Quantitative Determination of Tetraalkyllead by Lead-207 Nuclear Magnetic Resonance

by

Mohammed Abdullah Al-Ghamdi

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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TO MY PARENTS, WIFE, AND MY CHILDREN

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THESIS ABSTRACT

Name: Mohammed Abdullah Al-Ghamdi
Title: Quantitative Determination of Tetraethyllead by Lead-207 Nuclear Magnetic Resonance
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Tetraalkyllead products are available in Saudi Arabia from 3 different vendors; Ethyl (US), Octel (UK), and Novoktan (FRG). Saudi Arabia purchases $100,000,000 of this lead octane blending chemical per year, with only basic quality control methods in force. We have succeeded in developing the lead-207 NMR technique to observe lead impurities in TEL, and have developed the technique to measure tetraethyllead and tetramethyllead in gasoline at levels down to 50 ppm, with a precision of 2 % relative error. Lead-207 has also been shown to be a powerful tool to study the rate, degree, and composition in the formation of equilibrium mixtures of tetraalkyllead blending components. This technique can also be applied to the measurement of alkyllead species in biological fluids, environmental samples, and process development and improvement studies.

خلاصة الرسالة

إسم مقدم الرسالة : محمد عبدالله علي الغامدي
عنوان الرسالة : تعين كمية رباعي إيكيل الرصاص بواسطة الطنين النووي المغناطيسي.
التخصص : كيمياء
التاريخ : فبراير ١٩٩٧م

يتم الحصول على رباعي إيثيل الرصاص في المملكة العربية السعودية عن طريق ثلاث مصادر وهي شركة إيثل من الولايات المتحدة الأمريكية وشركة نوفكتان من المانيا وشركة أكتل من بريطانيا. وتشتري المملكة العربية السعودية من مادة رباعي إيثيل الرصاص الذي يخلط مع وقود البنزين لرفع كفاءة الإحتراق ما قيمته ١٠٠,٠٠٠,٠٠٠ دولار أمريكي سنوياً. وتتم مراقبة نوعية هذة المادة بطريقة تحليل تقليدية وطويلة. وقد تم في هذة الدراسة تطوير طريقة بإستخدام إسلوب الطنين النووي المغناطيسي لتحديد كمية مادة رباعي إيثيل الرصاص في كل من الشحنات التجارية من هذة المادة وفي وقود البنزين المستخدم في المملكة. وكذلك تم تطوير هذة الطريقة بحيث يمكن إستخدامها لقياس نسبة كل من مادتي رباعي إيثيل الرصاص و رباعي ميثيل الرصاص في وقود البنزين و الموجود فيه في حدود ٥٠ جزء من المليون وبدقة مقدارها ٢٪. و بإستخدام هذة الطريقة تم إثبات أنها أداة مناسبة لدراسة سرعة و درجة التكوين و المكونات في محاليل تحتوي على عدة أصناف من مركبات رباعي إيكيل الرصاص. ومن الممكن إستخدام هذة الطريقة أيضاً لقياس أصناف إيكيل الرصاص في السوائل البيولوجية وعينات البيئة وكذلك في دراسة تطوير عمليات المعالجة وتحسينها.

CHAPTER 1

1. THEORITICAL PRINCIPLES

1.1 INTRODUCTION

1.1.1 BACKGROUND

Tetraethyllead (TEL) is manufactured by electrosynthesis from alkyl halide and a lead-alkali metal amalgam. Impurities are expected to be other lead alkyls and possibly plumbanes, alkyl lead halides, lead oxygenates, and organolead multinuclear clusters(1).

Lead has 4 major isotopes, ^{204}Pb=1.5%, ^{206}Pb=23.6%, ^{207}Pb=22.6%, ^{208}Pb=52.3%. Only lead-207 isotope has nuclear spin and may be observed by NMR techniques (2). The total lead percentage in a TEL sample may be easily determined by atomic absorption spectroscopy, X-ray fluorescence, or iodine monochloride titration (3). Total lead does not refer to the variety of lead species in the sample, or their contribution to octane performance. Very little work is published in the area of nuclear magnetic resonance spectroscopy of the lead-207 isotope(4). Lead-207 has a receptivity twelve times greater than carbon-13, nuclear spin of 1/2, and no nuclear quadrapole. Also, it has a strong coupling with hydrogen which may be easily decoupled. The reasonable chemical shifts, rapid relaxation, a strong nuclear Overhauser effect advantage, and good spectral dispersion are other factors that make lead a good subject for NMR studies (5).

TEL is delivered as a 30-65% solution in various alkyl halide solvents such as 1-chloro-2-bromoethane, these solvents also function as lead scavengers in the automobile engine (6).

Saudi Arabia is currently purchasing $100,000,000 in TEL each year, for direct use and also to permit stockpiling, since continued manufacture or supply by the Ethyl corporation and others is uncertain. If it is found that the quality or storage stability of TEL is questionable, this will directly impact the value of the expenditure. For example, if one vendor's product is superior to the other by as little as 1%, Saudi Arabia could realize a saving of $1,000,000 per year, based on reduced consumption of TEL.

1.1.1.1 LEAD ALKYLS AND THE GASOLINE ENGINE

The thermal efficiency (E) of the theoretical Otto-cycle engine can be described by the relationship:

$$E = 1-\{ 1/C_R \}^{C_p/C_{v-1}}$$

where C_R is the compression ratio and C_p and C_V are the specific heats of the working fluids at constant pressure and volume respectively. When C_P and C_V are equal, the thermal efficiency (and hence the fuel economy) is a strict function of the compression ratio, E_R.

Increasing compression ratio to achieve higher thermal efficiency is limited by abnormal combustion phenomena such as spark knock, which can cause significant power loss and engine damage. The ability of a motor fuel to resist spark knock is measured in terms of its research octane number (R O N) and motor octane number (MON) ratings, which are determined by comparing or matching its knock performance to reference fuels in stationary laboratory engines. The most effective way of increasing octane number and knock resistance of fuel, and fuel engine economy, has historically been through the use of lead alkyls rather than refinery process upgrading. Recently, however, environmental regulations have forced the elimination of lead alkyls from gasoline pools due to their chronic toxicity, and oxygenated fuel additives such as methyl tertiary butyl ether (MTBE) have been used as a replacement. Manganese alkyls are permitted in Canada, however, and the USA, Environmental Protection Agency (EPA) has been petitioned to permit their use (7). Sophisticated approaches to achieving octane requirements by a combination of refinery upgrading, reformulation and octane enhancing additives is now routinely practiced throughout the world.

1.1.1.2 THE STATUS OF LEAD USAGE IN GASOLINE.

The average tetraalkyllead content in the total US gasoline pool reached a peak of 4 grams per US gallon in 1968-69 when the petroleum refining industry supplied high octane gasoline to satisfy the high compression ratio engines then popular with US automakers. Domestic consumption then reached its maximum of 312,000 tons of lead alkyls. Consumption began to decrease in 1971 with the appearance of automobiles with low compression engines designed to reduce exhaust emissions. Between 1974 and 1978 further declines in lead consumption occurred with the introduction of catalytic converters that were incompatible with leaded gasoline. The EPA mandated in 1973 a reduction in the lead content of the gasoline pool, and consumption decreased to 205,000 tons per year in 1978, with the average gasoline content of 2 grams per gallon. Thus, lead consumption in the US had declined by the year 1978, by 34 % from its peak in 1968. The following schedule (Table 1.1) was adopted for the removal of lead from gasoline (11).

Table 1.1 Timetable Used for US Lead Phase-out

Date	Target Lead Status
1. Late 1973	0.45 gram/liter
2. Mid 1974	Introduction of Lead Free Gasoline
3. July 1985	0.13 gram/liter
4. January 1986	0.03 gram/liter
5. January 1988	0.01 gram/liter
6. January 1990	Elimination of Lead from all Gasoline

Since January of 1992, Canada has banned the sale of leaded gasoline for automobile use, but a manganese additive is permitted. In the US, lead additives are prohibited in gasoline unless a waiver is granted by the EPA. Litigation is in progress to force the EPA to permit manganese additives (9).

In Latin America, the environmental legislation is way behind that of the US. But, leaded gasoline is not generally available in Brazil. A lead phase down program has been initiated in Mexico. The proposed lead reduction in Venezuela will not be implemented until the year 2000, although reconfiguration is already underway in domestic refineries. Unleaded gasoline was introduced in Chile in 1992, and legislation has been established to require all new cars to meet US emission standards.

In Western Europe, the European Economic Community (EEC) dropped its remaining trade barriers in 1992, and set the stage for common gasoline specifications. It requires member countries to set a maximum of between 0.15-0.40 g/l lead in the gasoline pool, permits members to ban the sale of leaded gasoline, and required the introduction of unleaded in 1989. West Germany and Luxembourg have already banned leaded gasoline.

In the Asia-Pacific region, market penetration of unleaded gasoline has been swift, including Australia, Taiwan, New Zealand, Hong Kong, Malasia, and Thailand. In Japan, all gasoline is now 96 % unleaded, and both regular and premium grades are widely available. South Korea banned the sale of leaded gasoline in 1993. Thailand has initiated several objectives: Lead phase-out to be completed over the next two years, aromatics to be reduced 30 %, and benzene trimmed to 3 vol. %. India requires gasoline to be reduced to a lead content of 0.15 g/l from the previous 0.5 g/l.

In the Middle East, Kuwait and the United Arab Emirates planned to introduce unleaded in 1996, but Iran and Iraq have not considered lead phase-down. Bahrain sells two grades of leaded gasoline. Saudi Arabia is the worlds largest producer of MTBE, but produces only one grade of leaded gasoline. In 1987 all Saudi domestic refineries switched to a single grade of gasoline at RON of 95 and lead content of 0.6 g/l. After 1996, the switch to unleaded is expected to take place. The joint-venture export refineries in Jubail, Yanbu, and Rabigh produce only unleaded gasoline. The switch-over to unleaded is under intense scrutiny, but plans are still undefined, and a definite timetable has not been set(11). Because of the greater than one billion dollar investment required for the Saudi Arabian switch over, the change may not be affected until the year 2005 (15).

In Africa, there is no restriction on lead before the year 2000, but South Africa has reduced lead content to 0.4 g/l, and introduced unleaded in 1995 (9).

1.1.1.3 ORGANOLEAD COMPOUNDS

Tetraethyllead was the first organolead compound known, and was formed by the reaction of a sodium-lead alloy with ethyl iodide. The antiknock properties of TEL were discovered in 1923. Tetramethyllead and redistribution mixtures of TEL and TML were introduced in 1960 for specific economic advantages in gasoline composition-automotive engine combinations. There were approximately 1450 organolead compounds known in 1968, with about 130 new ones each year. Due to their widespread use as gasoline motor fuel antiknock additives, organolead compounds are the largest single industrial application of organometallic chemistry (7).

The only large scale industrial use of organolead compounds is the antiknock application in internal combustion gasoline engines. The only other significant application is alkyllead halides for use as seed disinfectants and control of fungus, and these uses are limited because of environmental concerns. Experimental work is underway to evaluate trialkyllead derivatives as agents against marine borers, molds, and termites. Triphenyllead acetate has been commercialized in Germany as a marine antifouling paint. Tributyllead acetate is active against termites and fungi. Other applications under investigation are as catalysts, synthetic reagents, biocides, sternutators, and stabilizers (7).

1.1.1.4 PHYSICAL PROPERTIES OF LEAD ALKYLS

Lead tetra-alkyls appear to be typical organic compounds in physical properties, ranging from the liquid, volatile TML to the crystalline tetraaryleads. Hydrides (Plumbanes) are known but are relatively unstable. Solubility of lead alkyls is similar to corresponding hydrocarbons. Boiling points parallel molecular weights, and melting points reflect the usual symmetry and physical force factors. Compounds with lead to metal bonding exhibit largely non-polar properties. Physical properties such as dipole moment, heat of vaporization, heat capacity, and viscosity are comparable to analogous hydrocarbons. Densities naturally reflect the presence of the lead atom. Most tetra-alkyl lead compounds are colorless to yellow, and non-fluorescent. Symmetry for these compounds is tetrahedral, with bond angles near 109 degrees, and carbon-lead bond lengths of 2.25 A° (7).

Table 1.2 Physical Properties of Lead Alkyls

Properties	Tetramethyllead	Tetraethyllead
Melting Point, °C	-30.2	-137.6
Boiling Point, °C	110(@ 101 mm)	78(@ 1.3 mm)
Density^{20}, g/ml	1.9952	1.6528
Refractive Index ^{20},	1.5128	1.5195
Viscosity, cP	0.572	0.864
Log Vapor, kPa	6.06257 (-1335.317/ T+219.084)	8.8551 (-2960.0 / T+273.1)
Surface Tension, dyn/cm		28.48
Lat Heat of Vap., kJ/mole	38	54
Heat of Fusion, kJ/mole	10.86	8.80
Heat Capacity J/mole-C	101-152 (-173 to -121 C)	141-262 (-132 to -133 C)
Heat of Formation kJ/mole	98.4	53.6
Heat of Combustion kJ/mole	3507	6473

1.1.1.5 THE CHEMISTRY OF LEAD ALKYLS

The chemistry of the carbon-lead bond is similar to other unreactive organometallics. Although covalent, the bond is subject to a wide array of free-radical and ionic reactions. The carbon-lead bond in aliphatic plumbanes is only moderately stable to heat, with bond energies around 150 KJ/mole. Pyrolysis generates free lead and alkyl radicals, forming diethyllead and hexaethyldilead intermediates. Decomposition of TEL begins at about 100°C and is exothermic with first order kinetics and an E_a of 150 KJ/mole. TML decomposes at a higher temperature but with a faster rate and E_a of 115 KJ/mole. The decomposition temperature of tetraphenyl lead is 250_C. Although lead tetraalkyles are photochemically stable, they can be decomposed by near-uv light (1).

Reactions involving electron transfers or redox mechanisms are common, with diverse reagents such as oxidants, halogens, and reactive metals. Lead alkyls are electrochemically reactive with electrode processes reported for polarographic conditions. For a typical reactive metal replacement reaction, sodium or potassium, usually in liquid ammonia, donates an electron with simultaneous lead-carbon bond cleavage:

$$R_4Pb + 2\,Na + NH_3 \longrightarrow R_3PbNa + RH + NaNH_2$$

The R_3Pb^- ion can react further with ammonia to give R_2Pb. The R_3Pb^+ compounds can react by reduction with metals to give hexaalkyldilead species, R_3PbPbR_3.

Under mild conditions with direct mixing, even a very low temperatures, tetraalkyllead compounds react with halogens to form trialkyllead halides:

$$R_4Pb + Cl_2 \longrightarrow R_3PbCl + RCl$$

The reaction continues exothermically even at -10 _C with replacement of the second R group:

$$R_3PbCl + Cl_2 \longrightarrow R_2PbCl_2 + RCl$$

Replacement of the third alkyl group results in decomposition of the lead alkyl:

$$R_2PbCl_2 + Cl_2 \longrightarrow RCl + \{RPbCl_3\} \longrightarrow 2RCl + PbCl_2$$

Other oxidants such as oxygen, sulfur dioxide, nitrogen dioxide, sulfuryl chloride, chlorine, and even carbon tetrachloride remove one or two alkyl groups, and compounds with lead-metal bonds are equally reactive:

$$R_3PbPbR_3 + Cl_2 \longrightarrow 2\ R_3PbCl$$

Ionic processes without one-electron transfer steps also take place facialy. Acids produce cleavage of lead alkyl bonds, with both mineral and organic acids as effective reagents:

$$R_4Pb + HCl \longrightarrow R_3PbCl + RH$$

The weaker carboxylic acids react more slowly, and warming is helpful, but water and aqueous caustic solutions are unreactive; for example both $(CH_3)_4Pb$ and $(C_2H_5)_4Pb$ may be steam distilled. Many ionic chemical exchange reactions take place, such as with metal salts, organometallics, and nonmetal halides:

$$R_4Pb + PCl_3 \longrightarrow R_3PbCl + RPCl_2$$

$$R_4Pb + AlCl_3 \longrightarrow R_3PbCl + RAlCl_2$$

$$R_4Pb + HgCl_3 \longrightarrow R_3PbCl + RHgCl_2$$

$$R_4Pb + SiCl_4 \longrightarrow R_3PbCl + RSiCl_3$$

Most non-metal halides react similarly, as do most Group II, IV, and transition metal halides. Metal ions such as ferric, copper, silver, and gold are reduced in the process since the alkylated metal chlorides are unstable. The extent of the alkylation or replacement reaction varies considerably, and depends on the reagent. For example with phosphorus trichloride, two alkyl groups are replaced at 25_C, but the third requires 100 _C for replacement. Arsenic trichloride requires 100_C to replace two alkyl groups (16). Sulfur dioxide reacts by an insertion mechanism to form a sulfone:

$$(C_2H_5)_4Pb + 2\ SO_2 \rightarrow (C_2H_5)_3Pb(SO_2C_2H_5) \rightarrow (C_2H_5)_2Pb(SO_2C_2H_5)_2$$

The ease of cleavage of carbon-lead bonds by electrophilic reagents follows the decreasing order of reactivity: a-napthyl> b-toluyl > phenyl > methyl > ethyl > *n*-propyl > cyclohexyl. Another class of exchange reactions characteristic of lead alkyls is the disproportionation reaction in which lead alkyls exchange substituent groups:

$$2\,(C_2H_5)_2Pb(CH_3)_2 \rightarrow (C_2H_5)_3Pb(CH_3) + (C_2H_5)Pb(CH_3)_3$$

In the presence of Lewis acid catalysts such as iron or aluminum chloride, this reaction is accelerated. Exchange with other organometals such as mercury, tin, and aluminum alkyls is favored, and the redistribution reaction between TEL and TML is used to tailor-make gasoline additive systems:

$$2\,(C_2H_5)_4Pb + 2(CH_3)_4Pb \xrightarrow{AlCl_3} (C_2H_5)_3Pb(CH_3) + (C_2H_5)Pb(CH_3)_3 + 2(C_2H_5)_2Pb(CH_3)_2$$

Various ionic lead species such as R_3Pb^+ and R_2Pb^{2+} compounds undergo anion replacement in normal fashion, although disproportionation is a competing reaction. If the anion is a chelating agent, complexes that suggest coordination to lead can be formed (7).

1.1.1.6 SYNTHESIS OF LEAD ALKYLS

Synthesis of lead alkyls requires formation of a lead-carbon bond and consequently involve the use of organometallic synthetic techniques. Lead metal reacts with ethyl or methyl chlorides if the lead is first combined with sodium, usually as the 1:1 alloy. Catalysts such as acetone or higher alcohols are frequently used.

$$4\,NaPb + 4\,C_2H_5Cl \longrightarrow (C_2H_5)_4Pb + 4\,NaCl + 3\,Pb$$

Other alloys and other alkyl halides are less frequently employed and are either less efficient or fail to react. The presence of lead metal helps push reaction intermediates such as hexaethyldilead to completion.

Divalent lead such as $PbCl_2$ or PbO can also be alkylated but only by organometallics such as Grignards or aluminum alkyls. For the ethyl compound, the final product is a mixture of hexaethyldilead and tetraethyllead when Grignard reagents are used, or tetraethyllead when aluminum alkyls are used:

$$5\ PbCl_2 + 10\ C_2H_5MgBr \longrightarrow (C_2H_5)_4Pb + (C_2H_5)_3PbPb(C_2H_5)_3 + 10MgBrCl + 2\ Pb$$

Several electrochemical routes to the synthesis of tetraalkyllead compounds are known. Electrolysis of Grignard solutions in ethers is practiced by the Nalco Chemical Co., using alkyl halide reagent with a lead anode to give tetramethyllead:

$$2\ CH_3MgCl + 2\ CH_3Cl + Pb \dashrightarrow (CH_3)_4Pb + 2\ MgCl_2$$

Electrolysis using a tetraalkylammonium salt electrolyte in a solvent such as acetonitrile with lead anodes and a methyl chloride alkylating agent has been reported (17):

$$4\ CH_3Cl + Pb \longrightarrow (CH_3)_4Pb + 2\ Cl_2$$

1.1.1.7 MANUFACTURING AND PROCESSING OF LEAD ALKYLS

Tetraethyllead is produced by two different processes both involving the reaction of ethyl chloride with sodium-lead alloy. The original process was a batch operation in which the alloy was flaked under nitrogen then transferred to an agitated horizontal autoclave. Ethyl chloride together with acetone catalyst was added gradually with mixing, and reflux cooling along with jacket cooling controlled the reaction below 100_C. After stripping ethyl chloride from the product, the reaction mass was dropped as a viscous slurry to a still pot, where TEL was purified by steam distillation. Anti-agglomeration agents including sodium thiosulfate, ferric salts, and elemental sulfur prevented the finely divided solids from coalescing, and soaps were added to aid in removal of residual TEL. After distillation, the reaction mass which consisted of metallic lead and sodium chloride, was transferred to a wash tank for removal of sodium chloride. The washed metallic lead was then recycled to the melt furnace, where it was mixed with sodium metal to reform the alloy. At least 75% of the lead had to be recycled, but overall the yield was 82-92%. Byproducts include hydrocarbons, and sodium chloride, and several process poisons including carbon dioxide, acetylene, and water were of concern during operation. The product after aeration and washing was typically 99% pure, and was then formulated into antiknock products.

An improved process for the continuous manufacture of TEL was introduced by DuPont in 1953 at its New Jersey site, and a second plant was built in California in 1957. This process was based on the batch process outlined above and appears as a process flow diagram in Figure 1.1. Alloy is fed to an agitated cascade reactor along with excess ethyl chloride and catalyst. Cooling of the reactor is from refluxing ethyl chloride to maintain 150 degree C with 300 psi during residence time of several minutes. As the reaction slurry is charged to the stripper, water and steam are injected along with antiagglomeration agents. Lead and sodium chloride along with steam condensate drop to a wash tank from which the lead is augered to the remelt furnace, and the wash is sent to treatment. The stripper overhead is further fractionated to purify ethyl chloride for recycle and TEL to storage. Water is recovered as condensate and steam for reinjection (18).

Tetramethyllead is manufactured from methyl chloride in a batch process similar to that for TEL. Higher temperatures and pressures are required along with different catalysts. Two different catalysts are employed, one is simply variations of Lewis acids such as aluminum chloride along with aluminum alkyls. A second catalyst system employs a Lewis base, ammonia, along with an aqueous low molecular weight alcohol as co-catalyst. The second system involves much milder conditions. Reaction cooling, separation and purification are similar to the TEL process, but toluene is added as a solvent and diluent as a safety feature. This is because higher pressures of the TML process, as well as the more violent decomposition tendencies (19).

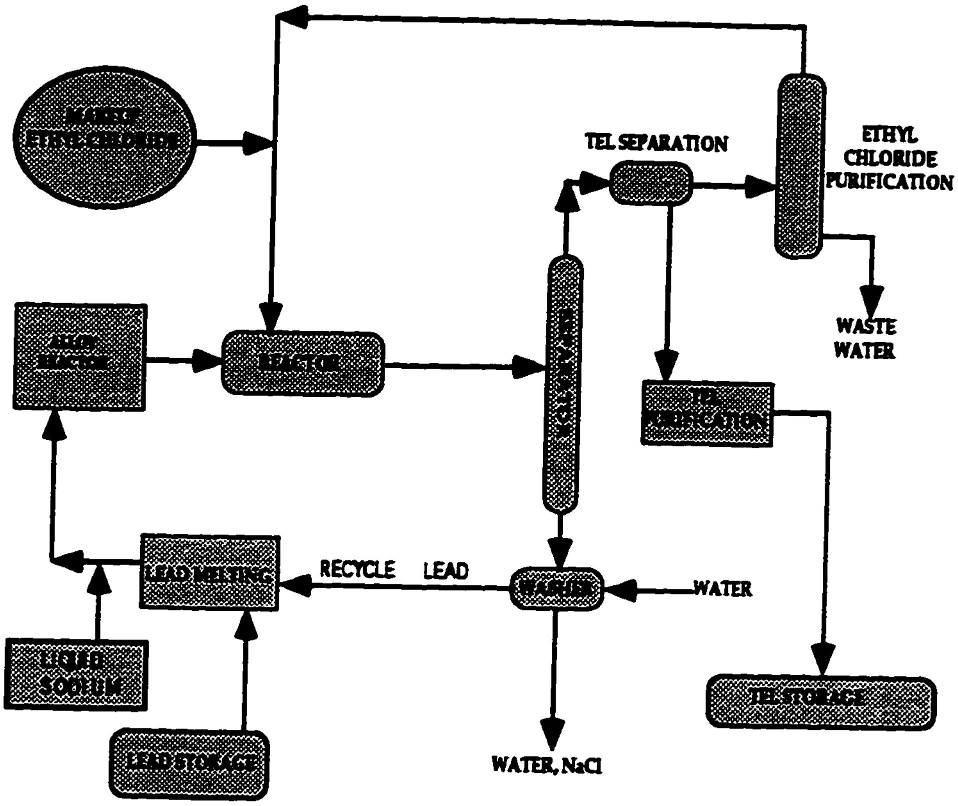


Figure 1.1 E.I DuPont Continuous Process for Tetraethyllead Manufacturing

Another process for TML was introduced by Nalco in 1962 based on an electrolytic Grignard reaction. Electrolytic cells containing a pelletized lead anode separated by a membrane from the surrounding steel vessel wall which functions as the cathode. The Grignard reagent in ether solution is passed through the cell where methyl anions react with lead in the electrode producing TML. $MgCl^+$ ions migrate to the steel wall where they are reduced to magnesium metal and magnesium chloride. Excess methyl chloride reacts with magnesium metal to produce more Grignard which continues to react. The process stream effluent from the electrolytic cell is separated by countercurrent extraction then distillation, then the methyl chloride and ether are recycled. Magnesium chloride is processed to recover the metal which is recycled, and TML is further purified and blended. The process has an overall yield of 96%, and avoids lead recycle, although magnesium costs and high power requirements are disadvantages (20).

Since commercialization of lead antiknock compounds, many other processes and modifications and improvements have been developed but have not been adopted because of practical and economic deficiencies. They include active metals other than sodium, alternative alkylating agents, alternative lead alloys, and alternative catalysts.

1.1.1.8 PRODUCTION OF LEAD ALKYLS

Manufacture of tetraethyllead was initiated by Standard Oil of New Jersey in 1922, but was discontinued after a few months. Production resumed in 1923 by DuPont at Deepwater, New Jersey, and had other plants at Antioch, California, Maitland, Ontario, and Coatzacoalcos, Mexico. Ethyl Corporation began manufacture in 1948 at Baton Rouge, Louisana, built another plant at Pasedena, Texas, and eventually manufactured at Sarnia, Ontario and Thessaloniki, Greece. Nalco Chemical manufactures lead alkyls in Freeport, Texas, and PPG Industries has a facility in Beaumont, Texas. Associated Octel has had manufacturing facilities for lead alkyls at Almwich, Ellesmere Port; Northwich in the UK; Biebesheim, FRG; Bussi, Italy, and Paimboeuf, France. Alcor Chemie AG (Novaktan) manufactures TEL at Walterswil, FRG. Total US production was 403,000 metric tons in 1978, and 164,000 the same year in the rest of the world (7).

1.1.1.9 HEALTH, SAFETY, ENVIRONMENTAL, TOXICOLOGY OF LEAD ALKYLS

Lead has been associated with civilization for thousands of years because of its many desirable properties, such as malleability, inertness, and ease of smelting. Hazards from lead poisoning have been recognized since antiquity. Only in this century have effective methods of preventing overexposure been practiced, and today there is a very low incidence of lead poisoning from industrial sources.

All lead compounds are considered toxic, especially the organoleads. Inorganic lead salts can be introduced into the body by ingestion or airborne dust, the volatile tetraalkyllead compounds can, in addition, be absorbed through the skin and inhaled in the vapor form. These routes of exposure generally are not available for inorganic lead compounds (7).

Overexposure to organolead compounds unlike inorganic lead compounds, produces symptoms that largely are related to effects on the central nervous system. Great care is taken in all manufacturing plants to prevent worker exposure to organolead vapors and liquid. In addition to the previously mentioned engineering controls, considerable effort is expended in the area of protective clothing, for example, gloves, suits and boots, and most manufacturers have ongoing programs to evaluate new protective materials. Some excellent barriers to penetration are selected fluoroelastomers, certain formulations of nitrile latexes, and poly(vinyl alcohol). The latter may be impractical in some situations because of its interaction with water. Lesser but adequate protection, is provided by poly(vinyl chloride), especially if it is overcured. Respiratory protection, when required, is provided adequately by National Institute of Occupational Safety and Health (NIOSH)-approved organic vapor cartridge respirators or combinations of air supplied masks, hoods, and suits. The result of these efforts is a safe working environment.

In further exposure control, the air at organolead manufacturing sites is one of the most closely monitored in the chemical industry. Routine monitoring was adopted early and has continued with increasing development and refinement. Today, plants use such devices as atomic absorption instruments which continuously draw air from designated sampling points; personal monitors;

and 24-h monitoring stations. The current (1979) Occupational Safety and Health Association (OSHA) permissible exposure limit for organolead is 75 ug Pb/m^3 (or about 9 ppb) at ambient conditions (22).

1.1.1.10 THE ANALYTICAL CHEMISTRY OF LEAD

Tetraalkyllead compounds may be determined by a wide array of analytical procedures. These include classical titrimetric, chromatographic, and spectroscopic techniques with a variety of precision and complexities (24).

1.1.1.10.1 TITRIMETRY

The most recognized titrimetric procedure is the iodine monochloride procedure accepted by the American Society of Testing Materials (ASTM) (25). In this method, a known volume of sample is diluted with heavy petroleum distillate and shaken with aqueous iodine monochloride reagent. Any tetraalkyl lead compounds present react with iodine monochloride and are extracted into the aqueous phase as dialkyl lead species. The aqueous extract is separated from the gasoline and boiled with nitric acid for about 30 minutes to convert the lead to inorganic nitrates. The residue is dissolved in distilled water, buffered to pH 5 using acetate buffer, and titrated with EDTA to xylenol orange endpoint. Typical precision is approximately 2%.

A rapid procedure has been reported for the titrimetric determination of TEL in gasoline using complexone to a calorimetric end point. The sample is pipeted into bromine solution in carbon tetrachloride until the color persists, then methanol is added. The solution is boiled, decolorized with a small excess of alcoholic KOH, diluted with water and boiled again. Then lead is determined indirectly using EDTA (26).

In another procedure, the sample is diluted with high boiling solvent then a 30% bromine in carbon tetrachloride is added until the brown color persists. The solution is shaken with 0.1 M nitric acid and this extract is boiled to expel bromine fumes. Tartaric acid, Erichrome black indicator, and an excess of 0.2 M magnesium chloride are added, along with 0.1% potassium cyanide and a buffer to pH 10. The sample is titrated with EDTA (27).

TEL may be determined by extraction from petroleum into concentrated hydrochloric acid and the lead precipitated as lead sulfate. The lead is then determined by titration with EDTA with Erichrome Black T as indicator. Interferences may be removed by oxidation of organic mater with sulfuric and nitric acids (28). Tetraalkyllead compounds have been determined colorimetrically using bromine and mercury(I) ion or with bromine in alcoholic solution (1).

1.1.1.10.2 SPECTROPHOTOMETRY

Tetraalkyllead (TAL) compounds may be determined spectrophotometrically by reaction with iodine, then measuring the increase in ionic lead. TAL may also be measured by extraction from petroleum with a solution of potassium chlorate and sodium chloride in dilute nitric acid (Schwartz

Reagent), then measured colorometrically as lead sulfide. In an alternate procedure, bromine in diisobutylene is added to petrol and the inorganic lead produced is measured spectrophotometricly. A rapid method measures triethyllead, diethyllead, and ionic lead as the dithizine complexes (1).

1.1.1.10.3 ELECTROCHEMISTRY

Tetraalkyllead compounds may be determined either polarographically or amperometrically after extraction with Schwartz Reagent. An alternative method is based on decomposition with hydrochloric acid, followed by polarographic analysis of the aqueous extracts at -0.2 to 0.7 volts (30). TEL compounds are determined coulometrically using bromine and mercury(I) ion in 0.5 M methanolic ammonium bromide. Hexaethyldilead may be determined in TEL by coulometric iodination at constant current with amperometric dead-stop end point indication. The titration of lead alkyls by electrolytically generated silver ion to an amperometric end point has been investigated, and titration of mixtures of lead alkyls have been titrated with silver ion in the presence of quinoline as a complexing agent. High frequency titration with potassium permanganate has been used to titrate acetone solutions of lead alkyls (1).

1.1.1.10.4 GAS CHROMATOGRAPHY

There has been an extensive amount of published work on the determination of lead tetraalkyls by gas chromatography. Almost all of the work is concerned with their analysis in petroleum solutions, or in the environment as a result of pollution from automotive emissions (1).

The problem of analysis of lead alkyls in gasoline is complicated by the hydrocarbon matrix, and by the fact that in some cases mixtures of lead alkyls are used to maximize octane. An early approach to the problem was that of Parker(30), who used gas chromatography to separate the lead alkyls, then determined the lead spectrophotometricly as the dithiazone complex. A selective electron capture detector has been reported which has essentially no interference from hydrocarbons. A silver nitrate scrubber pre-column was used to remove the halocarbon additives from the sample, and the analytical column was methylsilicone on Chromosorb W (31). Another approach is to use an analytical column containing 1,2,3-tris(cyanoethoxy)propane, a highly polar phase, which retains the halogenated scavengers until after the tetraalkyllead components have eluted (32). Two types of electron affinity detectors have been used, which were equipped with 100 mCi titanium tritide beta emitter sources. These were useful although the sensitivity of the detectors for halocarbons made special column configurations necessary (33). An elegant method of analysis combines pressure programming of the chromatograph with an atomic absorption spectrometer to produce a rapid and precise result for five tetraalkyllead components in gasoline.

The hydrogen atmosphere flame ionization detector(HAFID) was introduced in 1972, and has subsequently been proven to be a very sensitive and selective detector for lead in gasoline. A variety of methods based on gas chromatography have been reported using microwave emission detectors with argon or helium plasma and echelle gratings or diode array detectors. Mass spectrometry coupled to capillary gas chromatographs have been used for both identification and quantitation of lead alkyls in fuels(3). Some of the most promising methods are based on gas chromatography coupled to the pulsed flame photometric detector(PFPD) , the atomic emission detector (AED), inductively coupled plasma-mass spectrometry(ICP-MS), and atomic absorption spectrometer(AAS) detector(34).

1.1.1.10.5 LIQUID CHROMATOGRAPHY

Trialkyl and dialkyllead halides can be separated as the dithizonate complexes by thin layer chromatography. Mixtures of the tri- and dialkyllead acetates are best separated in an acetone-water system, and other mixtures can be separated in benzene. Color development after separation is done with dithizone spray to give yellow or red spots on a blue-green background. Inorganic lead does not migrate(35).

Mixtures of tetraalkyl lead, trialkyllead halides and dialkyllead halides may be determined by paper chromatography following conversion to the lead tetrachloride dianion and spectrophotometric measurement at 357 nm(36). A procedure for separation of tetralkyllead compounds in petroleum is based on conversion to the trialkyllead bromide, followed by ascending development on Schleicher and Schull 2043b paper with benzene:cyclohexane 1:6 saturated with water and visualization with ammonium sulfide(37). A similar method extracts tetraalkyllead compounds from petroleum and converts them to aqueous trialkyllead bromides with bromine solution. The extract is treated with ammonia and separated on Whatman #1 paper and developed decendingly with butanol-aqueous ammonia and visualized with dithizone. All metathesis products of TEL and TML were resolved(38).

High performance liquid chromatography permits concentrations as low as 10 mg of tetraethyllead per Imperial gallon to be determined, and other procedures for organic lead in gasoline by liquid chromatography are reported(39).

Lead alkyls and lead halide mixtures are separated by paper electrophoresis using aqueous lithium chloride as supporting electrolyte on Whatman #1 paper at 135 volts for 2 hours(40).

1.1.1.10.6 ATOMIC SPECTROSCOPY

Atomic absorption spectroscopy has been used for the direct determination of tetraethyllead in petroleum and offers a rapid reproducible result free from interference. Lead absorbs so strongly at 283.3 nm that samples may need to be diluted to between 0.0 and 100 mg/l. Several burner configurations have been used and several different fuel mixes are applicable, depending on the sample matrix and diluent. Precision is typically one percent, and the presence of other metals as well as sulfur, nitrogen, and halogens does not interfere below 1%

concentration. Mixtures of lead alkyls appear to suffer from some differences in absorption coefficients in the flame causing non-linearity. A rapid method for lead in gasoline is the ASTM D 3237, in which the sample is diluted with methyl isobutyl ketone, reacts with iodine, and is aspirated into the AAS flame (1).

1.1.1.10.7 X-RAY METHODS

X-ray fluoresence permits the determination of tetraethyllead in gasoline in the concentration range of 0.1-6 ml/Imperial gallon with a standard deviation of 0.28 ml/gallon(41). The error due to sulfur in the sample is very small, and that due to phosphorus additives is negligible. The time required for the analysis is 5-10 minutes. For samples of petroleum containing about 0.1 ml/gallon, a molybdenum anticathode (50kV, 13 mA), a curved crystal of lithium fluoride, and a scintillation counter have been used to insure maximum sensitivity. The lines LB_1 and LB_2 of lead and KB (second order) of molybdenum are used, but an internal standard of 0.25% bromine is added (as bromobenzene in tetralin) to compensate for interference by sulfur. Petroleum manufactured from different crudes does not affect the results significantly, and the standard deviation is typically 0.8%. Good overall agreement between results by XRF using platinum as an internal standard and other chemical, gravimetric, and spectroscopic methods has been reported(42).

TEL in petroleum products has been measured by X-ray absorption spectroscopy by monitoring the absorption increment corresponding to the sublevel L_{111} of the lead present in the sample. An apparatus of the General Electric type XRD3 was used with the anti-cathode of molybdenum (18kV). The emitted radiation, rendered monochromatic by a crystal of sodium chloride, is passed through the cell containing the petroleum sample, , and its intensity is measured at various angles using a Geiger counter(43). In another procedure, results were obtained using a radiation source of tritium Bremsstrahlung which gave a precision of .02 % with those by gravimetry for lead concentrations between 0.5-2.0 % in gasoline(45).

1.1.1.11 LEAD - 207 NMR

Lead has four major isotopes, ^{204}Pb=1.5%, ^{206}Pb=23.6%, ^{207}Pb=22.6%, ^{208}Pb=52.3%. Only the lead 207 isotope has nuclear spin and may be observed by NMR(2). The total lead percentage in a sample may be easily determined by atomic absorption spectroscopy, or iodine monochloride titration(3). This tells nothing about the variety of lead species in the sample, or their contribution to octane performance. Very little work is published in the area of Nuclear Magnetic Resonance spectroscopy of the lead 207 isotope(4). Lead is considered to be a good subject for NMR analysis, with receptivity twelve times greater than carbon-13. It has a nuclear spin of 1/2, no nuclear quadrapole, strong coupling with hydrogen which may be decoupled easily, reasonable chemical shifts, rapid relaxation, a strong nuclear Overhauser effect advantage, and good spectral dispersion(5).

Considering the ease with which the lead nucleus may be observed, the lack of quadrapolar line broadening, its high sensitivity, and its strong coupling with other nuclei, it is quite surprising that so few lead NMR studies have been reported. With an abundance of 24%, a receptivity equal to 0.2% that of the proton, a positive gyromagnetic ratio which leads to a potential nuclear Overhauser effect enhancement of up to η = 2.4, observation of lead spectra seems quite attractive in structural studies. This may be in part attributed to the extreme toxicity of organolead compounds, which requires great care in handling. Nevertheless, several lead NMR studies have been completed, including at least a dozen on organolead compounds(45-51). Prior to this work, direct observation of tetraalkyllead in gasoline has not been reported, and very little attention has been paid to use the technique for quality control in lead alkyl shipments and manufacturing, or structural elucidation purposes.

1.1.1.11.1 NUCLEAR OVERHAUSER EFFCT RELAXATION MECHANISMS

Five important mechanisms function with nuclear Overhauser effect relaxation. Those mechanisms are magnetic dipole-dipole interactions, quadrapolar, scaler coupling of 1st and 2nd kind, spin rotation, and chemical shift anisotropy. Chemical shift anisotropy mechanism, is especially important with heavy metals such as platinum and lead nuclei (52). Consequently, great care must be taken when comparing coupling in spectra taken at different applied field strength (53).

While several studies of organolead compounds by ^{207}Pb NMR have been reported, including a detailed study of vinyllead derivatives (54), one of the most interesting is the observation of direct coupling of ^{14}N-^{207}Pb nuclear spins in amine complexes of trimethyllead (55). Coupling constants of 170 Hz were observed with the ^{207}Pb nucleus appearing as an ill-defined triplet of 1:1:1 intensity (^{14}N, I=1). Coupling of heavy metal nuclei to ^{14}N is observed only rarely.

In tetramethyllead, $^{2}J(^{207}Pb-^{13}C)$ is = 131.5 Hz, and $^{2}J(^{207}Pb-^{1}H)$ is -60.5 Hz, sign inversion often is observed in carbon-13 and protons coupled to lead. In tetraethyllead, the 3-bond coupling to the methyl hydrogens is +128.6 Hz and the 2-bond coupling is -41 Hz. For plumbanes with directly bonded hydrogen the coupling constant is -2456 Hz.

A CP-MAS study by a group from Bruker of ^{207}Pb, reported a remarkably sensitive temperature dependence of chemical shift in magic angle spinning spectra of lead nitrate. This provided an excellent method for solid-state thermometry with uniform dependence of a range of -130 °C to + 150 °C. The sensitivity and NMR linewidth were favorable to the measurements, so that lead nitrate could be used to probe sample temperatures, MAS heating effects, and dynamics of temperature jumps(56).

In another solid state study of ^{207}Pb spectra, the earlier work from Bruker was confirmed and extended the chemical shift dependence of lead nitrate to variations in temperature. The Pb-207 chemical shift exhibited a linear dependence on temperature with a slope of 0.70 ppm per degree Kelvin. These results were consistent with measurements made on the static solid. At higher MAS speeds, the signal split into several components owing to localized heating effects. The effects were more pronounced in rotors made from zirconia than those made from silicon nitride (60).

A comprehensive examination of heteronuclear second order coupling between platinum and lead in bimetallic complexes has been reported. Metallation of benzene by both nuclei of ^{207}Pb-^{195}Pt of triphenylphosphine- triphenyl lead complexes was detected by observing ^{207}Pb, ^{195}Pt , and ^{31}P NMR spectra, and analysis of the asymmetry of coupled multiplets. Similar results were obtained for an extended series of platinum-lead bonded compounds with various substituents as well as for two lead atoms bound to one platinum(57).

The complexation of Pb(II) by carboxylic and aminocarboxylic acids was studied by ^{207}Pb NMR, with results indicating that the ^{207}Pb chemical shift provides a sensitive probe of the aqueous coordination chemistry of lead species. A single exchange-averaged resonance was observed for lead in solutions containing $Pb(NO_3)_2$ with pivalic, acetic, formic, or chloroacetic acids, with the lead chemical shift sensitive to mole ratios and solution pH. Formation consistence were determined for the lead-carboxylate complexes by fitting chemical shift data to a model involving the complexes and ligand protonation. Chemical shift data for lead complexed to glycine, histadine, or glycylglycine, indicate complexation of lead by the zwitterionic form of the ligands. Formation constants were determined for these complexes, which are difficult to obtain otherwise.

Complexation of lead by ethylenediaminetetraacetic acid, N-hydroxyethyl-ethylenediaminetetraaceticacid, nitrilotriaceticacid, and N-methyliminoaceticacid causes a large desheilding of the ^{207}Pb nucleus, by values in the range of 2500 ppm. The chemical shift in these complexes is sensitive to protonation, formation of mixed complexes and hydroxide complexes(58).

The ^{207}Pb spectrum of bis(triphenyllead) sulphide was obtained. The data were compared with the results of NMR measurements in solution and are discussed in relation to crystallographic considerations. Satellite resonances allow some metal-metal coupling constants to be determined. The existence of intramolecular crystallographic inequivalence makes this feasible even for $(Ph_3Pb)_2$. Use of a rotation- synchronized Carr-Purcell-Meiboom-Gill pulse sequence improves the ability to measure such coupling constants, as is demonstrated for $(Me_2SnS)_3$ (59).

CHAPTER 2

2. EXPERIMENTAL

2.1 MATERIALS AND INSTRUMENTATION

2.1.1 CHEMICALS

2.1.1.1 CHEMICALS FOR NMR METHOD

Dilute tetramethyllead-CB and tetraethyllead-CB manufactured in Great Britain by Associated Octel Company Limited. Chloroform-d and toluene-d8 from WILMAD.

2.1.1.2 CHEMICALS FOR IODINE MONOCHLORIDE TITRATION METHOD

Distilled deionized water, ammonia solution 14.8M, bromthymol blue indicator solution, EDTA standard solution 0.005M, isooctane Iodine monochloride reagent 1.0M, nitric acid 15.9M, sodium acetate, acetic acid buffer solution pH 5.2, and Xylenol orange indicator solution.

2.1.2 APPARATUS

2.1.2.1 NMR SPECTROMETER

All Lead-207 NMR spectra were obtained on a Varian Unity 400 Wide Bore Nuclear Magnetic Resonance Spectrometer equipped with a Sun Sparc IPX data station and driven by the program VNMR. The ^{207}Pb resonance frequency is 83.70 MHz and data were collected at 293K. Both broadband 5 and 10 millimeter probes and 5 mm and 10 mm WELMAD NMR tubes were used.

2.1.2.2 IODINE MONOCHLORIDE TITRATION METHOD

Separatory funnel, 250 mL, borosilicate glass, stoppered Erlenmeyer flask, 500 mL borosilicate glass, graduated cylinder, and hot plate thermostatically controlled.

2.2 EXPERIMENTAL DESIGN

2.2.1 NMR-METHOD

The original spectrum was obtained on a 0.1 M lead nitrate solution. Since the maximum spectral window on the Unity Spectrometer is 100,000 Hz, several attempts were necessary to find this signal. Resonance was finally observed at 83.40 MHz for $PbNO_3$. Subsequent observations revealed that all lead alkyls appeared at 0.3 MHz higher field, near 83.70 MHz

Broad-band Waltz-16 modulated ^1H decoupling was gated on during acquisition and off for the remainder of the pulse sequence in order to suppress the nuclear Overhauser effect (NOE). An acquisition time of 1.5 seconds and zero delay with 4096 transients (signal averaging) results in a total accumulation time of about 102 minutes per sample. A 21 μsec (90°) pulse width was used in order to yield data that are quantitative and free from baseline distortions. Collected FIDs were transformed with a 0.5 Hz line broadened weighting function.

All spectra were referenced to internal or external tetramethyllead ($\delta = 0.0$ ppm). The baseline was adjusted for linearity, using a cubic spline fit to zero, over non-absorbing regions of the spectrum. All spectral regions used in the calculations were compared to an assigned value of 10 for the tetramethyl lead integrated region (TML peak).

In order to measure longitudinal relaxation time and estimate optimum pulse width for the investigation, a spin recovery experiment was carried out using a spin-echo 180°-90°pulse sequence. T_1 measurements were performed on 9% tetraethyllead solutions in deuterochloroform to establish 90° pulse width for the 10mm broadband probe. Table 2.1 summarizes spectrometer conditions used for standard samples.

Table 2.1 Spectrometer Parameter Values Used For Standard Conditions of Lead-207 NMR Acquisitions

PARAMETER	VALUE	PARAMETER	VALUE
Transmitter Frequency	83.7 MHz	Line Broadening	1
Transmitter Power	55 Db	Decoupler Nucleus	^{1}H
Transmitter Offset	0 Hz	Decoupler Offset	0 Hz
Sweep Width	100000 Hz	Decoupler Power	49 Db
Acquisition Time	0.640	Decoupler Mode	nny
Pulse Width	19.5 µs (90°)	Decoupler Modulation	WALTZ
Delay Time	1 sec	Temperature	20 °C

The above mentioned lead-207 NMR technique has been used to analyze shipments of TEL at a nominal 65% concentration, as well as gasoline samples containing less than 1000 ppm tetraethyllead. Tetraethyllead shipments from three different vendors were analyzed in both the internal standard method, with tetramethyllead internal standard, and in the normalized mode without an internal standard, to measure total lead. In the internal standard mode, shipment samples were weighed into a vial, then diluted with a weighed quantity of deuterochloroform containing a standard amount of tetramethyllead internal standard. The spectra were acquired and integrated according to the spectrometer parameters in Table 2.1. For the normalized atomic purity mode of analysis, the samples of TEL were simply diluted in deuterochloroform and analyzed according to the same conditions. The normalized atomic purity method of analysis is based on the total integration of all lead nuclei in the sample which is set equal to 100 %. Then the percent of the integration attributable to tetraethyllead represents the atomic purity of TEL, or the percentage of lead atoms that exist as tetraethyllead. The internal standard method is based on the addition of a measured amount of a deuterated solvent containing a known amount of tetramethyllead, to a measured amount of tetraethyllead. The spectrum acquired from this mixture is integrated, and the concentration of tetraethyllead is calculated from the integral ratios of TEL/TML, and the respective molecular weights, as well as the known concentration of TML as the following:

$C_{TEL} = C_{TML} \times (MW_{TEL}/MW_{TML}) \times \text{NMR RATIO} \times \text{VOLUME RATIO}_{(TML/TEL)}$

2.2.2 IODINE MONOCHLORIDE METHOD

Iodine Monochloride Method was carried out according to the following procedure, in a 250 mL separatory funnel, 50 mL of 1.0 M ICl reagent and 25 mL of isooctane were added. Using a pipet, 25 mL gasoline sample which has a temperature of 60 °F was taken from a sealed container and added to the funnel. Immediately, the funnel was stoppered and shook for 60 seconds and then the contents were allowed to settle for about 5 minutes. When the layers were separated, the lower aqueous layer was run into a 500 mL Erlenmeyer flask. The gasoline was washed with three separate 20 mL portions of distilled water, the funnel was shaken each time and the contents were allowed to settle. The washings from the funnel were added to the contents in the Erlenmeyer flask. Several glass beads were placed in the flask, the mouth of the flask was covered with a ribbed watch glass, and then the flask was placed on a hot plate. The solution was heated and allowed to boil until its volume was reduced to between 15 to 20 mL. With the flask on the hot plate, the watch glass was removed and 5 mL of concentrated nitric acid was added down the side of the flask. The solution then was evaporated almost to dryness to oxidize any organic material. Another 5 mL of the nitric acid was added, and the solution was again evaporated almost to dryness to eliminate remaining organic material and until a white residue remained in the bottom of the flask. The flask was removed from the hot plate and the contents were allowed to cool. Distilled water (200 mL) was added to the flask and swirled around to dissolve the residue. Then, 5 drops of bromthymol blue indicator was added and was titrated with ammonia solution until the color just changes to blue. Sodium acetate-acetic acid buffer solution (10 mL) and 5 drops of xylenol orange indicator solution were added. The solution turned to a rose color indicating the presence of lead. Finally, the solution was titrated with 0.0050 M standard EDTA and the color changed to orange, and then to a bright lemon yellow at the endpoint.

2.2.3 X-RAY METHOD

The x-ray fluorescence technique was also used to determine the total lead levels in refinery blended gasoline using a dedicated Oxford Lab-X 3000 Energy Dispersive Spectrometer (EDXRF). This instrument is a multielement spectrometer, capable of measuring sulfur at the percent level and heavy elements up to uranium in the ppm range. It was equipped with Focus 5 software for calibration and instrument stabilization package to control wavelength and amplification drift with a system known as "Energy Lock". The excitation source is a one watt, 25 kilovolt x-ray tube, with programmable excitation from 8 to 25 kilovolts at 5 microamperes. The target is palladium, and the detector is a sealed, gas filled, proportional counter. Liquid gasoline samples were analyzed in replicate by filling a sample cup and sealing it, and collecting counts for 1 minute. Calibration was performed on the Focus 5 software by running unleaded reformat fortified with known amounts of TEL added.

CHAPTER 3

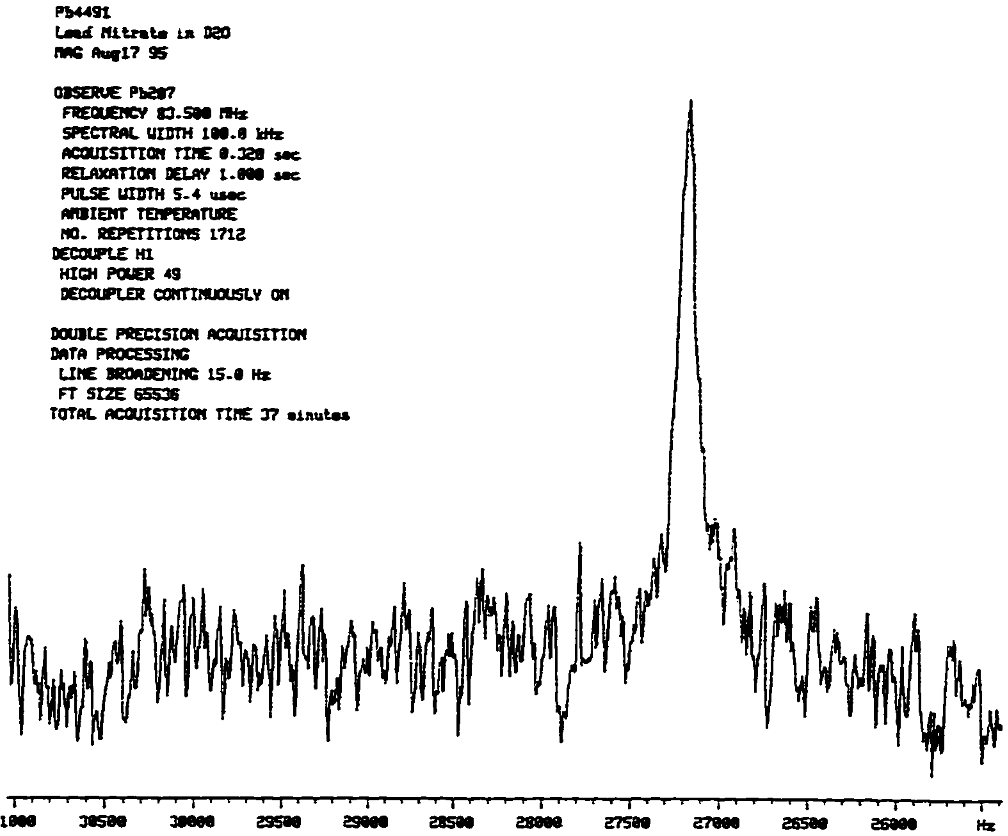
3. DISCUSSION

3.1 PRELIMINARY STUDY

As a preliminary NMR study the ^{207}Pb spectrum of a sample of 1.0 M lead nitrate solution in deuterium oxide was analyzed (Figure 3.1). The spectrum appears in Figure 3.1 shows a poor signal to noise ratio. It is assumed that this is due to lack of dipolar nuclei coupled to lead to provide relaxation mechanisms(61). The spectrum was acquired with an acquisition time of 0.32 sec, pulse width of 5.4 μs (90°), transmitter power of 55 decibels, and using 500 transients. A line broadening coefficient of 10 Hz was set to enhance the signal to noise ratio.

3.2 LONGITUDINAL RELAXATION TIME MEASUREMENTS

In order to measure longitudinal relaxation time and estimate optimum pulse width for the investigation of TEL, a spin recovery experiment was carried out using a spin-echo 180°-90° pulse sequence. The results appear in Figure 3.2 and are plotted in Figure 3.3, giving T_1 of 1.4 sec. A similar experiment for TML was carried out and gave a value of 0.70 sec. as T_1.



```
Pb4491
Lead Nitrate in D2O
MAG Aug17 95

OBSERVE Pb207
 FREQUENCY 83.500 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.320 sec
 RELAXATION DELAY 1.000 sec
 PULSE WIDTH 5.4 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 1712
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 15.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 37 minutes
```

Figure 3.1 Lead-207 NMR Spectrum of 0.1M Lead Nitrate

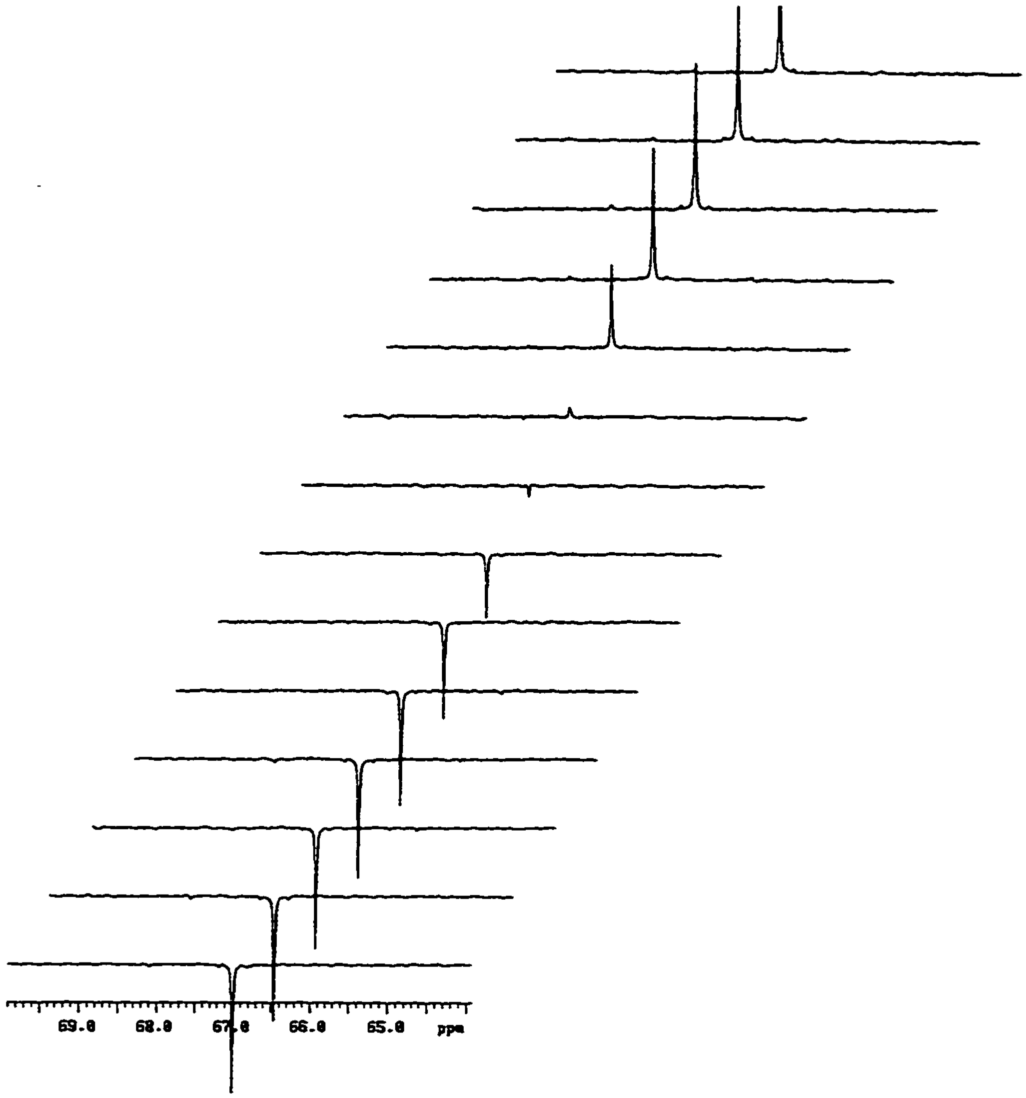


Figure 3.2 Inversion-recovery Measurement (T_1) of Tetraethyllead

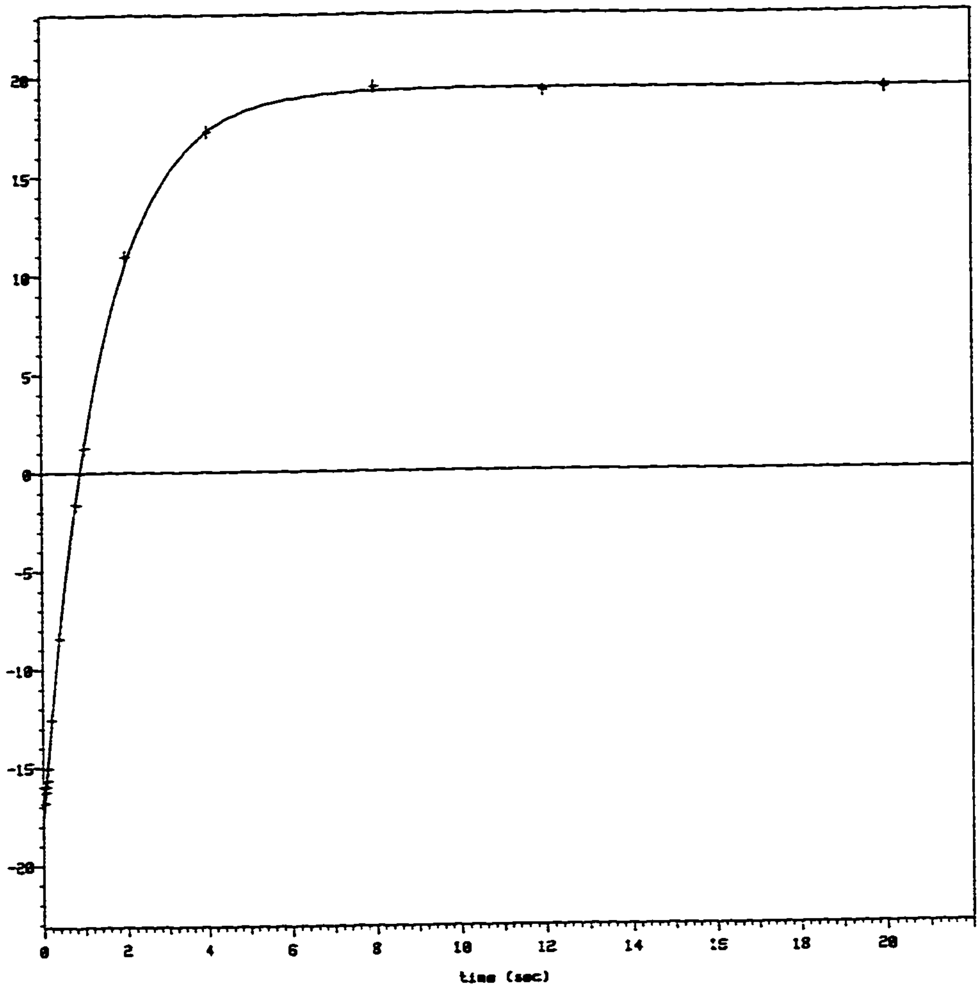


Figure 3.3 Plot of Lead-207 Nuclear Spin Inversion Recovery Data for T_1 Experiment on Tetraethyllead

3.3 CALCULATIONS FOR TETRAETHYLLEAD CONCENTRATION

The NMR signals for TEL and TML when observed under quantitative conditions, are equal to the mole ratio of TML and TEL present in the sample tube. If one of the amounts present is known, then the other may be calculated. This is the basis for quantitative analysis by NMR. In the first basic undiluted additive experiments, 5 ml of gasoline was added to one ml of toluene-d8 containing a known amount of TML. Then TEL concentration was calculated from the area of the NMR signals as follows:

$C_{TEL} = C_{TML} \times \text{NMR Ratio} \times (MW_{TEL}/MW_{TML}) \times 1/5$

OR

$C_{TEL} = 0.242 \times \text{NMR Ratio} \times C_{TML}$

Since the concentration of tetraethyllead was 5.84 G/L, the equation becomes:

$C_{TEL} = \text{NMR Ratio} \times 1.413 \text{ G/L}$

For the gasoline sample runs we used the insert tube method. An insert tube was prepared with a sample of TML dissolved in the lock solvent, benzene-d6, such that the integration of lead in the TML sample was about the same intensity as the integration of lead peaks obtained from the gasoline samples. This standard insert tube was sealed and standardized against a sample of ASTM gasoline of known concentration (543 mg/liter). A factor ($F_{Ext.\ Ref}$ =1.421) was calculated from the NMR ratio from table 3.3 and the known concentration of the ASTM sample. This factor was used for all other samples where the very same insert with TML was used, and the outer tube was filled to the same level with gasoline of an unknown concentration of TEL.

Then the calculation is performed according to the following equation:

$C_{TEL}=F_{Ext.Ref.} \times \text{NMR Ratio}$

$F_{Ext.Ref}$ may be determined when C_{TEL} is known and NMR RATIO is observed, as for ASTM gasoline. $F_{Ext.Ref}$ was found to be 1.421 G/L, so the equation for insert samples becomes:

$C_{TEL}= \text{NMR Ratio} \times 1.421\ \text{G/L}$

In the ICI, the concentration of lead was calculated using the following:

Lead, g/US gallon at 60°F (15.5 °C).= $T \times M \times F_{Temp}$

Where:

T= volume of EDTA solution used to titrate sample, mL

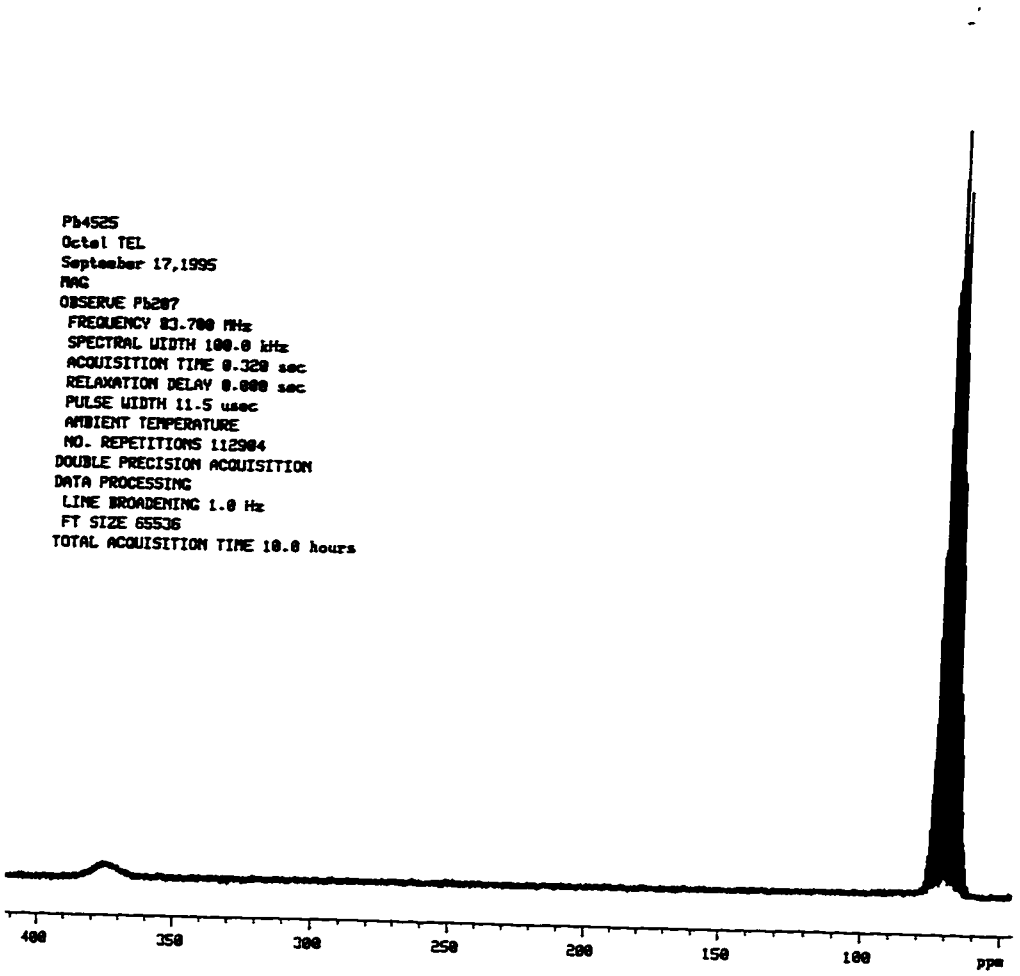
M= molarity of EDTA solution

F= is the temperature factor

3.4 PURE ADDITIVES ANALYSIS

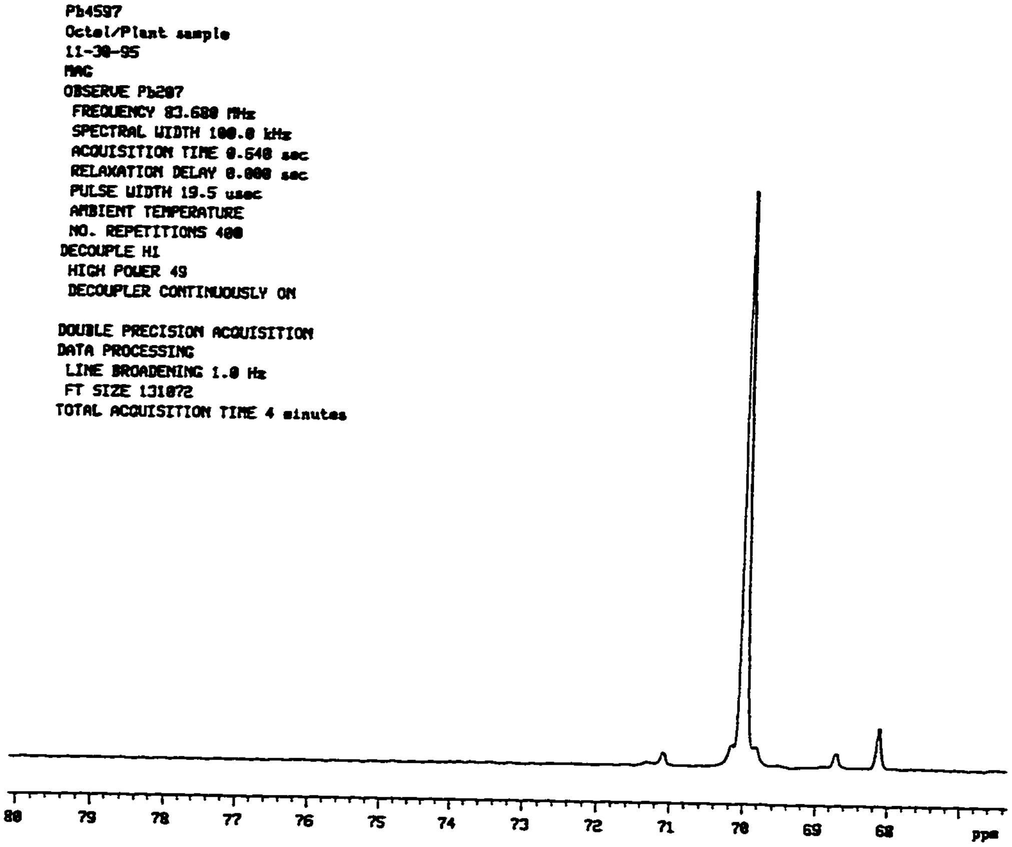
A sample of Associated Octel Tetraethyllead was obtained from Ras Tanura Refinery which contained (according to the Certificate of Analysis) by Iodine Monochloride Assay 64.9% tetraethyl lead (39.4% Pb), and by gas chromatography 17.86% dibromoethane and 18.81% dichloroethane. This sample was diluted with an equal volume of deutero-chloroform and observed at 83.5 MHz in the 5 mm probe. No signal was observed. Since the spectrometer can observe a maximum of a 100,000 hertz window, but the chemical shift range for lead-207 is 500,000 hertz, it was necessary to change the transmitter frequency to find resonance. At a transmitter frequency of 83.68 MHz, the TEL signal was acquired in the center of the spectral window. The spectrum appears in Figure 3.4 as a lead multiplet split by coupling with 8 methylene and 12 methyl protons. The coupling constant of the methylene protons, J_{Pb-H}, is almost three times the coupling constant of methyl protons with lead. This spectrum was obtained with the decoupler off under similar conditions for the lead nitrate sample(62). An impurity peak of approximately 10% is seen down field.

Figure 3.5 is the proton decoupled ^{207}Pb spectrum of the same sample using 2560 transients (about 15 minutes acquisition time). The multiplet has collapsed allowing observation of ^{13}C coupling of 100 Hz. In this decoupled spectrum there was an unassigned peaks at 65 ppm and 138 ppm. The carbon-13 satellites from the alpha (methylene) carbons J= 200 Hz, were observed. Also prominent in Figure 3.5 are the signals from triethylmethyllead (61 ppm), diethyldimethyllead (52 ppm), ethyltrimethyllead (29 ppm), and tetramethyllead (0 ppm) (63,64). From inspection of the spectrum and integration, it is possible to deduce that the atomic purity of TEL is 95.2%. See Table 3.1.



```
Pb4525
Octel TEL
September 17,1995
MAG
OBSERVE Pb207
 FREQUENCY 83.700 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.320 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 11.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 112904
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 10.0 hours
```

Figure 3.4 Proton Coupled Lead-207 NMR Spectrum of Associated Octel Tetraethyllead



```
Pb4597
Octel/Plant sample
11-30-95
MAC
OBSERVE Pb207
 FREQUENCY 83.680 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.640 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 400
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 4 minutes
```

Figure 3.5 Proton Decoupled Lead-207 NMR Spectrum of Associated Octel Tetraethyllead

Table 3.1 Atomic Purity of Associated Octel TEL by ^{207}Pb NMR

LEAD SPECIES	SHIFT PPM	INTENSITY	RELATIVE AREA%
Tetramethyl	0	2.5	0.5
Trimethylethyl	28	1.5	0.3
Dimethyldiethyl	51	1.0	0.2
Methyltriethyl	60	2.0	0.4
Unknown	65	1.0	0.2
Tetraethyl	70	465	95.2
Unknown	138	1.5	0.3

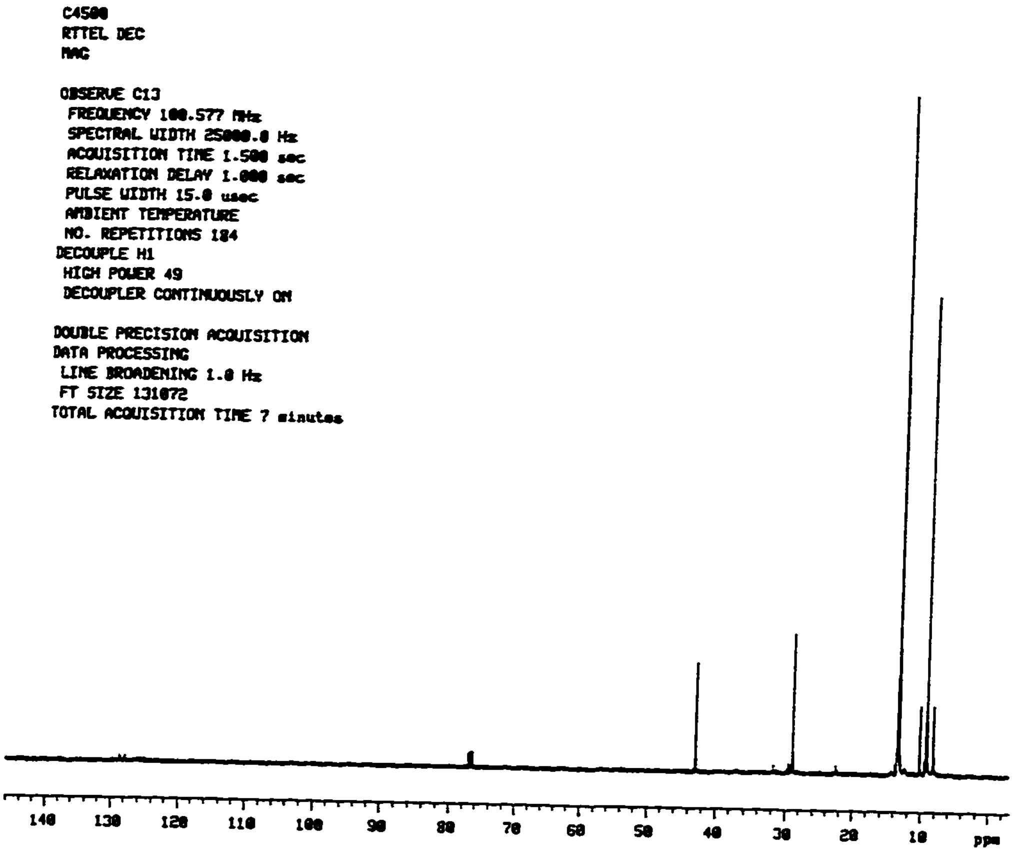
Figure 3.6 is the ^{13}C spectrum of the same sample, obtained with 184 transients in the 5 mm broadband probe. The spectrum is referenced to $CDCl_3$ at 77.0 ppm. The signal at 43 ppm is ethylene dibromide, the signal at 29 ppm is ethylene dichloride, and the signal at 13 ppm is due to the methyl carbons of the TEL. The methylene carbons appear at 9.4 ppm and are strongly coupled to the ^{207}Pb nuclei which comprise 22.6% of the lead isotopes. The expanded spectrum in Figure 3.7 clearly reveals the coupling of the ^{13}C nucleus to the ^{207}Pb nucleus of 100 Hz confirming the $J_{Pb\text{-}C}$ coupling constant determined from Figure 3.10. The signal appearing at 9.4 ppm is from the methylene carbons of TEL. It arises from the zero spin isotopes ^{204}Pb (1.5 %), ^{206}Pb (23.6 %), and ^{208}Pb (52.3 %). The lead-207 (22.6 %) isotope gives rise to the doublet at 8.4 and 10.4, with intensity of each equal to 22.6/2 % or 11.3 % of the total methylene area. The coupling constant $J_{C\text{-}Pb}$ is large at 100 Hz, due to the direct sigma bonding of methylene carbons to lead. This value agrees well with the coupling seen in the lead-207

spectrum of TEL, which gives $J_{Pb\text{-}C}$ of 100 Hz. Similarly, the signal centered at 13.6 ppm arises from the methyl groups of TEL. The coupling constant is smaller with $J_{C\text{-}Pb}$ equal to 20.0 Hz. The doublet is equal in area, however, to the percentage of lead-207 isotopic abundance of 22.6 %. In Figure 3.10, the satellites from splitting of the lead-207 nucleus appear at + and - 50 Hz from the main signal, which is to be expected from the $J_{Pb\text{-}C}$ of 100 Hz and they represent the carbon-13 abundance of 1.1%/2 or 0.55 percent of the lead-207 area. The shoulders of the lead signal at +/- 10 Hz are due to splitting of the lead signal by the methyl carbon-13 isotope. The tetramethyllead signal near zero ppm shows coupling of the methyl carbons at +/-100 Hz, since the $J_{Pb\text{-}C}$ is equal to 100 Hz for TML.

Figure 3.8 is the ^1H coupled ^{207}Pb spectrum of a mixture of Associated Octel tetramethyllead and Novoktan tetraethyllead in $CDCl_3$. This spectrum has been referenced at TEL=70.5 ppm, and clearly illustrates the proton-lead-207 coupling of J= 58.5 Hz for the 12 TML methyl protons, giving rise to the multiplet. The spectrum is split into a tridecet (the number of protons = N = 12, multiplicity = N+1). The lines of a tridecet (lead coupled to 12 protons) have the intensities predicted by the binomial expansion:

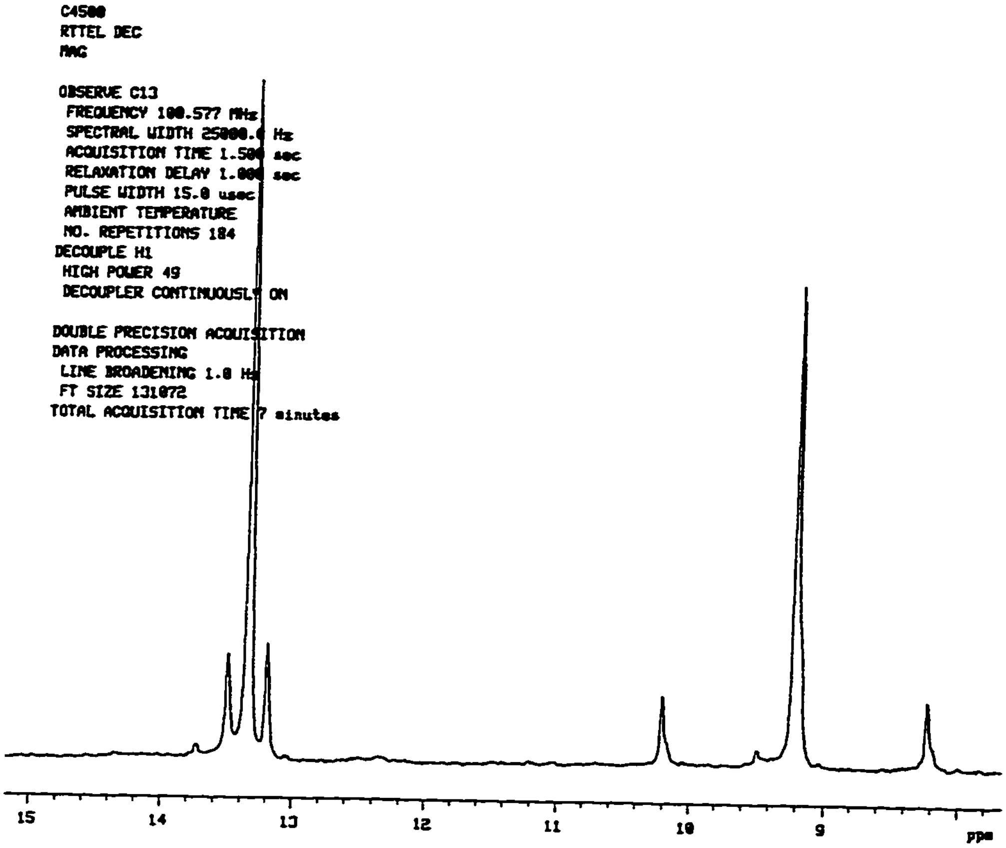
1 : 12 : 66 : 220 : 505 : 832 : 984 : 832 : 505 : 220 : 66 : 12 : 1

A synthesized spectrum which shows that the two outer peaks are almost disappeared, is shown in Figure 3.9.



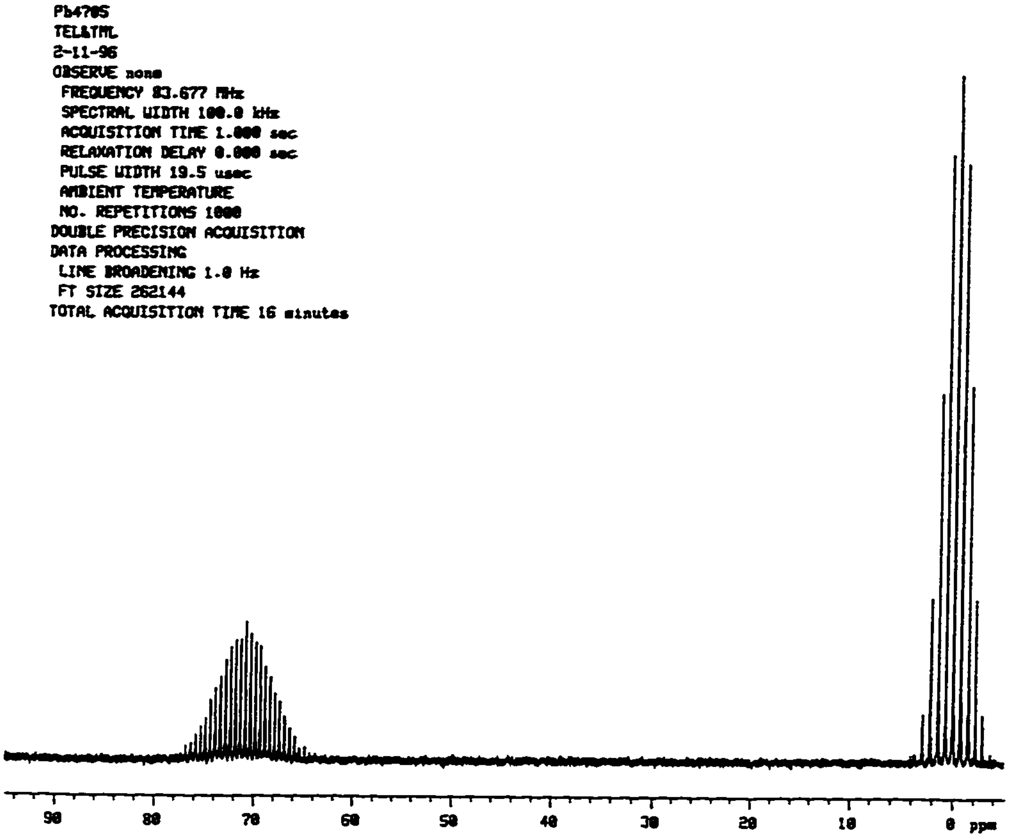
```
C4500
ATTEL DEC
MAC

OBSERVE C13
 FREQUENCY 100.577 MHz
 SPECTRAL WIDTH 25000.0 Hz
 ACQUISITION TIME 1.500 sec
 RELAXATION DELAY 1.000 sec
 PULSE WIDTH 15.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 184
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 7 minutes
```

Figure 3.6 Carbon-13 Spectrum of Associated Octel Tetraethyllead



```
C4500
RTTEL DEC
MAG

OBSERVE C13
 FREQUENCY 100.577 MHz
 SPECTRAL WIDTH 25000.0 Hz
 ACQUISITION TIME 1.500 sec
 RELAXATION DELAY 1.000 sec
 PULSE WIDTH 15.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 184
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 7 minutes
```

Figure 3.7 Expanded ^{13}C Spectrum of Associated Octel Tetraethyllead



```
Pb4705
TEL&TML
2-11-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 1000
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 16 minutes
```

Figure 3.8 Proton Coupled Lead-207 NMR Spectrum of TEL and TML Mixture

Figure 3.10 shows the ^{1}H decoupled ^{207}Pb spectrum of TML with 4.4% ^{13}C sidebands (TEL reference). Careful manual measurements of the TEL and TML lines have indicated that the TEL has a linewidth of 1.7 Hz, and TML has a linewidth of 2.3 Hz. This difference is a function of T_1 and their differences in relaxation modes, and must be considered when carrying out quantitative measurements.

In order to perform quantitative measurements of TEL purity, the magnitude of nuclear Overhauser effects (66) was investigated. Figure 3.8 is the ^{1}H coupled spectrum of a mixture of TEL (Novaktan) and TML (Associated Octel) in $CDCl_3$ obtained under standard conditions (Table 2.1). By using the TML as a reference, it was possible to calculate the assay value of TEL at 60.4 wt.%, or 98% of the certificate value of 61.6 wt.%. Figure 3.10 shows the spectrum of the same sample obtained with the decoupler on during excitation, delay, and acquisition, giving a ratio of 1.16 for the intensity of the TEL to TML lead signals. Figure 3.11 was obtained with the decoupler on only during acquisition, which gives no NOE enhancement. The ratio of TEL to TML was found to be 1.13. Thus the observed difference in the NOE enhancement was found to be positive in favor of TEL by a value of 2.6% (67). The theoretical value of the NOE for lead at the extreme narrowing condition may be calculated from the following equation(68)

$$\eta_{max} = g_S/2g_I = 227\ \%$$

where η is the percent NOE enhancement, g_s is the gyromagnetic ratio for the saturated nucleus (hydrogen=26.75 x 10^7 rad/sec-deg), and g_I is the gyromagnetic ratio for the observed nucleus (lead=5.895 x 10^7 rad/sec-deg). The theoretical value of NOE enhancement of 227% greatly exceeds the observed and reported values (69), indicating that other rapid longitudinal relaxation mechanisms are in force for the lead alkyls. It has been found that spin-lattice relaxation times ,T_1, decrease with increasing temperature and that relaxation is dominated by spin rotation mechanisms for heavy nuclei. It has been well documented that these other mechanisms include chemical shift anisotropy (CSA) (70), spin rotation, and dipolar contributions (71). Although the NOE enhancement difference for TEL and TML is small and probably insignificant, all quantitative measurements have been made with decoupler on during acquisition and off during excitation and delay, which supresses any NOE (72).

Figure 3.12 is the ^{207}Pb spectrum of Novaktan TEL, 61.49% assay. There are no discernable lead compound impurities in this sample indicating atomic purity of greater than 99%.

Figure 3.13 is a ^{207}Pb spectrum of Ethyl Corp. TEL under the same conditions, showing impurity peaks and giving atomic purity of 95%.

Figure 3.14 is a ^{207}Pb spectrum obtained from a mixture of Ethyl TEL and Octel TML, that was allowed to stand for 30 days in an NMR tube with $CDCl_3$ solvent. A number of impurity peaks are apparent, including the triethylmethyllead (62 ppm), diethyldimethyllead (54 ppm), ethyltrimethyllead (30 ppm), and tetramethyllead (0 ppm), along with unknowns at (68 ppm) and (139 ppm). The exchange of alkyl groups between lead alkyls is well documented (1,3). The exchange is greatly accelerated by Lewis acids such as $AlCl_3$, $FeCl_3$. These so-called "equilibration mixtures" are frequently used to optimize octane in fuels (3).

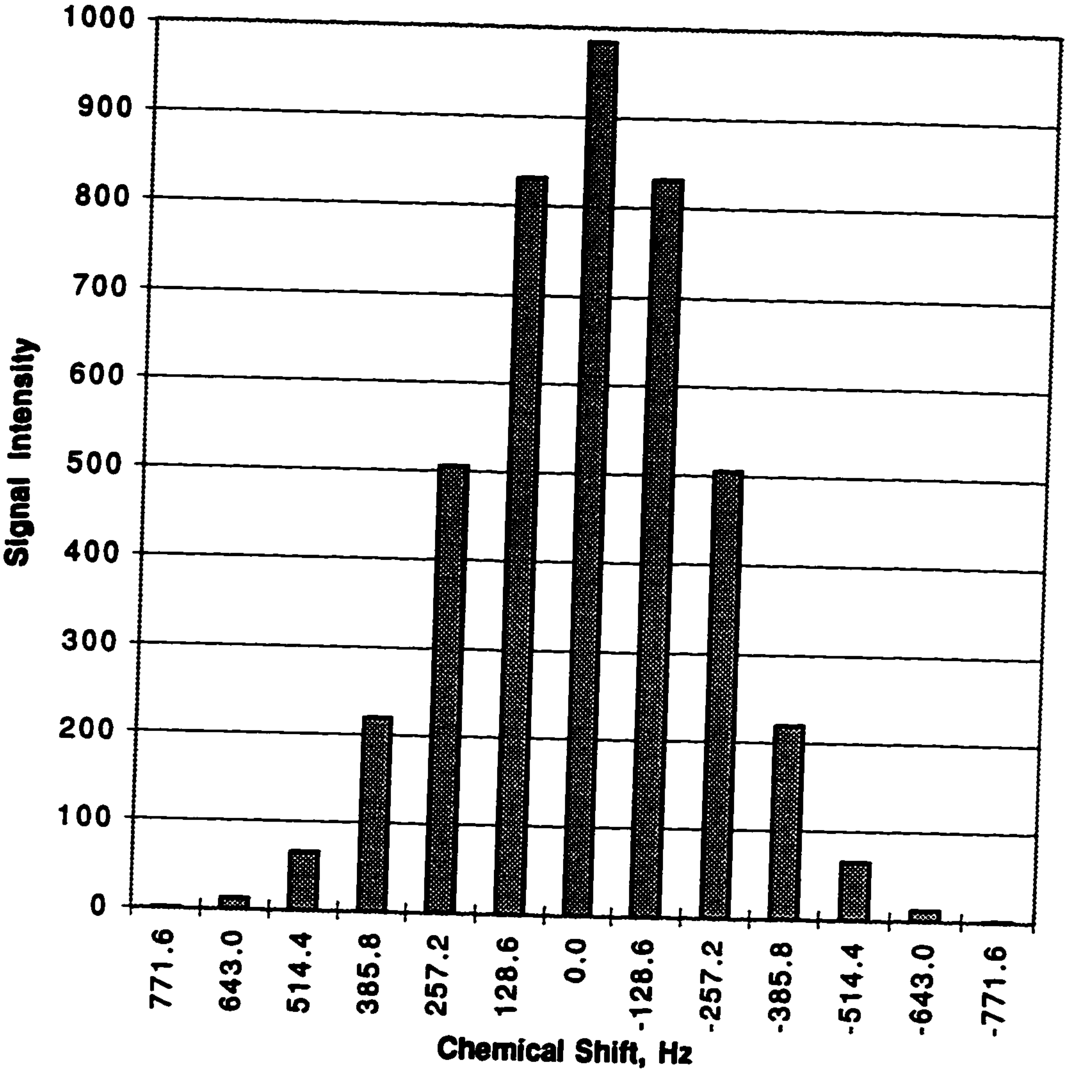
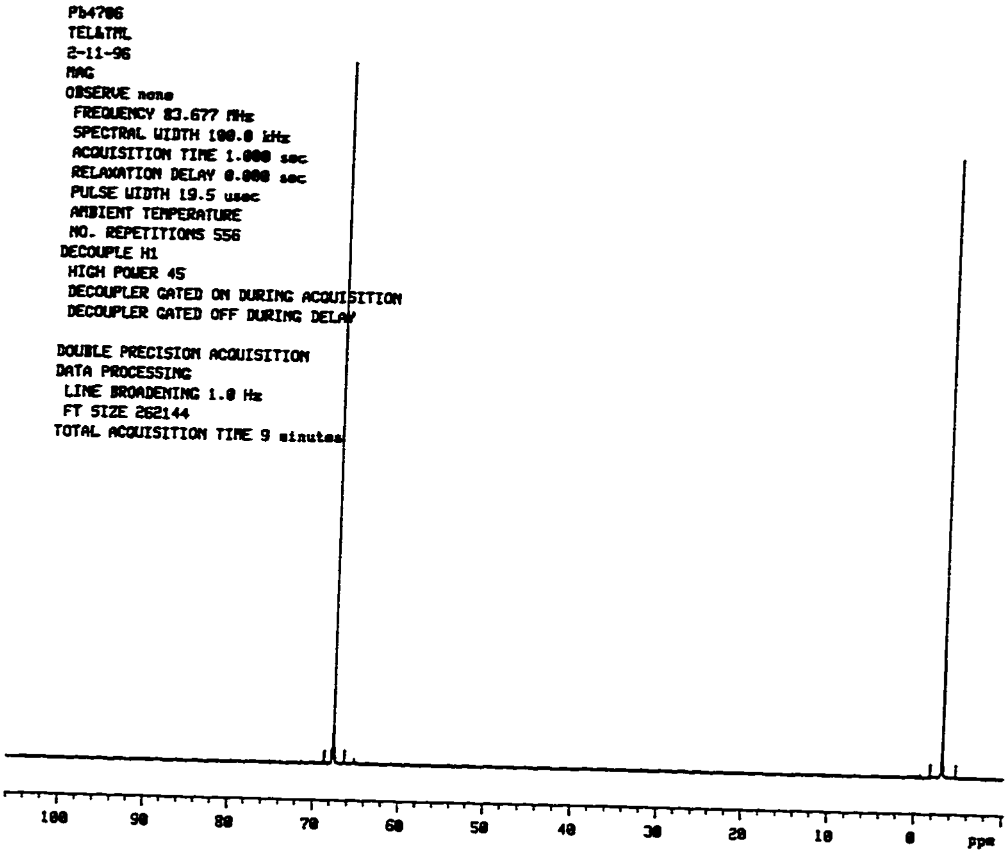
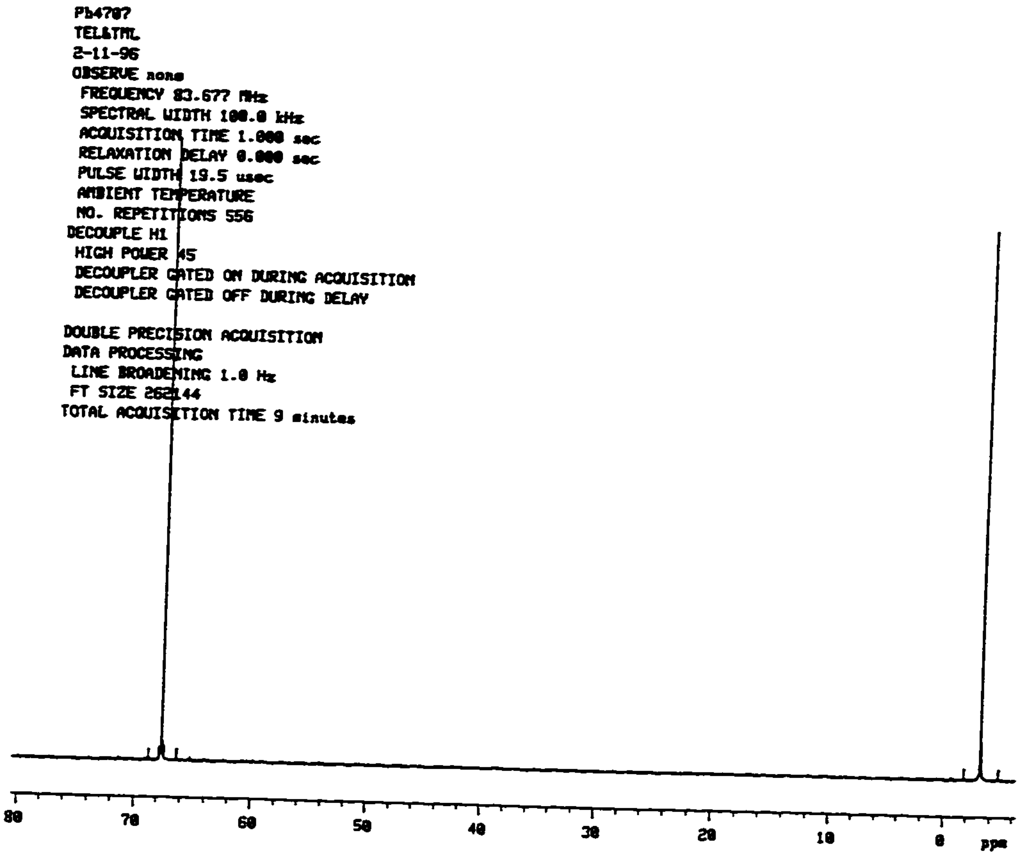


Figure 3.9 Predicted Line Intensity for Lead-207 NMR Spectrum of Tetramethyllead



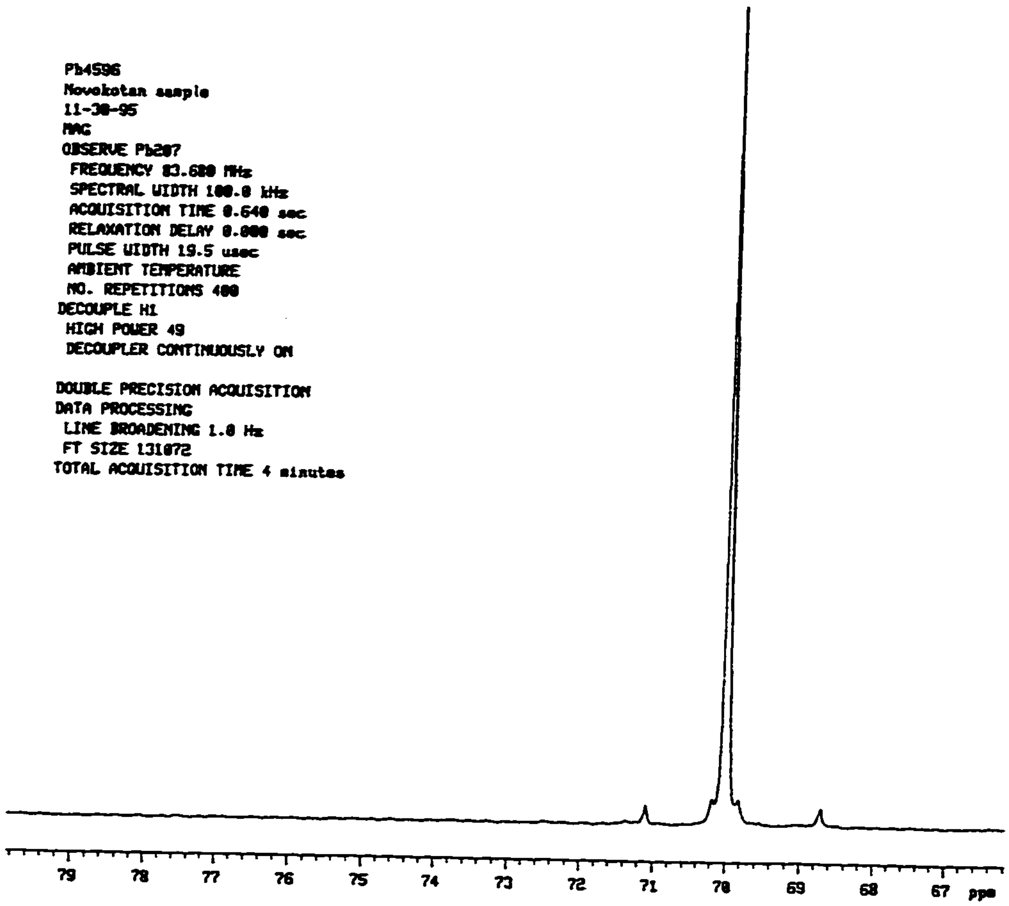
```
Pb4706
TEL&TML
2-11-96
MAG
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 556
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 9 minutes
```

Figure 3.10 Tetraethyllead and Tetramethyllead Mixture Under Nuclear Overhauser Effect Conditions



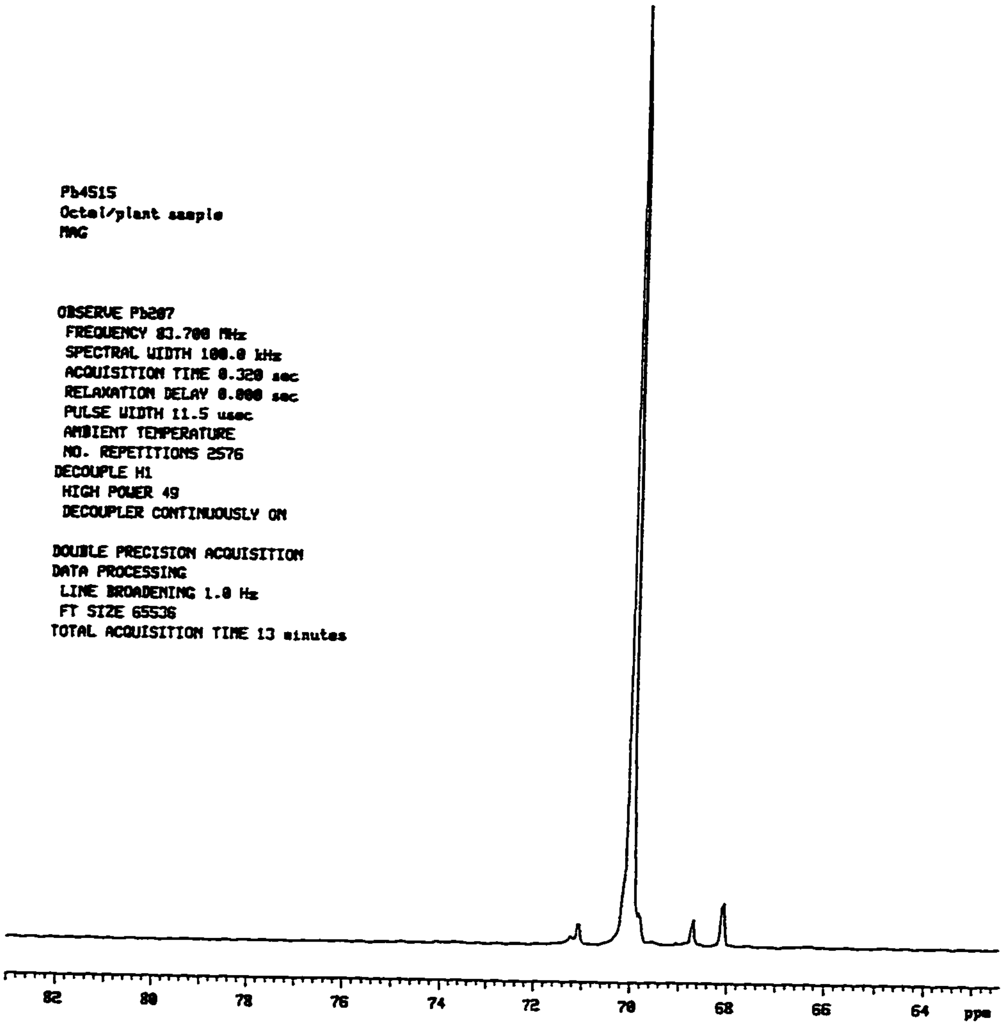
```
Pb4707
TEL&TML
2-11-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 556
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 9 minutes
```

Figure 3.11 Proton Decoupled Lead-207 NMR Spectrum of Tetraethyllead and Tetramethyllead Mixture without Nuclear Overhauser Effect Conditions



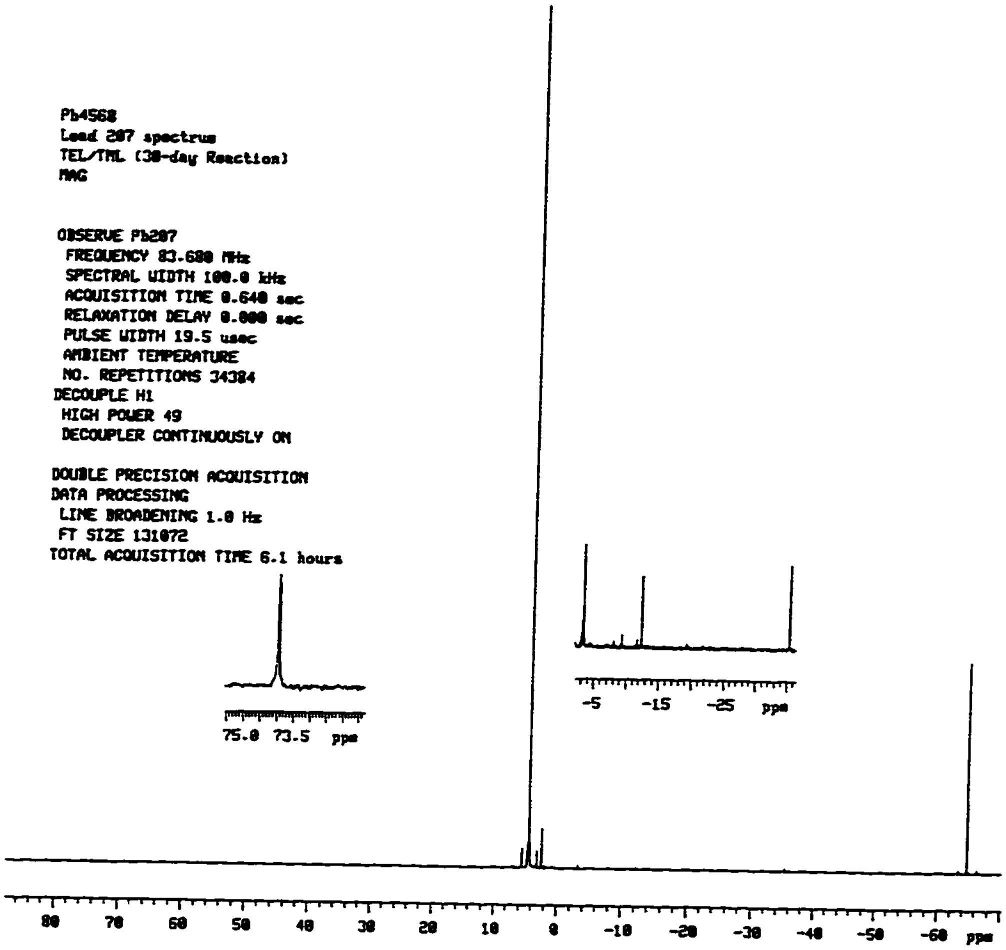
```
Pb4596
Novokotan sample
11-30-95
MAG
OBSERVE Pb207
 FREQUENCY 83.680 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.640 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 400
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 4 minutes
```

Figure 3.12 Lead-207 NMR Spectrum of Novoktan Tetraethyllead Shipment



```
Pb4S15
Octel/plant sample
MAG


OBSERVE Pb207
 FREQUENCY 83.700 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.320 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 11.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 2576
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 13 minutes
```

Figure 3.13 Lead-207 NMR Spectrum of Ethyl Coorporation Tetraethyllead Shipment



```
Pb4568
Lead 207 spectrum
TEL/TML (30-day Reaction)
MAG

OBSERVE Pb207
 FREQUENCY 83.680 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.640 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 34384
DECOUPLE H1
 HIGH POWER 49
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 6.1 hours
```

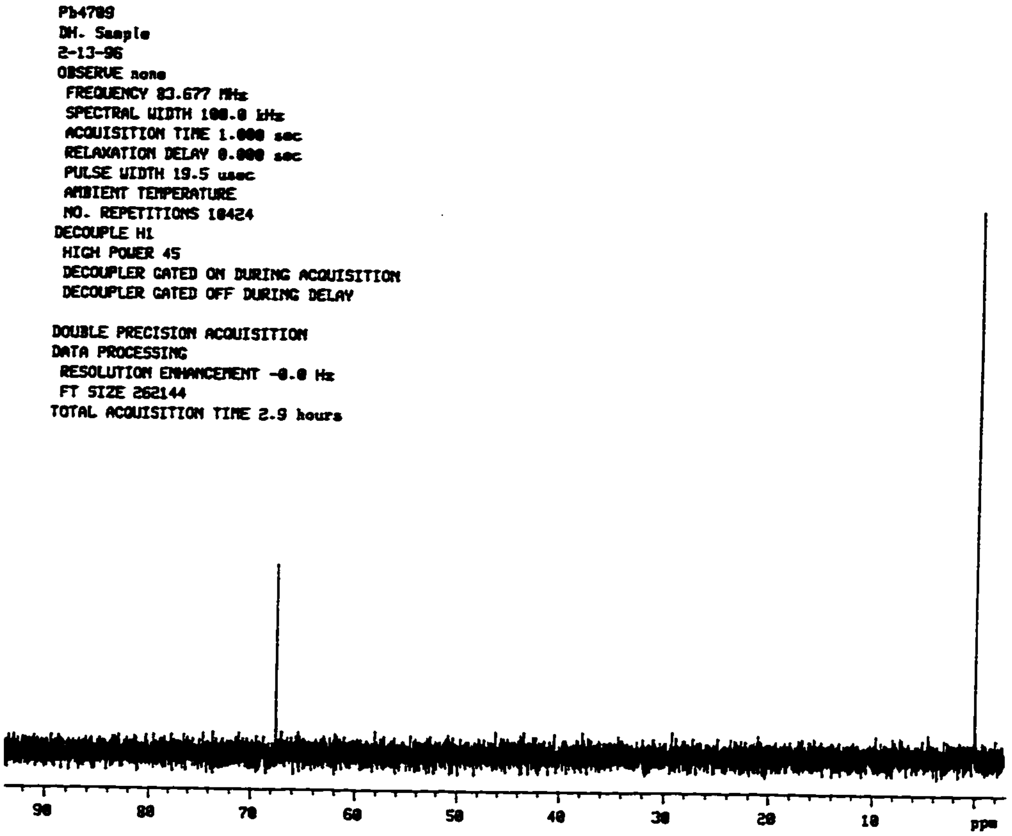
Figure 3.14 Lead-207 Spectrum of The 30-day Reaction Product of Tetraethyllead and Tetramethyllead

3.5 GASOLINE ANALYSIS - INTERNAL STANDARD:

Figure 3.15 is the ^{207}Pb spectrum obtained from a sample of Saudi Aramco leaded gasoline received from the Dhahran Terminal. This spectrum was acquired on a 5 ml sample fortified with 1 ml of 4.48 mg/ml lead as TML, in D-8 toluene in a 5 mm broadband probe. The observed value was 425 ppm. Figure 3.16 is the ^{207}Pb NMR spectrum of leaded gasoline obtained from the Riyadh refinery, certified at 400 ppm lead as TEL. Calculations, tabulated in Table 3.1, showed a value, based on TML internal reference, of 300 mg/l. Figure 3.17 is a spectrum obtained under identical conditions of an ASTM reference sample of gasoline containing 540 mg/l of lead as TEL, fortified with lead as TML. The calculated value was 501 mg/l, giving an accuracy of 93% for the NMR method. Figure 3.18 is a spectrum of gasoline prepared from naphtha processed in the reformer pilot plant at Saudi Aramco. TEL was added to a value of 418 mg/l then 5 ml of the gasoline was mixed with 1 ml of a TML standard of 4.48 mg/ml as lead in deuterated toluene. The results (Table 3.2) indicated a value of 355 mg/l lead as TEL, suggesting that some reaction may occur which depletes TEL.

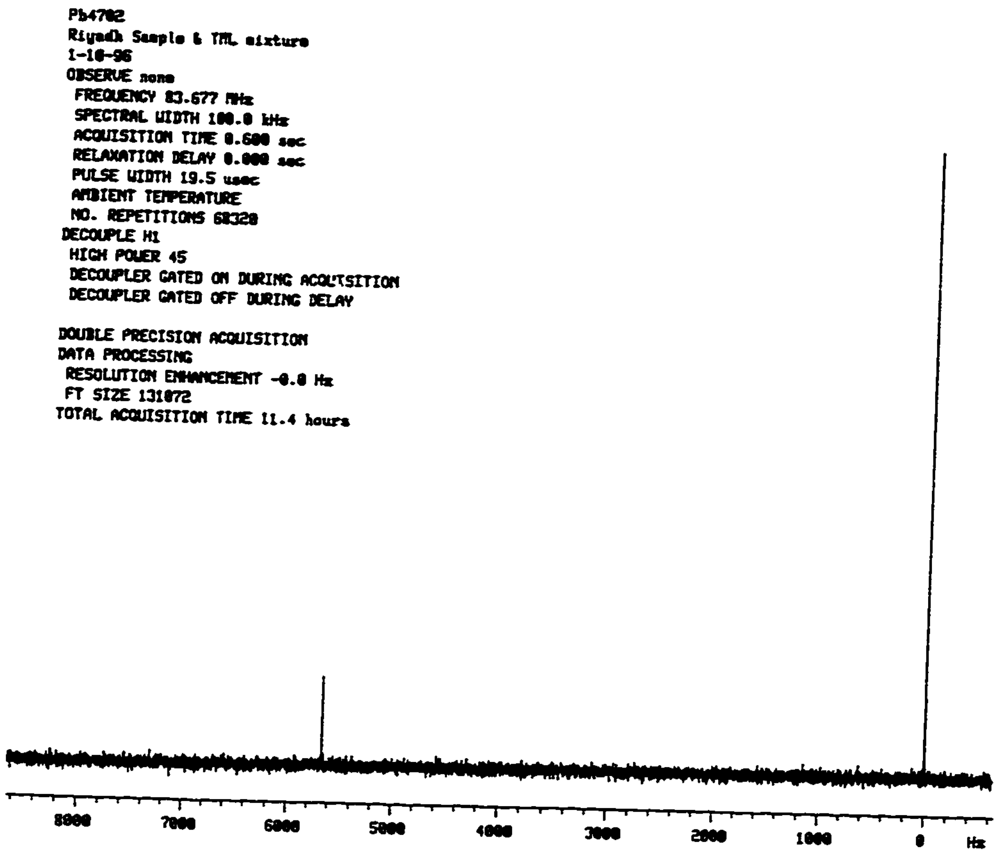
Table 3.2 Lead-207 NMR Measurement of Lead In Gasoline

SAMPLE	EXPECT. VAL.	Mred. VAL.	DIFFERENCE
Dhahran Bulk Terminal	400 mg/l	425 mg/l	+ 6.25 %
Riyadh Refinery Storage	400 mg/l	300 mg/l	- 25 %
Unleaded Spiked TEL	418 mg/l	355 mg/l	-15 %
ASTM SRM 2715	540 mg/l	501 mg/l	- 7.5 %



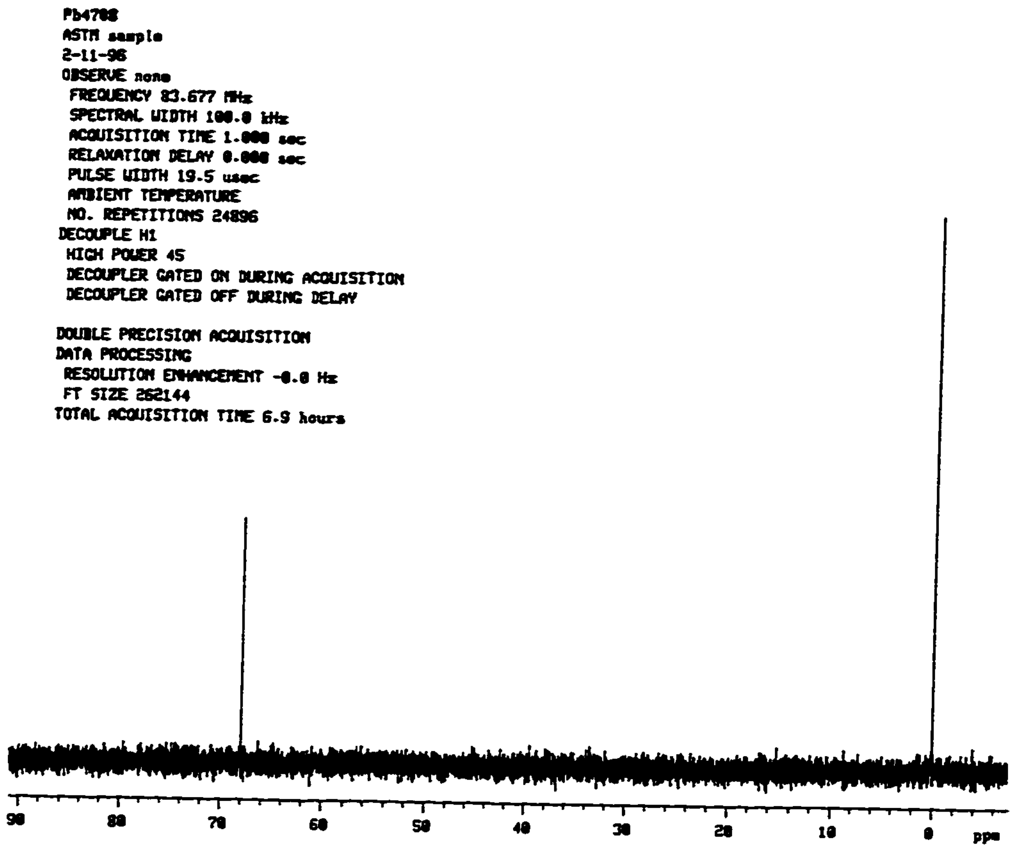
```
Pb4709
DH. Sample
2-13-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 10424
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 RESOLUTION ENHANCEMENT -0.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 2.9 hours
```

Figure 3.15 Lead-207 NMR Spectrum of Dhahran Terminal Leaded Gasoline with Tetramethyllead Reference



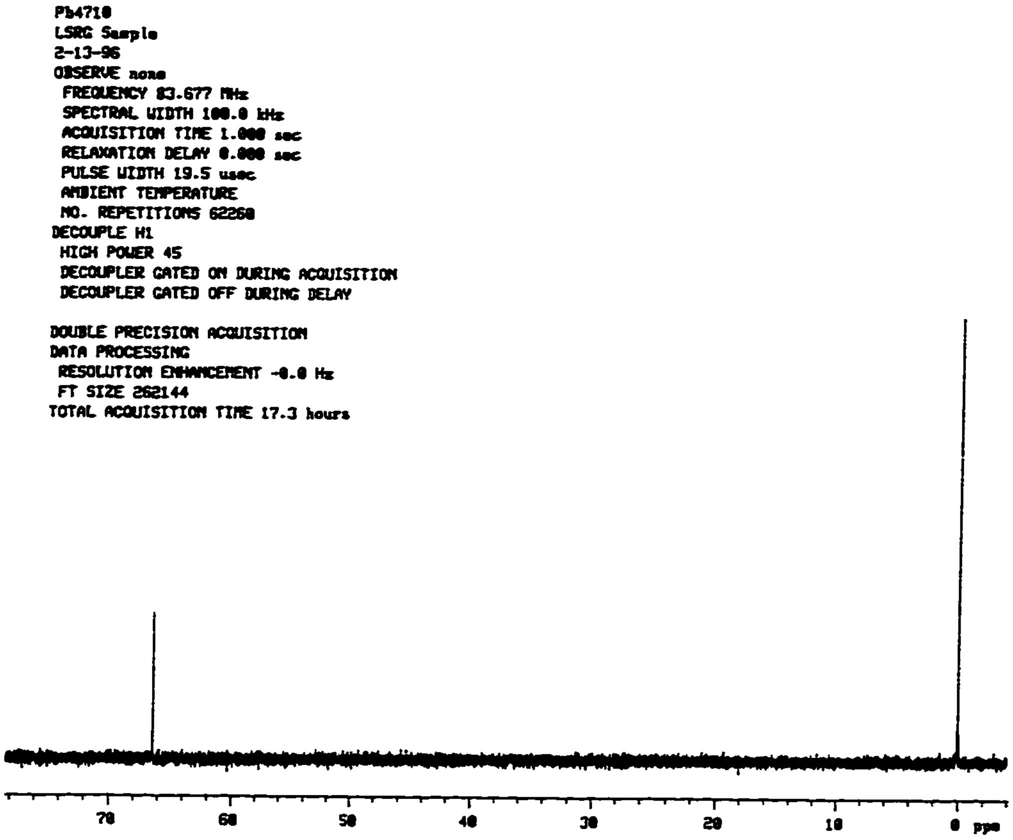
```
Pb4702
Riyadh Sample & TML mixture
1-10-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 0.600 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 68320
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 RESOLUTION ENHANCEMENT -0.0 Hz
 FT SIZE 131072
TOTAL ACQUISITION TIME 11.4 hours
```

Figure 3.16 Lead-207 NMR Spectrum of Riyadh Refinery Leaded Gasoline with Tetramethyllead Reference



```
Pb4708
ASTM sample
2-11-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 24896
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 RESOLUTION ENHANCEMENT -0.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 6.9 hours
```

Figure 3.17 Lead-207 NMR Spectrum of ASTM SRM2715 (540mg/l) Leaded Gasoline with Tetramethyllead Reference



```
Pb4710
LSRG Sample
2-13-96
OBSERVE none
 FREQUENCY 83.677 MHz
 SPECTRAL WIDTH 100.0 kHz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 19.5 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 62260
DECOUPLE H1
 HIGH POWER 45
 DECOUPLER GATED ON DURING ACQUISITION
 DECOUPLER GATED OFF DURING DELAY

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 RESOLUTION ENHANCEMENT -0.0 Hz
 FT SIZE 262144
TOTAL ACQUISITION TIME 17.3 hours
```

Figure 3.18 Lead-207 NMR Spectrum of Reformate with Tetraethyllead added, Referenced to Tetramethyllead

The expected value stated for a gasoline from a given refinery, is that level which is typically found, or thought to be added by the refiner. In fact, the TEL level often varies considerably from the target value. The quality of gasoline that must be held constant is the octane, which is measured by running the fuel in a stationary laboratory engine. In gasoline manufacture, naphtha is reformed by passing over a platinum-alumina catalyst at 500 deg °C, where the aromatics and isoparaffin content is increased, raising the octane level. The reformate is then blended with more naphtha, then treated with enough TEL to raise the octane level to the desired value (95 RON is KSA target value). The same effect can be had by adding TML, MTBE, manganese cyclopentadienyl carbonyl, or alkylate (made by reacting olefins and paraffins with HF catalyst). Thus the lead level varies from refinery to refinery, depending on the quality of their naphtha or it's reformability, the efficiency of it's catalytic reformer in boosting octane, the use of other octane enhancers, the availability of other blending components (which varies from week to week), the practice of extracting high octane components such as toluene and xylenes for petrochemical feedstocks. Often blending stocks such as fluidized catalytic cracker (FCC) gasoline, pyrolysis gasoline, chemical naphtha, natural gas condensates, hydrocracker naphtha and higher quality naphthas are available day to day on the spot market, and are purchased by refineries to maintain capacity or inventory. Variations in TEL quality may cause variations in TEL levels

Once a particular gasoline has been produced with a given level of TEL, it's TEL value may change. This can happen when gasoline from two different sources such as refineries or manufacturers, are blended in the same storage tank. Often, gasoline marketers can benefit from enhanced octane values by mixing TML and TEL, and then an interchange reaction between TEL and TML occurs diminishing the TEL and TML levels, forming other intermediates. TEL can react with other additives such as alcohols and antioxidants. Also, TEL may react with air to oxidize and form a lead sludge which precipitates. Moreover, TEL levels can increase if gasoline evaporates. Leaded gasoline may inadvertently or deliberately be mixed with unleaded gasoline, causing the TEL to be diluted.

3.6 GASOLINE ANALYSIS - EXTERNAL STANDARD

Samples were prepared in such a way to be run using the inserted tube external standard method. A 0.453 g of the lock solvent, deuterated benzene, along with 0.0380 g of tetramethyllead (reference) was sealed in the inside tube. The neat gasoline samples were put directly in the outside tube for the analysis. Figure 3.19 illustrates the inserted tube technique.

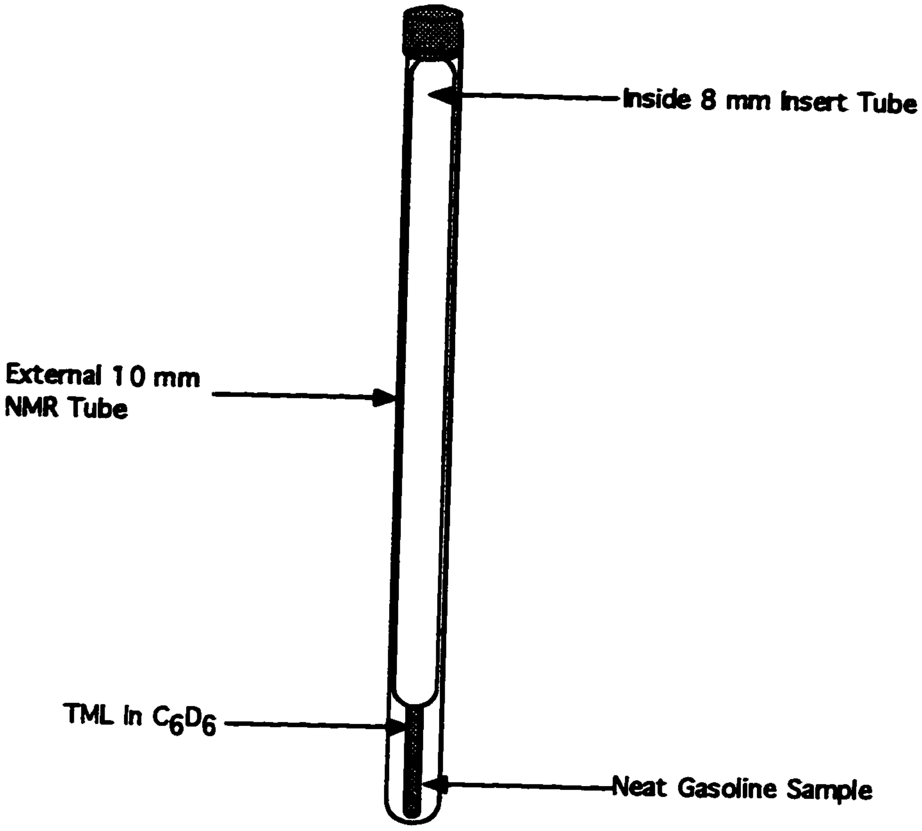


Figure 3.19 NMR Insert Tube Technique Diagram

3.6.1 ACQUISITION TIME EFFECT

To check the effect of the acquisition time on the results, five experiments were performed at different acquisition times. The maximum signal to noise value was found at an acquisition time of 1.5-2 seconds. For longer values of acquisition times, the signal to noise ratio remained constant. The results of these experiments are tabulated in Table 3.3 and their corresponding spectra are in the appendix as spectra 1-6.

Table 3.3 ASTM Sample (different acquisition time) Integral Values

pw= 21.0 μsec. (90°)

Acquisition Time (sec)	S/N
0.3	38.0
0.6	44.0
1.0	48.0
1.5	48.3
2.0	48.6
3.5	48.5

3.6.2 PRECISION OF THE METHOD

An ASTM sample (4.0ml) was placed in the outside tube and was run five times. Each time the sample was ejected, taken out of the spinner, replaced in the spinner, and then inserted into the instrument to perform an independent experiment. The instrument was retuned and reshimmed, after each sample insertion. The purpose of this step was to check the precision of the NMR method. The spectrum of each experiment was phased, referenced (TML =

0.0ppm), and integrated over the range where the TEL and TML peaks are appearing in the spectrum. The chosen range for all the analysis in this study were 71.0 to 74.0 ppm and -1.0 to 1.0 ppm for the TEL and the TML, respectively. The integral values are tabulated in Table 3.4 and their corresponding spectra are in the appendix as spectra 7-11.

Table 3.4 ASTM Sample (one sample five times) Integral Values

Mean=0.382, SD=0.00100

Run #	TML	TEL	TEL:TML	G/L TEL	G/Gal
1	10.0	3.83	0.383	0.544	2.177
2	10.0	3.84	0.384	0.546	2.183
3	10.0	3.82	0.382	0.543	2.171
4	10.0	3.82	0.382	0.543	2.171
5	10.0	3.84	0.384	0.546	2.183

3.6.3 UNIFORMITY OF NMR TUBES

A set of five ASTM samples were prepared in five different NMR tubes to check the uniformity of the nmr tubes. All samples were run under the same experimental conditions. The integral values are tabulated in Table 3.5 and their corresponding spectra are in the appendix as spectra 12-16.

Table 3.5 ASTM Sample (five different tubes) Integral Values

Mean=0.344, SD=0.00356

Sample #	TML	TEL	TEL:TML	G/L	G/Gal
1	10.0	3.41	0.341	0.485	1.938
2	10.0	3.41	0.341	0.485	1.938
3	10.0	3.48	0.348	0.495	1.978
4	10.0	3.48	0.348	0.495	1.978
5	10.0	3.46	0.346	0.492	1.967

3.6.4 PRECISION OF INTEGRATION METHOD

To check the reproducibility of the integration method, one spectrum was integrated five times. Each time the spectrum is rephased and the integration method is reapplied. The integral values are tabulated in Table 3.6 and their corresponding spectra are in the appendix as spectra 17-21.

Table 3.6 ASTM Sample (one run integrated five times) Integral Values

Mean=0.320

Run # 1	TML	TEL	TEL:TML	G/L	G/Gal
a	1.00	0.320	0.320	0.455	1.82
b	1.00	0.320	0.320	0.455	1.82
c	1.00	0.320	0.320	0.455	1.82
d	1.00	0.320	0.320	0.455	1.82
e	1.00	0.320	0.320	0.455	1.82

3.6.5 DETECTION LIMIT

Five different concentrations (500, 400, 300, 200, 100, and 50ppm) of ASTM sample were prepared by dilution. Ras Tanura reformate (naphtha) was used to make up the different concentrations. The purpose of this experiment was to ensure that levels as low as 50 ppm can be detected. The integral values are tabulated in Table 3.7 and plotted in Figure 3.20 giving a correlation coefficient of 0.996. The corresponding spectra are in the appendix as spectra 22-27.

Table 3.7 ASTM Sample (different concentration) Integral Values

Concentration (ppm)	TML	TEL	TEL:TML	G/L	G/Gal
500	10	3.41	0.341	0.485	1.938
400	10	2.68	0.268	0.381	1.523
300	10	2.09	0.209	0.297	1.188
200	10	1.35	0.135	0.192	0.767
100	10	0.69	0.069	0.098	0.392
50	10	0.33	0.033	0.047	0.188

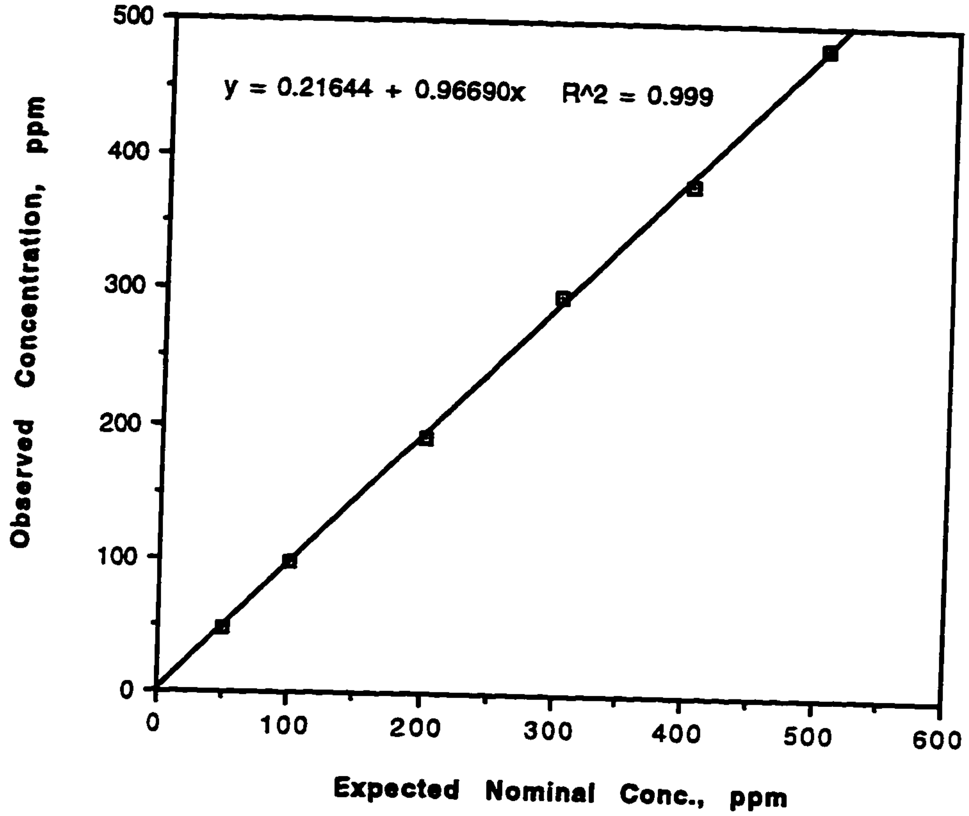


Figure 3.20 Observed vs. Expected Nominal Values of Different Concentrations of ASTM Samples

3.6.6 CONCENTRATION DETERMINATION

The next step was to apply the method to some real samples and compare the observed to the expected nominal concentration. Samples from Ras Tanura, Bahrain (regular & super), and Riyadh were analyzed. Table 3.8 shows the integral values of the tested samples. Their spectra are in the appendix as 28-31.

Table 3.8 Different Gasoline Samples

Sample	TML	TEL	Ratio	G/L	Merd. Val G/Gal	Exp.Nom. Val G/Gal
Ras Tanura	10.0	3.02	0.302	0.429	1.717	2.00
Bahrain Regular	10.0	1.86	0.186	0.264	1.057	1.00
Bahrain Super	10.0	3.61	0.361	0.513	2.052	2.00
Riyadh	10.0	2.95	0.295	0.419	1.677	2.00

3.6.7 COMPARISON OF METHODS OF ANALYSIS

In order to compare the NMR method to both the iodine monochloride (ICl) method and the X-Ray method, one sample was run ten times using all methods. In the NMR method, the sample was run using the external standard method. The ICl method was run according to ASTM Method D3341-91 Standard Test for Lead in Gasoline--Iodine Monochloride Method. The NMR results are tabulated in Table 3.9 and the corresponding spectra are in the appendix as spectra 32-41. The ICl results are tabulated in Table 3.10. Table 3.11 the X-Ray fluorescence method results.

Table 3.9 Ras Tanura Sample (Run ten times) Integral Values

Mean=1.07 , SD=0.018

Run #	TML	TEL	Ratio	G/L	G/Gal
1	10.0	1.97	0.197	0.280	1.12
2	10.0	1.96	0.196	0.279	1.12
3	10.0	1.95	0.195	0.277	1.11
4	10.0	1.96	0.196	0.279	1.12
5	10.0	1.93	0.193	0.274	1.10
6	10.0	1.92	0.192	0.273	1.09
7	10.0	1.90	0.190	0.270	1.08
8	10.0	1.91	0.191	0.271	1.08
9	10.0	1.90	0.190	0.270	1.08
10	10.0	1.96	0.196	0.279	1.12

Table 3.10 Iodine Monochloride Method (ICl) Results

Mean=1.04 , SD=0.009

Run #	Calculated Concentration g/US Gal
1	1.03
2	1.05
3	1.04
4	1.05
5	1.05
6	1.04
7	1.03
8	1.04
9	1.03
10	1.03

Table 3.11 X-Ray Fluorescence Method Results

Mean=1.04

Run #	Concentration g/US Gal
1	1.04
2	1.04
3	1.04
4	1.04
5	1.04

CHAPTER 4

CONCLUSION

Lead-207 NMR has been found to be an extremely sensitive, flexible, accurate, and simple method to examine lead alkyls in undiluted samples and gasoline. The lead nucleus is a very accessible subject for study by NMR with high sensitivity, good resolution and spectral dispersion, rapid relaxation, strong coupling, and large (227%) NOE advantage. Lead-207 NMR has been successfully developed as a technique to measure lead purity in tetraethyl and tetramethyl lead shipments, to indicate the level of organo-lead impurities, and to measure tetraethyllead and tetramethyllead in gasoline at levels to less than 50 ppm. Shipments of TEL from 3 different vendors; Ethyl (US), Octel (UK), and Novoktan (FRG) were examined. Quality questions at Saudi Arabian refineries concerning variations in the performance of these shipments and consistency of the quality have been addressed.

Although NMR is less precise (sd= 0.018) than x-ray fluorescence (with no deviation) or iodine monchloride titration (sd= 0.009), it has the unique advantage to discriminate among organolead, inorganic lead, and lead tetraalkyl components. It therefore serves as a technique to detect adulteration of lead shipments with inactive lead components. It also has the advantage of discerning degradation of lead alkyls in shipments, gasoline, and waste samples. Lead-207

NMR has been proven to be effective in studies of lead alkyl degradation and interaction between lead alkyls.

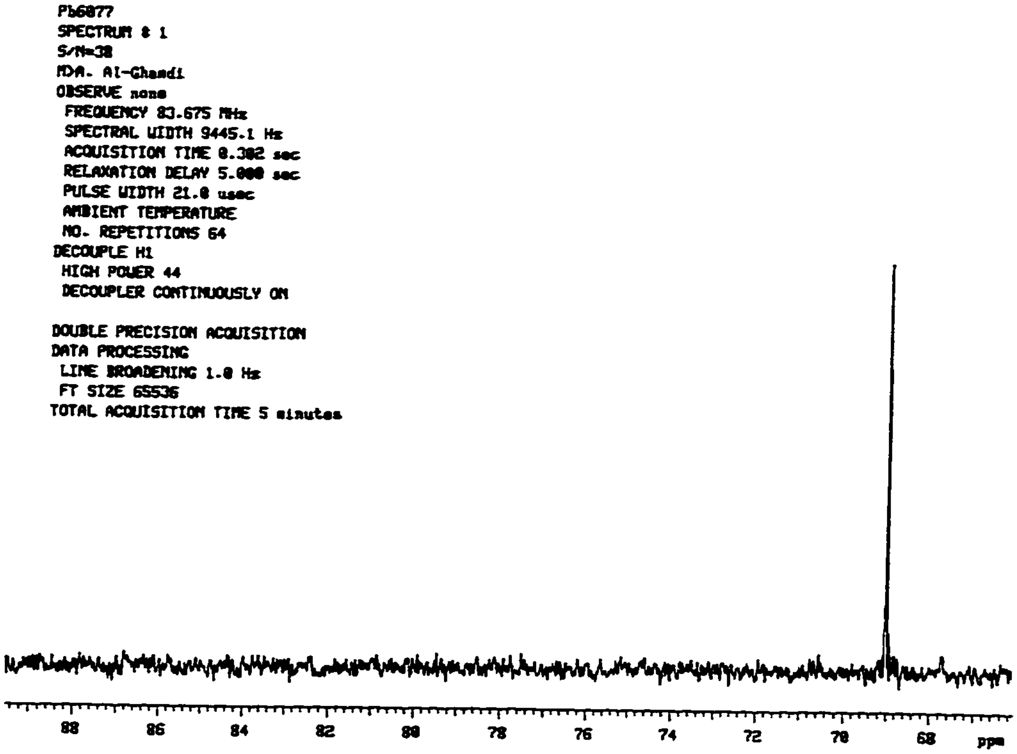
Further exploitation of the technique is anticipated to survey regular TEL shipments to the refineries, to study the fate and degradation of lead alkyls, and to evaluate environmental samples from land farms, tank drainage, waste disposal, out of specification gasoline, and lead sludge. The technique is also valuable to study process streams to improve process efficiency, yields, and by products from lead manufacturing. With a sensitivity at the level of a few tens of ppm, the technique is amenable to the study of fate in physiological fluids for the investigation of lead poisoning and metabolic.

APPENDIX A

ACQUISITION TIME EFFECT SPECTRA

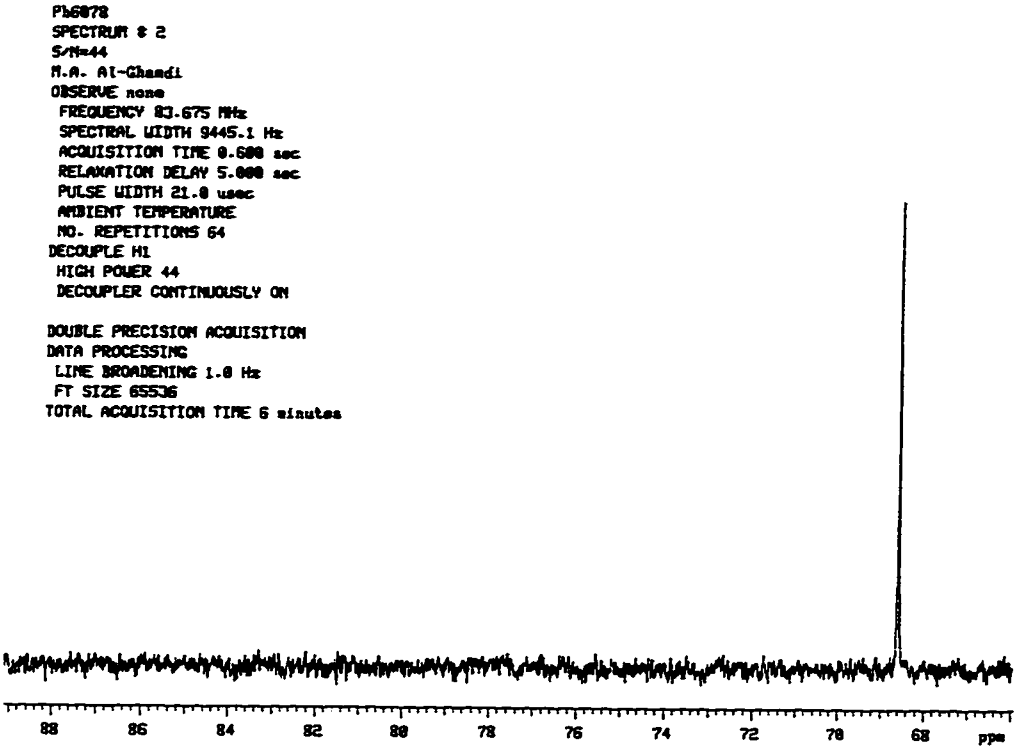
Spectra 1 through 6 have been used to determine the effect of the acquisition time on the signal to noise ratio.

SPECTRUM # 1



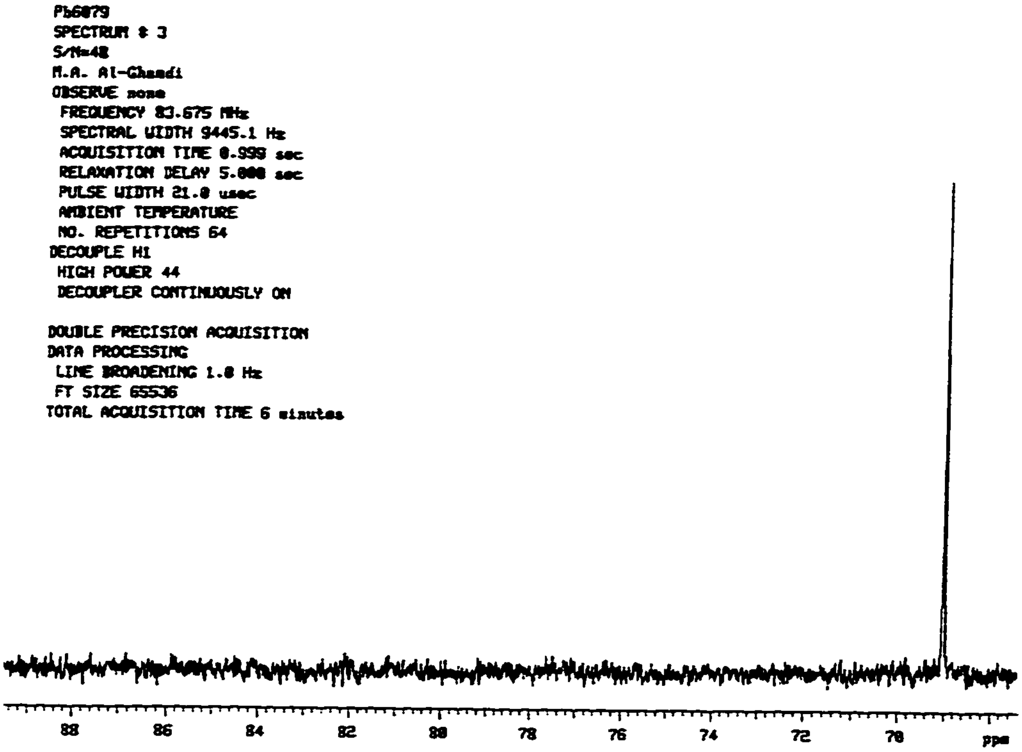
```
Pb6077
SPECTRUM # 1
S/N=30
MDA. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 0.302 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 5 minutes
```

SPECTRUM # 2



```
Pb6078
SPECTRUM # 2
S/N=44
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 0.600 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 6 minutes
```

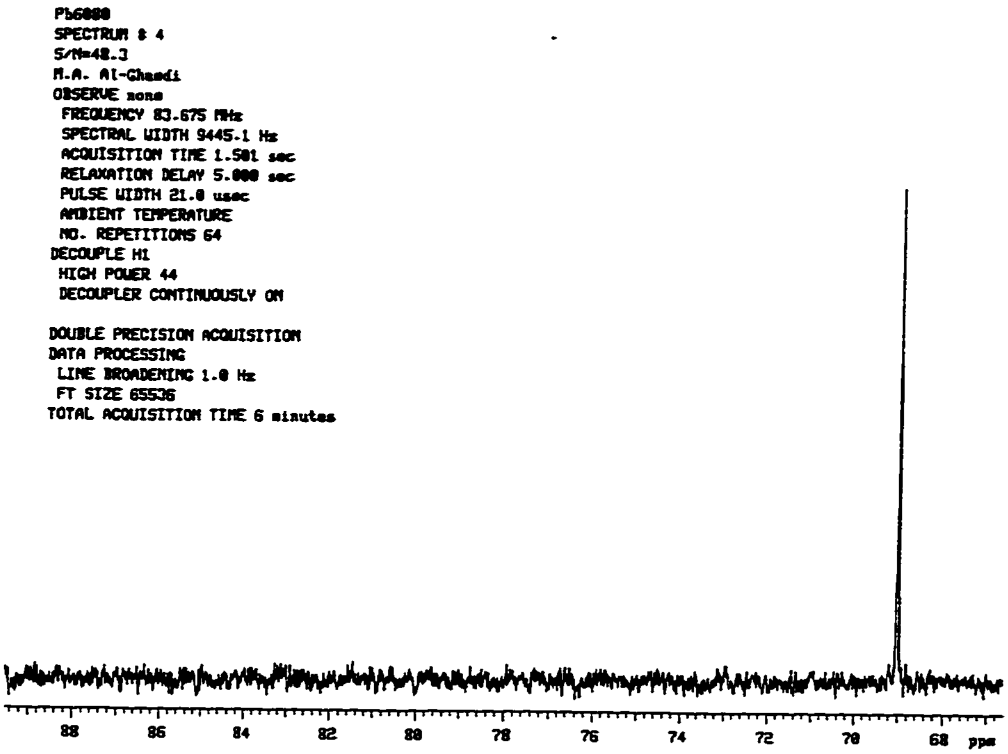
SPECTRUM # 3



Pb6079
SPECTRUM # 3
S/N=40
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 0.999 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

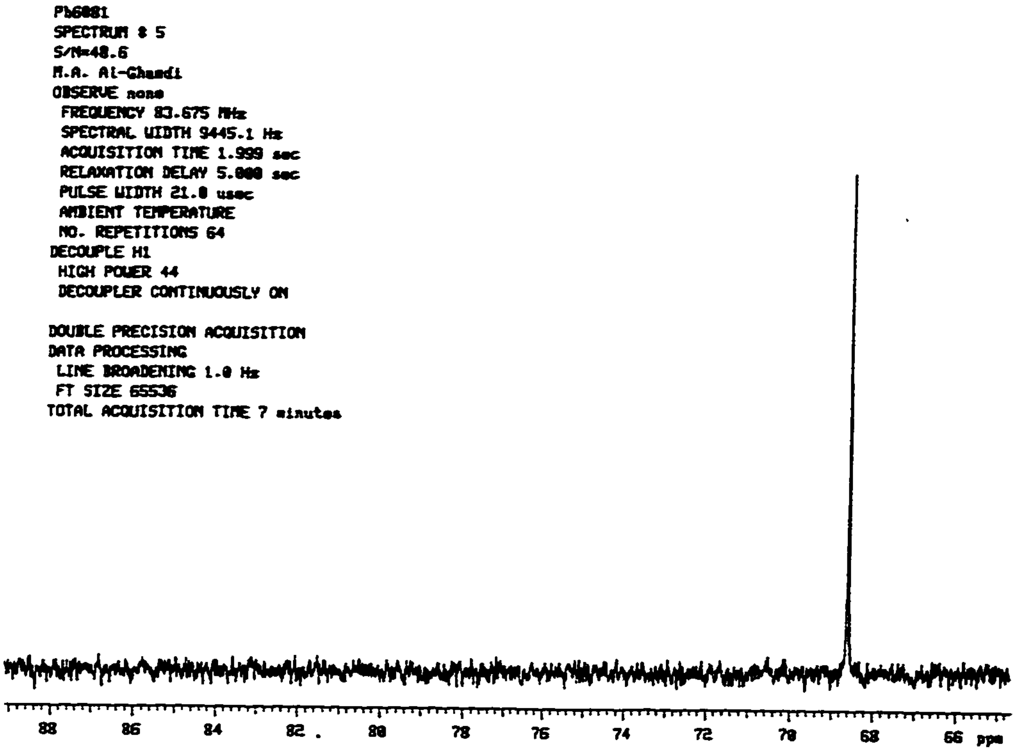
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 6 minutes

SPECTRUM # 4



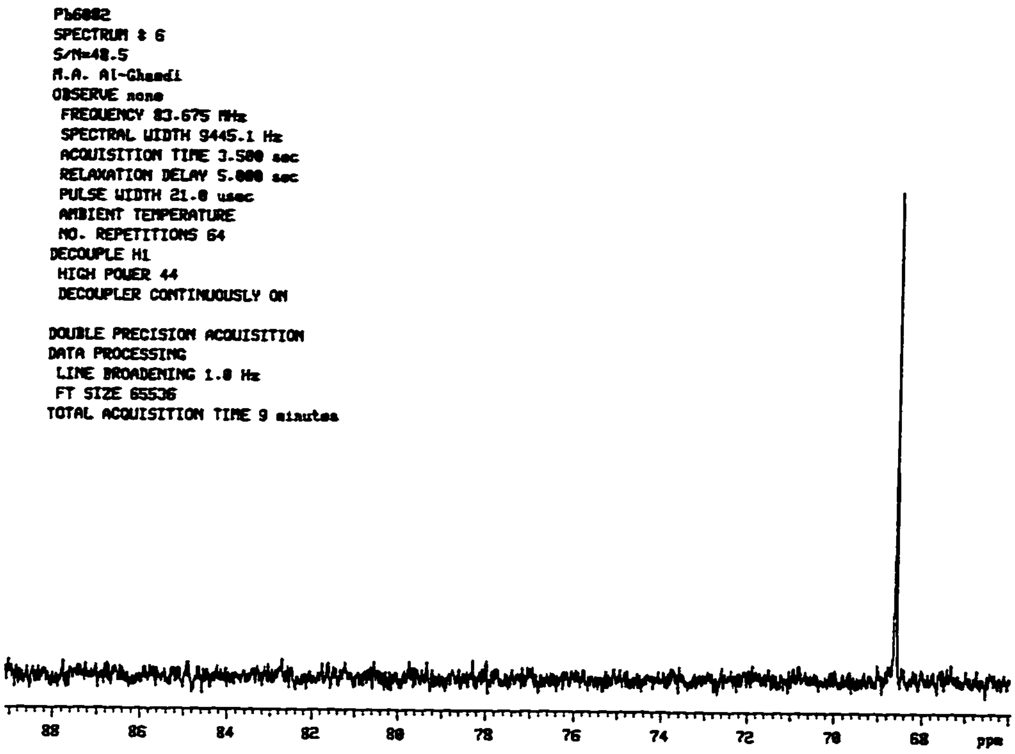
```
Pb6000
SPECTRUM # 4
S/N=48.3
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 6 minutes
```

SPECTRUM # 5



```
Pb6001
SPECTRUM # 5
S/N=40.6
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 7 minutes
```

SPECTRUM # 6



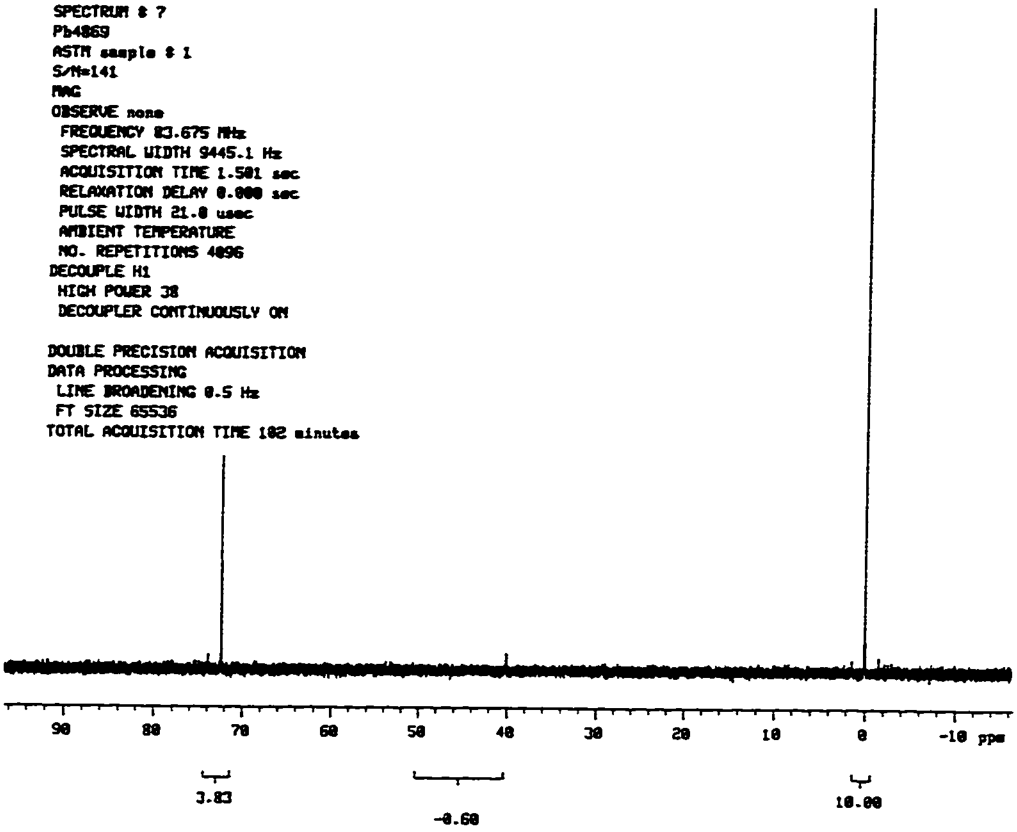
```
Pb6002
SPECTRUM # 6
S/N=40.5
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 3.500 sec
 RELAXATION DELAY 5.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 64
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 9 minutes
```

APPENDIX B

PRECISION OF THE METHOD SPECTRA

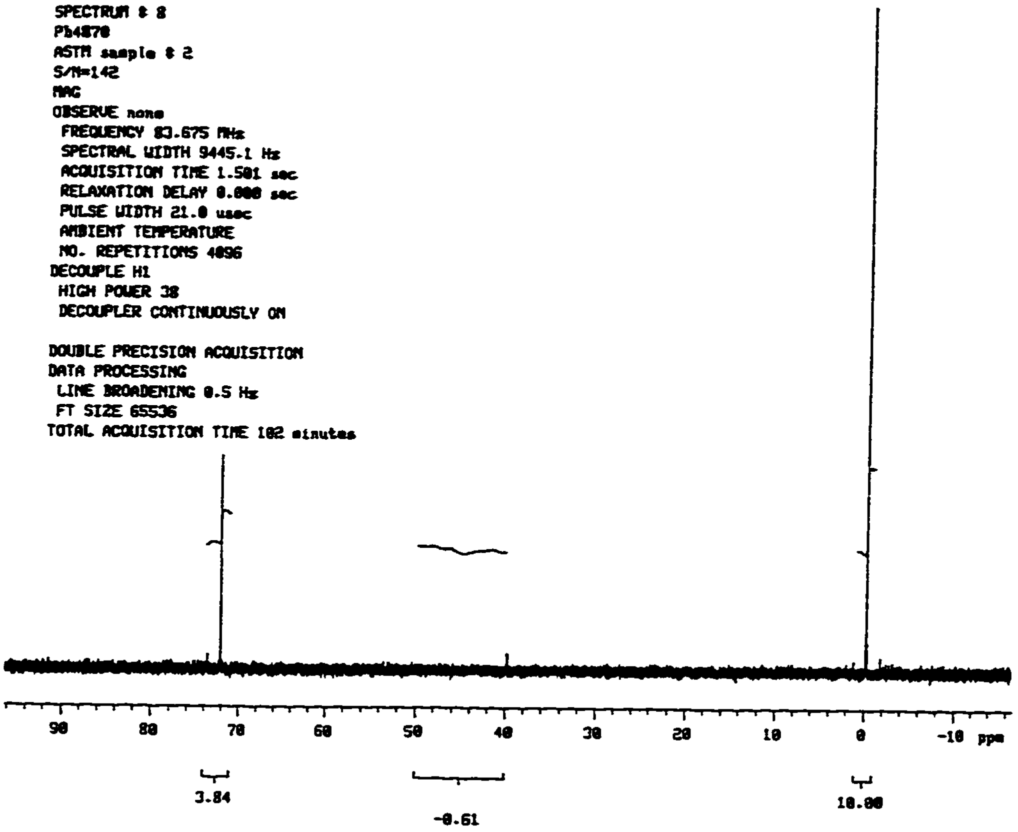
Spectra 7 through 11 have been used to test the precision of the experimental method.

SPECTRUM # 7



```
SPECTRUM # 7
Pb4069
ASTM sample # 1
S/N=141
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

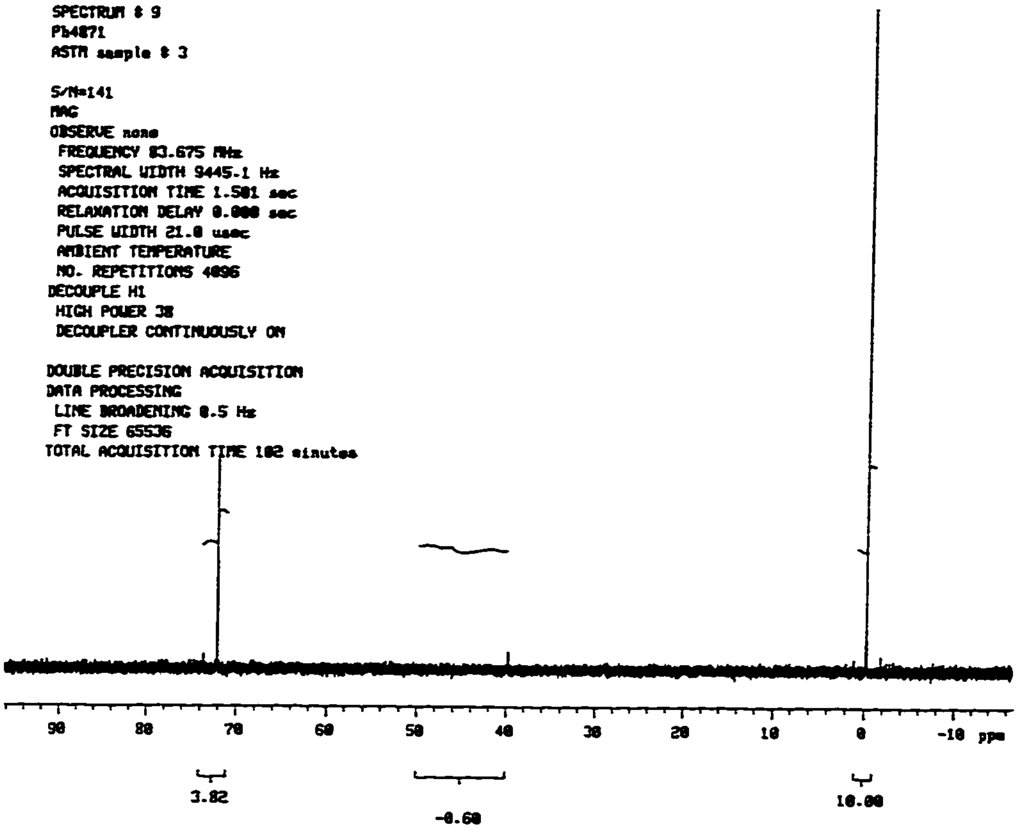
SPECTRUM # 8



SPECTRUM # 8
Pb4870
ASTM sample # 2
S/N=142
MAG
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.501 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 38
DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.5 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes

SPECTRUM # 9

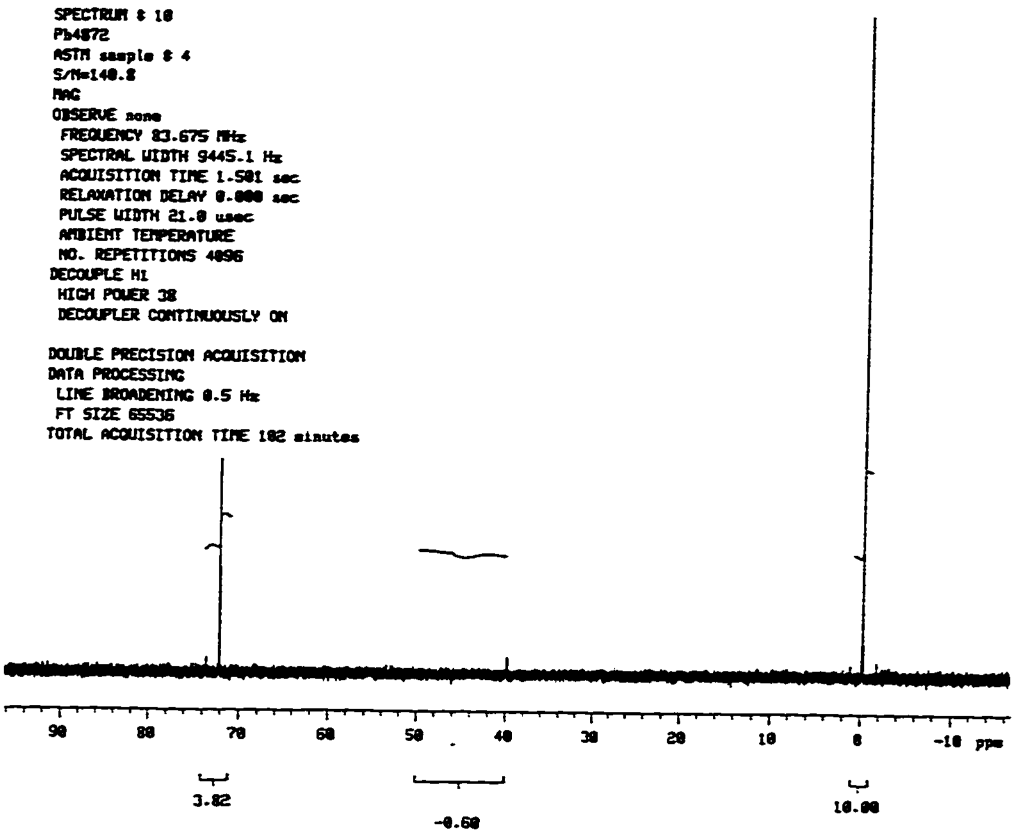


SPECTRUM # 9
Pb4071
ASTM sample # 3

S/N=141
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes

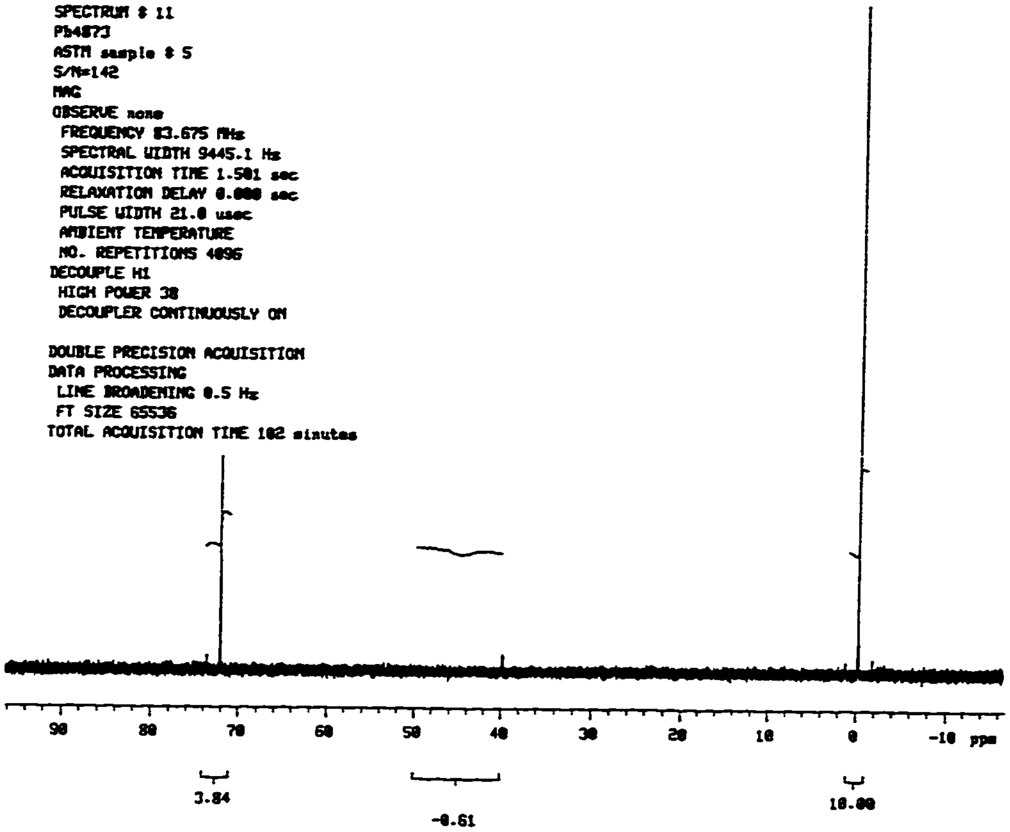
SPECTRUM # 10



SPECTRUM # 10
Pb4072
ASTM sample # 4
S/N=140.0
MAG
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.501 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 30
DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.5 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes

SPECTRUM # 11



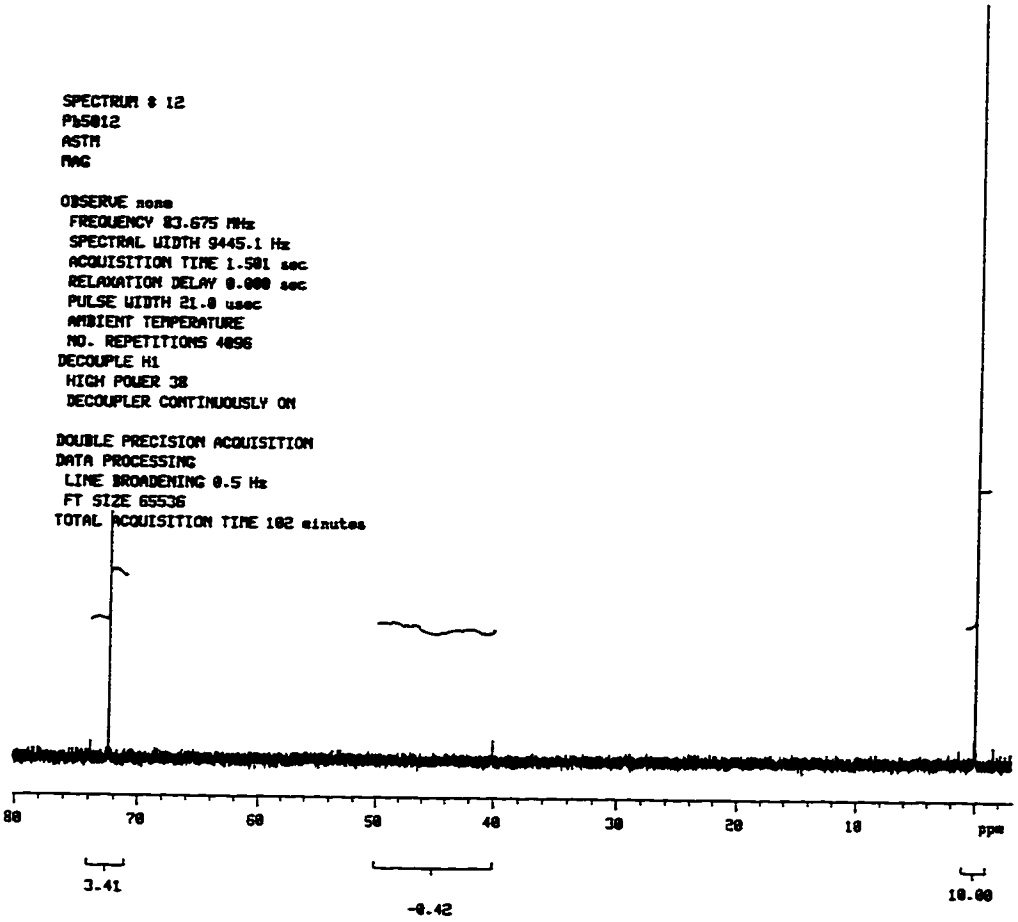
```
SPECTRUM # 11
Pb4873
ASTM sample # 5
S/N=142
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

APPENDIX C

UNIFORMITY OF NMR TUBES SPECTRA

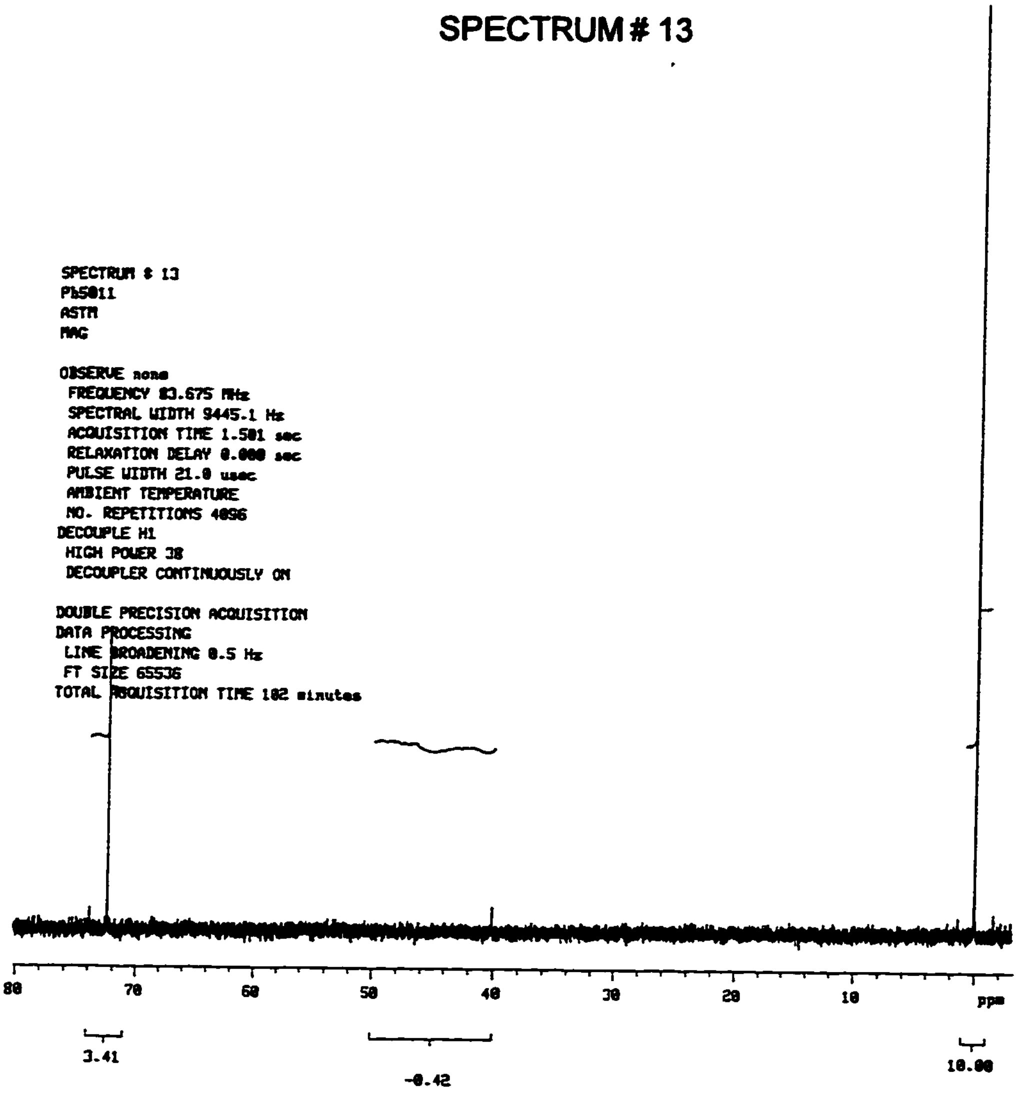
Spectra 12 through 16 have been used to test the uniformity of the NMR tubes.

SPECTRUM # 12



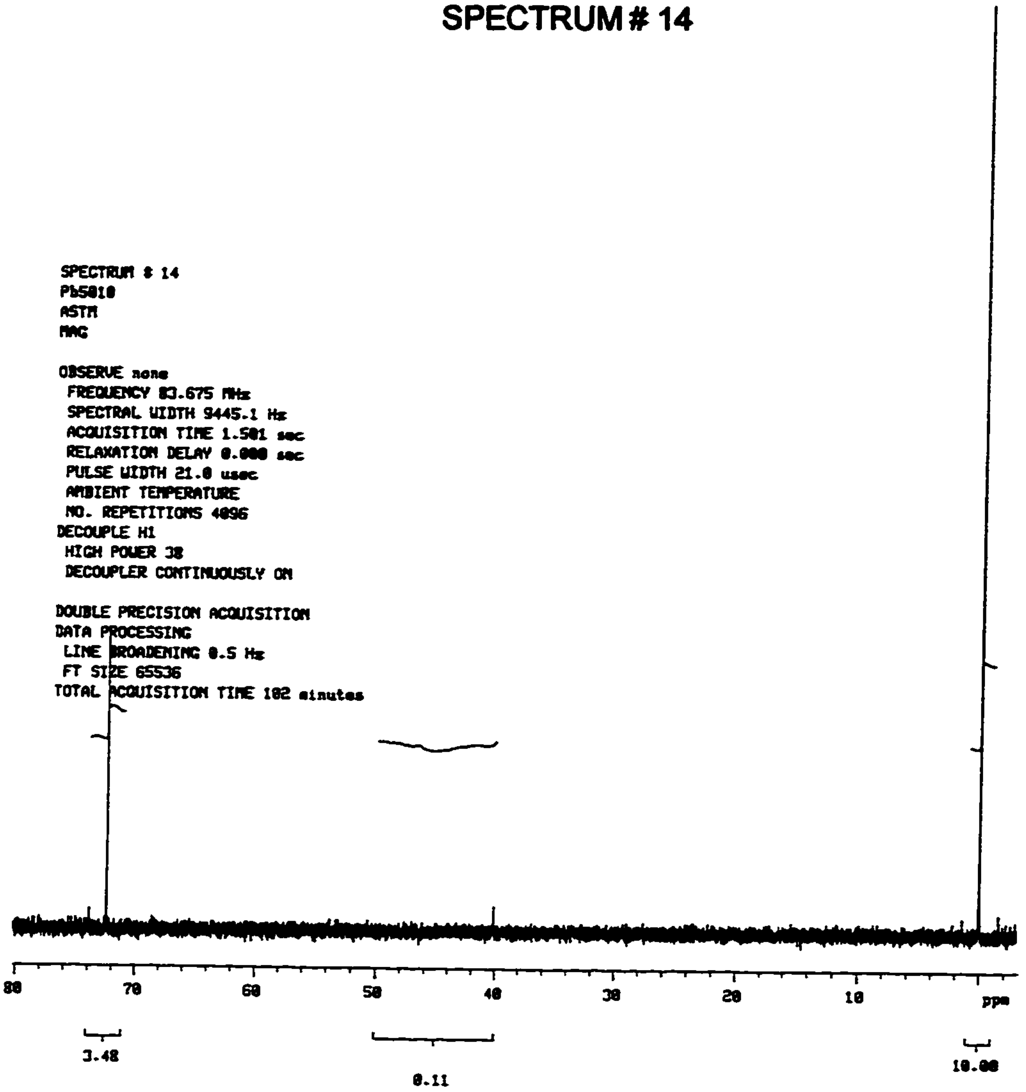
```
SPECTRUM # 12
Pb5012
ASTM
MAG

OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 13



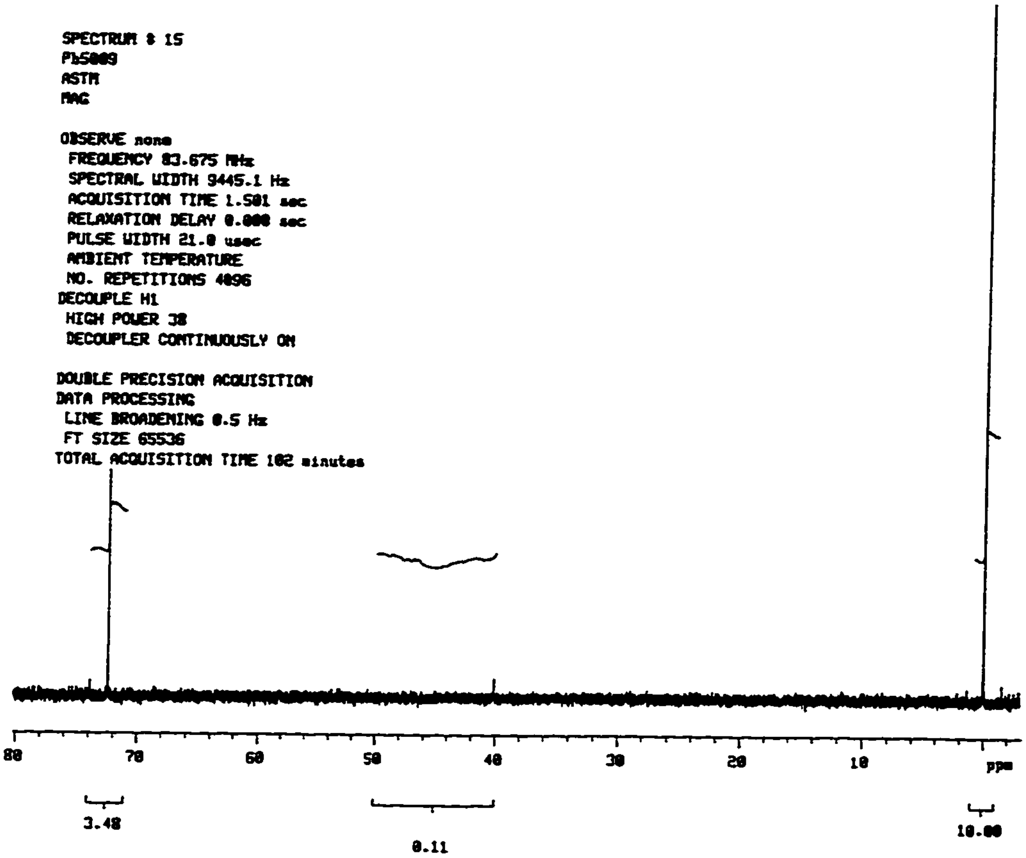
```
SPECTRUM # 13
PbS011
ASTM
MAG

OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 14



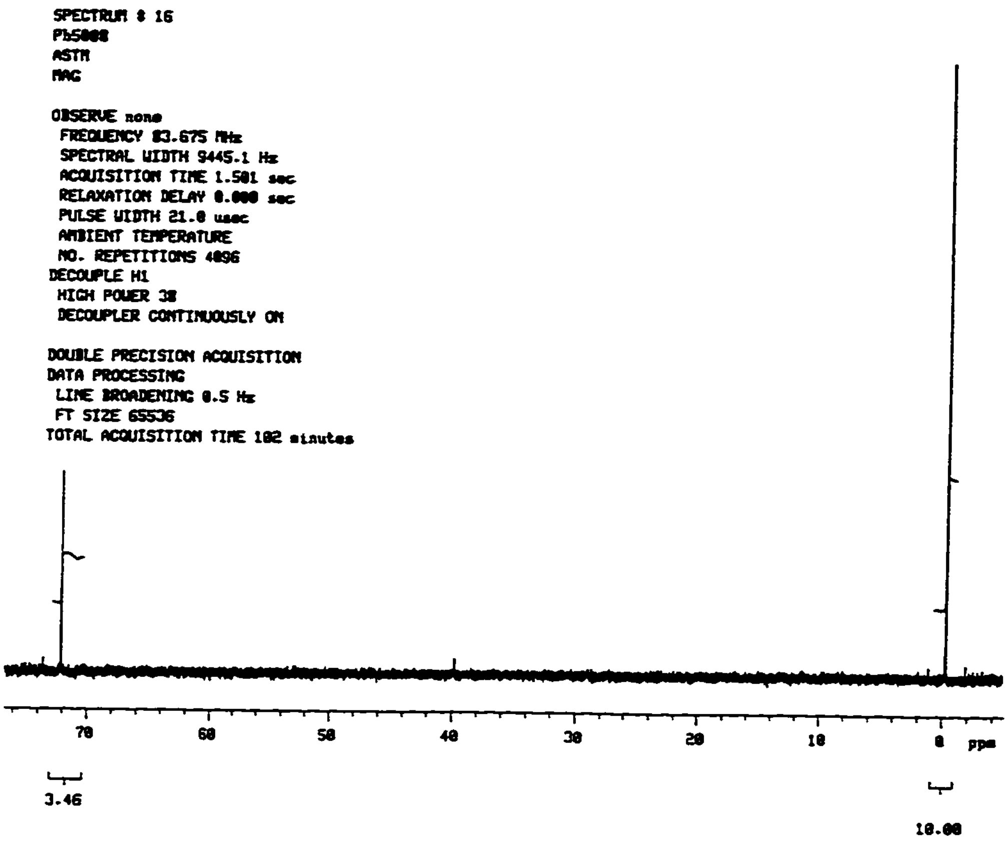
```
SPECTRUM # 14
Pb5010
ASTM
MAG

OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 15



```
SPECTRUM # 15
Pb5009
ASTM
MAG

OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 16



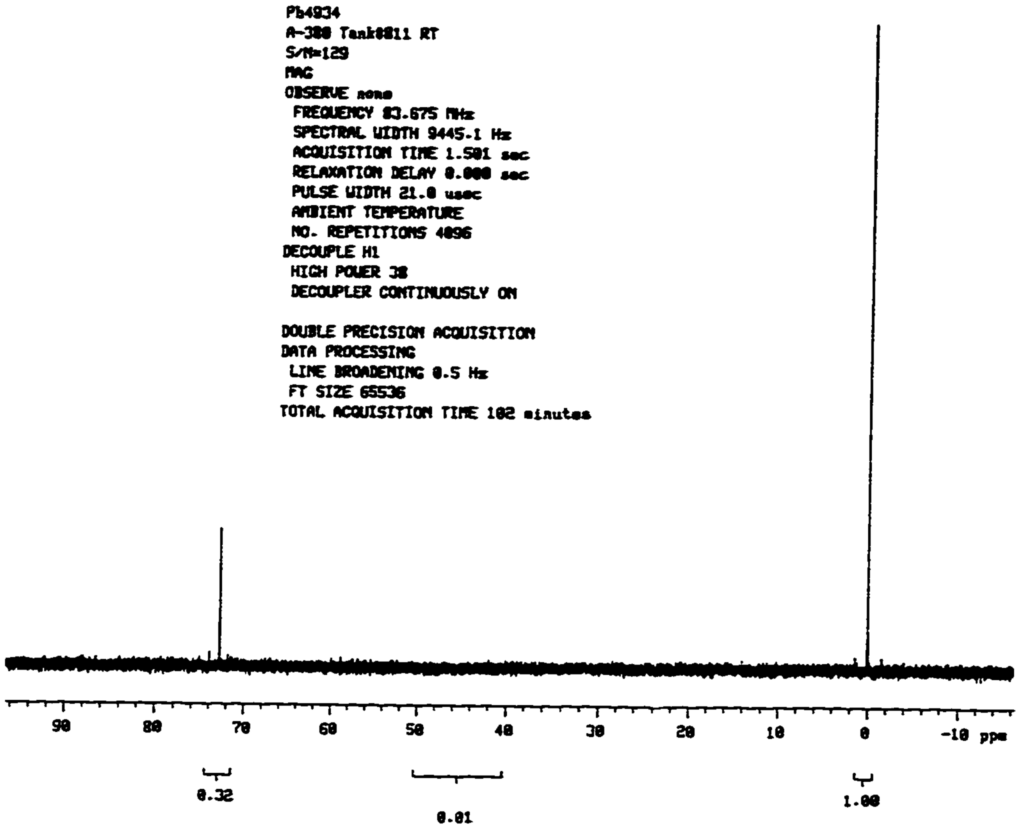
```
SPECTRUM # 16
Pb5000
ASTM
MAG

OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

APPENDIX D

PRECISION OF INTEGRATION METHOD SPECTRA

Spectra 17 through 21 have been used to determine the precision of the integration method.

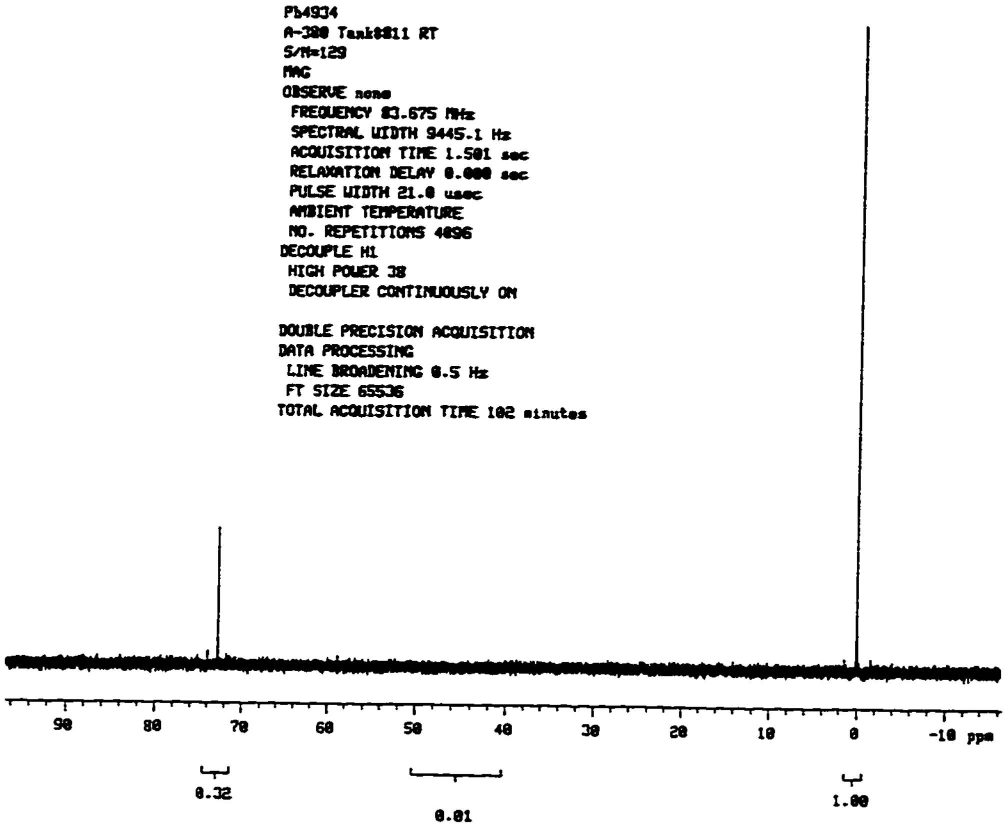
SPECTRUM # 17



Pb4934
A-300 Tank0011 RT
S/N=129
MAG
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.501 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 30
DECOUPLER CONTINUOUSLY ON

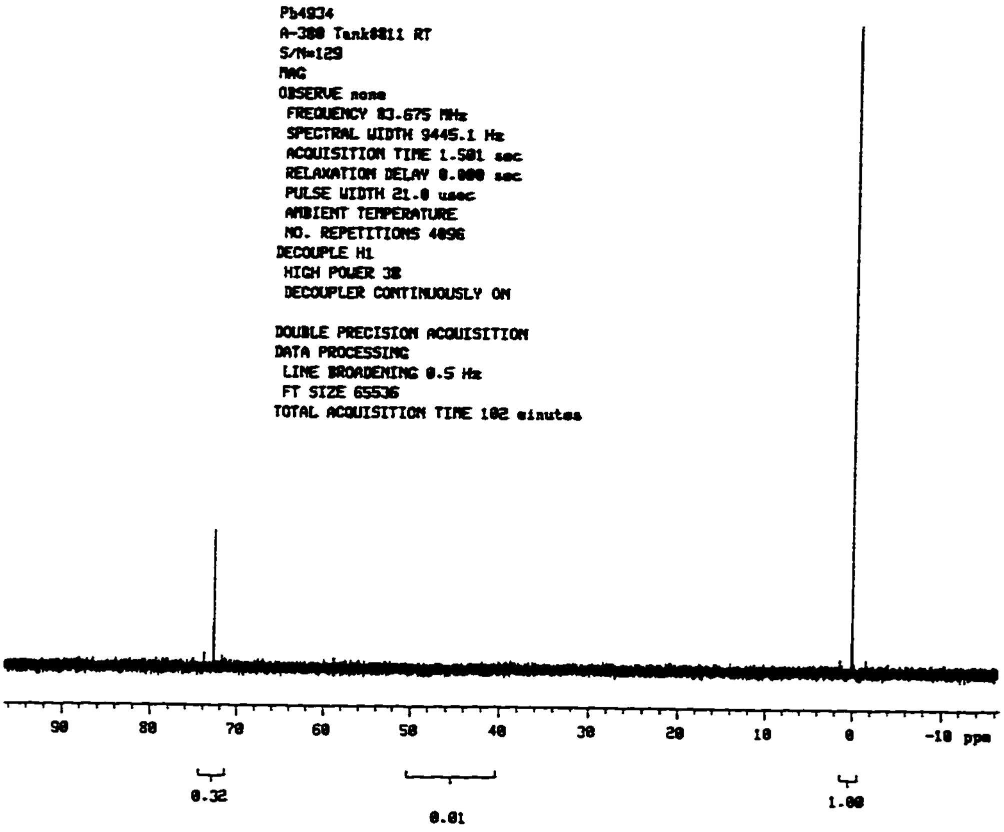
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.5 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes

SPECTRUM # 18



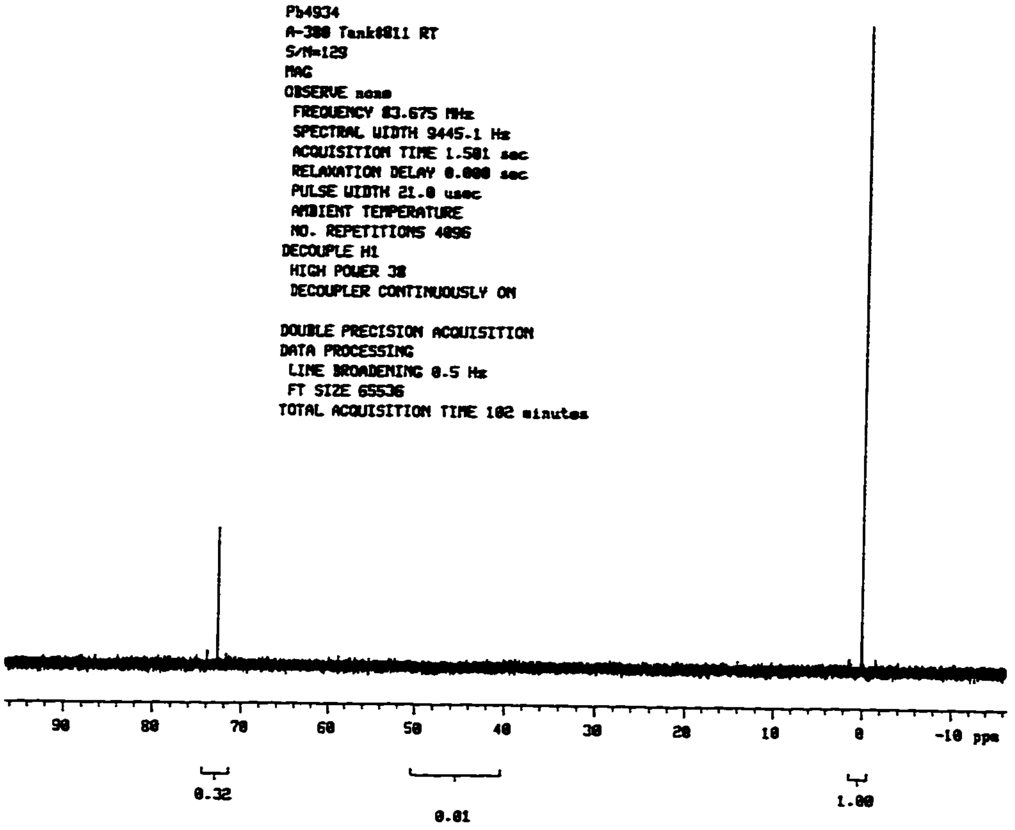
```
Pb4934
A-300 Tank#011 RT
S/N=129
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 19



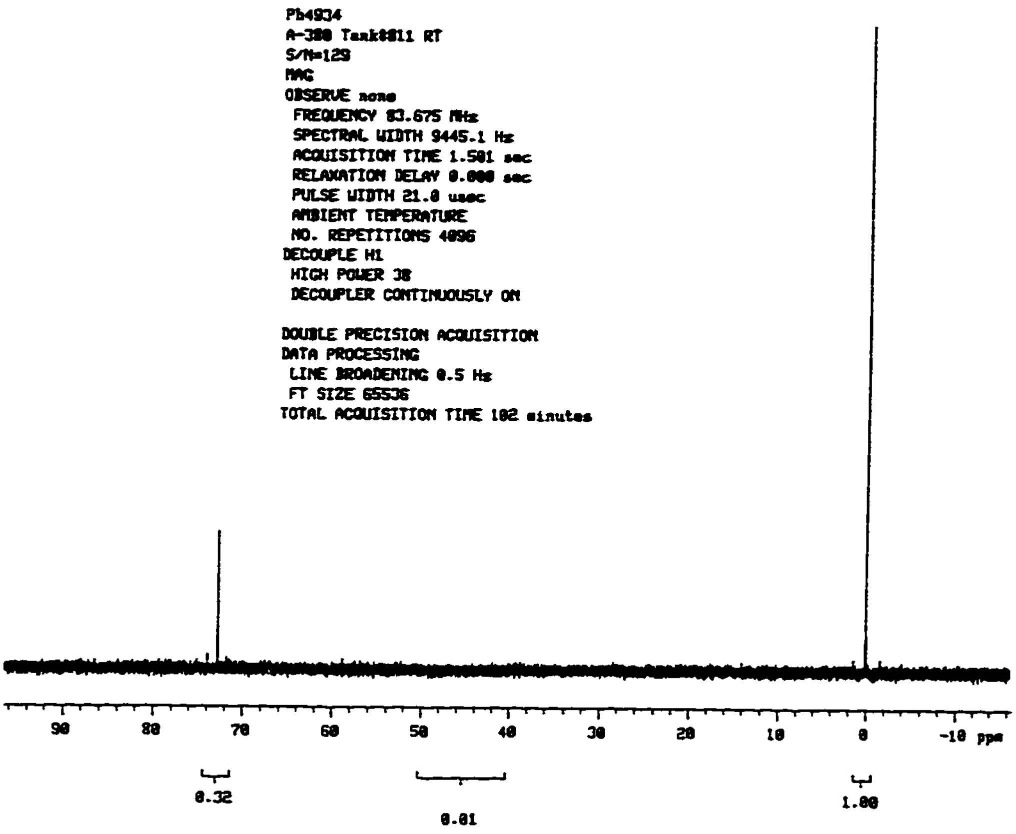
```
Pb4934
A-300 Tank#011 RT
S/N=129
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 20



```
Pb4934
A-300 Tank#011 RT
S/N=129
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 21



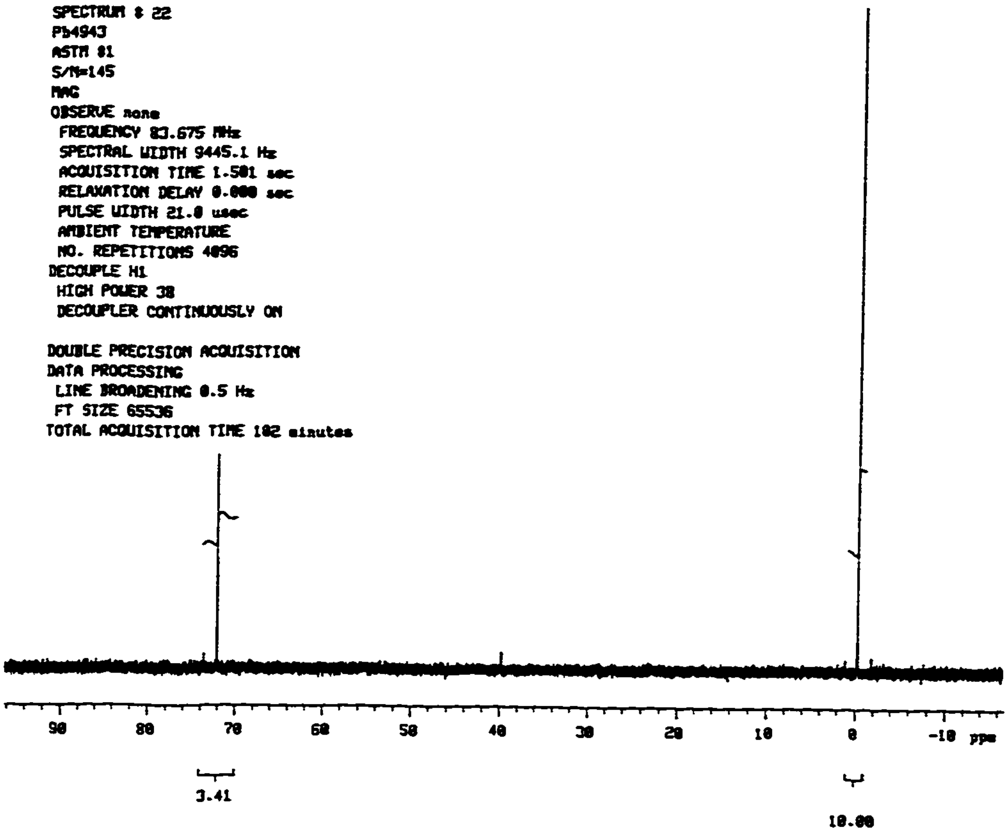
```
Pb4934
A-300 Tank#011 RT
S/N=129
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

APPENDIX E

Detection Limit Spectra

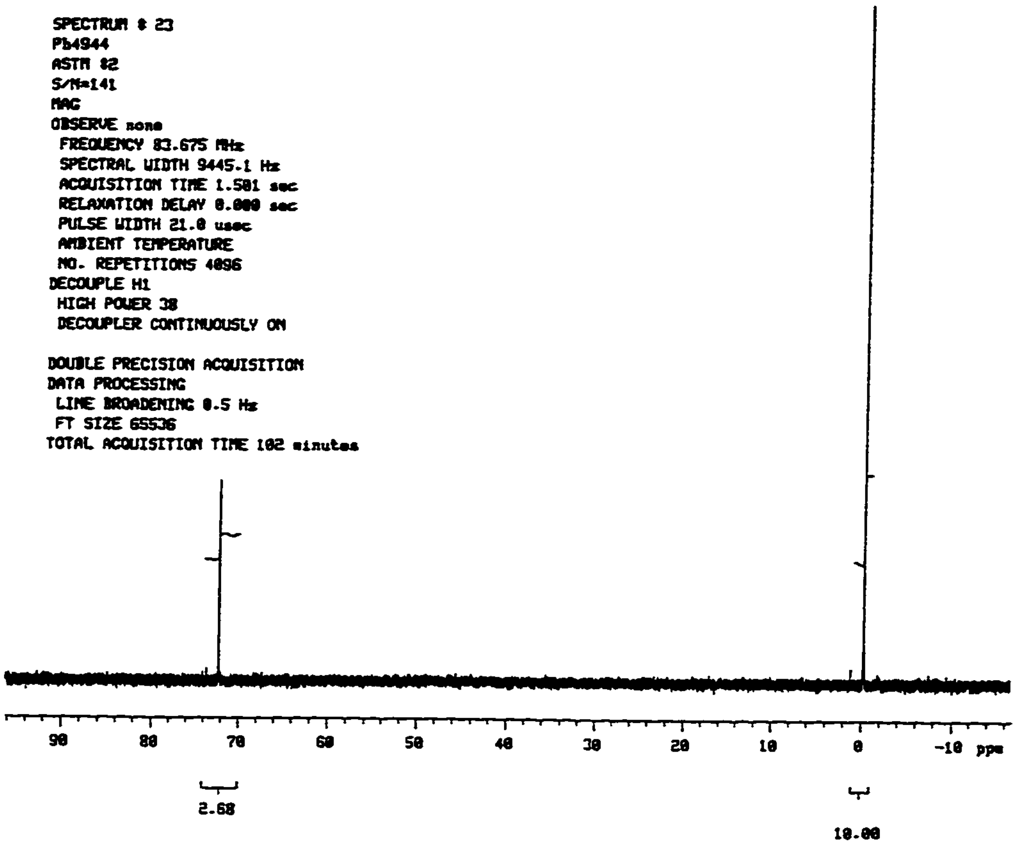
Spectra 22 through 27 have been used to determine the detection limit on the NMR method.

SPECTRUM # 22



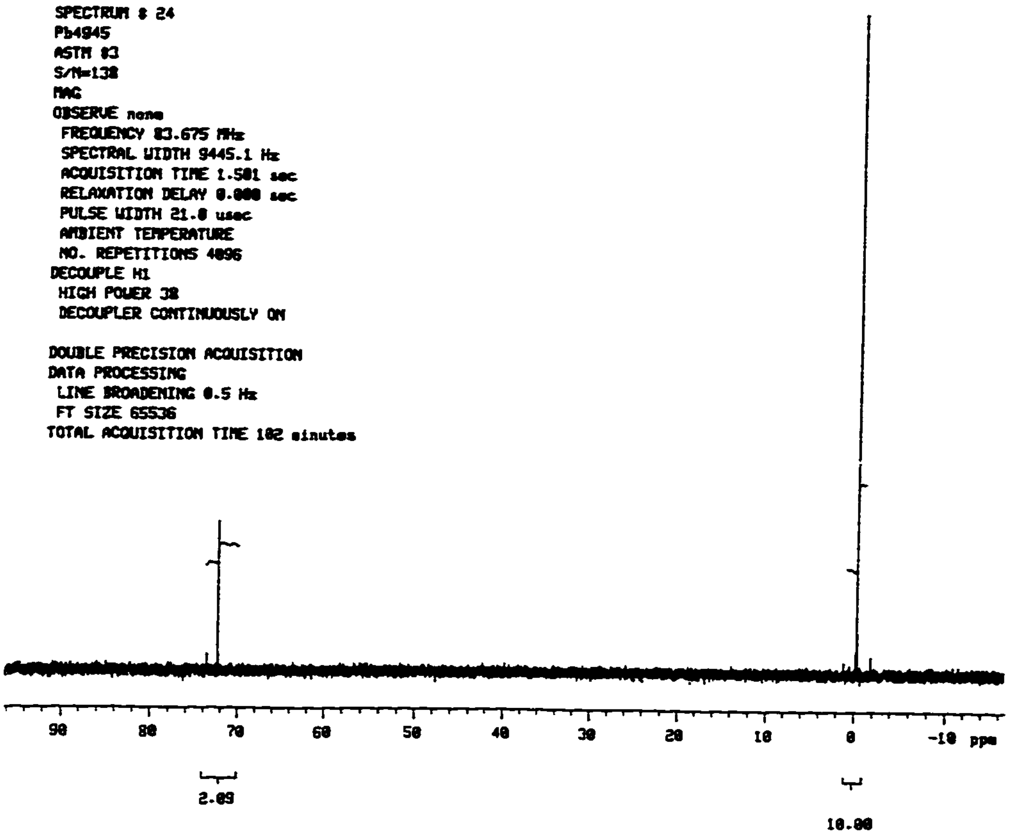
```
SPECTRUM # 22
Pb4943
ASTM #1
S/N=145
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 23



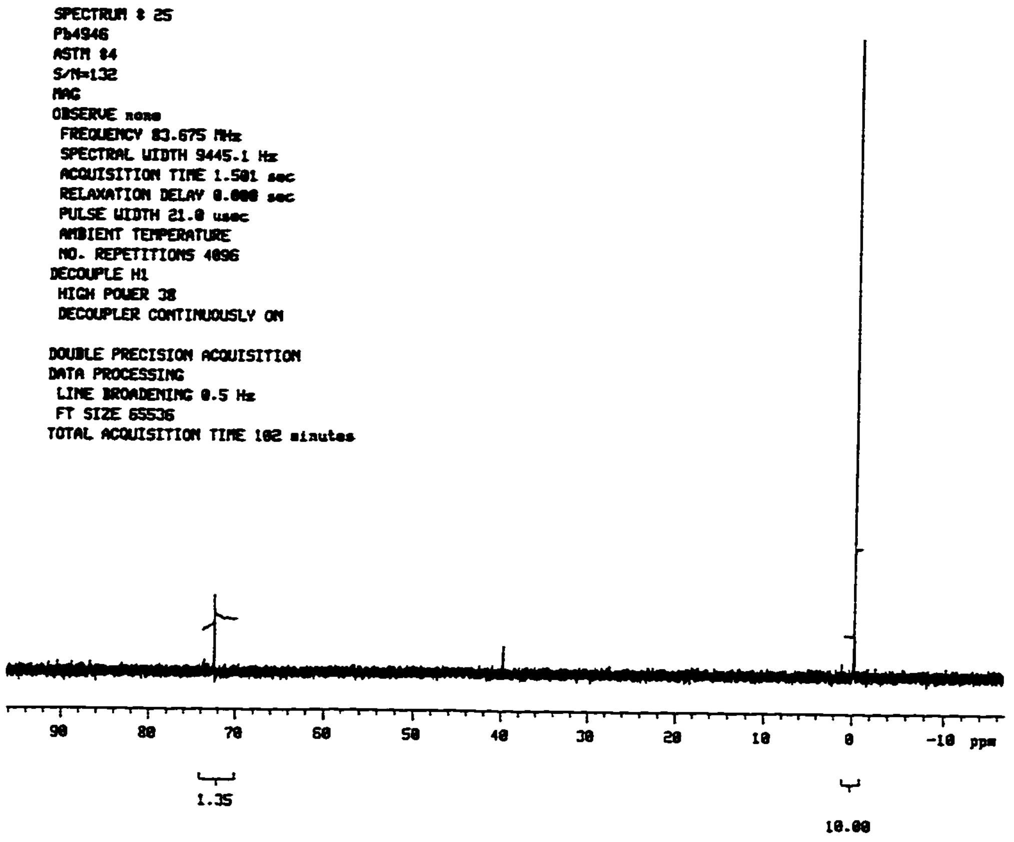
```
SPECTRUM # 23
Pb4944
ASTM #2
S/N=141
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 24



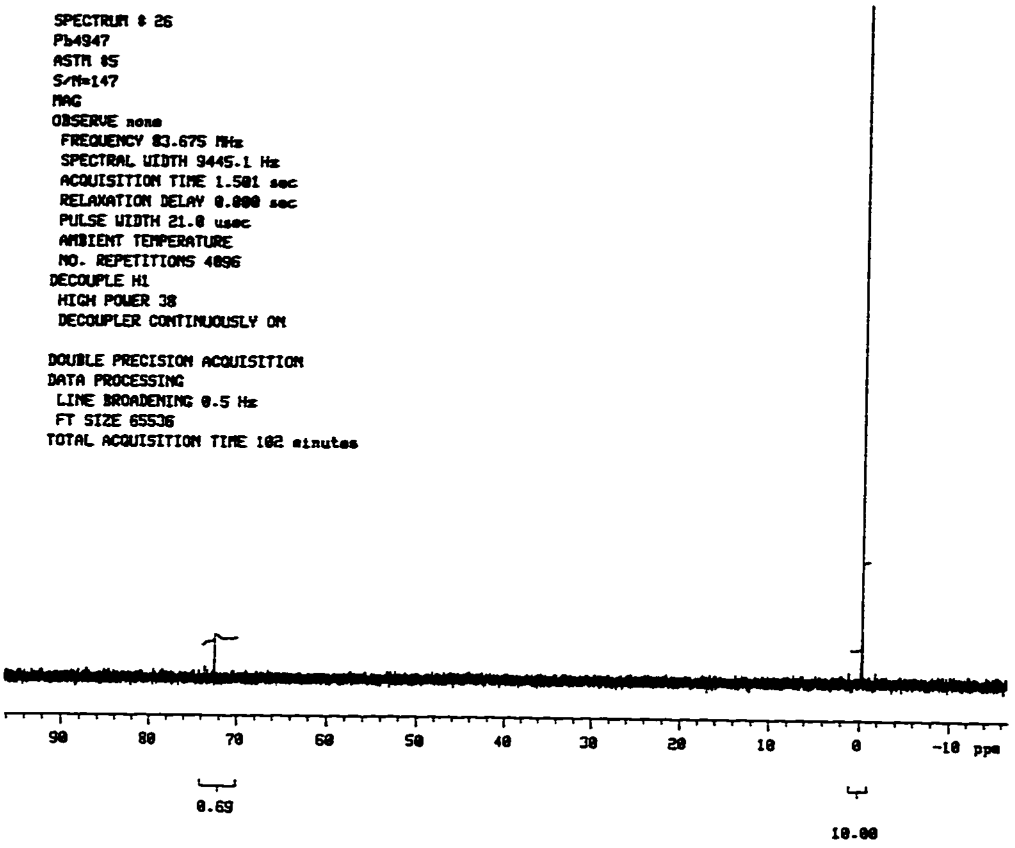
```
SPECTRUM # 24
Pb4945
ASTM #3
S/N=130
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 25



```
SPECTRUM # 25
Pb4946
ASTM #4
S/N=132
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

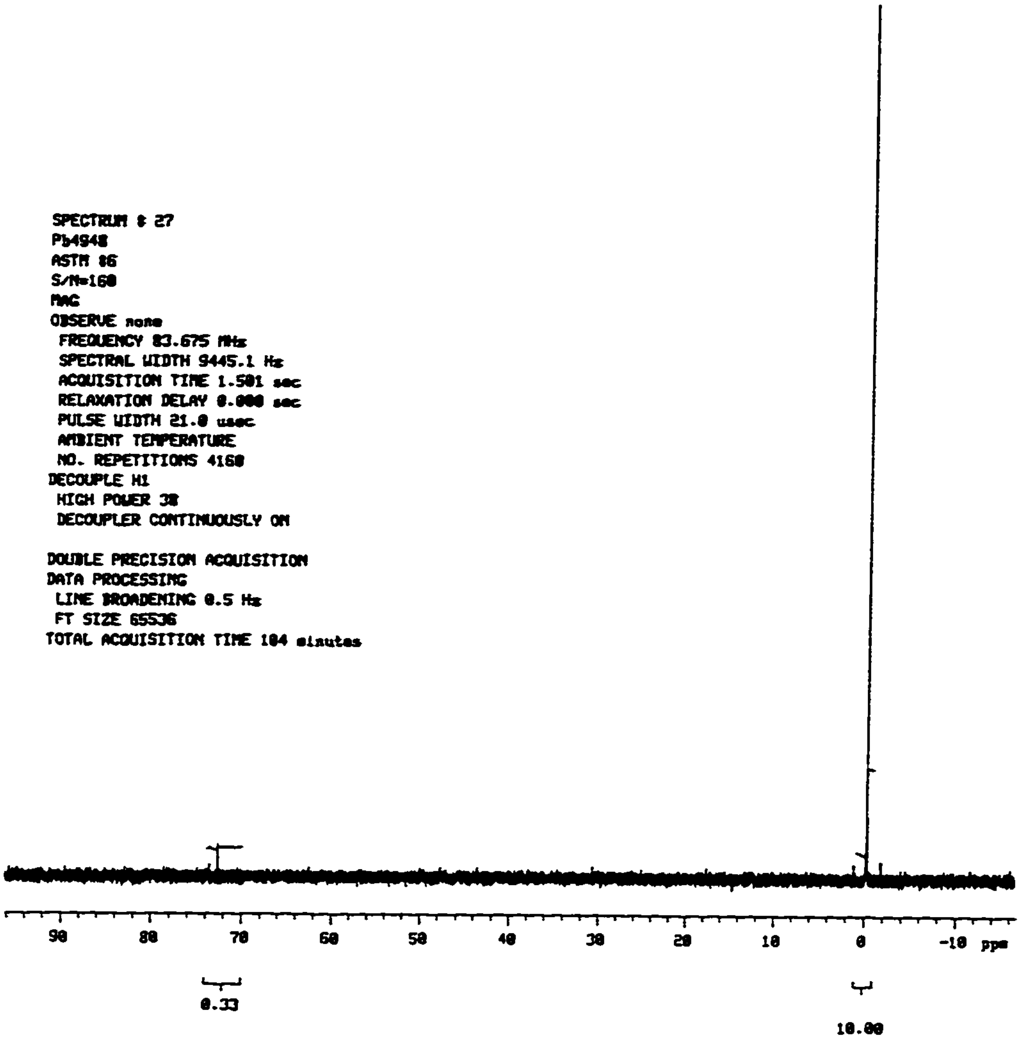
SPECTRUM # 26



SPECTRUM # 26
Pb4947
ASTM #5
S/N=147
MAG
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.501 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 38
DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 0.5 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes

SPECTRUM # 27



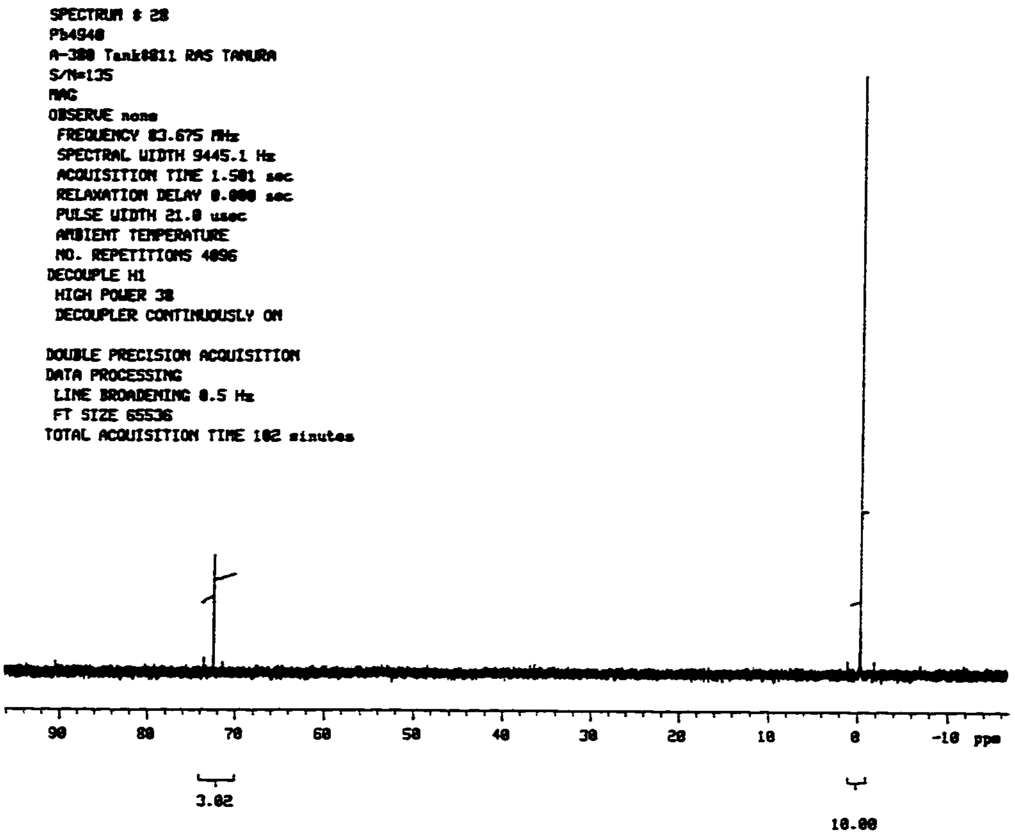
```
SPECTRUM # 27
Pb4948
ASTM #6
S/N=160
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4160
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 104 minutes
```

APPENDIX F

CONCENTRATION DETERMINATION SPECTRA

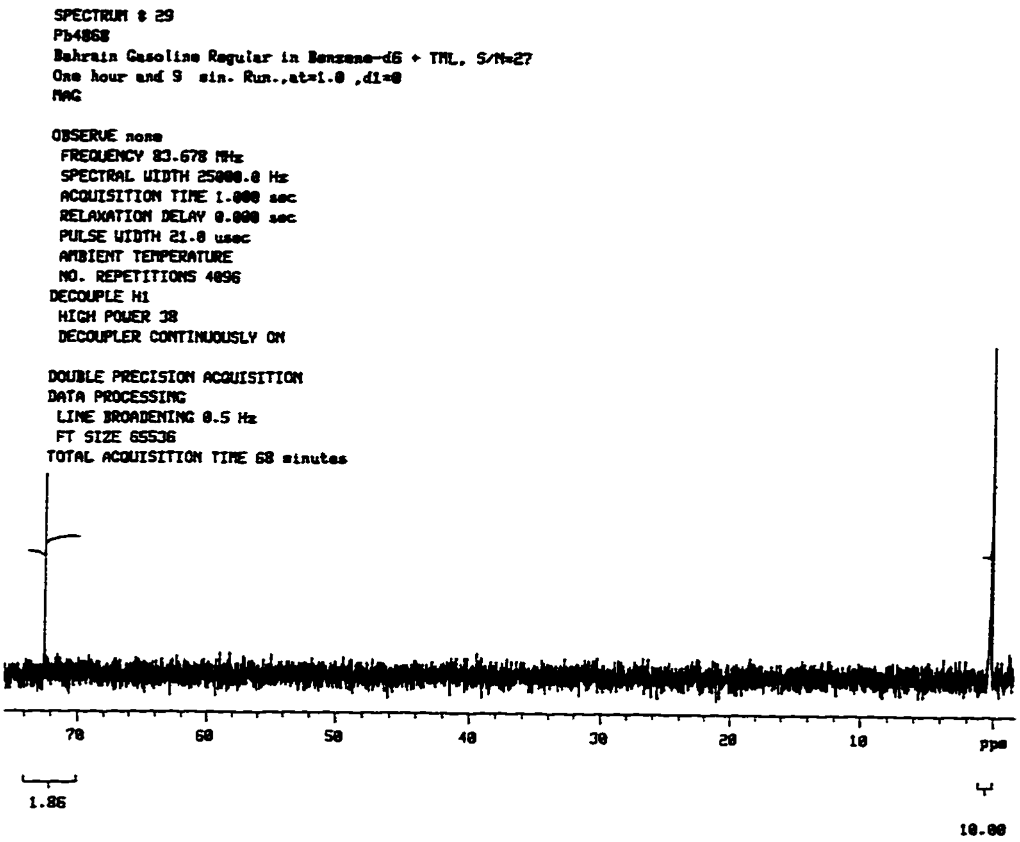
Spectra 28 through 31 have been used to determine the concentration of various unknown gasoline samples.

SPECTRUM # 28



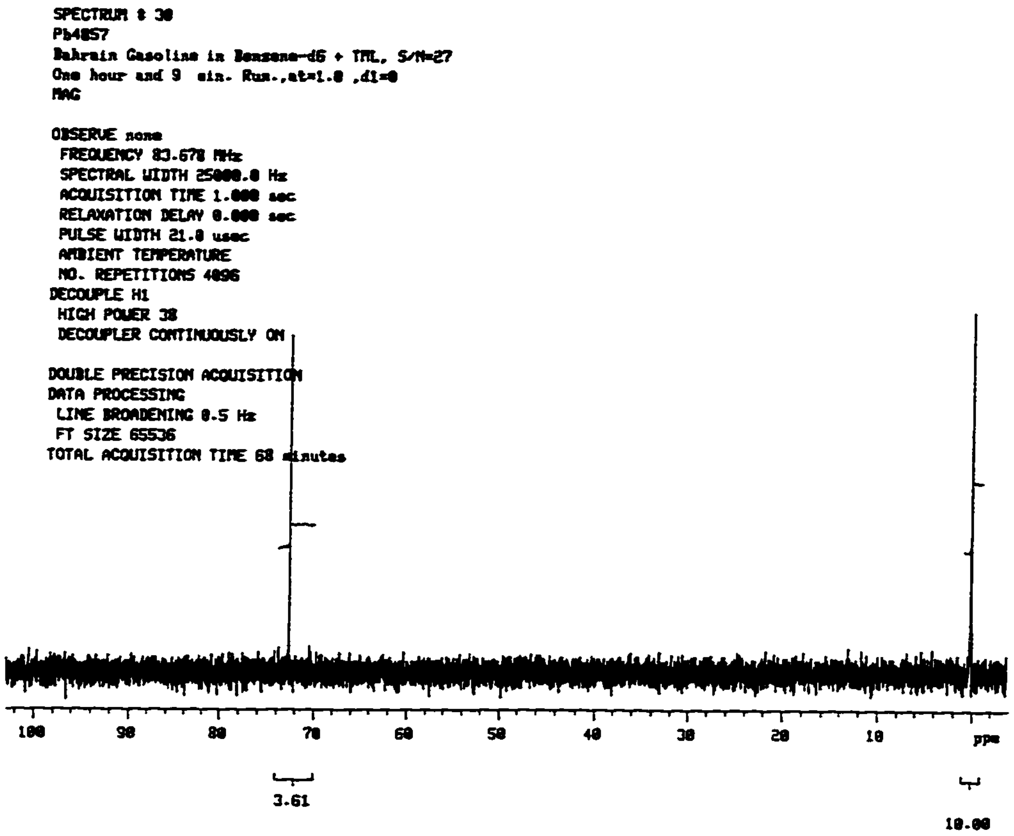
```
SPECTRUM # 28
Pb4940
A-300 Tank#011 RAS TAMURA
S/N=135
MAG
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.501 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 102 minutes
```

SPECTRUM # 29



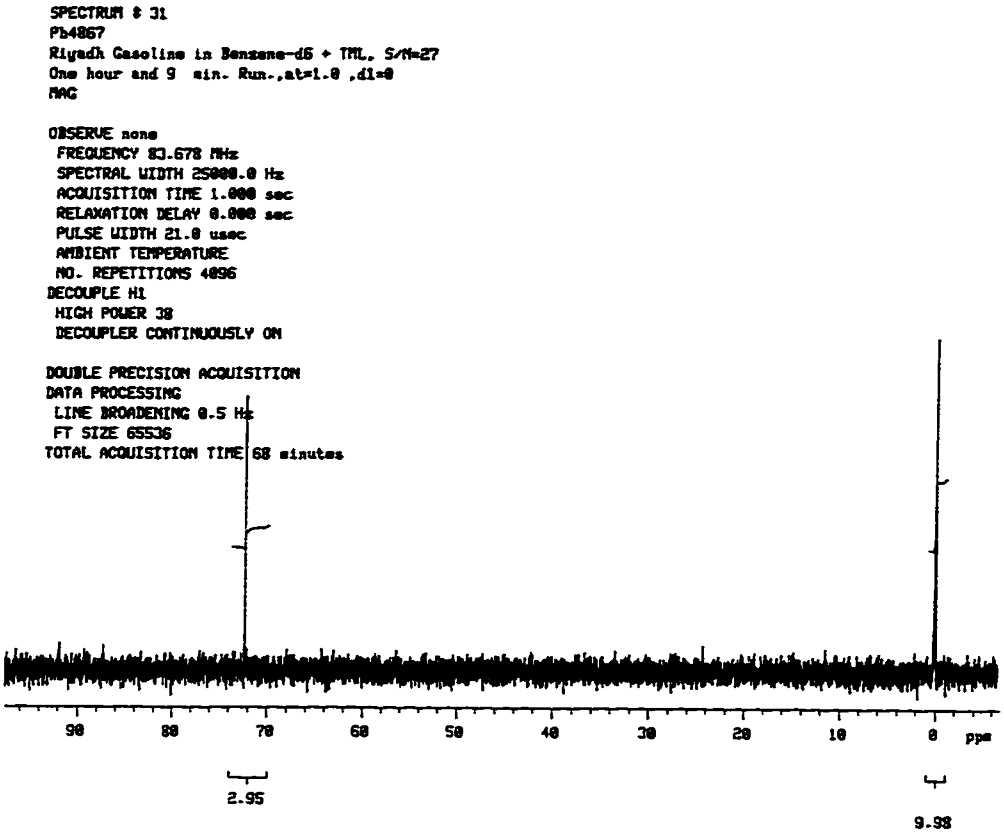
```
SPECTRUM # 29
Pb4068
Bahrain Gasoline Regular in Benzene-d6 + TML, S/N=27
One hour and 9  min. Run.,at=1.0 ,d1=0
MAG

OBSERVE none
 FREQUENCY 83.678 MHz
 SPECTRAL WIDTH 25000.0 Hz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 68 minutes
```

SPECTRUM # 30



```
SPECTRUM # 30
Pb4057
Bahrain Gasoline in Benzene-d6 + TML, S/N=27
One hour and 9  min. Run.,at=1.0 ,d1=0
MAG

OBSERVE none
 FREQUENCY 83.678 MHz
 SPECTRAL WIDTH 25000.0 Hz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 30
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 68 minutes
```

SPECTRUM # 31



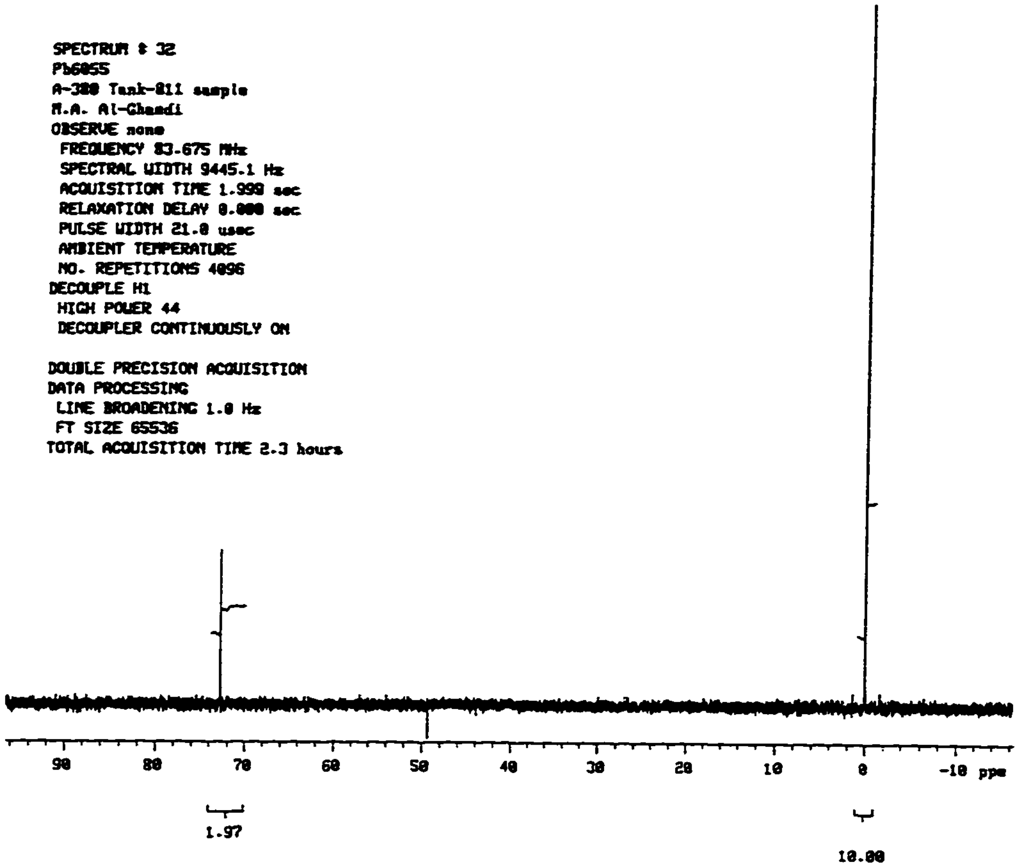
```
SPECTRUM # 31
Pb4867
Riyadh Gasoline in Benzene-d6 + TML, S/N=27
One hour and 9  min. Run.,at=1.0 ,d1=0
MAG

OBSERVE none
 FREQUENCY 83.678 MHz
 SPECTRAL WIDTH 25000.0 Hz
 ACQUISITION TIME 1.000 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 38
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 0.5 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 68 minutes
```

APPENDIX G

COMPARISON OF METHODS (NMR METHOD SPECTRA)

Spectra 32 through 41 have been used to compare the NMR method to the Iodine monochlorid method.

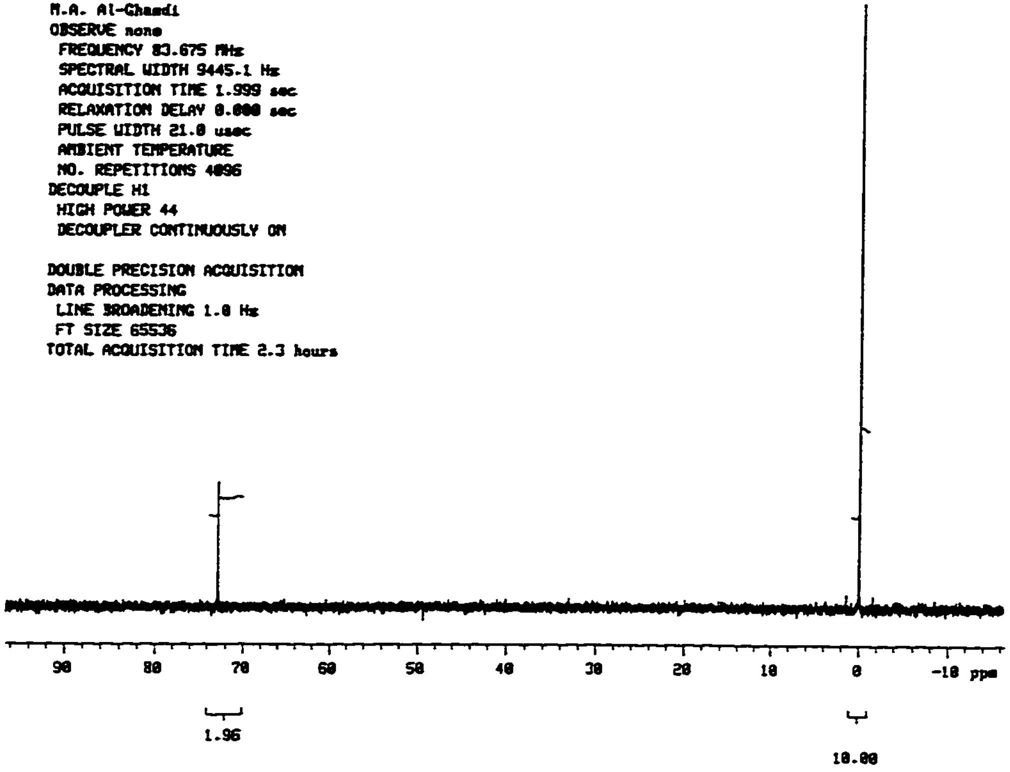
SPECTRUM # 32



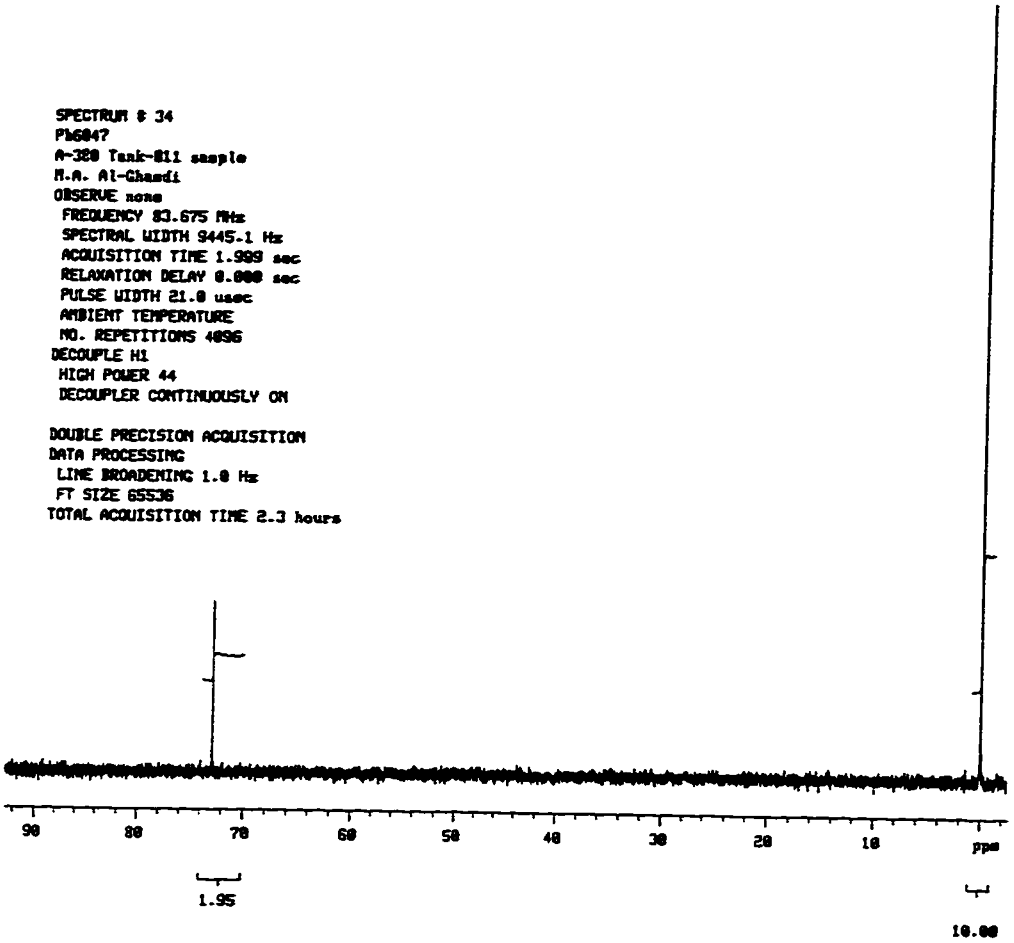
```
SPECTRUM # 32
Pb6055
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

SPECTRUM # 33

```
SPECTRUM # 33
Pb6046
A-300 Tank-811 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```



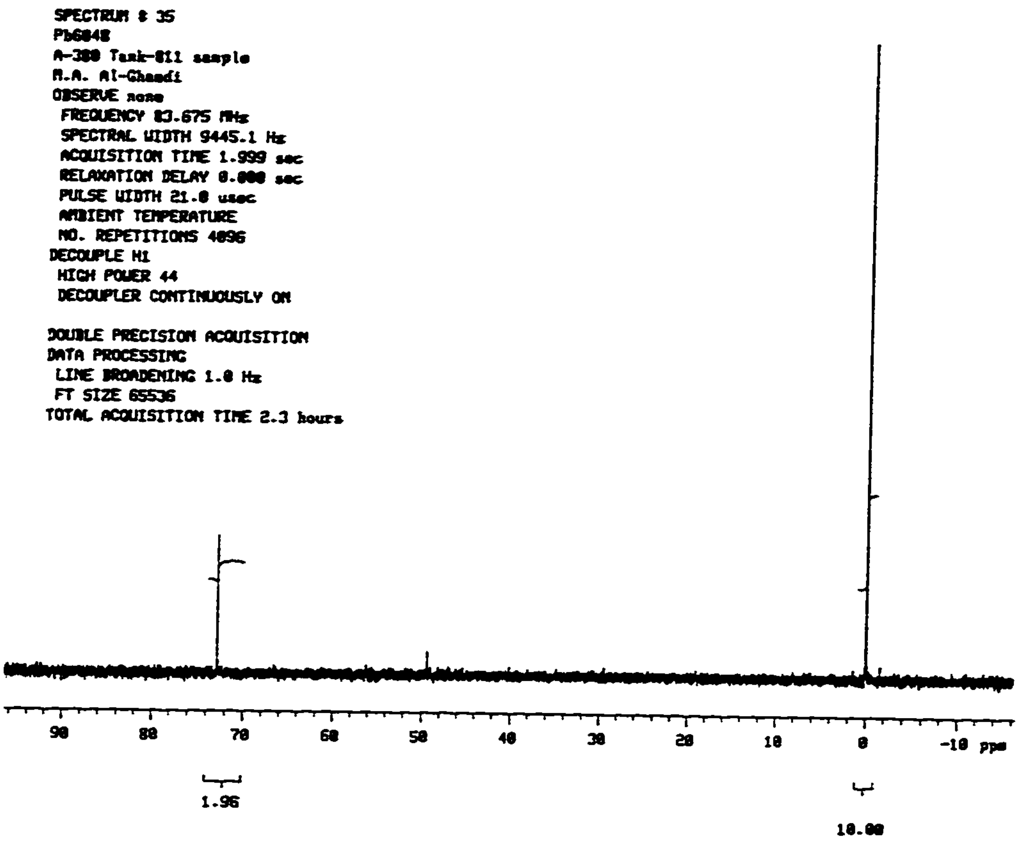
SPECTRUM # 34



SPECTRUM # 34
Pb6047
A-320 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.999 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 44
DECOUPLER CONTINUOUSLY ON

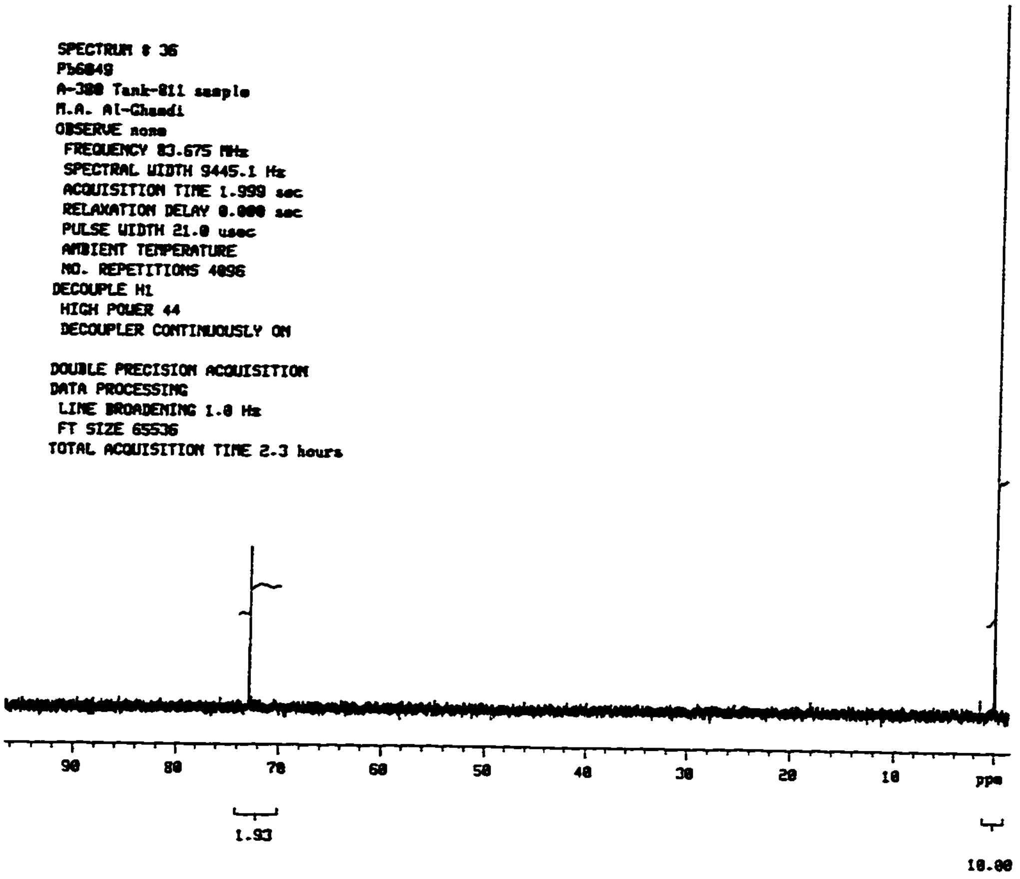
DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 1.0 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours

SPECTRUM # 35



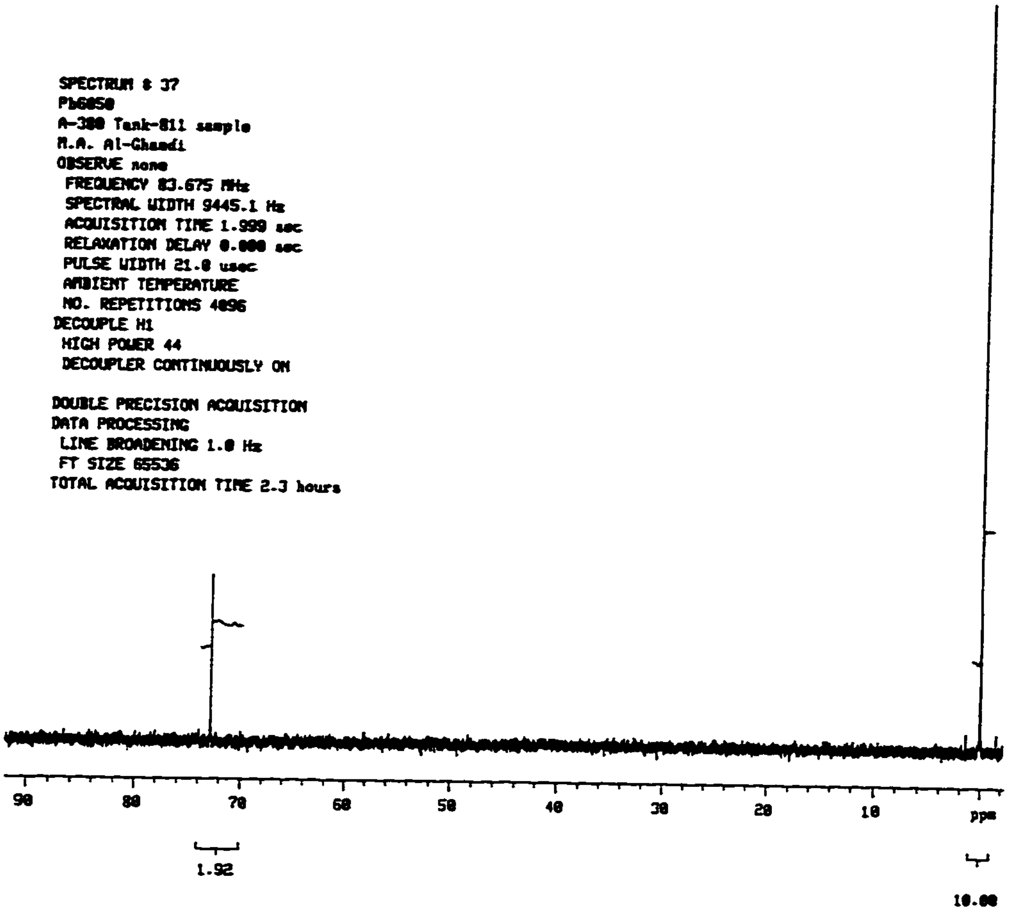
```
SPECTRUM # 35
Pb6048
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

SPECTRUM # 36



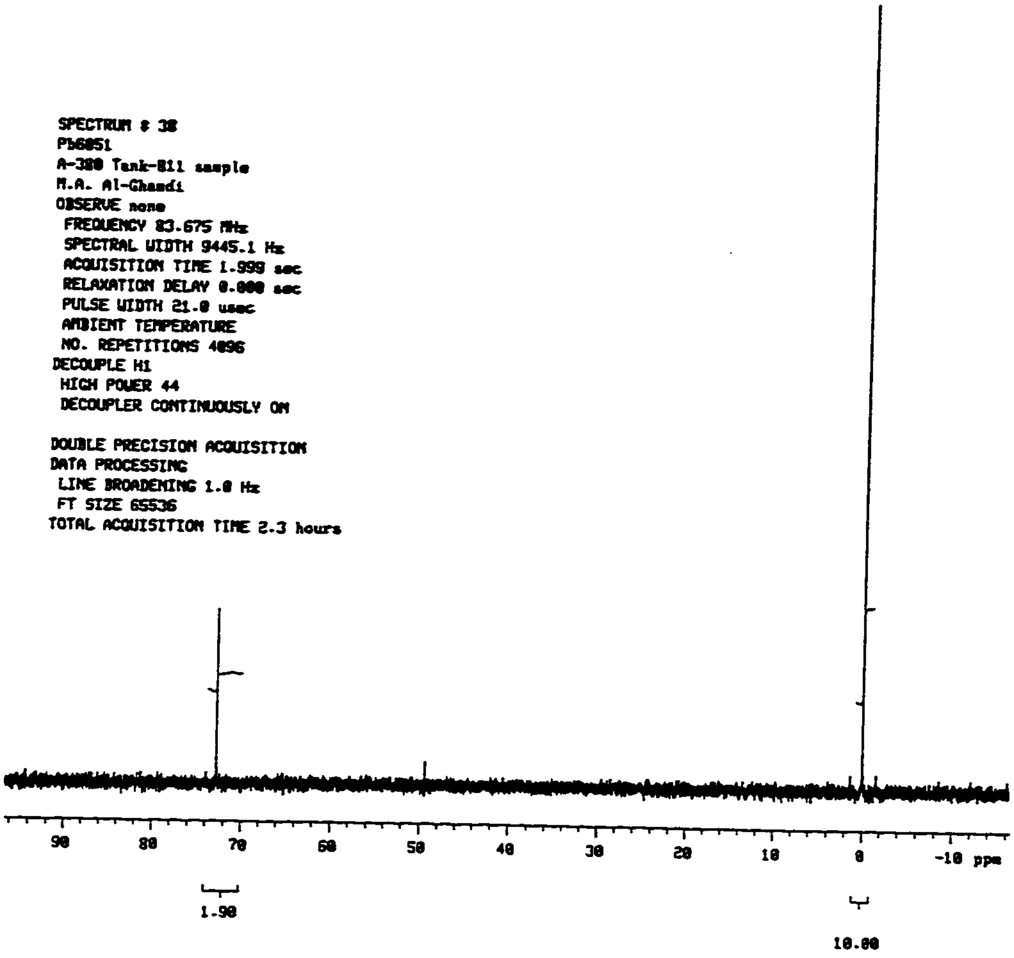
```
SPECTRUM # 36
Pb6049
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

SPECTRUM # 37



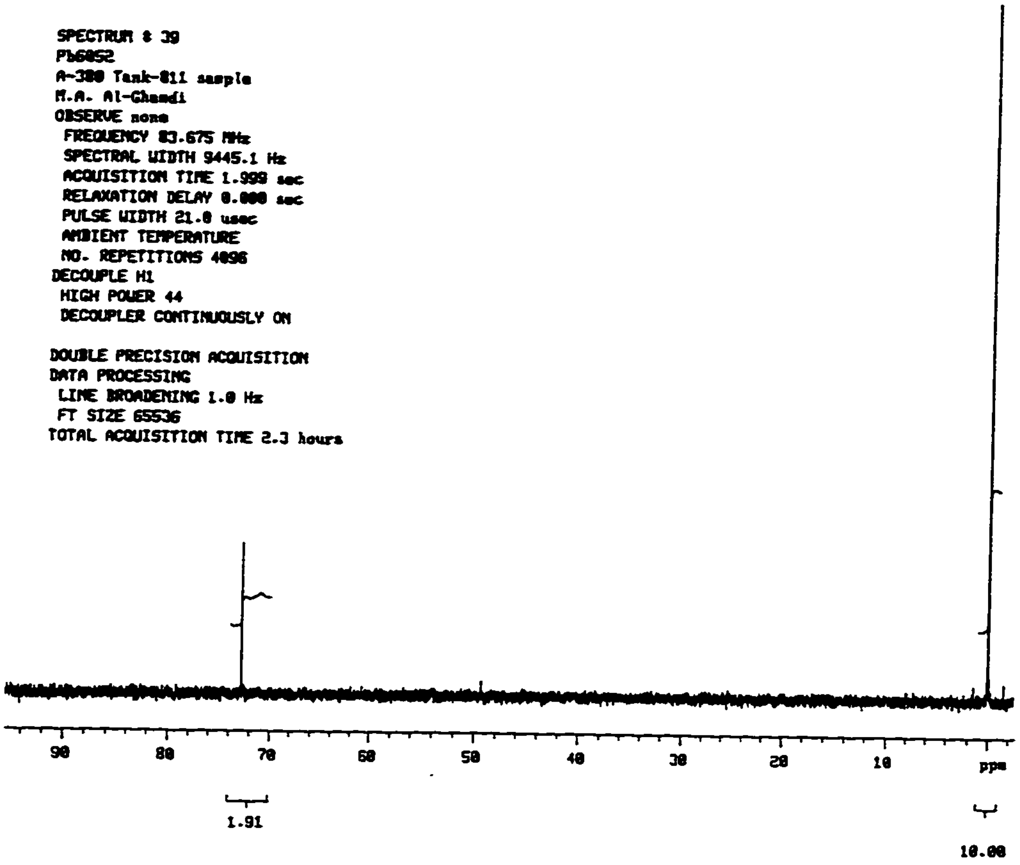
```
SPECTRUM # 37
Pb6050
A-300 Tank-811 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

SPECTRUM # 38



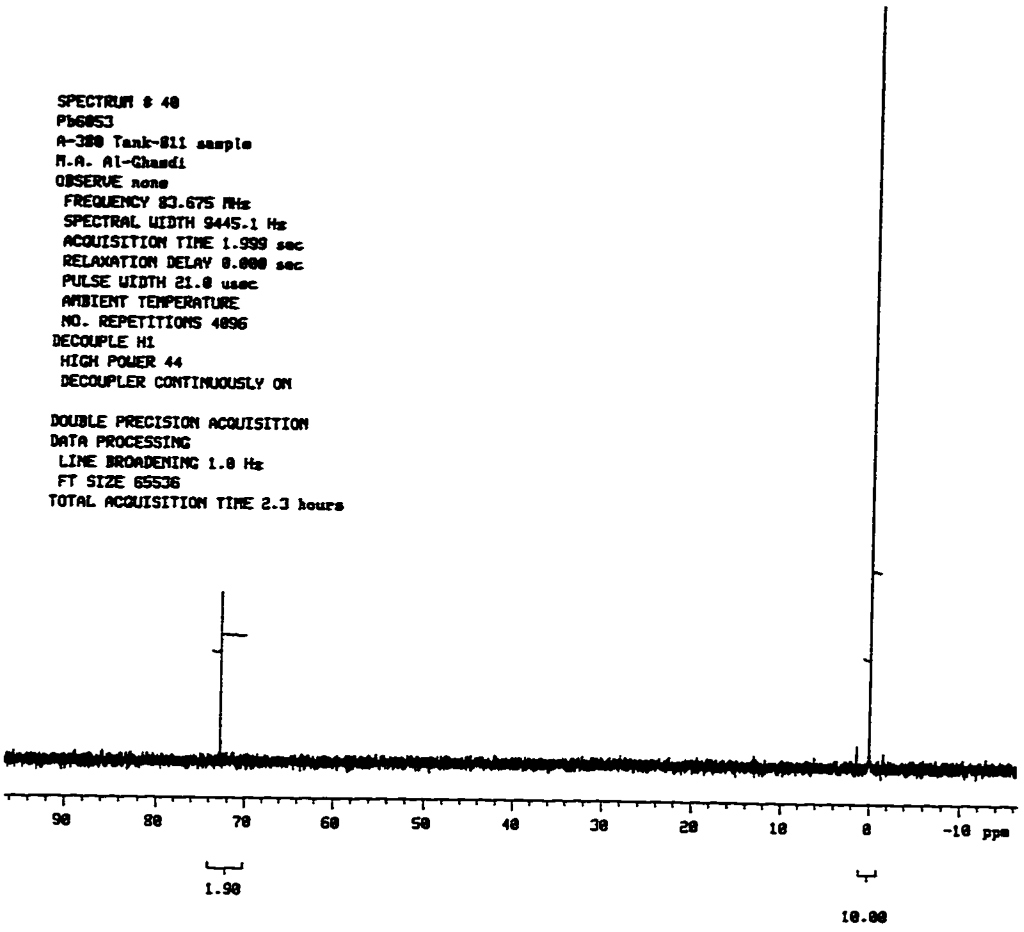
```
SPECTRUM # 38
Pb6051
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

SPECTRUM # 39



```
SPECTRUM # 39
Pb6052
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours
```

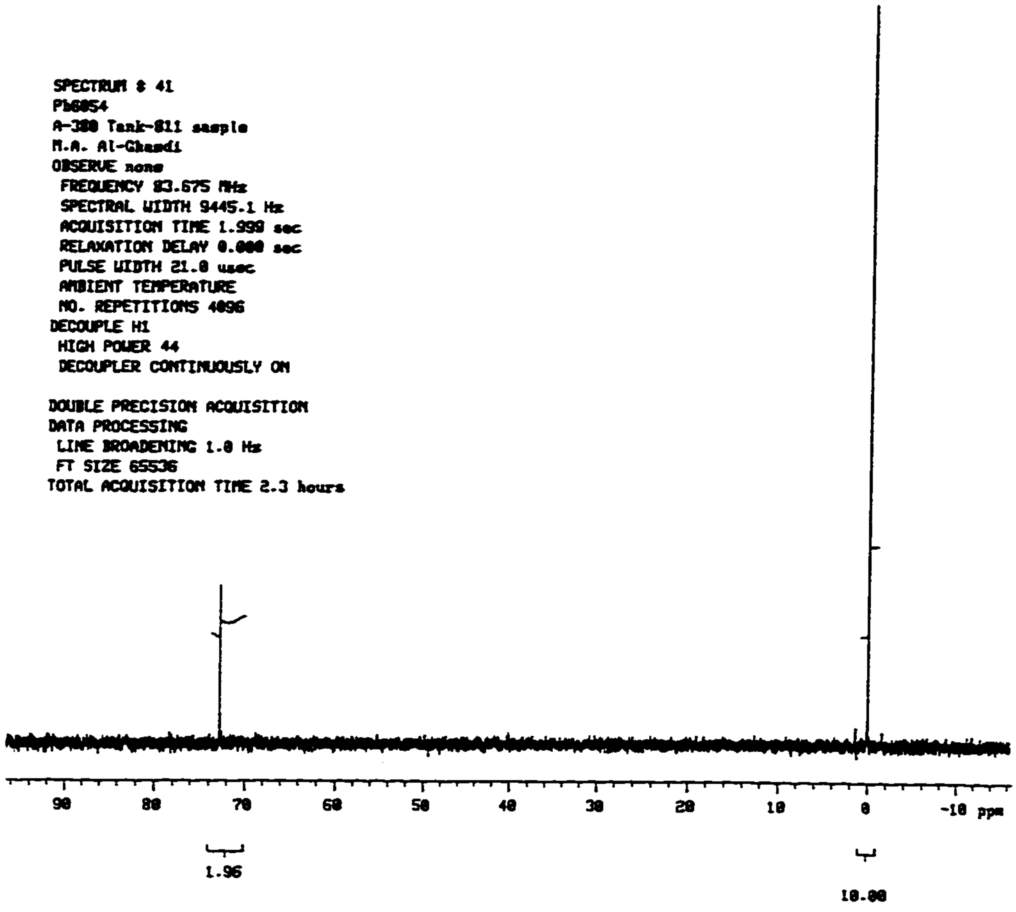
SPECTRUM # 40



SPECTRUM # 40
Pb6053
A-300 Tank-011 sample
M.A. Al-Ghamdi
OBSERVE none
 FREQUENCY 83.675 MHz
 SPECTRAL WIDTH 9445.1 Hz
 ACQUISITION TIME 1.999 sec
 RELAXATION DELAY 0.000 sec
 PULSE WIDTH 21.0 usec
 AMBIENT TEMPERATURE
 NO. REPETITIONS 4096
DECOUPLE H1
 HIGH POWER 44
 DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
 LINE BROADENING 1.0 Hz
 FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours

SPECTRUM # 41



SPECTRUM # 41
Pb6054
A-300 Tank-811 sample
M.A. Al-Ghamdi
OBSERVE none
FREQUENCY 83.675 MHz
SPECTRAL WIDTH 9445.1 Hz
ACQUISITION TIME 1.999 sec
RELAXATION DELAY 0.000 sec
PULSE WIDTH 21.0 usec
AMBIENT TEMPERATURE
NO. REPETITIONS 4096
DECOUPLE H1
HIGH POWER 44
DECOUPLER CONTINUOUSLY ON

DOUBLE PRECISION ACQUISITION
DATA PROCESSING
LINE BROADENING 1.0 Hz
FT SIZE 65536
TOTAL ACQUISITION TIME 2.3 hours

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