REACTIONS OF ORGANOLEAD COMPOUNDS UNDER NATURAL CONDITIONS

by

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A thesis presented for the degree
of Doctor of Philosophy in the
University of Aston in Birmingham.
October, 1977.

SUMMARY

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Certain compounds containing lead atoms bonded to alkyl groups are of much greater toxicity than their non-alkylated analogues. The tetra-alkyl lead compounds are used as antiknock additives in petrol and are discharged into the atmosphere by exhaust emission, spillage and evaporation. Because of their toxicity the concentration and reaction of such compounds in natural waters is of great importance.

Little data is available on the concentration and properties of organolead compounds in the environment and the information which is available is concerned mainly with the concentration of tetra-alkyl lead compounds in the atmosphere. This dissertation seeks to establish the fate of organolead compounds washed from the atmosphere into natural water systems.

Procedures for the extraction and estimation of alkyl lead compounds in water and on sediment were developed. The reactions of soluble organolead compounds in aqueous systems under conditions of light, dark and added metal ions were studied as were the reactions of alkyl lead compounds adsorbed on silica.

Some exploratory work on the biological methylation of inorganic and alkyl lead ions was carried out to substantiate studies by other workers and it was concluded that the reported results could, in many cases, be explained by a chemical disproportionation mechanism involving sulphide ions rather than a biological mechanism.

This dissertation concludes that it is unlikely that any organolead compounds entering natural waters will remain dissolved and unreacted for any length of time, and that all reactions lead to a reduction in total alkyl lead content of the system with inorganic lead as the final product.

Key Words: Natural Water, Organolead.

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CHAPTER ONE

INTRODUCTION

INTRODUCTION

1.1. COMMERCIAL USES OF ORGANOLEAD COMPOUNDS.

The synthesis of tetraethyl lead (TEL), was first reported in 1853 by Lowig[1] however it was not until 1916 that a most important commercial use for this material was discovered. Kettering Midgely and Boyd[2] in the U.S.A. had been carrying out a series of tests on various organic compounds to establish their antiknock properties when added to engine fuel, and of the compounds screened TEL proved to have the highest antiknock value by far.

As a consequence of this work commercial fuel containing TEL was sold for the first time in the U.S.A. in 1923 and has been sold ever since, apart from a short period in 1925 when its use was suspended on health grounds. In the U.K. TEL was first introduced around 1940 and again is still in use today as an antiknock additive.

In 1960 tetramethyl lead (TML), the first serious competitor to TEL as an antiknock additive was introduced. This introduction of TML was closely followed by the use of the mixed ethyl methyl tetra-alkyl lead compounds (Me_3EtPb, Me_2Et_2Pb, and $MeEt_3Pb$).

TML although basically similar to TEL had a number of more favourable properties, such as increased volatility and higher antiknock ability, weight for weight, than TEL where the base fuel contained in excess of 20% aromatic hydrocarbons[2]. The mixed tetra-alkyl leads also gave increased antiknock performance with particular base fuel stocks. In the U.K. in 1973 over 12,000 tonnes of lead in the form of lead alkyls was used as petrol additives[3]. The present day use is approximately 50% TEL and 50% TML, the use of the mixed tetra-alkyl leads is not encouraged for economic reasons[4]. In 1972[5] it was announced that the lead content of fuel would be reduced from 0.64 gl^{-1} at the end of 1972 to 0.55 gl^{-1} by the end of 1973 and 0.045 gl^{-1} by the end of 1975. This reduction in tetra-alkyl lead (TAL) content of fuel follows from world wide apprehension as to the long term health effects of lead compounds in the environment, and in particular in urban areas. The movement towards leadless fuel has now been suspended due to the recent energy crisis and increased cost of producing high octane fuel with low levels or without added TAL.

The major commercial use of the TAL compounds used is as fuel additives, however there are a number of other minor uses for organolead compounds.

Tributyl lead acetate and triphenyl lead acetate both have excellent biocidal properties when added to marine paints for use on the hulls of ships. The use of such paints can greatly increase the time interval, previously twelve months, between dry docking. In the past the fouling layer of marine plants and animal organisms were removed by mechanical means. If the fouling is allowed to build up and left untreated, operating efficiency drops due to increased fuel consumption, decreased manoverability and increased corrosion[6,7].

Tributyl lead acetate has been recommended for both interior and exterior use in a vinyl copolymer emulsion paint as a fungicide, the organolead compound still being active after 250 hours of artificial weathering[8]. Under the same conditions an organotin and phenyl mercuric compound had both failed.

The actual toxic species present in a paint system has not been studied, nor has the nature or composition of the organolead compounds leached from the surface of the paint by weathering.

Preliminary studies on the effect of dibutyl lead diacetate on tape worms in sheep has been carried out by Graber[9]. His results have shown that the majority of tape worms were eliminated while the toxicity of the dibutyl lead diacetate to the sheep themselves was generally low except with lambs.

Triphenyl lead acetate has been used to control snails which act as the carrier for the debilitating tropical disease Bilharzia, this disease affects over 200 million people in the tropics. The triphenyl lead acetate is active at a 0.1ppm concentration for 24 hours. Four days after dosage the compound is no longer detectable or effective in the aqueous phase, but appears to be concentrated in the silt and mud at the bottom of the water course[10].

Organolead compounds have been shown to have excellent properties as lubricant additives, as well as fuel additives. Beatty[11] found that of the compounds tested, organolead nitrogen compounds had by far the best antiwear properties under varying conditions of load and temperature.

Aryl lead triacylated are useful catalysts in the production of polyurethane foams[12]. Formerly to produce a flexible foam two catalysts were used, one forming the polymer, the other to produce carbon dioxide in the foam. Aryl lead triacylates have been shown to catalyse both reactions satisfactorily, thus offering a cost and convenience advantage.

Stroganov[13] has proposed the use of a number of organolead compounds of the type $R_{4-n}MX_n$, (where R = methyl, ethyl or phenyl; X = acetate, hydroxide, or chloride and n = 0 or 1), for the control of plankton and daphnia in water reservoirs in Russia, how extensive is the use for this purpose is unknown.

The toxicity of organolead compounds to many forms of life is the property on which most of their applications are based, their use as an antiknock additive being a major exception, however it is this same toxic property which has caused handling problems, and has restricted their more diverse use.

1.2. TOXIC PROPERTIES

Seventeen months after the commercial production of TEL had commenced in the U.S.A., thirteen deaths and one hundred and thirty nine cases of poisoning were caused by exposure to this compound[14]. These involved not only workmen handling the neat TEL but also included industrial chemists who at that time were unaware of the toxic action of TEL on the human system. Once the toxicity of TEL had been established, stringent safety rules for its handling and manufacture were introduced, and this served to eliminate further incidents of poisoning, except in cases where the safety rules were ignored or not known, or where TEL was used in error[15]. TAL is adsorbed into the body by inhalation of the vapours, or by skin adsorption.

The toxicity and toxicology of organolead compounds has been reviewed by Shapiro and Frey[16] and more recently by Thayer[17]. Most of the available information is concerned with the toxicity of the lower alkyl organolead compounds i.e. methyl to butyl. Cremer[18], has shown that the toxic species in TAL poisoning is the trialkyl lead ion. In rats TEL is converted to triethyl lead by the liver, with the symptoms for both TEL and triethyl lead poisoning being identical, but different from diethyl lead or inorganic lead, which were again similar.

Thayer[17] states that trialkyl lead compounds are more toxic than inorganic lead compounds, and that the symptoms and distribution of the lead in the body is different. The relative toxicity of TAL compounds depends on the animal to which the TAL is administered. Rats have been shown to be about ten times more susceptible to TEL than TML[19], due to the differing rates of conversion of TAL in the animal body.

Rabbits injected intravenously with similar quantities of TML and TEL showed marked differences in response, the rabbits receiving TML showed no ill effects even after three weeks, whilst rabbits injected with TEL died after sixteen hours.

TEL is more toxic than TML to rabbits and rats, however for mice the reverse is true, 50% of the TML lead administered to mice had been converted to the trimethyl lead after two days and was slow to disappear. The corresponding figure for TEL was only 30% conversion after three days.

In one of the few studies actually carried out on humans[15] it was found that the distribution and breakdown products in the human body following fatal exposure to TEL, were similar to that found in rats by Cremer[18]. Most of the TEL was converted to the triethyl lead ion.

A study of the cause of death among workers associated with the production of TEL[21] has demonstrated that it is no different from that of a control group. This investigation was carried out over a twenty year period, which the author considered to be the minimum time for the results to have any significance.

The mechanism of action of TAL compounds as antiknock additives in fuel is still not fully understood. It is generally accepted however that for the TAL to be effective it must first decompose to lead oxide[22], which exists as a mixture of the orthorhombic and tetragonal forms, the percentage of each being determined by several factors including engine temperature. The build up of this lead oxide on the wall of the combustion chamber and piston head is prevented by the addition of the alkyl halides, 1, 2-dichloraethane and 1, 2-dibromaethane[2], to the petrol. The alkyl halides acting as scavengers, remove the lead from the chamber as the mixed halide PbBrCl and as the mixed ammonium halide/lead halide complex, and it is these compounds that are emitted from the exhaust pipe of a motor car[23].

1.3. CONTAMINATION OF THE ENVIRONMENT

It was reported by Hirschler[23] that organolead compounds of unknown composition are present together with inorganic lead compounds in exhaust fumes. This organolead was equivalent to 0.023% of the total TAL input of the engine. The corresponding value for incompletely burnt hydrocarbons in the exhaust gasses was 1.7% of the total input reflecting the instability of the TAL compared with the hydrocarbons. Laveskog[24] using a combined G.L.C. and M.S. technique, identified TEL and TML emitted from the exhaust of motor vehicles, he also reported that the maximum emissions occurred from cold engines during the warm up period, with values reaching 5,000 μgm^{-3} compared to 30 μgm^{-3} for a warm engine under load. Values for an idling engine were given as 50-100 μgm^{-3}. When crank case emissions were checked a value of the order of 1.9 mgm^{-3} was found, this is high considering that the fuel and air mixture as supplied to the engine has a value of only 50 mgm^{-3} for TAL.

Further loss of TAL to the atmosphere can arise, due to evaporation from fuel tanks and from minor spillages during the filling of motor car fuel tanks[5]. Localised high concentration contamination can occur where large amounts of "leaded" fuel are lost during storage or transport. It has recently been reported[25] that in July 1974, some six miles off the coast of Italy, two ships collided, as a result of this collision one ship subsequently sank, this ship's cargo was 900 drums of neat lead alkyls, both TML and TEL. The drums are now lying in 300 feet of salt water and the metal must eventually corrode, releasing their lethal contents on the sea bed, causing as yet unknown contamination and damage to the environment. A similar incident occurred in 1966, in which 157 drums were lost at sea, off an unnamed coastal resort. As yet no ill effects have been reported as a result of either incident.

Used engine oil is contaminated by alkyl lead compounds[26] and when disposed of in the illegal but much practised way, down road side drains or on to waste land, this organolead will constitute another source of lead alkyls, eventually contaminating natural waters.

The concentration of inorganic and organic lead in the atmosphere has been measured at a variety of sites and by a variety of methods. The basis of most methods is to filter a measured quantity of air and define the inorganic lead as that retained by a filter while the lead passing through the filter and subsequently removed by another method is assumed to be organolead. The inorganic lead in the filter is determined by acid digestion of the filter and measuring the lead by a suitable method. The quantitative measurement of the organolead depends on its method of removal after passing through the filter.

The concentration of volatile and particulate lead in the atmosphere has been determined for four road side sites by Colwill and Hickman[5], who used a method developed by Moss and Browett[27], the inorganic lead is removed using a 0.8μm pore filter, and the organolead is removed by passage through a 0.1M aqueous solution of iodine monochloride. The lead was then extracted from the iodine monochloride as the dithizone complex by shaking with 4-methyl pentan-2-one (MIBK) and analysed by A.A.S.. The results obtained indicated organolead concentrations of 55% and 30% of a total lead concentration of $2\mu gm^{-3}$ at two of the sites close to petrol filling stations, at the other two sites, a motorway central reservation and a tunnel, a 10% organolead concentration was determined of a total lead concentration of $10\mu gm^{-3}$ and $15\mu gm^{-3}$ respectively.

Snyder[28] replaced iodine monochloride with activated charcoal in the removal of organolead from filtered air. The charcoal on acid digestion gave 98% - 100% recovery when known amounts of TAL were added. The accuracy claimed was ± $0.008\mu gm^{-3}$ at a $0.1\mu gm^{-3}$ level of organolead in the atmosphere. The average value found for organolead in the atmosphere by this method was $0.078\mu gm^{-3}$.

Harrison and co-workers[29] used a G.L.C. column, cooled to liquid nitrogen temperatures, to collect the organolead passing through the filters. When the required volume of air had been sampled, the column was sealed, warmed to 130°C, connected to the burner of an A.A. spectrometer, then purged with nitrogen gas. The resultant peak is said to represent the organolead collected by the column. They determined a range of $0.02 - 0.59\mu gm^{-3}$ of organolead in the air. In the vicinity of petrol filling stations, higher values of alkyl leads were obtained.

Contuti and Cartoni[30] used a similar technique for measuring more highly contaminated air near an alkyl lead manufacturing works. The column they used relied on a favourable distribution between the liquid on the solid support and the air passing through it. The collection column was then connected to a normal G.L.C. column and rapidly heated, the resulting peaks were analysed using an electron capture detector. For the normal levels of TAL found in street air, this method proved insensitive.

Laveskog[24] used a 'U' tube containing chromosorb W (60 - 80) coated with apiezon M at a temperature of -80°C to collect TAL compounds at a variety of sites. The TAL compounds were eluted from the column by heating, then separated and studied by G.L.C. / M.S. The latter is one of the few methods for the direct analysis of organoleads in the atmosphere. Levels of TAL varied from 0.1 - 1.0μgm^{-3} depending on the location and time of sampling

Despite all the work carried out on the analysis of organolead compounds in the atmosphere, the literature appears to contain no reference to the detection of organolead compounds other than TAL. The dialkyl and trialkyl lead salts are likely to be intermediates in the conversion of TAL to inorganic lead, and methods for their individual analysis are available[31].

If dialkyl or trialkyl lead salts were present in the atmosphere, they would be removed by rainfall due to their relatively high solubility in water[32]. The rainfall would be further contaminated by contact with organolead salts present on the earths surface. The solubility of the TAL compounds[33] is very low, however so is their concentration in the atmosphere, hence rainfall would also be expected to contain some TAL.

As a result we would expect some contamination of natural water by these various sources of alkyl lead compounds.

1.4. AIM OF PRESENT WORK

Very little recorded data is available on the reactions of organolead compounds at low concentration.

This investigation is concerned with the fate of alkyl lead compounds in natural water systems and their determination, with particular reference to the potential toxicity of the main products and intermediates.

CHAPTER TWO

PROPERTIES, PREPARATION AND EXTRACTION

PROPERTIES, PREPARATION AND EXTRACTION

2.1. PROPERTIES

2.1.1. INTRODUCTION

Natural waters are exposed to two distinct groups of organolead compounds, firstly the tetra-alkyl leads (TALs); tetramethyl lead (TML), tetraethyl lead (TEL) and the mixed alkyl leads i.e. methyl triethyl lead ($MeEt_3Pb$), dimethyl diethyl lead (Me_2Et_2Pb) and trimethyl ethyl lead (Me_3EtPb). Some or all of these TAL compounds are present in all commercially available antiknock fluids, and are the only organolead compounds so used[34]. The second group consists of the possible breakdown products of the TALs, i.e. $Me_nEt_{3-n}PbX$ ($n = 0-3$) and $Me_nEt_{2-n}PbX_2$ ($n = 0-2$), where X is a suitable anion, included in this group are the higher alkyl lead salts used in antifouling paints[7] and as molluscides[10], e.g. tributyl lead acetate, the mono alkyl lead salts $RPbX_3$ are unstable and have not been identified.

In aqueous solution these organolead salts are dissociated[16] and the nature of the anion (X) is of little importance. For this work we found the organolead chlorides to be the most convenient species to study, being easy to prepare, purify and store. An exception to this is the organolead sulphides, which are unstable (see Chapter 6).

The properties of TEL and TML have been investigated extensively, the mixed TAL compounds have not been investigated to such an extent, but in general it has been found that their properties and behaviour lie between the two symmetrical compounds. The properties and reactions of TALs have been reviewed elsewhere[16, 34, 35, 36].

TEL and TML have been extensively studied because of their commercial significance as antiknock fluids. The alkyl lead salts have no commercial use and this is reflected in the smaller amount of data available on their properties, however studies have been carried out and this work has been reviewed[16, 35].

2.1.2. PHYSICAL PROPERTIES AND LABORATORY USE

Pure TAL compounds are clear, colourless, volatile liquids, which are soluble in common organic solvents but insoluble in water[16]. The actual solubility of TEL in water has been reported[33] to be between 0.2 and 0.3 μgml^{-1}. TEL boils at 200°C and has a vapour pressure of 0.26 mm Hg at 20°C. TML boils at 110°C and has a vapour pressure of 23.7 mm Hg at 20°C. Both TEL and TML are heavy liquids, their densities being 1.650 and 1.995 gml^{-1} respectively.

The TALs are highly toxic and care must be taken to avoid inhalation of the vapour or contact of the liquid with the skin. They are stable to air, hydrolysis and shock, when handling in the laboratory no special precautions are necessary, except they must always be used and stored in an efficient fume cupboard. Ultra-Violet light catalyses the decomposition of TALs and they should therefore be stored in the dark and not handled in direct sunlight. We observed that dilute solutions of TML and TEL (1-10 p.p.m. $^{v}/v$) in benzene were stable for at least three months if stored in the dark.

TALs are thermally unstable above 100°C and in the absense of air TEL may explode. TML will explode if ignited, but may be distilled in the absence of a hot spot or spark without any decomposition, in practice TML is best kept at room temperature or below. Commercially TML is manufactured in the presence of toluene, 80% TML $^{w}/w$ in toluene being the normal concentration, no attempt is made to separate this mixture[37].

The alkyl lead salts R_3PbX and R_2PbX_2 are white crystalline solids. If X is the anion of a strong acid the compound is usually stable to air, water and shock. If X is the anion of a weak acid the salt tends to disproportionate[34]. For maximum stability the salts should be stored in the dark below 0°C. The purity of salt should be checked by T.L.C. before use.

The toxicity of R_2PbX_2 compares with that of inorganic lead, while that of R_3PbX is comparable with TAL. Care must be taken to avoid exposure to R_3PbX, however since they are generally solids, inhalation of the vapour is not a problem and the possibility of skin adsorption is reduced. Concentrated solutions of R_3PbX should be treated as TAL with regard to skin adsorption. An interesting property of many R_3PbX compounds is that air borne dusts have sternutatory properties, the possible use of these as offensive weapons lead to the preparation of a large number of organolead salts[38, 39, 40, 41].

The concentrations of alkyl lead compounds in the environment is generally so low as to make solubilities irrelevant. Table 1 lists the solubilities of a number of alkyl lead salts in a range of solvents[32, 42]. We found the table useful in the preparation and purification of organolead salts and it might be of use in the event of a gross pollution incident resulting from a spillage.

2.2. PREPARATION OF ALKYL LEAD SALTS

2.2.1. TETRA-ALKYL LEAD COMPOUNDS

The TAL compounds used in this work were kindly donated by Associated Octel Ltd. It was not necessary to prepare and isolate

TABLE 1

SOLUBILITIES OF ALKYL LEAD SALTS ($g l^{-1}$)

	Water	$CHCl_3$	CCl_4	Acetone	Ether	Benzene	Hexane	Alcohol
Et_3PbCl	20	s	50	50	6	800	0.9	50
Et_3PbBr	13		50	50	50	700	9	50
Et_3PbOH	198	s		42.1	1.8	8	0.6	
Et_3PbOAc	60	450		21 (r)	2.3	8.6	6	450
$(Et_3Pb)_2CO_3$	8.3		0.017	0.72	0.023	0.016	0.018	17.5
Me_3PbBr	100	275		350	25	50	3	450
Me_3PbOAc	135	13		4	0.3	1	2	100(r)
Et_2PbCl_2	50	i	0.04	22.2	0.03	0.04	0.02	21
Et_2PbBr_2	15		0.02	50	0.09	0.08	0.0	10
$Et_2Pb(OH)_2$	34						0.0	
Et_2PbCO_3	0.21		0.006	0.016	0.01	0.009	0.03	0.013
$PbCl_2$	9.9		0.0	0.003	0.0	0.0	0.0	0.015
$PbBr_2$	8.4		0.0	0.1	0.0	0.0	0.0	0.053

s soluble

i insoluble

r solvent suitable for recrystallisation any TAL compounds except those required as intermediates in the preparation of alkyl lead salts.

2.2.2. TRIALKYL LEAD SALTS

Associated Octel Ltd also supplied pure samples of triethyl and trimethyl lead chloride, a number of other trialkyl lead salts were prepared.

Triethyl lead chloride (Et_3PbCl) was prepared using the method of Heaps and co-workers[39] and its identity was confirmed by thin layer chromatography (T.L.C.). An alternative method was also used which involved the preparation of TEL as an intermediate. The TEL was prepared from lead chloride and the appropriate grignard and then reacted with HCl gas (see Experimental, section 2.1.1.2. pp. 109). Both methods gave products contaminated with diethyl lead dichloride and inorganic lead.

Triethyl lead bromide (Et_3PbBr) was prepared by reacting TEL with bromine at -70°C, again the product was found to be contaminated with the diethyl lead salt.

Triethyl lead hydroxide (Et_3PbOH) was prepared by the method of Calingaert and co-workers[43]. T.L.C. of the product gave a spot with the characteristic yellow colour of a trialkyl lead salt but with a different R_f value from Et_3PbCl. The salt gave no reaction with silver nitrate solution indicating the adsence of any chloride ion.

Triethyl lead acetate (Et_3PbOAc) was prepared according to the method of Heap and co-workers[38], by reacting TEL with glacial acetic acid using silica as a catalyst. The identity of the product was confirmed by T.L.C. and melting point measurements.

Trimethyl lead iodide (Me_3PbI) and trimethyl lead bromide (Me_3PbBr) were prepared by reacting TML with iodine and bromine respectively at -70°C. The resulting products were contaminated with dimethyl lead salts and inorganic lead.

Tributyl lead chloride (Bu_3PbCl) was prepared by chlorination of hexabutyl dilead[42]. The hexabutyl dilead was prepared using lead chloride and the appropriate grignard. Certain precautions must be observed in this preparation, the temperature should be maintained at -70°C and there should be an insufficiency of chlorine, excess chlorine leads to the formation of dibutyl lead dichloride, also excess chlorine can lead to an explosion as the mixture warms up, as chlorine reacts rapidly with the tributyl Bu_3PbCl to form Bu_2PbCl_2 at room temperature (see Experimental. section 2.1.7. pp. 111).

2.2.3. DIALKYL LEAD SALTS

Dimethyl lead dichloride (Me_2PbCl_2) and diethyl lead dichloride (Et_3PbCl_2) were kindly supplied by Associated Octel Ltd. The dialkyl lead halides were prepared by reacting the appropriate TAL with excess halide at 0°C in a suitable solvent.

Diethyl lead hydroxide ($Et_2Pb(OH)_2$) was prepared by the method of Heap and co-workers[41] and its identity confirmed by a method similar to that used for Et_3PbOH.

2.2.4. STORAGE OF SALTS

All organolead salts were stored in the dark at 0°C or below. Before use the purity of the salts was checked by T.L.C. and the materials repurified if necessary.

2.3. PREPARATION OF STANDARD SOLUTION OF ORGANOLEAD COMPOUNDS

2.3.1. TETRAETHYL LEAD

Standard solutions of TEL required for G.L.C. work were prepared by suitable dilution of pure TEL with the appropriate solvent.

The accuracy of the dilution was checked by A.A.S.. The TEL was converted to a diethyl lead salt, then extracted into nitric acid solution, the solution was then analysed by A.A.S., good agreement was found between calculated and measured concentrations, (see Experimental, section 2.2.1. pp. 112).

2.3.2. TETRAMETHYL LEAD

The TML supplied by Associated Octel Ltd was a nominal 80% $^{w}/_{w}$ solution in toluene. Standard solutions were prepared by suitable dilution with an appropriate solvent.

The absolute concentration of the standard was determined by a number of different methods: (i) the TML was decomposed to dimethyl lead ion using bromine, the solvent was then evaporated, the residue dissolved in nitric acid solution and the lead concentration determined by A.A.S.. (ii) For water immiscible solvents following reaction with bromine, the dimethyl lead ion was extracted into distilled water and the concentration was then determined by using the P.A.R. method (see Chapter three). (iii) For water miscible solvents the TML was converted to dimethyl lead by iodine monochloride, then using a suitable aliquot, the dimethyl lead concentration was determined by the P.A.R. method. All three methods were in good agreement, giving an average concentration of 71% TML (1.42 gml^{-1}) by volume in the solution as supplied by Associated Octel Ltd., (see Experimental, section 2.2.2. pp. 113).

2.3.3. TRIALKYL LEAD SALTS

Standard solutions of trialkyl lead salts were prepared by dissolving the appropriate amount of pure solid in distilled water to give a 1,000 p.p.m. solution. Lower standards were prepared by suitable dilution. The purity of the standard was checked by determining its dialkyl lead content using the P.A.R. method. If any dialkyl lead was found the standard was discarded and the salt repurified before repeating the process.

2.3.4. DIALKYL LEAD STANDARDS

A similar process for the preparation of dialkyl lead standard solutions was followed as for the trialkyl lead solutions. In this case the purity was checked by determining the trialkyl lead content of the solution.

2.4. EXTRACTION OF ALKYL LEAD SALTS FROM AQUEOUS SOLUTION BY ADSORPTION AND ION EXCHANGE

2.4.1. INTRODUCTION

It was anticipated that there might be a need to extract and concentrate alkyl lead salts present in a very low concentration in aqueous solutions. Three possible chromatographic materials were evaluated for this purpose, activated charcoal, a cation exchange resin and a macroreticular resin without ionic groups but capable of removing neutral and weakly ionic organic molecules from aqueous solutions.

2.4.2. ACTIVATED CHARCOAL

The use of activated charcoal for the adsorption and concentration of both organic[45] and inorganic[46] trace impurities in water has been reported. The properties of activated charcoal have been reviewed by Parkash[47]. Lead containing by-products from the manufacture of TAL have been reclaimed by the use of activated charcoal[48], while TEL, itself, is reported to be unstable when adsorbed on charcoal, and is not reclaimable by extraction with steam or benzene[49]. The breakdown products were not identified.

Activated charcoal is reported to adsorb alkyl lead salts ($200 \mu g g^{-1}$) from a dilute aqueous solution[26]. Subsequent elution of the alkyl lead salt was difficult even with the most efficient solvent, aqueous acetic acid (5% $^{v}/v$). This solvent gave only 40% and 70% recovery of triethyl and diethyl lead salts respectively from charcoal. It has also been reported that the conversion from triethyl lead to diethyl lead is catalysed by the carbon[26]. We conclude that activated charcoal was not a suitable adsorbent for our purposes and it was not evaluated any further.

2.4.3. CATION EXCHANGE RESINS

2.4.3.1. INTRODUCTION

A strongly basic anion exchange resin has been used to concentrate cadmium, copper and lead in samples of natural non-saline waters[50]. The metals are adsorbed as their anionic bromide complexes and eluted using aqueous nitric acid solutions. Heavy metals have also been removed from aqueous effluents using a starch xanthate - cation polymer complex[51].

In this work we evaluated the use of Zeolit 225, a cross linked polystyrene - divinyl benzene cation exchange resin. This was a standard cation exchange resin whose normal application is in the water softening and deionization field.

2.4.3.2. ADSORPTION BY THE RESIN

The resin (15 ml) totally removed Et_2PbCl_2 (100 mg) from distilled water (250 ml) with the resin in the hydrogen or sodium form. A similar result was obtained with Et_3PbCl, where the resin in the sodium or hydrogen form was again capable of exchanging over 100 mg of the salt from distilled water. The resin was also shown to be capable of exchanging inorganic lead ions in aqueous solution.

No attempt was made to determine the total capacity or break through point of the resin, since 100 mg was anticipated to be in excess of the concentration of alkyl lead which would be present in solution.

2.4.3.3. ELUTION

Elution of the exchanged cations was carried out using aqueous sodium hydroxide (4% $^w/v$) and hydrochloric acid (4% $^v/v$) solutions for the sodium and hydrogen forms of the resin respectively. Successive fractions of eluate (90 ml) from the column were collected and analysed by A.A.S.. The results are shown in table 2.

We also investigated a number of organic solvents as possible eluants for Et_3Pb^+. The results of this study are shown in table 3.

The elution of Et_3Pb^+ with both NaCl and HCl proved inefficient giving incomplete recovery and high elution volumes, the recoveries for 500 ml being only 46% and 72% respectively.

In the case of Et_2Pb^{++} the percentage recoveries were reversed, with NaCl giving 71% recovery while HCl gave only 43% with 500 ml of eluate. With HCl the percentage recoveries per fraction were low, less than 10%, increased elution volumes would have increased the total recovery of Et_2PbCl_2, but at the expense of a high total volume.

TABLE 2

ELUTION OF LEAD SALTS FROM A CATION EXCHANGE RESIN BY AQUEOUS SOLVENTS

	Exchanged Salt	Et_3PbCl	Et_3PbCl	Et_2PbCl_2	Et_2PbCl_2	$PbCl_2$
	Weight Adsorbed (g)	0.111	0.113	0.101	0.117	0.115
	Resin Form	H^+	Na^+	H^+	Na^+	Na^+
	Eluant	HCl	NaOH	HCl	NaOH	NaOH
	Fraction 1	21.3	15	3.4	30	38
(Percentage Extracted of Total Adsorbed)	" 2	17.8	13	7.8	17	38
	" 3	11.1	7.6	9.6	9.9	17
	" 4	8.5	4.4	8.3	7.2	8.7
	" 5	7.2	3.2	7.6	4.4	2.6
	" 6	5.7	2.3	6.4	3.2	1.6
	" 7	4.7	-	5.6	2.1	0.7
	" 8	3.2	-	5.1	2.5	0.3
	" 9	2.5	-	4.8	1.9	-
	" 10	-	-	4.6	-	-

TABLE 3

ELUTION OF Et_3Pb^+ FROM A CATION RESIN USING ORGANIC SOLVENTS

SOLVENT	ACETONE	METHANOL	METHANOL + HCl (1% $^v/v$)
Resin Form	H^+	H^+	H^+
Weight of Et_3PbCl adsorbed (g)	0.103	0.111	0.114
% Extraction for 50 ml fractions of solvent			
1st Fraction	< 0.1	< 0.1	57
2nd Fraction	< 0.1	< 0.1	11.4
3rd Fraction	< 0.1	< 0.1	7.6
4th Fraction	< 0.1	< 0.1	6.8
5th Fraction	< 0.1	< 0.1	6.4
6th Fraction	< 0.1	< 0.1	5.7
7th Fraction	< 0.1	< 0.1	4.7

The extraction of inorganic lead ions was carried out for completion. Recovery from the resins in the sodium form was good with 76% recovery after 180 ml and 100% recovery after 500 mls of eluate had been collected.

Neither acetone nor methanol removed any organolead salts from the resin, this was to be expected as the elution is an ion exchange process and neither solvent is strongly ionic in character. With methanol containing HCl (1% $^v/v$) Et_3Pb^+ was eluted and gave a 68% recovery in the first 100 ml and 89% recovery for the first 250 ml of eluant.

2.4.3.4. SUMMARY

We have established that alkyl lead salts can be removed from aqueous solution by cation exchange and subsequently recovered. The presence and effect of other cations which may be present in natural waters was not investigated. It is to be expected that other cations would be exchanged along with alkyl lead ions and this could affect the capacity of the resin and the subsequent elution of alkyl lead salts. If solutions other than distilled water are to be used the method should first be checked for suitability.

2.4.4. MACRORETICULAR RESINS

2.4.4.1. INTRODUCTION

Macroreticular resins have been used to identify and estimate neutral organic contaminants in potable[52] waters. The resin, a cross linked polystyrene polymer without ionic groups, is reported to retain 100% of neutral and weakly ionic organic compounds, while strongly ionic inorganic compounds are not retained. The weakly ionic compounds are readily eluted from the resin by varying the pH of the eluant while the neutral organic compounds are eluted using methanol or diethyl ether.

This resin has the advantage over ion exchange resins that solutions of high ionic content can be extracted without the resin becoming rapidly exhausted, this assumes the absence of large quantities of other organic compounds in the water.

Trialkyl lead salts are known to be ionic[16] and may not be adsorbed by the resin, however the extraction of Et_3PbCl by benzene from a solution saturated with sodium chloride has been reported[53]. The ionization of Et_3PbCl (Equation 1) in aqueous solution is

$$Et_3PbCl \rightleftharpoons Et_3Pb^+ \quad + \quad Cl^- \qquad 1$$

suppressed by the addition of high concentrations of chloride ion thereby increasing the solubility in non polar solvents. It was thought that the addition of chloride or some other anion might increase the adsorption of Et_3PbCl by the resin.

The suppression of ionizations and the extraction by non polar solvents is not possible for dialkyl lead salts. This is scarcely surprising since the dialkyl leads are more strongly ionized in aqueous solutions and are insoluble in non polar solvents.

We studied the adsorption of alkyl lead salts from a range of aqueous solutions and their subsequent elution from the resin, using methanol, (see Experimental, section 2.4. pp. 115).

2.4.4.2. Et_3PbCl IN DISTILLED WATER AND AQUEOUS NaCl SOLUTIONS

Two solutions containing Et_3PbCl (10 $\mu g ml^{-1}$) were prepared in distilled water and aqueous NaCl solution (1% $^W/v$). Each solution was slowly passed through the resin until 90 ml had been extracted, the column was then washed with distilled water (30 ml) and then extracted with methanol. Each 10 ml fraction of eluate was collected and analysed for lead, the concentration being expressed as the percentage of the total lead added to the column. The results are shown in table 4.

From table 4 it can be seen that the resin only extracted 60% of the Et_3PbCl from distilled water, with methanol removing only 66% of the adsorbed Et_3PbCl.

When NaCl (1% $^W/v$) was added to the alkyl lead solution the ionization of Et_3PbCl was suppressed and the resin extracted over 90%, subsequent extraction with methanol gave 100% recovery of the adsorbed alkyl lead. It is interesting to note that when the column was washed with distilled water prior to extraction with methanol some alkyl lead was removed.

TABLE 4

EXTRACTION OF Et_3PbCl FROM AQUEOUS SOLUTION BY A MACRORETICULAR RESIN AND ITS SUBSEQUENT REMOVAL BY METHANOL

	Concentration of Et_3PbCl expressed as a % of the total added Et_3PbCl	
FRACTION	DISTILLED WATER	NaCl (1%)
1st 10 ml of Et_3PbCl solution	0	0
2nd " " " "	0	0
3rd " " " "	< 1.0	< 1.0
4th " " " "	< 1.0	< 1.0
5th " " " "	1.2	< 1.0
6th " " " "	2.4	< 1.0
7th " " " "	4.0	< 1.0
8th " " " "	4.2	< 1.0
9th " " " "	4.4	< 1.0
1st 10 ml of Distilled Water	4.0	2
2nd " " "	-	12
3rd " " "	-	8.4
1st 10 ml of Methanol	14	47
2nd " " "	10	11
3rd " " "	6.3	3.7
4th " " "	5.1	3.7
5th " " "	4.7	3.4
1st 50 ml of Methanol	12	8.4

TABLE 5

CONCENTRATION OF DIETHYL AND TRIETHYL LEAD SALTS BY A MACRORETICULAR RESIN

Fraction	% of total lead added present in each fraction Solution A	Solution B	Solution C	Solution D	Solution E
1st 25 ml of eluate	0	0	< 2.0	9.4	5.8
2nd 25 ml of eluate	< 2.0	< 2.0	4.1	20.4	9.8
3rd 25 ml of eluate	< 2.0	< 2.0	5.4	24.4	13.5
4th 25 ml of eluate	< 2.0	< 2.0	7.5	8.4	16.1
1st 25 ml of methanol	83	57	62	< 2.0	45.4
2nd 25 ml of methanol	0	14	< 2.0	< 2.0	2.0

Solution A = Et_3PbCl ($10 \mu g ml^{-1}$) in HCl (1% $^v/v$)

Solution B = Et_3PbCl ($10 \mu g ml^{-1}$) in NaOAc (2% $^w/v$)

Solution C = Et_3PbCl ($10 \mu g ml^{-1}$) in NaOH (1% $^w/v$)

Solution D = Et_2PbCl_2 ($25 \mu g ml^{-1}$) in Distilled Water

Solution E = Et_2PbCl_2 ($20 \mu g ml^{-1}$) in NaOAc

2.4.4.3. SUPPRESSION OF IONIZATION OF Et_3PbCl BY HCl, NaOAc AND NaOH

Three solutions containing Et_3PbCl ($10 \mu g ml^{-1}$) were prepared in aqueous HCl (1% $^v/v$) aqueous NaOAc (2% $^w/v$) and aqueous NaOH (1% $^w/v$). 90 ml of each solution was passed through the resin (10 ml) followed by 10 mls of the solution without added lead, the resin was then extracted with methanol. The eluate was collected in suitable fractions and analysed for lead by A.A.S.. The lead concentration was expressed as a percentage of the total lead added. The results are shown in table 5.

Both, solutions of Et_3PbCl in HCl and NaOAc, are totally adsorbed by the resins, which shows that acetate also suppresses the ionization, and that the nature of cation is not important for this work. Extraction with methanol resulted in 83% and 71% recovery from the HCl and NaOAc column respectively. The adsorption from the 1% NaOH was not complete with 83% of the Et_3PbCl extracted by the resin. The methanol extracted 71% of the alkyl lead adsorbed by the resin.

2.4.4.4. Et_2PbCl_2 IN DISTILLED WATER AND AQUEOUS NaOAc SOLUTION

Pure Et_2PbCl_2 was added to distilled water and aqueous NaOAc (2% $^w/v$) to give concentrations of 25 μgml^{-1} and 20 μgml^{-1} respectively. These solutions were passed through the resin as above, the results are shown in table 5.

Solutions in distilled water gave poor adsorption with only 37.5% adsorbed. The methanol failed to elute any diethyl lead. Solutions in NaOAc were more strongly adsorbed with 55% removal of which methanol eluted 86%.

2.4.4.5. INORGANIC LEAD CHLORIDE IN AQUEOUS NaCl SOLUTION

An aqueous $PbCl_2$ solution (14 μgml^{-1}) was passed through the resin and 25 ml portions of eluate were analysed for lead. The results are shown in table 6. The lead results are expressed as percentage lead removed from that fraction. Over 290 μg of lead was removed from the first 25 ml of solution, however after 75 ml the percentage adsorption was only 4%.

TABLE 6

EXTRACTION OF $PbCl_2$ FROM AN AQUEOUS SOLUTION BY A MACRORETICULAR RESIN

	% of $PbCl_2$ adsorbed from each fraction
1st fraction of eluate (25 ml)	86
2nd fraction of eluate (25 ml)	22
3rd fraction of eluate (25 ml)	4

2.4.4.6. CAPACITY OF THE RESIN

From the results obtained it is clear that the resin will remove both Et_3PbCl and to a lesser extent Et_2PbCl_2 from aqueous solutions, while the addition of an inorganic salt, such as NaCl or NaOAc, increases the amount adsorbed. For Et_3PbCl this could form the basis of a method for its isolation and concentration. We therefore decided to examine the capacity of the resin for aqueous NaCl solutions (1% $^w/v$ and 5% $^w/v$). Solutions of Et_3PbCl ($20\,\mu g ml^{-1}$) were prepared in aqueous NaCl solution (1% $^w/v$ and 5% $^w/v$), these solutions were passed through the resin and the eluate collected in fractions. Each fraction was analysed for lead and the results expressed as the percentage not adsorbed. The results are shown in table 7.

From table 7 the adsorption from NaCl (5% $^w/v$) is superior to NaCl (1% $^w/v$), this is to be expected since the higher concentration of NaCl would supress the ionization more and so increase the adsorption. With NaCl (5% $^w/v$) the resin had adsorbed 5 mg Et_3PbCl and was still removing over 92% of the Et_3PbCl from solution. In the case of NaCl (1% $^w/v$) the resin was only removing 75% of the lead from solution at a similar stage. After 500 ml of solution had been extracted only 56% removal was being obtained with 1% NaCl.

TABLE 7

TOTAL CAPACITY OF A MACRORETICULAR RESIN WHEN ADSORBING Et_3PbCl FROM AN AQUEOUS NaCl SOLUTION

Fraction of Eluate (25 ml)	% of lead not adsorbed from each fraction	
	NaCl (1%)	NaCl (5%)
1st	0	< 4.0
2nd	< 4.0	< 4.0
3rd	< 8.0	< 4.0
4th	11.4	< 8
5th	13.0	< 8
6th	15	< 8
7th	18	< 8
8th	20	< 8
9th	22	< 8
10th	24	< 8
11th	28	
12th	31	
13th	33	
14th	34	
15th	35	
16th	37	
17th	42	
18th	41	
19th	41	
20th	44	
21st	46	
22nd	47	

2.4.4.7. SUMMARY

The resin can be used to remove Et_3PbCl from aqueous solutions provided the ionization is suppressed by the addition of an inorganic salt such as sodium chloride (5% $^{w}/v$). The alkyl lead salt can then be eluted by the use of methanol. The capacity of the resin is high with 10 ml adsorbing at least 5 mg. For diethyl lead the adsorption and extraction is less efficient but could still be used on a qualitative basis. The resin will also adsorb a small amount of inorganic lead ions and therefore cannot be used as a method of separation.

CHAPTER THREE

ANALYTICAL TECHNIQUES

ANALYTICAL TECHNIQUES

3.1. GENERAL

In this particular investigation there was a need to detect and quantitatively analyse low levels of alkyl lead compounds.

Because of the wide variation in the properties of TAL, alkyl lead salts and inorganic lead no single method is universally applicable. The method chosen must suit the type of lead compound and its expected concentration, often several methods must be applied to the same sample in order to determine the whole range of lead compounds present.

The common instrumental methods of analysis used in organic chemistry (e.g. I.R. and N.M.R.) were not applicable to this investigation due to their lack of sensitivity. Only G.L.C., M.S. and T.L.C. had sufficient sensitivity for our purposes.

For quantitative analysis we used G.L.C., A.A.S. and Colorimetry.

3.2. GAS LIQUID CHROMATOGRAPHY

3.2.1. INTRODUCTION

The methyl and ethyl TAL compounds are liquids with a range of boiling points from 110°C to 200°C. This property enables the separation of the five TALs to be readily achieved by G.L.C..

Most of the published work on the G.L.C. of TALs has been concerned with the analysis of commercial petrol. Many different columns have been used effectively, but the most critical variable is the detector.

3.2.2. DETECTORS AND COLUMNS

The Katharometer is not sufficiently sensitive to TALs for use with the levels found in this investigation.

The flame ionization detector (F.I.D.) is more sensitive than the katharometer and will readily detect low levels of TALs, however it is also particularly sensitive to hydrocarbon and other organic solvents. Most of the TAL analysis was concerned with solutions in an organic solvent, interference from the solvent made qualitative and quantitative analysis impossible using this detector system.

A number of specific detectors have been used in the determination of TALs in petrol. Parker and co-workers[54] used a 40% nujol on chromosorb at 70°C to separate the five TAL compounds. The separated compounds were then collected in an iodine scrubber and analysed as inorganic lead by a colorimetric method using dithizone.

Soulages and co-workers[55] determined TAL in petrol using a 200 mm long by 4 mm dia. column containing chromosorb P coated with P.E.G. 400. After separation the alkyl groups were hydrogenated and the hydrocarbons produced were then analysed quantitively using F.I.D.

More recently Mutsaars[56] has employed a flame photometric technique to measure quantitatively TALs eluted from a gas chromatagraphic column. Coker[57], utilising an A.A.Spectrometer as a detector, quantitatively determined TAL compounds eluted from a 900 mm long by 6 mm dia. G.L.C. column packed with 10% P.E.G. 20 M on 100 - 120 mesh Porasil C.

The electron capture detector (E.C.D.) has been widely used because of its very high sensitivity to electron capturing materials and low sensitivity to the hydrocarbon matrix of petrol.

The presence of dichloroethane and dibromoethane as scavangers in petrol has lead to a number of problems in the analysis of TAL by E.C.D., both scavangers used exhibit strong electron capturing properties, and depending on the column used can separate in a position causing peak overlap with one of the TALs. One solution to this problem has been suggested by Dawson[58] who found that a pre-column (containing silver nitrate in carbowax 400) placed immediately before the detector retained the halogen scavengers while permitting the TALs to pass through unchanged. An alternative procedure adopted by a number of workers, has been the use of 1,2,3 tris-(2-cyanoethoxy) propane as a stationary phase[59, 60]. With this liquid the halogen compounds were eluted after the final TAL. A number of other stationary phases, SE 30[61], P.P.G.[62] and Apiezon L[63], are also effective.

3.2.3. ELECTRON CAPTURE DETECTOR

3.2.3.1. BASIC THEORY

The E.C.D. utilises the fundemental principle that the conductivity of gases in an ionization chamber can be altered by the presence of a contaminant.

The E.C.D. consists of an ionization chamber containing a radioactive source. In early detectors tritium was used as a source, however this has now been superceded by the more versatile nickel[63]. The carrier gas elutes directly from the column into the ionization chamber where, under the influence of the ionizing radiation, it dissociates into a positive ion and an electron, as shown in equation 2 where nitrogen is the carrier gas.

$$N_2 + \beta \text{ ray} \rightleftharpoons N_2^+ + e^- \qquad 2$$

By the application of a potential across the chamber all the free electrons produced can be collected at the anode. The recombination reaction is slow due to the difference in mobility between the fast moving electron and the relatively slow moving positive ion. When a steady state is reached a constant standing current can be measured across the ionization chamber.

When an electrophilic compound is eluted along with the carrier gas, this steady state is disrupted. The electrons generated from the carrier gas react with the electrophilic compound in one of two ways; either a dissociative reaction (see equation 3), or a non-dissociative reaction (see equation 4).

$$e^- + AB \rightleftharpoons A^o + B^- \qquad 3$$

$$e^- + AB \rightleftharpoons AB^- \qquad 4$$

As a result of these reactions the fast moving electron is replaced by a slow moving negative ion, the negative ion because of its lack of mobility, now has a high chance of recombination with any positive ions before it is collected at the anode. The overall effect of this is a reduction in the standing current, this is measured and recorded as a conventional G.L.C. trace.

In the earlier detectors a constant potential was applied across the chamber to collect the electrons, this lead to a number of inconsistencies. Lovelock[64] has reviewed these irregularities and discussed an alternative pulsed potential procedure.

With the pulsed potential, the potential is only applied for about 0.5 µsec with a delay between pulses of about 100 µsecs. Since there is no potential difference for most of the time, the electron density in the chamber is not reduced by migration to the anode, which increases the electron density and hence the number of negative ion produced will increase. The negative ions produced will have a higher chance of recombination as they are not migrating towards the anode during the periods of zero potential. During the short pulses only the electrons are sufficiently mobile to be collected at the anode, as a result there is an overall increase in sensitivity compared to the non-pulsed or D.C. mode.

The period between pulses increases both the sensitivity and the response to background contamination within the detector, this contamination can cause non linear base lines and in practice a balance must be achieved between sensitivity and base line stability. The normal operating pulse space is 150 µsec[65].

3.2.3.2. IONIZATION SOURCE

Tritium was the main radioactive source used from 1961 to 1965, between 100 and 250 millicuries of tritium was occluded in titanium and plated onto stainless steel or copper. The maximum operating temperature for this source was 225°C, this comparatively low temperature was inconvenient and lead to the development of a nickel ^{63} source, with a maximum operating temperature of 350°C[65]. The advantages of a high maximum operating temperature are two fold, it prevents condensation in the detector and hence contamination, and also promotes increase in the electron capture properties of some compounds. Where the column temperature is close to or even above that of the detector, condensation can occur within the detector body, leading to the presence of a permanently electron capturing species and hence, a permanent reduction in the standing current.

The dissociative process of electron capture (equation 3) is promoted at high temperatures and hence an increased sensitivity occurs where the electron capture process is of this nature.

3.2.3.3. LINEAR RANGE

The linear range of the detector is low, normally about two and a half orders of magnitude, even with a clean detector, and is usually taken as being 20% of the standing current. Detectors cannot be kept clean.

As a detector is contaminated then the number of electrons available for reaction with incoming electrophiles is reduced, therefore the standing current is reduced and so the linear range. In extreme cases of contamination the base line becomes unstable and a negative peak follows a normal positive peak, making quantitative analysis impossible.

In practice the amount and rate of build up of contamination can be kept to a low level if a number of precautions are observed: The detector should always be operated at least 50°C above the column temperature, thereby preventing condensation within the detector body. The maximum working temperature of the stationary phase should never be exceeded and where possible not approached, in order to reduce column bleed. When not in use the column should be disconnected from the detector.

3.2.4. ANALYTICAL CONDITIONS FOR TETRAETHYL LEAD ANALYSIS

3.2.4.1. INTRODUCTION

The initial analysis of TEL was conducted using the conditions of Maggs and Swan[61] with minor modifications. The carrier gas flow and column temperature were adjusted to give a retention time of approximately eight minutes for TEL, (see Experimental, section 3.1.2.2. pp. 117).

3.2.4.2. SOLVENT

A number of solvents were tested for suitability as diluant for TEL standard solutions. Of the solvents examined 60 - 80 pet spirit and benzene (after purification) gave the most acceptable traces. Benzene was chosen as this was a more easily defined solvent.

3.2.4.3. DETECTOR TEMPERATURE

The response of the detector to a 10 p.p.m. TEL standard was measured over a range of detector oven temperatures. We found that the response increased with temperature from 150°C to 350°C, the maximum operating temperature. For this work a temperature of 300°C was chosen which gave a balance between maximum response while still retaining the ability to increase the temperature, in order to thermally clean the detector.

3.2.4.4. ANALYTICAL COLUMNS

Following the procedure of Dawson[58] a column was prepared by coating 15% SE 30 on caustic coated chromosorb W 60 - 80. The column was conditioned at 200°C for 24 hours with a 50 cc per minute nitrogen flow, this column proved totally unsatisfactory due to excess column bleed which made analysis impossible.

Following the advice of Pye-Unicam[66] a similar column was prepared, however instead of conditioning at 200°C for 24 hours, as above, the column was conditioned by slowly raising the temperature from room temperature to 200°C over a period of 7 days. This column was satisfactory and remained so for several months, after which time column bleed became evident. The column bleed could not be removed by conditioning and it was necessary to replace it with another.

SE 30 is a methylsilicon polymer, which in the presence of a strong base or acid decomposes to a volatile cyclic silicon containing compound[67]. This volatile material could have been the cause of column bleed, however no attempt was made to identify the compound. The function of the caustic coating on the chromosorb support is to prevent cross alkylation if TML and TEL are present[58]. In this work only a single TAL was present in the majority of cases so we decided to prepare further columns without caustic. No problems were experienced with these columns and as an additional safe guard the column was conditioned for a minimum of 2 hours at 175°C each day before use.

An alternative column, using a 1,2,3 tris-(2-cyanoethoxy) propane (TCEP) as stationary phase, was also prepared and found to give suitable separation for TEL dissolved in benzene.

3.2.5. ANALYTICAL CONDITIONS FOR TETRAMETHYL LEAD

3.2.5.1. DETECTOR CONDITIONS

Detector conditions were identical for both TML and TEL.

3.2.5.2. SOLVENT

A range of solvents were examined for their suitability as diluants for TML solutions. As with TEL, benzene and pet spirit (40 - 60) were found to be suitable, benzene was again chosen.

3.2.5.3. COLUMNS

Both the SE 30 and TCEP gave base line separation for benzene and TML, provided the flow rate and temperature of the column were suitably adjusted to give a retention time for TML of 6 to 8 minutes.

3.2.6. CALIBRATION GRAPHS

Calibration graphs for both TML and TEL were determined in the range 0 - 10 p.p.m. using a 1μl injection of standard, (see Experimental, section 2.2. pp. 112). The graphs obtained were straight lines passing through the origin. These graphs had to be recalculated daily due to the varying sensitivity of the detector.

3.2.7. ANALYSIS OF SAMPLES

The normal injection was 1μl. When the concentration of the sample was outside the normal working range i.e. 1 p.p.m. to 10 p.p.m., then the calibration graph could not be used without some amendment.

With samples below 1 p.p.m. it was possible to increase the sample volume to a maximum of 10μl provided no adverse effects, such as peak distortion or failure to achieve base line separation, were experienced. Samples over 10 p.p.m. were diluted with an appropriate solvent until the concentration was within the normal working range.

3.2.8. LIMITS OF DETECTION

The quantitative limit of detection for TALs was taken as a 1μl injection of a 1 p.p.m. $^{v}/v$ solution of the TAL in benzene. This limit can be increasing by up to a factor of ten by injecting 10μl subject to the above conditions.

The qualitative limit of detection was very much dependant on the sensitivity of the detector at the eime of analysis. The sensitivity being proportional to the degree of contamination of the detector. Apart from contamination, the sensitivity could be increased by higher amplification and by increasing the pulse space to 500 μsecs. The qualitative limit can be increased by at least a factor of 10, compared with the quantitative limit by these methods. The quantitative limit however cannot be increased in the same manner due to the lack of base line stability under these conditions.

3.2.9. ANALYSIS OF MIXED LEAD ALKYLS

Only the qualitative analysis of the mixed methyl-ethyl lead alkyl was carried out. The column conditions could be altered to give base line separation for all five TALs.

3.2.10. CONTAMINATION OF THE DETECTOR

The detector can be contaminated by any electron capturing substance, which, if it remains in the detector, reduces the number of available electrons and hence the standing current. The change in sensitivity of the detector with time could be attributed to contamination, in most cases the source of contamination was not identified. The most likely agents were thought to be column bleed material, carrier gas, and impurities in the sample. The contamination was not apparently caused by the TAL compounds themselves, as there appeared to be no relationship between contamination and the amount or number of injections of TAL. When the contamination reached a limit where quantitative analysis, within the normal working range was impossible, the detector was cleaned, (see Experimental, section 3.1.4. pp. 117).

3.2.11. DECONTAMINATION OF THE DETECTOR

The manufacturer of the detector provided a detector cleaning service, this service however was costly and very time consuming, so wherever possible the detector was cleaned without removal from the instrument by one of the following procedures:

The temperature was first raised to 350°C and left for up to 24 hours with a low flow of nitrogen passing through the detector. If this failed to clean the detector then relatively large quantities of water and hexane were injected, this latter method never failed to clean the detector to a level at which quantitative analysis was again possible.

3.3. COLORIMETRIC TECHNIQUES

3.3.1. INTRODUCTION

Whilst G.L.C. is the ideal analytical technique for the quantitative analysis of TALs, it is not applicable to the tri-and di-alkyl lead salts. A literature search suggested a limited number of quantitative methods for the analysis of the alkyl lead salts, all of which involve colorimetry in the final stage.

Henderson and Snyder[31] with dithizone determined trialkyl, dialkyl and inorganic lead. A quantitative estimation of their concentration in aqueous solution could be obtained by measuring the chloroform soluble dithizone complexes at three wavelengths. The dithizonates formed are unstable to daylight as is dithizone itself, and the analysis has to be carried out in the dark. Dithizone is also non-selective forming coloured complexes with Fe^{++}, Zn^{++}, and Mn^{++}, all of which have maximum adsorption values which interfere with those of the dithizone-lead complexes during analysis[69].

3.3.2. ANALYSIS OF Et_3Pb^+ USING HNPAN-Na

The formation of a complex between 1-hydroxy-4(p-nitrophenylazo)

-2-sodium naphthoate (HNPAN-Na) and Et_3Pb^+ has been used as a selective method for the estimation of Et_3Pb^+ in aqueous solution[70], with the complex being extracted into chloroform from a weakly alkaline aqueous solution. Interferences from Et_2Pb^{++} are eliminated by the addition of ethylene diamine diorthohydroxyphenyl acetic acid. Cupric ions and Fe^{+++} ions also form a complex with HNPAN-Na but these are not soluble in chloroform at the pH used to extract the Et_3Pb^+-HNPAN-Na complex.

Exploratory work suggested the method was indeed practical, however we decided not to continue with this method but to adopt instead, the method based on the formation of a complex formed between dialkyl lead and 4(2-pyridyl-azo) resorcinol (P.A.R.), (see Experimental, section 3.2.2. pp. 120).

3.3.3. PYRIDYL-AZO RESORCINOL METHOD

3.3.3.1. P.A.R.-R_2Pb^{++} COMPLEX

The reagent 4(2-pyridyl-azo) resorcinol disodium salt (P.A.R.) has been shown to be a selective reagent for dialkyl lead ions (R_2Pb^{++})[71] forming a stable yellow complex. There is no complex formed between P.A.R. and trialkyl lead ions (R_3Pb^+). The complex formed between P.A.R. and inorganic lead is destroyed by the addition of E.D.T.A. while the P.A.R. - R_2Pb^{++} complex remains unchanged. Thus R_2Pb^{++} can be estimated spectrophotometrically after complexing with P.A.R.[72].

The P.A.R. method has been used not only for the estimation of Et_2Pb^{++} alone, but also for Et_2Pb^{++} in the presence of Et_3Pb^+, and for total Et_3Pb^+ and Et_2Pb^{++}. Triethyl lead ions, by the addition of iodine monochloride solution, are converted to Et_2Pb^{++} before complexing[73]. We found that the conversion of Et_3Pb^+ to Et_2Pb^{++}

by iodine monochloride is quantitative and no loss of Et_2Pb^{++} occurs. Any TEL present will also be converted to Et_2Pb^{++} which can lead to falsely high Et_3Pb^+ reading.

3.3.3.2. INTERFERENCES

Ions which may interfere in the analysis, including inorganic lead but excluding iron, are removed by the addition of 1,2 diamino cyclohexane N,N',N',N' tetra acetic acid (C.D.T.A.). Using this reagent we found samples containing up to 200 μg of inorganic lead could be analysed without interference.

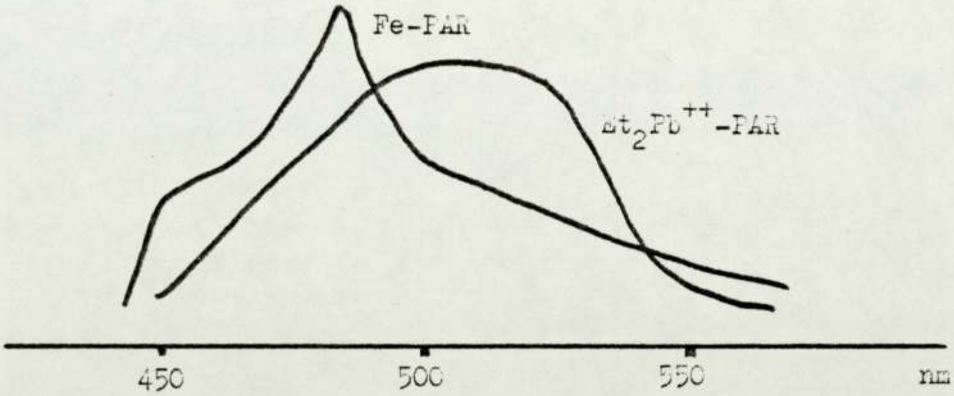
3.3.3.3. CALIBRATION GRAPHS

The calibration graph we obtained by plotting optical density against concentration of Et_2Pb^{++} (μg) gave a straight line passing through the origin. Although this method was used initially for Et_2Pb^{++} ions, we found that an identical procedure can be followed for dimethyl (Me_2Pb^{++}) and dibutyl lead (Bu_2Pb^{++}) ions. The ϵ_{max} for all three ions occurs at 515 nm and as with Et_2Pb^{++} we found the plot of concentration versus adsorbance was a straight line passing through the origin for both ions. This method can be used to distinguish between R_3Pb^+ and R_2Pb^{++} but cannot be used to differentiate between lead species if two or more dialkyl lead ions are present, in this case only an estimation of their total concentration can be obtained.

3.3.3.4. INTERFERENCE BY THE IRON - P.A.R. COMPLEX

The only metal ion which interfered in the P.A.R. method was iron. The Fe-P.A.R. complex has a ϵ_{max} at 485 nm and contributes a significant interference to the R_2Pb-P.A.R. peak at 515 nm (see figure 1) when present in the sample.

FIGURE 1. INTERFERENCE OF IRON IN P.A.R. METHOD



There were no known complexing reagents to remove this interference so the iron had to be removed by a chemical precipitation technique. We found that iron could be removed by co-precipitation with lead hydroxide. Lead nitrate was added to the sample followed by sufficient aqueous sodium hydroxide to attain pH 8. The sample was then filtered and the filtrate analysed in the normal way. Using this procedure, interference from iron is totally eliminated.

3.3.3.5. STABILITY OF Et_2Pb-P.A.R. COMPLEX

We investigated the stability of the Et_2Pb-P.A.R. complex and found that the optical density decreased by about 5% in the light over a three hour period, there was a 33% decrease over twenty four hours. In the dark the reduction in optical density was much less, with only an 8% reduction in sixteen hours and 24% over three days. In the light of these observations we decided that the complex once formed should be stored in the dark, and analysed within one hour of formation.

3.4. ATOMIC ABSORPTION SPECTROMETRY

Total lead in a sample was determined using atomic absorption spectrometry (A.A.S.), (see Experimental, section 3.3. pp. 123). Previous workers have analysed TAL in petrol directly after dilution with a suitable organic solvent[74], it was shown that standards must also be prepared using TAL and the same solvent, inorganic lead or a lead complex was not suitable because of their different atomization efficiencies[75].

In our work we decided to use only aqueous samples for total lead analysis to eliminate any problems associated with organic solvents. Most samples were prepared as an aqueous nitric acid solution (1% $^{v}/v$). If the sample was initially in an organic solvent it was first treated with iodine monochloride, this converted any TAL to a non volatile salt. The solvent was then evaporated to dryness and the residue taken up in aqueous nitric acid.

A.A.S. gives a total lead value. If two or more different types of organo or inorganic lead species are present, individual concentrations of each can only be obtained if they are first separated.

3.5. THIN LAYER CHROMATOGRAPHY

The separations of Ph_4Pb, Ph_3PbCl and Ph_2PbCl_2 on alumina and of R_3PbX and R_2PbX_2 (R = Me or Et) on silica plates using benzene[42] or benzene/acetic acid[76] as eluant have been reported. A dithizone in chloroform solution (0.1%) was used to develope the plates, this produced characteristic yellow spots for trialkyl lead, salmon red for dialkyl lead and red for inorganic lead, there is no reaction between TALs and dithizone.

Initially we used an acetic acid in benzene solution (25% $^v/v$) as eluant for silica plates, the substitution of toluene for benzene on health grounds made no difference to the separation. We also found it advantageous to use alumina plates with acetic acid in toluene (5% $^v/v$) solution as eluant, when small quantities of alkyl lead were being examined. This method gave a large increase in the lower level of detection (see table 8). Table 9 gives some typical R_f values for the systems studied, inorganic lead remained on the base line in all cases.

In some instances, if an organic solvent was concentrated and the residue run on a T.L.C. plate, a yellow spot developed in the area typical of a trialkyl lead compound. Following some initial confusion we established that this interference was not due to a lead containing species. To prevent further confusion a confirmatory test for trialkyl lead was developed. The plates were sprayed once with dithizone and any coloured spots were marked, the plates were then exposed to iodine vapours for 10 to 15 minutes, at the end of this time excess iodine was removed in a stream of air. The plate was then resprayed with dithizone. If yellow spots were due to trialkyl lead ions a colour change to the salmon red would occur, iodine converts trialkyl to dialkyl lead. If the yellow spot remains yellow, then it can be discounted. This confirmatory test for trialkyl lead does not change the colours of either the di or inorganic lead species, the test also has the added advantage of increasing the detection limit for R_3Pb^+.

It should be noted that U.V. - activated plates cannot be used as the U.V. active agent is normally a heavy metal salt, and will complex with the dithizone. The adsorbents used in this work were non U.V. - active materials.

TABLE 8

LIMITS OF DETECTION OF SOME ALKYL LEAD CHLORIDES BY T.L.C.

Alkyl lead Chloride	Silica Plates Acetic Acid/Toluene 25 : 75	Alumina Plates Acetic Acid/Toluene 5 : 95
Et_3PbCl	5	0.5
Me_3PbCl	5	1
Me_2PbCl_2	3	0.5
Et_2PbCl_2	2	0.5

Values in μg

TABLE 9

T.L.C. R_f VALUES

SYSTEM	Et_3PbCl	Me_3PbCl	Et_2PbCl_2	Me_2PbCl_2
Silica Plates				
25% AcOH/Benzene	.5	.3	.2	.1
25% AcOH/Toluene	.5	.3	.2	.1
Alumina Plates				
5% AcOH/Toluene	.5	.2	.3	.1

3.6. MASS SPECTROMETRY

As both TML and TEL are volatile liquids their mass spectra are well documented and have been reviewed elsewhere[77].

A number of workers have used M.S. for the quantitative estimation of TALs. Laveskog[24] has identified trace quantities of TAL in motor vehicle exhaust fumes using a G.L.C./M.S.. Howard[78] has reported the use of M.S. to determine TEL and TML in petrol. The peak hights at $^{m}/e$ values of 295 and 253 corresponding to Et_3Pb and Me_3Pb respectively, were compared.

The relative abundances of the ions produced by R_4Pb are in the order:

$$R_3Pb > RPb > Pb > R_2Pb \gg R_4Pb$$

where R is either methyl or ethyl. The parent ion peak accounts for only about 0.5% of the total[79, 80]. If both methyl and ethyl groups are bonded to the same lead atom, the ethyl group is preferentially lost[81, 82].

The mass spectra of the alkyl lead salts have not been reported, probably because of their lack of volatility. We determined the mass spectra of a number of the trialkyl lead salts in order to evaluate the potential of the technique as a quantitative or qualitative method of analysis, (see Experimental, section 3.5. pp. 124). The spectra produced showed all the ions which could be formed by the loss of a varying number of alkyl groups or the halide radical, the abundance was in the order:

$$R_3Pb = R_2PbX = RX = RPb > R_2Pb = RPbX \gg R_3PbX$$

$$X = Cl,\ I,\ \text{or}\ Br \qquad R = Me\ \text{or}\ Et$$

TABLE 10

SOME $^{m}/e$ VALUES FOR ORGANOLEAD IONS

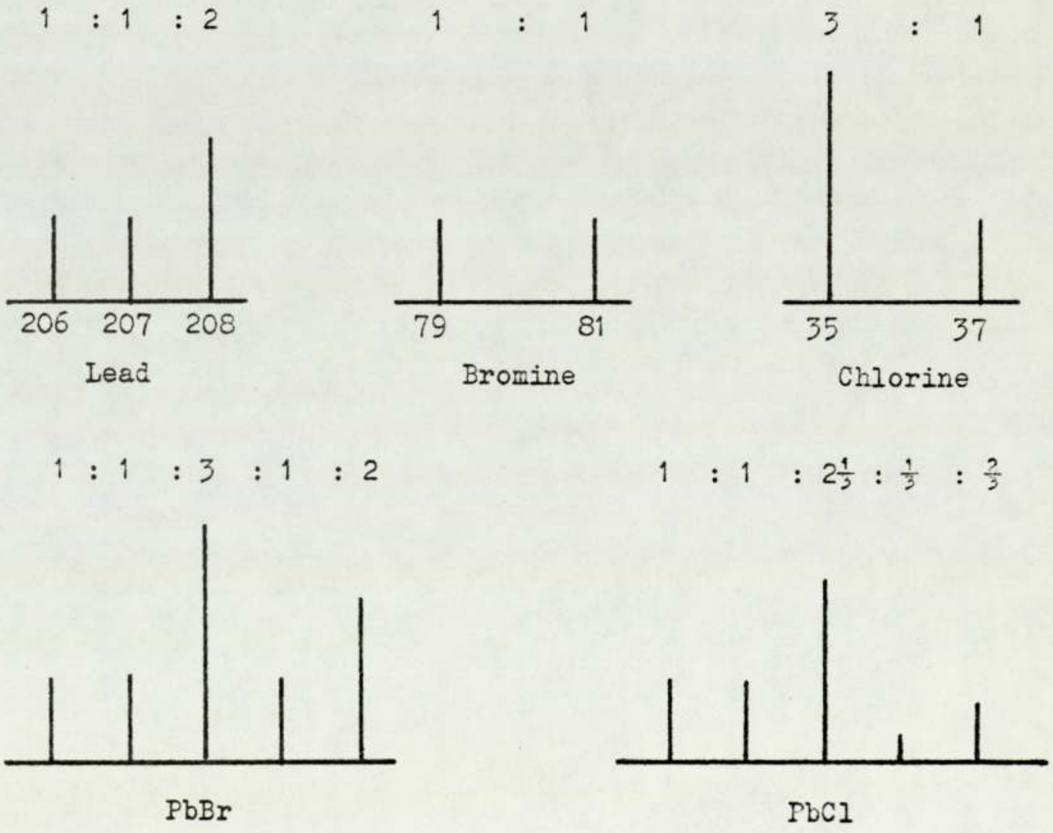
Based on Lead 208, Bromine 79, Chlorine 35, Iodine 127.

$^{m}/e$	ION
208	Pb
209	PbH
223	MePb
237	EtPb
238	$\mathrm{Me_2Pb}$
243	PbCl
252	MeEtPb
253	$\mathrm{Me_3Pb}$
258	MePbCl
266	$\mathrm{Et_2Pb}$
267	$\mathrm{Me_2EtPb}$
268	$\mathrm{Me_4Pb}$
272	EtPbCl
273	EtHPbCl
273	$\mathrm{Me_2ClPb}$
281	$\mathrm{MeEt_2Pb}$
285	PhPb
287	PbBr
287	MeEtPbCl
288	$\mathrm{Me_3PbCl}$
295	$\mathrm{Et_3Pb}$
301	$\mathrm{Et_2PbCl}$
302	$\mathrm{Me_2EtPbCl}$
316	$\mathrm{MeEt_2PbCl}$
316	EtPbBr
317	EtHPbBr
317	$\mathrm{Me_2PbBr}$
324	$\mathrm{Et_4Pb}$
330	$\mathrm{Et_3PbCl}$
331	MeEtPbBr
332	$\mathrm{Me_3PbBr}$
335	PbI
345	$\mathrm{Et_2PbBr}$
346	$\mathrm{Me_2EtPbBr}$
350	MePbI
360	$\mathrm{MeEt_2PbBr}$
362	$\mathrm{Ph_2Pb}$
364	EtPbI
365	EtHPbI
365	$\mathrm{Me_2PbI}$
374	$\mathrm{Et_3PbBr}$
379	MeEtPbI
380	$\mathrm{Me_3PbI}$
393	$\mathrm{Et_2PbI}$
394	$\mathrm{Me_2EtPbI}$
408	$\mathrm{MeEt_2PbI}$
422	$\mathrm{Et_3PbI}$
439	$\mathrm{Ph_3Pb}$
516	$\mathrm{Ph_4Pb}$

Regardless of the nature of the alkyl lead halide, peaks corresponding to other halides were always observed e.g. in the spectrum of Et_3PbBr, peaks corresponding to Et_3PbCl and Et_3PbI were also present. Table 10 lists the major peaks found and their $^m/e$ value based on the major halogen and lead isotope.

The analysis of trialkyl lead salt spectrum is simplified by the characteristic isotope patterns found where both lead and a halogen atom are present together in the same radical. The presence of bromine or chlorine is readily established by comparison with the isotope patterns shown below, figure 2.

FIGURE 2 LEAD - HALOGEN ISOTOPE PATTERNS



Iodine has only one significant isotope and therefore any Pb - I containing radicals will have the normal lead pattern. These are found much higher in the spectrum due to the high atomic weight of iodine.

We decided following this work, that mass spectrometry had only limited use on a qualitative basis.

CHAPTER FOUR

REACTIONS OF ORGANOLEAD COMPOUNDS IN AQUEOUS SOLUTIONS IN THE LIGHT AND DARK

REACTIONS OF ORGANOLEAD COMPOUNDS IN AQUEOUS SOLUTIONS IN THE LIGHT AND DARK

4.1. INTRODUCTION

Although it was not known when this work was started, it has now been established in these laboratories that the concentration of organolead compounds in natural waters is low, except in the vicinity of localized spillages[83]. As yet however there is no published work on the stability or reactions of alkyl lead compounds at these very low concentrations. In general organolead compounds are reported to be stable to hydrolysis and in many cases steam distillation is used in their purification[16]. TAL compounds are insoluble in water while the organolead salts are generally ionic and readily soluble in water at the expected concentrations and due to the ionic nature the anion is unimportant.

In this work we have attempted to expand our knowledge of the stability and reactions of organolead compounds in aqueous solutions, under conditions of light, dark and added metal ions.

4.2. GENERAL ANALYTICAL TECHNIQUE

To determine the organolead content of a sample it was first extracted with benzene to remove TAL and then the aqueous phase was analysed by the P.A.R. method, the TAL was determined by G.L.C.. The weight of the organolead compounds are expressed as μg of R_2Pb^{++}.

4.3. STABILITY OF DIALKYL LEAD IONS

4.3.1. IN THE DARK

4.3.1.1. DIMETHYL LEAD DICHLORIDE AND DIBUTYL LEAD DICHLORIDE

Aqueous solutions of Me_2PbCl_2 (8.1 μgml^{-1}) and Bu_2PbCl_2 (11.1 μgml^{-1}) were prepared and stored in the dark. The solutions were analysed for R_3Pb^+ and R_2Pb^{++} concentration, with time and the results are shown in table 11.

TABLE 11

STABILITY OF AQUEOUS SOLUTIONS OF Me_2PbCl_2 AND Bu_2PbCl_2 IN THE DARK

Time	concentration as R_2Pb^{++} (μgml^{-1})			
(Days)	Me_2Pb^{++}	Me_3Pb^+	Bu_2Pb^{++}	Bu_3Pb^+
0	8.1	0.0	11.1	0.0
28	7.3	0.33	10.8	0.0
46	7.1	0.21	10.9	0.0
71	6.8	0.21	10.7	0.09

It can be seen from table 11 that there is a 16% loss of Me_2Pb^{++} over 71 days, whilst only a 3% loss of Bu_2Pb^{++} occurs during the same period. A small amount of R_3Pb^+ was found in each case.

4.3.1.2. DIETHYL LEAD DICHLORIDE

An aqueous solution of Et_2PbCl_2 (10.1 μgml^{-1}) was prepared and stored in the dark. The concentration of Et_2Pb^{++} and Et_3Pb^+

was determined with time. The results are shown in table 12.

TABLE 12

STABILITY OF AN AQUEOUS SOLUTION OF Et_2PbCl_2 IN THE DARK

Time (days)	concentration as Et_2Pb^{++} ($\mu g ml^{-1}$)	
	Et_2Pb^{++}	Et_3Pb^{+}
0	10.1	0.0
15	9.5	0.03
16	9.6	0.03
25	9.5	0.0
101	8.7	0.21
120	8.8	0.30
192	8.4	0.33
270	7.8	0.27
288	7.5	0.51
313	7.1	0.51

It can be seen from table 12 that slow decomposition of Et_2Pb^{++} takes place with 30% reduction in concentration over 313 days. A small amount of Et_3Pb^{+} was also found.

4.3.1.3. SUMMARY

All three dialkyl lead ions exhibited some instability over the period studied, however the least stable, Me_2Pb^{++}, only suffered a reduction of 15% in 71 days. The order of stability was:

$$Bu_2Pb^{++} \gg Et_2Pb^{++} > Me_2Pb^{++}$$

The formation of R_3Pb^+ in small quantities with all three ions suggests that the decomposition is at least in part a disproportionation reaction.

4.3.2. EXPOSED TO LIGHT

Aqueous solution of Me_2PbCl_2 (10.3 μgml^{-1}), Et_2PbCl_2 (7.4 μgml^{-1}) and Bu_2PbCl_2 (8.5 μgml^{-1}) were prepared and exposed to normal daylight. The alkyl lead salt concentrations were determined with time and the results are shown in table 13. All three solutions were irradiated for equal lengths of time.

TABLE 13

STABILITY OF AQUEOUS SOLUTIONS OF R_2Pb^{++} IN THE LIGHT

Time	concentration as R_2Pb^{++} (μgml^{-1})					
(Days)	Me_2Pb^{++}	Me_3Pb^+	Et_2Pb^{++}	Et_3Pb^+	Bu_2Pb^{++}	Bu_3Pb^+
0	10.4	0.30	7.4	0.06	8.5	0.0
1	9.9	0.24	7.4	0.06	8.1	0.0
6	10.2	0.15	7.1	0.09	7.2	0.0
12	9.9	0.33	6.8	0.06	6.2	0.04
23	9.7	0.0	6.2	0.04	4.6	0.01
30	10.2	0.33	6.0	0.14	3.8	0.10
40	9.9	0.65	5.5	0.01	2.6	0.0
58	9.7	0.30	4.5	0.03	1.5	0.04
82	9.0	0.54	2.1	0.0	0.08	0.46
111	8.7	0.83	0.48	0.0	0.0	0.0
134	9.0	1.0	0.18	0.0	-	-
167	8.0	1.4	0.06	0.03	-	-
204	6.2	1.5	0.09	0.0	-	-

From table 13 it can be seen that the order of stability in the light is:

$$Me_2Pb^{++} > Et_2Pb^{++} > Bu_2Pb^{++}$$

This is a reversal of the order of stability in the dark and indicates that a different mechanism of decomposition is dominant in the light reaction.

4.4. STABILITY OF TRIALKYL LEAD IONS

4.4.1. IN THE DARK

4.4.1.1. Me_3PbCl AND Bu_3PbCl

Aqueous solutions of Me_3PbCl ($10.4\,\mu gml^{-1}$) and Bu_3PbCl ($10.6\,\mu gml^{-1}$) were prepared and stored in the dark. The concentrations of organolead salts were determined with time. No dialkyl lead ions were produced by either system. The results are shown in table 14.

From table 14 it can be seen that Bu_3Pb^+ appears stable while the concentration of Me_3Pb^+ shows some fluctuations, however if any breakdown is occurring it is at most 10% over 220 days.

4.4.1.2. Et_3PbCl

Aqueous solutions of Et_3PbCl ($8.6\,\mu gml^{-1}$) and Et_3PbCl ($16.3\,\mu gml^{-1}$) plus Cu^{++} ($20\,\mu gml^{-1}$), were prepared and stored in the dark. The concentration of alkyl lead ions was determined with time over a period of 200 days.

Both solutions showed complete stability over the period analysed.

TABLE 14

STABILITY OF AQUEOUS SOLUTIONS OF Bu_3PbCl AND Me_3PbCl IN THE DARK

Time (Days)	concentration as R_2Pb^{++} (μgml^{-1})	
	Bu_3Pb^+	Me_3Pb^+
0	10.8	10.4
1	10.8	10.0
2	10.8	9.0
3	10.6	10.2
4	10.7	10.3
5	10.8	9.7
7	10.8	9.9
9	10.7	10.0
14	10.7	10.0
19	10.7	9.3
44	10.1	10.1
63	10.9	9.1
74	10.8	9.7
220	10.1	9.1

4.4.1.3. SUMMARY

All R_3Pb^+ ions studied appeared stable in the dark and no reaction occurred between Cu^{++} ions and Et_3Pb^+ ions. Triethyl lead ion is a product of the reaction between TEL and Cu^{++} as reported later in this chapter (4.5.2.2.).

4.4.2. EXPOSED TO LIGHT

4.4.2.1. Me_3PbCl AND Bu_3PbCl

Aqueous solutions of Me_3PbCl ($17.1\mu gml^{-1}$) and Bu_3PbCl ($18.2\mu gml^{-1}$) were prepared and exposed to normal daylight. No dialkyl lead ions were formed in either reaction. The results are shown in table 15.

TABLE 15

STABILITY OF AQUEOUS SOLUTIONS OF Me_3PbCl AND Bu_3PbCl IN THE LIGHT

Time (Days)	concentration as R_2Pb^{++} (μgml^{-1})	
	Bu_3Pb^+	Me_3Pb^+
0	18.2	17.1
1	17.4	16.8
2	16.9	15.6
3	16.5	16.3
4	16.0	16.6
6	15.6	15.5
8	14.5	15.0
13	13.3	15.8
21	11.2	16.5
44	7.2	15.8
52	6.5	15.8
63	4.7	16.0
74	4.0	14.6
136	-	15.6

From table 15 it can be seen that Bu_3Pb^+ ions undergo a fairly steady decomposition to inorganic lead while Me_3Pb^+ again exhibits erratic behaviour, however the overall trend seems to be a very slow decomposition. The lack of formation of dialkyl lead suggests that the reaction is not a disproportionation.

4.4.2.2. Et_3PbCl

An aqueous solution of Et_3PbCl ($21.2\,\mu g ml^{-1}$) was prepared and exposed to daylight. The variation of concentration of organolead salts with time is shown in table 16.

TABLE 16

STABILITY OF AN AQUEOUS SOLUTION OF Et_3PbCl IN THE LIGHT

Time (Days)	concentration as Et_2Pb^{++} ($\mu g ml^{-1}$)	
	Et_3Pb^+	Et_2Pb^{++}
0	21.2	0.03
1	12.2	0.16
2	6.8	0.19
3	5.2	0.35
4	3.9	0.18
5	2.5	0.42
8	0.36	0.26
9	0.27	0.22
11	0.17	0.13
15	0.22	0.14

Table 16 shows a fairly rapid breakdown of Et_3Pb^+. There is a small amount of Et_2Pb^{++} produced during the decomposition, suggesting that disproportionation may be occurring to a small extent, although it is not the dominant reaction.

4.5. STABILITY OF TAL COMPOUNDS

4.5.1. INTRODUCTION

The solubilities of TAL compounds are very low, TEL is only soluble at 0.2 - 0.3μgml^{-1} in aqueous solution[33]. For our purposes this was too low to study the reaction of dissolved TAL. As a compromise, higher concentrations of TAL in water were prepared and the solutions were shaken regularly. To sample a solution a portion was removed immediately after shaking, and analysed for organolead content in the normal way.

4.5.2. IN THE DARK

4.5.2.1. TEL IN DISTILLED WATER WITH ADDED Ni^{++} IONS

A solution of TEL (38.7μgml^{-1}) was prepared in distilled water and an aqueous Ni^{++} (20μgml^{-1}) solution. The samples were shaken to disperse the TEL and then stored in the dark. The aqueous layer was analysed immediately after shaking. The results for distilled water are shown in table 17. The results of the Ni^{++}/TEL solution were similar.

In both cases no Et_2Pb^{++} was produced and only a small amount of Et_3Pb^+ was detected. There appeared to be a rapid loss of TEL from solution without any corresponding product, which suggested that adsorption on to the glass walls could be occurring. Analysis of the aqueous phase by A.A.S. indicated the absence of inorganic lead.

After prolonged extraction with benzene, 71% of the remaining TEL was recovered from the glass walls. The reactions of TEL adsorbed by silica are discussed in Chapter 5.

TABLE 17

STABILITY OF AN AQUEOUS SOLUTION OF TEL IN THE DARK

Time	concentration as Et_2Pb^{++} (μgml^{-1})	
(Days)	TEL	Et_3Pb^+
0	38.7	0.0
1	23.4	0.0
2	23.2	0.07
6	17.5	0.23
9	17.9	0.15
13	20.0	0.05
16	18.4	0.06
23	19.9	0.25
41	17.3	0.27
50	12.3	0.55
77	8.5	0.81

4.5.2.2. TEL IN AQUEOUS SOLUTIONS OF Cu^{++} AND Fe^{++}

Solutions of TEL ($38.7\mu\ gml^{-1}$) were prepared in aqueous solution of Cu^{++} ($20\ \mu gml^{-1}$ and $1\ \mu gml^{-1}$) and Fe^{++} ($20\ \mu gml^{-1}$). The solutions were stored in the dark and analysed for organolead content with time. The results are shown in tables 18 and 19 and in figure 3 for Cu^{++} ($20\mu\ gml^{-1}$).

From tables 18 and 19 it can be seen that TEL reacts with Cu^{++} and Fe^{+++} ions to produce Et_3Pb^+.

The reactions of Cu^{++} with TEL in alcoholic solutions has been studied by a number of authors[84, 85, 86] and a mechanism has been proposed for this reaction, Cu^{++} is reduced to Cu^+ which is then alkylated, as shown below.

$$Cu^{++} + R_4Pb \longrightarrow Cu^{+} + R_3Pb^{+} + R^{o}$$

$$Cu^{+} + R_4Pb \longrightarrow RCu + R_3Pb^{+}$$

At room temperature the alkyl copper reacts with the solvent.

The reaction of Fe^{+++} with TEL at room temperature has also been reported[87], the Fe^{+++} being reduced to Fe^{++}, this reaction has been used to remove TEL from petrol[88]. In this work we initially used a Fe^{++} solution, however this would be rapidly oxidised to Fe^{+++}. We studied iron solutions because it has been established that it is a common element in natural waters.

Traces of Et_2Pb^{++} were found in both systems.

TABLE 18

STABILITY OF TEL IN AN AQUEOUS SOLUTION OF Cu^{++} (20 μgml^{-1}) IN THE DARK

Time	concentration as Et_2Pb^{++} (μgml^{-1})		
(Days)	TEL	Et_3Pb^{+}	Et_2Pb^{++}
0	38.7	0.0	0.0
1	26.3	2.1	0.03
2	14.8	3.3	0.0
3	22.49	5.0	0.0
4	13.82	6.5	0.0
9	8.26	10.1	0.14
10	12.33	11.5	0.15
15	3.39	15.5	0.27
18	7.18	17.8	0.98

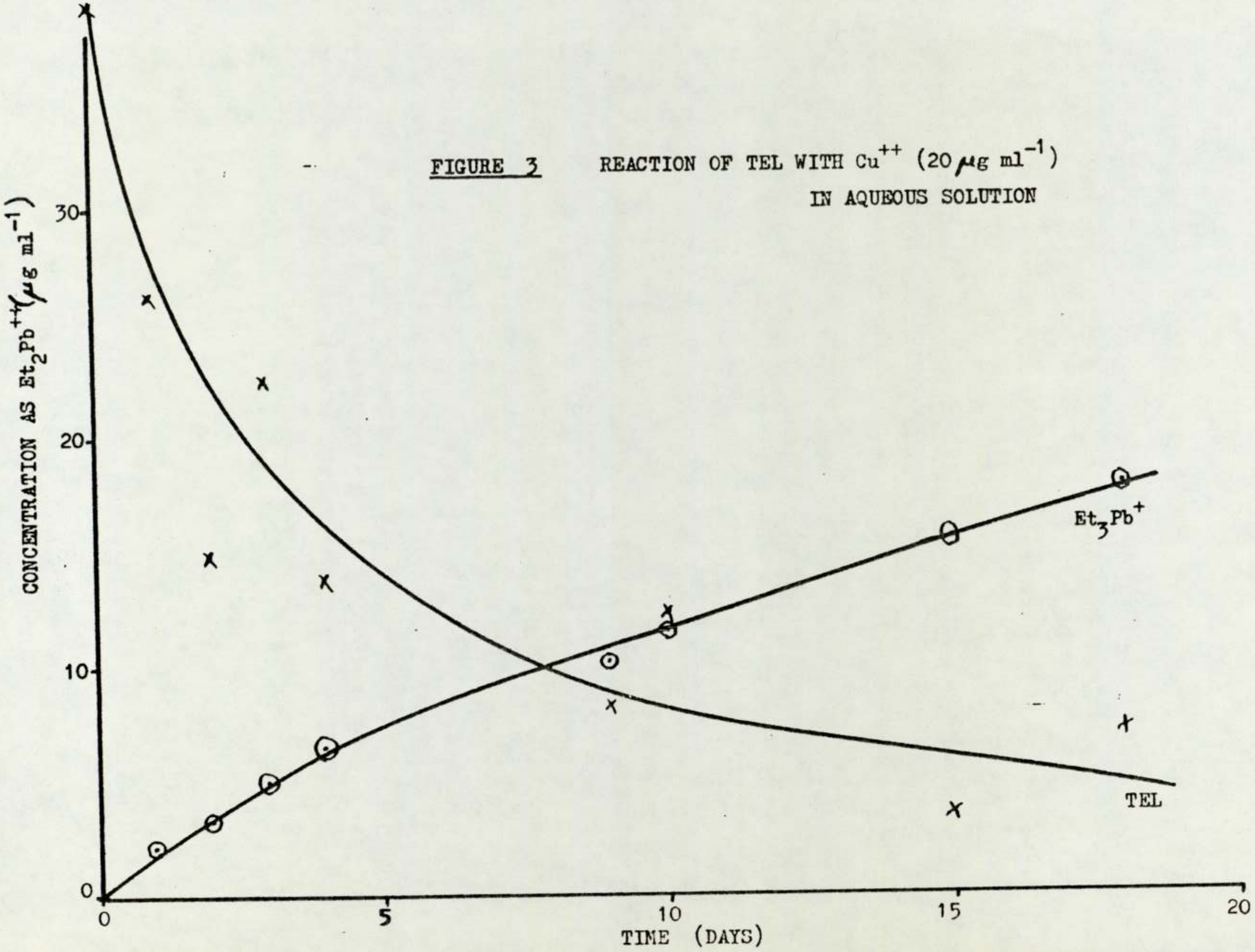


FIGURE 3 REACTION OF TEL WITH Cu^{++} ($20\ \mu g\ ml^{-1}$) IN AQUEOUS SOLUTION

TABLE 19

STABILITY OF TEL IN AQUEOUS SOLUTIONS OF Cu^{++} ($1\ \mu gml^{-1}$) AND Fe^{++} ($20\ \mu gml^{-1}$) IN THE DARK

Time (Days)	concentration as Et_2Pb^{++} (μgml^{-1})					
	Fe^{++} ($20\ \mu gml^{-1}$)			Cu^{++} ($1\ \mu gml^{-1}$)		
	TEL	Et_3Pb^+	Et_2Pb^{++}	TEL	Et_3Pb^+	Et_2Pb^{++}
0	38.7	0.0	0.0	38.7	0.0	0.0
1	26.0	-	-	24.6	0.12	0.0
2	21.3	-	-	18.6	0.23	0.0
4	20.2	0.41	0.14	16.1	0.36	0.0
7	19.1	0.17	0.08	15.0	0.61	0.05
10	18.6	0.22	0.0	11.4	0.69	0.0
17	17.2	1.8	1.4	6.3	1.4	0.0
24	16.2	0.63	0.09	2.6	1.8	0.0
35	11.1	0.94	0.13	-	2.8	0.0
44	10.7	1.6	0.54	0.45	3.3	0.0
51	12.6	1.4	0.0	0.45	3.4	0.0
71	-	2.6	0.24	-	4.3	0.0
314	-	7.6	0.24	-	7.1	0.0

4.5.3. EXPOSED TO LIGHT

An aqueous solution of TEL ($38.7\ \mu gml^{-1}$) was prepared and exposed to natural daylight. The organolead content of the system was determined at frequent intervals. The results are shown in table 20 and figure 4.

From table 20 the major reaction of TEL is the formation of Et_3Pb^+ which in daylight will itself decompose to inorganic lead. It is to be expected that adsorption onto glass will occur in the light also. Traces of diethyl lead are again observed.

FIGURE 4 REACTION OF TEL IN AQUEOUS SOLUTION IN THE LIGHT

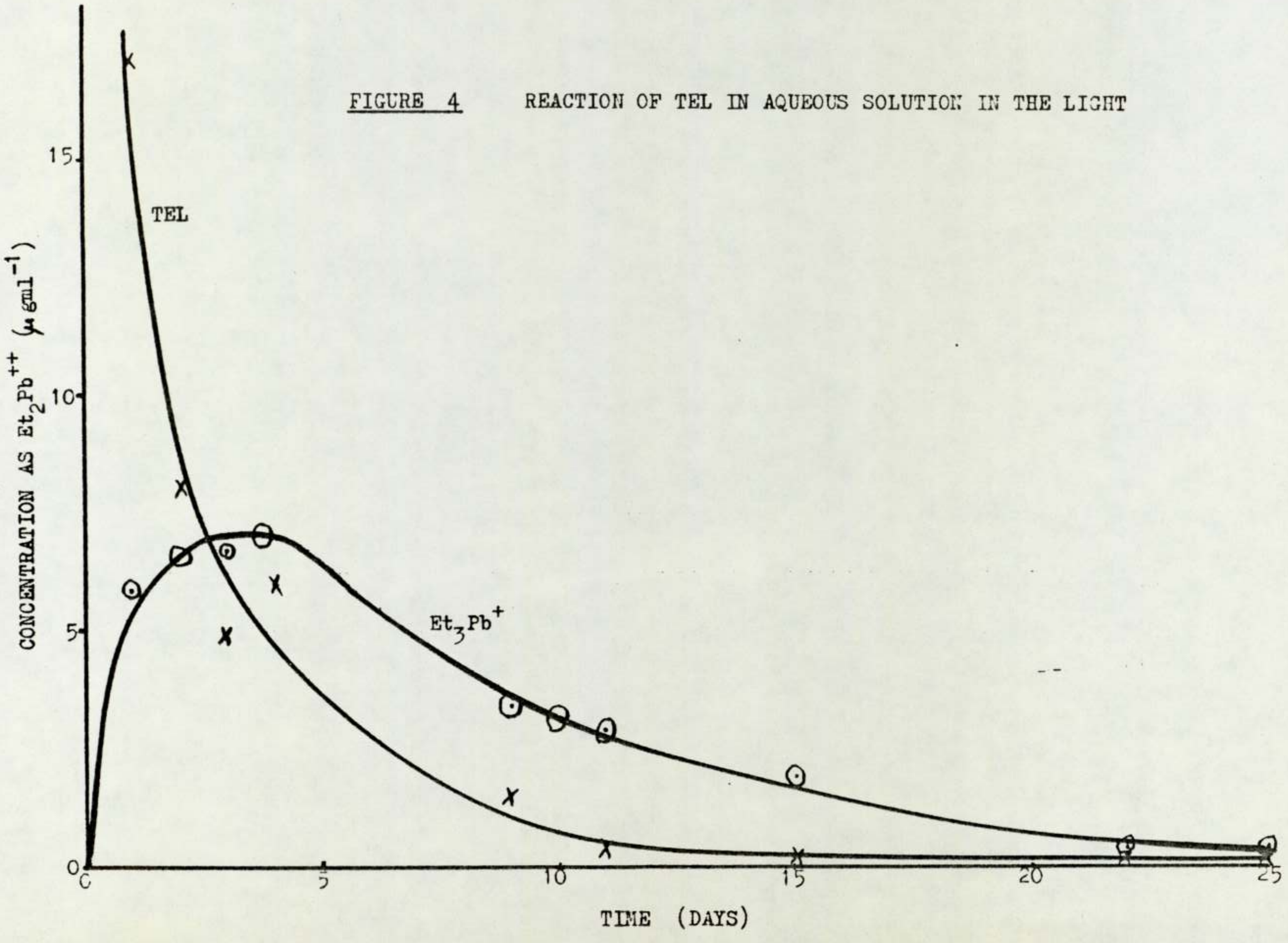


TABLE 20

STABILITY OF AN AQUEOUS SOLUTION OF TEL IN THE LIGHT

Time (Days)	concentration as Et_2Pb^{++} (μgml^{-1})		
	TEL	Et_3Pb^+	Et_2Pb^{++}
0	38.7	0	0.0
1	17.1	5.8	0.0
2	8.1	6.6	0.15
3	4.9	6.7	0.0
4	6.0	7.0	0.0
9	1.2	3.3	0.20
10	0.65	3.1	0.0
11	0.34	2.9	0.18
15	0.17	1.9	0.11
22	0.12	0.39	0.08
25	0.15	0.37	0.03
38	-	0.21	0.0

4.5.4. STABILITY OF TML IN THE LIGHT AND DARK

Two aqueous solutions of TML (30.6μgml^{-1}) were prepared, one was stored in the light the other in the dark. The organolead content of each was analysed with time, no Me_2Pb^{++} was found in either sample, the results are shown in table 21.

From table 21 it can be seen that TML is unstable both in the light and the dark. The initial rate of loss of TML greatly exceeds the formation of Me_3Pb^+ and this would indicate, especially in the dark, that adsorption onto the walls is again occurring, the TML still appears to be available for reaction even after adsorption. The rate of formation of Me_3Pb^+ is greater in the light than the dark.

TABLE 21

STABILITY OF AQUEOUS SOLUTIONS OF TML IN THE LIGHT AND THE DARK

Time	concentration as Me_2Pb^{++} ($\mu g ml^{-1}$)			
	Light		Dark	
(Days)	TML	Me_3Pb^+	TML	Me_3Pb^+
0	30.6	0.0	30.6	0.0
1	4.2	0.86	6.4	1.9
2	3.7	1.6	3.6	2.5
5	3.1	3.8	4.3	3.5
8	1.6	6.3	1.5	4.1
12	1.8	10.3	3.0	4.6
14	1.5	12.7	2.0	4.5
16	1.3	15.4	1.1	4.8
19	0.53	16.3	0.98	4.6
22	0.09	18.3	0.56	4.9

4.5.5. SUMMARY

TEL is stable in the dark but decomposes in the light. TML decomposes in the light and the dark, however the rate of reaction is far greater in the light.

TAL compounds absorb U.V. light, decomposing by a free radical mechanism[16]. In the vapour phase the products are hydrocarbons and metallic lead, however in aqueous solutions it would appear that the first stage is the loss of one alkyl group and the formation of R_3Pb^+. This will in turn decompose to inorganic lead by a mechanism not involving the formation of R_2Pb^{++}.

CHAPTER FIVE

REACTIONS OF ALKYL LEAD COMPOUNDS WHILE ADSORBED ON SILICA GEL

REACTIONS OF ALKYL LEAD COMPOUNDS WHILE ADSORBED ON SILICA GEL

5.1. INTRODUCTION

In natural water systems heavy metals are adsorbed by the sediment[89]. Oliver[90] suggested that the highest concentration of heavy metals are to be found in the finer silts due to the high surface area. Maxfield and co-workers[91] have investigated the sediment down stream from a mining operation. After separation into four fractions, the concentration of lead in each fraction was estimated and found to be in the order:

clay > organic matter > silt > sand

It has been reported that cadmium is adsorbed onto glass surfaces from aqueous solutions during storage[92], we observed a similar behaviour with TEL where very dilute aqueous solutions were adsorbed, during storage, onto the walls of glass vessels.

In natural water systems it is to be anticipated that organolead compounds will be adsorbed onto sediment and that sediment concentration will generally be much higher than found in water. Since it is almost impossible to obtain a uniform, well defined natural sediment, with which to study adsorption and sediment reactions, we decided to use silica gel (100 - 200 mesh), we were aware of the many differences between this and natural sediment.

5.2. ADSORPTION AND EXTRACTION

5.2.1. TETRA-ALKYL LEADS

TEL (825 μg) and TML (687 μg) were totally adsorbed by suspensions of silica (10 g) in distilled water (50 ml).

The TEL was extracted from the silica suspension with benzene. The extraction of TEL from water gave an average recovery of 97% for four samples, whereas the recovery of TEL in the presence of silica was reduced to 78%.

The time taken for extraction appeared to be an important factor in the recovery of TEL. For distilled water alone maximum recovery was achieved by extracting for 2 minutes, with distilled water and silica, TEL was still extractable after a 2 hour extraction period and to achieve maximum recovery, samples were usually shaken overnight using an automatic shaker.

The recovery of TML from distilled water was 100% and complete within 2 minutes, maximum extraction from silica could be achieved within 5 minutes, but in this case recovery was only 67%.

5.2.2. ALKYL LEAD SALTS

5.2.2.1. INTRODUCTION

Westoo[93] found that the recovery of alkyl mercury salts from tissue could be increased by the addition of an inorganic mercury salt to the system. This improvement was attributed to the replacement of the alkyl mercury at adsorption sites by inorganic mercury salts. In consequence of this observation we decided to use a similar technique for the extraction of alkyl lead salts from silica.

Our initial experiments were carried out with Et_3PbCl (approx 500μg) adsorbed on silica (10 g) suspended in distilled water (50 ml).

5.2.2.2. AQUEOUS LEAD NITRATE AS ELUANT

Lead nitrate (5 g) was added to the suspension and shaken for 30 minutes, the silica was then removed by filtration. The large excess of lead nitrate in the filtrate interferes with the P.A.R. method of analysis for Et_3Pb^+, to overcome this the lead is removed, prior to analysis, by precipitation as the insoluble hydroxide. Sodium hydroxide is added to give a pH of 8.0 and the sample is filtered, the filtrate is then suitable for analysis by the P.A.R. method.

Utilising the above method the recovery of added Et_3Pb^+ ion was only 45%, a further extraction of the silica by aqueous $Pb(NO_3)_2$ (10% $^W/v$) gave a similar recovery of the remaining Et_3Pb^+. The extraction of the alkyl lead was complete in 30 minutes, overnight shaking produced no further increase.

It was then decided that a more efficient way of extracting the silica would be to transfer it to a column and elute with aqueous lead nitrate solution (10% $^W/v$). By this method we achieved a 92% recovery, eluting with 200 ml of solution.

The use of aqueous lead nitrate as an extraction solution gives high recoveries but has the disadvantage that the inorganic lead must be removed before analysis. The removal of the inorganic lead does not result in any serious loss of alkyl lead salts, 98% recovery being achieved when inorganic lead was removed from a dialkyl lead solution, but the procedure is time consuming and we decided therefore to seek alternative extraction reagents.

5.2.2.3. AQUEOUS ACETIC ACID SOLUTION AS ELUANT

We found that an aqueous acetic acid solution (2% $^{v}/v$) gave good recoveries for all the ethyl and methyl salts adsorbed on silica. The results were 96%, 94%, 96%, and 93% for Et_3PbCl, Et_2PbCl_2, Me_3PbCl, and Me_2PbCl_2 respectively. The analysis was carried out by the P.A.R. method after neutralisation of the acetic acid solution with NaOH.

There was no detectable conversion of dialkyl lead to trialkyl lead or trialkyl lead to dialkyl lead while adsorbed on the silica or during the extraction procedure. When silica containing TML (680 μg) was extracted with aqueous acetic acid solution (2% $^{v}/v$), Me_3Pb^+ (41 μg) was recovered. It has been reported that silica catalyses the conversion of TEL to triethyl lead acetate using glacial acetic acid[44]. In the light of this observation it was our practice to extract first the TALs, before extracting the alkyl lead salts.

5.2.2.4. AQUEOUS SODIUM ACETATE AS ELUANT

Another solvent system was investigated for the extraction of Me_3PbCl adsorbed on silica, this solvent, an aqueous sodium acetate solution (2% $^{w}/v$), gave poor recoveries with 16% recovery in the first 100 ml and only 4% recovery in the second. No further work was carried out in this solvent.

5.2.2.5. ADSORPTION EFFICIENCY

We observed that Et_3PbCl (500 μg), Et_2PbCl_2 (500 μg), Me_3PbCl (500 μg) and Me_2PbCl_2, were totally adsorbed from distilled water (50 ml) by silica (10 g).

5.2.3. METHODS OF EXTRACTION

Using benzene, for complete extraction 10 minutes shaking was required for TML and overnight for TEL. After removal of the TALs the silica was transferred to a column and the alkyl lead eluted with aqueous acetic acid solution (2% $^{v}/v$). After extraction the pH of the eluate was adjusted to between 7 and 8 using sodium hydroxide solution and analysed by the P.A.R. method, usually 200 ml of acid was sufficient for removal of all the lead salts. The benzene layer is analysed by G.L.C, to determine the concentration of TAL.

5.3. DECOMPOSITION OF ALKYL LEAD COMPOUNDS ON SILICA

5.3.1. TETRAETHYL LEAD

A number of identical samples were prepared consisting of silica (10 g) suspended in distilled water (50 ml) to which TEL (677 μg as Et_2Pb^{++}) was added . The samples were stoppered, shaken and then stored in the dark. Extraction of the aqueous layer indicated total adsorption of the TEL by the silica.

The stability of TEL on silica was measured by determining the change in the concentration of the various organolead species with time, the results are shown in table 22 and in figure 5 .

Table 22 indicates that the major reaction of TEL adsorbed on silica is conversion to Et_3Pb^+ which does not appear to undergo further reaction to Et_2Pb^{++}. After 29 days only 3% of the TEL added is extractable as TEL while 70% is extractable as the trialkyl salt, which leaves 27% unaccounted for, this material must be irreversibly adsorbed by the silica or have reacted to give another product such as inorganic lead. We did not attempt to

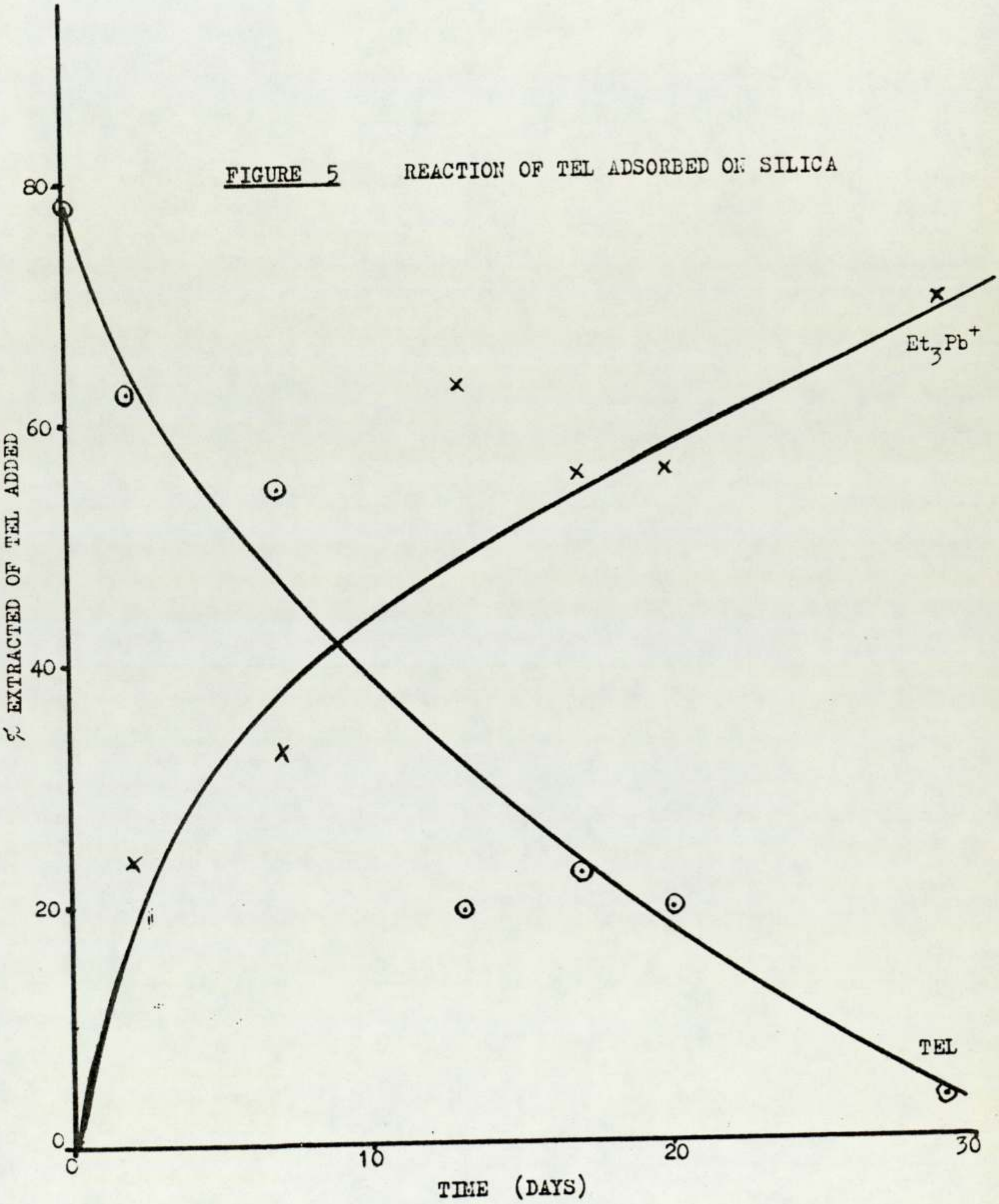


FIGURE 5 REACTION OF TEL ADSORBED ON SILICA

isolate or identify this 27%. The analysis after 13 days appears anomalous to the general trend of results, no reason for this anomaly is immediately apparent.

TABLE 22

STABILITY OF TEL ADSORBED ON SILICA

Time (Days)	% Extracted of TEL Added TEL	 Et_3Pb^+	 Et_2Pb^{++}
0	78	-	-
2	62.5	23.3	0
7	54.4	32.7	0
13	19.2	63	0
17	22.2	55.4	0
20	19.4	55.9	0
29	3.1	69.7	0

5.3.2. TETRAMETHYL LEAD

As with TEL a number of identical samples were prepared consisting of silica (10 g) suspended in distilled water (50 ml) to which TML (530 μg as Me_2Pb^{++}) was added. The samples were stoppered, shaken then stored in the dark. Analysis of the aqueous layer indicated total adsorption of the TML by the silica. The change in concentration of the organolead compounds adsorbed on the silica was determined with time. Each analysis was carried out in duplicate and the results are shown in table 23 and figure 6 . As can be seen from table 23 there is poor agreement of duplicate samples, despite identical procedures, however figure 6

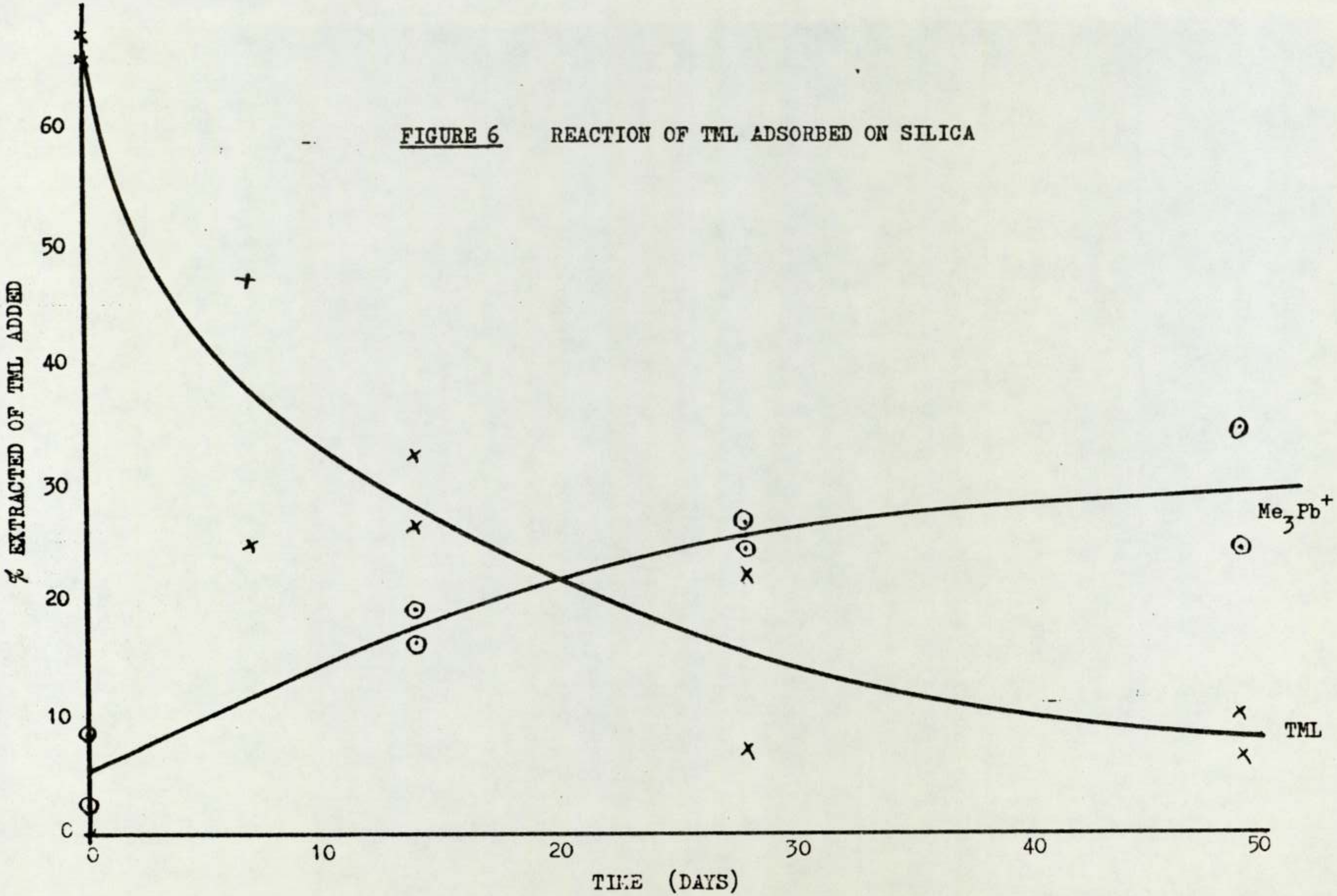


FIGURE 6 REACTION OF TML ADSORBED ON SILICA

shows that the general trend is a breakdown of TML to give Me_3Pb^+, Me_2Pb^{++} was undetectable except at time 0 when 1.7% and 0.6% of Me_2Pb^{++} were recovered. As with the TEL there is a percentage of material unaccounted for, again this is assumed to be irreversibly adsorbed or to have reacted to give inorganic lead.

TABLE 23

STABILITY OF TML ADSORBED ON SILICA

Time (Days)	% recovery of TML added TML	Me_3Pb^+	Me_2Pb^{++}
0	67.5	2.4	1.7
	65.7	8.4	0.6
7	24.4	-	-
	47	-	-
14	26	16.3	0
	32	19.1	0
28	7	24	0
	22	25.2	0
49	10	34.2	0
	6.3	24.1	0

The effect of allowing the silica to dry while TML was adsorbed on it, was also examined. Two samples were filtered 2 hours after the addition of TML, the silica was then air dryed overnight. Some 24 hours later the silica was analysed by the usual procedure. Neither TML or Me_2Pb^{++} were detected in either sample. Trimethyl lead (83 μg as Me_2Pb^{++}) was recovered from both samples. It is unlikely that the TML evaporated from the silica and therefore it would appear that drying greatly increases the rate of breakdown to inorganic lead.

5.3.3. TRIETHYL LEAD CHLORIDE

A number of identical samples were prepared consisting of silica (10 g) suspended in distilled water (50 ml) to which Et_3PbCl (650 µg as Et_2Pb^{++}) was added. The samples were shaken and stored in the dark. The samples were analysed for alkyl lead salt content with time. The results are shown in table 24. In all cases total adsorption of the Et_3PbCl occurred.

TABLE 24

STABILITY OF Et_3PbCl ADSORBED ON SILICA

Time	% recovery of Et_3PbCl added	
Days	Et_3Pb^+	Et_2Pb
0	94	0
	95	0
21	78.2	1.9
	74.5	4.6
42	77	3.7
	78.1	6
84	68	6.9
	69.4	5

It can be seen from table 24 that Et_3PbCl is relatively stable while adsorbed on silica with only a 26% decomposition in 84 days, and of this only 6% reacted to form Et_2Pb^{++} , the remaining 20% was not identified and was probably inorganic lead. The maximum decomposition was during the first 21 days, when 18 % of the Et_3PbCl added underwent decomposition.

5.3.4. TRIMETHYL LEAD CHLORIDE

A number of samples were prepared consisting of silica (10 g) suspended in distilled water (50 ml) to which Me_3PbCl (666 μg as Me_2Pb^{++}) had been added. The samples were shaken and stood in the dark, they were analysed in duplicate for methyl lead salt content, with varying time. The results are shown in table 25.

TABLE 25

STABILITY OF Me_3PbCl ADSORBED ON SILICA

Time (Days)	% recovery of Me_3PbCl added	
	Me_3Pb^+	Me_2Pb^{++}
0	95	0
	96	0
14	84	0
	85	0
28	84	0
	81	0

Other samples of Me_3PbCl were filtered and the silica was allowed to air dry in the dark, it was then analysed for alkyl lead salt content after 5 and 15. The results are shown in table 26.

TABLE 26

STABILITY OF Me_3PbCl ADSORBED ON SILICA AND AIR DRYED

Time	% recovery of Me_3PbCl added	
(Days)	Me_3Pb^+	Me_2Pb^{++}
5	100	0
15	92	0

Total adsorption of the Me_3PbCl occurred in all cases. Me_3PbCl shows no tendency to form Me_2Pb^{++} while adsorbed on silica, whether the silica is wet or dry. Table 26 shows that 8% decomposition occurred during a 10 day period on the dry silica. Table 25 indicates that maximum reaction took place during the first 14 days, when 11% decomposition occurred, compared with only 2% in the second 14 day period. Again the decomposition product or products were not identified but were assumed to be inorganic lead.

CHAPTER SIX

REACTIONS BETWEEN ALKYL LEAD COMPOUNDS AND SULPHIDE IONS

REACTIONS BETWEEN ALKYL LEAD COMPOUNDS AND SULPHIDE IONS

6.1. INTRODUCTION

When other workers in these laboratories reacted organolead salts with natural sediments, the evolution of a pungent odour was noticed, this odour only occurred after the organolead salt had been added. When Et_3PbCl was the added salt, an analysis of the odour established the presence of diethyl sulphide, which has a pungent odour, and TEL. If Me_3PbCl was the added salt, then dimethyl sulphide and TML were identified in the atmosphere above the sediment. The formation of TAL from trialkyl lead ions suggests that an alkylation reaction could be taking place, possibly involving sulphur.

Biological methylation of certain metals and metalloids was established many years ago[94], while that of mercury has only recently been discovered[95] following the deaths of 41 people and 111 cases of poisoning in the Minamata area of Japan. Inorganic mercury was disposed of by industry into a river estuary, this underwent bacteriological methylation forming the highly toxic monomethyl mercury, and this was then concentrated in the tissue of fish which formed the staple diet of the local inhabitants[96]. The natural methylation of mercury has been reviewed[97, 98]. It has been shown that two mechanisms exist for the methylation of mercury. A non-enzymatic route involving methyl cobalamin, a vitamin B_{12} derivative, which readily methylates mercuric salts[99, 100] and which is present in many natural species known to methylate mercuric salts. However other organisms have been known to methylate mercuric salts when methyl cobalamin is absent, and for them an enzymation route has been proposed[101].

The biological methylation of lead was first reported in 1975 by Wong and co-workers[102], who stated that the addition of lead nitrate or trimethyl lead acetate to lake sediment incubated under anaerobic conditions, greatly increased the formation of TML. All sediments produced TML from trimethyl lead acetate but only certain sediments produced TML from lead nitrate or chloride, no TML was produced from lead hydroxide, cyanide, oxide, bromide or palmitate when added to sediment.

A more detailed investigation of this work seemed desirable because in the U.K. alone over 12,000 tonnes of inorganic lead are released into the environment annually from motor vehicles, and should all or part of this total be methylated to TAL or trialkyl lead ions, serious consequences could result[103].

6.2. METHYLATION OF LEAD

By analogy with the methylation of mercury a possible mechanism for the methylation of lead is by a methyl group transfer from methyl cobalamin. However in the case of lead this would lead to the formation of a monomethylated species as an intermediate and such a species is known to be very unstable[35]. The di and trialkyl lead compounds should if methylated form trialkyl and TAL compounds respectively.

No reaction is reported to occur between methyl cobalamin and Me_3PbOAc, Me_3PbCl, Me_2PbCl_2 and $Pb(NO_3)_2$ in aqueous solution over 21 days[104], nor was any ^{14}C-TML formed from Pb^{++} and ^{14}C-methyl cobalamin[105]. The demethylation of methyl cobalamin however has been reported[106], when it reacted with $Pb(OAc)_4$, no reaction was evident with Pb^{++}. No organolead product was identified and the methyl group was lost by volatilisation. Thus the methylation observed by Wong[102] must be via an enzymatic pathway or possibly via a chemical reaction.

Using natural sediment and anaerobic incubation it was found that the formation of TML from Me_3Pb^+ ions was repeatable but that the formation of TML from Pb^{++} was not[104].

It is known that salts of the type R_3PbX tend to disproportionate as follows:

$$2R_3PbX \longrightarrow R_4Pb + R_2PbX_2$$

where the weaker is the acid HX, the greater is the tendency to disproportionate[34]. Hydrogen sulphide is a weak acid and the organolead sulphide would be expected to undergo extensive disproportionation reactions.

When dilute solutions of Me_3PbCl were reacted with Na_2S the formation of TML was evident within 24 hours, while solutions of Me_3PbCl without added Na_2S produced no detectable amount of TML. It seems likely therefore that the apparent methylation of trimethyl lead ions is in fact a two stage chemical reaction where the trimethyl lead sulphide is initially formed and then undergoes a disproportionation reaction to give TML as one of the products.

When Et_3PbCl was added to sediment and incubated under anaerobic conditions, the only detectable TAL compound produced was TEL[104], the formation of Et_3PbMe would have been anticipated if the reaction is a biological methylation, where as the formation of TEL supported the chemical disproportionation theory.

Sulphur is present throughout the environment in a number of oxidation states[107], as hydrogen sulphide it is liberated by many organisms under anaerobic conditions. This would normally react with dissolved heavy metal ions forming the insoluble sulphide. If alkyl lead salts were present we would expect that they would compete with other cations for the sulphide. Wong and co-workers[102] suggest that autoclaving the sediment, prior to the addition of Me_3PbOAc, prevented the formation of TML. Autoclaving of the sediment has the effect of destroying all biological activity which includes the formation of hydrogen sulphide, thus if the sulphide disproportionation mechanism is correct the formation of TML from Me_3PbOAc would not be expected following autoclaving of the sediment.

This mechanism explains the formation of TML from Me_3PbOAc in natural sediment, however it offers no explanation of the reported formation of TML from inorganic lead ions[102]. This mechanism however must be very selective since TML is formed from lead nitrate and dichloride by certain sediments only, but not from lead bromide, hydroxide, cyanide, oxide or palmitate[102]. The mechanism must also involve the transfer of two alkyl groups before the lead species becomes free in order to overcome the instability of the monoalkyl lead ion[35]. We decided to study the reactions between organolead compounds and sulphide ions in more detail following the above observations.

6.3. PROPERTIES OF ORGANOLEAD SULPHIDES

Alkyl lead sulphides are usually prepared by metathetical reactions of the type:

$$2R_3PbX \quad + \quad Na_2S \longrightarrow (R_3Pb)_2S \quad + \quad 2NaX$$

They are usually covalently bonded and show a tendency to be unstable, oxidizing slowly in air to the alkyl lead sulphate, this reaction is used as a method of preparation of the alkyl lead sulphates[16]. Triethyl lead sulphide ($(Et_3Pb)_2S$) is a liquid (m.p. -45.1 °C). The synthesis of organolead sulphide compounds has been reviewed[108], while the preparation of a number of them has been patented because of their potential antiknock properties[109,110].

6.4. ANALYTICAL TECHNIQUE WITH ORGANOLEAD SULPHIDES

To separate TAL and organolead salts in aqueous solution the TAL compounds are normally removed by solvent extraction with benzene, where organolead sulphides were also present it was found that they too were extracted by the benzene. In the presence of excess sulphide ions, total extraction of Et_3Pb^+, Et_2Pb^{++}, Me_3Pb^+ and Me_2Pb^{++} occurred, if organolead ions were in excess then it was found that the dialkyl lead ions were extracted preferentially. When the aqueous layer was acidified prior to extraction, no organolead salts were extracted by the benzene. Any organolead sulphide previously extracted by benzene, could be transferred back to an aqueous phase by shaking with dilute acid.

In this work, when sulphide ions were present the sample was acidified prior to extracting the TAL compounds. The acidification had no effect on the determination of the alkyl lead salts by the P.A.R. method.

6.5. STABILITY OF ALKYL LEAD SULPHIDE

6.5.1. INITIAL OBSERVATIONS OF THE REACTION BETWEEN TRIALKYL LEAD ION AND SULPHIDE ION

When the atmosphere in a sealed flask containing an aqueous solution of Me_3PbCl and Na_2S was analysed for TAL content, TML was detected, no TML was detected above a similar solution containing only Me_3PbCl. Similar results were obtained with a corresponding aqueous solution of Et_3PbCl and Na_2S. When equimolar concentrations of Me_3PbCl and Et_3PbCl were reacted with Na_2S, four of the possible five ethyl methyl TAL compounds were detected. The concentrations in decreasing order of magnitude were:

$$\mathrm{TML} > Et_3MePb > Et_4Pb > EtMe_3Pb$$

The results suggest a single alkyl group transfer, with the methyl group migrating more readily than the ethyl group, hence the higher concentration of Et_3MePb compared to $EtMe_3Pb$. The absence of Et_2Me_2Pb indicates that a single alkyl group migration is occurring.

A strong characteristic odour of an alkyl sulphide was noticed in all cases, no attempt was made to identify this other product at this stage.

Low concentrations of sulphide ions in distilled water were unstable, with the sulphide being oxidized to sulphate. An aqueous solution of Na_2S (10^{-4} M) was fully oxidised in under 48 hours. To overcome this problem when studying a reaction over a period of time, additional sulphide was added every 24 - 48 hours.

6.5.2. STABILITY OF BIS TRIMETHYL LEAD SULPHIDE

An aqueous solution (500 ml) of Me_3PbCl (27 $\mu g\,ml^{-1}$ as Me_2Pb^{++}) was reacted with $Na_2S.7H_2O$ (0.01 g) in a stoppered flask and stored in the dark. The concentration of the methyl lead salts was determined with time, and the results are shown in table 27.

TABLE 27

STABILITY OF $(Me_3Pb)_2S$

Time (Days)	concentration in $\mu g\ ml^{-1}$ (as Me_2Pb^{++})	
	Me_3Pb^+	Me_2Pb^{++}
0	27	0.15
3	23	1.4
5	21.2	1.4
7	18.0	0.0
10	14.6	0.0

After each analysis $Na_2S.7H_2O$ (0.01 g) was added to the reaction. In the atmosphere above the reaction TML and dimethyl sulphide were identified.

A further experiment was carried out to determine the amount of TML produced. Trimethyl lead chloride was reacted with excess sulphide ions over 12 hours, after which period the system was analysed for organolead content. The results of duplicate samples are shown in table 28. Of the Me_3Pb^+ that reacted, 22% was found to be TML, 11% to be Me_2Pb^{++} and the remaining 67% was inorganic lead.

TABLE 28

MASS BALANCE OF DECOMPOSITION OF $(Me_3Pb)_2S$

	SAMPLE A	SAMPLE B
Me_3Pb^+ initially present	568	568
Me_2Pb^{++} " "	0.0	0.0
Me_3Pb^+ present after 12 hours	471	478
Me_2Pb^{++} " " "	11.0	11.0
TML " " "	21.9	20.8

All values as Me_2Pb^{++} (μg)

6.5.3. STABILITY OF DIMETHYL LEAD SULPHIDE

An aqueous solution (500 ml) of Me_2PbCl_2 (19 μgml^{-1} as Me_2Pb^{++}) was reacted with $Na_2S.7H_2O$ (0.02 g) and stored in the dark. After 12 hours a black precipitate indicated the presence of inorganic lead. An analysis of the aqueous indicated the total absence of Me_2Pb^{++}, however Me_3Pb^+ ions were determined at a concentration of 8.0 μgml^{-1}. A large amount of TML together with a trace of dimethyl sulphide was determined in the atmosphere above the solution.

6.5.4. STABILITY OF BIS TRIETHYL LEAD SULPHIDE

To an aqueous solution (500 ml) of Et_3PbCl (25.7 μgml^{-1} as Et_2Pb^{++}) $Na_2S.7H_2O$ was added, the solution was shaken then stored in the dark. The variation in concentration of ethyl lead salts with time is shown in table 29. Following each analysis a further $Na_2S.7H_2O$ (0.01 g) was added. In the atmosphere above the reaction both TEL and diethyl sulphide were identified.

TABLE 29

STABILITY OF $(Et_3Pb)_2S$

Time (Days)	concentration as Et_2Pb^{++} (μgml^{-1})	
	Et_3Pb^+	Et_2Pb^{++}
0	25.7	0
3	24.6	0
5	23.0	0
8	21.7	0

6.5.5. STABILITY OF DIETHYL LEAD SULPHIDE

An aqueous solution of Et_2PbCl_2 (500 ml) was reacted with $Na_2S.7H_2O$ (0.02 g). The variation in concentration of ethyl lead salts with time is shown in table 30. Following each analysis $Na_2S.7H_2O$ (0.02 g) was added.

TABLE 30

STABILITY OF Et_2PbS

Time (Days)	concentration as Et_2Pb^{++} (μgml^{-1})	
	Et_3Pb^+	Et_2Pb^{++}
0	2.73	11.03
1	2.95	6.59
2	2.71	3.70
4	3.05	0

From table 30 it can be seen that diethyl lead ion is rapidly decomposed. As the initial sample of Et_2Pb^{++} was contaminated with

Et_3Pb^+ the formation of Et_3Pb^+ as a product is not clear. To establish this, a further experiment was carried out using pure Et_2Pb^{++}. The results are shown in table 31.

TABLE 31

PRODUCTION OF Et_3Pb^+ FROM Et_2PbS

Time	weight as Et_2Pb^{++} (μg)	
(Days)	Et_3Pb^+	Et_2Pb^{++}
0	0	366
1	13.6	29.1

A large quantity of diethyl sulphide was also detected above the reaction mixture. From table 31 it can be seen that the decomposition of Et_2PbS (357 μg as Et_2Pb^{++}) produced only 13.6 μg of Et_3Pb^+.

6.6. REACTION OF TEL WITH SULPHIDE IONS

The reaction of TEL with sulphide ions in the absence of light gives a result typical of the reaction of TEL in distilled water under similar conditions.

6.7. CONCLUSION

Sulphide ions have been shown to react positively with both di and tri methyl and ethyl lead salts. The salts appear to be reacting according to previously reported disproportionation reaction for alkyl lead salts[16], equations

$$2R_3PbX \longrightarrow R_2PbX_2 + R_4Pb$$

$$2R_2PbX_2 \longrightarrow R_3PbX + RX + PbX_2$$

The final product of any reaction will therefore depend on the relative rates of disproportionation together with the amount of excess sulphide present. However the overall effect is the formation of TAL but with a large reduction in the total organolead content of the system. The alkyl sulphides, also formed as a product, are already present in the environment from natural biological processes[111].

CHAPTER SEVEN

SUMMARY OF RESULTS AND THEIR RELEVANCE TO THE ENVIRONMENT

SUMMARY OF RESULTS AND THEIR RELEVANCE TO THE ENVIRONMENT

7.1. INTRODUCTION

We have investigated the effect of a number of parameters on the breakdown of alkyl lead compounds in aqueous systems. This investigation was conducted using relatively simple model systems which differ markedly from complex natural water systems, however we feel that the results of these studies could make a significant contribution to the study of the pollution of the aqueous environment by alkyl lead compounds.

The parameters which were investigated included light, surface area, and the effect of a number of anions and cations. It was not possible in the time available to investigate the influence of such parameters as temperature, pH or redox potentials.

7.2. TETRA-ALKYL LEAD COMPOUNDS

In the dark a solution of TEL in distilled water was stable with only 2% decomposition to Et_3Pb^+ over 77 days, there was however extensive loss of TEL from solution by adsorption onto the glass walls. The TEL was recoverable from the walls by extraction with benzene. Solutions containing Cu^{++} or Fe^{+++} ions in the absence of light promoted the breakdown of TEL to form Et_3Pb^+, the rate of reaction being proportional to the concentration of the metal ion. In solutions containing 20 mgl^{-1} and 1 mgl^{-1} of Cu^{++}, 30% and 2% respectively of TEL reacted to give Et_3Pb^+ over a ten day period. Only traces of Et_2Pb^{++} were produced in these reactions.

When exposed to sunlight, aqueous solutions of TEL rapidly decomposed, initially to give Et_3Pb^+ and finally to Pb^{++}. The maximum concentration of Et_3Pb^+ was attained after 4 days and corresponded to an 18% conversion of TEL, after 15 days only 1% of TEL remained unreacted. Aqueous solutions of TML reacted fairly rapidly in both the light and the dark. Over a 22 day period 59% and 16% respectively reacted to give Me_3Pb^+, also only in the dark was there evidence that TML was removed from solution by adsorption onto the glass walls.

The order of stability in the light and the dark is shown below:

Light TML $>$ TEL

Dark TEL $>$ TML

The fact that the order is reversed between the light and the dark implies that the dark and light reactions follow different mechanisms. We have not made any mechanistic studies, however on the basis of other evidence, one possible explanation of the different reactivity in the light and dark is that the light reaction is a free radical process and the dark reaction a polar process[16].

Both TML and TEL were totally adsorbed from aqueous solutions onto silica, once adsorbed both underwent decomposition with R_3Pb^+ being the only detectable organolead product. Analysis of the silica after 29 days indicated that 99% of the TEL had decomposed to give 70% of Et_3Pb^+ and no other organolead product, the remaining products were not determined, but were assumed to be inorganic lead. In the case of TML, after 28 days, 85% had decomposed to give only 25% of Me_3Pb^+, again no other organolead product was found and the remaining TML was assumed to have reacted to give inorganic lead.

The order of stability of the TML and TEL on silica is the same as that observed for the reaction in aqueous solution in the light i.e. TML $>$ TEL, however from the analysis of the products formed it would appear that on silica Et_3Pb^+ is more stable than Me_3Pb^+ (vide infra).

7.3. TRIALKYL LEAD COMPOUNDS

In the absence of light, aqueous solutions of the trialkyl lead compounds (Me_3PbCl, Et_3PbCl and Bu_3PbCl) appeared stable, the only minor exception to this being Me_3PbCl which decomposed by 10% over 220 days. Cu^{++} ions in solution did not promote the decomposition of Et_3PbCl.

In the light the order of stability was:

$$Me_3Pb^+ > Bu_3Pb^+ > Et_3Pb^+$$

over a 15 day period there was some 4% loss of Me_3Pb^+, 25% loss of Bu_3Pb^+ and 99% loss Et_3Pb^+. The final product in all cases was inorganic lead, however with Et_3Pb^+ a trace of Et_2Pb^{++} was also detected.

The normal order of stability in the light is again apparent with Me_3Pb^+ the most stable. The solutions of Me_3Pb^+ and Bu_3Pb^+ were studied under identical conditions, however the Et_3Pb^+ solution was studied under different conditions (i.e. different time of the year, therefore different amounts of light) and therefore we feel that we cannot compare the reactivity of Et_3Pb^+ to the other two compounds on a strict basis.

Both Et_3Pb^+ and Me_3Pb^+ were totally adsorbed from aqueous solution by silica. After 28 days 16% of the Me_3Pb^+ had decomposed to give inorganic lead with no formation of Me_2Pb^{++}. After 84 days 26% of the Et_3Pb^+ had decomposed to give 6% of Et_2Pb^{++} and the rest as inorganic lead. These results agree with those observed during the decomposition of TEL and TML while adsorbed on silica when R_3Pb^+ is formed as a product

$$\text{i.e.} \quad Et_3Pb^+ > Me_3Pb^+$$

In the presence of sulphide ions the R_3Pb^+ compounds reacted to give the trialkyl lead sulphides, which are unstable even in the dark, and disproportionate to give R_4Pb and R_2Pb^{++}. In the presence of excess sulphide ion the R_2Pb^{++} will react further to give the dialkyl lead sulphide which also undergoes disproportionation to give R_3Pb^+ and inorganic lead, hence the final product will depend on the relative concentration of organolead salts and sulphide ions. In the case of excess sulphide ions the final product will be R_4Pb and inorganic lead. The decomposition of alkyl lead sulphide takes place over a matter of hours and proceeds in the absence of light. Alkyl sulphides are also produced during these reactions. Due to the complex nature of reactions no attempt was made to establish the relative stabilities of the methyl and ethyl lead sulphides.

7.4. DIALKYL LEAD COMPOUNDS

Aqueous solutions of R_2Pb^{++} compounds in the dark are less stable than R_3Pb^+ solution under identical conditions. After 71 days, 16% of a Me_2Pb^{++} solution had decomposed, some 3% of which had formed Me_3Pb^+, similarly a Bu_2Pb^{++} solution decomposed some 4% with about 1% formation of Bu_3Pb^+. Over 101 days a solution of Et_2Pb^{++} reacted to give a 14% loss of starting material and 2% formation of Et_3Pb^+, while the same solution over 313 days decomposed by 30%, giving some 6% Et_3Pb^+ as a product. These results suggest an order of stability of:

$$Bu_2Pb^{++} \gg Et_2Pb^{++} > Me_2Pb^{++}$$

This agrees with the relative stabilities found for aqueous solutions of R_4Pb and R_3Pb^+ in the dark. The formation of R_3Pb^+ as a product suggests the reaction is in part at least a disproportionation reaction.

In the light the order of stability, as normal, is reversed as shown below, together with the percentage reacted over 40 and 204 days.

	Me_2Pb^{++} >	Et_2Pb^{++} >>	Bu_2Pb^{++}
40 Days	5	26	69
204 Days	40	99	100*

* Bu_2Pb^{++} had completely decomposed after 101 days.

In all cases R_3Pb^+ ions were again found suggesting a disproportionation reaction, however only with Me_2Pb^{++} was there a significant build up in concentration of the trialkyl lead ion determined. After 204 days, 14% of the Me_2Pb^{++} had been converted to Me_3Pb^+. This ion was observed to be the most stable of the R_3Pb^+ ions studied during the investigation of their stability in the light.

7.5. ENVIRONMENTAL ASPECTS

It has been shown that the toxic species in TAL poisoning is the trialkyl lead ion, with the symptoms for both TEL and Et_3Pb^+ poisoning being identical but different from diethyl lead or inorganic lead poisoning which are themselves similar[18]. Trialkyl lead salts are by far more toxic than either dialkyl lead or inorganic lead compounds[17]. The toxicity of R_2Pb^{++} compares with inorganic lead, however the solubility of the R_2Pb^{++} will be greater permitting increased mobility.

The conversion of TAL to the toxic species R_3Pb^+ by sunlight, Cu^{++} and Fe^{+++} also means that a more readily soluble form of organolead is produced, this could help to spread any localized pollution aided by natural water movements. In the light however R_3Pb^+ is unstable and will be converted to inorganic lead, and only in the case of Me_3Pb^+ is there the slight possibility that any trialkyl lead ions would persist. The fate of any dialkyl lead ions in solution in the light will be the same with again the Me_2Pb^{++} being the most stable dialkyl lead species studied. In the environment it is unlikely that in any aqueous system exposed to sunlight, appreciable concentrations of organolead compounds could remain.

If it is assumed that silica behaves in a similar manner to natural particulate matter, then all three forms of organolead compounds (TAL, R_3Pb^+, and R_2Pb^{++}) will be removed from solution by adsorption and concentrated in the sediment[10] where a slow decomposition will occur to give inorganic lead as the final product. The adsorption effectively removes the alkyl lead from the solution, however it could still pose a toxic threat to animals or fish, ingesting sediment as part of their normal life style. Following ingestion the alkyl lead species may then be desorbed from silica and retained within the creatures body. This could lead to the poisoning of a whole range of creatures in a food chain.

The major environmental consideration of the reactions involving sulphide ions, is that the total organolead content of a system will be rapidly reduced to give the TAL and inorganic lead, assuming an excess of sulphide ions. (Sulphide ions are readily formed under anaerobic conditions in bottom sediments, and under such conditions would normally be in excess). If other species are present, capable of reacting with TAL to give an alkyl lead salt, then the only product will be inorganic lead, in the absence of such species it should be remembered that a toxic volatile organolead compound will be produced.

7.6. CONCLUSIONS

When consideration is given to our observations it is difficult to envisage how, other than under exceptional conditions, the concentration of alkyl lead compounds in the aqueous environment could reach any significant level.

The biological methylation of lead which has been reported by several authors[102,112], is beyond the scope of this present work, and cannot be commented on except to say that the TML, once formed, would be subject to the reactions studied in this work.

The methyl lead compounds are more stable, and on this evidence the use of TEL should be encouraged so as to reduce the amount of TML used as a petrol additive. However, regardless of the type of organolead compounds the final product in any decomposition of organolead must inevitably be inorganic lead, a toxic element which is accumulative and particularly dangerous to the embryonic and infant stages of all species, therefore the use of any lead compound should be kept to a minimum and, where suitable alternatives exist, eliminated.

EXPERIMENTAL

EXPERIMENTAL

1. GENERAL

Unless otherwise stated the following terms, reagents and experimental conditions were used throughout this work.

1.1. REAGENTS

All reagents were A.R. grade.

Ether unqualified refers to diethyl ether.

Water refers to distilled water.

HNO_3 refers to concentrated nitric acid.

HCl refers to concentrated hydrochloric acid.

Samples of the following chemicals were kindly supplied by the Associated Octel Company Ltd:

Tetraethyl lead (pure)	(Et_4Pb, TEL)
Tetramethyl lead (80% in toluene)	(Me_4Pb, TML)
Mixed alkyl leads (TEL/TML, 50/50 catalytically redistributed)	
Triethyl lead chloride	(Et_3PbCl)
Trimethyl lead chloride	(Me_3PbCl)
Diethyl lead dichloride	(Et_2PbCl_2)
Dimethyl lead dichloride	(Me_2PbCl_2)

1.2. GENERAL TECHNIQUE

Evaporation of solvents was carried out using a rotary evaporator the vacuum for which was provided by a water pump.

Wide range universal indicator paper (Johnsons) was used for pH measurements.

2. EXPERIMENTAL WORK RELATING TO CHAPTER TWO

2.1. PREPARATION OF ALKYL LEAD SALTS

All confirmatory T.L.C. work was carried out on silica plates eluted with acetic acid/toluene (1:3).

2.1.1. Et_3PbCl

2.1.1.1. To ether (25 ml) saturated with HCl gas, TEL (4.0 ml) was added dropwise with continuous stirring and cooling. A white precipitate formed immediately. The mixture was maintained at 0°C for 20 minutes then at room temperature for 30 minutes, the white solid was then filtered off. Yield 4.9 g (74%). Its identity was confirmed by T.L.C. against a genuine sample. The prepared Et_3PbCl was impure with a second spot corresponding to Et_2PbCl_2 present.

2.1.1.2. To EtMgBr, prepared from Mg (10 g) and EtBr (44 g) in anhydrous ether (200 ml), lead chloride (56 g) was added over 5 - 10 minutes with vigorous stirring, while the temperature was maintained at 0°C - 10°C. The mixture was stirred for 1 hour at 0°C, then refluxed for 1 hour. The excess Grignard was quenched with water and the ether layer was separated and dried using anhydrous $MgSO_4$.

The ether layer was cooled using a dry ice/acetone mixture, and then HCl gas was bubbled through until all reaction had ceased, the mixture was allowed to attain room temperature and the white solid was filtered off. Yield 21.5 g (65%). T.L.C. confirmed its identity when run against pure Et_3PbCl. The sample was again contaminated with Et_2PbCl_2 as indicated by a salmon red spot.

2.1.2. Et_3PbBr

TEL (1 ml) in ether (50 ml) was maintained at -70°C using dry ice/acetone. Bromine solution (1% $^{V}/v$ in ether) (12.5 ml) was added dropwise with stirring. After addition of the bromine was complete the mixture was stirred for 10 mins at -70°C then allowed to attain room temperature. The ether was filtered to remove Et_2PbCl_2 and then evaporated leaving Et_3PbCl. Yield 1.3 g (68%). T.L.C. confirmed the presence of a trialkyl salt contaminated by dialkyl lead ions.

2.1.3. Et_3PbOH

Et_3PbCl (1 g) in benzene (15 ml) was shaken with NaOH (5.6 g) in water (8.4 ml) for 20 minutes. The white solid formed in the lower layer was filtered off, extracted with hot benzene, filtered and recrystallised at 0°C. The identity was confirmed by T.L.C.. The absence of chloride ions was confirmed by a negative reaction with aqueous silver nitrate solution under acid conditions.

2.1.4. Et_3PbOAc

TEL (3.3 ml) in glacial acetic acid (1.0 ml) and a small amount of silica (M.F.C., 80 - 200 mesh) were heated under reflux. After 60 minutes the mixture, which had solidified, was filtered and the solid recrystallised from benzene. Yield 3.5 g (58%). T.L.C. confirmed the sample was a trialkyl lead salt. M.p. 158°C (lit, 160°C).

2.1.5. Me_3PbI

TML (2.5 ml) in pentane (20 ml) was maintained at -70°C using dry ice/acetone. Iodine (4 g) in pentane (200 ml) was added dropwise over 20 minutes while the solution was continuously stirred. Stirring was continued for a further 10 minutes then the solution was allowed to attain room temperature. A yellow solid was filtered off. Yield 3.9 g (55%). T.L.C. of the product indicated the presence of trialkyl lead contaminated with both dialkyl and inorganic lead. No attempt was made to purify the product.

2.1.6. Me_3PbBr

TML (2.5 ml) in pentane (20 ml) was maintained at -70°C using dry ice/acetone. Bromine (2.4 g) in pentane (100 ml) was added dropwise over 20 minutes. The reaction was stirred continuously. After a further 10 minutes the mixture was allowed to attain room temperature. The white solid which had formed was filtered off. The solid was dissolved in ether, filtered then recrystallised by the addition of pentane. Yield 4.2 g (68%). T.L.C. confirmed the presence of a pure trialkyl lead salt.

2.1.7. Bu_3PbCl

The Grignard reagent was formed from Mg (14 g) and butyl bromide (68.7 g) in anhydrous ether (250 ml). Lead chloride (69.5 g) was added with vigorous stirring over 10 to 15 minutes, and the temperature was maintained below 10°C. Stirring was continued for 1 hour at 0°C and for a further hour while refluxing. Excess Grignard was quenched with water and the ether layer separated and dried with anhydrous $MgSO_4$.

Hexane (250 ml) was added to the mixture and ether was distilled off until the temperature of the distillate reached 55°C. The mixture was then cooled using dry ice/acetone, chlorine gas was added until in excess (i.e. a positive reaction with wet starch iodide paper). The mixture was then allowed to attain room temperature slowly. The mixture was filtered to remove dibutyl lead dichloride and inorganic lead, the solvent was evaporated to give Bu_3PbCl. Yield 44 g (84%). T.L.C. confirmed its identity.

2.1.8. $Et_2Pb(OH)_2$

Et_2PbCl_2 (3 g) in ether (30 ml) was shaken with NaOH (3 g) in water (10 ml). The white suspension disappeared from the ether layer and the aqueous layer turned cloudy. The mixture was left overnight, the ether decanted and the solid at the interface filtered off and dried under vacuum over P_4O_{10}. The T.L.C. gave a salmon red spot. The absence of chloride ions was confirmed by a negative reaction with an acidified aqueous solution of silver nitrate.

2.2. STANDARD SOLUTIONS

2.2.1. TEL

With a 10μl syringe TEL (10μl) was added to benzene (200 ml) in a volumetric flask to form a 50 p.p.m. standard solution. This solution was freshly made every three months, however good agreement was always found between old and new indicating the standard was stable over those three months. Lower standards were prepared by suitable dilution with benzene.

The accuracy of the standard solutions was checked by A.A.S.. To 5 ml of standard (50 p.p.m.) excess bromine (0.1 ml) was added and then evaporated to dryness. Any residue was dissolved in aqueous nitric acid (1% $^{V}/v$) (250 ml) and the Pb^{++} concentration determined by A.A.S..

2.2.2. TML

TML (10μl) was added, using a 10μl syringe to benzene (200 ml) forming a 50 p.p.m. standard solution. Since TML was supplied as a mixture with toluene its true concentration was determined as follows:

Excess bromine (0.1 ml) was added to 5 ml of standard, followed by evaporation of the solvent. Any residue was dissolved in aqueous nitric acid (1% $^{V}/v$) (250 ml) and the Pb^{++} concentration determined by A.A.S..

5 ml of 50 p.p.m. standard was diluted with benzene (approx 45 ml), then excess bromine (0.1 ml) was added followed by water (50 ml). After shaking, sodium thiosulphate (1% $^{W}/v$ aqueous solution) was added to remove excess bromine. The aqueous layer was separated and the extraction repeated with a further 25 ml of water. The aqueous layers were combined and made up to 100 ml in a volumetric flask. The dimethyl lead ion content of the solution was determined by the P.A.R. method using 5 ml samples.

For water miscible solvents a suitable aliquot (1.0 ml) containing between 10 and 100μg R_2Pb^{++} was analysed as a normal sample by the P.A.R. method.

2.2.3. TRIALKYL LEAD SALT STANDARDS

All salts were purified immediately before the preparation of standard solutions. Me_3PbCl and Et_3PbCl were purified as follows:

The salt (1 g) was dissolved in the minimum amount of CCl_4, filtered to remove dialkyl lead and inorganic lead salts, and hexane was added to precipitate pure trialkyl salt.

Bu_3PbCl was purified by recrystallization from acetone at -60°C.

2.2.4. DIALKYL SALTS

All salts were purified immediately before the preparation of standard solutions.

2.2.4.1. Bu_2PbCl_2 AND Et_2PbCl_2

The salt (1 g) was washed with ether (50 ml) to remove trialkyl salts. The salt was then dissolved in acetone and filtered to remove inorganic lead. The addition of ether precipitated the pure dialkyl salt.

2.2.4.2. Me_2PbCl_2

No suitable solvent could be found to recrystallise Me_2PbCl_2. However the salt was freed of Me_3PbCl by washing with ether. Hence solutions of Me_2PbCl_2 were standardised against a standard solution of Me_3PbCl by the P.A.R. method.

2.3. CATION EXCHANGE RESINS

The cation exchange resin used throughout was Dowex 50W - X8 (18 - 52 mesh), supplied in the hydrogen form. New resin (15 ml) was used for each experiment. When used on the H^+ form, the resin was washed with aqueous HCl solution (4% $^v/v$) (100 ml) then water until the eluate was chloride free as shown by a negative reaction with silver nitrate solution. When used in the Na^+ form the resin was washed with aqueous NaCl (4% $^w/v$) (100 ml) then water, until the eluate was again chloride free.

2.3.1. ANALYSIS OF FRACTIONS

All fractions collected were analysed by A.A.S.. Aqueous samples were adjusted to 1% $^{v}/v$ nitric acid by the addition of concentrated acid. Organic solvents were evaporated to dryness and the residue taken up in aqueous nitric acid (1% $^{w}/v$).

2.3.2. COLUMN

A 20 mm dia. glass column with a glass stop cock was used. The resin was supported on a glass wool plug, flow rates were 10 - 15 ml min^{-1} for all solutions.

2.4. MACRORETICULAR RESINS

The macroreticular resin used was Amberlite XAD - 2 (20 - 50 mesh). New resin (10 ml) was used for each experiment, and was washed with 100 ml distilled water before use. A column, as described above, 2.3.2., was used to contain the resin. All flow rates were approximately 10 ml min^{-1}.

All samples were analysed by A.A.S.. Aqueous samples were adjusted to a concentration of 1% $^{v}/v$ nitric acid by the addition of HNO_3. Organic solvents were evaporated to dryness and the residue taken up in aqueous nitric acid (1% $^{v}/v$).

3. EXPERIMENTAL WORK RELATING TO CHAPTER THREE

3.1. GAS LIQUID CHROMATOGRAPHY

3.1.1. INSTRUMENT

Chromatography: Pye Unicam Model 104.

Detector: Pye Unicam Electron Capture Detector, Ni^{63} source.

Operating Temperature: 300°C.

Operating Mode: pulsed, pulse space 150 µsec.

Purge Gas: nitrogen, purified by molecular sieve.

Integrator: Kent Chromalog Mk. 1.

Carrier gas: Nitrogen purified by molecular sieves.

3.1.2. COLUMNS

All columns were 6 mm dia. glass.

SE 30 : 150 cm, 10% SE 30 on Chromosorb W (60 - 80 mesh)

SE 30 (OH) : 150 cm, 10% SE 30 in 8% NaOH coated chromosorb W (60 - 85 mesh)

TCEP : 300 cm, 10% 1,2,3-tris(2-cyanoethoxy)propane on chromosorb W (60 - 85mesh)

3.1.2.1. PREPARATION OF COLUMNS

SE 30 was dissolved in dichloromethane, NaOH in methanol and TCEP in acetone. Solvents were evaporated using a rotary evaporator.

SE 30 (OH) was conditioned slowly over seven days. The temperature was maintained at 60°C for 24 hours, then raised 20°C every 24 hours until 200°C was reached, the nitrogen flow was 40 ml min^{-1}. SE 30 was conditioned at 200°C for 48 hours with a nitrogen flow of 40 ml min^{-1}. TCEP was conditioned at 150°C for 48 hours with a nitrogen flow of 50 ml min^{-1}. Immediately before use SE 30 columns were conditioned at 175°C for 2 hours and TCEP columns at 120°C for 2 hours.

3.1.2.2. CONDITIONS

For	Column	Operating Temp(°C.)	Flow Rate
TEL	SE 30/SE 30(OH)	100	80 ml min^{-1}
TML	SE 30	60	40 ml min^{-1}
TEL	TCEP	60	40 ml min^{-1}

The above conditions are only approximate and were adjusted to give a suitable retention time for TAL, usually 8 minutes.

3.1.3. CALIBRATION

Calibration graphs were prepared by injecting 1 μl samples of 2, 4, 6, 8 and 10 p.p.m. standard solutions. Peak areas were measured using the integrator. Calibration graphs were recalculated daily. Standard solutions were stored in the dark at all times.

3.1.4. DECONTAMINATION OF THE DETECTOR

Decontamination of the detector was initially carried out thermally, if this failed a more severe technique was adopted:

An empty column was connected to the detector and a nitrogen flow of 30 ml min^{-1} was set. The column oven was adjusted to 150°C and the detector oven to 350°C, and then left for 24 hours.

If this failed to decontaminate the detector, then hexane (100μl) and water (100μl) were injected alternately into the empty column while the conditions were maintained as above. Two injections of each were normally sufficient. The outlet from the detector was connected to an efficient fume cupboard during this process. After injection of the hexane and water the thermal cleaning process was repeated.

3.2. COLORIMETRIC TECHNIQUE

3.2.1. HNPAN - Na

3.2.1.1. REAGENTS

HNPAN - Na Solution

HNPAN - Na	0.072 g
water	to 200 ml

HNPAN - Na was dissolved in water and made up to 200 ml in a volumetric flask. The solution was stored in a dark bottle.

EDDHA Solution (10^{-2}M)

Ethylene diamine diorthohydroxyphenyl acetic acid (EDDHA)	0.36 g
Ammonium hydroxide (s.g. 0.880)	2.5 ml
Water	to 100 ml

EDDHA was dissolved in ammonium hydroxide and water (2.5 ml) and made up to 100 ml with water in a volumetric flask. The solution was stored in a dark bottle.

C.D.T.A. Solution (10^{-2}M)

1,2 diamino cyclohexane N,N',N',N', tetra acetic acid (CDTA)	3.6 g
Aqueous NaOH (10% $^{w}/v$)	20 ml
Water	to 1000 ml

CDTA was dissolved in NaOH solution and made up to 1 l in a volumetric flask.

Phenolphthalein Indicator (P.P.)

Phenolpthalein (P.P.)	1 g
Ethanol	90 ml
Water	to 100 ml

P.P. was dissolved in ethanol and made up to 100 ml in a volumetric flask with water.

Buffer Solution

Ammonium hydroxide solution (1:4)

Ammonium Chloride

Ammonium hydroxide solution was added to ammonium chloride solution so as to give a pH of 8.3.

Sodium Chloride

Sodium Chloride 10% $^W/v$ aqueous solution

Chloroform

3.2.1.2. METHOD

Samples were less than 30 ml in volume containing no more than 120 μg of Et_3Pb^+ and 100 μg of Et_2Pb^{++}. The concentration of NaCl in the sample was adjusted to a 1% $^W/v$ solution.

To the sample, EDDHA solution (2 ml) and CDTA solution (2 ml) were added with shaking, followed by 1 drop P.P. indicator. Weak ammonia (20% $^V/v$) or nitric acid (5% $^V/v$) was added to give a faint red colour. Buffer (10 ml) and HNPAN - Na solution (2 ml) were then added. The solution was made up to volume (50 ml) with water, and extracted with chloroform (10 ml) for 1 minute. The chloroform was filtered and the O.D. measured against a reagent blank at 440 nm in 10 mm cells. A calibration graph was prepared by determining the optical density of samples containing 20, 40, 60, 80 and 100 μg of Et_3Pb^+.

3.2.1.3. PREPARATION OF HNPAN - Na

HNPAN - Na was not a commercially available reagent, so it was prepared according to the method of Hewitt and Mitchell[44].

SOLUTION A

To water (10 ml) p-nitroaniline (4 g) was added followed by HCl (10.4 ml). The mixture was cooled to 0°C and $NaNO_2$ (3 g) dissolved in water (6 ml) added, keeping the temperature below 8°C.

SOLUTION B

1 hydroxy-2-napthoic acid (5.4 g) and NaOH (6 g) were dissolved in water (20 ml), and cooled in ice.

Solution A was added to solution B slowly with stirring, keeping the temperature below 8°C. HCl acid was added to give an acid reaction to congo red, followed by excess Na_2CO_3. The product was filtered off and recrystallised from THF. Yield 4.9 g.

3.2.2. PYRIDY - AZO - RESORCINOL METHOD (P.A.R. METHOD)

3.2.2.1. REAGENTS

ICL (1.0M)

Potassium Iodide	27.75 g
HCl acid (s.g. 1.18)	111.25 ml
Potassium Iodate	18.75 g
Water	to 250 ml

HCl was added to the KI dissolved in water and cooled to 0°C. KIO_3 was added with stirring, then the solution was made up to 250 ml with water in a volumetric flask.

Buffer Solution

Sodium Sulphate hydrated $Na_2SO_3.7H_2O$	60 g
Triammonium Citrate	46 g
Potassium Cyanide	5 g
Ammonium Hydroxide (s.g. 0.880)	100 ml
Water	to 1000 ml

Sodium sulphate and triammonium citrate were dissolved in water (ca 500 ml) and transferred to a 1 l volumetric flask. KCN was dissolved in water (ca 50 ml) and was added to the flask followed by ammonium hydroxide and water to volume.

P.A.R. Solution (1.04×10^{-3} M)

Pyridyl - azo - resorcinol sodium salt (P.A.R.)	0.282 g
Water	to 1000 ml

P.A.R. was dissolved in water and made up to 1 l in a volumetric flask.

C.D.T.A.

1,2, diamino cyclohexane N,N',N',N', tetra acetic acid (C.D.T.A.)	14.56 g
Sodium Hydroxide	4 g
Water	to 200 ml

C.D.T.A. was dissolved in a solution of NaOH in water and made up to 200 ml in a volumetric flask.

3.2.2.2. METHOD

Analysis for Et_2Pb^{++}

ICL solution (1 ml) was pipetted into a 25 ml volumetric flask and was washed from the sides with a small volume of water. Buffer solution (5 ml) was added from a pipette and the solution shaken to dissolve the liberated iodine. A measured volume of sample (1 - 10 ml) containing no more than 100 μg Et_2Pb^{++} was pipetted into the flask. P.A.R. solution (5 ml) was added followed by C.D.T.A. (1 ml), the solution was then shaken and made up to volume with water. The formation of a red colour following the addition of P.A.R. and its removal by C.D.T.A. indicates the presence of inorganic lead in the sample.

The absorbance of the solution at 515 nm was measured in 10 mm glass cells against a reagent blank.

Analysis for Et_3Pb^+

The concentration of Et_3Pb^+ was determined by the difference in the absorbance between the above solution estimated for Et_2Pb^{++} and a solution estimated for total (Et_2Pb^{++} and Et_3Pb^+). The estimation of Et_2Pb^{++} plus Et_3Pb^+ was carried out by the addition of the sample to ICl solution before the addition of the buffer. The mixture of ICl and sample was left for 5 minutes to allow complete reaction before the addition of the buffer and the remaining reagents.

3.2.2.3. INSTRUMENTATION

Routine analysis was carried out on a Pye-Unicam SP 500 spectrophotometer. Visible spectra were determined on a Pye-Unicam SP 800. 10 mm glass cells were used in all instances.

3.2.2.4. INTERFERENCES

Samples containing Pb^{++} (200μg), Cu^{++} (200μg) and Ni^{++} (200μg) were analysed as above to determine any interference. None was noted.

3.2.2.5. CALIBRATION GRAPHS

The optical densities (O.D.) of samples containing 0, 20, 40, 60, 80, and 100μg of alkyl lead were determined for Me_2Pb^{++}, Et_2Pb^{++} and Bu_2Pb^{++}. All three gave straight lines passing through the origin. The following factors for conversion of O.D. to concentration were calculated:

Me_2Pb^{++} : O.D. X 148.88 = μg Me_2Pb^{++}

Et_2Pb^{++} : O.D. X 151.38 = μg Et_2Pb^{++}

Bu_2Pb^{++} : O.D. X 190.48 = μg Bu_2Pb^{++}

3.2.2.6. STABILITY OF P.A.R. - Et_2Pb^{++}

Two samples containing Et_2Pb^{++} (500μg) were analysed by the P.A.R. method using a 10 fold increase in reagent volumes. One solution was stored in the light, the other in the dark. Each was analysed with time to determine the stability.

3.3. ATOMIC ABSORPTION SPECTROMETRY

Atomic absorption spectrometry (A.A.S.) was carried out on a Perkin Elmer PE 303 Spectrometer using the 283.3 nm line of a hollow cathode lead lamp with an air/acetylene flame. Aqueous samples were present as 1% $^v/v$ nitric acid solutions and run against standards of lead nitrate in nitric acid solution (1% $^v/v$). Organic solvents were evaporated and the residue taken up in aqueous nitric acid solution (1% $^v/v$).

3.4. THIN LAYER CHROMATOGRAPHY

3.4.1. GENERAL

Silica and alumina refer to M N Kleselgel G. and M N Aluminoxid G. respectively. These materials were used at a thickness of 0.25 mm on 20 cm glass plates and were equilibrated with the atmosphere before use.

Plates were eluted in a closed atmosphere saturated with eluant vapour and developed using dithizone (0.1% $^w/v$) solution in carbon tetrachloride.

Salts were applied from an appropriate solution, chloroform was found to be suitable for R_3PbX and acetone or water for R_2PbX_2. With systems giving low R_f values care was necessary not to overload the plates to prevent streaking and consequently false R_f values.

The results of the elution of alkyl lead salts under different conditions is given in table 9.

3.4.2. LIMITS OF DETECTION

Solutions were made up of Et_3PbCl and Me_3PbCl in chloroform at 1 mg ml^{-1} and of Et_2PbCl_2 and Me_2PbCl_2 in water at 1 mg ml^{-1}. Measured volumes were applied to T.L.C. plates from a calibrated microsyringe (10 μl), the solvent was allowed to evaporate and the plates eluted and developed with dithizone solution. Plates were studied visually, and those on which spots were not observed were placed in iodine vapour for 15 minutes. On removal from the iodine, the plates were left in a stream of air until all the adsorbed iodine had been evaporated (ca 1 hour), when the plates were resprayed with dithizone solution.

Sample volumes of 5, 3, 2, 1, 0.5 and 0.2 μl were applied and the corresponding limits of detection for the various systems are tabulated in table 8.

3.5. MASS SPECTROMETRY

Mass spectrometry was carried out on an A.E.I. M.S. 9 mass spectrometer, the conditions being:

Accelerating Voltage	8000 V
Electron Energy	70 V
Source Temperature	250°C
Probe Temperature	110°C

4. EXPERIMENTAL WORK RELATING TO CHAPTER FOUR

4.1. GENERAL

All solutions were prepared using distilled water. Organolead salt solutions were prepared by suitable dilution of 1000 p.p.m. standard solutions. Solutions containing metal ions were prepared from 1000 p.p.m. standard solutions of the metal chloride. In the case of Fe^{++} solution these were initially prepared as the ferrous salt solution, however at low concentrations these would oxidize to ferric ions. Solutions of TAL were prepared by the addition of TAL from a calibrated microsyringe (10 μl).

All solutions were stored in glass conical flasks with glass stoppers. TAL solutions were vigorously shaken by hand for 10 minutes immediately after the addition of the TAL, daily, and immediately before analysis.

Samples exposed to light were placed on an east facing window ledge and exposed to natural daylight.

4.2. ANALYSIS

4.2.1. TAL

Following the shaking of the sample, 50 ml of solution was transferred to a separating funnel (100 ml) benzene(50 ml) was added and the solution shaken for 5 minutes. The layers were allowed to separate, the benzene layer was analysed for TAL content by G.L.C. while the aqueous was analysed for organolead salt content.

4.2.2. ORGANOLEAD SALTS

The trialkyl and dialkyl lead concentrations were determined by the P.A.R. method using 5 ml samples.

4.2.3. IRON INTERFERENCE

The interference of iron was eliminated by the following method:

To the sample (50 ml), $Pb(NO_3)_2$ (1 g) was added and shaken until dissolved. Aqueous NaOH solution (5N) was added dropwise until pH 8 was attained. Filtration through a Whatman No 1 filter paper removed the precipitate, and the aqueous was analysed for tri- and dialkyl lead by the P.A.R. method.

4.3. REMOVAL OF TEL FROM GLASS

Following the suggestion that TEL was being adsorbed by glass surfaces, TEL was removed from the glass by the following method:

The flask was extracted with benzene (100 ml) for 1 hour, after which time the TEL content was determined by G.L.C.. The process was repeated with fresh benzene until TEL was no longer being extracted from the glass walls.

5. EXPERIMENTAL WORK RELATING TO CHAPTER FIVE

5.1. GENERAL

Silica gel (100 - 200 mesh) was used throughout. The silica was suspended on 50 ml of water before the addition of organolead compounds. Organolead salts were added to the suspension by suitable additions of a $500\mu gml^{-1}$ aqueous standard solution of the salt. Dilute solutions of TEL and TML were prepared by adding TAL ($50\mu l$) to methanol (10 ml) using a calibrated syringe ($100\mu l$). For the addition of TAL to silica, $100\mu l$ of this dilute solution was added using a $100\mu l$ syringe ($100\mu l$ of the dilute solution is equivalent to $0.5\mu l$ of TAL).

All suspensions were prepared in glass conical flasks (100 ml) with glass stoppers, mixtures were stored in the dark prior to analysis.

5.2. DETERMINATION OF ORGANOLEAD CONTENT

The suspension was transferred to a separating funnel and benzene (50 ml) was added. The sample was shaken for 10 minutes (TML) or overnight (TEL) to achieve maximum extraction of TAL. The silica was run off into a glass column and the benzene was analysed by G.L.C. for TAL content.

A column, 20mm dia. with a glass stop cock was used to extract the silica. The silica was supported on a glass wool plug. The aqueous solution used to suspend the silica was collected and analysed to check total adsorption of the salts by the silica. The silica was then extracted by slowly passing aqueous acetic acid solution (2% $^{v}/v$) through the column at 15 ml min^{-1} successive fractions (50 ml) were collected and neutralised by the addition of aqueous NaOH (5N). The alkyl lead content was then determined by the P.A.R. method using 5 ml samples. Fractions were collected until no alkyl lead was determined in the eluant, usually 200 ml was sufficient.

Initial experiments involving $Pb(NO_3)_2$ solutions as eluant meant that samples were deleaded before analysis by the P.A.R. method. The method used was described above in 4.2.3.

6. EXPERIMENTAL WORK RELATING TO CHAPTER SIX

6.1. EXTRACTION OF ALKYL LEAD SULPHIDES BY BENZENE

Prepare 5×10^{-3}M aqueous solutions of Me_3PbCl, Et_3PbCl, Et_2PbCl_2, Et_3PbCl, and Na_2S from the corresponding pure solid and water.

6.1.1. TRIALKYL SALTS

Aqueous R_3PbCl (5×10^{-3}M) (2 ml) and aqueous Na_2S (5×10^{-3}M) (1 ml), were added to a separating funnel containing water (97 ml) followed by benzene (50 ml). The mixture was shaken for 5 minutes. The aqueous layer was analysed for tri- and dialkyl lead compounds by the P.A.R. method using 5 ml sample volumes.

The above experiment was repeated using 96 ml of water and 2 ml of Na_2S solution instead of 97 ml and 1 ml respectively.

6.1.2. DIALKYL LEAD SALTS

Aqueous R_2PbCl_2 (5×10^{-3}M) (2 ml) and aqueous Na_2S (5×10^{-3}M) (2 ml) were added to a separating funnel (250 ml) containing water (96 ml), benzene (50 ml) was then added and the mixture extracted for 5 minutes. The aqueous layer was analysed for di- and trialkyl lead content by the P.A.R. method using 5 ml sample volumes.

The above experiment was repeated using water (94 ml) and Na_2S (4 ml) instead of water (96 ml) and Na_2S (2 ml).

6.1.3. RESULTS

Where equimolar concentrations of lead Me_2PbCl_2, Me_3PbCl_2, Et_3PbCl and Et_2PbCl_2 were mixed with sulphide ions, only 80%, 75%, 85% and 83% extraction of the alkyl lead sulphide was achieved, however with excess sulphide all salts were totally extracted.

6.1.4. ACIDIFICATION

The above experiments (6.1.1. and 6.1.2.) were repeated except the solutions were acidified by the addition of aqueous nitric acid solution (10% $^{v}/v$) (1 ml) prior to extraction by benzene. In all cases no alkyl lead salt was extracted by the benzene.

6.2. METHOD OF ANALYSIS USED WHEN SULPHIDE IONS ARE PRESENT

When sulphide ions were present in aqueous solution the following method was used when analysing for organolead compounds:

The sample was acidified with sufficient aqueous nitric acid solution (10% $^{v}/v$) such that the final concentration of acid was 0.1% $^{v}/v$, this prevented the extraction of organolead sulphides by benzene but did not influence the P.A.R. method of analysis.

TAL compounds were extracted from the aqueous solution, after acidification, using equal volumes of benzene and shaking for 5 minutes. The layers were allowed to separate and the TAL content of benzene was determined by G.L.C.

The aqueous was analysed by the P.A.R. method using 5 ml samples.

6.3. INITIAL STUDIES ON REACTIONS BETWEEN R_3Pb^+ AND S^{2-}

6.3.1. GENERAL

All reactions were carried out in glass conical flasks (250 ml) sealed with rubber subaseals. The atmosphere above the reaction was analysed by G.L.C. withdrawing 100μl samples through the subaseal using a syringe (100μl). Because we were analysing the vapour of a volatile liquid only a qualitative analysis could be performed with regard to the concentration of TAL in the flask. The conditions used were those normally used for TAL analysis. The dialkyl sulphides were identified by comparison with authentic samples.

6.3.2. REACTION BETWEEN Et_3Pb^+ AND SULPHIDE IONS, AND Me_3Pb^+ AND SULPHIDE IONS

Et_3PbCl (0.015 g) was dissolved in water (100 ml) in a conical flask (250 ml) to which $Na_2S.7H_2O$ (0.011 g) was added and the flask was sealed with a subaseal. The mixture was then stored in the dark. The atmosphere was analysed after 24 hours as detailed above 6.3.1.

This experiment was repeated replacing Et_3PbCl with Me_3PbCl (0.013 g).

6.3.3. REACTION BETWEEN A MIXTURE OF Me_3PbCl AND Et_3PbCl AND ADDED SULPHIDE IONS

To water (100 ml) contained in a conical flask, 2 ml of an aqueous solution of Et_3PbCl (5×10^{-3}M) and 2 ml of an aqueous solution of Me_3PbCl (5×10^{-3}M) were added with shaking. An aqueous solution of Na_2S (5×10^{-3}M) (4 ml) was then added and the flask was sealed with a subaseal, shaken and stored in the dark. Analysis after 24 hours was carried out by the method detailed above 6.3.1.

In all cases blanks of the organolead solutions were prepared without added sulphides and analysed by a similar procedure.

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