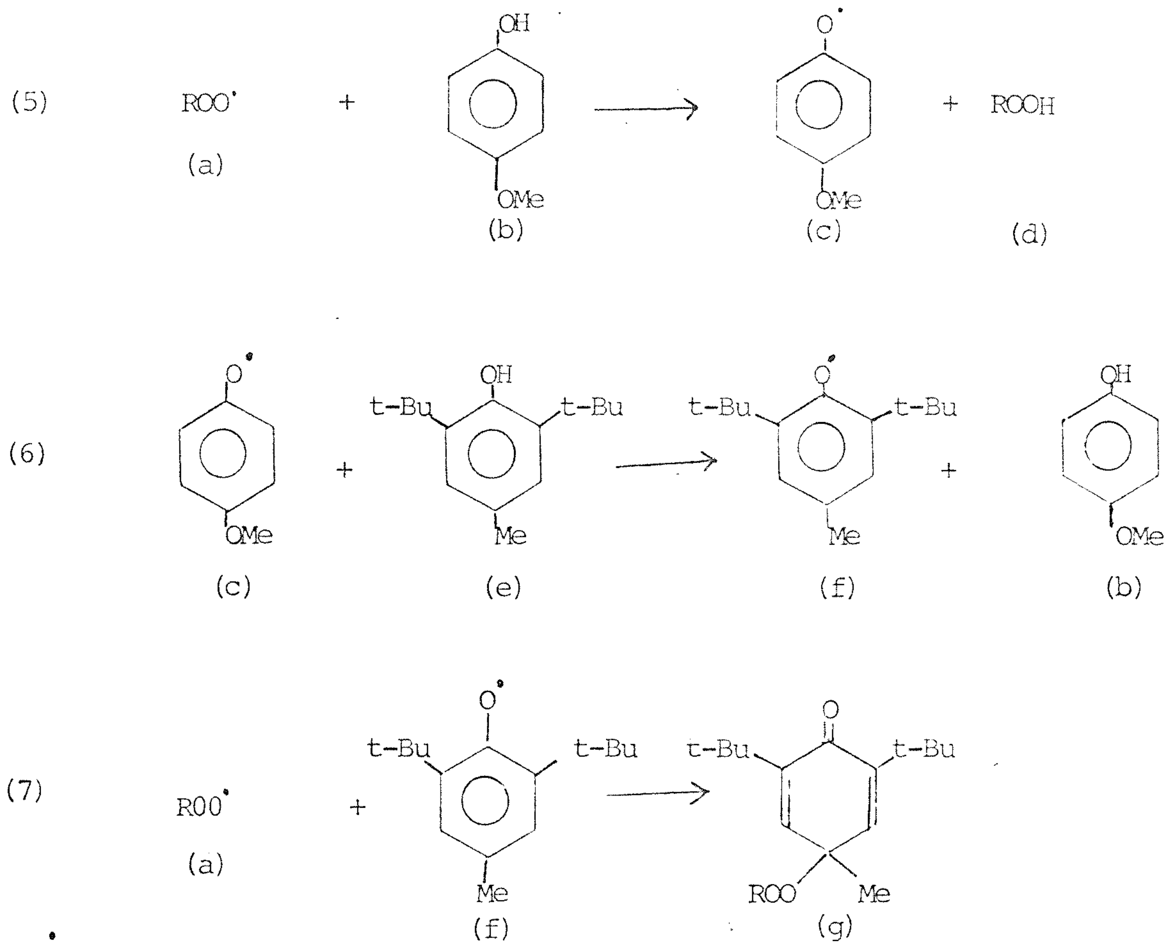
$$(3)\quad ROO^{\bullet} + ArOH \rightarrow ROOH + ArO^{\bullet}$$

$$(4)\quad ROO^{\bullet} + ArNH_2 \rightarrow ROOH + ArNH^{\bullet}$$

Equations (3) and (4) illustrate the function of anti-oxidants, ArOH and $ArHN_2$.

Gasolines studied in this project have been classified into three groups. Reflecting the relatively large proportion of olefinic components, the first and third groups of gasolines have large numbers of different phenolic and amine compounds. The second group of gasolines is characterized by high aromatic content and very little olefinic molecules. This fact is collaborated by its anti-oxidant data. Looking at data on Tables VII-1 through VII-4, there are hindered and unhindered phenols. Relatively unhindered phenols are phenol, 3-methylphenol, 4-methylphenol, 3,5-dimethylphenol, 3,4-dimethylphenol, 4-ethyl-3-methylphenol, 3-ethyl-5-methylphenol, and 3,5-bis-(1-methylethyl)phenol. Hindered phenols are 2-methylphenol, 2-ethylphenol, 2,3-dimethylphenol, 2-ethyl-5-methylphenol, 2,3,6-triethylphenol. The reasons for the presence of both hindered and unhindered anti-oxidants in gasoline have been

Fig. 4. Mechanistic Illustration of Synergistic Behavior of Hindered and Unhindered Phenolic Anti-oxidants*



ROO• = hydroperoxide radical
–OMe = methoxy
–t-Bu = tertiary butyl
–Me = methyl
–O• = oxy radical

(a) = hydroperoxide radical
(b) = p-methoxyphenol
(c) = p-methoxyphenol radical
(d) = hydroperoxide
(e) = 2,6-di-t-butyl-4-methylphenol
(f) = radical of (e)
(g) = peroxycyclohexadienone

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* (5), (6), and (7) are equations respectively. This illustration is referenced from L. R. Mahoney, Ange. Chemie. (Int. Ed.), 1969, 8, p 547.

explained by Mahoney[16]. According to reference 16, the reaction rate of equation (3) is very much dependent on both steric and electronic factors. Therefore, 2,6-dialkylphenols react much less rapidly than simple phenols because of the steric protection of the reaction center and, hence, they are less efficient antioxidants. However, the mixture of a hindered and unhindered phenol is a much more efficient antioxidant than either, alone, as observed for a mixture of 2,6-dit-butyl-4-methylphenol and p-methoxyphenol. The reason for this synergistic behavior of the two phenols arises from the regeneration of p-methoxyphenol in the reaction. This reaction, as shown in equation (6), is favored instead of its reverse reaction because of the relief of steric strain accompanying the formation of 2,6-disubstituted phenoxy radicals. In the absence of a hindered phenol, however, the reaction (5) would be reversible and the retardation would be less marked. See Figure 4 for illustrations of this kinetic mechanism. A similar reaction mechanism can be rationalized for aromatic amines, such as 4-methylbenamine and 2,5-dimethylbensenamine. Some suspected anti-oxidants could not be positively identified.

Corrosion inhibitors are long chain molecules with at least one strong polar group. Some of the corrosion inhibitors found are butyl-2-methoxypropyl-1,2-benzenedicarboxylic acid, 1,4-benzenedicarboxylic acid, 3-nitro-1,2-benzenedicarboxylic acid, bis(2-ethylhexyl)phthalate, and 1,2-benzenedicarboxylic acid diisooctyl ester. Although an organophosphate class of anti-corrosion agent was not detected, this may be due partially to difficulty in the computer library search of mass spectra for organophosphate compounds. This class of molecules often loses its phosphate group in the mass fragmentation process initiated by the EI source, and its spectra is not too discriminating. Some standard compounds were difficult to obtain. Without chromatographic data to complement the less discriminating mass spectrum, identification is not possible.

API Gravity. A statistical summary of API gravity data from Table III is listed in Table IX.

Reid Vapor Pressure. Although Hawaii is not affected, a recent enactment of Reid vapor pressure regulation by the Environmental Protection Agency has limited the Reid vapor pressure values of gasolines on the mainland United States. With few exceptions, most Reid vapor pressure values are similar for all the samples collected from the 20 different service stations. Due to the nature of this testing, Reid vapor pressure could not be retested once the sample cover had been opened to recheck some of our results. Analyzing the Reid vapor pressure data, even the most volatile components, such as butane, did not significantly evaporate from the storage tanks.

Water. Although the amount of water dissolved in all the gasoline samples is not unexpected, the standard deviations are high. The ppm level of water dissolved in all the samples collected from the 20 service stations were random. A gasoline is contaminated with water either at a refinery, during transport, or by condensation with atmospheric water vapor which may enter through a vent which is connected to a gasoline tank. Usually a gasoline tank at a service station is tilted in one direction. When there is water accumulation in the tank, a mixing of water and gasoline occurs whenever there is a gasoline delivery or pumpage of gasoline. Water contamination is a serious problem in gasoline storage, and the presence of free water can create ideal media for bacterial growth which can lead to fuel degradation and corrosion[17,18,19]. All the samples collected during this study did not contain any free water.

Implication of the Data from This Study on Preparing Proper Alcohol Blend. Azeotropic formation, miscibility, and water will be discussed. Azeotropic Formation: The hydroxyl group of both methanol and ethanol will readily form the minimum boiling azeotropic combination with a number of gasoline components found in this study. These data are listed in Table X. These alcohols cause lowering of the boiling point of the azeotropic mixture. Note that methanol has a greater effect than ethanol on lowering the boiling point of a benzene azeotropic mixture. During hot summer months or after an engine has reached a certain temperature, a vapor-lock may occur in some cars using alcohol blends. They may be related to the formation of a binary azeotropic mixture of methanol and ethanol with benzene. Xylenes do not form azeotrope with either ethanol or methanol. <u>Miscibility</u>: When preparing alcohol blends with gasoline, miscibility of ethanol and methanol with different components of gasoline should be considered. For certain gasoline co-solvents, for example, 1-butanol has to be added to enhance miscibility. A phase separation may occur during cool December and January, months even in Hawaii when an alcohol blend is left in an automobile tank for some time. There are a number of empirical tables on the miscibility of alcohols and components of gasoline[20,21,22]. These tables show that aromatic solvents are more miscible with methanol and ethanol than aliphatic solvents. Xylenes (meta, para, and ortho) are aromatic molecules and yet do not form an azeotropic mixture with both ethanol and methanol. When fully implementing alcohol blend gasoline, a refining process should be modified to prepare gasoline which is more favorable to blending. Among the three classes of gasolines studied in this project, the second class of gasolines should be most favorable for preparing alcohol blend gasoline than either the first or the third group of gasolines. <u>Water</u>: Water in alcohol blends is one of the major problems which must be corrected. While the amount of water found in gasoline samples collected in this study is not alarming for use in gasoline engines, it could cause problems in alcohol blend fuel. Alcohols have a great tendency to attract water molecules, especially from the atmosphere. Vents for both alcohol blend gasoline and gasoline tanks must be modified to eliminate water contamination of these fuels during storage at the service station. Also, free water, which accumulates in gasoline tanks at the service station, must be removed more often than it is now.

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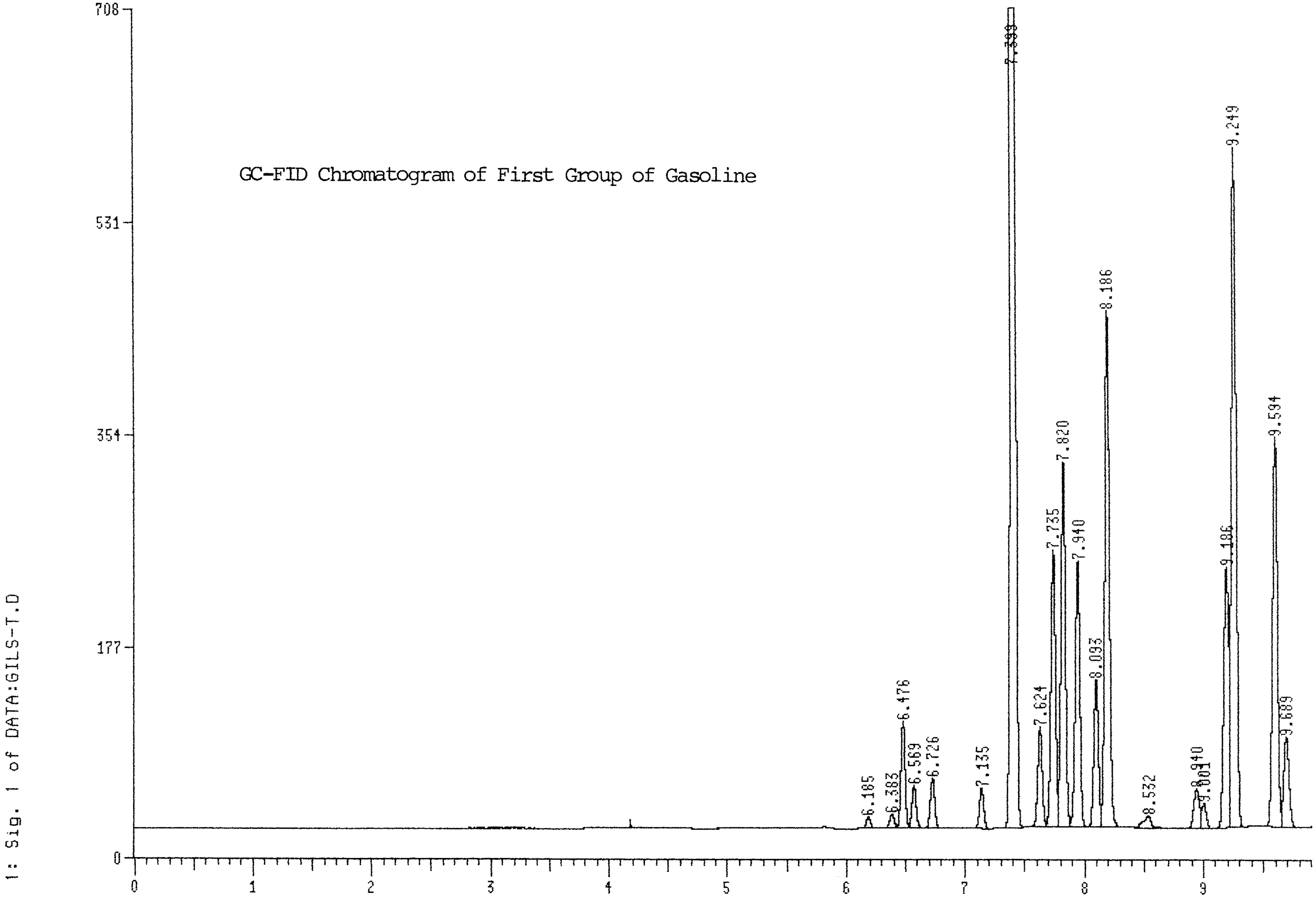
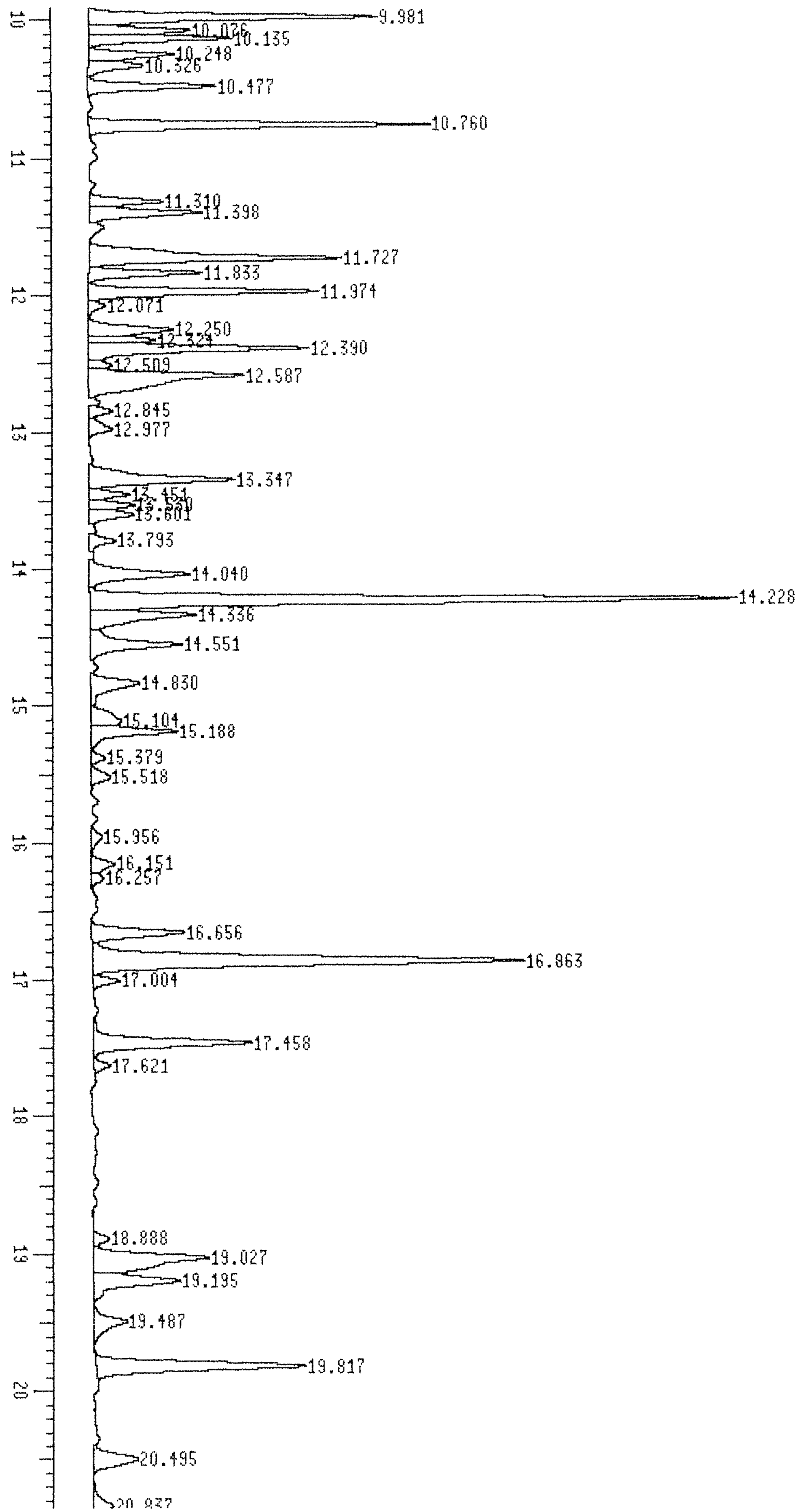


GC-FID Chromatogram of First Group of Gasoline

10
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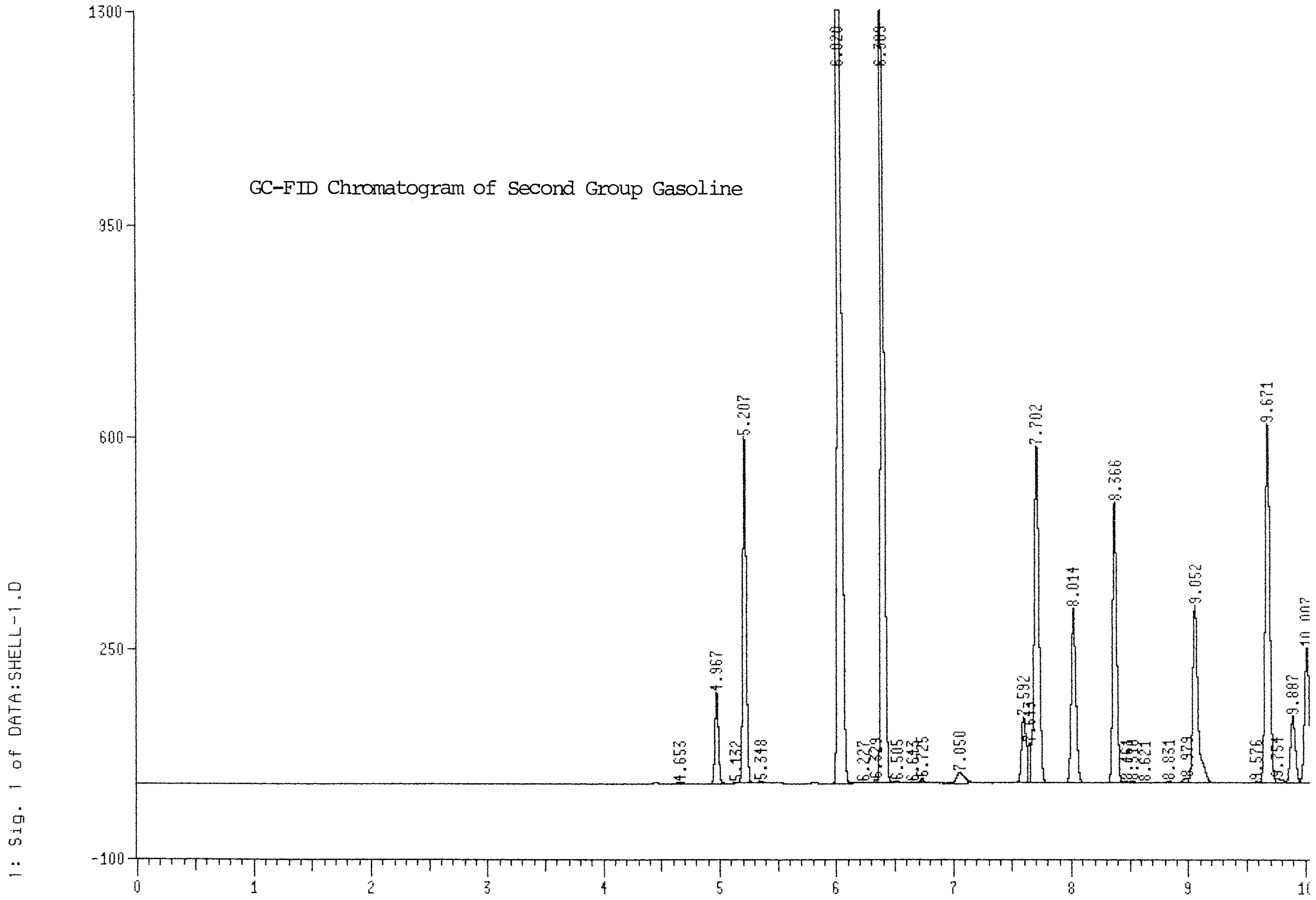
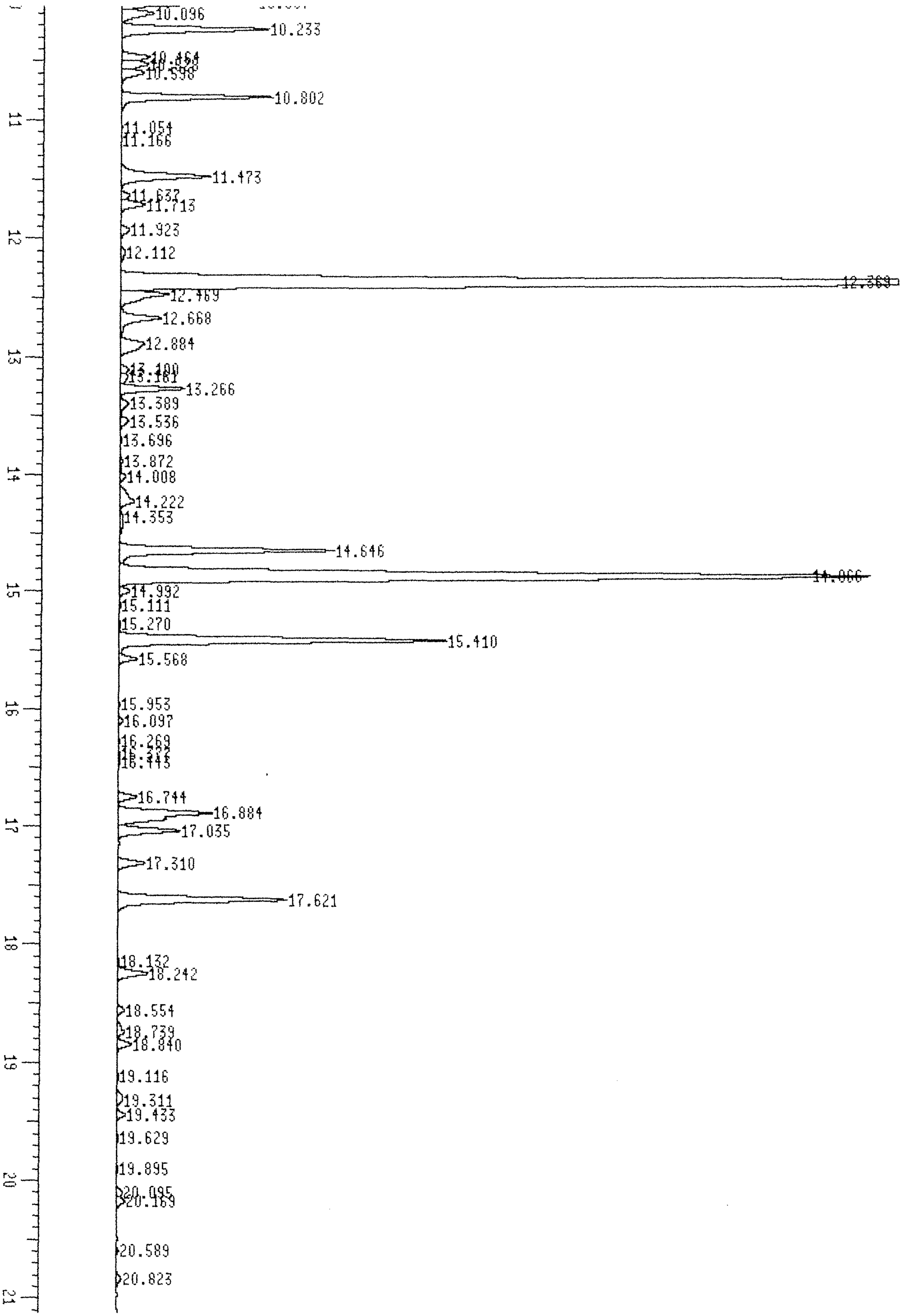

GC-FID Chromatogram of Second Group Gasoline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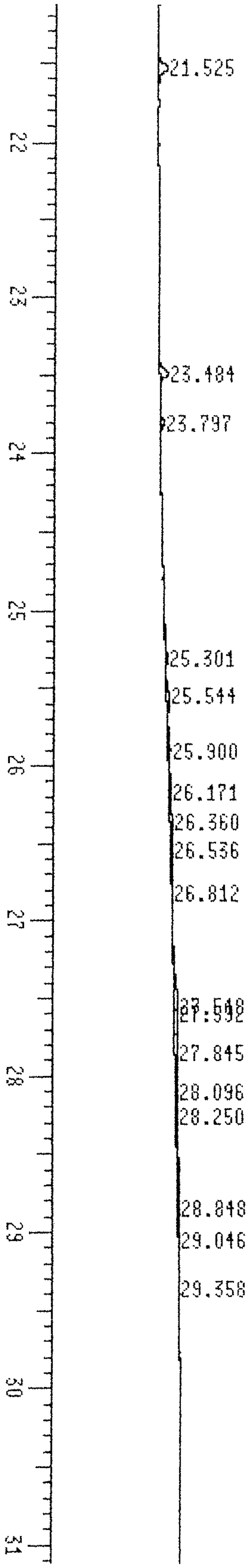

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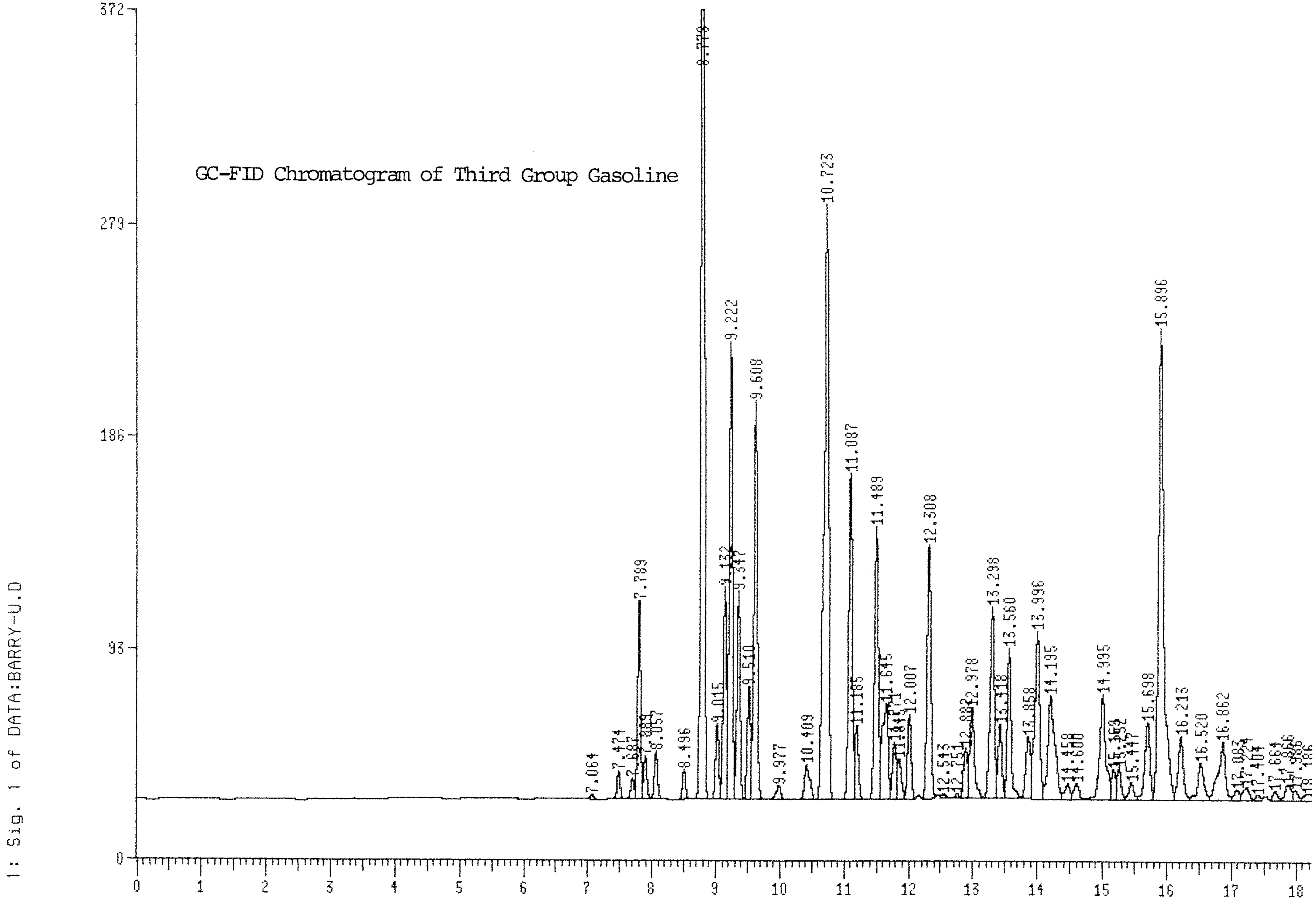

GC-FID Chromatogram of Third Group Gasoline