FINAL REPORT

TO

SOUTHWESTERN ELECTRIC POWER COMPANY

OF

A STUDY OF THE DECOMPOSITION OF TRANSFORMER OIL

BY

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ABSTRACT

Using sophisticated modern chemical separation techniques and analytical procedures we find dramatic changes in electric insulating oils that have failed in service. Highly volatile and flammable compounds are formed. These compounds are readily ignited in a transformer environment.

The compounds detected are typically a benzene molecule with one or more side chain substituents. These molecules could well be the residues of the larger molecules from the napthalenic hydrocarbons in the original insulating oil. The volatile compounds produced have been found in concentrations exceeding 2% of the oil in the tap changer.

There is great promise that in-situ measurement devices can be developed to guard against these events in the future. Real time monitoring devices and compound specific detectors are now available. These devices could be used to initiate service of the transformer before an explosive mixture is produced.

I. INTRODUCTION

Due to environmental concerns, the very stable polychlorinated biphenyls have been replaced with non-chlorinated hydrocarbons. There has been a series of previously unexplained failures (fires and explosions) in these hydrocarbon transformer oils. At the request of Southwestern Electric Power Company, a team of chemists, chemical engineers and electrical engineers have considered this problem. This is their first written report.

Transformer electrical insulating oil is a complex mixture of light naphthenic hydrocarbons. It contains many isomers of with an average molecular weight of approximately 255. The molecular framework for the oil usually contains 18 to 25 carbon atoms. The oil has been hydrotreated to insure that the molecular structures are stable up to the boiling point of the oil, about 238 °C. Oil is classified according to its basic composition, or series. The most familiar one is the saturated, or paraffin, series that contains compounds such as methane, propane, butane, and octane. The paraffins have a general formula of C_nH_{2n+2}. The napthenic hydrocarbons are unsaturated and usually have a general formula of C_nH_{2n} . Some napthenic stocks have higher degrees of unsaturation. Formulae of C_nH_{2n-8} have been reported. The napthenes may contain both cyclic and aromatic structures. The high molecular weight of the oil insures that it has a low vapor pressure, ~ .01 mm Hg at 20 °C.

We have conducted an extensive series of analysis to determine the causes of the failure of this oil to perform as desired. An extensive review of available literature has been conducted to find out what has been reported in this area. Samples of new oil were tested along with samples used oil of varying service ages. Some samples were provided from failed transformers as well as samples before and after filtration.

The results of these tests provide us with the predictive tools necessary to monitor the degradation of the oil. It should be possible to measure the increase in the concentration of these explosive decomposition products in the tap changer, possibly in real time, so that appropriate preventative measures can be taken long before a catastrophic failure.

II. LITERATURE SEARCH

TITLE: Oxidation Stability of Insulating Oil

AUTHOR: A.C.M. Wilson

REFERENCE: Proceedings of IEE, Volume 112, No. 3, March 1965

SYNOPSIS: The rate of oxidation is known to depend on four factors: (a) oxygen availability, (b) temperature of operation, (c) copper/oil ratio and (d) oil consumption. These conditions vary widely in service. Any test, therefore, which uses one set of accelerated conditions can be no more than an effective screening or routine control test.

The article looks only at the accelerated tests performed on the oil in the main tank. These tests have been studied for many years with several changes in the procedures. The benefit of accelerated tests, is believed to be limited. Future research does include looking at the copper/oil ratio in tap changer using atomic absorption analysis.

TITLE : The Role of Copper During the Oxidation of Transformer Oils

AUTHOR: John J. Melchoire and Ivor W. Mills

REFERENCE: Journal of the Electrochemical Society, April 1965

SYNOPSIS: This article gives insight to the degree that copper plays in the degradation of transformer oils with or without metal deactivators. The oil without the deactivator is rapidly degraded in the presence of metallic copper. The copper enters solution in a conductive form contributing to power factor losses in the early stages of the oxidation. In the presence of copper, a metal deactivator is very effective in preserving the oil. The quanity of copper dissolved is less, the rate of appearance and concentration of oxidation intermediates is less. Dielectric loss, as measured by power factor, seems to be related to the carbonyl content of the oil.

The article points to further investigate the following two areas: 1) the use of metal deactivators in the load tap changer and 2) the study of copper content in the tap changer using the Atomic Absorption Spectrophotometer. It has been observed the tap changer contacts are made of copper and will release copper during normal operation. Copper can lead to problems in oil oxidation.

TITLE: Simulated Service Aging Tests of Insulating Oils in Transformers
AUTHOR : H.A. Adler and M.F. Cosgrove
REFERENCE: Electrical World, August 1965
SYNOPSIS: Tests were conducted over a period of 124 months on a sealed and free breathing (open) 10 kVa transformer. Both inhibited and non-inhibited oils were tested. The tests performed on the oil were standard tests. Tests were color number, power factor and the Alcoa Test. An interesting point was that the sealed transformer were sludge free and had unobstructed ducts. The open transformer on the other hand experienced severe sludge buildup. The acid formation increased over time. There is a relation between acid formation and the breakdown of the transformer. The article stated that there was no measurable amounts of inhibitor left after five months of testing.

TITLE: Oil Tests Show Incipient Power Transformer Faults
AUTHOR: Leander C. Levy
REFERENCE: Electrical World, April 29, 1968
SYNOPSIS: This article claims, as suspected, there are too many peaks to identify completely, but to consider the acid region of 1710 cm^{-1} in the infrared . The article exams only the paraffinic based mineral oil samples from the main tank.

From current research data collected the Infrared is a valuable tool in determining the fractions contained in the naphthenic based oil samples taken from the tap changer. The Infrared can be used along with the GC/MS and the NMR to better identify the fractions.

TITLE: Take a Close Look at Insulating Oils

AUTHOR: J.J. Melchoire and I. W. Mills

REFERENCE: Power, August 1968

SYNOPSIS: The research work done in this article studied the continuos power factor behavior of various transformer oils in a controlled, accelerated laboratory oxidation test, both in the presence and absence of copper. There are three important conclusions stated in the paper. First, soluble copper has a large adverse effect on oil stability. Second, certain compounds tend to solubilize copper and thus lead to rapid oil degradation. Third, aromatic hydrocarbons tend to preserve oil stability.

Research data collected does not agree with the third point. Aromatic buildup is a large problem that can contribute to the ignition of the transformer.

TITLE: Transformer Fault Diagnosis by Dissolved-Gas Analysis

AUTHOR: Joseph J. Kelly

REFERENCE: IEEE Transactions on Industry Applications, Vol. IA-16, No. 6, November/December 1980

SYNOPSIS: A transformer in subjected to two types of stress electrical and thermal. The insulating materials within the transformer can break down as a result of these stresses to yield gases. The procedure for the analysis consists of three steps: 1) extracting the gases from the oil by some type of vacuum apparatus, 2) introducing the gases into a gas chromatograph and 3) quantifying the sample.

The dissolved gas analysis has not proved to be an accurate measure of volatile components. There are several problems associated with this method. Due to the dead volume of the extraction system, oils containing very low levels of gas cannot produce enough gas to perform the chromatographic analysis. Factors affecting the extraction system dead volume include the volumetric collection ratio and the gas collection tube design. Additionally, due to the handling of the gas sample, the more volatile gases can be lost, in particular the aromatics produced such as benzene and xylene. Oxygen and nitrogen can contaminate the sample due to air absorption.

TITLE: Comparative Performance of Paraffinic and Naphthenic Insulating Oils

AUTHOR: G. St-Jean, J. Castonguay, M. Landry, D.R. Pugh, H. St-Onge

REFERENCE: IEEE Transactions on Power Apparatus and Systems, Vol. PAS-99, No. 6, Nov/Dec 1980

SYNOPSIS: The performance of insulating oil in circuit-breakers relies upon the arc-quenching characteristics of the oil and its ability to withstand the recovery voltage. The research in this article investigates the arc-quenching characteristics of two experimental paraffinic oils made from western Canadian crudes was performed in comparison with Voltesso 35 (naphthenic based). The test was to subject low-voltage circuit breakers to both resistive and short-circuit arcing conditions. The problems that are seen in circuit breakers may help in the investigation of tap changer oil.

As suspected, the arcing between the contacts of the circuit breakers produce localized high temperatures in the oil. The elevated temperature produces degradation products such as dissolved gases and more important, suspended carbon particles. A change of property is seen in the case of the dielectric strength.

The carbon particle distribution of the arced oils were studied using a model 345 Royco particle counting instrument. The suspended carbon particles can fall out of solution and form the coking products as seen on the tap changer contacts. Carbon particle counting can be used as an excellent method in determining the amount of coke products deposited inside the tap changer.

TITLE: Particle Contamination Levels in Oil-Filled Large Power Transformers
AUTHOR: T.V. Oommen and E.M. Petrie
REFERENCE: IEEE Transactions on Power Apparatus and Systems, Vol. PAS-102, No. 5, May 1983.
SYNOPSIS: Particle content in transformer oils were determined using a HIAC Model 600 Particle Analyzer, available from HIAC-Royco Instruments. The instrument uses the principle of light blockage to estimate the size of each particle. Particles pass through a micro cell in which a transverse light beam is applied. The cross sectional area of the particle is automatically estimated and is converted to an equivalent ellipse. Most particles for instance, dust particles and wear particles are non-spherical in shape.

The topic of research in this article was concerned mainly with observed particle levels in operating transformers. Attention was given to sources of particle generation such as cellulosic fibers and metallic material from pump failure.

The same basic principle can be applied to tap changer units. The difference would be the source generation. Two sources of particle generation are from the electrical arcs between the tap changer contacts. The electrical arcs produce carbon particles as well as metallic copper from the surface material of the contact. Carbon particles form the coke product that builds up on the components of the tap changer. Future research work could be to correlate the aromatic content with the particle contamination as a part of the transformer preventative maintenance program.

TITLE: Influence of Oxidation on the Electrical Properties of Inhibited Naphthenic and Paraffinic Transformer Oils

AUTHOR: C. Lamarre, J. P. Crine and M. Duval

REFERENCE: IEEE Transactions on Electrical Insulation Vol. EI-22 No. 1, February 1987.

SYNOPSIS: The tan-delta and conductivity of mineral oils depend on the dissolved copper, peroxide, and soluble acid contents. Sludge formation is when the copper dissolution, peroxide and acidity contents increase sharply.

The different amounts of copper, peroxides, and acidity depend on the chemical nature of the oil. The naphthenic oil resist thermal oxidation slightly better than the paraffinic oil. The naphthenic oil has a greater ability to dissolve copper, therefore the electrical properties for naphthenic oil is not as good as for the paraffinic oil.

III. DISCUSSION OF RESULTS

The extensive analytical procedures used in this project were necessary to enable us to identify the decomposition products present in the used oil samples. A separation procedure was used to isolate these products. Previous reports have indicated little or no change in the oil as a function of age.(R1) The molecular complexity of the insulating oil and its much greater concentration will mask the signals of these relatively minor components. The elaborate vacuum separation scheme we used enabled us to trap the products at successively lower temperatures. Figure 1. shows a schematic diagram of the separation apparatus. The liquid nitrogen, LN2, trap collects the most volatile components. This separation procedure used on the virgin oil produced no such volatile fraction. Several analytical methods were employed on this fraction to confirm the identification of these compounds.

Gas chromatography was used to separate the volatile components according to their retention time in a column packed with an appropriate absorbing material. Known samples were used to calibrate the chromatograph. Once calibration was accomplished the retention times of the unknown components were measured and compared to the standards. The relative amounts of each component were determined by comparing the areas under the peaks.

Infra-red spectroscopy was used to identify the molecular structure of the unknown components. Incident IR radiation is absorbed by the atoms in the molecule and cause specific vibrations to occur based on the relative bond activation energies . The wavelength of the absorbed radiation is a measure of the composition and structure of the molecular species. The IR absorption spectrum is a "fingerprint" of the compound. The fingerprint of the unknown is compared to that of known compounds for confromation. Since the LN2 fraction is actually a mixture of compounds only the general types of compounds present can be inferred from this analysis.

Nuclear magnetic resonance, NMR, was also used to identify the molecular structure of the unknown. The hydrogen atoms magnetic field is influenced by its chemical environment. The magnetic fields of the hydrogen atoms in a compound are measured by placing the sample in a very strong magnetic field. Since the compounds are made mostly of carbon and hydrogen, this is a specially useful analytical tool. H atoms in aliphatic compounds, H atoms in aromatic compounds and H atoms combined with oxygen all have strong unique signals. Figure 2 shows an NMR analysis of P7124 that indicates aromatic compound are present. The intensity of the aromatic H signal is obvious when this spectrum is compared to that of the new oil in Figure 3.

Vacuum Separation Apparatus

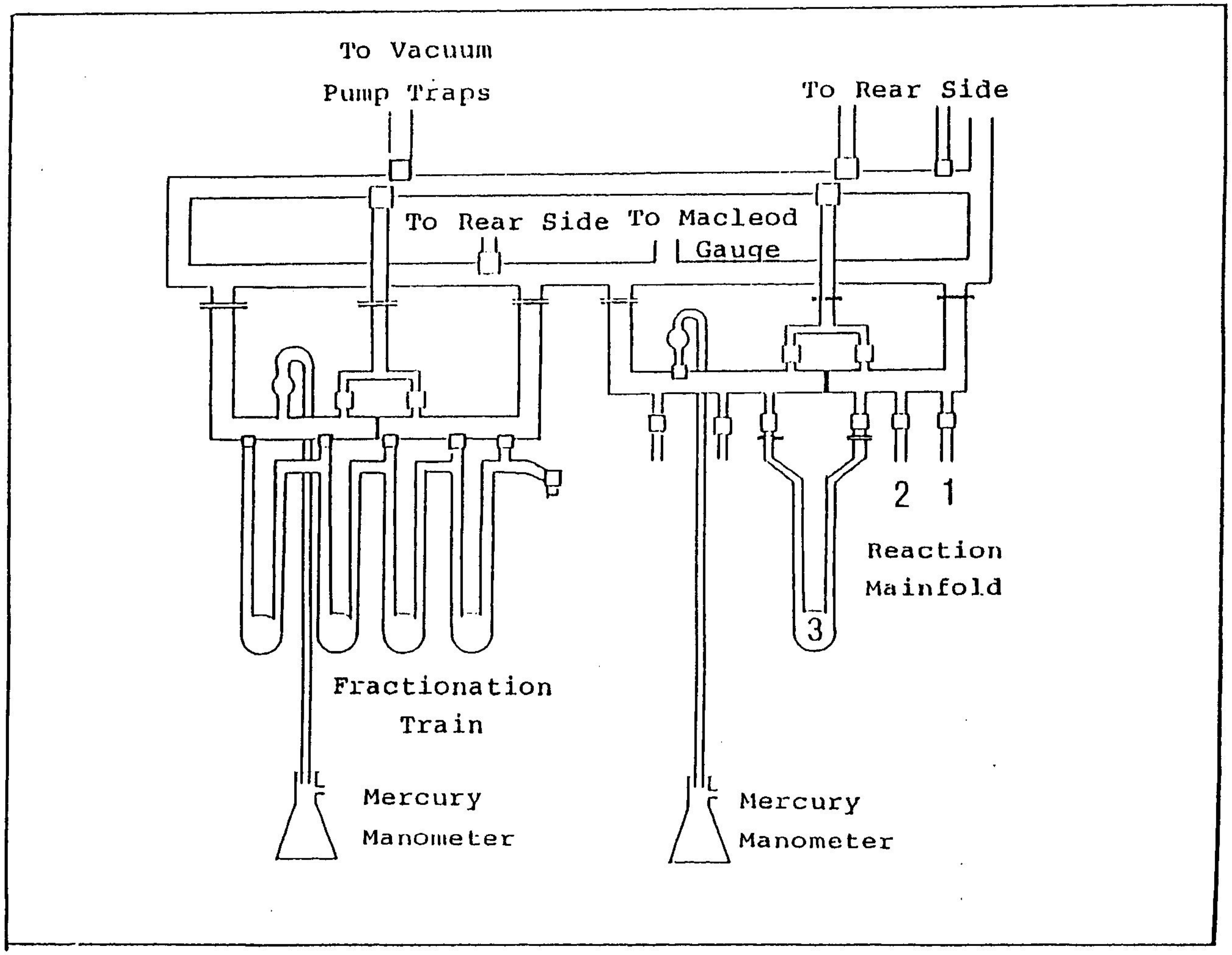
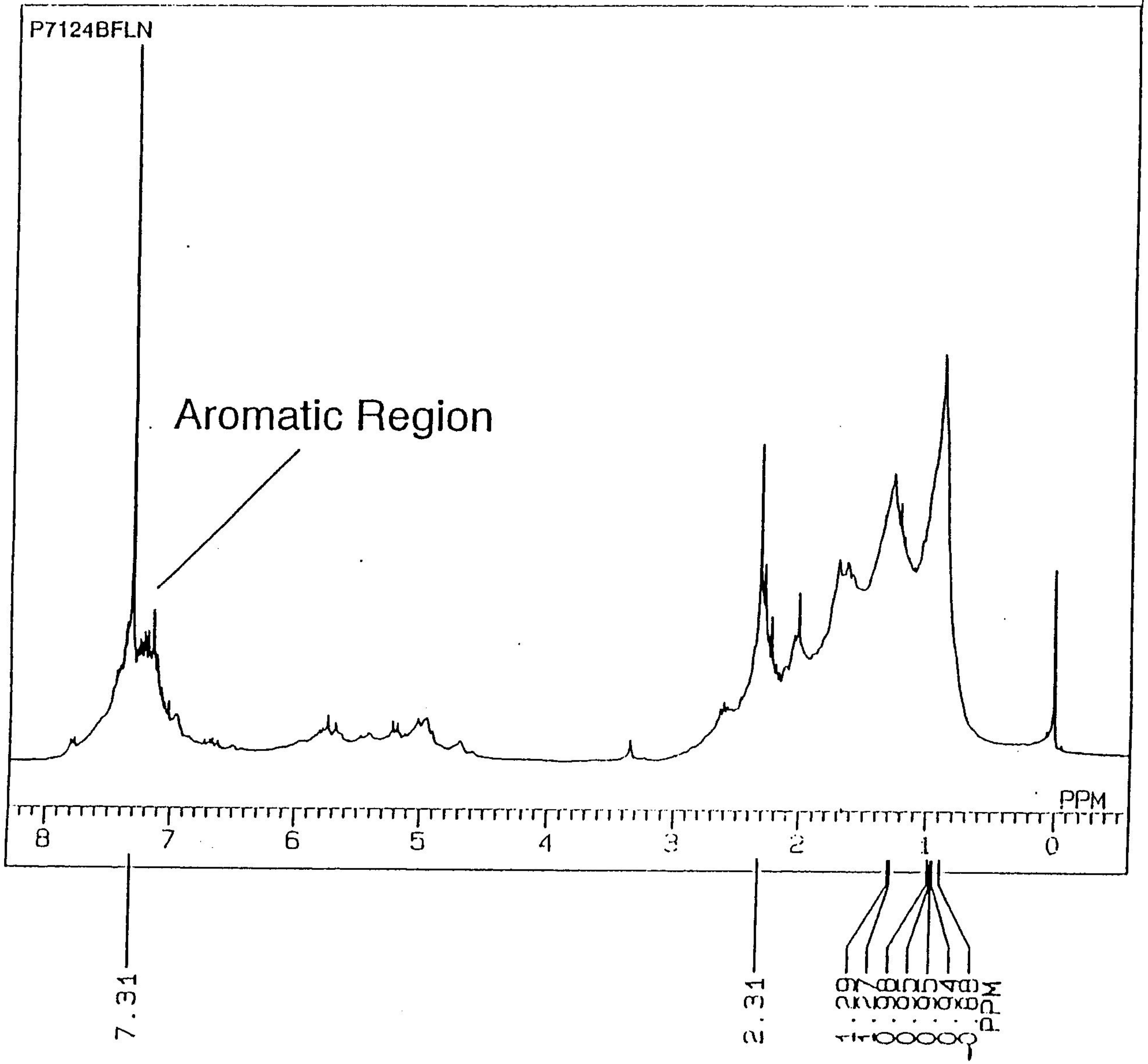


Figure 1



JEOL
CPF-270

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27-AUG-92 15: 43: 45
EXMOD SGNON
OBNUC 1H
OBFRQ        270.05 MHz
OBSET        112.00 kHz
OBFIN        5400.0 Hz
POINT         16384
FREQU        5405.4 Hz
FILTR          2700 Hz
SCANS           100
ACQTM         1.516 sec
PD            3.000 sec
PW1            10.0 us
ADBIT     12
TEMP.   27.0 c
SPEED            15 Hz
SLVNT  CDCL3
EXREF          0.00 ppm
BF             0.10 Hz
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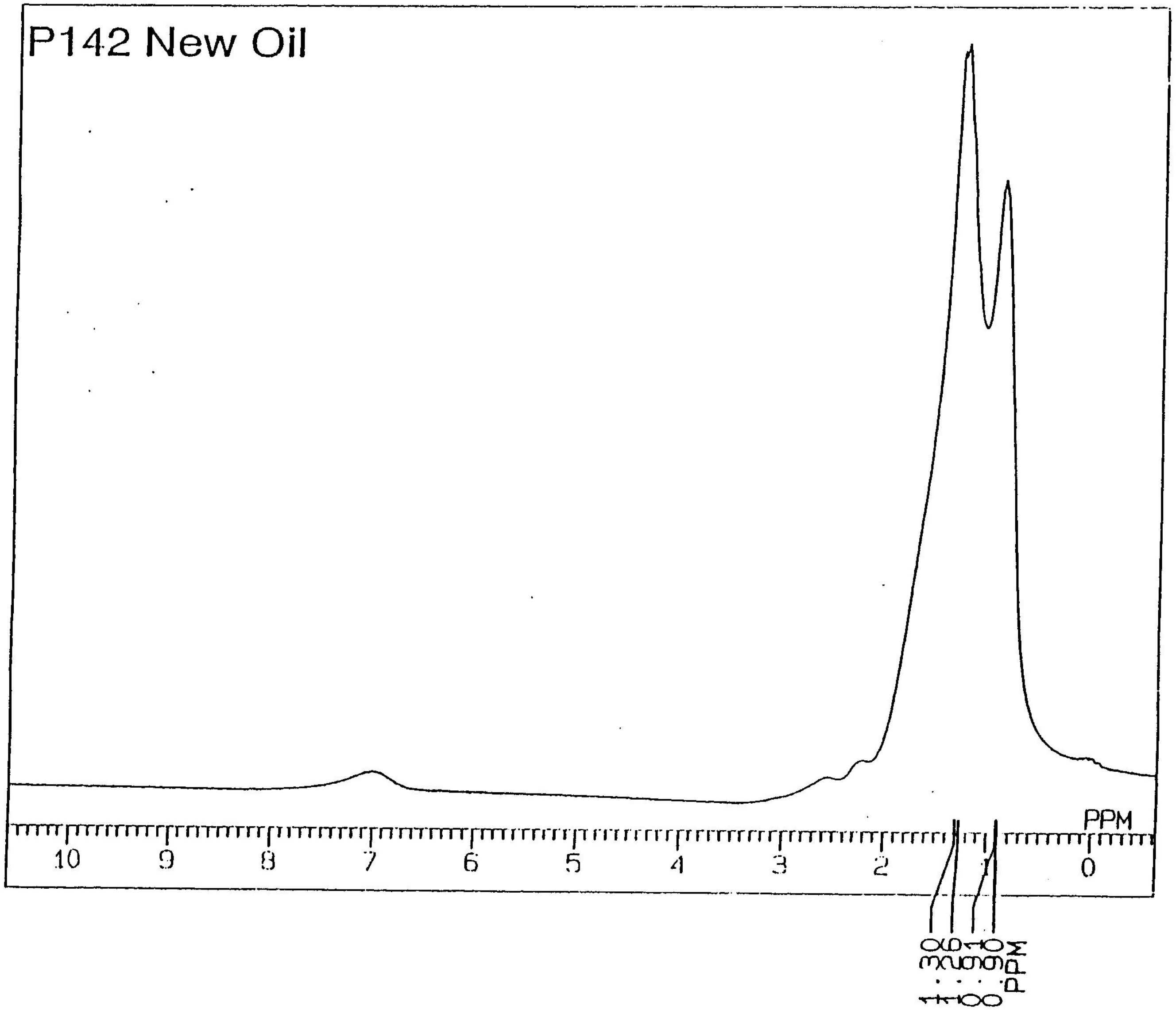
Figure 2



JEOL
CPF-270

06-OCT-92 15: 43: 45
EXMOD SGNON
OBNUC 1H
OBFRQ 270.05 MHz
OBSET 112.00 kHz
OBFIN 4591.7 Hz
POINT 16384
FREQU 5405.4 Hz
FILTR 2700 Hz
SCANS 50
ACQTM 1.516 sec
PD 3.000 sec
PW1 10.0 us
ADBIT 12
TEMP. 27.0 c
SPEED 15 Hz
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.10 Hz

Figure 3

Table 1. provides a summary of the major absorption peaks in the infrared spectra of the samples tested. Since these peaks are masked in the spectrum of a bulk sample, this data proves the advantage of separating the volatile fraction from the insulating oil. Table 3. is a comparison of the samples. It shows an obvious increase in the decomposition products when the older samples are compared to a new oil sample. The sample P142BF from the Texas Eastman location shows the presence of a only small amount of both aromatic and oxidation products. The concentration of these products was greatest in sample P7124 from the transformer that failed at Carthage Texas. Figure 4. is the infrared spectrum of the LN2 fraction from sample P7124 before filtration. Comparison of this sample with new oil, Figure 5, reveals considerable absorption in the aromatic region, 600-900 cm^{-1}.

Nuclear magnetic resonance, NMR, was also used to identify the molecular structure of the unknowns. The hydrogen atom's magnetic field is influenced by its chemical environment. The magnetic fields of the hydrogen atoms in a compound are measured by placing the sample in a very strong magnetic field. Since the compounds are made mostly of carbon and hydrogen, this is a specially useful analytical tool. H atoms in aliphatic compounds, H atoms in aromatic compounds and H atoms combined with oxygen all have strong unique signals. Figure 2 shows an NMR analysis of P7124 that indicates aromatic compounds are present. The intensity of the aromatic H signal is obvious when this spectrum is compared to that of the new oil in Figure 3.

Mass spectrographic analysis was used to get information on the molecular weight of the unknowns. Each compound produces certain stable ions in this procedure that enable calculation of the molecular weight and structure of the compound. It is one of the most specific of the analytical methods. The results of this analysis are illustrated in figures 7 and 8. This mass spectral data combined with the previous analyses provides conclusive evidence of the presence of aromatic components in significant concentrations. The explosive limits for mixtures are a complex function of the composition of the mixture. A summation of mole fractions of just the benzene and toluene present in sample P-7124 would probably be sufficient to exceed this limit.

A plot of the concentration of the volatile decomposition products is shown in figure 6. There is a definite correlation with the increase in volatiles and tap changer problems. Values of greater than 1% would indicate potential problems.

TABLE 1: INFRARED DATA

Sample Number	Major Peaks (cm^{-1})	Graph Location
P7124NO6 BATCH	3240, 2955, 2924, 2856, 1458, 1377	
P7124NO8- I.B.	3240, 2955, 2924, 2866, 1456, 1377	
P7124NO9 - L.N.	3211, 2955, 2924, 2866, 1456, 1375	
P7124BF4 - L.N.	3211, 2955, 2928, 2868, 1716, 1641, 1456, 1377, 991, 908, 729, 677	
P7124AF12 - I.B.	3344, 2955, 2928, 2868, 1716, 1456, 1377, 908	
P7124AF13 - L.N.	3344, 2955, 2928, 2868, 1716, 1641, 1456, 1377, 991, 908, 729, 677	
P142BF14 - BATCH	3383, 2955, 2924, 2866, 1458, 1377	
P142BF15 - I.B.	3344, 2955, 2924, 2872, 1456, 1377	
P142BF16 - L.N.	3184, 2955, 2922, 2858, 1464, 1375,1072, 920	
P25BF23 - BATCH	3373, 2955, 2924, 2877, 1460, 1377	
P25BF24 - I.B.	3377, 2955, 2926, 2868, 1456, 1377	
P25BF25 - L.N.	3421, 2955, 2926, 2877, 1716, 1643,1456, 1377, 991, 910	
P25AF26 - BATCH	3240, 2955, 2924, 2872, 1458, 1377	
P25AF27 - I.B.	3240, 2955, 2924, 2872, 1458, 1377	
P25AF28 - L.N.	3240, 2955, 2924, 2872, 1458, 1377, 910	

PEAK REFERENCE

Peak Range (cm^{-1})	Description of Peak
3184 - 3421	O-H stretch, water
2955	CH3 methyl
2928 - 2924	CH2 methylene stretch
2877 - 2856	CH3 methyl stretch
2355	Absorbed CO2 in sample
1716	C=O, carbonyl group, carboxylic acid
1643 - 1641	C=C, alkene
1464 - 1456	CH2, CH3 stretch, asymmetrical vibration
1375 - 1377	CH3 of CH3CO unit, symmetrical bending vibration
991	-CH , out of plane bending
908 - 920	C-H bend , olefinic or aromatic
729	Aromatic, out of plane -C-H bend or CH2 rock
677	Aromatic, out of plane ring C=C bend

TABLE 3: RESULTS OF VACUUM EXTRACTION

SAMPLE NUMBER FROM SWEPCO	WEIGHT OF OIL grams	LN2 FRACTION grams	WEIGHT % VOLATILES
P7124 BF	130.89	3.52	2.7
After filtering			2.5
P25 BF	130.62	1.48	1.13
After filtering			1.14
P7123BF	130.47	1.18	0.91
After filtering			0.9
P25 NEW	130	0	0
P24 NEW	130	0	0

TABLE 2 : A COMPARISON OF SAMPLES

Sample Number	Location	Summary of Analysis
P7124 Before Filtration, Failed Transformer	Carthage, Tx	Severe degradation. Found aromatics, aldehydes, alkenes and carboxylic acids. 2.7% of sample collected in the liquid nitrogen distillate.
P7124 After Filtration, Failed Transformer	Carthage, Tx	Severe degradation. Found aromatics, aldehydes, alkenes, and carboxylic acids. 2.4% of sample collected in the liquid nitrogen distillate. Filtration made no change in the compounds detected, nor their concentration.
P25 Before Filtration	Longview, Tx	Found some degree of degradation. Aromatics, aldehydes, alkenes, and carboxylic acids. 1.13% of sample collected in the liquid nitrogen distillate.
P25 After Filtration	Longview, Tx	Found some degree of degradation. Found aromatics, aldehydes, alkenes and carboxylic acids. 1.13% of sample collected in the liquid nitrogen distillate. Filtration made no change in the compounds detected, nor their concentration. Replaced tap changer contacts.
P142BF	Tx Eastman	Degradation was not bad. Found small concentration of aldehydes, alkenes and aromatics. 0.43% of sample found in liquid N2 distillate.
P7124 New Oil	Carthage, Tx	No degradation products. No liquid N2 fraction observed.
P25 New Oil	Longview, Tx	No degradation products. No liquid N2 fraction observed.

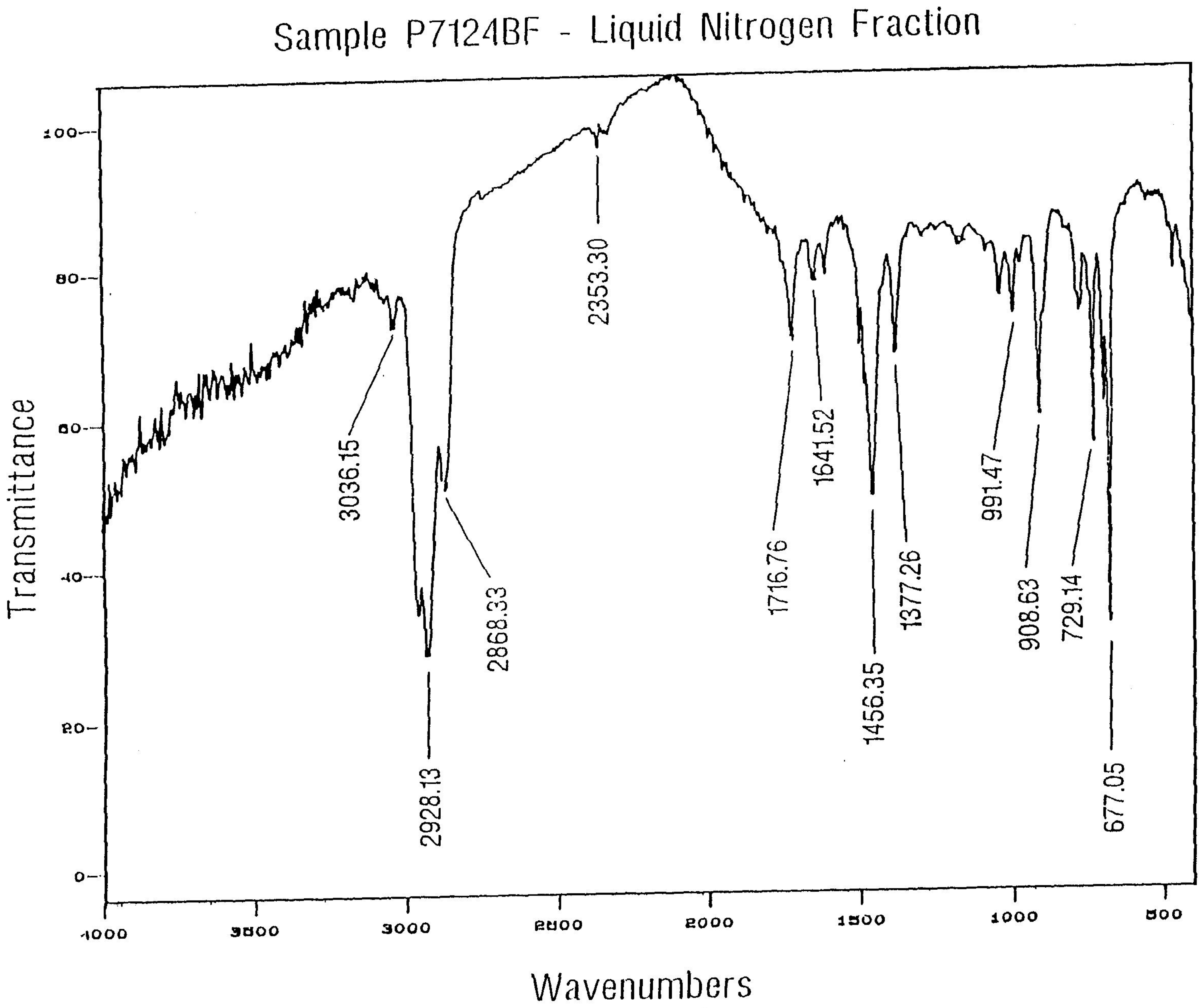

Sample P7124BF - Liquid Nitrogen Fraction
Transmittance
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers
3036.15
2928.13
2868.33
2353.30
1716.76
1641.52
1456.35
1377.26
991.47
908.63
729.14
677.05

Figure 4

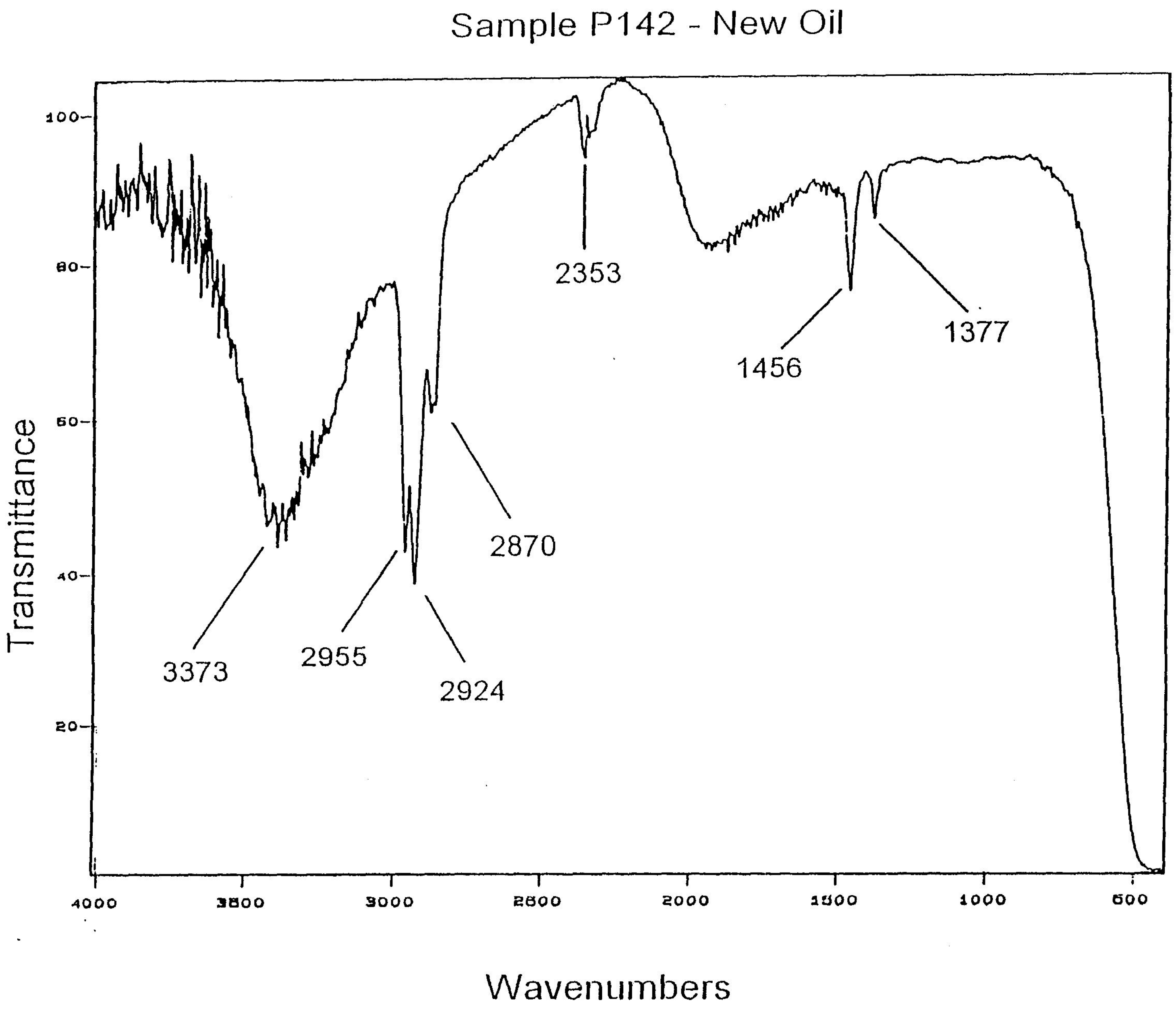

Sample P142 - New Oil
Transmittance
100
80
60
40
20
3373
2955
2924
2870
2353
1456
1377
4000
3500
3000
2500
2000
1500
1000
500
Wavenumbers

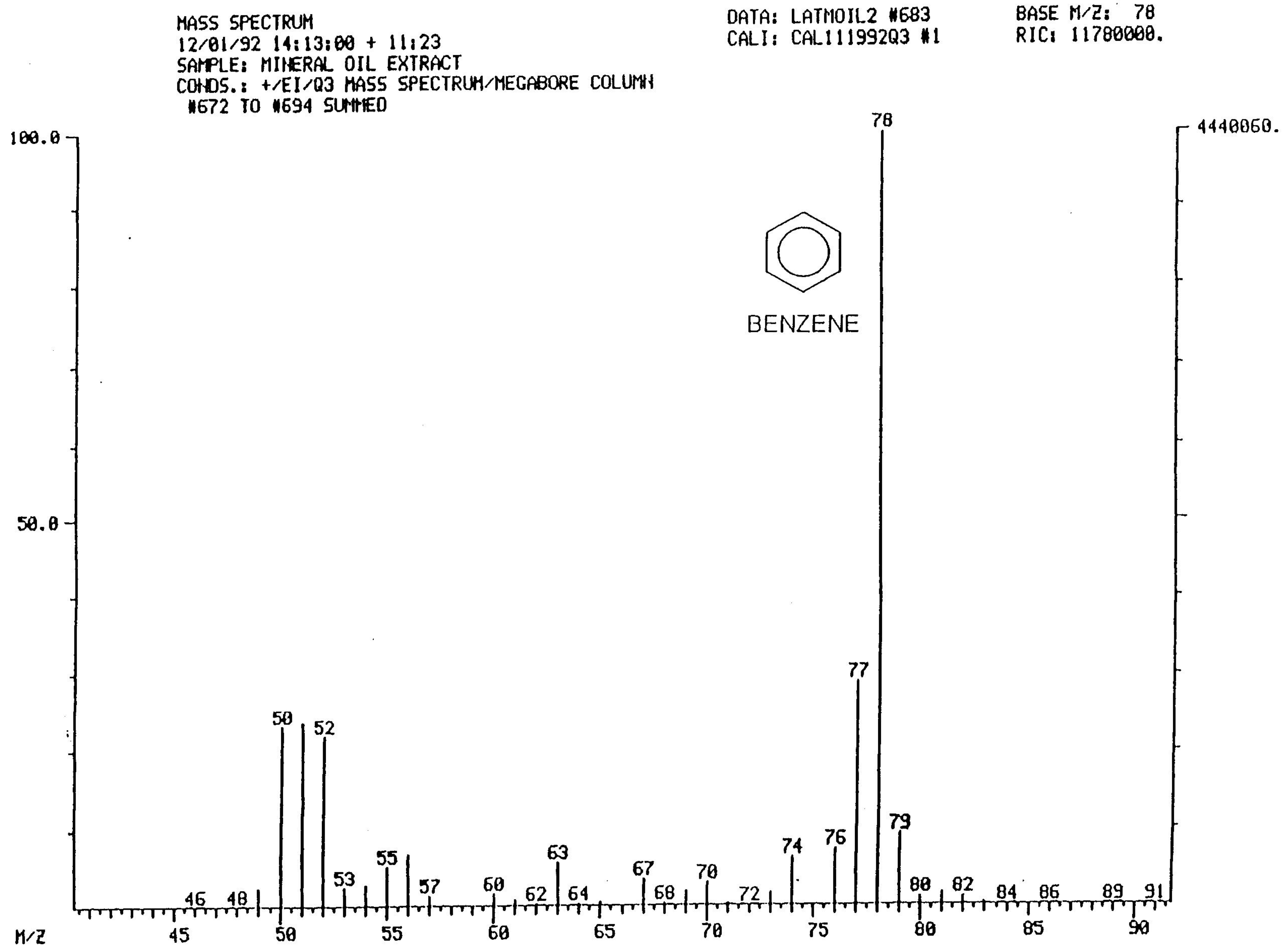
Figure 5

gasoline or gasoline to diesel. A small amount of the original material remained in the tank and when the new material began to flow in somewhere early in the process a fire or explosion might occur. These explosions have now been eliminated by blanketing the tank with nitrogen. The earlier ventings of these tanks (which allowed air to fill the tank and supply oxygen for fires and explosion) have been eliminated anyhow for environmental reasons.

THE SPECIAL CASE HERE

The highly flammable components that appear in our analysis of these oils is most significant. Even if they were not within their pure component flammable limits our ignorance of the flammability of mixtures must warn us of the great hazard that has been created.

Figure 7 - Mass Spectrum Analysis of Sample P7124BF - Liquid Nitrogen Fraction



MASS SPECTRUM
12/01/92 14:13:00 + 11:23
SAMPLE: MINERAL OIL EXTRACT
CONDS.: +/EI/Q3 MASS SPECTRUM/MEGABORE COLUMN
#672 TO #694 SUMMED

DATA: LATMOIL2 #683
CALI: CAL111992Q3 #1

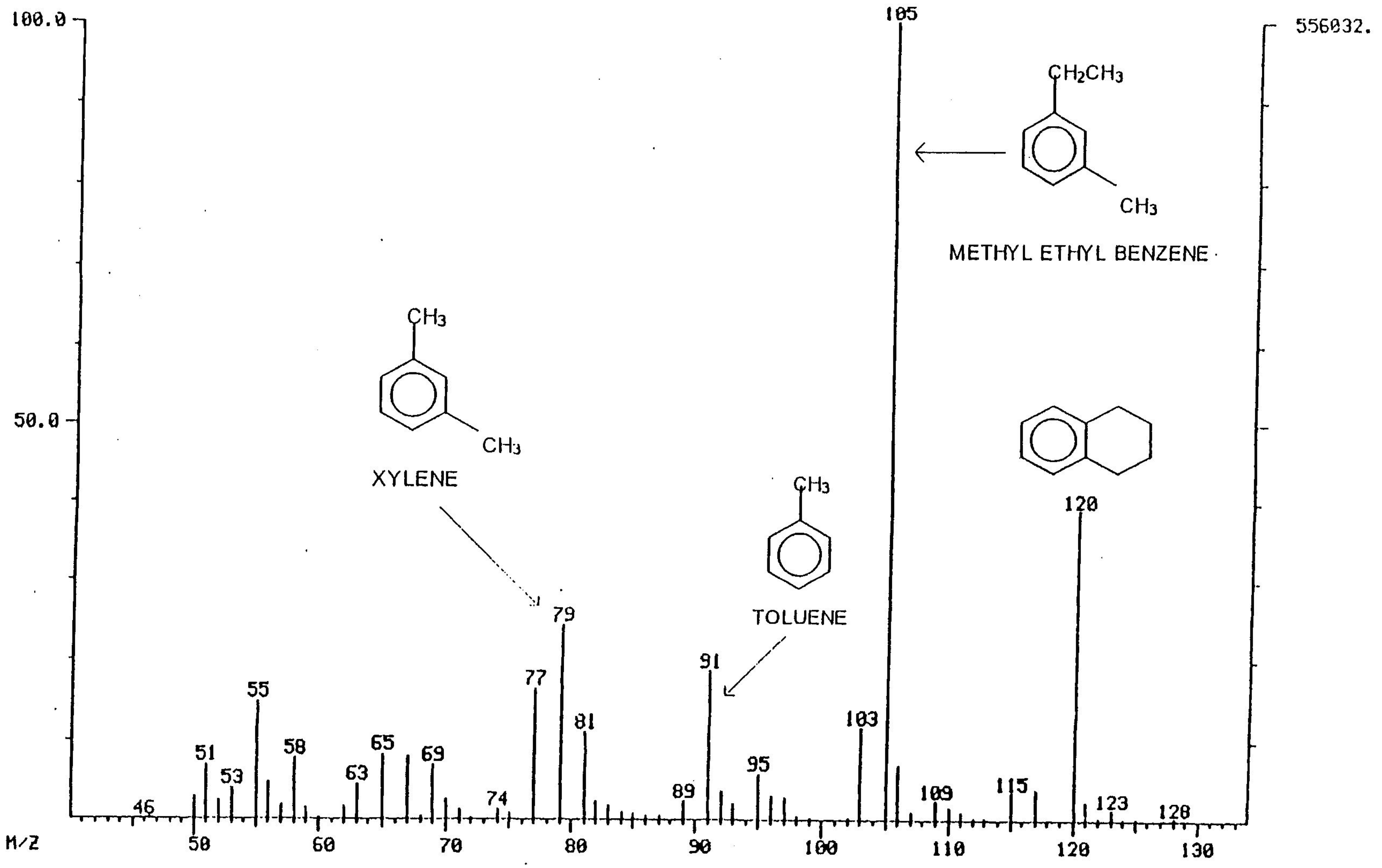
BASE M/Z: 78
RIC: 11780000.

Figure 8 - Mass Spectrum Analysis of Sample P7124BF - Liquid Nitrogen Fraction

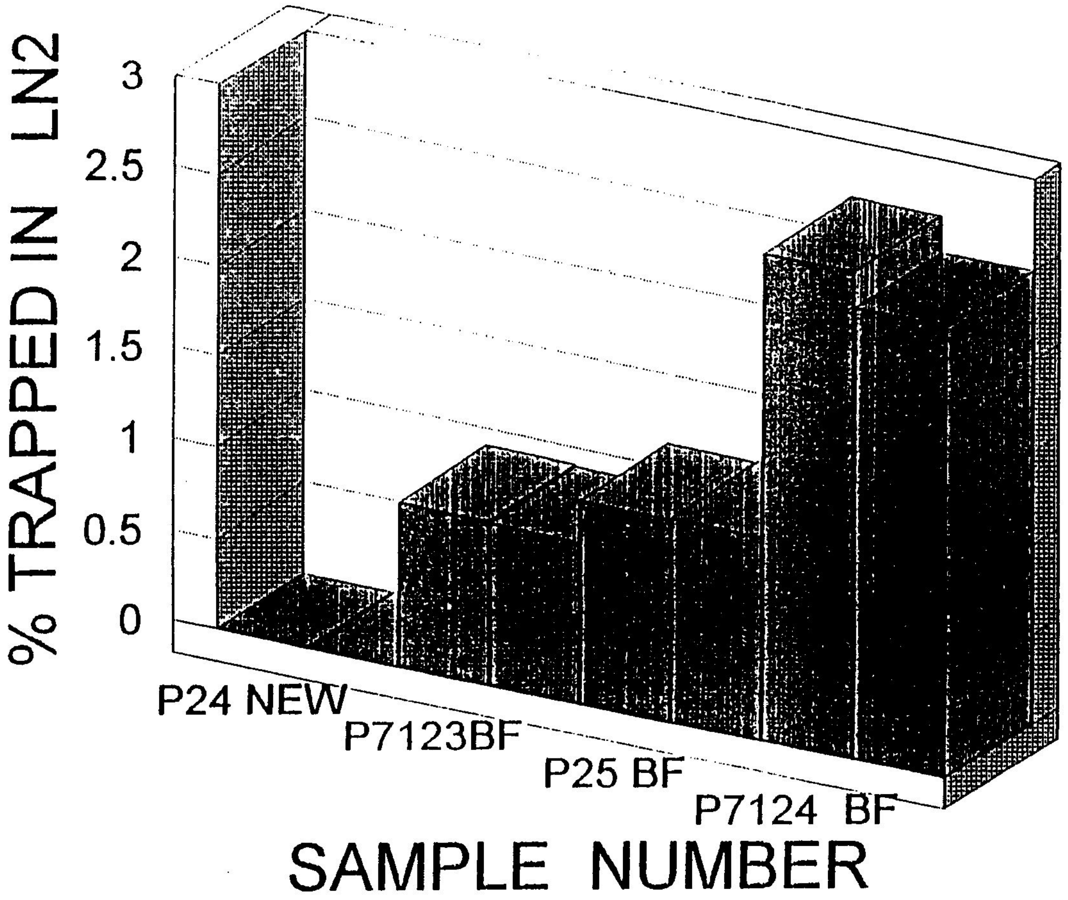
MASS SPECTRUM
12/01/92 14:13:00 + 33:15
SAMPLE: MINERAL OIL EXTRACT
CONDS.: +/EI/Q3 MASS SPECTRUM/MEGABORE COLUMN
#1991 TO #1999 SUMMED

DATA: LATMOIL2 #1995
CALI: CAL111992Q3 #1

BASE M/Z: 105
RIC: 2015230.



VOLATILE COMPONENTS



Appendix 1. FLAMMABILITY

GENERAL

Anytime we have present the three apexes of the five triangle: fuel, oxygen, and ignition, a fire/explosion may occur. Fuel and oxygen must be present in the proper amounts (this being referred to as the flammable or explosive limits) and an ignition source of sufficient energy must be introduced.

The terms fire and explosion are used interchangeably since one form of explosion is simply instantaneous (or at least very rapid fire). In addition to this, however, we know substances which will not burn very well but may explode catastrophically (ammonia fertilizer dust, and flour being examples). Finally, there are the true explosives ranging from nitrocellulose to nitroglygerin. Nitrocellulose, depending on its degree of nitration, is used in various smokeless gun powders. It requires an external ignition source to ignite and then its "explosion" is really a very rapid controlled burn. On the other hand, nitroglycerine is very unstable and may explode with impact, heating or freezing.

MIXTURES

The testing of flammability limits and flash points has been done exclusively on simple pure components. There is no such body of knowledge for mixtures. As a first assumption, we might guess that an equal mixture of two flammable liquids would have the ignition characteristics of an average of the two components. There is some work that appears to support this on simple hydrocarbons. However, there are very disturbing instances which appear to contradict this. These are the so called "cross-over" fires which occurred some two decades ago in the petroleum industry. These "cross-over" fires were always associated with changing over a large storage tank either from diesel to