MICROWAVE ASSISTED DECOMPOSITION

OF TRI-BUTYL PHOSPHATE IN AQUEOUS

EFFLUENT STREAMS

by

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collaboration with British Nuclear Fuels Plc

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DECLARATION

I declare that while registered as a candidate for the degree which submission is made I have not been registered as a candidate for another award at an academic institution. No material contained in this thesis has been used in any other submission for an academic award.

All the work presented in this thesis was carried out within the University of Central Lancashire's Catalysis and Microwave Laboratory.

John Rawcliffe, August 2000

Acknowledgements.

Abstract.

An investigation into the microwave assisted remediation of organic containing aqueous solutions has been conducted. Tri-n-butyl phosphate (TBP), the nuclear fuel reprocessing solvent, and its diluents, are known to be responsible for the formation of interfacial deposits (cruds) in the alkali solvent wash stage of the Purex process for reprocessing spent nuclear fuel.

The presence of cruds in the process is managed by regular wash out and the collected cruds are separated from aqueous washings and stored.

Chemical oxidation of the cruds is one way of destroying them. This project explored microwave assisted oxidation, using TBP as a simple simulant for the crud.

Low concentration TBP streams were circulated through an activated carbon loaded glass reaction vessel. The vessel was then subject to microwave radiation applied in short pulses.

Studies were performed to assess the variation in reaction parameters using two oxidants; air and hydrogen peroxide. The analytical techniques used to assess the extent of decomposition were ion chromatography and UV-Vis spectroscopy.

Results showed TBP was found to decompose to orthophosphate ions in solution and to di-butyl phosphoric acid (HDBP).

Contents.

Glossary of Terms Used in the Thesis.

Butex $BuO(CH_2)_2O(CH_2)_2OBu$

D Distribution ratio of metal concentration in organic phase to aqueous phase

DBP Di-n-butylorthophosphate

F.P.s Fission Products

G value Number of molecules of TBP destroyed per 100eV absorbed energy.

H_2MBP Monobutylphosphoric Acid

HBLP Butyl-laurylphosphoric Acid

HDBP Di-n-butylphosphoric Acid

HTTA Thenoyltrifluoroacetone

LWR Light Water Reactor

MBP Monobutylorthophosphate

MIBK Methylisobutyl ketone

MOX Fuel Mixed Oxide Fuel

MWd Megawattday

nDD n-Dodecane

NPH Normal Paraffin Hydrocarbon

OK Odourless Kerosene

PCBs Polychlorinated Biphenols

PUREX Plutonium Uranium Refining by Extraction or Plutonium and Uranium

   Redox Extraction

TBP Tri-n-butylorthophosphate

THORP Thermal Oxide Reprocessing Plant

Trigly $Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl$

1. Introduction.

1.1. Nuclear Fuel Cycle.

The nuclear fuel cycle comprises the handling of all fissile and fertile material required for the production of nuclear power and of the radioactive products formed in this process. The nuclear power station divides the two ends of the cycle. The front end involves uranium mining, refining, enrichment and processing, whilst the back end involves the treatment of the spent fuel, i.e. reprocessing and waste management.[1] A diagram of the fuel cycle can be seen in Figure 1.1.

In most nuclear reactors the fuel is uranium dioxide, UO_2. This fuel is normally enriched to give an increased percentage of radioisotope ^{235}U. Some reactors have been developed that use uranium in which plutonium is distributed whereas some use plutonium mixed with ^{238}U and also ^{232}Th oxides.[2] Due to deformations and corrosion which occur at the high temperatures and pressures found in reactors, the fuels are produced as ceramic pellets and stacked in zircaloy or stainless steel tubes. In the reactor very high heat gradients are observed as a result of poor heat conduction, and it is possible for the ceramic pellet to melt in the centre under these circumstances (m.p UO_2 = 2865^{0}C) even though the surface temperature is much below the melting point. The steep temperature gradients result in cracks appearing due to thermal expansion.[1]

1.1.1. Fission Products.

The temperature gradients that exist in the ceramic pellets lead to a distribution of the fission products (F.P.s) throughout the fuel. This is because the F.P.s accumulate where their chemical potential is a minimum. In this case the low chemical potentials lead to higher concentration gradients. In the cladding, the noble gases,

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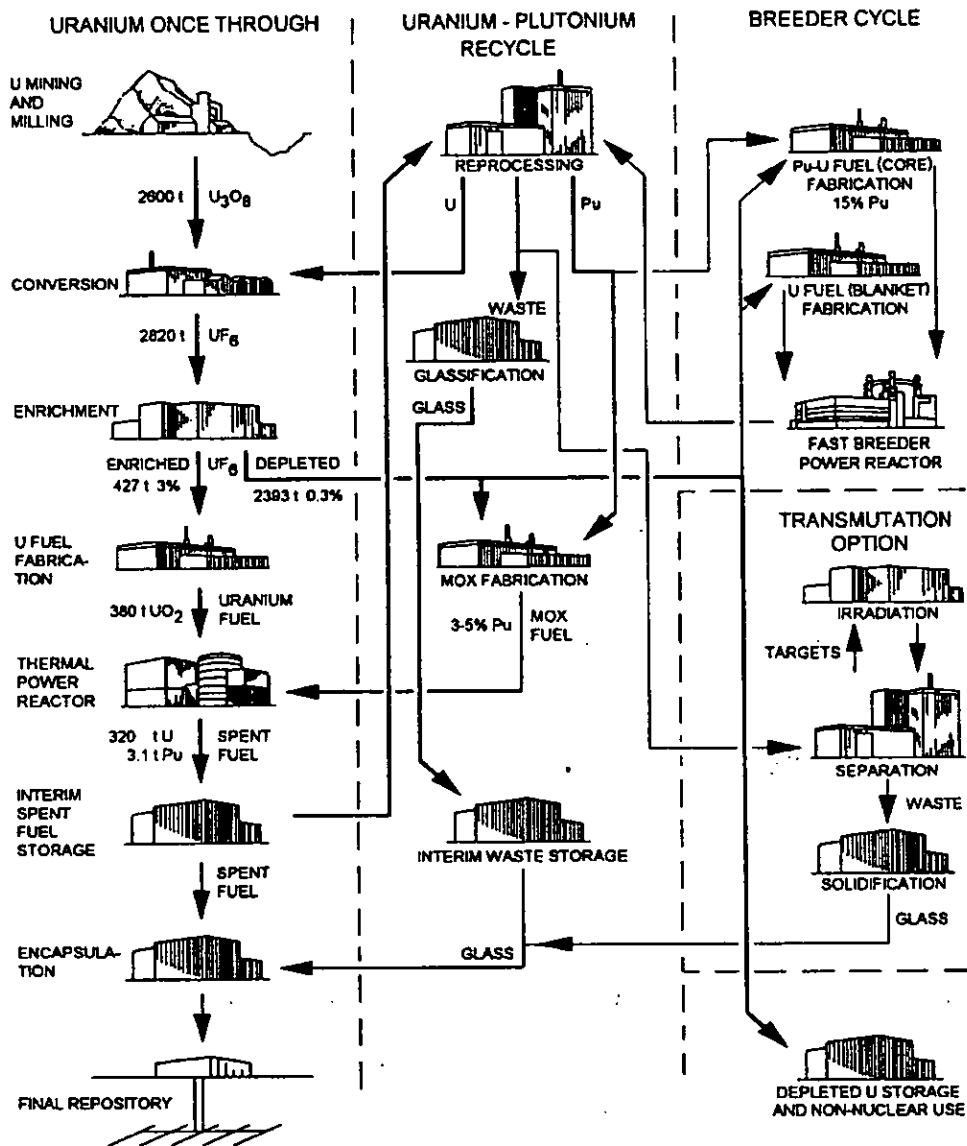
Figure 1.1 The Nuclear Fuel Cycle.

Cs and I predominate. However, the high temperatures of the pellet centre cause Zr and Nb migrate. The Pu formed is distributed near the fuel surface with little near the fuel centre.

The overall composition of spent reactor fuels is variable and dependent on input composition, pin design, position in the reactor, amount of cooling, time in core, and neutron spectrum. Hence spent fuel from different reactors will differ, depending on the reactor type used, which is also true for different pins in the same reactor including pins that are adjacent. These differences though do not require drastically

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different reprocessing techniques the only prerequisite being that the fuel is U or UO_2 based. One tonne of uranium irradiated to 33000MWd results in 34kg of fission products.

In general, spent fuel cooled for ten years contains the following as stable isotopes: Ga, Ge, As, Br, In, Xe, La, Nd, Tb, Dy and Er. There are also a variety of very low activity isotopes: Zn, Se, Rb, Mo, Pd, Ag, Sn, I, Gd, Ho and Tm. Some of those active after ten years have disappeared by 100 years (Sb, Ce, Eu, Pm, Ru, Rh and Kr) leaving only ^{90}Sr-^{90}Y and ^{137}Cs-^{137}Ba pairs, ^{99}Tc, ^{135}Cs, ^{79}Se, and ^{151}Sm. Neutron capture and β-decay result in the formation of higher actinides including ^{237}Np, ^{238}Pu, ^{241}Am and ^{242}Cm.[1]

The total amount of Pu formed varies and is dependant on the reactor type as are the amount of fissile Pu isotopes and quality of the plutonium. Figure 1.2 shows the decay process for uranium-238.[1]

1.1.2. U-Pu Fuel Cycle.

The fissile fraction in spent light water reactors (LWR) fuel amounts to 0.9% ^{235}U and 0.5-0.7% $^{239+241}$Pu. By recovering these and returning them to the LWR fuel cycle the demand for new U and enrichment services is reduced by ≈ 30%. The U recovered can either be re-enriched for use as normal UO_2 fuel or incorporated with the Pu recovered to give a mixed oxide fuel; which can also be generated using depleted U and recovered Pu.

The plutonium recovered changes its isotopic composition and this leads to a large increase in the most radioactive Pu isotope, ^{238}Pu (an alpha emitter). The presence of this leads to an increase in the radiolysis of the reprocessing solutions.

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Figure 1.2 The U²³⁸ Decay Series.

1.1.3. Reprocessing of Uranium and Mixed Oxide Fuels.

Figure 1.3 shows a flow sheet for nuclear fuel reprocessing.

The main purpose of commercial reprocessing is:[1,2]

   1. To increase the available energy from fissile and fertile atoms;

   2. To reduce hazards and costs for handling the high level radioactive wastes;

   3. To reduce the costs of the thermal reactor fuel cycle.

The type of system used for reprocessing depends on the nature of the reactor, for instance, light water reactor fuel is chopped prior to dissolution. In high temperature gas cooled reactors burning of the graphite fuel matrix is the technique employed. Liquid-metal fast breeder reactors are more problematic but the high proportion of plutonium (10x LWR) provides an economic incentive.

LWR fuel reprocessing occurs in the following stages:

   1. Head end section; fuel preparation prior to separation;

   2. Partitioning of U, Pu and F.P.s;

   3. Purification of U;

   4. Purification of Pu;

   5. Waste treatment;

   6. Recovery of chemicals.

1.1.4. Head End Plant.

Upon arrival the fuel containing flasks are decontaminated. They are next dismantled and chopped in a radiation shielded environment, known as the dry shear cave.[3] In the Thermal Oxide Reprocessing Plant (THORP) at Sellafield, U.K, dry chopping is used.[1, 3-5] Dissolution of the fuel is achieved by a reflux in 6-10M nitric

acid (no greater than 7.7M in THORP), under these conditions the can remains

insoluble. Since fluoride ions complex readily with Zr, an amount of AlF_3 may be

HEAD END PLANT | CHEMICAL SEPARATION PLANT

DISSOLVER OFF-GAS TREATMENT — CONDENSER — BUFFER STORAGE

FUEL RECEIPT

DISSOL-VER OFF-GAS — ACCOUNTANCY

U PURIFICATION → ACCOUN-TANCY — U PRODUCT

1ST CYCLE EVAPORATION

U

EVAPORATION → CONV. TO OXIDE

POND STORAGE → REMOVAL FROM CONTAINER → SHEARING → DISSOLUTION → LIQUOR CLARIFI-CATION

Pu

Pu PURIFICATION → EVAPORATION — Pu PRODUCT

FEED POND WATER

HULLS FINES — PARTICULATE MATTER

ACCOUNTANCY → CONV. TO OXIDE

HIGH ACTIVE WASTE EVAPORATION — MED. ACTIVE WASTE DISPOSAL

MONITORING → DISCHARGE — CEMENT ENCAPSULATION

VITRIFICATION

Figure 1.3 Nuclear Fuel Reprocessing Flow Sheet.

added, to improve the dissolution. Certain alloys of metal fission products are

insoluble under these conditions (Ru, Rb, Mo, Tc and Pd) and are filtered off and

disposed of as high level waste.[1] Cutting the fuel pins can release gaseous fission

products (^{85}Kr, ^{3}H, ^{129}I and ^{131}I), although this is not the case in THORP, and these are

collected and routed to the dissolver off-gas treatment system. Other gaseous

contaminants are released upon dissolution: Kr, Xe, I_2, T_2, THO, RuO_4, CO_2 are treated similarly; H_2O, HNO_3 and NO_x are recycled.[3]

The overall reaction for the dissolution is:

$$U(IV)O_2 + 2HNO_3 + (O) \longrightarrow U(VI)O_2(NO_3)_2 + H_2O$$
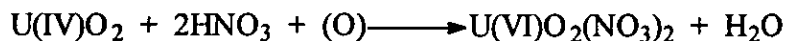
1.1.5. Chemical Separation Methods.

Separation is a complex procedure mainly due to the variety of species present (F.P.s, actinides and corrosion products). Other complications arise from the radioactive nature of these components including radiation decomposition, safety regarding criticality and the need for the process to be remotely controlled behind heavily shielded areas. Most processes take advantage of the stability of U^{6+} complexes and the redox lability of Pu (+3, +4, +6) and all use the principle of oxidising and reducing Pu at various stages in the purification.[1,4]

Originally (1940's) the technique of choice was to precipitate out the plutonium as a plutonium phosphate (+3 and +4).[1] Unfortunately this method was not suitable for the large scale continuous remote separation of very pure plutonium and uranium. The replacement technique used thus was solvent extraction. This technique involves the dissolution of the fuel using nitric acid as described above, followed by the formation of uncharged organic species which are soluble in organic solvents.

There are three main types of compound formed:

1. Organic chelate complexes such as plutonium tetraacetylacetonate.

2. Inorganic metal complexes forming adducts with solvating organic compounds i.e., TBP (tri-n-butyl phosphate), and hexone, which forms $UO_2(NO_3)_2(hexone)_2$.

3. Ion-pair complexes between large organic cations (R_3NH^+) and negatively

   charged inorganic complexes such as $UO_2(SO_4)_3^{4-}$.

The nature of the solvent thus determines the process.

1.1.5.1. Choice of Solvent.

At Hanford, USA, the first solvent used was methylisobutylketone (MIBK), which

formed adducts with actinide nitrates.[1] The advantage of this was that the complexes

formed, $Pu(NO_3)_4(MIBK)_2$, were soluble in MIBK itself; although it is unstable at

high nitric acid concentrations. In comparison the U.K initially used Butex (β- β'-

dibutoxydiethylether) as the solvent and this formed complexes analogous to those of

MIBK.[4] It was preferred since it had greater stability, was less flammable and gave

better separations. Thenoyl trifluoroacetone (HTTA) was tested for use in the U.S.A,

and a solvent comprising of 15% dibutylether in CCl_4 in the U.S.S.R. Canada tested a

solvent known as Trigly $(Cl(CH_2)_2O(CH_2)_2O(CH_2)_2Cl)$.[4]

These solvents were found to be problematic. Trigly only extracts plutonium and

chlorine evolution from the solvent occurs under radiolytic attack, this is also the case

found when using 15% dibutylether in CCl_4. HTTA extraction is slow.[4] Butex and

MIBK also have disadvantages: high viscosity, low flash point[4], a density near to that

of water and a tendency to form complexes under certain conditions.[2] In order to

achieve sufficiently high extraction factors these two solvents both required the

addition of salts to obtain a sufficiently high nitrate concentration to salt U and Pu

into the organic phase. In the case of Butex this could be achieved by the addition of

HNO_3 alone, but MIBK is unstable at high nitrate concentrations so $Al(NO_3)_3$ is

added as a salting agent, leading to an increase in the waste material. On the other

hand, a salting agent is added to the Butex flowsheet to assist in the back-extraction of

Pu. These problems further highlighted the need for a solvent that used a salt-free flowsheet. At Windscale, Pu purification used TBP and this solvents use was extended to cover the whole uranium/plutonium/fission product separation.[4] A molecular model representation of a TBP molecule is shown in Figure 1.4, where the colour-atom relationship is: purple-phosphorous, green-oxygen, red-carbon, yellow-hydrogen.
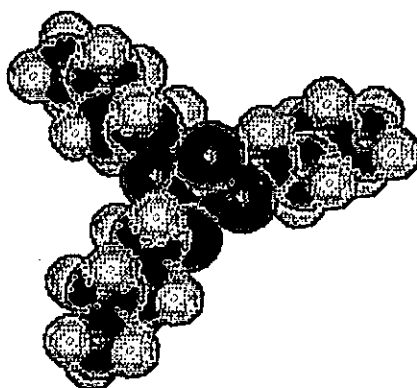
Figure 1.4 A Molecular Model Showing the Structure of TBP.

TBP is currently the solvent used in all reprocessing plants.[1, 4, 6] It forms adducts and is more stable, less flammable, cheaper and gives better separations than Butex. It is often used as a 30% solution in odourless kerosene.

Its advantages include

1. Good physical properties.

2. Reasonably sufficient radiolytic and nitric acid stability.

3. Sufficient extraction powers.

4. No salting agents required.

5. Good decontamination from fission products.

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There are certain prerequisites that the solvent must fulfill in order to function successfully. Some of these constraints include:

1. The avoidance of precipitates.

2. The avoidance of excessive liquor volumes.

3. Minimisation of corrosion.

4. Minimisation of solvent degradation.

5. The needs for all product and waste streams to be in suitable forms for further treatment.

In purex plants this can be achieved readily by means of:

1. Stainless steel equipment.

2. A HNO_3 concentration of medium or low strength in the first extraction contractor.

3. A suitable TBP concentration.

4. Extraction of the actinides as the first step leaving the fission products in the aqueous raffinate.

5. Minimal addition of metal cations or anions other than nitrate.

There are as would be expected certain disadvantages that include:

1. Separation, while good is not 100% and it is not possible to attain very pure U and Pu in a one-step extraction.

2. The build-up of TBP and diluent degradation products. This causes a number of problems which are discussed in full in Section 1.3.

1.1.5.2. Purex Separation Scheme.

(Plutonium and Uranium Redox Extraction or Plutonium Uranium Refining by Extraction)

The dissolved fuel from the head end plant then enters the chemical separation plant. The chemical separation plant used in THORP employs a Purex extraction process.[1, 3, 5, 7]

In the system 30% TBP in kerosene and aqueous solution of nitric acid the extracted metal, M, is obtained in the M(VI), M(IV) and M(III) oxidation states as $MO_2(NO_3)_2(TBP)_2$, $M(NO_3)_3(TBP)_2$ and $M(NO_3)_3(TBP)_3$ respectively. The stability of the complexes varies with oxidation state in the order:

$$M^{4+} \geq MO_2^{2+} > M^{3+} \geq MO_2^+$$
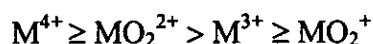
MO_2^{2+} occurring before M^{3+} since the metal atom in the linear $[OMO]^{2+}$ species has a higher charge density than in M^{3+}. Of importance in reprocessing are the low distribution ratios (Section 1.2.1.) of fission products like Cs, Sr, Ru and Zr in the TBP/kerosene/HNO_3 system. I, II, III, V, VII valent fission products have distribution ratios (D values) $\ll$ 0.01 and are thus not extracted. Therefore at high nitric acid concentrations Pu (IV), Pu (VI) and U (VI) are extracted with very little of the fission products. At low nitric acid concentrations the D value for all actinides regardless of oxidation state is $\ll$ 1. As a result of this the tetra- and hexavalent actinides are stripped from the organic phase by dilute HNO_3.

Figure 1.5 shows the solvent extraction process. The HA cycle separates the bulk of the fission products from the uranium and plutonium and then separates the uranium from the plutonium. The UP and PP cycles further purify the uranium and the plutonium nitrate product streams from certain partially extractable fission products, notably, technetium, ruthenium, cesium, zirconium, cerium and neptunium.[1, 4, 8-15]

The purified uranyl and plutonium nitrate liquors are then converted to uranium trioxide and plutonium dioxide powder products which can then be used as nuclear fuel. In the first cycle the fission products from the spent fuel mean high levels of β and γ radiation are present.

As a result of the high plutonium content of the irradiated fuel, criticality control is of major importance and this is achieved mainly by the use of safe by geometry equipment. Pulse columns, are used as the solvent extraction contactors in the HA
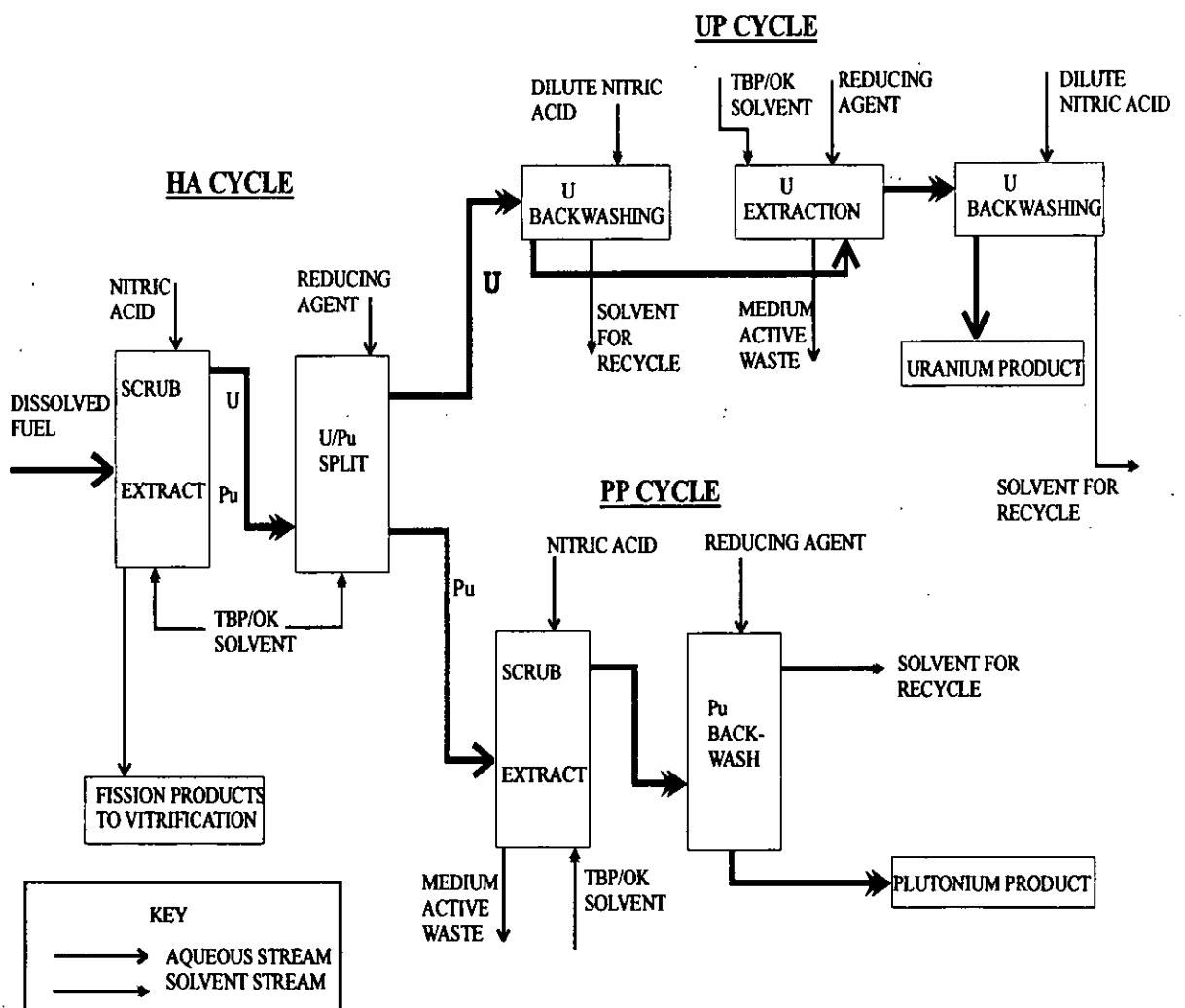
Figure 1.5 Flow Diagram of the Purex Solvent Extraction Process.

and PP cycles because of their high surface area to volume ratio. These have the advantage of short liquor residence times that help minimise the extent to which the solvent can become degraded.

1.1.5.3. The HA Cycle.

The THORP HA cycle (Figure 1.6) employs four pulse columns, two mixer settlers and equipment to remove solvent from the waste and plutonium product streams.[3] The HA and HS columns extract the U and Pu in the dissolved fuel into the solvent (30% TBP in OK), and scrub out partially extracted fission products, using a nitric acid feed. Highly active waste flows out of to the steam strip column (SS), prior to vitrification and storage. In the contactors the aqueous and organic phases flow counter-current to one another. The first cycle co-extracts >99.8% uranium and plutonium as U(VI) and Pu(IV) from HNO_3 into the kerosene-TBP phase, leaving >99% of the fission products in the aqueous raffinate.[1, 3, 4]

The 1BX column separates U from Pu by chemically reducing Pu from the +4 state to +3. Plutonium in this oxidation state is no longer extractable and is back-washed in the aqueous phase. This aqueous stream then flows to the 1BS column where uranium traces are removed by extraction with solvent, before passing through an OK wash column to remove traces of TBP, and finally to the Pu purification cycle.

The uranium contained in the organic phase of column 1BX flows to the mixer settler 1BXX, where further reduction removes Pu traces, before the U is backwashed into an aqueous phase in the 1C mixer settler and onto the U purification cycle.

Chemical reduction of the plutonium is achieved by use of uranium (IV) nitrate, a salt free reducing agent which is oxidised to U(VI) nitrate which then joins the uranium stream. Reduction occurs in the aqueous phase. The reduction of Pu(IV) by
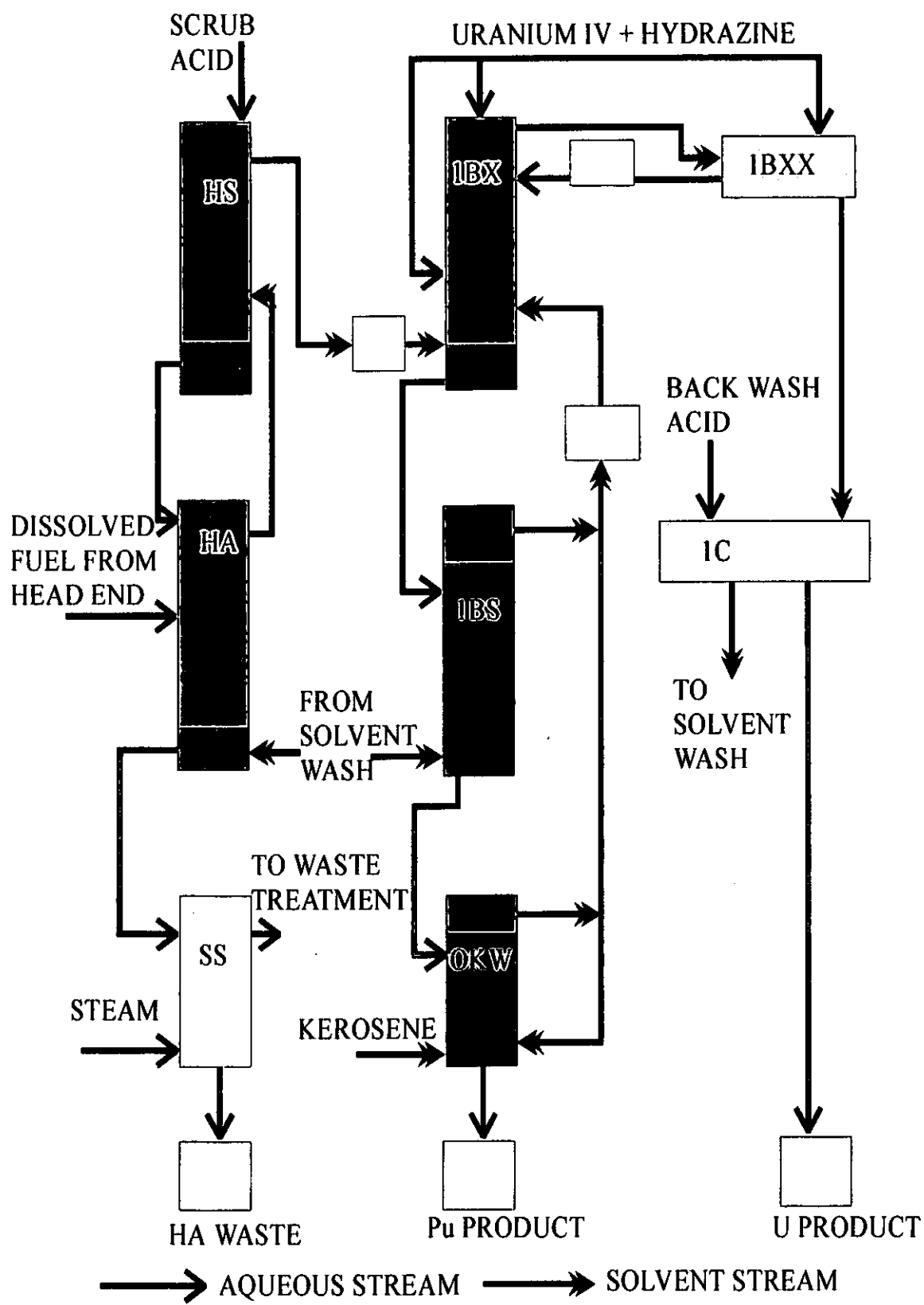
Figure 1.6 Flow Diagram of the Purex HA Cycle.

U(IV) nitrate is as follows:

$$U^{4+} + 2Pu^{4+} + 2H_2O \longrightarrow UO_2^{2+} + 2Pu^{3+} + 4H^+$$
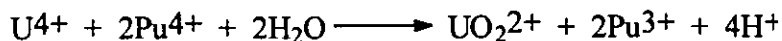
The U(IV) nitrate is stabilized with hydrazine to prevent reaction with HONO,[3] and prevents re-oxidation of the Pu as it is formed. Hydrazine is preferred to ferrous sulphamate as it avoids the addition of cations to the waste streams.

1.1.5.4. Problems Associated With The Purex Process.

As could be expected with most processes, the Purex process is not exactly problem free. The problems are detailed below:

1. Reductant- Problematic since the use of U(IV) nitrate to reduce Pu^{4+} to Pu^{3+} introduces new uranium into the streams which will require treatment (in THORP this is only 5% of the total). Ferrous sulphamate (Fe $(SO_3NH_2)_2$) introduces inorganic salts to the aqueous streams thereby increasing the volume of high level waste. The ferrous ion and the sulphamate ion act separately. The ferrous / ferric couple reduces Pu (IV and VI); the sulphamate ion stabilises the ferrous ion in nitric acid solutions by destroying nitrous acid which would otherwise oxidise the Fe^{2+} ion and so interfere with the formation of Pu(III).[2]

2. Solvent Degradation - TBP decomposes radiolytically into di-butlyphosphate (DBP) and subsequently the mono-butylphosphate(MBP). These have a tendency to form complexes with many of the fission products as well as Pu. This affects the efficiency of the decontamination and heralds an increase in fissile material waste streams. One solution to this problem is the introduction of an alkaline solvent wash stage; which recycles degraded solvent by eliminating acidic degradation products such as DBP. Problems due to these degradation products may affect the treatment of effluent streams in that some of the fission products

are retained in the solvent.[8-15] This is in addition to the deposition of interfacial zirconium containing material, leading to a loss of this element as well as problems through emulsification.

The operation of solvent extraction processes may inevitably become problematic and this is most commonly observed as the formation of a stable phase called "crud". In certain circumstances cruds adversely affect the performance of the solvent extraction processes by emulsification, hindered mass transfer and process disturbances. The crud disturbs the operation of the extracting equipment; the mixer settlers generally suffer the greatest effect from crud formation because they have as many interfaces as stages.[4, 9, 16-19] Crud is defined as "the material resulting from the agitation of an organic phase, an aqueous phase and fine solid particles, that form a stable mixture"[17] and is discussed in more detail in Section 1.4.3.

1.2. TBP as an Extracting Solvent.

Tri-n-butyl orthophosphate (TBP), $(C_4H_9O)_3PO$, is a colourless almost odourless liquid and is well established as the major extractant for the reprocessing of nuclear fuels. Figure 1.4 shows a diagram of the molecule. In this process it is employed to separate uranium and plutonium from fission products and to assist in their purification.[1-6] Other nuclear applications include the recovery of thorium from spent fuel and the separation of neptunium.[20]

The extensive use of TBP as an industrial solvent is due both to its excellent chemical resistance and to the physical properties of the substance. TBP is a highly polar compound with only slight solubility in water and very low vapour pressure. Table 1.1, contains the physical properties of TBP.

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The applications of TBP are not limited to the nuclear industry and it has roles that are widespread throughout industrial scale hydrometallurgy.[6] These include its use in the preparation of rare earth metals, iron recovery and zirconium and hafnium separation.[6] TBP also has applications as a catalyst, an antifoaming agent[21] an antioxidant, and as a corrosion inhibitor.[4]

The emergence of TBP as a solvent for metal extraction was recorded by US workers involved in the Manhattan Project.[4] In this work undiluted TBP was shown to be capable of extracting thorium and plutonium. However, using TBP in an undiluted form caused process problems, which were thought at the time to inappropriate further use.

TBP first occurred in the open literature in 1949 in a paper by Warf[22] that related to the use of TBP as an extractant for cerium (IV). TBP was found to be satisfactorily resistant to the strongly oxidising action of cerium (IV) nitrate, a useful property which lends itself to nuclear reprocessing. Indeed, the solvent is stable to nitric acid upto concentrations as high as 16M.[23] Warf[22] also reported the extraction of thorium and uranyl nitrates by TBP along with iron, zirconium and lanthanum. However, extraction of zirconium and lanthanum was not as considerable as that of iron.

After using mixtures of TBP and other extractants it was found that by adding non-extracting diluents, the extracting power of the TBP-diluent mixture increased.

Table 1.1   Physical Properties of TBP at 25°C.

Molecular weight		266.32
Boiling point, °C		284 ± 5
Freezing point, °C		~ -80
Density, ρ, g ml^{-1}	Pure	0.9727 ± 0.0004
	Water-saturated	0.9758 ± 0.0006
Refractive index, η_D	Pure	1.4225
	Water-saturated	1.4173
Dielectric constant, $\in'$		8.09 ± 0.04
Dipole moment, μ, debyes		3.1
Surface tension, γ, mN m^{-1}		27.2 ± 0.5
Solubility, mol l^{-1} TBP in water Water in TBP Organic liquids		 1.6×10^{-3} 3.58 ± 0.02 Miscible, most compounds
Viscosity, c poise	Pure	3.32 ± 0.07
	Water-saturated	3.99 ± 0.09

1.2.1. Extraction of Metal Cations Using TBP.

The distribution of a particular metal between aqueous and organic phases is defined by the equation:[6]

$$D = [M]_{org} / [M]_{aq}$$

where D is the distribution coefficient or ratio, $[M]_{org}$ is the analytical concentration of metal in organic phase, and $[M]_{aq}$ is the analytical concentration of metal in aqueous phase.

TBP can be categorised as a neutral extractant due to it forming adducts or solvates. This is achieved by way of donation of electrons from the oxygen atom of the phosphoryl group to the metal cations. It has been noted that as the basicity of the phosphoryl group increases, there is an accompanied increase in extractability.[4] Thus the order of extracting power for phosphorus esters is: phosphine oxide > phosphinate > phosphonate > phosphate. There is no evidence that the ether oxygen atoms between the butyl groups and the phosphorus atom are involved in the bonding between TBP and the extracted species.[4]

TBP most readily extracts metals that form triply or quadruply charged cations, including the actinides. Hexa-valent cations of the form MO_2^{2+}, e.g. uranyl ion, where M=U, are also readily extracted. On the other hand, many I- and II- valent metals are poorly extracted.[6, 23, 24]

Nitrate and other anions including chloride, bromide, iodide, thiocyanate, and perchlorate usually accompany the extraction of cations. However, fluorides, carbonates, sulphates, and phosphates are almost insoluble in TBP. This inability to extract from sulphate media renders TBP ineffective as an extractant in metallurgy,

where sulphate liquors are commonplace. Despite this high extracting power, TBP and water are only slightly soluble in one another.

Table 1.2 contains a selection of TBP solvation numbers.

Table 1.2 TBP Solvates.

Elemental Group	Solvates, specific or general
Alkali metals, +1	$LiNO_3 \cdot 2H_2O \cdot 2TBP$
Li, Na, K, Cs, Rb	$NaClO_4 \cdot 5TBP$
	$LiCl \cdot 0$ to $2TBP$
Alkaline earths, +2	$M(NO_3)_2 \cdot 2TBP$
Be, Mg, Ca, Sr, Ba, Ra	$Sr(ClO_4)_2 \cdot 5TBP$
+3 States	$M(NO_3)_3 \cdot 3TBP$
Sc, Y, Ac, lanthanides,	$Ln(ClO_4)_3 \cdot 6TBP$
Actinides	$Eu(ClO_4)_3 \cdot 5$ and $7TBP$
+4 States	$M(NO_3)_4 \cdot 2TBP$
Ti, Zr, Hf, Ce, Th,	
Actinides	$Th(NO_3)_4 \cdot 2$ and $3TBP$
+6 States	$MO_2(NO_3)_2 \cdot 2TBP$
U and other actinides	$MO_2Cl_2 \cdot 2TBP$
	$MO_2(ClO_4)_2 \cdot 4TBP$

1.2.1.1. The Effect of Diluents on the Extractability of Metal Cations Using TBP.

Undiluted TBP is physically difficult to work with because of its viscosity and density complicating mixing and phase separation. As a result, undiluted TBP is used mainly in bench- scale work. For scaled-up tasks such as counter current multistage operations diluted TBP solutions are employed. Dilution of the TBP lowers all distribution coefficients. Distribution coefficients for elements differ between diluted and undiluted TBP because of the different dependencies on TBP strength as a result of the different solvation numbers.

The diluents are usually inert with regard to metal extraction, and serve two main roles:

1. The diluent reduces the extracting power of TBP, which is often too high for most purposes. A too powerful extractant would hinder attempts to complete the solvent extraction cycle by stripping the metal(s) into an aqueous phase.

2. It modifies the physical properties of the extractant, resulting in density and viscosities akin to that of the diluent itself, which are usually lower than TBP.

Dilution enhances the disengagement of the phases, lowers the solubility of TBP in aqueous solutions and the solubility of acids or water in the solvent phase. It also increases the organic/aqueous phase interfacial tension and alters the flashpoint of the extractant.

There are currently three types of diluent used in the Purex processes, they are:

1. Normal paraffin hydrocarbons (NPH), either pure i.e. n-dodecane (nDD) or mixtures of C_9 to C_{14} carbon chains.

2. Alkylated and polymerisation products (e.g., hydrogenated polypropylene tetramer; branched paraffins).

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3. Saturated petroleum fractions, for example odourless kerosene (OK).

In the USA the tendency is towards the use of n-dodecane or NPH as the diluent[4], however, in the UK odorless kerosene is used.[3-5] The composition of odourless kerosene is variable depending on the source but a typical analysis could be n-alkanes 62%, cycloalkanes 26%, branched alkanes 7% and aromatics 5%, with an average carbon chain length of C_{10}-C_{16}.[4,18] The stability of hydrocarbons to radiolytic degradation is: n-alkanes > branched alkanes > cycloalkanes > alkenes[4] and therefore it would be expected that odourless kerosene would not be as stable towards degradation as n-dodecane or NPH. OK can be distilled to give a more stable product [4]but this method too has drawbacks in a resultant lower flashpoint and a 25% loss of starting material. Aromatic diluents have been shown to decrease the extent of TBP degradation by radiolysis[25-27] this is because the resonance structure of the aromatic ring acts as an energy sink thus giving enhanced stability towards the ionising radiation. Among the disadvantages is the increased susceptibility towards nitric acid degradation.

The ratio of solvent to diluent effectively dictates the strength of the extractant. Too low a TBP percentage (v/v) gives inadequate extraction of U and Pu, whilst too high results in the problems found in the use of undiluted TBP, namely unacceptable viscosity and density. The optimum TBP concentration has been found to be within the range 20-30%. The Magnox fuel reprocessing plant at Sellafield uses 20% solutions for its solvent extraction program, whilst most other plants employed 30%; Marcoule used 40% until 1961.[4] THORP uses 30% mixtures and now all modern reprocessing plants tend to use 30% mixtures.[3, 5] The choice seems to depend on the flow sheet for the operation and the tendency is to use 30% where U(IV) is used as a reductant for Pu. At this percentage the U(IV) can be extracted along with U(VI)

without any alterations to the system. However, in the reprocessing of fast reactor fuel low percentages (3, 5-10) have been studied[28]. The conclusions show increased decontamination factors and lower concentrations of solvent degradation products. The low percentage means an increased volume of both TBP and diluent are required since the same amounts of U and Pu have to be recovered.

It was first reported in 1958 in a report by Blake *et al.*[29] that when a dialkyl hydrogen phosphate, $(RO)_2PO_2H$, is used in conjunction with TBP, the extracting power of the mixture exceeds the sum of the individual extracting powers of the components.

1.2.2. Reactions of TBP.

The reactions of TBP with various reagents are of importance to both research and process applications. Reactions in acidic and basic media result in the formation, generally, of the same compounds, albeit via different mechanisms.

1.2.2.1. Alkaline Hydrolysis of TBP.

Hydrolysis of TBP and other alkyl phosphates results in the formation of dibutylphosphoric acid (HDBP), as the stable product. Monobutylphosphoric acid (H_2MBP), phosphoric acid (H_3PO_4), and some butanol are also formed as secondary products.[4, 30, 31] The reaction is first order with respect to both phosphate ester and hydroxide ion. Hydrolysis only occurs in the aqueous phase, thus yields are affected by the solubility of TBP in the alkali.[30]

The reaction is known to proceed via P-O bond rupture[31] and the following mechanism represents the reaction:

$$(RO)_3PO + OH^- \longrightarrow (RP)_2PO(OH) + RO^-$$

$$(RO)_2PO(OH) + OH^- \longrightarrow (RO)_2PO(O)^- + H_2O$$

$$RO^- + H_2O \longrightarrow ROH + OH^-$$
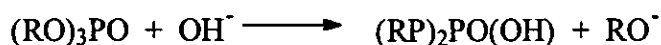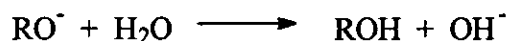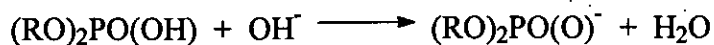
Sodium carbonate solutions are used in the clean-up of Purex process degraded TBP. No report of hydrolytic attack by the carbonate solution on the solvent has been made.[4]

1.2.2.2. Acid Hydrolysis of TBP.

The acid catalysed dealkylation of TBP occurs in both the aqueous and organic phases. Much work has been done[4, 9, 10, 30-34] with regard to this reaction because of the implications to the Purex process where the system TBP-diluent-HNO_3-H_2O is encountered.

The initial step in the reaction yields HDBP and butyl alcohol, with H_2MBP and then phosphoric acid formed by further hydrolysis.

$$(C_4H_9O)_3PO + HOH \xrightarrow{H^+} (C_4H_9O)_2PO(OH) + C_4H_9OH$$

$$(C_4H_9O)_2PO(OH) + HOH \xrightarrow{H^+} (C_4H_9O)PO(OH)_2 + C_4H_9OH$$

$$(C_4H_9O)PO(OH)_2 + HOH \xrightarrow{H^+} H_3PO_4 + C_4H_9OH$$
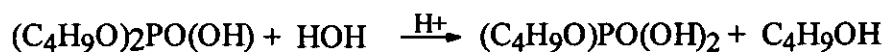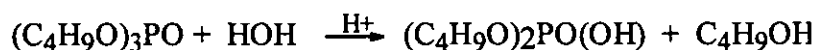
Blumenthal and Herbert[31] showed that acid-catalysed hydrolysis of tri-methyl phosphate occurred primarily (70%) by C-O bond cleavage rather than P-O rupture, thus forming methyl chloride as a product. So, in the TBP-nitric acid-water system, butyl nitrate as well as phosphoric acid and its mono- and dibutyl esters are the products and this was found in reactions using concentrated nitric acid.[32]

These reactions are of importance to the nuclear fuels reprocessing industry. For the decomposition reaction in the system 30%TBP-n-paraffin diluent-aqueous nitric acid, the order of catalyst effectiveness is: HI > HBr > HCl > $HNO_3 \geq H_2SO_4$. Rates

for the acid catalysed organic-phase hydrolysis of TBP increase when the organic phase contains U(IV), zirconium, or thorium nitrates. While, on the other hand, U(VI) increases rates at low nitric acid concentrations, but decreases them at high acid strengths. Overall, the order of decreasing effect of metal ion on the rate of hydrolysis is: Zr(IV) > U(IV) > Th(IV) > U(VI).

The reaction of tri-ethyl phosphate and phosphoric acid was studied by Cherbuliez and Leber[35] :

$$(C_2H_5O)_3PO + H_3PO_4 \longrightarrow (C_2H_5O)_2PO(OH) + (C_2H_5O)PO_3H_2$$
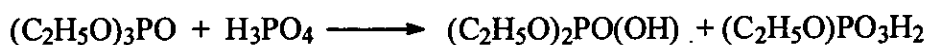
they found that the reaction proceeded one third by hydrolysis (water the active agent) and two thirds by acidolysis (H_3PO_4 the active agent).

1.2.2.3. Oxidation of TBP by Air or Oxygen.

Work has been carried out on the thermal chemical oxidation of organic compounds used in the extraction systems.[36] It was found that destructive oxidation began at elevated temperatures greater than 103°C, accompanied by gas evolution. The thermochemical oxidation of TBP includes a number of consecutive and concurrent reactions, such as acid hydrolysis, the oxidation of the TBP hydrolysis products, and destructive TBP oxidation. Some of these reactions can proceed with heat explosion and two known accidents have happened in the past as a result of this; at Savannah River, USA (1976) and at Tomsk, Siberia (1993).[4]

Various investigators[37-39] have studied thermal and pyrolytic decomposition of TBP and the subsequent products formed. But-1-ene was the major product of these reactions. Some butan-1-ol was reported by Paciorek et al[39] and the oxidation of this lead to the presence of butyraldehyde. Other studies[37, 38, 40] showed that small amounts of butanol, dibutylether, and tetrabutyl pyrophosphate were formed.

1.2.2.4. TBP as an Alkylating Agent.

TBP was found to react with $AlCl_3$ by Berman and Lowry[41] in an attempt to use the TBP as an alkylating agent in Friedel-Crafts reactions.

$$(C_4H_9O)_3PO + 3C_6H_6 + AlCl_3 \longrightarrow 3(C_4H_9)C_6H_5 + AlPO_4 + 3HCl$$

1.3. Radiolytic Behaviour of the Components of Solvent Extraction Systems.

1.3.1. The Chemical Effects of Ionising Radiation.

The chemical effects of radiation depend on the composition of the matter exposed and the amount of energy given to this matter by the radiation. Direct ionising radiation is caused by charged particles (e^+, α, e^-, etc.) whereas indirect ionising radiation is a result of uncharged particles (n) and electromagnetic radiation (γ).[1] Exposure of water to ionising radiation results in the formation of the radiolysis products within 10^{-7}s and these include e_{aq}^-, H·, ·OH, H_2, H_2O_2, and H_3O^+. In the absence of dissolved species, reactions occur between these particles and between water. In pure gamma or X-ray irradiated water the net result of these reactions is the reformation of water, thus no net decomposition is incurred. In irradiated aqueous solutions at concentrations <0.1 mol dm^{-3}, energy is absorbed by the water molecules and changes observed are due to the interaction between the solutes and the radiolysis products of water. At greater concentrations the solute may be liable to direct ionisation.

With regard to organic compounds, in general they have more electrons than water and thus a greater variety of products can be obtained from their radiolysis. The effects are strongly dependent on the structure of the molecule. Smaller molecules than the original are generated along with the substantially larger polymeric products.[1, 26, 27]

1.3.2. Radiolysis of TBP.

The phosphate anion in TBP is very stable towards radiolytic attack with the rupture of a C-O bond more likely than that of a P-O bond.[4]

The radiolysis of TBP either wet or dry results in the degradation products HDBP, H_2MBP, H_3PO_4, H_2, CH_4, C_2H_4, C_2H_6, C_4H_9OH, various hydrocarbons, and a polymeric product.[4, 9-12, 16, 18, 25, 26, 30, 34, 42-47] The formation of and the identification of the degradation products of TBP is of great importance to the Purex process since intense radiation fields are encountered in the first extraction stage.[1,3-5, 7]

The yields of the principal degradation products follows the decreasing order HDBP $> H_2MBP > H_3PO_4$,[4, 30, 42-47] and these yields are often measured in terms of the G value, where G is the number of molecules of TBP transformed per 100eV of energy absorbed from the radiation source. Most reactions have G-values < 10.[1] A summary of reported G values is contained in Table 1.3, H_3PO_4 was not reported.

Table 1.3. TBP Radiolysis.

Radiation Source	HDBP	H₂MBP	H₂	CH₄	C₂	C₃+C₄	Ref.
1.25 MeV electrons	1.52	0.12	1.11	0.005	0.24	0.45	48
⁶⁰Co gamma	1.7-1.8	0.3	-	-	-	-	25
1 MeV electrons	2.25	0.39	1.59	0.07	0.13	0.75	47
1.66 MeV electrons	2.44	0.14	1.73	0.07	0.18	0.65	46

Radiolysis also occurs in both aqueous and organic phases and in the aqueous layer the attack on TBP is believed to be from the radiation produced hydroxyl radicals originating from water:

$$H_2O \longrightarrow H^{\cdot} + {}^{\cdot}OH$$

27
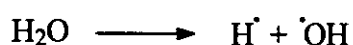
followed by DBP formation via attack at the α-C:[43]

$$OH^{\cdot} + CH_3(CH_2)_2CH_2O\underset{\underset{O}{\|}}{P}(OBu)_2 \longrightarrow CH_3(CH_2)_2\overset{\cdot}{C}HO\underset{\underset{O}{\|}}{P}(OBu)_2 + H_2O$$
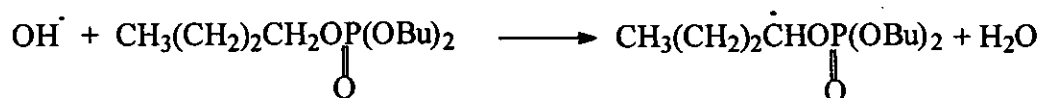
and the formation of butyraldehyde was believed to be as a result of O-addition in oxygenated solutions to the TBP radical. Thus in less oxygenated solutions the yield of DBP was less; although in nitric acid containing systems no oxygen effect was noted.

Lesage et al.[44] investigated the formation of minor radiation degradation products and concluded that one feature of the reprocessing process is that an accumulation of trace quantity products occurs. Lesage found that individual product identification was not possible as a result of the complexity of the resulting mixtures. However, he proposed that the radiolysis of TBP proceeded by the preferential loss of radical H· from the C-H bond, followed by O-C, C-C or O-P bond cleavage. Recombination of radicals can result in a wide variety of molecules. In a nitric acid media the TBP radical dimerises and is transformed under the oxidative conditions into several butyl chains substituted hydroxy or nitro phosphates as well as alkylated TBP. The butyl chain hydroxylated phosphate leads to ketones, ethers and O-ester derivatives.

In the TBP-nDD-nitric acid system, a large amount of material has been published.[3, 4, 9-14, 16, 18, 19, 24, 25-30, 42-53] Along with thermal and radiolytic degradation, U.V illumination was investigated.[34]

Irradiation has also been found to generate radiation modified phosphates: diphosphates and phosphate phosphonates[45] as organic phase products, although the yields of the diphosphate and phosphate phosphonate were less in a system containing nitric acid. Of note is that the use of benzene as a diluent not only improves the extraction capability of TBP but also reduces the extent of radiolytic degradation.[26]

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Figure 1.7 Radiolytic Degradation Reactions.

Aromatic additives act as protectors, whereas certain saturated hydrocarbons (hexane, dodecane) sensitise or enhance the decomposition of TBP. It is thought that mixtures of, for example, dodecane and toluene, could be employed to provide a degree of resistance to radiation,[27] although are not used in industry. Benzene is not used as diluent because of its high density and low flash point.[4] Figure 1.7 presents a summary of radiolytic degradation reactions of TBP and hydrocarbon diluents.

Carboxylic acids were formed from the irradiation of TBP in n-dodecane,[54] but were generated from the diluent, whereas the TBP radiolysis products were alkyl-phosphoric acids, as would be expected.

1.3.3. Radiolysis and Degradation of Diluent Systems.

The second component of the solvent used for extraction is also prone to degradation as a result of exposure to ionising radiation or high temperatures. The extent to which degradation occurs and the nature of the degradation products is dependent on the diluent employed. The order of susceptibility to radiolytic attack of hydrocarbons is olefins > napthenes > isoparaffins > n-paraffins.[18] Thus, the OK diluent employed in THORP is fairly stable to radiolytic attack but is not as stable as n-dodecane would be, for example.

In the past[18] a distinction has been made between radiolytic and chemical degradation. However, since both proceed by via free-radical mechanisms, the degradation products formed may be similar.[53] The species resultant from the thermal degradation of the diluent are :

1. Aliphatic nitro compounds, which result from nitration by nitrous or nitric acids.

2. Aliphatic carboxylic acids, resulting from oxidation reactions of nitric and nitrous acids.

3. Aliphatic nitroso compounds, formed by the action of nitrous acids on secondary nitro compounds.

4. Nitro and nitroso derived aromatics.

5. Ketones and aldehydes which lead to the formation of carboxylic acids.

The deterioration of the solvent is believed to be due to the diluent degradation products rather than those originating from TBP. Degradation products from TBP can be removed by a simple alkaline wash,[4, 10, 18] and this is the procedure employed in THORP.[3]

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There are a number of hypotheses postulated to explain diluent degradation and these are summarised in a review on the decomposition of solvent extraction media by Tahraoui and Morris.[9] Hydroxamic acids were suggested to be the main complexing species from the degradation of the diluent.[49, 50] The precursors to these compounds were believed to be primary nitroparaffins formed by nitration of hydrocarbon -CH_3 groups. These then reacted in the manner of the Victor-Meyer and Nef reactions[55] to yield the hydroxamic acids. Lane[49] believed that the hydroxamic acids would not retain metal ions until a substantial concentration had built up. It is not in doubt that the hydroxamic acids are capable of retention of metals ions, but whether they are actually produced in the system.[9] Becker and co-workers[56] reported that the presence of hydroxamic acids was not confirmed, whilst Nowak[33] suggested that the hydroxamic acids were destroyed by the action of nitrous acid.

More recently Mailen et al.[53] performed a series of experiments to develop reactions for the degradation of the NPH diluent. This work concl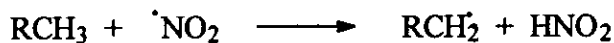uded that nitric acid does not chemically effect the nitration of paraffins but serves as a source for the formation of radical-like species.[57] The radical-like species being monomeric $NO_2^{\bullet}$ formed thus:

$$HNO_3 \xrightarrow{\gamma} {}^{\bullet}OH + {}^{\bullet}NO_2$$
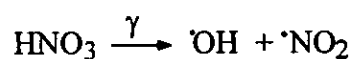
the radical then reacts with n-alkanes giving nitrous acid, water and free hydrocarbon radicals:

$$RCH_3 + {}^{\bullet}NO_2 \longrightarrow RCH_2^{\bullet} + HNO_2$$

and $$\qquad RCH_3 + {}^{\bullet}OH \longrightarrow RCH_2^{\bullet} + H_2O$$
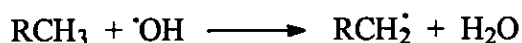
the hydrocarbon radical may then react with a further molecule of $^{\bullet}NO_2$ to give nitro or nitrite compounds:

$$RCH_2^{\bullet} + O\overset{\bullet}{N}O \underset{\searrow}{\overset{\longrightarrow}{}} \begin{array}{l} RCH_2NO_2 \\[1em] RCH_2ONO \end{array}$$

31
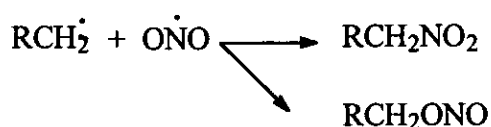
the nitro compound RCH_2NO_2 can then further react with the nitrous acid formed giving a nitroso compound:

$$RCH_2NO_2 + HNO_2 \longrightarrow R\overset{\displaystyle |}{\underset{\displaystyle NO}{C}}HNO_2 + H_2O$$
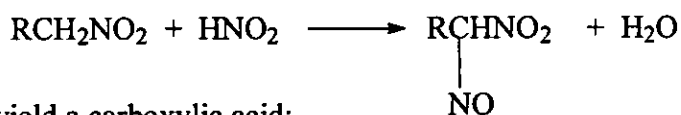
or be hydrolysed to yield a carboxylic acid:

$$RCH_2NO_2 + HNO_2 \longrightarrow RCO_2H + H_2NOH$$
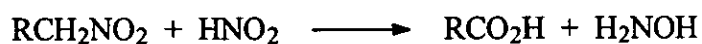
other reactions can occur; for example the nitrite formed can undergo hydrolysis to the alcohol:

$$RCH_2ONO + H_2O \rightleftharpoons RCH_2OH + HNO_2$$
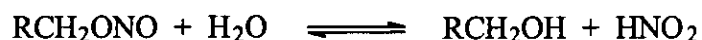
which may then be oxidised to give a carboxylic acid:

$$RCH_2OH + 2(O) \longrightarrow RCO_2H + H_2O$$
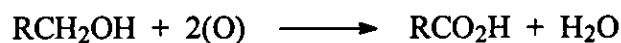
This mechanism is thought to apply to the PUREX process since it fits the facts concerning the identity of the products formed.[18, 45, 53, 56]

It was found that gamma irradiation of a 30% TBP solution in nDD in contact with 3M nitric acid resulted in the formation of C_4 to C_{12} carboxylic acids[54], lauric acid being the principal product. Fracture of the hydrocarbon chain was energetically more favourable than end carbon fission. Long chain aliphatic acids are regarded as the end product of the normal paraffin hydrocarbon (NPH) degradation[53] and these are among the most chemically stable of the degradation products formed. Tallent[53] found by spectrophotometric detection that the main compounds formed by NPH chemical degradation were long chain nitro, nitrite, and nitroso compounds; GC-MS analysis also revealed the presence of alcohols, unsaturated alcohols, nitro alkenes, nitro alcohols and esters. Smith et al.[18] also reported similar observations in chemically degraded diluent systems.

1.4. The Effects of the Degradation Products on Solvent Extraction.

1.4.1. The Effects of TBP Degradation Products.

The products of primary degradation of greatest relevance are TBP, HDBP, H_2MBP, H_3PO_4 and BuOH. Butanol is preferentially distributed into the aqueous phase and can be removed in the aqueous waste streams.[4, 30] Phosphoric acid is usually formed in small amounts. DBP and MBP though are more problematic. DBP is a strong acid with pKa = 1.00, in most organic solvents it exists as a dimer. Problems occur in the process due to the retention in the organic phase by DBP of metal cations, most notably niobium and zirconium, ruthenium [8, 12-16, 19, 34, 42, 58-61], which decrease metal recovery and decontamination efficiences and lead to physical problems. Other adverse effects include undesirable effects on the equipment operation and extraction process, such as loss of uranium and plutonium to waste streams, insufficient phase separation and formation and deposition of solids.[17] These strong complexes decrease metal recovery and decontamination efficiencies and are capable of causing physical problems. This is complicated by the synergism displayed when a dialkyl hydrogenphosphate is used in conjunction with a neutral organophosphorus reagent, e.g. TBP. The extracting power of the mixture exceeds the sum of the extracting power of its components.[29]

It was found that the precipitates, often containing zirconium, generated by the degradation products in the TBP phase are conducive to the formation of interfacial cruds.[4, 8, 16, 18, 52, 58, 60, 62, 63] In the system 30% TBP-nDD-Zr-nitric acid containing 250ppm HDBP of which the aqueous phase had a pH of $\approx$ 1.5, a precipitate of $ZrO(DBP)_2$ was formed, which was residual in the organic phase.[52] In comparison, using 250ppm H_2MBP in analogous conditions, it was found that zirconium precipitates were formed only at concentrations below 1 mol HNO_3 / litre, which is

below Purex extraction conditions (6M HNO_3). Precipitates of zirconium phosphate were also reported.

Finely divided solids can produce stable emulsions (cruds) at the aqueous/organic interface in solvent extraction processes. In a system containing 0.01M $ZrO(NO_3)_2$ in aqueous 6M nitric acid solution with radiochemically degraded 30%TBP in odourless kerosene diluent containing 50ppm H_3PO_4 the formation of cruds was observed.[60] These contained micro-crystalline deposits of carbonate in the interface which was deemed to have arisen from the wash solution. The purpose of the aqueous sodium carbonate wash is to remove from the organic phase DBP and MBP. Also reported in the aqueous-organic interface of the same system were non-crystalline crud aggregate particles. Smith et al.[60] concluded that a zirconium bis(di-n-butylphosphate) dinitrate complex was responsible for these and several structures were proposed, and these are shown in Figure 1.8.

1.4.2. The Effects of Diluent Degradation Products.

It is thought that with the exception of carboxylic acids the primary products of degradation are not directly responsible for fission product retention in the organic phase. [9, 18, 50, 51, 53] Long-chain aliphatic acids give phase separation problems when the solvent is washed with aqueous sodium carbonate solutions, even at concentrations as low as 1×10^{-3}M, and the retention of Pu.[51] The sodium salts of these acids are surface active and will stabilise emulsions by reducing interfacial tension[64] in addition to the TBP degradation products that are emulsion stabilisers. Micelle formation may also be involved.[56] Adamov[46] found that carboxylic acids with a chain length $<C_{11}$ are removed from solvent by the alkali wash.
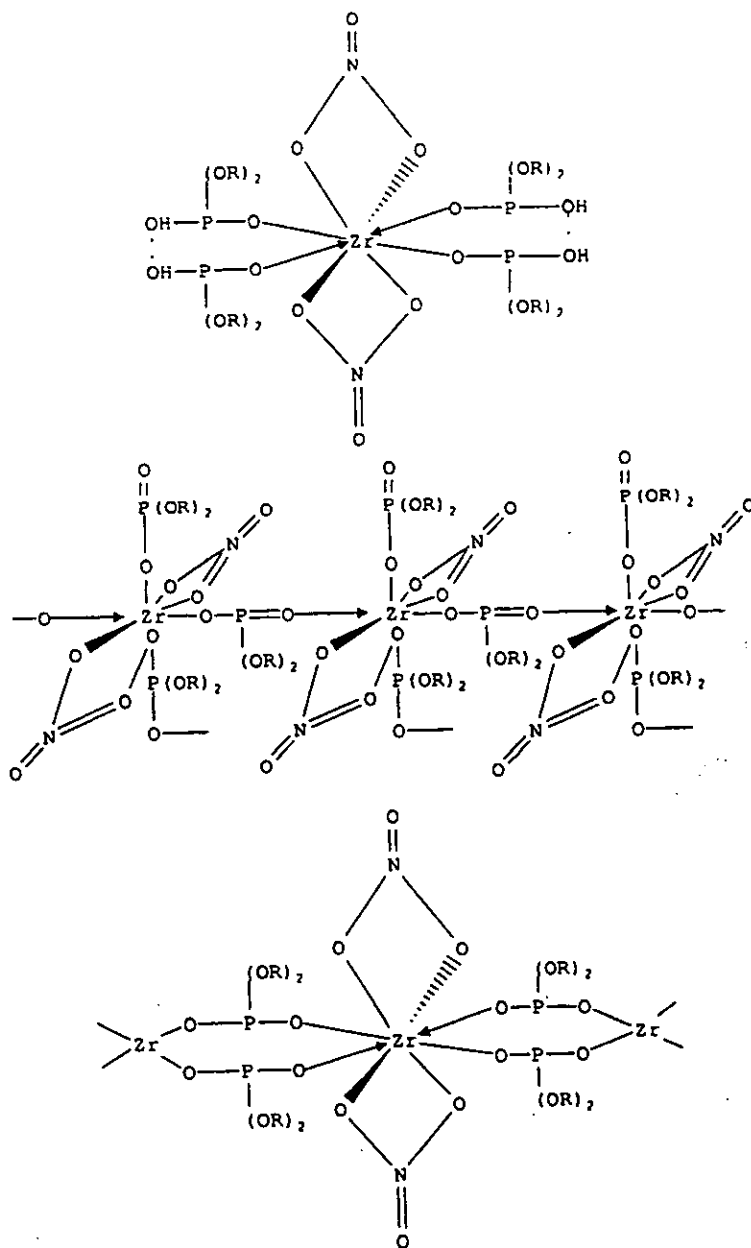
Figure 1.8 Structures Proposed for Zirconium bis(di-n-butylphosphate)dinitrate Complex.

The retention of low levels of fission products in the solvent from one extraction cycle to the next is attributable to degradation products formed in secondary reactions yielding long chain alkyl butyl-phosphoric acids.[53] Dilute Na_2CO_3 solutions do not remove these from TBP-diluent systems.[65]

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Through secondary reactions the solvent and diluent degradation products generate various surfactants, complexants, and crud formers. No practical means for removal of diluent degradation products from TBP phases has been found.

Secondary reactions include:

1. Reaction of a carboxylic acid and alcohol yielding an ester and water.

2. Ester alkaline hydrolysis producing a surfactant as does the reaction of long chain aliphatic acids and alkali.

3. Attack by surfactants on TBP to give complexants e.g. butyl lauryl-phosphoric acid.

Radionuclides sorbed by interfacial crud are later discharged into the product stream during stripping operations.[51] Neace[52] showed that reactions involving TBP and organic soluble cationic surfactants in the hydroxide form produce strong complexants for Zr and Nb which, unlike DBP, are not removed by contact with dry lime or carbonate solutions. One of these complexants butyl lauryl phosphoric acid has been shown to extract Zr into TBP phases[65] and Nb.[66] It was found that a wash with water was sufficient for its removal. Neace in his paper on diluent degradation[51] demonstrated that the principal diluent degradation products: carbonyls, alkyl nitrates and nitroalkanes could be removed by the solid sorber activated alumina. Healy[10] also examined the use of solid absorbents in the clean-up of degraded 20% TBP/OK solvent and found that titania could be used as an effective replacement for the alkali solvent wash. Aluminium oxide and aluminosilicate dust were also shown to be effective methods.[67]

In systems employing OK as TBP diluent it would be expected that there are a greater variety of chain primary and secondary products formed due to the varied composition of the mixture.[50]

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1.4.3 Formation of Interfacial Cruds.

Most of the species responsible for the formation of interfacial cruds have already been discussed, while the mechanism has not. As already noted, the chemical and physical aspects of crud can differ for each separation operation and variables include inorganic composition, organic content, colour, density, etc. Figure 1.9 shows a proposed summary of interfacial crud formation.
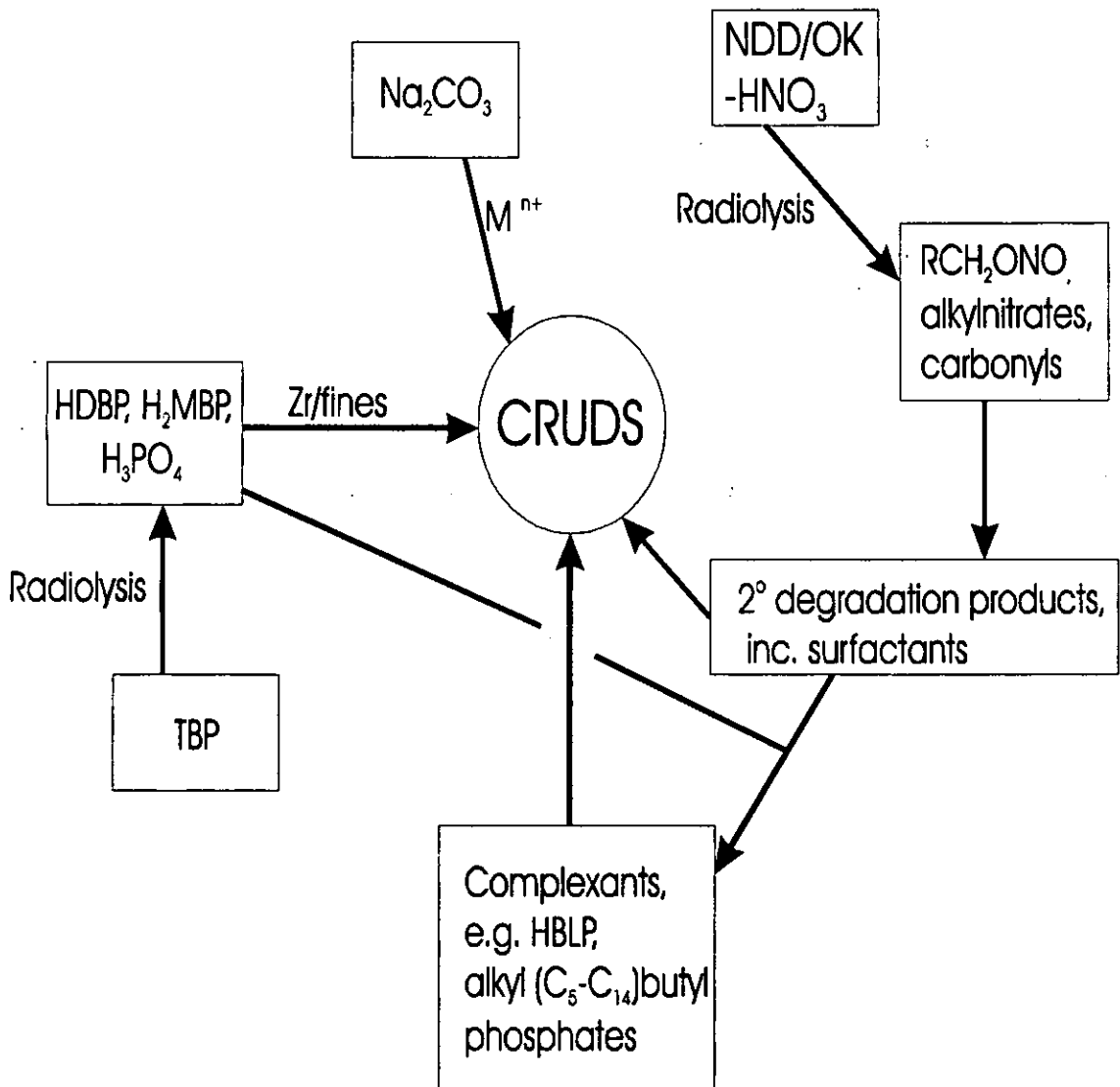
Figure 1.9 Summary of Crud Formation.

Operational disturbances cause the formation of emulsions commonly called crud. Emulsions are described as a dispersed system in which the phases are immiscible or partially miscible liquids.[64]

First Contactor Stage Cruds.

For stable cruds/emulsions an emulsifying agent must be present; there are three broad categories:

1. Surface active materials.

2. Naturally occurring materials.

3. Finely divided solids.

The emulsifying agent promotes stability by forming an adsorbed film around the dispersed droplet that helps to diminish any coagulation or coalescence.

As covered, these cruds are formed by complexes of Zr with degradation products of TBP, mainly DBP, and/or fines from the dissolution process, fines from the extraction or fines generated as a result of corrosion.[16, 18, 59, 60, 62] Zirconium MBP complexes are important in the formation of zirconium precipitates and interfacial cruds.[59] When MBP is added to aqueous nitric acid solutions of zirconium, a gelatinous precipitate forms.[13, 65] The precipitate has an empirical formula of $Zr(MBP)_2 \cdot 2H_2O$. Addition of MBP to extracts of zirconium in TBP also results in the precipitation of solids with a Zr : MBP ratio of two, and these precipitates did not include the nitrate ion.[58] Precipitates of chemical formula $Zr(NO_3)_2(HDBP)_2(OH)_2$ and $Zr(H_2MBP)_2(OH)_2$ have also been observed.[58, 63]

Emulsions which are stabilised by fines were first described by Pickering.[68] The emulsions generated were of the oil in water type. Later, Briggs[69] reported the stabilisation of water in oil emulsions by fines. Adsorbed surfactants at oil-water

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interfaces lower the interfacial energy, thus aiding the growth and enhancement of stability of the large interfacial areas associated with emulsions.

The underlying mechanism is the different wetting of the fines by the two liquids. In an oil in water emulsion, the hydrophilic fines are adsorbed on the oil drops but the majority of the fines' surface is immersed into the aqueous phase and thus stabilisation occurs because the dispersed phase cannot coalesce due to the covering of the fines. Zimmer and Borchardt[52] found that the cruds produced by $ZrO(H_2PO_4)_2$, silica and bentonite fines were of the oil in water type. In contrast, cruds formed by $ZrO(DBP)_2$ were of the water in oil type.

Alkali Solvent Wash Cruds.

Smith et al.[18] in their study on the nature of interfacial cruds formed in the alkali solvent wash stage during the Purex process found that three types of crud were possible under varying conditions of the system $OK-TBP-Na_2CO_3$. These are classified as follows:

1. Type I $\rightarrow$ interfacial fines / emulsions.

2. Type II $\rightarrow$ amorphous interfacial deposits.

3. Type III $\rightarrow$ multilayers of interfacial film.

NB chemically degraded nDD, contacted with 0.25M Na_2CO_3 generated Type I crud.

1. Type I Crud.

Tallent[53] as previously mentioned described the problems that could be caused by long chain carboxylic acids in the solvent system. Smith et al.[18] showed in tests that lightly degraded OK doped with C_6-C_{10} chain acids produced Type I crud and C_{10}-C_{12} gave emulsions. The sodium salts of longer chain acids being

surface active lower the interfacial tension and produce emulsions. Smith[18] proposed that the factors involved in the formation of this crud include the interaction of the acid with other degradation products as well as the balance between the hydrophilic and hydrophobic properties of the crud.

2. Type II Crud

Smith[18] proposed this to be a "nonstoichiometric agglomerate of degradation products", that, due to their surface active properties accumulate at the liquid interface. This crud was observed in conditions where more highly degraded OK had been used than that which formed Type I crud, thus implying that the Type I crud may have acted as a "nucleating agent for the formation of Type II crud". Added fines, in an attempt to affect the formation of Type II crud, were unsuccessful, although Type I crud forming characteristics were observed.

OK was found to become crud forming after approximately one hour reflux with 6M nitric acid[18], yielding a degradation product concentration of $0.012gL^{-1}$. It was found that the instability of nDD to form Type II cruds could be explained by the greater chemical stability of nDD relative to OK, thus the yield of degradation products formed over a period of time would be less and also less varied. It was also postulated that the degradation products obtained from nDD were not the degradation products responsible for Type II cruds.

3. Type III Crud

It was reported[18] that the occurrence of this crud was more unpredictable, and that any Type I crud formed never formed Type III crud. Smith et al.[18] proposed this type of crud was, as was the case for Type I crud, a result of long chain

carboxylic acids and other diluent degradation products. Smith proposed that this type of crud consisted of "lamellae of orientated surface-active degradation products".

1.5. The Interaction of Microwaves With Matter.

The ability to generate electromagnetic radiation as microwaves was developed under secrecy during war-time research into radar systems.

The breakthrough was made possible by the invention of a device known as a magnetron. The remarkable heating effects this form of electromagnetic radiation could achieve soon led to domestic and commercial microwave ovens appearing on the market. This originally began in the U.S.A in the 1950s, while later in the 1980s more effective production techniques and subsequently more affordable cost resulted in a rise in occurrence of microwave ovens in the domestic kitchen. Since, a whole industry of convenient "ready meal" foods has emerged to exploit the heating capabilities.

Heating effects that have not been ignored by the manufacturing industry since applications can be found in industrial processes such as drying, curing, hardening, sterilizing, dye fixing and melting.[70]

1.5.1. The Electromagnetic Spectrum.

Microwave is the name given to the electromagnetic waves arising as radiation from electrical disturbances at high frequencies. In the electromagnetic spectrum the region corresponding to microwave radiation lies between wavelengths of 1 cm and 1m (frequencies of 300 MHz and 3000 000 MHz). This region occurs sandwiched between the infra-red and radio region (Figure 1.10).

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The wavelengths between 1 cm and 25 cm are designated for RADAR transmissions, while telecommunication applications use the remainder. Domestic and industrial microwave heaters have been allocated wavelengths of 32.8 cm (900 MHz), 12.2 cm (2.45 GHz), 5.17 cm (5800 MHz), and 1.35 cm (22125 MHz), so as not to interfere with RADAR and telecommunication uses. Domestic ovens usually operate at 2.45 GHz.
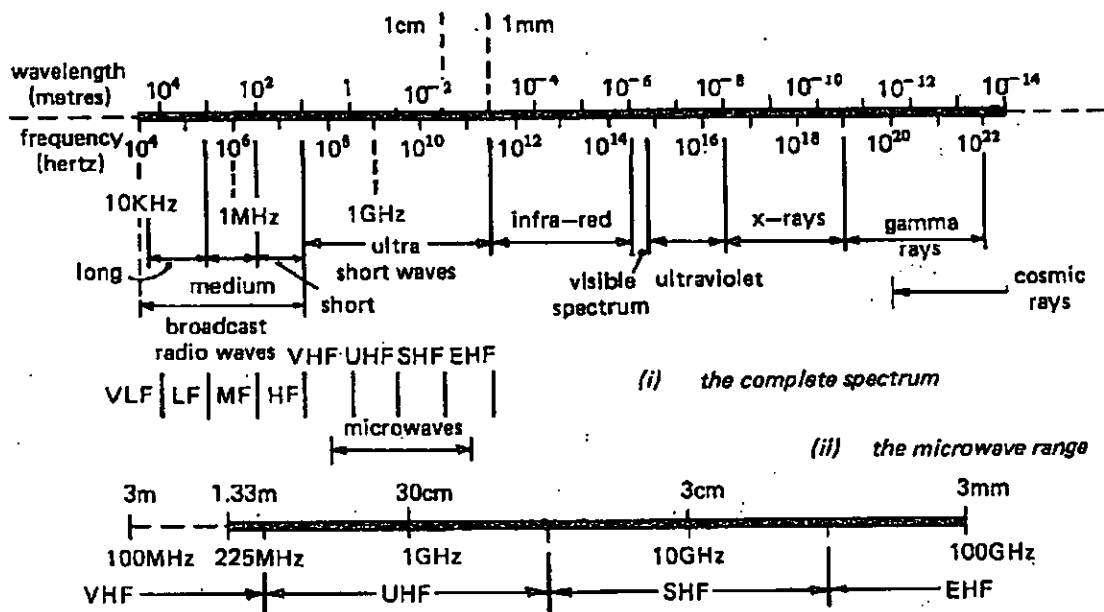
Figure 1.10 The Electromagnetic Spectrum.

1.5.2. Dielectric Polarization.

The ability of an electric field to polarize charges in a material and the inability of this polarization to follow rapid reversals of an electric field is one source of dielectric heating.

When a suitable dielectric is placed in an electric field, changes in the charge distribution occur and the total polarization is given by the following expression:

$$\alpha_t = \alpha_e + \alpha_a + \alpha_d + \alpha_i + \alpha_v$$

Where :

α_e = the electric polarization arising from the realignment of electrons around specific nuclei,

α_a = the atomic polarization which results from the relative displacement of nuclei due to he unequal distribution of charge within the molecule,

α_d = the dipolar polarization which occurs due to the orientation of permanent dipoles by the electric field,

α_I = the interfacial polarization which occurs when there is a build-up of charges at the interface (Maxwell-Wagner effect) and,

α_v = the vibrational polarization, occurring because of forces between atoms.

When an oscillating electric field is applied α_e and α_a do not contribute to the dielectric heating of a material because the time-scales of the polarization and depolarization of these quantities are so fast (compared to microwave frequencies). The opposite is the case for α_d and α_i, these quantities have time-scales comparable to microwave frequencies and thus effect the dielectric heating.

(i) The dipolar polarization, α_d, is a result of the dipole moment of a molecule, for instance in a molecule of water the dipole moment arises from the differing electronegativities of the O and H atoms. At low frequencies the dielectric polarization is in phase with the electric field since the time required to change the field direction is longer than the response time of the dipole. The field provides the energy for the molecules to rotate into alignment. A negligible amount of energy loss, as heat, occurs as the dipole is displaced from its alignment and is realigned. If the field alternates at some high frequency then the oscillations occur at a faster rate than the response time of the dipoles. Thus the dipoles do not rotate and hence no energy is absorbed and heating does not occur.

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Ideally the frequency should be such that the time-scale for the field to oscillate is approximately equal to the response time for the dipole. In this situation the polarization lags behind the changes in the field. This indicates that the molecule is absorbing energy from the field and is heated.

The magnetic field of the electromagnetic wave has an insignificant effect because there is nothing in most dielectrics it can work on.
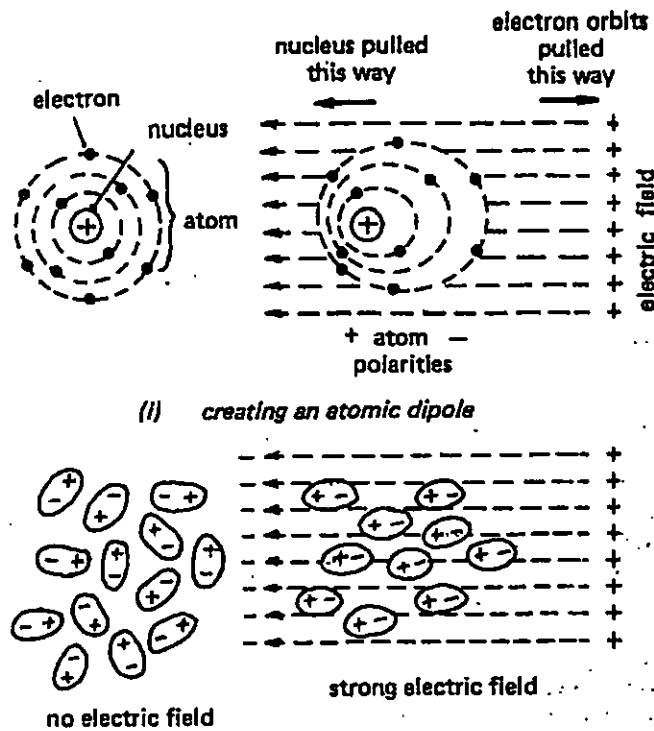
Figure 1.11 Schematic Diagram Showing Dielectric Polarisation.

The power generated within a dielectric is given by the product $2\pi f E^2 \varepsilon_o \delta$ and measured in watts per unit volume (i.e. W/m^3); where E is the applied voltage at a frequency, f, ε_0 is the electric constant (permittivity of free space) and δ is the dielectric loss factor.

For a given electric field the heat generated is proportional to the power factor, and the greater the overall loss within a dielectric the more power which will be absorbed from an electromagnetic wave.

The dielectric properties of a material are governed by two factors:

1. ε', the dielectric constant which defines the ability of a molecule to be polarized by the applied field, where:

$$\varepsilon' = \frac{C}{Co} \quad , C \text{ being the conductance,}$$

C_o the conductance of free space.

At low frequency the value of ε' will reach a maximum as the maximum amount of energy is stored in the material.
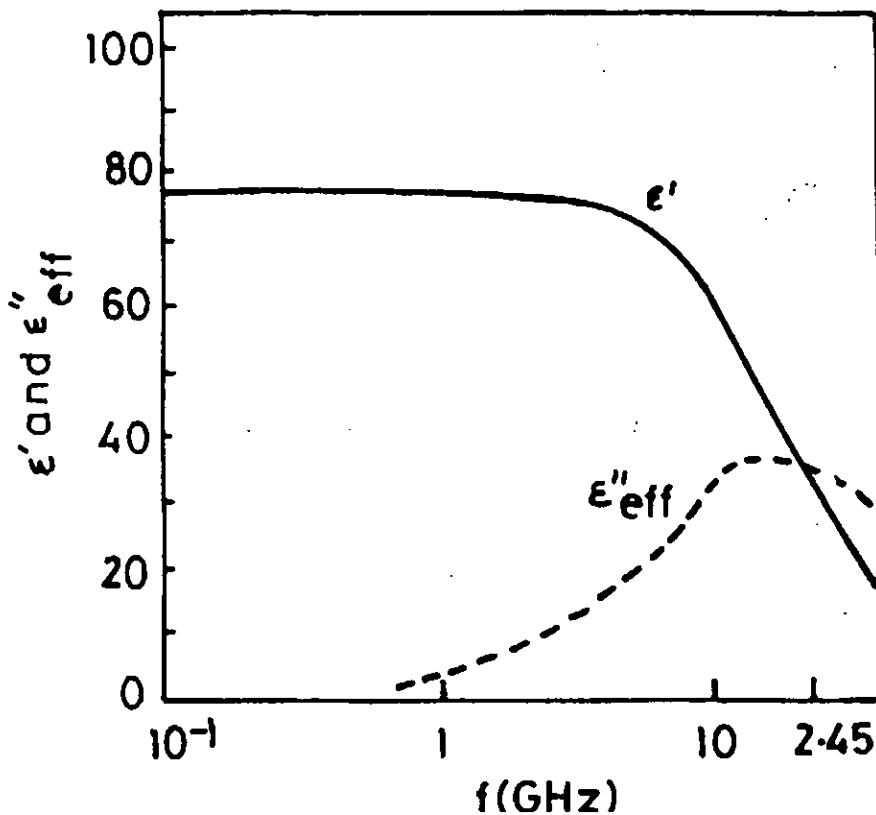
Figure 1.12 Dielectric Properties of Water as a Function of Frequency.

2. ε'', the dielectric loss which describes the efficiency of the conversion of electromagnetic radiation to heat, and is given by the following expression:

$$\varepsilon'' = \frac{\sigma}{2\pi f} , \text{ where } \sigma \text{ is the dielectric conductivity.}$$

The dielectric loss goes through a maximum as the dielectric constant diminishes, and this is evident in Figure 1.12, which shows the relationship between dielectric properties and frequency for water. The ratio of the dielectric loss to the dielectric constant is called the loss tangent and is defined as thus:

$$\tan \delta = \frac{\varepsilon''}{\varepsilon'}$$

and is a measure of the ability of a material to convert electromagnetic radiation into heat.

1.5.3. Debye Equation for Relaxation Time.

In liquids it is necessary to consider the behaviour of a molecule in an alternating field, arising from the rotation of a spherical dipole in a viscous medium dominated by friction. It is assumed the dipoles can point in any direction and are continually changing due to thermal agitation.[71] Thus, Debye derived the following expression for the relaxation time of spherical dipoles:

$$\tau = \frac{4\pi r^3 \eta}{KT},$$

where τ = relaxation time constant, r = radius of the dipole molecule, η = the viscosity of the medium and K is Boltzmann's constant.

Some liquid and solid dielectrics have relaxation times longer than those generated by the equation, and they are still inaccurate when a correction factor is introduced. Debye introduced the idea of an activation energy U, which is equal to the energy required for a dipole to acquire a new position. In a gas U<< KT, since the molecules are free there is less force on each one. In solids U>>KT, since the inter-atomic forces are large due to the spatial arrangement and the number of equilibrium positions available. In order to change from one position to another a potential energy

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barrier must be overcome. If two equilibrium positions are possible with opposite dipole directions then the energy separating them is U_a, as shown in Figure 1.13.
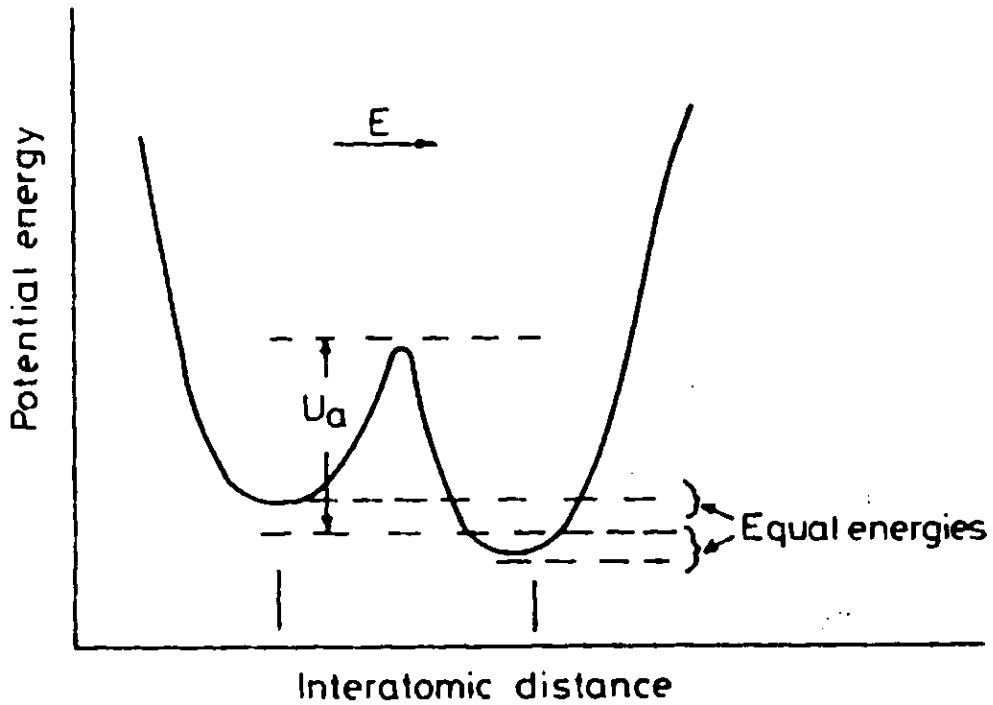
Figure 1.13 Potential Energy Diagram for Two Alternative Positions of a Dipole Relative to an Electric Field.

Using Boltzmann statistics it follows that the number of transitions from one state to another is proportional to $\left(1 - e^{\frac{t}{\tau}}\right)$, where t is the time and τ the relaxation time constant.

The dielectric relaxation time is the time required for the molecules to return to 63% disorder, and occurs at $\omega = 1/\tau$ where $\omega = 2\pi f$. If $1/\tau$ corresponds to the angular frequency of the microwave energy the dissipation will be high. If $1/\tau$ differs from ω dissipation will be low. If a sample is heated this changes τ, *tan δ* and ultimately the penetration depth.

1.5.4. Interfacial Polarization.

This is also known as Maxwell-Wagner polarization and is very important in heterogeneous dielectrics. It relates to the build-up of charge particles at interfaces in heterogeneous dielectrics. The effect is seen as the build-up of charge between the interfaces of a suspension of conducting particles in a non-conducting medium.

Wagner[72] devised a simple model for this type of polarisation. It consisted of conducting spheres distributed through a non-conducting medium, where this frequency variation of the loss factor is similar to that of dipolar relaxation. A model for interfacial polarisation was suggested by Maxwell and Wagner in their two layer capacitor model and is shown in Figure 1.14.
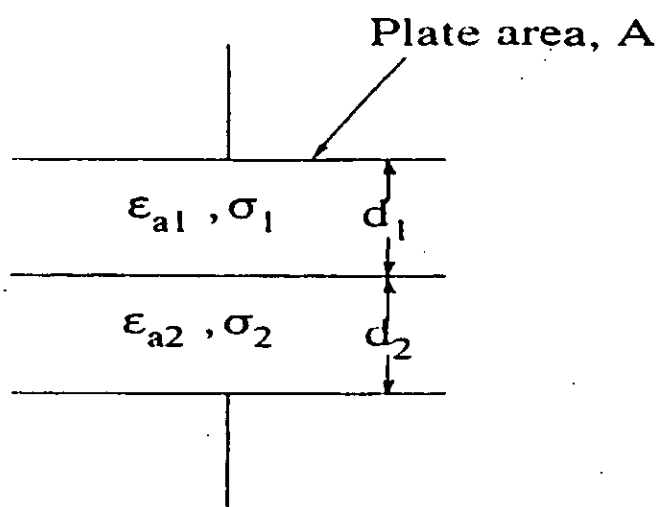
Figure 1.14 The Maxwell-Wagner two layer capacitor (ε_x and σ_x refer to dielectric and conductivity, d_x is the distance).

The total effect is seen as a combination of areas of differing dielectric constants and conductivities. The dielectric loss is related to d.c. conductivity.

1.5.5. Microwave Heating.

The power dissipated by a material will depend upon the materials dielectric constant properties. The average power is thus:

$$P_{AV} = 2\pi f \varepsilon_o' \varepsilon'' \int_v (\mathbf{E}^* \mathbf{E}) dV$$

E is not constant due to the variations occurring in space. In a multi-mode microwave it can be considered constant since $\mathbf{E}.\mathbf{E}^* = \mathbf{E}^2$, where $\mathbf{E}^*$ is the complex conjugate of E, then:

$$P_{AV} = 2\pi f \varepsilon' \varepsilon'' \mathbf{E}_{RMS}^2 V$$

where E is measured in volts per metre and V in m^3.

Hence the dielectric field generated at microwave frequencies can be calculated. The frequency and the value of ε'' are vital in establishing the magnitude of the electric field to obtain the same power dissipation in the material.

The rate of rise of temperature incurred by the electric field of microwave radiation is given by :

$$\frac{\delta T}{\delta t} = \frac{CONSTANT.\varepsilon'' f \mathbf{E}_{RMS}^2}{\rho C_P}$$

where $\mathbf{E}_{RMS}^2$ equals the field intensity, ρ is the density, C_P is the specific heat capacity. The radiation losses are given by:

$$\frac{\delta T}{\delta t} = -\frac{e\sigma}{\rho C_P} \left(\frac{area}{volume} \right)_{SAMPLE} T^4$$

where e is the sample emissivity and σ is the Stefan-Boltzmann constant.

Thus temperature rise is dependent on:

  1. Dielectric constant

  2. Specific heat capacity

  3. Emissivity of the sample

4. Strength of the applied field

All of which are also temperature dependent.

1.5.5.1. Thermal Runaway.

To a sample under microwave irradiation the effect of an uncontrolled rise in temperature is known as thermal runaway (Figure1.15). It can be seen in the diagram that initially absorption of the microwave energy occurs, ε'' increases with temperature and at a critical temperature, tan δ increases such that the material is subject to the thermal runaway effect; conversion of the majority of the microwave energy into heat. The phenomena is disadvantageous due to the inherent lack of control over temperature rise, resulting in undesired temperatures at which samples may degrade.
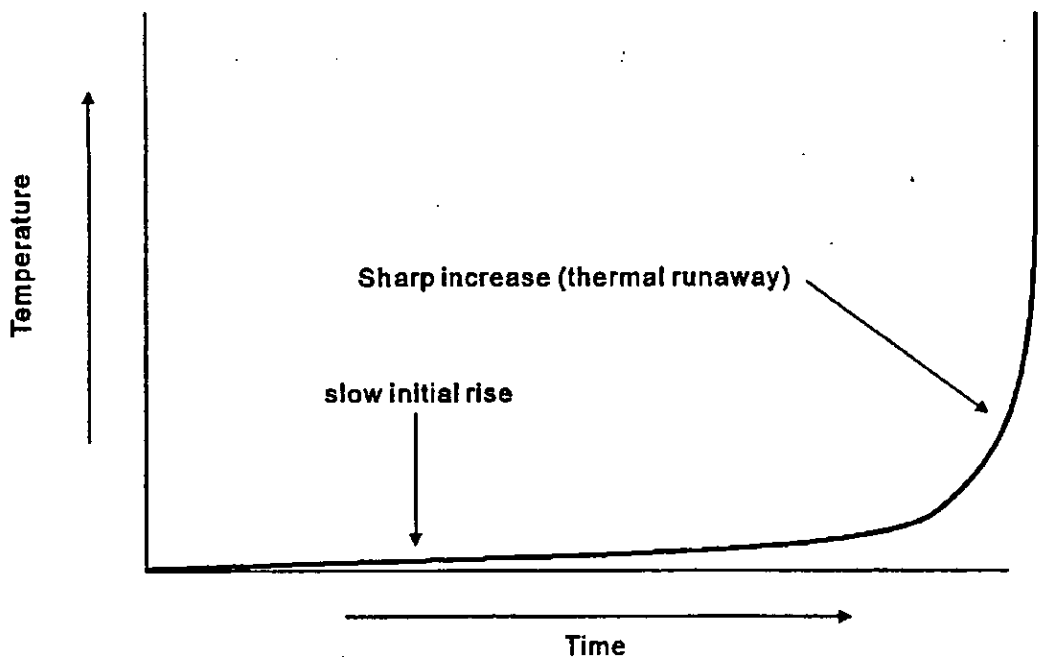
Figure 1.15 The Thermal Runaway Effect Under Microwave Irradiation.

1.5.6. Microwave Cavities.

1.5.6.1. Multimode Cavities.

These are relatively cheap and are useful for a variety of chemical applications. The disadvantage is that the microwave energy is distributed around the cavity and thus the sample does not absorb all the energy.

In principle the multimode applicator is a closed metal box with some means of coupling in power from a generator. A modern domestic microwave oven is an example of a multi mode device (Figure 1.16). The variable power settings available in a domestic oven are produced by switching the magnetron on and off according to a duty cycle. For example a 600W oven with a 30s duty cycle can be made to deliver an average of 300W by switching the magnetron on and off every 15s.
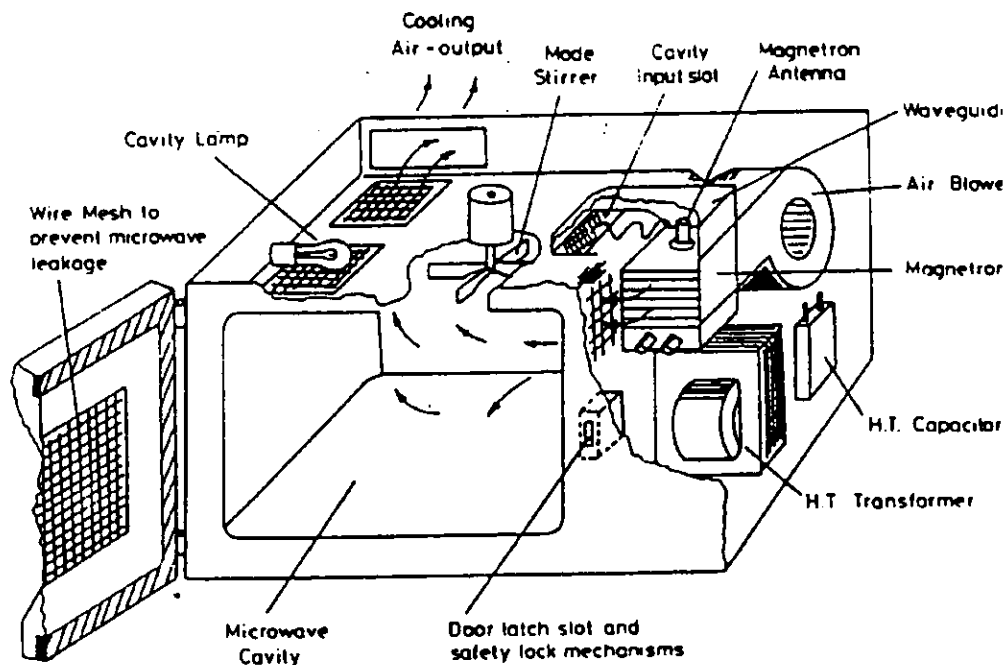
Figure 1.16 The Major Features of a Modern Domestic Microwave Oven.

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1.5.6.2. Magnetron.

The principal features of the magnetron in which microwaves are generated are shown in Figure 1.17.

The magnetron is a thermionic diode incorporating an anode and a directly heated cathode. The anode is a circular block of metal (usually copper) in which are cut eight holes and slots as shown. These holes are cavities that act as tuned circuits due to constant resonating. To one is coupled a waveguide as the output port.

The cathode is fixed in the centre of the block, leaving an interaction cavity between it and the inner surface of the anode. A permanent magnet is used to create the magnetic field. Random effects set up weak oscillations in the cavity resonators and these give rise to electric fields crossing the slots and extending into the interacting space as shown in the diagram "for a particular instant". In this arrangement alternate slots support fields in opposite directions and the alternate cavities are linked by two wire straps which ensure the correct phase relationship. A very strong magnetic field is induced axially through the anode, an electron liberated from the cathode is bent to the right by the magnetic flux which causes it to enter the r.f electric field of cavity 1 (rather than straight to the anode). Energy is transferred to the field as the electron moves away, and is accelerated towards cavity 2, here the process is repeated although the field direction has changed by π radians. As energy is given up the electron eventually moves closer to the anode and is seized by it. The process continues until the oscillations induced in the cavity are of a sufficient magnitude, it is then removed via an antenna. In a typical system the 1200W power used by the magnetron, 600W is converted into electromagnetic energy. The remainder is heat and needs removal.
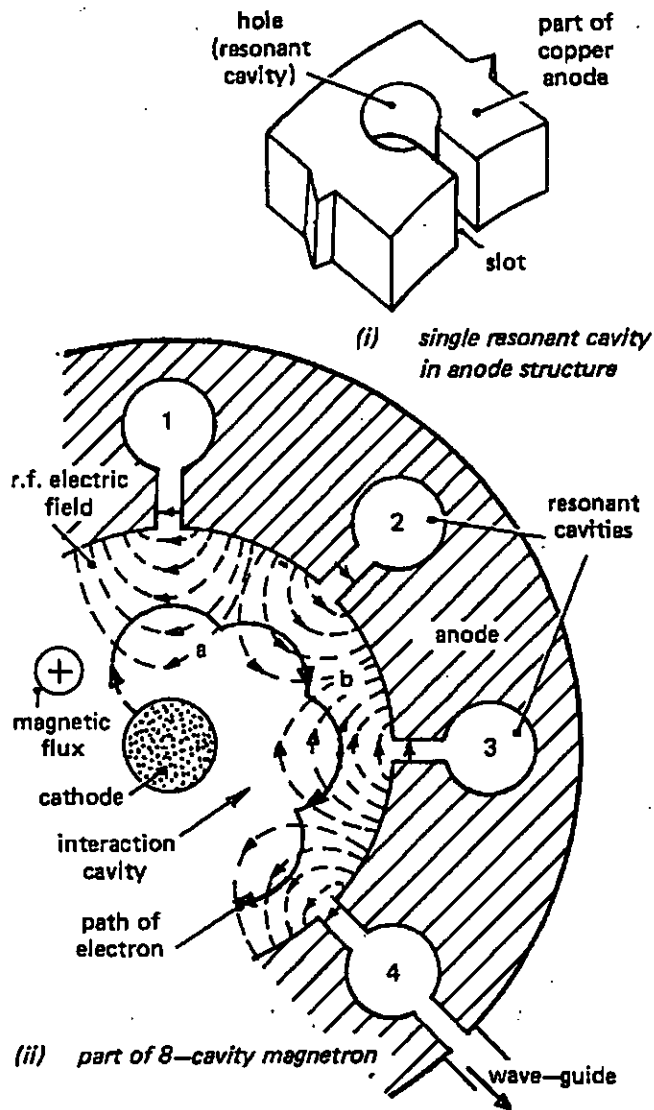
Figure 1.17 The Magnetron.

1.5.6.3. Waveguide.

The microwaves generated by the magnetron are channeled to the cavity via the waveguide, which are made of metal and found rectangular in cross-section. The electromagnetic wave is propagated by continual reflections off the interior walls of the waveguide and the minimum frequency which can be propagated is related to the dimensions of the rectangular cross-section via: $c/f=2d$, where c is the speed of light, f is the cut-off frequency and d is the largest cross-sectional dimension.

1.5.6.4. Cavity.

In order to optimise the efficiency of the oven for heating samples the walls of the cavity are reflective. Thus waves which are not directed on the sample are reflected in order to strike it. With small samples, too much energy could be reflected back into the magnetron causing damage and most ovens have an automatic cut-off or some form of circulator which directs excess energy into a dummy load to avoid this problem. In certain situations it may be that some areas of the cavity receive large amounts of energy while others negligible amounts. In order to evenly distribute the energy in the cavity a mode-stirrer is used, these are metallic fans which rotate in the cavity when the magnetron is operating. Mode-stirrers are often used alongside turntables, which expose both the sample to different areas of the cavity and different areas of the sample to the radiation in order to achieve uniform heating.

1.5.6.5. Singlemode Cavities.

In this set-up all the energy is focused onto a very small volume, with the disadvantage being greater cost. Multimode devices are inefficient with loads that are poor absorbers of microwave energy or small sample amounts which require high temperature heating. The single-mode device overcomes this. It allows the sample to be exposed to much higher electric field strengths than would be obtained in a multi-mode arrangement by tuning to the characteristics of the material being heated. The cavity consists of a metallic enclosure into which a microwave signal of the correct electromagnetic field polarisation is directed. The superposition of the incident and reflected waves gives rise to a standing wave pattern which for some simple structures is well defined in space. Since the configuration of the field can be determined this enables the sample to be placed in the position of maximum electric field strength for

optimum transfer of the electromagnetic energy to it. Whilst lacking the versatility of a multimode microwave heater a single mode resonant heater will establish much higher electric field strengths.

1.6. Treatment of Aqueous Effluent.

Remediation is any process, either chemical, physical or biological or a combination of, that is either introduced or enhanced in order to reduce the concentration of contaminants.

The problems aqueous effluent contaminant streams pose and the handling of them are more complex than if the wastes were simply gases. Aqueous streams may contain varying concentrations of dissolved substances, these may be gases or solids.

Physical characteristics of the waste include temperature, odour and colour. The nature and concentration of any dissolved matter in the flow stream would also be of concern. The chemical factors which dictate the choice of remediation treatment are varied. These include pH of the waste stream, radioactive nature, and the amounts and nature of any inorganic or organic solids or liquids present.

A more demanding problem is posed by any inorganic or organic solid contaminants. These may be present as a suspension or dissolved in the aqueous phase. Suspended solids are the most readily removed contaminants and dissolved solids the most difficult; thus requiring the most expenditure to remove. Biological characteristics of the waste relate to any kind of bacteria present and whether or not these will breakdown organic compounds.

Modern industrial processes generate large volumes of various contaminants each causing its own problems. Refinery sites produce waste water streams containing hydrogen sulphide, oil, and suspended solids.[73] Nuclear reprocessing produces

streams containing radioisotopes, fission products and acidic streams which contain organic and inorganic contaminants.[74] Heavy metal contamination of process and run-off waters[75] are caused by the metal finishing, mining and mineral processing, coal mining, and oil refining industries. The paint and dye industries produce wastes contaminated with organic chemicals, solvents, paint wastes and oil/water mixtures[76]; leather industries generate wastes consisting of sulphides, chromium and precipitated lime. Food and drug manufacturing produces wastes high in suspended solids, organic matter, nitrogen containing compounds and dissolved organics, all with variable pH. Wastes from chemical manufacture include acids, colouring, organic compounds, fluorides, clays, phosphorous containing compounds, silicas, metals, soaps and oils.[77]

The contamination and subsequent treatment of aqueous effluent as outlined above is extensive and a comprehensive discussion can be found in "Unit Operations for Treatment of Hazardous Industrial Wastes".[73]

1.6.1. Treatment of Aqueous Effluent Organic Contaminants.

1.6.1.1. Carbon Adsorption.

These systems take advantage of the adsorptive capabilities of activated carbon. Activated carbon is a highly porous, carbonaceous material, which is produced from various raw materials such as peat, wood, lignite, anthracite, fruit pits or shells.

The very large porosity provides a large surface area, typically in the region 500-1500 m^2g^{-1}, which results in excellent adsorptive properties. The raw material is carbonised by pyrolysis in the absence of air to form an intermediate product. The carbonised intermediate is then activated using steam (steam activated carbon) or acid, usually H_3PO_4 (chemically activated carbon). The activation process creates

pores in the carbon and a variety of sizes are found (Table 1.4). Conventional types of activated carbon generally have what is termed a tridisperse structure, i.e. micropores, mesopores and macropores present in the structure. The majority of the surface is non-polar, but as a consequence of manufacturing, the interaction with oxygen produces specific active sites containing acid and aldehyde groups which give the surface a slightly polar nature. The structure of activated carbon consists of elementary microcrystallites, which are quite similar to graphite in two dimensions, being composed of several parallel planar layers formed by carbon hexagons. Unlike graphite, however, the planar layers are arranged at different angles to a perpendiculer axis passing through them, and they overlap in an irregular manner. The orientation of microcrystallites to one another is completely random.

Table 1.4 Activated Carbon Pore Types.

Pore Definition	Pore Radii (Å)
Micropores	<18-20
Mesopores	20-1000
Macropores	1000<Radius<20 000

Adsorption on the carbon surface itself mainly takes place as a result of the effect of the dispersion component of the van der Waals forces. Adsorption of polar and polarisable adsorbates increases with sites in the activated carbon surface, on which the orientational or polarising component of the van der Waals force become effective or where a hydrogen bond can form. Such sites can be formed by heteroatoms (as described above).

When deciding what carbon is required for a particular application it is not always best to opt for the greatest surface area carbon. Most of the total surface area is found

in the micropores and in many instances not all the total surface area is accessible. In many applications the molecules to be adsorbed are too large to fit into the micropores. For liquid applications, since most of the molecules have a high molecular weight, a carbon of high mesoporosity is required, and a high total surface area is of no use. On the other hand, gas phase applications require a high total surface area since the adsorbing molecules are small.

The adsorptive capacity of the carbon is dependent of the nature of the carbon, the amount used, the source of the carbon and the concentration of pollutants.[78]

The pore structure is the most important aspect of activated carbon; the removal of impurities by activated carbon takes place by adsorption; the activation process increases the internal surface area and thus the number of available sites for adsorption. Adsorption is more suited to organic solutes which have a high molecular weight, low water solubility, low polarity and low degree of ionisation.

There are two forms of activated carbon available:

1. Granular.

For use in packed beds, it can be thermally reactivated for reuse thus avoiding problems of waste disposal and minimising carbon consumption. This treatment is very suitable for continuous processes and involves greatly reduced carbon consumption in comparison with powdered carbon.

2. Powdered.

This can be used in packed beds or in suspension. It is less expensive than the granular form and has a slightly higher adsorption capacity. Although disadvantages, which are mainly handling difficulties, coagulation problems and regeneration being uneconomical due to high losses (15%), exist.

Activated carbon is suitable for the removal of dissolved organic compounds such as saturated oils, alkanes, alkenes, chlorinated hydrocarbons, dyes, phenols, benzene and high molecular weight organics. It is also used in detoxification plants to remove residues of pesticides and insecticides. The downside of this treatment is the reacted carbon sludge must be bagged and removed.[74] Another application is the recovery of nitrophenol as byproduct[77], with the nitrophenol subsequently leached from the carbon bed using NaOH. Other compounds adsorbed are molybdenates and iodine, whilst silver salts and potassium permanganate are reduced by the carbon, precipitated out, and removed by filtration. Activated carbons are used in the recovery of thermally desorbed pesticides.[79]

1.6.1.2. Phenol Destruction.

The presence of these compounds when combined with chlorine in waste water discharges can cause health problems in the drinker and a foul taste is also prevalent. These compounds are present in waste streams in plastic industries, coke plants, oil refineries, and chemical companies. Ozone is used as a successful decontaminant.[79]

1.6.1.3. Photocatalysis.

Semiconductor photocatalysis with a focus on TiO_2 as a durable photocatalyst has been applied to a variety of environmental problems, including air purification, water disinfection, hazardous waste remediation, and water purification. It has also been shown to be useful for the destruction of bacteria and viruses, for odour control, and for the clean-up of oil spills.

The application of illuminated semi-conductors for the remediation of contaminants has been used successfully for a wide variety of compounds such as alkanes, aliphatic

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alcohols, aliphatic carboxylic acids, alkenes, phenols, aromatic carboxylic acids, dyes, PCB's, simple aromatics, halogenated alkanes and alkenes, surfactants and pesticides as well as for the reductive deposition of heavy metals (e.g., Pt^{4+}, Rh^{3+}, $Cr(VI)$) from aqueous solutions to surfaces.

Semiconductors (e.g., TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitisers for light-reduced redox processes due to their electronic structure which is characterised by a filled valence band and an empty conduction band. When the energy of an incident photon equals or exceeds the bandgap energy of the semiconductor, an electron is promoted to the higher energy conduction band leaving a positively charged hole behind. The valence band holes are powerful oxidants while the promoted electrons in the conduction band prove good reductants. Thus thermal and photocatalytic reactions to yield mineralisation products can occur, with the general stoichiometry for the heterogeneously photocatalysed oxidation of a generic chlorinated hydrocarbon to complete mineralisation given below.

$$C_xH_yCl_z + \left(x+\frac{y-z}{4}\right)O_2 \xrightarrow{hv, TiO_2}$$
$$xCO_2 + zH^+ + zCl^- + \left(\frac{y-z}{2}\right)H_2O$$
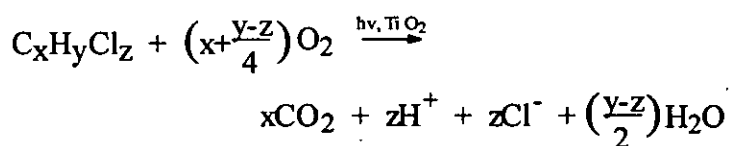
1.7. Objectives of the Work.

TBP is one of the main contributory factors to the presence of interfacial cruds in the alkali solvent wash stage of the PUREX process and its decomposition difficult to achieve without resorting to incineration.

The microwave assisted removal of organic contaminants from aqueous streams has been previously shown to be successful when applied to aqueous streams containing methylene blue[80] and flourescein.[81] These previous studies have shown that for the decomposition to be effective it is necessary to use a porous sensitiser in conjunction with the microwave radiation. The effect of the radiation on the sensitiser causes the formation of a localised plasma, which facilitates the decomposition.

The main objective of this work is to devise an experimental arrangement such that low concentrations of TBP can be decomposed from aqueous solutions. In order to achieve this it was recognised that the following required investigation:

1. The construction and arrangement of the equipment to be used.

2. A suitable experimental method.

3. A suitable method of analysis.

4. The variation of experimental parameters.

2. Experimental.

2.1. Apparatus.

2.1.1. The Microwave Cavity.

The microwave cavity used in this work can be seen in Figure 2.1 and was a single mode device, capable of operating at power outputs of up to 700W. The device was purpose built by Microwave Systems Ltd. The microwave cavity was fitted with a double plunge tuner to permit the maximum E-field to occur at the test section, where the sample was located. Positioning the sample at this point ensures optimum transfer of electromagnetic radiation. The PC interface allowed the pulse timing to be 3 seconds "on" followed by 5 seconds "off" and this 8 second cycle was repeated throughout the duration of the experiment (typically 150 minutes) with a pulse power of 490W employed.

2.1.2. Reaction Vessels.

The reaction vessels used initially suffered from a series of problems. Carbon was continually lost from the reaction vessel, and the vessels had a limited capacity. As a result, new, improved reaction vessels were designed.

A diagram of the reactors designed for use in this work can be seen in Figure 2.2. The material used for construction of the reactors was glass which is transparent to microwave radiation, the reactors were made by York Glassware and in this work had the following diameters: 10,15 and 40mm. The glass reaction vessels are loaded with an activated carbon, mesh 8-12 (Sutcliffe & co.). A porous frit (Grade 1) was placed in the upper most section of the glass bulb, this served to stop the loss of activated carbon from the reaction vessel whilst allowing liquid flow. For a particular experiment a mass of carbon was weighed out (Sartorius balance) and transferred
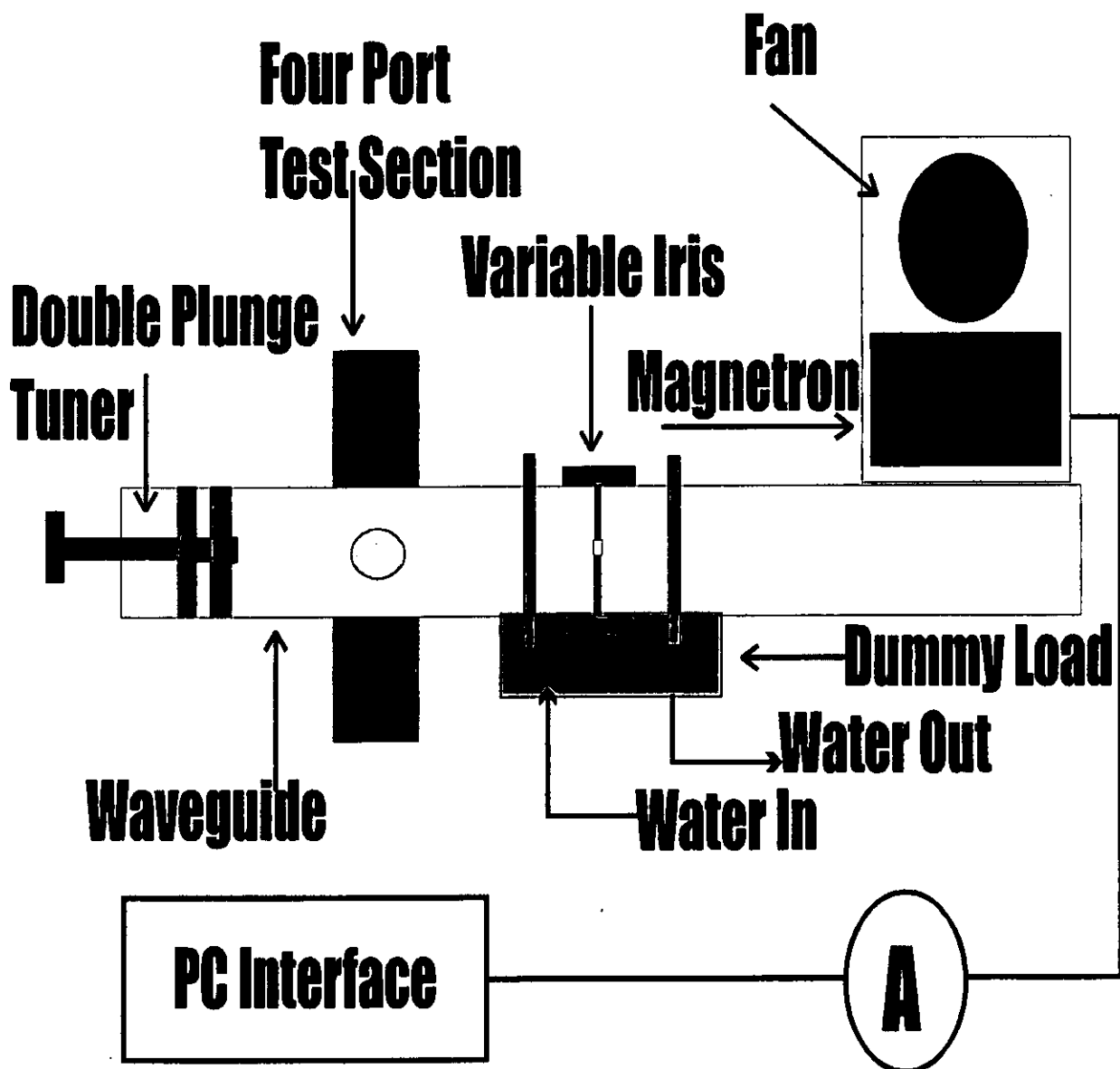
Figure 2.1 Microwave System.

accurately to the reaction vessel. A small plug of glass wool was used to prevent

carbon loss from the bottom end of the vessel. The reaction vessel was mounted in

the centre of the test section of the cavity for reasons described previously.
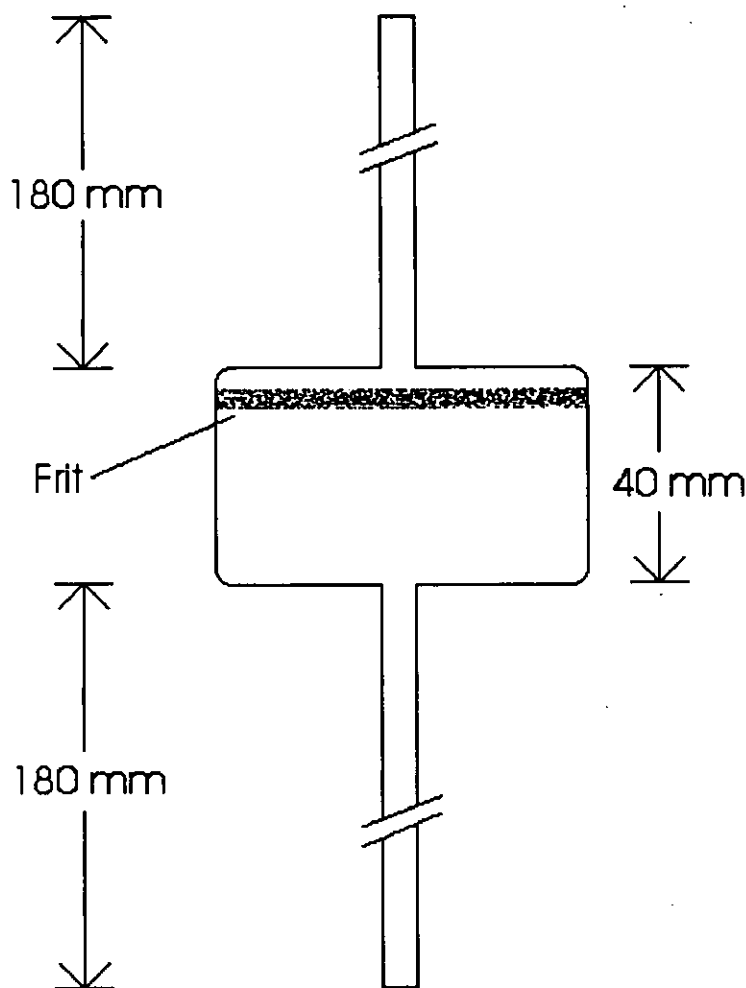
Figure 2.2 Diagram of the Reaction Vessel.

2.1.3. Activated Carbon.

Surface area measurement of the activated carbon was performed by the University of Huddersfield using N_2 adsorption / desorption at 77k. The instrument used was a Omnisorp 100CX (Beckman-coulter), and the surface area of the carbon was found to be $988.28 m^2 g^{-1}$.

2.1.4. Experimental Arrangement When Using Hydrogen Peroxide as Oxidant.

An aqueous solution of TBP (Aldrich) was pumped by a dual head chemical metering pump (Omega Engineering, Inc) from a reservoir (Figure 2.3). The

reservoir was a sealed glass beaker with in/out tubing and magnetic stirrer to maintain

inter-dispersion of the phases. It is placed in an ice bath during reactions to ensure
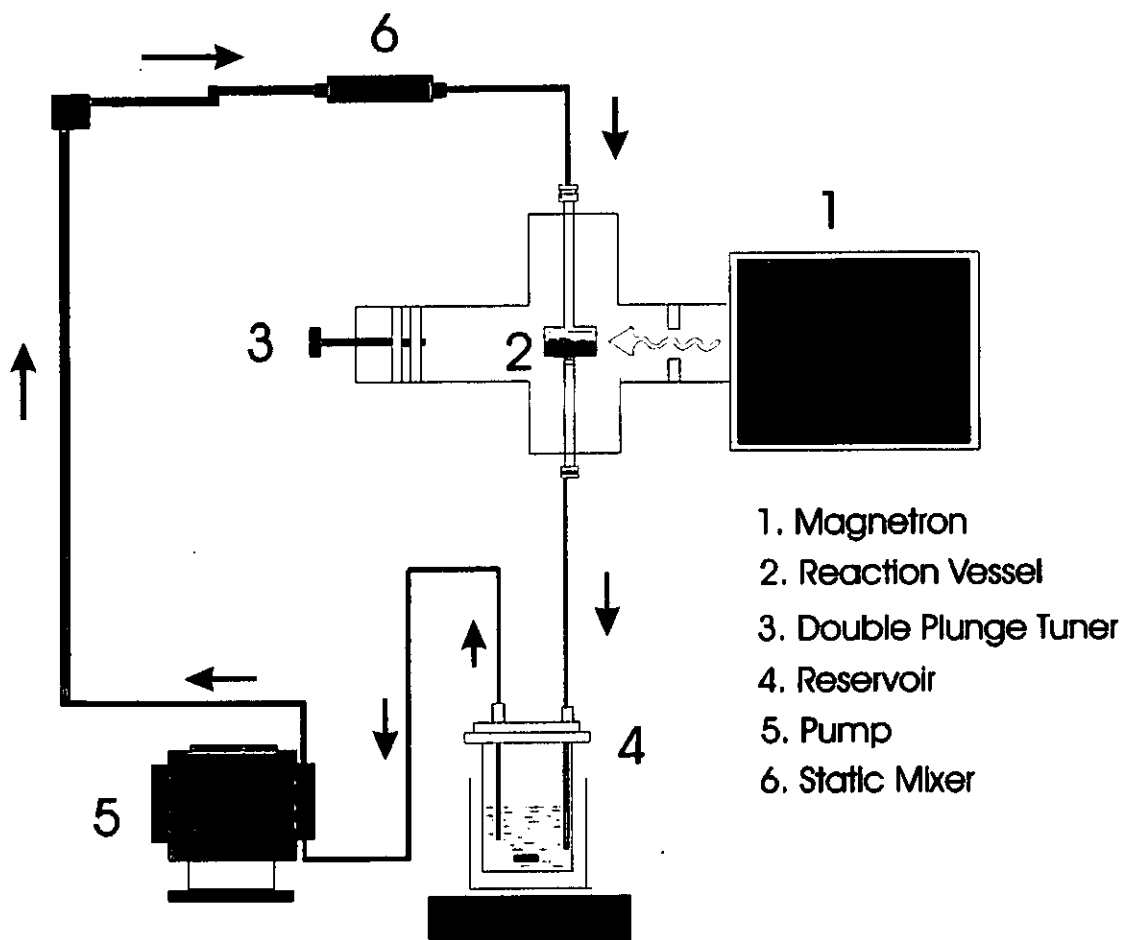
Figure 2.3 Experimental Arrangement with Hydrogen Peroxide as Oxidant.

1. Magnetron
2. Reaction Vessel
3. Double Plunge Tuner
4. Reservoir
5. Pump
6. Static Mixer

sufficient cooling of the hot exit solution. Upon passing through the pump-heads the

solution then entered the reaction vessel. Upon the filling of the reaction vessel by the

reaction mixture and emergence of solution from the exit tube, microwave radiation

was applied. Upon the application it is necessary to tune the radiation so to ensure the

microwaves are focused on the reaction vessel so as to give maximum scintillation of

the carbon. The reaction mixture was recycled for the duration of the experiment,

typically 2.5 hours.

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2.1.5. Experimental Arrangement When Using Air as Oxidant.

In these experiments, air is incorporated into the system. The apparatus used was the same although certain modifications were incorporated to facilitate the use of air. The solution is mixed with cylinder air in a static mixer (Omega) before being pumped into the glass reaction vessel (York Glassware). A rotameter is used to gauge the airflow and is connected to an in-line check valve to prevent liquid flow into it (Figure 2.4).

2.2. Reaction Procedures.

2.2.1. Reaction Procedures - Air as Oxidant.

2.2.1.1. Variation of Mass of Carbon.

Experiments were conducted to study the relationship between the mass of activated carbon used in the reaction vessel and the decomposition of TBP to produce inorganic phosphate. Experiments were performed using the 15mm diameter reaction vessel and carbon loadings in the range 0.5-3.0g. TBP was reacted in a 5% (v/v) solution in de-ionised water. Airflow was difficult to keep constant due to pressure variations in the system, thus the rotameter response varied between 70-120 ml min^{-1}. The solution flow rate was 30 ml min^{-1}. Airflow was started prior to microwave irradiation, whereby the magnetron operated using the pulse cycle described previously (Section 2.1.1.). The reaction mixture was recycled for a period of 2 hours. Upon termination of the reaction, liquid remaining in the tubing and reaction vessel was pumped out, then 100 ml of distilled water was run through the system to flush out any remaining reaction mixture. The mixture was transferred to a separating funnel prior to the addition of 25 ml dilute hydrochloric acid. The HCl removes any DBP or MBP from the aqueous phase.[29] The organic phase was removed by solvent extraction using 3 x
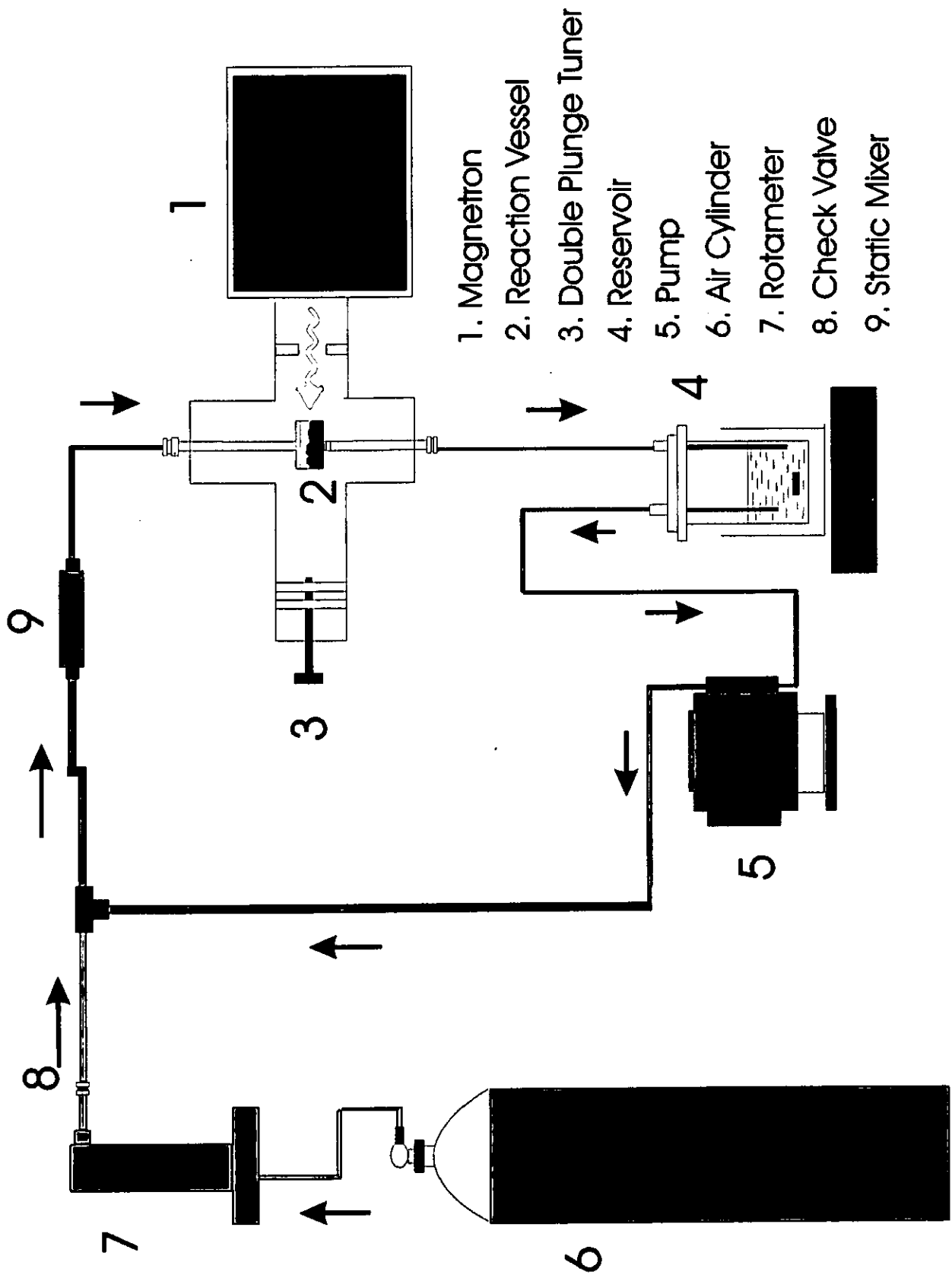
Figure 2.4 Experimental Arrangement with Air as Oxidant.

1. Magnetron
2. Reaction Vessel
3. Double Plunge Tuner
4. Reservoir
5. Pump
6. Air Cylinder
7. Rotameter
8. Check Valve
9. Static Mixer

5 ml chloroform. The resulting aqueous phase was then analysed by UV-Vis spectroscopy for inorganic phosphate. In order that the mass of carbon could be further increased a 40 mm diameter reaction vessel was used. This permitted studies to be carried using between 1 and 14 g of carbon. All other reaction parameters were maintained as in the experiments described above.

The analysis of these experiments was performed using ion chromatography and hence a modification to the product pretreatment was necessary. Prior to extraction 20 ml 0.5M NaOH was added to force DBP and MBP into the aqueous phase.[29] Removal of the remaining organic phase was performed using solvent extraction as described above. The aqueous phase was analysed by ion chromatography as described in Section 2.3.2.2.

2.2.1.2. Lifetime Studies.

Reactions were performed to study the decomposition of TBP (5% v/v in water) as a function of time. In these experiments 1ml aliquots of the aqueous phase were withdrawn at 15 minute intervals over a period of 180 minutes. The reaction vessel (15 mm dia.) was loaded with 1.3 g activated carbon and the reaction mixture circulated at a flow rate of 30 ml min^{-1}. Each 1 ml aliquot was made up to 100 ml with distilled water in a volumetric flask and analysed by UV-Vis spectroscopy as described in Section 2.2.1.1.

2.2.1.3. Variation of TBP Concentration.

Experiments were carried out over the concentration range 0.5-3.0% (v/v) TBP in water. A 15 mm reaction vessel loaded with approximately 1.3g of activated carbon was used. The duration of the experiments was 150 minutes with a duty cycle as

described in Section 2.1.1. Upon completion of the reaction the mixture was divided into two equal portions, to one half analysis was carried out by UV-Vis spectroscopy (Section 2.2.1.1.), whilst the other was analysed by ion-chromatography as described in Section 2.2.1.1.

2.2.2. Reaction Procedures - Hydrogen Peroxide as Oxidant.

2.2.2.1. Variation of Mass of Carbon.

Studies were performed on a 5% mixture of TBP in a 1:1 mixture of hydrogen peroxide (10 vol.) and water. The reaction vessel (40mm dia.) was loaded with activated carbon and the reaction mixture circulated at a flow rate of 30 ml/min. The amount of carbon for the experiments was varied between1 and 7 g . The length of each experiment was 150 minutes. The magnetron output was identical to that described in Section 2.1.1. The procedure for work-up and analysis were identical to those concerning ion-chromatography as described in Section 2.2.1.1.

2.2.2.2. Lifetime Studies.

The reaction using 90 vol. hydrogen peroxide was used to establish the variation of TBP decomposition as a function of time using peroxide as oxidant. The mass of activated carbon employed was approximately 3g. The other experimental parameters were the same as those above (Section 2.2.2.1.). The reaction was interrupted every 15 minutes so that 1ml aliquots of the aqueous phase could be sampled. A 5 minute settling time was used prior to sampling, to allow sufficient separation of the phases. Each 1 ml aliquot was made up to 10 ml with distilled water in a volumetric flask. Analysis of the aliquots was performed by Dionex ion-exchange chromatography.

2.2.2.3. Variation of Peroxide Concentration.

The effect of varying hydrogen peroxide strength was investigated using peroxide concentrations varying from 10 vol. to 100 vol. The quantity of activated carbon used was approximately 3 g. The other experimental parameters were identical to those employed in the experiments involving variation of mass of carbon with peroxide as oxidant (Section 2.2.2.1.). The procedure for work-up and analysis were identical to those described in Section 2.2.2.1.

2.2.2.4. Variation of TBP Concentration.

Experiments were conducted to study the variation of TBP decomposition with TBP concentration. Studies were performed on a range of concentrations (0.5, 1, 2, 3 and 4%) of TBP in a 1:1 mixture of hydrogen peroxide (10 vol.) and water. The reaction vessel (40 mm dia.) was loaded with approximately 3g of activated carbon. Other experimental parameters were akin to those used in Sections 2.2.2.1. and 2.2.2.2. Work up and analysis of the reaction mixtures was by the method outlined in Section 2.2.2.1.

2.3. Analytical Procedures.

2.3.1. Uv-Vis Spectroscopy.

2.3.1.1. Beer-Lambert Law.

For a solution the intensity of absorption at a given wavelength is related to the concentration of the absorbing molecule (c, $moldm^{-3}$), the path length of the sample cell (l, cm) and a measure of how easily photons of that wavelength are absorbed by the absorbing molecule, the molar absorptivity (ε, $mol^{-1}dm^3cm^{-1}$) by the following expression:[82]

$$A = \varepsilon c \, l$$

Thus, the spectrophotometer is calibrated by measuring the absorbance of a sample of standard of known concentration, then the concentration of analyte can be determined by measuring its absorbance at the same wavelength, usually the absorbance maxima.

2.3.1.2. Method for the Determination of the Concentration of Orthophosphate Ions.

In this work the method used was an adaptation of a method given in Vogel,[83] in which orthophosphate ions and molybdate ions condense in acidic solution to give molybdophosphoric acid, which upon selective reduction with hydrazinium sulphate (BDH) produces a blue colour due to molybdenum blue of "uncertain composition". The intensity of the blue colour is proportional to the amount of PO_4^{3-} initially incorporated in the heteropoly acid. Experiments were performed to ensure no response was obtained from organic phosphates.

The spectrophotometer used was Philips PU 8740. A series of calibration standards were prepared of varying concentration of orthophosphate ions 4.038 x 10^{-6} to 4.043x

10^{-5} mol dm^{-3} remembering that the absorbance values should be below 1 for accurate analyses. These solutions were prepared by dilution of a stock solution of KH_2PO_4 (BDH) and the absorbances measured at a wavelength of 826.4 nm, in a glass sample cell of pathlength 1cm.
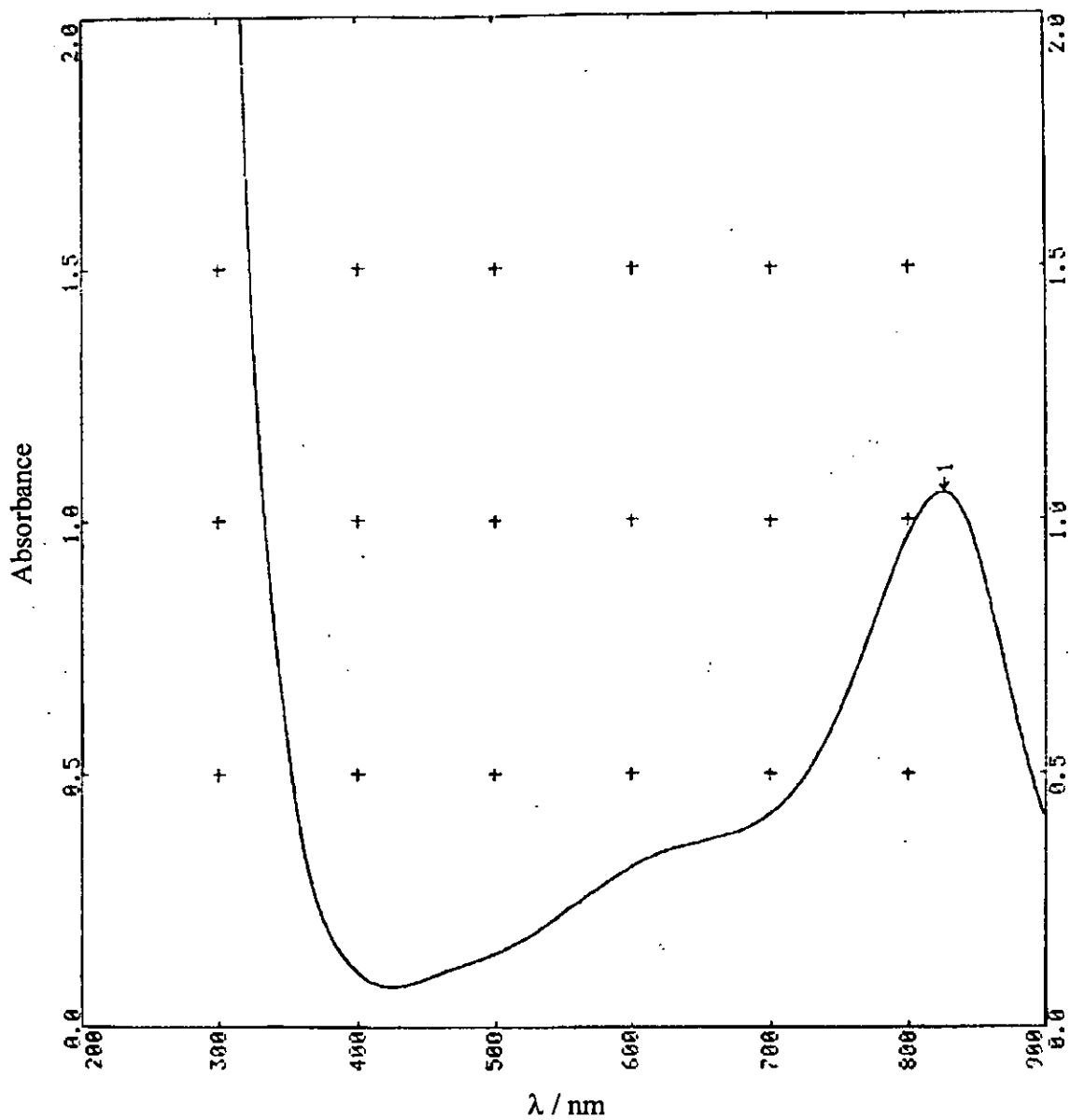

**Figure 2.5** Wavelength Scan Acquired for Phosphate Standards.

2.3.2. Dionex Ion Chromatography.

2.3.2.1. Theory.

The colorimetric method of analysis was not possible to use on solutions reacted with hydrogen peroxide as the oxidant because of an irreversible reaction between hydrogen peroxide and molybdate ions resulting in a yellow colouring. Hence, other avenues of analyses needed to be explored.

The technique of ion-chromatography makes use of synthetic ion-exchange resins which are high molecular weight polymeric materials containing ionic functional groups. For anion determination, anion exchange resins containing basic amine functional groups attached to the polymer molecule are used.[82]

Phosphate can be separated on an ion exchange resin in its basic form. In this application, the sample is first introduced onto the head of the column, where the anions are retained by the reaction:

$$3RN(CH_3)_3{}^+OH^- + PO_4{}^{3-} \rightleftharpoons [RN(CH_3)_3{}^+]_3PO_4{}^{3-} + 3OH^-$$
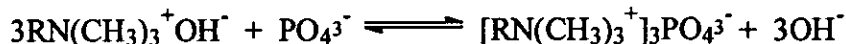
Elution is then carried out with a dilute solution of a base, which causes the foregoing reaction to be reversed and the anions to be released. Conductivity measurements provide a convenient method for the detection and determination of the eluted species. Although there are problems caused by the high electrolyte concentrations required to elute most analyte ions in a reasonable time. As a consequence, the conductivity from the mobile phase components tends to swamp that from the analyte ions. In order to negate this problem eluent suppressor columns are used which convert, by use of an ion-exchange resin, the ions of the eluting solvent to a form of limited ionisation without affecting the conductivity due to the analyte ions. For anion separations, the suppressor packing is the acid form of a cation-exchange resin and sodium bicarbonate or carbonate is the eluting agent.

The reaction in the suppressor is:

$$Na^+_{(aq)} + HCO_3^-_{(aq)} + resin^-H^+_{(s)} \longrightarrow resin^-Na^+_{(s)} + H_2CO_3_{(aq)}$$
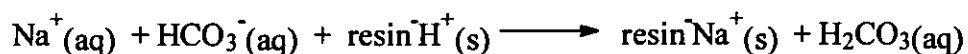
The largely undissociated carbonic acid does not contribute significantly to the conductivity.

2.3.2.2. Method for the Determination of the Concentrations of Orthophosphate Ions and Di-butylphosphoric Acid.

The method was adapted from that described by Lash and Hill.[84] The ion-exchange chromatogram used was manufactured by Dionex Corp. and consisted of an Ion Pac AG II 4 mm (10-32) pre-column (P/N 44078), an Ion Pac AS II 4 mm (10-32) separating column (P/N 44076) and a ASRS II 4 mm anion self-regenerating suppressor (P/N 46081). Detection was made using a Dionex Conductivity Detector-II (CDM). The required eluent was a 3 mM sodium carbonate (BDH), 1 mM sodium hydroxide (Fisher) solution. Chromatographic conditions are contained in Table 3.1.

Calibration standards were prepared by diluting phosphoric acid (90%, May and Baker) in water to yield concentrations ranging from 0 to 1000 µg/ml, although the linear range proved to be 0-500 µg/ml (standards of concentration 0.2618×10^{-3} to 5.236×10^{-3} mol dm^{-3} were used). This produced the calibration curve shown in Figure 3.2. For di-butylphosphoric acid, calibration standards were prepared by dissolving DBP (97%, Acros) in 0.5M sodium hydroxide (Fisher) and the concentration range for these standards was 0 to 1000 µg/ml (standards of concentration 0.1199×10^{-3} to 4.797×10^{-3} mol dm^{-3} were used). The calibration curve for DBP is shown in Figure 3.3. Tests were performed to understand the role of any TBP in the aqueous phase with regard to any co-elution problems with DBP. The

conclusion was that co-elution existed, but TBP had a negligible effect regarding the calculation of DBP concentrations.

Table 2.1 Chromatographic Conditions.

Eluent	3mM Na_2CO_3, 1mM NaOH
Flow Rate	2 mlmin^{-1}
Analytical Columns	Ion Pac AG II 4 mm (10-32) P/N 44078 Ion Pac AS II 4 mm (10-32) P/N 44076
Suppressor Columns	ASRS II 4 mm P/N 46081
Injection Volume	0.5 ml

2.3.3. Analysis using GC-MS.

Initial tests to evaluate GC-MS analysis was carried out using a Perkin Elmer 8500 Gas Chromatograph incorporating a Perkin Elmer Ion Trap Detector. This method of analysis is reliant on **all** the remaining organic phase being removed from the reactor and associated pipe-work which is extremely difficult to achieve. This coupled with the notorious unreliability of ion trap detectors for quantitative analysis accounts for the unreliability of this method of analysis. After the initial tests this method of analysis was not followed up.

2.4. Chemical Metering Pump Calibration.

The pump was calibrated by measuring the time taken to pump 50ml of water. The calibration data is contained in Table 2.2.

Table 2.2 Calibration of the Chemical Metering Pump.

Pump Setting/%	(i)	Time taken/s (ii)	(iii)	Average time	Flow rate/ ml per min
10	717	699	696	704	4.26
20	401	414	414	409.7	7.32
30	264	266	265	265	11.32
40	208	213	210	210.3	14.27
50	165	166	168	166.3	18.04
60	140	140	142	140.7	21.32
70	130	126	128	128	23.44
80	110	111	111	110.7	27.10
90	100	100	100	100	30.00
100	95	95	96	95.7	31.35

3. Results.

3.1. Quantification of Reaction Products.

The calibration graphs, Figures 3.1-3.3, were generated using Microsoft Excel, the R^2 values were obtained using the linear regression facility within the software program. Each point on the graph is an average of three replicate analyses.

All experiments were performed individually, and thus information on the reproducibility of the data is obtainable only between sets of data. A large number of experimental variables exist, particularly in the application of microwave radiation and the formation of localised plasmas. In this respect it is difficult to estimate the level of scintillation observed between experiments, and obviously is something to examine in future work. Thus no standard deviations are available to comment on error, and trend lines have been added for the purpose of being "guides to the eye" with the functional form of the fit being unimportant. All lines on the graphs (3.5-3.7, 3.9-3.12) were fitted using Microsoft Excel.

3.1.1. Calibration of the UV-Vis Spectrophotometer.

Orthophosphate was determined spectrophotometrically as described in Section 2.3.2.2. The spectrophotometer response was calibrated over the concentration range 4.038×10^{-6} to 4.043×10^{-5} moldm^{-3} (Table 3.1). The molar absorptivity, ε, for the species under study was calculated as being $2.516 \times 10^4 \pm 1.77\%$ mol^{-1}dm^{3}cm^{-1}. A linear response was achieved (Figure 3.1), confirming Beers Law was being obeyed.

Table 3.1 Spectrophotometer Response for Phosphate Standards.

$[PO_4^{3-}]$ / x 10^{-6} mol dm^{-3}	Absorbance
4.038	0.099
8.076	0.205
12.12	0.307
16.15	0.406
20.20	0.518
24.23	0.593
28.27	0.715
32.30	0.824
36.35	0.930
40.43	0.990
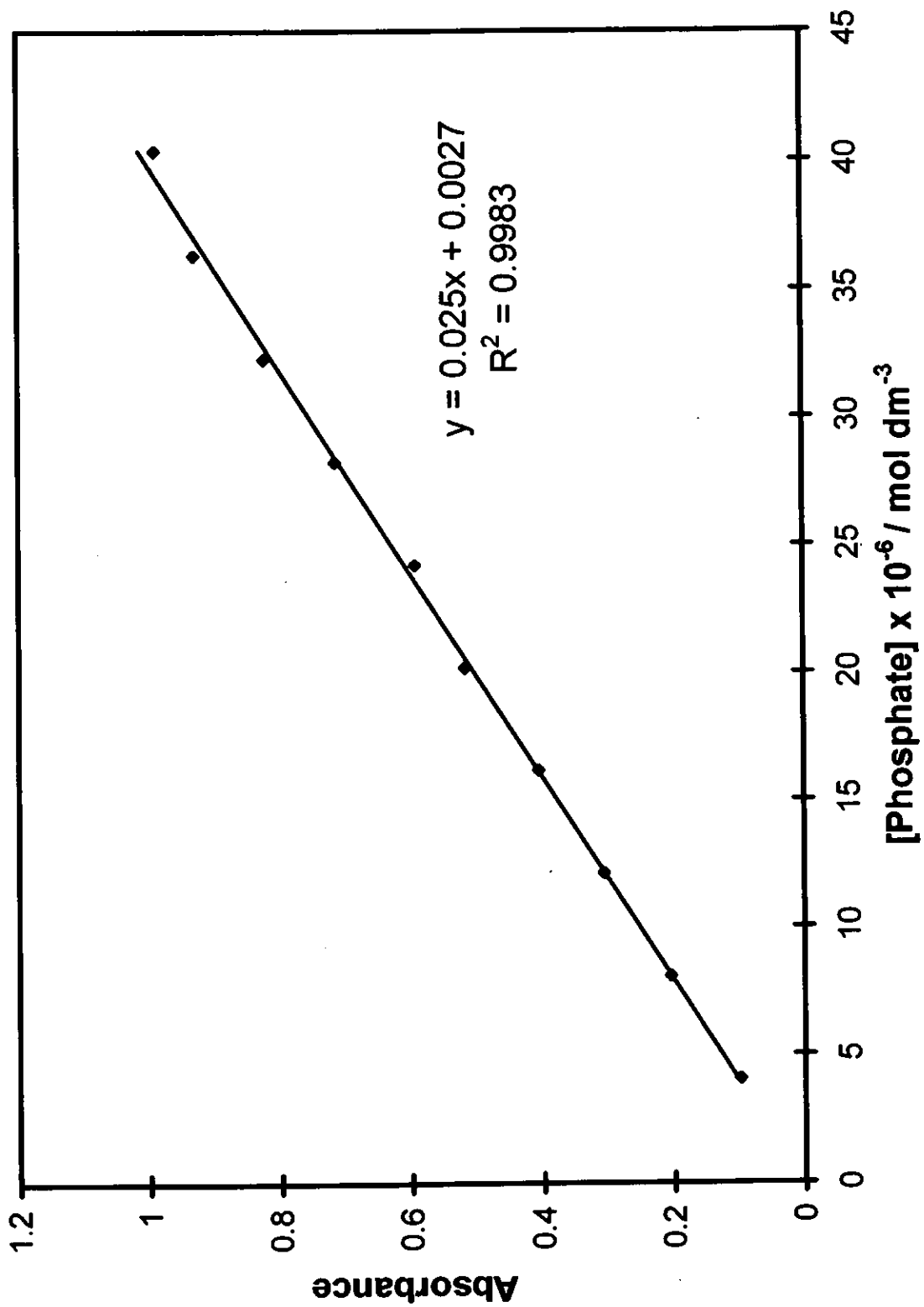
Figure 3.1 Phosphate Calibration Curve as Determined by UV-Vis Spectroscopy.

The figure shows a calibration plot of Absorbance (y-axis, 0 to 1.2) versus $[\text{Phosphate}] \times 10^{-6} / \text{mol dm}^{-3}$ (x-axis, 0 to 45), with the fitted line:

$$y = 0.025x + 0.0027$$
$$R^2 = 0.9983$$

3.1.2. Determination of Orthophosphate Ions and HDBP Using Ion Chromatography.

The ion chromatograph was calibrated for both orthophosphate ions and HDBP from aqueous solutions of known concentration. The peak areas produced are recorded in Table 3.2. Plots of area vs. concentration, Figures 3.2 and 3.3 respectively, confirm that a linear response is achieved over the concentration ranges. The threshold limit for HDBP detection is 1.5 $mgdm^{-3}$.

Table 3.2 Ion-Chromatogram Response for Phosphate and HDBP Standards.

[PO$_4$$^{3-}$] / μgml^{-1}	Peak Area	[HDBP] / μgml^{-1}	Peak Area
24.86	4322	25.21	8984
49.73	10587	50.42	11390
74.59	16580	100.84	24149
99.45	22196	201.68	47480
198.90	45752	403.36	98543
298.35	70729	605.4	160617
397.80	86422	806.72	203781
497.25	114039	1008.4	234153

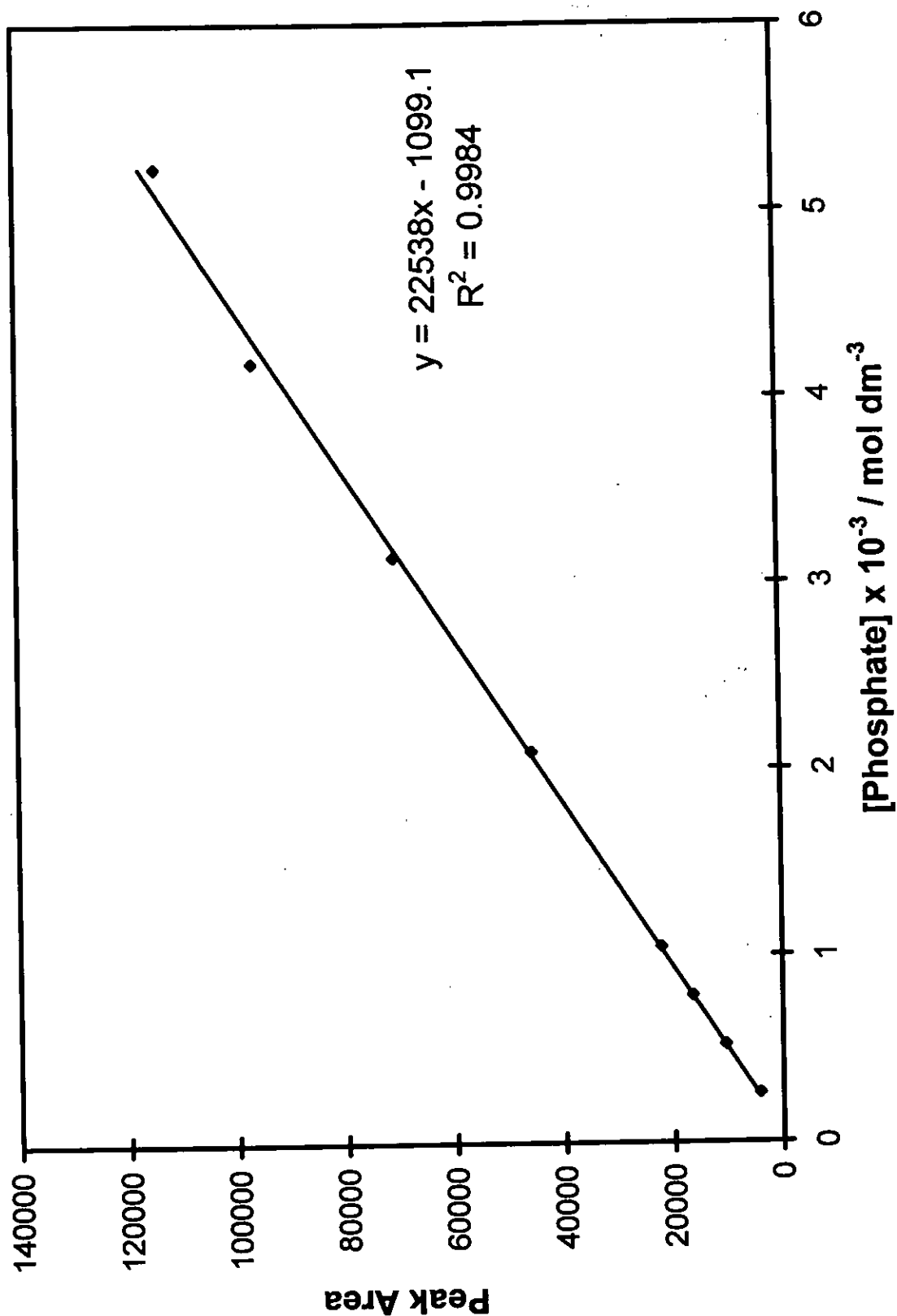**Figure 3.2** Phosphate Calibration Curve as Determined by Ion-Chromatography.

The fitted equation is $y = 22538x - 1099.1$ with $R^2 = 0.9984$, where the x-axis is $[\text{Phosphate}] \times 10^{-3} / \text{mol dm}^{-3}$ and the y-axis is Peak Area.

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Figure 3.2 Phosphate Calibration Curve as Determined by Ion-Chromatography.

The graph shows a plot with y-axis labeled "Peak Area" (0 to 140000 in increments of 20000) and x-axis labeled "[Phosphate] x 10^{-3} / mol dm^{-3}" (0 to 6). The linear fit equation is:

$$y = 22538x - 1099.1$$
$$R^2 = 0.9984$$

Figure 3.3 HDBP Calibration Curve as Determined by Ion-Chromatography.

The plot shows Peak Area (y-axis, 0 to 300000) versus $[HDBP] \times 10^{-3}$ / mol dm^{-3} (x-axis, 0 to 6).

$y = 50911x + 1612.2$
$R^2 = 0.9946$

3.2. Results for the Microwave Decomposition of TBP Using Air as Oxidant.

3.2.1. Analysis Using Ion Chromatography.

Figure 3.4 shows a typical chromatogram that exhibits a number of peaks not all of which have been identified. The peaks at 0.755, 1.364, and 4.958 minutes can be attributed to OH^- from NaOH, HDBP, and orthophosphate respectively. Some unknown substance formed from the action of sodium hydroxide on chloroform is responsible for the peak at 1.001 minutes. Attempts to identify the unknown peaks observed at retention times of 1.593, 1.741, and 2.320 minutes proved unsuccessful. This was achieved by injecting solutions of 1-butanol, 2-butanol, butanone, butyric acid, and dibutyl ether and hence these substances can be ruled out as oxidation products.

3.2.2. Variation of Mass Carbon.

The effect of varying the mass of carbon was investigated as described in Section 2.2.1.1. Results were produced using both the 15 mm and 40 mm diameter reaction vessels and these are shown in Figures 3.5 and 3.6 respectively. It can be seen (Figure 3.5) that maximum conversion is 0.3 mmoles, and was achieved using 1.9 g carbon. Results using the 40 mm reaction vessel show that the optimum loading for conversion to both orthophosphate and HDBP was 5 g carbon. For orthophosphate the maximum conversion was 1.2 mmoles, and for HDBP the maximum conversion attained was 0.3 mmoles.

Data for the reaction using the 15 mm diameter vessel was acquired by spectrophotometric analysis. Whereas ion chromatography provided the results for the variation of mass carbon acquired using a 40 mm diameter vessel.
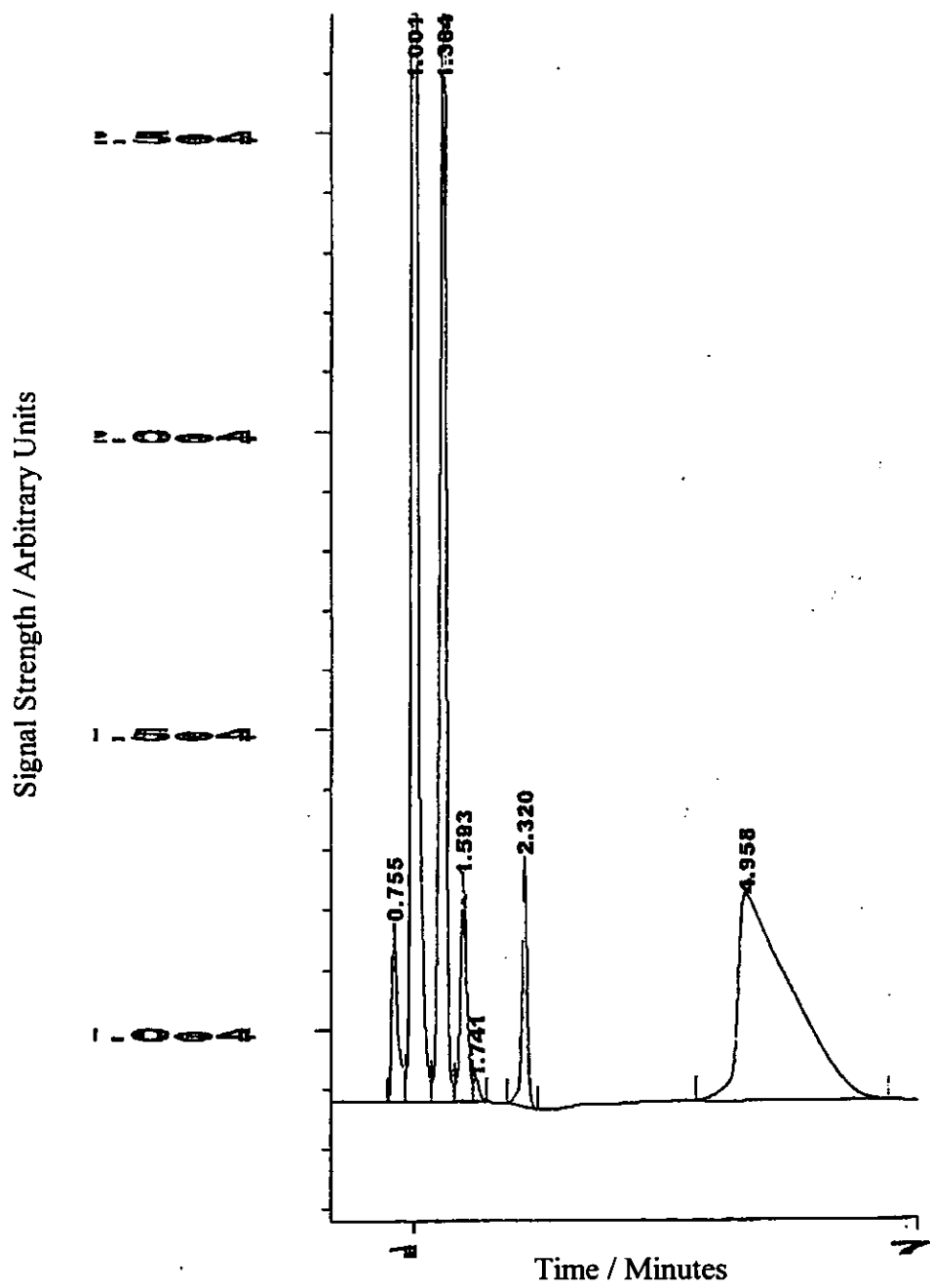
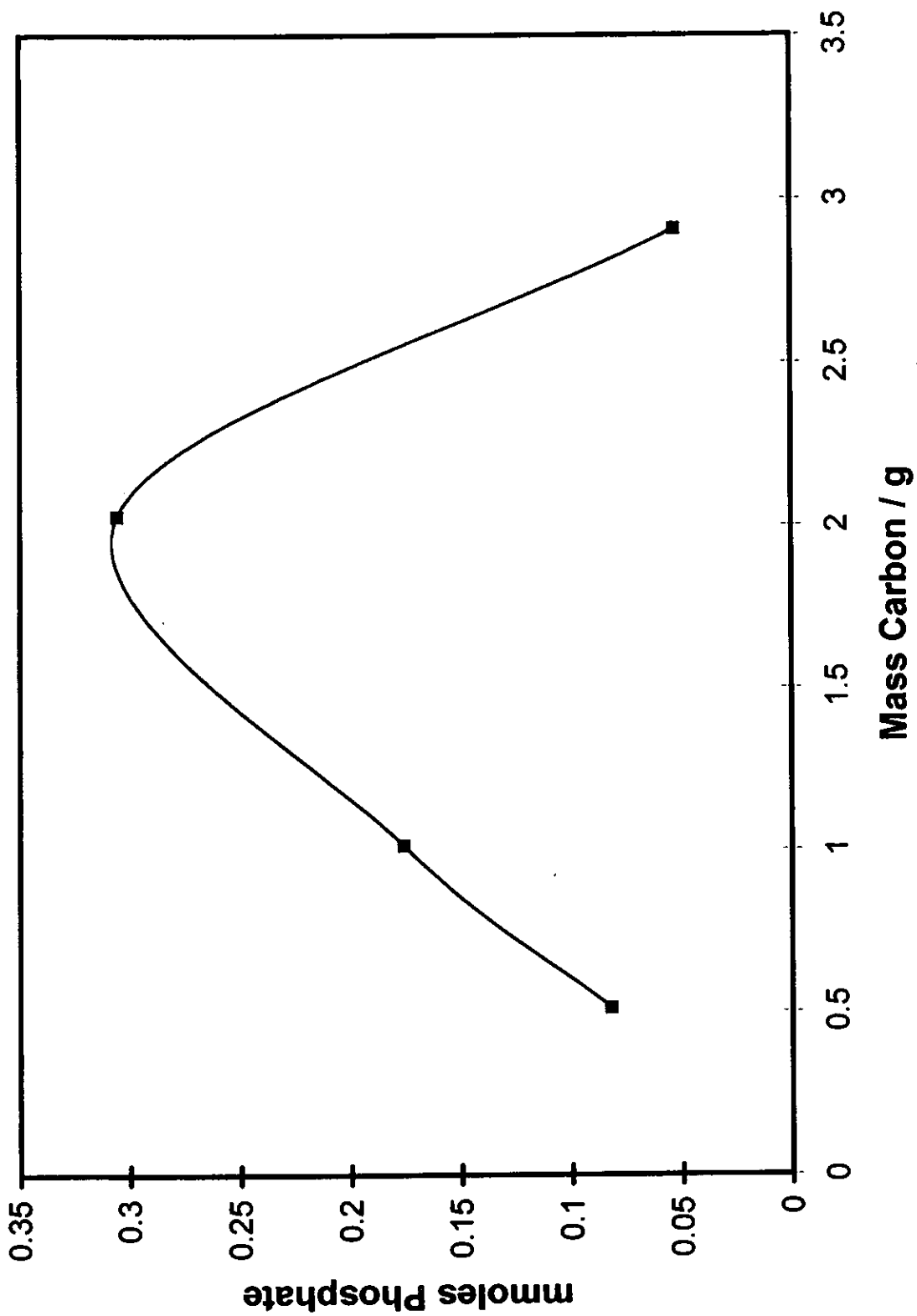**Figure 3.4** Dionex Ion-Chromatogram when Using Air as Oxidant.

Figure 3.5 Effect of Varying Mass of Carbon on the Decomposition of TBP Using Air as Oxidant and a 15 mm Reaction Vessel.
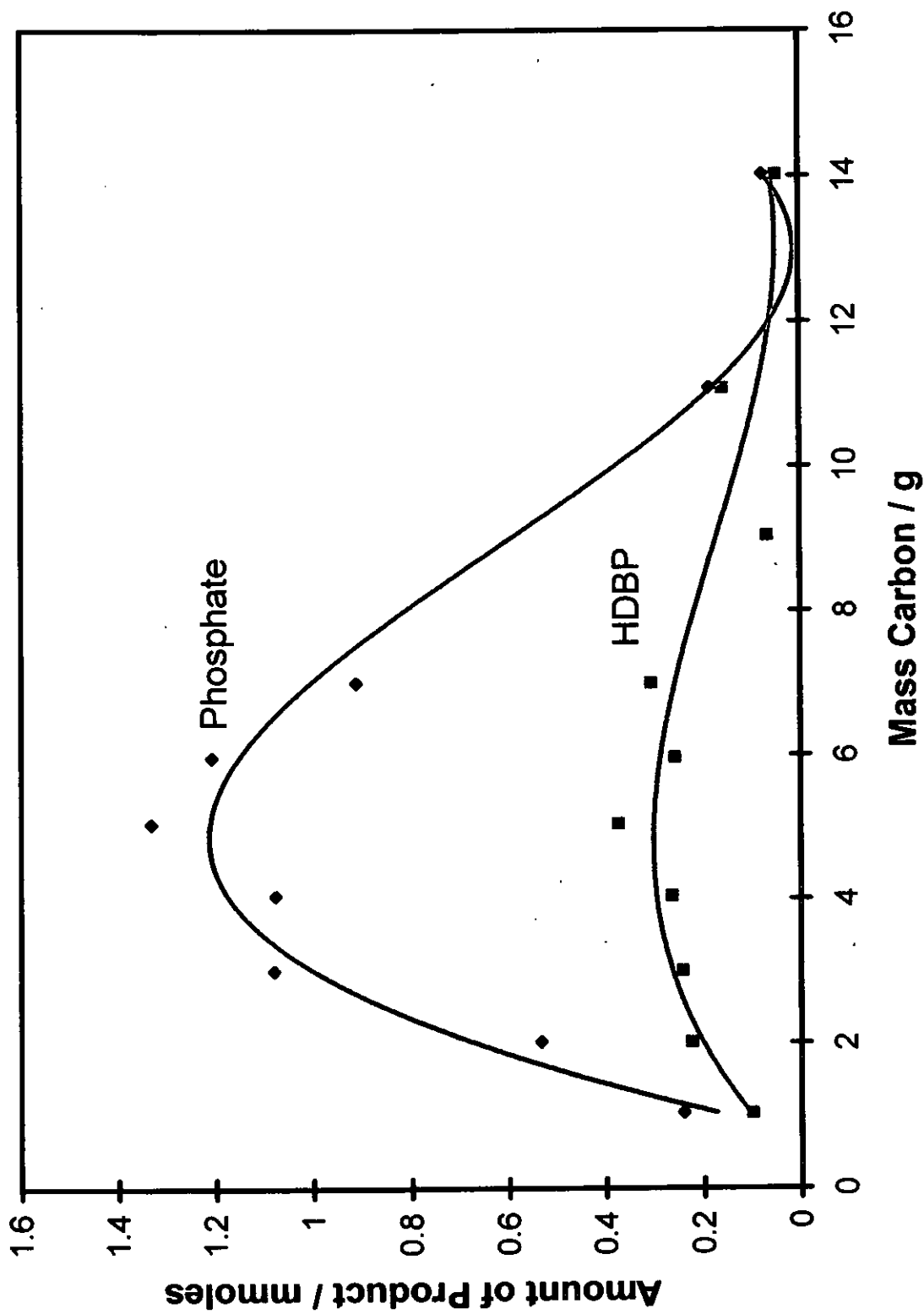
Figure 3.6 Effect of Varying Mass of Carbon on the Decomposition of TBP Using

Air as Oxidant and a 40 mm Reaction Vessel.

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3.2.3. Lifetime Studies.

The effect of decomposition of TBP as a function of time was carried out over the
duration 0-150 minutes, as described in Section 2.2.1.2. Experiments were performed
in the 15mm reaction vessel with a carbon loading of 1.3g. The data, acquired by
spectrophotometric analysis, is shown in Figure 3.7. Details of the additional data
points are contained in Section 3.2.4.

3.2.4. Variation of TBP Concentration.

Experiments were carried out as described in Section 2.2.1.3. to establish the effect
of varying the concentration of TBP over the range 0.5 to 3%. For concentrations 0.5
and 1.0 % there was no determinable orthophosphate by either spectrophotometric or
ion chromatographic methods. The data for the 3.0% sample is contained in Table
3.3. The data points have been added to Figure 3.7 and each is an average of three
replicate analyses. This method of data treatment, whilst no means statistically
complete, is included as a basis for comment on the precision of the analytical
procedures.

Table 3.3 Comparison of Analytical Methods.

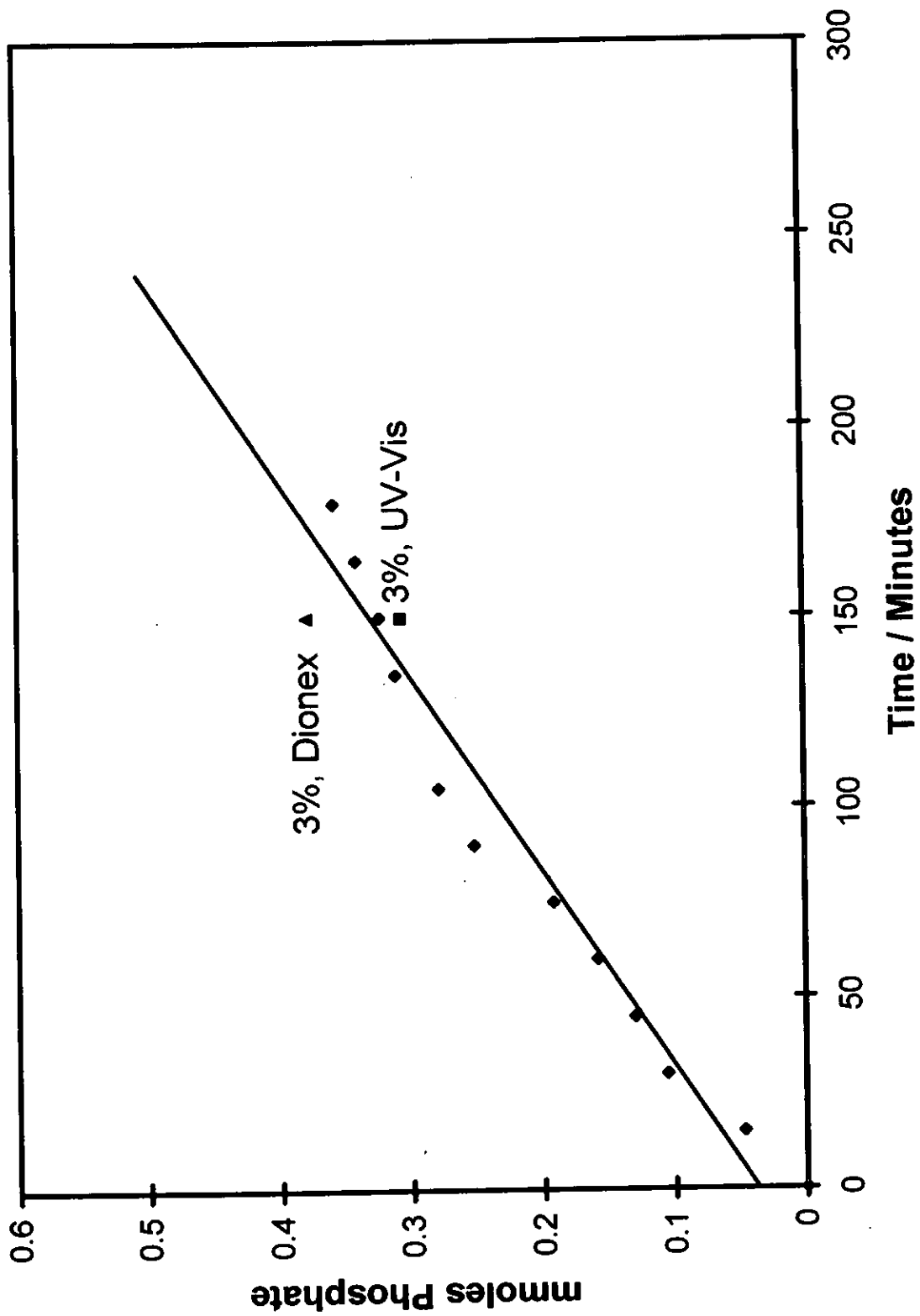| Analytical Method	Mmoles Phosphate Formed
UV-Vis Spectroscopy	0.3065
Ion Chromatography	0.3790

Figure 3.7 TBP Decomposition as a Function of Time.

3.3. Results for the Microwave Decomposition of TBP Using Hydrogen Peroxide as Oxidant.

3.3.1. Analysis Using Ion Chromatography.

A typical chromatogram produced in this type of reaction is shown in Figure 3.8. The number of peaks displayed is greater than in the cases where air is the oxidant. The peaks at 0.924, 1.313, and 4.747 minutes can be attributed to OH⁻ from NaOH, HDBP and orthophosphate ions respectively. The peak at 1.032 minutes is again believed to be due to the presence of a substance formed by the interaction between sodium hydroxide and chloroform. Hydrogen peroxide is responsible for the peaks occurring at retention times of 1.218, 3.119, and 3.233 minutes. Attempts to characterise the unknown peaks at 1.677 and 1.965 minutes proved unsuccessful. Methods used for the identification were the same as those described in Section 3.2.1., and the substances discussed there can also be ruled out as oxidation products when using this oxidant.

3.3.2. Variation of Mass Carbon.

The effect of varying the mass of carbon loaded in the reactor (40mm diameter) was investigated while using hydrogen peroxide as the oxidant. Experiments were performed as described in Section 2.2.2.1. and the analysis performed using ion chromatography. The conversion of TBP to both orthophosphate and HDBP as a function of the mass of carbon used is shown in Figure 3.9. It can be seen that the optimum carbon loading for both analytes is 3.0 g, yielding 1.0 mmole orthophosphate and 0.1 mmole HDBP.
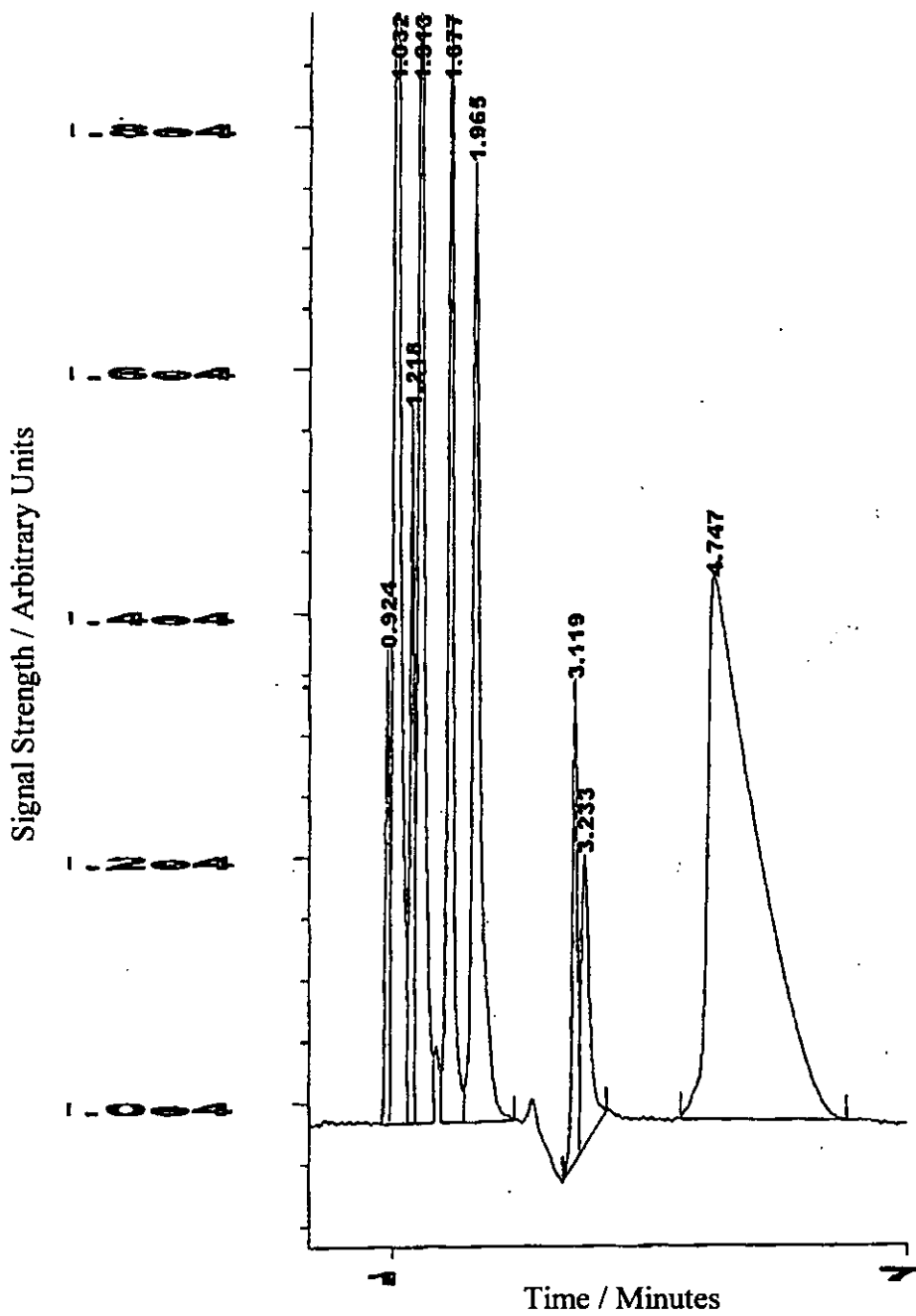
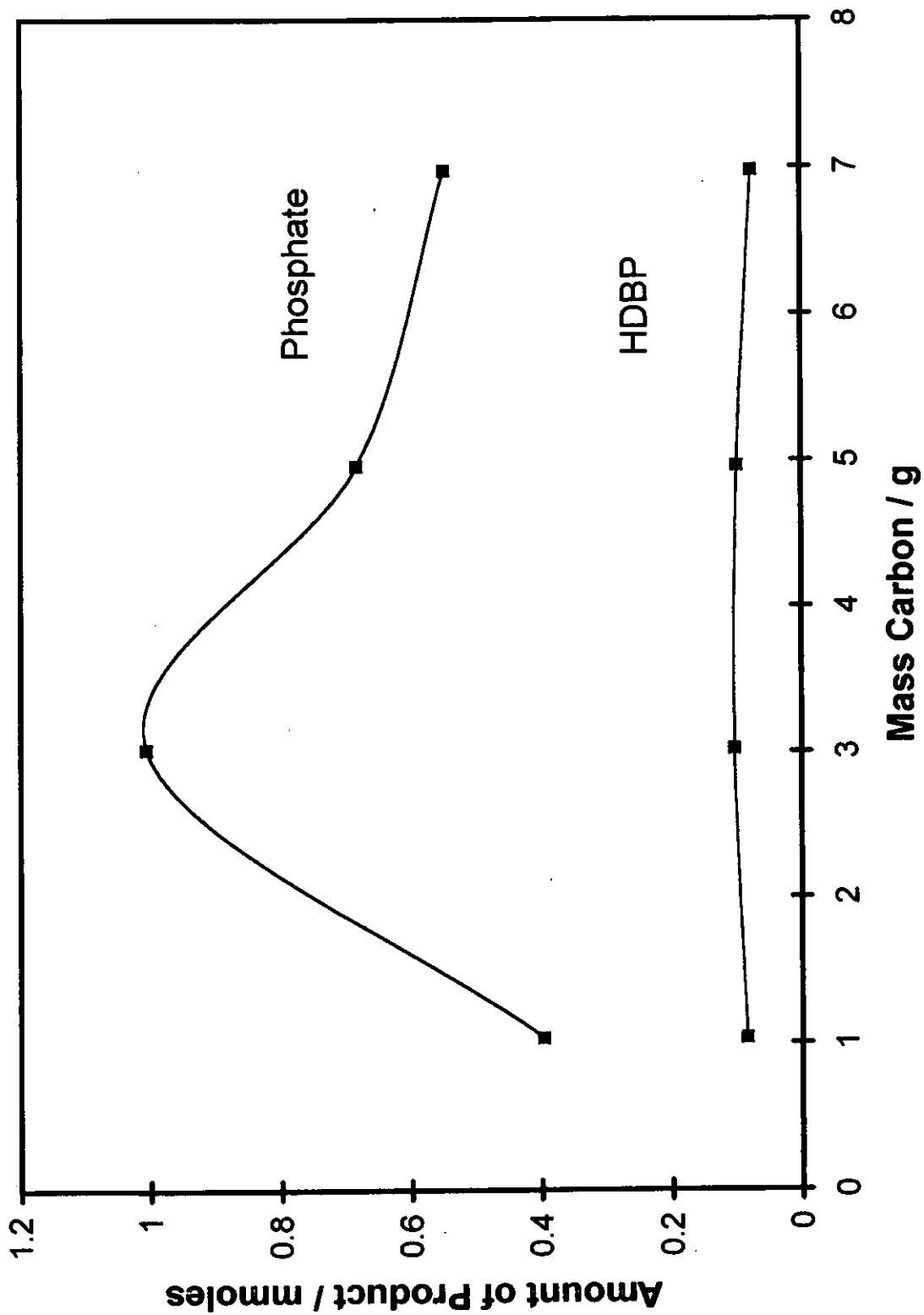**Figure 3.8** Dionex Ion-Chromatogram when Using Hydrogen Peroxide as Oxidant.

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Figure 3.9 Effect of Varying Carbon Mass on TBP Decomposition Using Hydrogen Peroxide as Oxidant.

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3.3.3. Lifetime Studies.

Experiments were performed to investigate the conversion to orthophosphate and HDBP as a function of time. The experiments were performed as described in Section 2.2.2.2. analysis being performed by ion chromatography. The plot of conversion versus time is shown in Figure 3.10. The linear trend-line serves as a visual guide, deemed to represent the perceived nature of the reaction.

3.3.4. Variation of Peroxide Concentration.

An investigation of the effect of varying the concentration of hydrogen peroxide was carried out over the range 10-100 vol. H_2O_2. Experiments were performed in the 40mm diameter vessel using 3 g of carbon as this had previously shown to be most effective (Section 3.3.2). The conversion to both orthophosphate and HDBP is shown in Figure 3.11. While a straight line has been fitted to Figure 3.11 there is obviously a large degree of scatter in the data. This is probably a reflection on the uncertainty in being able to reproduce the experimental conditions giving rise to exactly the same degree of plasma generation. This is obviously an area of concern and increasing the reproducibility would be a feature of future-work.

3.3.5. Variation of TBP Concentration.

Experiments were performed to investigate the decomposition of TBP with varying TBP concentration (0.5-5% v/v). The reaction vessel used was of 40 mm diameter and was loaded with approximately 3 g carbon. Analysis was conducted using ion chromatography and a plot of decomposition versus TBP concentration is shown in Figure 3.12. The trend-line for HDBP was applied using Microsoft Excel, while the corresponding line for inorganic phosphate was drawn in by hand. The fits were

chosen to serve as a guide to the eye to indicate the nature of the reaction as would be
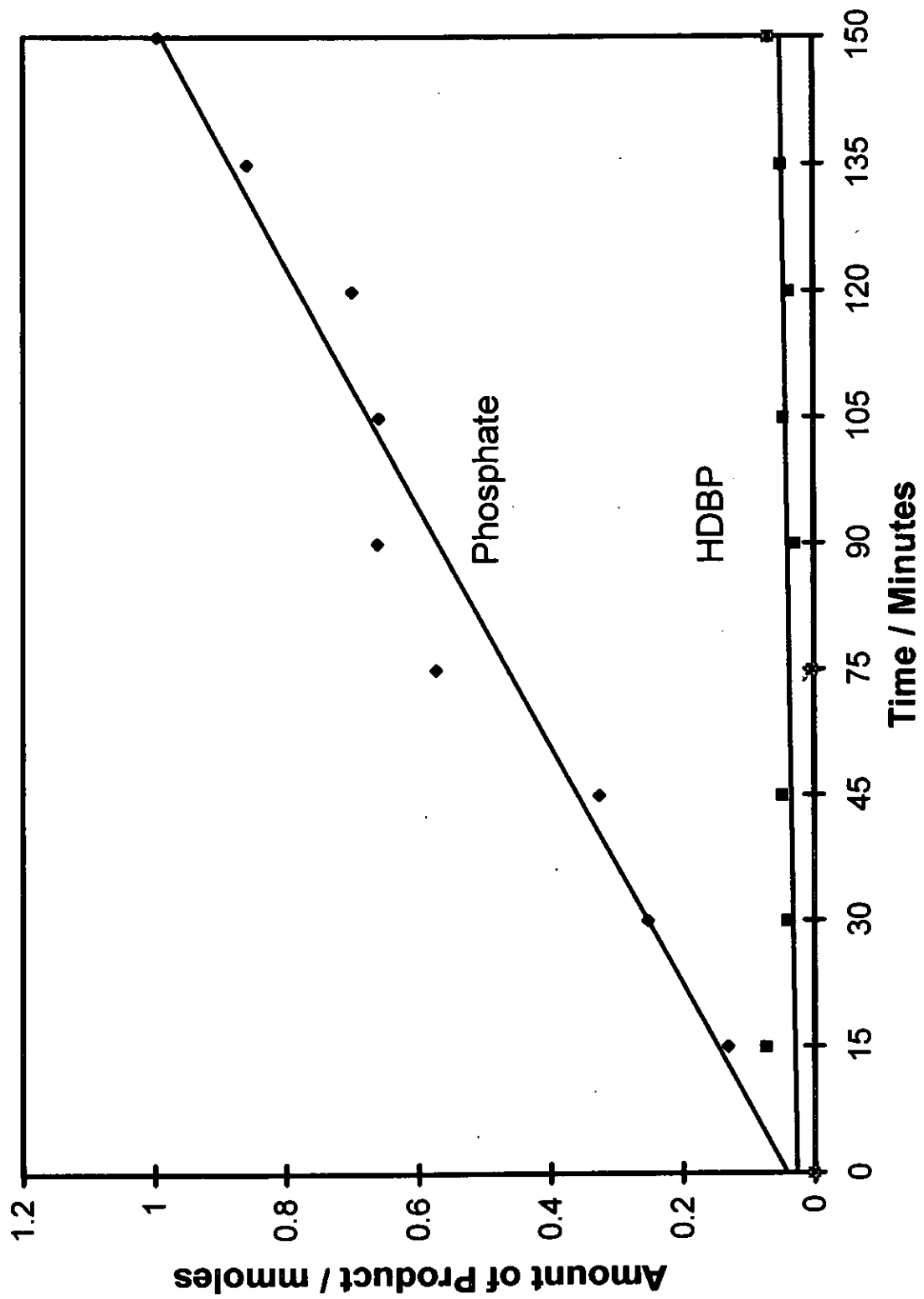
expected for the variable examined.

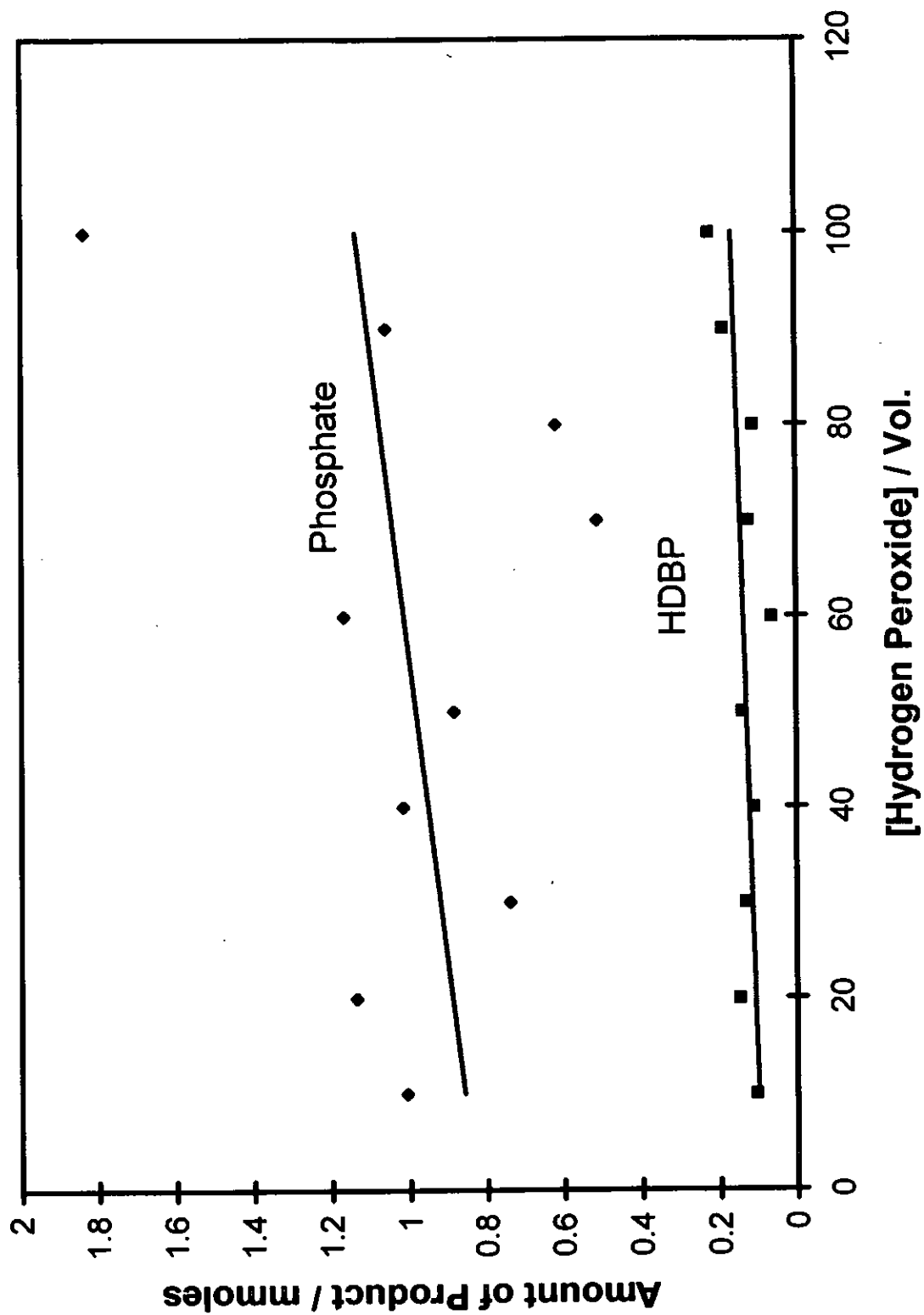**Figure 3.10** Conversion of TBP as a Function of Time Using Hydrogen Peroxide as Oxidant.

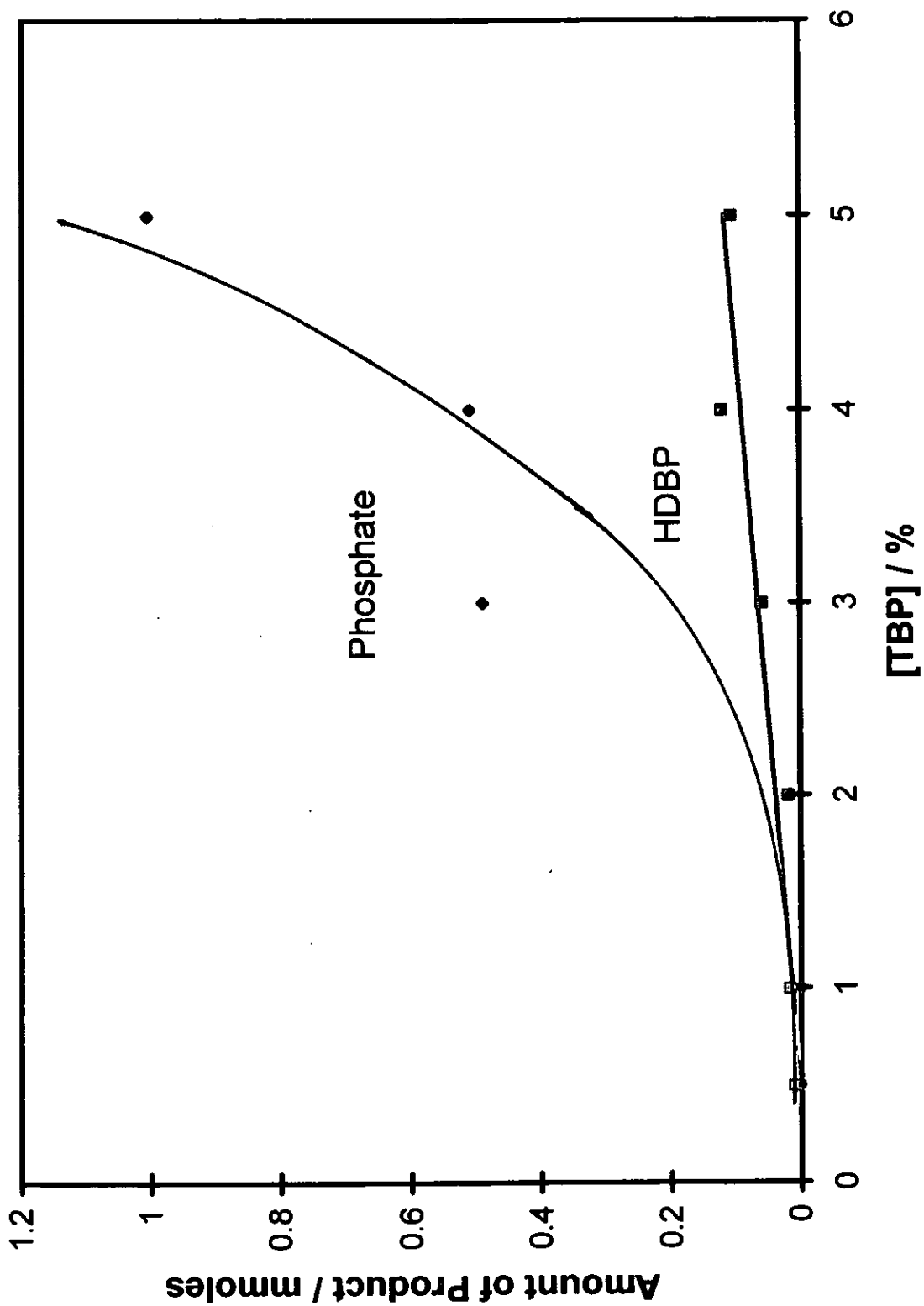**Figure 3.11** Decomposition TBP as a Function of Hydrogen Peroxide Concentration.

Figure 3.12 TBP Decomposition as a Function of TBP Concentration Using Hydrogen Peroxide as Oxidant.

4. Discussion.

4.1. Microwave Decomposition of TBP Using Air as Oxidant.

4.1.1. Variation of Mass Carbon.

Experiments performed in both 15 and 40 mm reaction vessels, Figures 3.5 and 3.6 respectively, show that a maximum conversion is achieved. These maxima occur at loadings of 1.9 and 5 g respectively. The 15 and 40 mm reaction vessels both show a parabolic curve whereas it might have been expected that there would be a direct relationship between the mass of carbon and the conversion of TBP. This is obviously not the case therefore we must conclude that there exists other factors which must be taken into consideration.

In reactions such as these using air as the oxidant, at low carbon levels the air bubbles through into the reaction vessel causing disruption to the carbon layer that floats at the top; in effect a fluidised carbon-bed is generated. In the upslope portion of the curve, conversion increases with an increase in carbon mass, whilst a sufficient level of fluidity is in operation. With increasing carbon mass a decrease in the bed fluidity occurs. Upon reaching the peak maxima, the bed takes on more of the characteristics of a packed bed as the vessel approaches fullness and there is less space for movement with air bubbling through. This may limit the extent to which adsorption of the organic can occur.

The % of the reactor volume that is filled is plotted against the rate of conversion normalised for the mass of carbon (Figure 4.1), with the trend-line fitted to the data series using Microsoft Excel. The software generated third order polynomial expressions to serve as a "guide to the eye". There appears to be a broad maximum between 20 and 40 % filled. Increasing the % fill above this clearly

has a detrimental effect for reasons outlined above. This result has significant

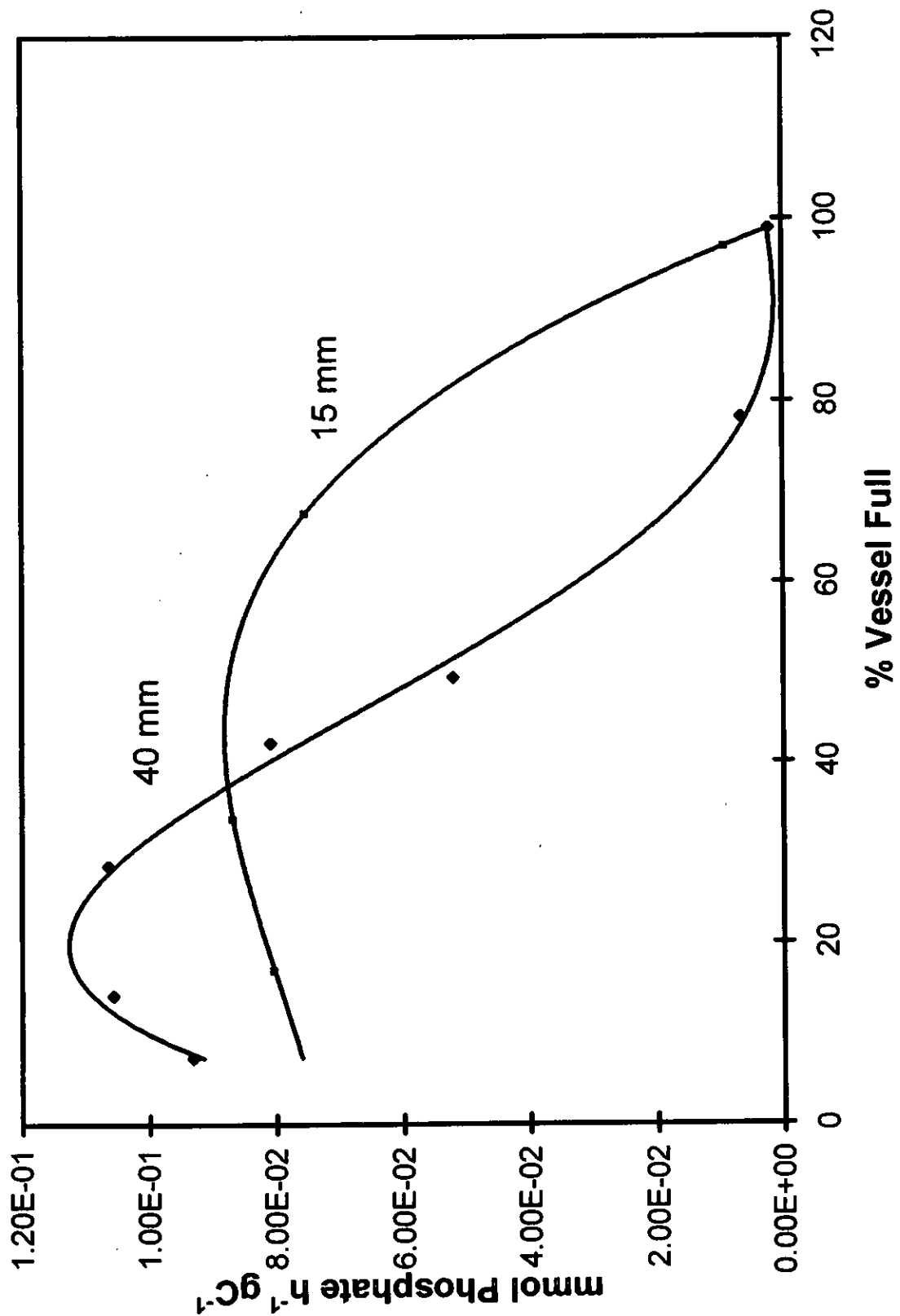**Figure 4.1** Graph of % Vessel Full versus mmol Phosphate per Hour per Gram

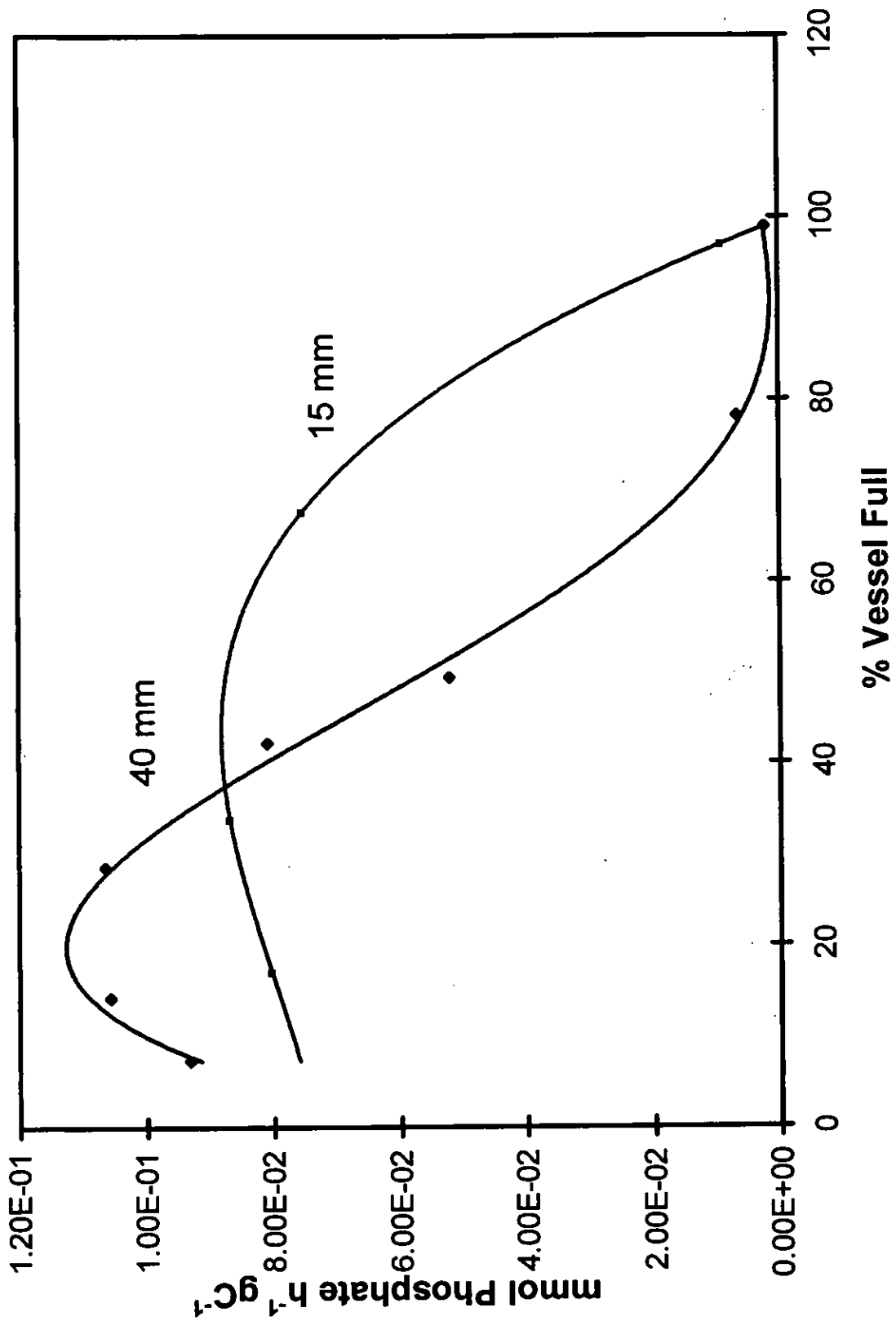Carbon for both 15 and 40 mm Reaction Vessels.

Figure 4.1 Graph of % Vessel Full versus mmol Phosphate per Hour per Gram

Carbon for both 15 and 40 mm Reaction Vessels.

implications for future work where the reactor size may be scaled up.

4.1.2. Lifetime Studies.

Monitoring the conversion of TBP to orthophosphate as a function of time shows that increased reaction gives rise to increased conversion. A smooth curve can be fitted to the data points, however a more detailed analysis indicates that there may be a step-like nature to the data.

Further evidence to this hypothesis is provided from work using hydrogen peroxide as the oxidant, where again a similar observation can be seen. Currently there is no explanation for a stepped reaction profile and longer reaction times would be required to further probe this phenomenon.

An insight into the reproducibility of these experiments can be given by comparison of Figures 3.5 and 3.7. In both cases a 15 mm vessel was used, regarding Figure 3.7, at a time of 2 hours with a vessel containing 1.3g carbon, conversion is approximately 0.275 mmoles. In comparison with Figure 3.5 the conversion achieved after 2 hours using 1.3 g carbon is approximately 0.235 mmoles, which is not a great difference given the variety of experimental parameters that exist.

4.1.3. Variation of TBP Concentration.

The data points collected from these experiments have been plotted on Figure 3.7 for comparison, since they were performed under comparable conditions (with the exception of TBP concentration: 5% for Figure 3.7, 3% for the added data points). For the result achieved using UV-Vis analysis the conversion is 0.31 mmoles and it is in good proximity to the line, hence showing reproducibility between the analytical methods. The conversion acquired by ion-chromatography is 0.38 and is above the

line, but the difference between both the line and the point for the conversion using UV-Vis analysis is not great. Thus, it is reasonable to suggest that data acquired by both methods of analysis is comparably precise.

4.2. Microwave Decomposition of TBP Using Hydrogen Peroxide as Oxidant.

4.2.1. Variation of Mass Carbon.

Conversion to phosphate at approximately 1 mmole is much greater than conversion to HDBP (approx. 0.1 mmole), which was also the case observed using air as oxidant (Figure3.6). With air as oxidant, these maximum values were greater, with conversion to phosphate at 1.2 mmoles and HDBP, 0.3 mmoles.

Reasons for the greater conversion to phosphate than HDBP will be discussed in Section 4.2.2.

It appears that a number of these observations can be attributed to the lack of bed fluidity when compared to the results using air as oxidant. With no air bubbling through to cause agitation of the carbon, the tendency is for the carbon to clump together and float at the top of the vessel. The scintillation observed is markedly less in some cases at higher fill levels and occurs only at certain areas of the carbon "clump". Reasonable conversion to phosphate can be achieved only at a lower percent full since the smaller mass of carbon is mildly disturbed by the direction of the aqueous input stream, and when "clumping" happens it is spread over the aqueous surface in the vessel. This, therefore, means that greater quantities of carbon are not excluded from being subject to scintillation, which is the case at greater carbon loadings.

4.2.2. Lifetime Studies.

First, it is apparent that as the reaction proceeds the rate of phosphate production is greater than that for HDBP (Figure 3.10). The conversion to phosphate behaves in a linear fashion, as opposed to the apparent constant HDBP level. Presumably, the conversion to phosphate would continue until there was no further starting material available for conversion, as long as oxidant remained available. Otherwise fresh oxidant could be added intermittently.

The lifetime study results were acquired using 90 vol. hydrogen peroxide and by looking at Figure 3.11 it is reasonable to suggest that hydrogen peroxide concentration is not a controlling factor. The lifetime study was achieved using 3 g carbon in a 40 mm reaction vessel and in comparison with Figure 3.9 it is evident that a degree of reproducibility has been achieved, with conversion at 150 minutes in the lifetime study at 1 mmole whilst an identical figure is present in Figure 3.9.

4.2.3 Variation of Peroxide Concentration.

It is evident, particularly with the phosphate results, that a great deal of scattering exists (Figure 3.11). Despite this the results indicate that there is little or no effect on varying the peroxide concentration.

An explanation for this lack of influence by the concentration could be that even at 10 vol., the number of moles of oxidant is substantially greater than the number of moles TBP. A 5% (v/v) solution of TBP in water contains 0.0184 moles of TBP, whereas 10 vol. H_2O_2 contains 0.08379 moles peroxide (4.5 times the number of moles TBP) and 100 vol., 0.8379 moles (45 times).

As the peroxide concentration is always in excess, hence changes in concentration in the range employed have no observable effect.

4.2.4. Variation of TBP Concentration.

The results presented in Figure 3.12 show that initially at low TBP concentrations the conversion is small possibly as a result of the small amounts of phosphate formed being undetectable. The graph then goes through an upturn before proceeding to show a linear relationship at higher concentrations.

4.3. Mechanism for the Microwave Assisted Decomposition of TBP Using Activated Carbon.

Reasons for the differences in amounts of the two analytes formed could provide an insight into the mechanism of conversion. With air, particularly in the experiments varying mass of carbon, HDBP formation was low, but maintained the trend displayed by phosphate conversion. Using hydrogen peroxide as oxidant, HDBP formation is very small and does not display the same trend as observed for phosphate. This may be attributable to a number of possibilities:

1. Hydrogen peroxide is more selective towards the formation of inorganic phosphate than towards HDBP.

2. It may suggest that the decomposition mechanism when using this oxidant could predominantly be TBP $\rightarrow$ H_3PO_4, rather than step-wise loss of butyl groups, i.e. TBP $\rightarrow$ HDBP $\rightarrow$ H_2MBP $\rightarrow$ H_3PO_4. Hence the major product would be phosphoric acid, with the presence of HDBP being a minor reaction product, formed from some step-wise decomposition.

3. The step-wise decomposition is the mechanism in operation, but conditions exist such that any HDBP formed is readily converted into the mono form and further reacted to give the inorganic phosphate. However, this would depend on whether the species formed are desorbed and later resorbed to achieve further conversion,

implying that some of the intermediate species would be detected if they failed to resorb. One other possibility is that the species remained adsorbed to the carbon, awaiting the conditions to arise for further conversion, before desorption as the inorganic phosphate. This would mean only phosphate being detected in large quantities.

4. One other possibility is that HDBP once formed may react more readily with hydrogen peroxide than with air, and this may also account for the differences in trends.

5. Conclusion and Future Work.

5.1 Conclusion.

A procedure has been developed to successfully decompose tri-butyl phosphate from aqueous solutions. The chosen method made use of a suitable oxidant, either air or hydrogen peroxide, which was mixed with the organic containing aqueous solution. This then passed into a reaction vessel loaded with activated carbon. The vessel was then subject to cycled pulses of microwave frequency radiation to facilitate the decomposition of tri-butyl phosphate. 100% decomposition was not achieved.

This study has shown that decomposition can be achieved using both air and hydrogen peroxide as oxidant and two products were identified; orthophosphate, and in smaller quantities, HDBP. Regarding both oxidants, it has been shown that conversion of tri-butyl phosphate to orthophosphate ions has been achieved, and that at the concentrations studied, neither oxidant is superior. Oxidation was attainable at low peroxide concentrations.

Perhaps, from an industrial point of view it would be more beneficial, economically and environmentally, to use air as the oxidant.

Conversion to orthophosphate is at an optimum when the carbon bed has the characteristics of a fluidised bed, as is shown in the non-linearity of the relationship between carbon loading and conversion for both 15 mm and 40 mm reaction vessels.

Studies on the variation of TBP concentration showed that with increasing TBP concentration, increasing decomposition was observed.

There were two methods of analysis suitable for use, depending on the oxidant. Reactions using air could be analysed using either ion-chromatography or UV-Vis Spectroscopy, whereas the reactions using hydrogen peroxide were limited to ion-chromatographic analysis. Both as would be expected had advantages and

disadvantages, although importantly they were precise in that a phosphate concentration derived from one was similar to the concentration derived from the other.

Ion-chromatography had the advantage of being able to quantify a variety of analytes providing they were identified, but was time consuming and subject to equipment inconsistencies. On the other hand, Uv-Vis Spectroscopy, was easy to use, giving quick analyses, but in the context of this work was only suitable for one analyte.

5.2. Future Work.

1. To scale-up the system so as to be able to decompose larger quantites of organic material. Initially this would be done by deciding on a reaction vessel size, and fitting the other pieces of equipment around this. Modifications could then also be incorporated into the design, such as reaction vessel material, frit alterations, stirring mode, number of reservoirs, etc. Naturally, a larger cavity would be required to house a larger reaction vessel.

2. Further optimisation of the experimental parameters to ensure greater reproducibility of the localised plasma formation. This would involve tests so as to find the most suitable duty cycle for maximum decomposition. In this study, because of time constraints an arbitrary cycle was decided on, which was maintained throughout the experiments. Variation of the pulse timing would possibly allow greater adsorption of organic material on to the carbon. Plasma formation in this work is not an exact science and thus it is imperative to hone the variables so as to give greater reproducibilty.

3. Improved product characterisation. In this study positive identification could only be made for two products using ion-chromatography. A better understanding of the compounds formed would give a more revealing insight into the mechanism of the decomposition. The methods of analyses used in this work served as a means to an end, with more time and better equipment, perhaps GC-MS could be used to establish what products are resident in the organic phase.

4. Variation of sensitiser/adsorbent. The work here centred solely on the use of activated carbon and was successful for what was required. Perhaps though testing a variety of catalysts would be more beneficial for example copper on carbon or other metals selective towards TBP on carbon.

5. Future work may be carried out on model cruds to ascertain the effect of the process on them. It would also be interesting to apply the technology to other organic waste remediation problems.

6. References.

1. Choppin, G., Rydberg, J., and Liljenzin, J.O., in Radiochemistry and Nuclear Chemistry, 2nd Edn. Butterworth-Heinemann Ltd., Oxford, 1995.

2. Howells, G.R., Hughes, T.G., and Saddington, K., "The Chemical Processing of Irradiated Fuels from Thermal Reactors" in Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 2 (Bruce, F.R., Fletcher, J.M., and Hyman, H.H.) Eds, Pergamon Press, London, 1958.

3. Philips, C., *Trans.I.Chem.E.*, **71**, Part A. (1993).

4. Navratil, J.D., Schultz, W.W., and Talbot, A.E., Science and Technology of Tributyl Phosphate, Vol.I: Synthesis, Properties, Reactions and Analysis, CRC Press, Inc., Florida, 1984.

5. Multern, J., "Thorp", *atw.40.Jg.* (1995) HEFT-8/9.

6. Chalmers, R.A., De, A.K., and Khopkar, S.M., Solvent Extraction of Metals, Van Nostrand Reinhold, London, 1970.

7. Marr, I., "Thorp", *Pow.Eng.I.*, pp.206-210, (1997).

8. Bender, K.P., Burger, L.L., Navratil, J.D. and Schulz. W.W., Science and Technology of Tributyl Phosphate, Vol.III: Applications of Tributyl Phosphate in Nuclear Fuel Processing, CRC Press, Inc., Florida, 1990.

9. Tahraoui, A., and Morris, J.H., *Sep.Sci.Tec.*, **30** (13) pp.2603-2630, 1995.

10. Healy, T.V., Fuel Reprocessing Solvent Tributyl Phosphate: Its Degradation, Clean-up, and Performance, IAEA-SM-207/23.

11. Miyake, C., Hirose, M., Yoshimura, T., Ikeda, M., and Imoto, S., *J.Nuc.Sci.Tec.* **27** (2) pp.157-166, 1990.

12. Siczek, A.A., and Meisenhelder, J. H., *Radiochimica Acta,* **27**, 217-221 (1980).

13. Solovkin, A.S., *Radiokhimiya*, **24**, 56, 1982; *(transl.), Sov.Radiochem.*, **24**, 49, 1982.

14. Siczek, A.A., and Steindler, M.J., *Atomic Energy Review*, **16**, 575, (1978).

15. Hardy, C.J., and Scargill, D., *J.Inorg.Nuc.Chem.*, **17**, 337-349, (1961).

16. Zimmer, E., Printz, G., and Merz, E., *Fuel.Reprocess.Waste.Manage.*, pp.459-466 (1986).

17. Ritcey, G.M., *Hydrometallurgy*, **5**, 97-107 (1980).

18. Smith, D.N., Edwards, H.G.M., Hughes, M.A., and Courtney, B., *Sep.Sci.Tec.*, **32** (17) pp.2821-2849, 1997.

19. Gonda, K., Oka, K., and Nemoto, T., *Nuc.Tec*, **57**, 1982.

20. Culler, F.L., Progress in Nuclear Energy, SeriesIII, Process Chemistry, Vol.I, Pergamon Press, London, 1956, 172.

21. Jha, B.K., Patist, A., and Shah, D.D., *Langmuir*, 1999, **15**, 3042-3044.

22. Warf, J.F., *J.Am.Chem.Soc.*, **71**, 3257, 1949.

23. Alcock, K., Grimley, S.S., Healy, T.V., Kennedy, J., and M^{c}kay, H.A.C., "The Extraction of Nitrates by Tri-n-butyl Phosphate", *J.Chem.Soc.Faraday.Trans.* **52**, pp.39-47, 1956.

24. M^{c}kay, H.A.C., and Healy, T.V., in "TBP as an Extracting Solvent" in Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 2 (Bruce, F.R., Fletcher, J.M., and Hyman, H.H.) Eds, Pergamon Press, London, 1958.

25. Goode, J.H., *Nucleonics*, **15**, 2, 1957.

26. Burger, L.L., and McClanahan, E.D., *Gamma Radiolysis*, **50**, 2, (1958), pp.153-156.

27. Bellido, A.V., and Rubenich, M.N., *Radiochimica Acta*, **36**, 61-64, (1984).

28. M^ckay, H.A.C., "Extractants and Diluents for Fast Reactor Reprocessing", in Fast Reactor Fuel Reprocessing, Society of Chemical Industry, London, 1980, pp.105-121.

29. Blake, C.A., Baes, C.F.N., Brown, K.B., Coleman, C.F., and White, J.C., *Proc.2nd Intern. Conf. Peaceful Uses At. Energy, Geneva,* **28**, 289 (1958).

30. Burger, L.L., "The Decomposition Reactions of Tributyl Phosphate and its Diluents and their Effect on Uranium Recovery Processes", in Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 2 (Bruce, F.R., Fletcher, J.M., and Hyman, H.H.) Eds, Pergamon Press, London, 1958.

31. Blumenthal, E., and Herbert, J.B.M., *Trans.Faraday.Soc.,* **41**, 611, 1945.

32. Moffatt, A.J., and Thompson, R.D., *J.Inorg.Nucl.Chem.,* **16**, 365, 1961.

33. Kondakov, V.M., Korotkevich, V.M., Semenov, E.N., and Mikhailova, N.A., *Radiokhimiya,* **41**, 1, 78-79, (1999), *(transl.) Radiochemistry,* **41**, 1, 81-82, (1999).

34. Nowak, Z., and Nowak, M., *Radiochem.Radioanal.Letters,* **14**, 3, 161-168, (1973).

35. Cherbuliez, E. and Lieber, J.P., *Helv.Chim.Acta.,* **35**, 2589, 1952.

36. Kazarinov, V.E., Egorov, G.F., Afanes'ev, O.P. and Nazin, E.R., *J.Radioanal.Nuc.Chem.,* **218**, 1, 87-92, (1997).

37. Higgins, C.E., and Baldwin, W.H., *J.Org.Chem.,* **30**, 3173, (1965).

38. Higgins, C.E., and Baldwin, W.H., *J.Org.Chem.,* **26**, 246, (1961).

39. Paciorek, K.J.L., Kratzer, R.H., Kaufman, J., Nakahara, J.H., and Christos, T., *J.Am.Ind.Hyg.Assoc.,* **39**, 633, (1978).

40. Filipov, A.P., and Krutova, G.I., *Sov.Radiochem (transl.),* **11**, 527, 1969.

41. Berman, N., and Lowry, A., *J.Am.Chem.Soc.,* **60**, 2596, 1938.

42. Rigg, T., and Wild, W., "Radiation Effects in Solvent Extraction Processes" in Progress in Nuclear Energy, Series III, Process Chemistry, Vol. 2 (Bruce, F.R., Fletcher, J.M., and Hyman, H.H.) Eds, Pergamon Press, London, 1958.

43. Clay, P.G., and Wittort, M., *Radiochem.Radioanal.Letters*, **19**, 2, 101-107, 1974.

44. Lesage, D., Virelizier, H., and Jankowski, C.K., *Spectroscopy*, **13**, 275-290, (!990).

45. Adamov, V.M., Andreev, V.I., Belyaev, B.N., Markov, G.S., Polyakov, M.S., Ritari, A.E., and Shil'nikov, A.Yu., *Kerntechnik*, **55**, No.3, 1990.

46. Burr, J.G., *Radiat.Res.*, **8**, 214-221, (1958).

47. Wagner, R.M., Kinderman, E.M., and Towle, L.H., *Ind.Eng.Chem.*, **51**, 1, 1959.

48. Wilkinson, R.W., and Williams, T.F., *J.Chem.Soc.*, 4098, 1961.

49. Lane, E.S., *Nuc.Sci.Eng.*, **17**, 620-625, (1963).

50. Huggard, A.J., and Warner, B.F., *Nuc.Sci.Eng.*, **17**, 638-650, (1963).

51. Neace, J.C., *Sep.Sci.Tec.*, **18**, (14&15), 1581-1594, (1983).

52. Zimmer, E., and Borchardt, J., *Nuc.Tec.*, **75**, 1986.

53. Tallent, O.K., Mailen, J.C., and Dodson, K.E., *Nuc.Tec.*, **71**, 1985.

54. Bykov, G.L., *Radiokhimiya*, **37**, 5, 475-479, 1995.

55. Warren, S., "Organic Synthesis", Wiley and Sons, 1981.

56. Becker, R., and Stieglitz, L., Proc. Conference on Reprocessing of Fast Breeder Fuel, Obertraum, Austria, 1981, p.31.

57. Titov, A.I., *Tetrahedron*, **19**, 557-580, 1963.

58. Miyake, C., Hirose, M., Yoshimura, T., Ikeda, M., and Imoto, S., *J.Nuc.Sci.Tec.*, **27**, 2, 157-166, 1990.

59. Sherrow, S.A., Toth, L.M., and Begun, G.M., *Inorg.Chem.*, **25**, 1992-1996, (1986).

60. Edwards, H.G.M., Hughes, M.A., and Smith, D.N., *Vib.Spec.*, **10**, 281-289, (1996).

61. Solovkin, A.S., Teterin, E.G., Shesterikov, N.N., and Kokanov, S.A., Russian *J.Inorg.Chem.*, **18** (1), 1973.

62. Edwards, H.G.M., Hughes, M.A., Smith, D.N., and Courtney, B., *J.Mol.Structure*, **351**, 65-76, (1995).

63. Miyake, C., Hirose, M., Yoneda, Y., *J.Nuc.Sci.Tec.*, **27** (3), 256-261, (1990).

64. Shaw, D.I., in "Introduction to Colloid and Surface Chemistry", 4th Edn., Butterworth-Heinemann, Oxford, 1998.

65. Maya, L., and Bopp, C.D., *J.Inorg.Nucl.Chem.*, **40**, 1147-1151, (1978).

66. Maya, L., Hydzik, R.J., and Haas, J.A., *J.Inorg.Nucl.Chem.*, **41**, 1193-1198, (1979).

67. Egorov, G.F., Zemlyanukhin, V.I., Shmidt, V.S., and Afanas'ev, O.P., *Radiokhimiya*, **22**, 3, 394-400, (1980).

68. Pickering, J., *J.Chem.Soc.*, **91**, p.2001, (1907).

69. Briggs, *J.Ind.Eng.Chem.*, **13**, 11, 1008-1010, (1921).

70. Frohlich, H., "Theory of Dielectrics", 2nd Edn., Oxford University Press, London, 1958.

71. Wagner, K.W., *Arch.Elektrotech.*, **2**, 371, (1914).

72. "Unit Operations for Treatment of Hazardous Industrial wastes", edited by De Renzo, D.J., Noyes Data Corporation, New Jersey, 1978.

73. Hutson, G.V., *Nuc.Energy.*, **35**, 6, pp.393-398, (1996).

74. Ouki, S.K., and Kavannagh, M., *Waste Management and Research*, **15**, 383-394, 1997.

75. Schulte, P., Bayer, A., Kuhn, F., Luy, Th., and Volkner, M., *Ozone Science and Engineering*, **17**, 119-134, 1995.

76. "Industrial Waste Disposal", edited by Ross, R.D., Van Nostrand Rheinhold, New York, 1968.

77. Gharaibeh, S.H., Moore, S.V., and Buck, A., *J.Chem.Technol.Biotechnol.*, **71**, 291-298, 1998.

78. Kearney, P.C., "Pesticide Remediation in Soils and Water", Wiley and Sons Ltd., 1998.

79. Hanks, K.S., Final Year BSc Project, 1997.

80. Christopher, J., Final Year BSc Project, 1996.

81. Skoog, D.A., West, D.M., and, Holler, F.J., "Fundamentals of Analytical Chemistry", 6th Edn., Saunders College Publishing, 1992.

82. Vogel, A.I., in "Quantitative Inorganic analysis", 3rd Edn., Longman, London, 1961.

83. Lash, R.P., and Hill, C.J., *J.Liq.Chrom.*, **2(3)**, 417-427, 1979.