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SEPARATION AND RECOVERY OF MATERIALS FROM SCRAP PRINTED CIRCUIT BOARDS

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ABSTRACT

Printed circuit boards from waste computers, televisions, and mobile phones were pyrolysed in a fixed bed reactor with the aim of separating and recovering the organic and metallic materials. A selection of printed circuit boards from each of the three waste classes was pyrolysed at 800°C and the pyrolysis products were analysed using GC-FID, GC-TCD, GC-MS, GC-ECD, ICP-MS, and SEM-EDX. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethyl)phenol, and p-hydroxyphenol, as well as bisphenol A, tetrabromobisphenol A, methyl phenols, and bromophenols. The pyrolysis oils also contained significant concentrations of organo – phosphate compounds and a number of tetrabromobisphenol A pyrolysis products were also identified.

The pyrolysis residues were very fragile and the organic, glass fibre, and metallic fractions could easily be separated and the electrical components could easily be removed from the remains of the printed circuit boards. The ash in the residue mainly consisted of copper, calcium, iron, nickel, zinc, and aluminium, as well as lower concentrations of valuable metals such as gallium, bismuth, silver, and gold, silver was present in particularly high concentrations. Many other metals were also identified in the ash by ICP-MS and SEM EDX. The pyrolysis gases mainly consisted of CO_2 and CO but all of the $C_1 – C_4$ alkanes and alkenes were present, as were some inorganic halogens.

Keywords: printed circuit board, recycling, pyrolysis, materials recovery
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INTRODUCTION

The European Commission’s Waste Electrical and Electronic Equipment Directive (European Commission, 2003) requires that member states re-use, recycle, and recover all waste electrical and electronic equipment rather than simply disposing of it in landfill sites. As part of this approach to waste processing, the WEEE Directive requires that printed circuit boards are processed in an environmentally sustainable manner. Many pieces of electrical equipment such as televisions and computers contain printed circuit boards as well as other electrical items such as washing machines, which are increasingly using printed circuit boards for features such as timers and pre-programming. Printed circuit boards are particularly problematic to recycle because of the heterogeneous mix of organic material, metals, and glass fibre. In 2002, only 15% of the 50,000 tonnes of scrap printed circuit board produced in the UK was recycled (Goosey and Kellner, 2002). Currently, waste printed circuit boards are either incinerated, which can lead to the formation of toxic brominated compounds derived from the brominated flame retardants contained in the circuit boards, or sent to landfill, which can lead to toxic compounds leaching into the water supply (Fisk et al., 2003).

Many printed circuit boards are made up of either polymer films such as polyimides, or less frequently polyethylene terephthalate or polyethylene naphthalate, or glass fibre composites bonded with a thermoset resin. Common resins include difunctional epoxy resins such as bisphenol A, multifunctional epoxy resins such as phenol and creosol based epoxy novolacs, BT epoxy blends, cyanate esters, and polyimides. As well as a resin, a hardener is needed to form the cross-linking required to create a thermoset plastic, the most common hardener is dicyanodiamide, but 4,4'-diaminodiphenyl sulfone and 4,4'-diaminodiphenyl methane are also used.

The choice of manufacturing materials used for printed circuit boards depends on the application, for example, difunctional epoxy resins are adequate for simple two-sided circuit boards but more sophisticated multifunctional epoxy resins or cyanate esters are required for thick multi-layered boards (Jawitz, 1997). The most common type of printed circuit board used in computers and communication equipment is made from glass fibre reinforced epoxy resin (referred to commercially as FR-4) but televisions and home electronics predominantly use printed circuit boards made of cellulose paper reinforced phenolic resin (FR-2), although high-value equipment increasingly contains FR-4 boards (Danish EPA, 1999). As well as glass fibre, paper, and resin, printed circuit boards also contain significant quantities of metals, the most significant of which is copper, which is used to form the electrical circuits on the printed circuit boards. Other metals that are present in printed circuit board waste include iron, nickel, silver, gold, and palladium from the electrical components themselves and the solder used to attach them to the boards (Goosey and Kellner, 2002).

One possible method of recycling printed circuit boards and recovering both the organic and non-organic fraction is pyrolysis. Pyrolysis is a thermal recycling technique that has been widely researched as a method of recycling synthetic polymers (Bhaskar et al., 2004, Brebu et al., 2005, Kaminsky et al., 2004, Hall and Williams 2006) including polymers that are mixed with glass fibres (Cunliffe et al., 2003). Pyrolysis of polymers leads to the formation of gases, oils, and chars which can be used as chemical feedstocks or fuels. Additionally, the pyrolysis process, if the temperature is high enough, will melt the solder used to attach the electrical components to the printed circuit boards. The combination of the removal and recovery of the organic fraction of printed circuit boards and the removal of the solder should aid the separation of the metal components from the organic material.

Although a significant amount of research into the pyrolysis of printed circuit board waste has been reported, most of the work has been carried out using analytical pyrolysis techniques or very small batch reactors (Barontini and Cozzani, 2006, Barontini et al., 2005, Blazso et al., 2002, Bradna and Zima, 1991, Luda et al., 2005, Williamson et al., 1980). Also, most of the work into the pyrolysis of printed circuit boards has concentrated on the composition of the organic products, particularly the brominated organics. In this work we have pyrolysed a selection of different printed circuit board wastes in a laboratory-scale batch reactor and as well as characterising the organic pyrolysis products we have also qualitatively identified the metals that can be recovered after pyrolysis of the waste boards. We have also reported upon the ease with which the metal and glass fibre components can be separated from the pyrolysis char compared to the relative difficulty of removing metal components directly from printed circuit boards.

A further aspect of the research investigated the presence of bromine and phosphorus compounds in the product pyrolysis oil. A major concern over the recycling of printed circuit boards by pyrolysis is the presence of flame retardants. Brominated and/or phosphated additives are added to circuit boards and circuit board components to reduce the flammability of the boards, these additives are often toxic (Tohka and Zevenhoven, 2002). FR-4 is fire retarded with tetrabromobisphenol A (TBBPA) while FR-2 is fire retarded with either TBBPA if the boards are manufactured in Europe or penta-bromodiphenyl ether (penta-BDE) if the boards are manufactured in Asia, although the use of penta-BDE is decreasing (Danish EPA, 1999). Due to the toxic nature of many brominated flame retardants, manufactures are increasingly using alternative, phosphate based flame retardants such as triphenyl phosphate and tricresyl phosphates (Danish EPA, 1999). Although there has been a significant amount of work that has investigated the pyrolysis of brominated circuit boards (Balabanovich et al., 2005, Barontini and Cozzani, 2006, Barontini et al., 2005, Blazso et al., 2002, Chien et al., 2000, Luda et al., 2002) the authors could find little work investigating the pyrolysis of phosphate containing printed circuit boards. In this work we have investigated the presence of both brominated and phosphated compounds in the pyrolysis oil.

EXPERIMENTAL

MATERIALS

Printed circuit boards were removed from a selection of televisions, computers and computer monitors, and mobile phones. The batteries were removed from the boards which were then broken into pieces that were 1.5 – 2 cm^2, which was the maximum size that would fit into the fixed bed reactor, and the boards from each category were then mixed together. Most of the boards were multi-layered but some boards, most notably the ones from televisions, were single layered. The multi-layered boards all contained glass fibres but the single layered boards did not. A wide variety of components were present on all the boards, the larger easily recyclable components such as transformers were removed during the dismantling process, leaving the circuit boards and the minor components. The global composition of each category of printed circuit board used in this work is given in table 1.

FIXED BED REACTOR

Each of the three printed circuit board types was pyrolysed in a fixed bed reactor. The reactor measured 260mm in length by an internal diameter of 44.5mm and was externally heated by a 1.5kW tube furnace (figure 1). A crucible that contained 20g of printed circuit board sample was placed in the reactor at the start of the experiment and the reactor was then sealed and purged with nitrogen before being heated to 800°C at a rate of 10°C min^{-1}. Once the reactor had reached 800°C it was held at this temperature for 135 minutes to ensure that pyrolysis of the sample was complete.

After exiting the fixed bed reactor, the pyrolysis gases and oils passed through a water-cooled condenser and then two ice-cooled condensers that collected any oils and waxes released during the pyrolysis process. In addition, a glass wool trap was used to remove any oils or waxes that were not trapped by the condensers. Any inorganic gaseous halogens were collected by bubbling the pyrolysis gases through an alkali solution, the fluorine, chlorine, and bromine concentration of the alkali trap solution was analysed off-line using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column. The organic and permanent gases were sampled from the pyrolysis gases by drawing off gas samples into a syringe at pre-arranged intervals. The organic gases were analysed using a Varian 3380 GC fitted with a stainless steel 2m by 8mm column packed with n-octane Porasil C of 80-100 mesh size and a FID detector. The permanent gases were analysed by a second Varian 3380 GC fitted with twin TCD detectors, one for N_2, CO, O_2, and H_2 and one for CO_2.

The mass balance was calculated by weighing the mass of char and oil produced and analysing the pyrolysis gases by ion chromatography, GC-FID, and GC-TCD. The mass of each gas was determined by converting the volume concentrations determined by the ion chromatograph, GC-FID and GC-TCD to mass concentrations. The gas therefore contributed to the mass balance of the experiment, rather than being calculated as 'mass of gas by difference'. Each category of circuit board was tested at least twice.

The pyrolysis oils were recovered from the water-cooled condenser, only a small amount of oil was collected by the ice-cooled condensers and the glass wool trap. The pyrolysis oil was often mixed with a significant quantity of water which was removed by centrifuging the oil in a Gallenkamp centrifuge. A small fraction of the oils could not be poured from the condensers and this oil was recovered by washing the water-cooled condenser with acetone.

The dry oils and the oils recovered from the condensers with acetone were analysed by GC-MS, GC-ECD, and GC-FID. The GC-MS was a Shimadzu QP2010 fitted with a 30m RTX-5 column. The injector temperature was 285°C and the oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C min^{-1}, and then held for 15 minutes. The mass spectrometer electron energy was 70eV and the ion source and coupling temperatures were 220°C and 300°C respectively. The GC-FID and GC-ECD was a Varian 3380 fitted with a Varian CP-sil 5CB column (15m x 0.25mm x 0.25µm). The injector and FID temperatures were 290°C and 300°C respectively and the ECD temperature was 310°C. The GC oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C min^{-1}, and then held for 15 minutes.

The GC-MS was used to determine the compounds present in each of the pyrolysis oils and the GC-FID was calibrated to determine the concentration of the major components in each oil and to confirm the GC-MS identification of the compounds by comparing the retention times. The GC-ECD was used to determine the number of brominated compounds in the oil and the quantification of brominated phenols and bisphenols. The GC-FID was also used to quantify and confirm the identity of the phosphated compounds that were identified by the GC-MS. The pyrolysis oils were also characterised using a Nicolet 560 FT-IR. A small aliquot of each pyrolysis oil was coated between two KBr disks and then analysed over the range 4000 – 400 cm^{-1}.

The pyrolysis chars were recovered from the reactor after it had cooled and were examined by scanning electron microscopy coupled with energy dispersive X-ray analysis (SEM-EDX) to determine their elemental composition using a CamScan 4 SEM-EDX. The chars were ashed at 600°C according to EN ISO 3451-1:1997 to determine the metal and organic content of the chars. The ash was acid digested and then analysed using ICP-MS.

RESULTS AND DISCUSSION

PRODUCT YIELD

Table 2 shows the product yield from the pyrolysis of the three different types of printed circuit boards. In general good repeatability was achieved when the heterogeneous nature of the samples is taken into consideration. The total mass balance was very high for the pyrolysis of the printed circuit boards from mobile phones but not so high for the computer and television circuit boards. This was due to the production of significant quantities of water during pyrolysis, this water was mostly either condensed by the water-cooled condenser or captured by the glass wool filter. However, as the pyrolysis test progressed the water on the glass wool would evaporate, presumably because of the drying action of the pyrolysis gas passing over the filter. It is therefore quite likely that the mass losses during the pyrolysis of some of the circuit boards can be attributed to the loss of water from the glass wool filter. Some organic gases could not be identified by the GC-FID analytical system, and these gases would also have contributed to the low mass balance.

The computer printed circuit boards pyrolysed to form an average of 68.9 wt% residue, 22.7 wt% oil, and 4.7 wt% gas. Pyrolysis of the television circuit boards led to an average mass balance of 60.0% residue, 28.5% oil, and 6.5% gas and pyrolysis of the mobile phone circuit boards led to an average mass balance of 82.2 wt% residue, 15.2 wt% oil, and 2.3 wt% gas.

The composition of the pyrolysis gases is shown in table 3. By far the most abundant gases were CO_2 and CO, which presumably formed during the decomposition of the epoxy group but could also have been formed by the decomposition of calcium carbonate fillers in the polymer. The printed circuit boards from mobile phones formed less CO_2 and more CO than the printed circuit boards from the computers and televisions. The other significant components of the pyrolysis gases were methane, which could have originated from the methyl groups in bisphenol A, and hydrogen.

Gas samples were taken at regular intervals during the pyrolysis of each of the printed circuit board samples so the amount of pyrolysis gas being produced at any given temperature can be plotted against time (figure 2 - 4). It can be seen in figure 2 that peak gas production during the pyrolysis of the computer circuit boards occurred at 400°C. CO_2 release from the computer circuit boards peaked at 400°C and 750°C while CO release peaked at 400°C and 800°C and methane peaked at 600°C. Of the minor gases, the release of ethene and propene peaked at 400°C, propane, butane and butene/butadiene peaked at 500°C, and ethane and hydrogen release peaked at 550°C. Propene release during the pyrolysis of the computer circuit boards occurred very rapidly for a short time peaking at 400°C, the same temperature that CO_2 and CO release peaked at. The fact that propene, CO_2, and CO were all released at the same time suggests that the decomposition of the epoxy group either leads to the release of CO that is later oxidised to CO_2 or the release of a hydroxyl group leaving an allyl radical which reacts with a hydrogen radical to form propene. As the temperature increased above 600°C, the release of CO_2 and CO increased, presumably due to further decomposition of the char.

The total gas production from the television printed circuit boards peaked at 360°C (figure 3), CO_2 and CO production also peaked at 360°C. The release of hydrogen and methane peaked between 550°C and 600°C. Of the minor gases, propane, propene, butane, and butene/butadiene release peaked at 500°C, ethene peaked twice at 500 and 600°C, and ethane, the most abundant minor gas, peaked at 550°C.

The release of gases from the mobile phone circuit boards as the pyrolysis temperature increased is plotted in figure 4. Overall, gas release from the mobile phone boards peaked three times at 400°C, 550°C, and 800°C. CO_2 release peaked at 400°C and 550°C but CO release did not peak until 800°C. Methane was produced throughout the pyrolysis of the mobile phone boards and peaked at 550°C. Hydrogen production peaked at 500°C before gradually declining. Of the minor gases, propene and ethene release peaked at 400°C, propane, butane, and butene/butadiene release peaked at 460°C, and ethane release peaked at 500°C. Propene was released very rapidly coinciding with the first stage of CO_2 release.

None of the pyrolysis gases contained any fluorine or sulphur and only the mobile phone pyrolysis gas contained any chlorine. However, all the printed circuit board pyrolysis gases contained small concentrations of bromine. The low concentration of halogens in the pyrolysis gases is an advantage if the gases are to be used as a fuel because hydrogen halides are particularly corrosive to boiler tubes. The small amounts of halogens that are present could easily be removed from combustion gases using existing technologies such as wet or dry scrubbing systems that are currently used in municipal waste incineration. The pyrolysis gases contain a significant proportion of CO_2 which will lower the calorific value of the gas, however, systems now exist for removing CO_2 from gas streams (International Energy Agency, 2004).

Barontini et al (2005, 2006) used TGA-FT-IR and a very small batch reactor to investigate the pyrolysis of printed circuit boards, which had had their metal content entirely removed, and reported that the most prominent gas was hydrogen bromide followed by CO_2 and CO, only small amounts of CH_4 were reported. In this work, less than 1% of the pyrolysis gas was inorganic bromine, which suggests that the metal content of the printed circuit boards might have captured the bromine.

PYROLYSIS RESIDUE

After each of the printed circuit board samples was pyrolysed in the fixed bed reactor the solid residue was removed from the reactor crucible. The mobile phone board residue consisted of flexible pieces of pyrolysed board which could be easily broken apart and the copper power boards and track, electrical components, and glass fibre were easy to separate, although some of the electrical components could not be separated from the copper power boards and all the electrical components were very small. The pyrolysed television printed circuit board residue was different from the mobile phone board residue; the boards were very brittle and no glass fibre was present. Never-the-less, the electrical components could easily be separated from the residue, indeed, some components had come loose from the residue during the pyrolysis process and small lumps of solder were also present in the pyrolysis residue. The computer printed circuit board residue was a mixture of the flexible, glass fibre containing boards found in the mobile phone residue and the brittle boards found in the television residue and consisted of pieces of boards, very fine residue, and lumps of solder. The residue could be easily broken and the copper tracks and power boards, electrical components, and glass fibre could be quickly separated. The nature of the residues from the pyrolysis of the different printed circuit boards suggests that the mobile phone boards were constructed of FR-4 while the television boards were constructed from FR-2 and the computer boards were a mixture of FR-4 and FR-2. An example of the effect of pyrolysis on printed circuit boards, and the separation of the electrical components from the pyrolysis residue, is shown in figure 5.

To analyse the metals present in the pyrolysis residues, each of the residues was ashed at 600°C in an ashing furnace. The resulting ashes consisted of large metal pieces and a fine powder that were separated using a 600μm sieve. Both size fractions from each ash were then acid digested and then analysed using a ICP-MS, the results are presented in table 4. It was relatively easy to take a representative sample of the sub-600μm fraction but taking a representative sample of the larger fraction was very difficult, the results shown in table 4 should therefore be treated only as a qualitative indication of the metals present in the large fraction.

Copper was the largest fraction present in all of the ashes with concentrations of up to 33% and high concentrations of calcium, iron, nickel, zinc, aluminium, lead, and silver were also found in most of the residues. Gold was not detected in the television ash but it was detected in very low concentrations in the computer and mobile phone ash, palladium was not detected in any of the ashes. The concentrations of mercury and cadmium, which are toxic, were very low in all of the ashes. However, barium, another highly toxic metal, was present in significant concentrations, particularly in the mobile phone ash. Barium sulphate is used as a filler in many plastics to increase the hardness and stiffness of the polymer (Murphy, 2001) and is one of the few non-toxic forms of barium due to it being almost completely insoluble in water. Gallium was found in low concentrations in all of the ashes, gallium arsenide is used in the semi-conductor industry (Rajput, 2005) and is a valuable resource because gallium arsenide is difficult to manufacture and the only commercial source of gallium is bauxite, which contains just 0.01% gallium. Low concentrations of bismuth were found in the television and computer ashes, bismuth can be used to alter the properties of solder (Jawitz, 1997) and is also used to make low-melting point casting alloys with tin.

As well ICP-MS analysis of the ashes, each of the residues was also examined by SEM-EDX. In addition to the metals listed in table 4, bromine, carbon, oxygen, phosphorous, silicon, and tin were found in all of the residues. The carbon was obviously the char, while the silicon and oxygen were the glass fibres, which were not digested and were therefore not analysed by the ICP-MS. Tin is a component of solder, while bromine was probably present due to the reaction of metals with the bromine released during the decomposition of brominated organic fire retardants. Phosphorus was probably present due to the decomposition of organo - phosphate fillers, which are discussed in more detail later in this work. The residues from the pyrolysis of the computer printed circuit boards contained scandium and sulphur and the residues from the pyrolysis of the television printed circuit boards contained vanadium.

To further investigate the non-metal components of the pyrolysis residue we performed a water leaching test on each residue and analysed the results using ion chromatography. Each of the residues contained a high concentration of soluble bromines and also contained some soluble chlorides, sulphates, and fluorine, but no soluble phosphates were found in any of the residues. These results suggest that the halogens were forming soluble salts, such as calcium chloride and calcium bromide, in the residue.

The material recovered from the boards was obviously a mixture of a wide variety of different metals which would require further processing if they were to be recycled. Cui and Forssberg (2003) carried out a review of the mechanical recycling options for waste electrical and electronic equipment in which they discussed several options for the separation of small metal particles. The separation of metals after the oxidisation of the organic fraction of printed circuit boards has also been reported (Lee et al., 2005).

PYROLYSIS OIL

The oil resulting from the pyrolysis of each type of printed circuit board was characterised using GC-MS, GC-FID, and GC-ECD. Table 5 shows the quantification of the major components in the pyrolysis oils and the most important brominated and phosphated compounds in the oils and figure 6 shows an example of the GC-MS chromatograms. The identity of each of the components listed in table 5 was confirmed by comparing the retention time to standard compounds. As well as the compounds shown in table 5, a large number of other compounds were present which were mostly identified by the GC-MS as substituted phenols and substituted benzofurans.

The major components of the pyrolysis oils can all be attributed to the direct decomposition products of bisphenol A epoxy resin or epoxy novolac resin. The most significant product in all the oils was phenol, followed by 4-(1-methylethyl)phenol, which must originate from the splitting of the bisphenol A structure. 4-Methylphenol and 4-ethylphenol were also present in the pyrolysis oils, presumably from the further breakdown of 4-(1-methylethyl)phenol. The bisphenol A structure did not completely break down in any of the oils, which each contained some bisphenol A as well as p-hydroxydiphenyl. As well as bisphenol A decomposition products, the pyrolysis oils also contained 2-methylphenol, 2,6-dimethylphenol, and 2-ethylphenol, compounds which have been reported to be present during the pyrolysis of epoxy novolac (Bradna and Zima, 1991). Overall, we were able to quantify 42.1 % of the computer pyrolysis oil, 21.4 % of the television pyrolysis oil, and 60.7 % of the mobile phone pyrolysis oil.

As can be seen from table 5, the composition of each of the three pyrolysis oils was very different. The composition of each pyrolysis oil is probably determined by the type of organic resin used to construct the original circuit boards and the degree of curing applied to the resin. The degree of curing applied to epoxy resins has previously been shown to affect the pyrolysis products from epoxy resins (Balabanovich et al., 2004, Bradna and Zima, 1991). The metals present in each type of circuit board may have affected the organic pyrolysis products because Blazso et al (2002) have reported that basic metals alter the amount of bromophenols formed during the pyrolysis of brominated epoxy resin and various authors have reported on the effect of metals on the pyrolysis of polycarbonate of bisphenol A and epoxy resin (Blazso, 1999, Sivalingam and Madras, 2004).

Each of the three pyrolysis oils were analysed by GC-ECD to confirm the presence of 2,4-dibromophenol, 2,6-dibromophenol, and tetrabromobisphenol A (table 6) and the results are presented in table 5. As well as the three major brominated products several other brominated compounds were identified by the GC-MS and these are listed in table 7. Most of the compounds shown in table 7 were not identified by the GC-MS software but were identified by manual comparison of mass spectra presented in the literature. No standards could be used to confirm the presence in the oil of the compounds listed in table 7, but they are all compounds that have been reported in the literature to be decomposition products of tetrabromobisphenol A or brominated epoxy resin, with the exception of 2,6-dibromo-4-(1,1-dimethylethyl)phenol. The mass spectra for 2,6-dibromo-4-(1,1-dimethylethyl)phenol and its chemical structure are shown in figure 7. It would seem likely that 2,6-dibromo-4-(1,1-dimethylethyl)phenol is the sister product of 2,6-dibromophenol when tetrabromobisphenol A decomposes.

The brominated compounds in the pyrolysis oils are most likely due to the presence of brominated epoxy resin in the printed circuit boards. Brominated epoxy resin pyrolyses to form tetrabromobisphenol A, which is then involved in a competition between evaporation and pyrolysis (Barontini and Cozzani, 2006); the thermal decomposition of tetrabromobisphenol A is discussed in detail elsewhere (Barontini et al., 2004a, Barontini et al., 2004b, Marsanich et al., 2004). The printed circuit board pyrolysis oils all contained at least 0.1% 2,6-dibromophenol and at least 0.01% 2,4-dibromophenol as well as trace amounts of tetrabromobisphenol A (table 5).

The pyrolysis oils all contained a significant number of phosphated compounds, the most abundant of which is triphenyl phosphate. Triphenyl phosphate is itself used as a fire retardant additive (Danish EPA, 1999) but it is also the pyrolysis product of several other phosphated fire retardants including bisphenol A bis(diphenyl phosphate) (Balabanovich, 2004), triphenyl (diphenoxyphosphinyl)phosphorimidate (Fukushima et al., 1998), and tetraphenyl imidodiphosphate (Shimasaki et al., 1992). The highest concentrations of triphenyl phosphate occurred in the oil resulting from the pyrolysis of the television printed circuit boards with a significant concentration also being present in the computer boards pyrolysis oil (table 5). Very little triphenyl phosphate was identified in the mobile phone pyrolysis oil.

The oils resulting from the pyrolysis of the computer and mobile phone boards contained cresyl diphenylphosphate, a plasticizer which also has flame retardant properties (Lee, 1989) and is mainly used in PVC but which can also be used in other thermoplastics (Whelan, 1994). Unfortunately, we were only able to obtain a commercial grade of cresyl diphenylphosphate that also contained triphenyl phosphate and tri-cresyl phosphates, a problem previously encountered by Vainiotalo et al (1987). The impurities in the cresyl diphenylphosphate sample meant that it could not be used for quantification but only to confirm its presence in the pyrolysis oil by comparing retention times. However, by comparing the peak areas of the two cresyl diphenylphosphate isomers to the peak area of triphenyl phosphate it was possible to estimate that the computer and mobile phone printed circuit board pyrolysis oil contained 1.7% and 0.2% cresyl diphenyl phosphate respectively.

Two isomers of cresyl phosphate, which is used as a plasticizer and flame retardant in PVC and polystyrene, were also present in the computer printed circuit board pyrolysis oil in low concentrations (table 5). The presence of m-cresyl phosphate might be expected but the presence of the o-cresyl phosphate isomer is unexpected because it is usually removed from commercial products due to concerns about its toxicity (Danish EPA, 1999). As well as the phosphated compounds mentioned above, other triphenyl phosphate derivatives were identified by the GC-MS; however, the appropriate standards were not available so we were unable to confirm their identification. The presence of phosphated flame retardants, which are mainly used in thermoplastics, suggests that they might be present in the pyrolysis oil due to the pyrolysis of plastic-containing components that were attached to the printed circuit boards, rather than the pyrolysis of the circuit boards themselves.

As well as characterisation by gas chromatography, the types of functional groups present in each of the pyrolysis oils was determined by FT-IR analysis (figure 8). The spectra for all three of the oils contained a large peak around 3400 cm^{-1} that is associated with O-H stretches in either alcohols or phenols and the small peak at 3045 cm^{-1} can be associated with benzene ring C-H stretches, either in phenols or in other aromatic compounds. The three peaks between 2850 – 2970 cm^{-1} can be associated with methyl groups (2960, 2926, and 2858 cm^{-1}) and methylene groups (2930 and 2853 cm^{-1}). The peaks at 1500 and 1595 cm^{-1} can be associated with aromatic C=C stretches and the peaks between 650 and 900 cm^{-1} are associated with C-H out-of-plane deformation vibrations in benzene rings. The bands at 1365 and 1230 cm^{-1} are always present when phenols are being analysed, although they can associated with other functional groups. Analysis of the FT-IR spectra for the oils resulting from the batch pyrolysis of printed circuit boards would suggest that the major components are phenols with the presence of methyl and methylene groups suggesting that they may be substituted phenols. The FT-IR spectra corroborate the gas chromatography characterisation of the oils, which found that most of the oil consisted of phenols and substituted phenols.

Printed circuit boards pose a huge disposal problem because they consist of a heterogeneous mixture of organic and metallic chemicals as well as glass fibre. As we have shown in this paper, pyrolysis has the potential to recover a large number of valuable metals and chemicals. Before being treated by pyrolysis, it is practically impossible to safely separate the different fractions of waste printed circuit boards. However, the pyrolysis process not only produces an oil that contains valuable chemicals such as phenol and bisphenol A, but also produces a residue that can easily be separated into metals, glass fibre, and any remaining organic material. The pyrolysis process also produces organic gases which can be used as a fuel to provide the heat necessary for the pyrolysis of printed circuit boards. The pyrolysis oil also contains flame retardant chemicals such as tetrabromobisphenol A and triphenyl phosphate which could be recovered and reused. The use of pyrolysis to treat waste printed circuit boards has the potential to recover valuable resources rather than further diminishing virgin supplies.

CONCLUSIONS

Printed circuit boards from three waste fractions, computers, televisions, and mobile phones, were pyrolysed in a fixed bed reactor at 800°C. The computer printed circuit boards pyrolysed to form an average of 68.9 wt% residue, 22.7 wt% oil, and 4.7 wt% gas. Pyrolysis of the television circuit boards led to an average mass balance of 60.0% residue, 28.5% oil, and 6.5% gas and pyrolysis of the mobile phone circuit boards led to an average mass balance of 82.2 wt% residue, 15.2 wt% oil, and 2.3 wt% gas.

The pyrolysis gases consisted mainly of CO_2 and CO, but all of the C_1 – C_4 gases and some inorganic bromine were also present, inorganic chlorine was also present in the mobile phone pyrolysis gas. The pyrolysis oils contained high concentrations of phenol, 4-(1-methylethylphenol), and p-hydroxyphenol, which are all regarded as decomposition products of epoxy resins. The composition of the pyrolysis oils suggested that most of the printed circuit boards were constructed from bisphenol A epoxy resin and epoxy novolac. The pyrolysis oils also contained tetrabromobisphenol A (TBBPA) and a variety of recognised TBBPA pyrolysis products as well as a variety of tri-aryl phosphates that are commonly used in plastics as plasticizers and fire retardants.

The pyrolysis residue contained both organic and metallic fractions which were easily separated. Following pyrolysis, the electrical components and glass fibre could be easily removed from the remains of the printed circuit boards. The ashes consisted mainly of copper, calcium, iron, nickel, zinc, and aluminium as well as more valuable metals such as silver.

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Table 1 Global composition of each category of circuit board that was pyrolysed in the fixed bed reactor (wt%)

wt%	Computers	Televisions	Mobile phones
Metal + glass fibre	32.0	32.1	83.1
Organic	68.0	67.8	16.9
Moisture	0.0	0.1	0.0

Table 2 Mass balances when each type of printed circuit board was pyrolysed in the fixed bed reactor (wt%).

	Computers		Televisions		Mobile phones	
	Expt 1	Expt 2	Expt 1	Expt 2	Expt 1	Expt 2
Residue	67.0	70.7	59.6	60.4	82.8	81.6
Oil	24.4	21	29	27.9	14.7	15.7
Gas	5.2	4.2	6.5	6.4	2.1	2.4
TOTAL	96.6	95.8	95.1	94.7	99.7	99.6

Table 3 Mass composition of the pyrolysis gases produced by each printed circuit board type on a nitrogen free basis (wt%)

Component	Computers	Televisions	Mobile phones
H_2	4.6	3.2	5.7
CO	27	21.8	36.1
CO_2	51	51.5	45.8
Methane	10.3	14	6.4
Ethene	0.6	1.1	0.5
Ethane	1.9	2.7	0.6
Propene	2	1.1	2.7
Propane	1	1.6	0.4
Butene	0.8	1.8	1
Butane	0.5	1.2	0.2
Cl	0	0	0.1
Br	0.3	0.1	0.5

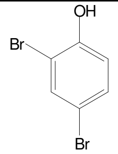
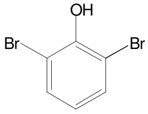
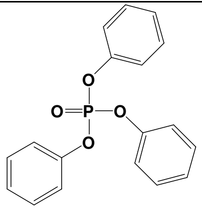
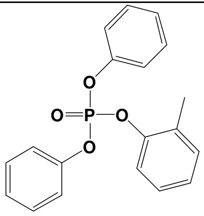
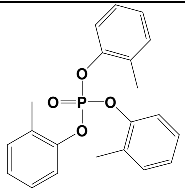
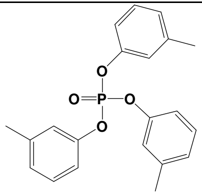
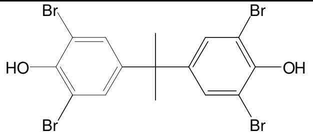
Table 4 An analysis of the metals present in the char produced by the pyrolysis of printed circuit boards at 800°C in a fixed bed reactor (mg/kg)

	Computers		Television		Mobile Phone	
	>600µm	<600µm	>600µm	<600µm	>600µm	<600µm
Li	6	13	<5.6	<5.6	13	15
Na	474	1,206	140	554	897	1,197
K	151	519	1,332	697	236	347
Mg	448	1,317	414	4,315	635	947
Ca	25,167	50,647	2,578	24,905	33,901	40,984
Sr	185	658	<5.6	20	334	372
Ba	618	8,050	41	285	10,739	6,786
Cr	42	268	118	787	1,792	139
Mn	372	177	674	592	654	569
Fe	69,729	11,355	159,671	31,461	15,089	5,366
Co	12	<5.6	93	56	64	39
Ni	10,660	1,331	24,388	1,863	13,454	6,870
Cu	242,986	167,105	260,404	185,190	333,228	323,163
Zn	13,139	700	14,695	10,149	1,011	960
Ga	45	27	94	29	210	184
Al	10,479	21,618	3,215	6,426	14,949	18,333
In	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6
Bi	301	77	75	68	<5.6	<5.6
Pb	128,242	21,466	76,900	91,577	1,405	2,495
Cd	8	<5.6	13	<5.6	<5.6	<5.6
Ag	6,458	800	15,020	1,164	8,118	4,125
Sb	<5.6	7	<5.6	12	44	8
Au	6	211	<5.6	<5.6	18	28
Hg	7	6	6	<5.6	12	7
Pd	<5.6	<5.6	<5.6	<5.6	<5.6	<5.6
Ti	19	70	65	90	1,508	708

Table 5 Quantification of the major products in the oil resulting from the pyrolysis of printed circuit boards at 800°C in a fixed bed reactor (%)

	Computers	Television	Mobile phone
Phenol	25.23	10.06	38.49
2-Methylphenol	1.04	1.60	1.07
4-Methylphenol	1.45	2.20	0.31
2,6-dimethylphenol	0.27	0.50	0.15
2-ethylphenol	0.22	0.20	0.24
4-ethylphenol	0.47	0.26	0.61
4-(1-Methylethyl)phenol	8.61	1.26	16.11
p-Hydroxydiphenyl	1.47	0.08	2.87
Bisphenol A	1.38	0.11	0.67
triphenyl phosphate	0.92	4.25	0.09
o-Cresyl phosphate	0.55	0.00	0.00
m-Cresyl phosphate	0.10	0.00	0.00
2,4-dibromophenol	0.03	0.35	0.01
2,6-dibromophenol	0.34	0.56	0.10
TBBPA	0.0006	0.0013	0.000

Table 6 Fire retardant additives and their pyrolysis products identified by GC-MS/FID/ECD in the oil of pyrolysed printed circuit boards

Retention time (mins)[a]	Name	Structure
33.7	2,4-dibromophenol	
34.4	2,6-dibromophenol	
55.1	Triphenyl phosphate	
56.4, 56.8	Cresyl diphenyl phosphate (2 isomers)	
58.1	o-cresyl phosphate	
58.8	m-cresyl phosphate	
	Tetrabromobisphenol A	

a: on the GC-MS system using a 30m DB-5 column

Table 7 Brominated compounds which were tentatively identified by GC-MS in the oil resulting from the pyrolysis of printed circuit board pyrolysis

Retention Time (mins) [a]	Name	Also reported by (Ref)
33.3	2-bromo-4-(1-methylethyl)phenol	(1-3)
35.0	2-bromo-4-(1-methylethenyl)phenol	(1,2)
45.0	bromo-p-hydroxybiphenyl	(1)
53.6	2,6-dibromo-4-(1,1-dimethylethyl) Phenol	-
53.8	Bromobisphenol A	(1-5)
55.8	dibromopbisphenol A	(1-5)

References;
(1) Balabanovich, et al., 2005,
(2) Blazso et al., 2002
(3) Barontini et al 2004a
(4) Marsanich et al., 2004
(5) Barontini et al., 2004b

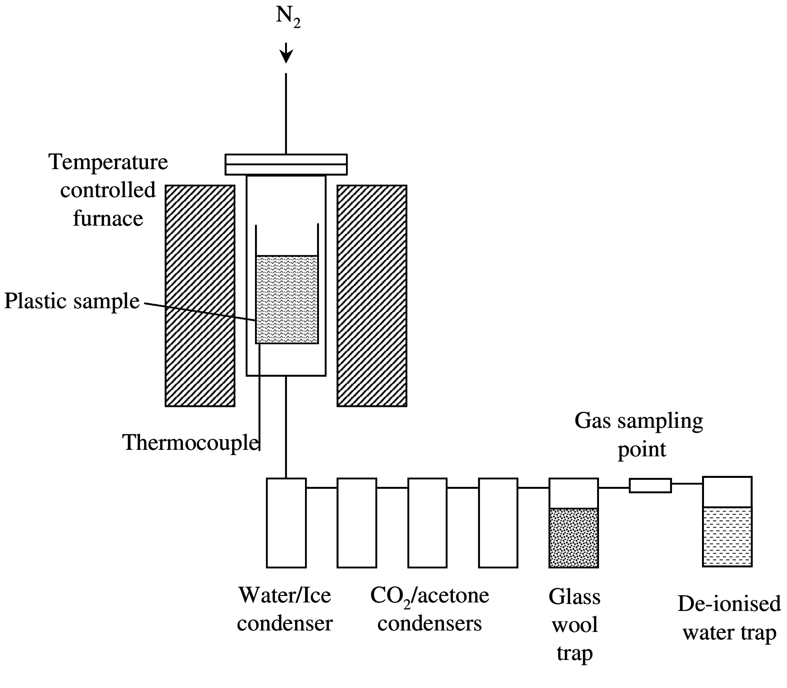


Fig. 1. Schematic diagram of the fixed bed reactor

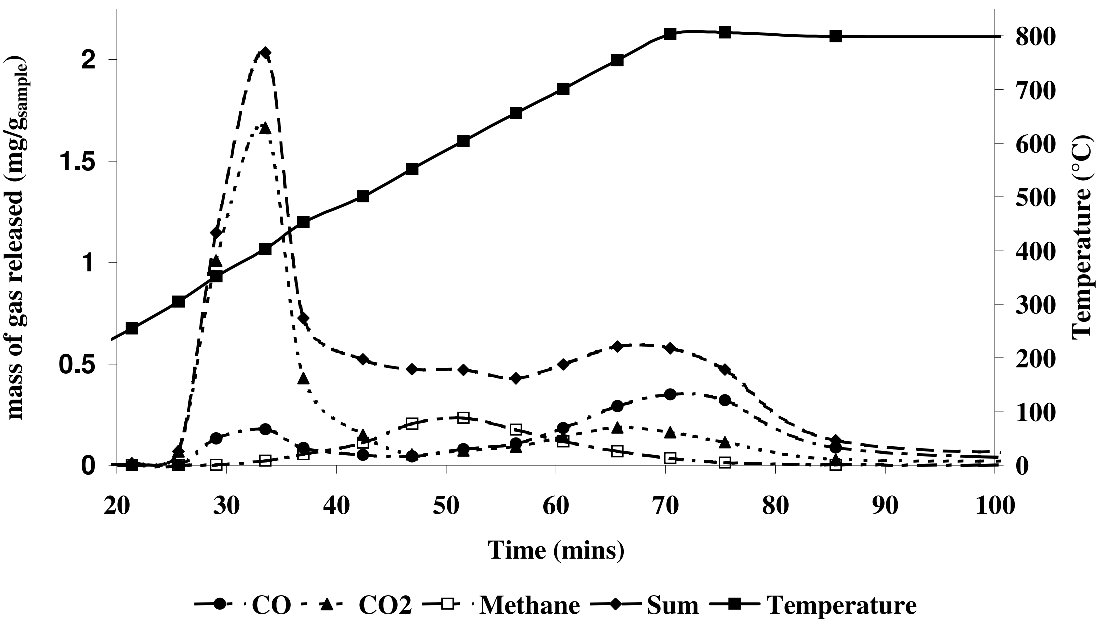


Fig. 2. Profile of the release of gases during the batch pyrolysis of computer printed circuit boards

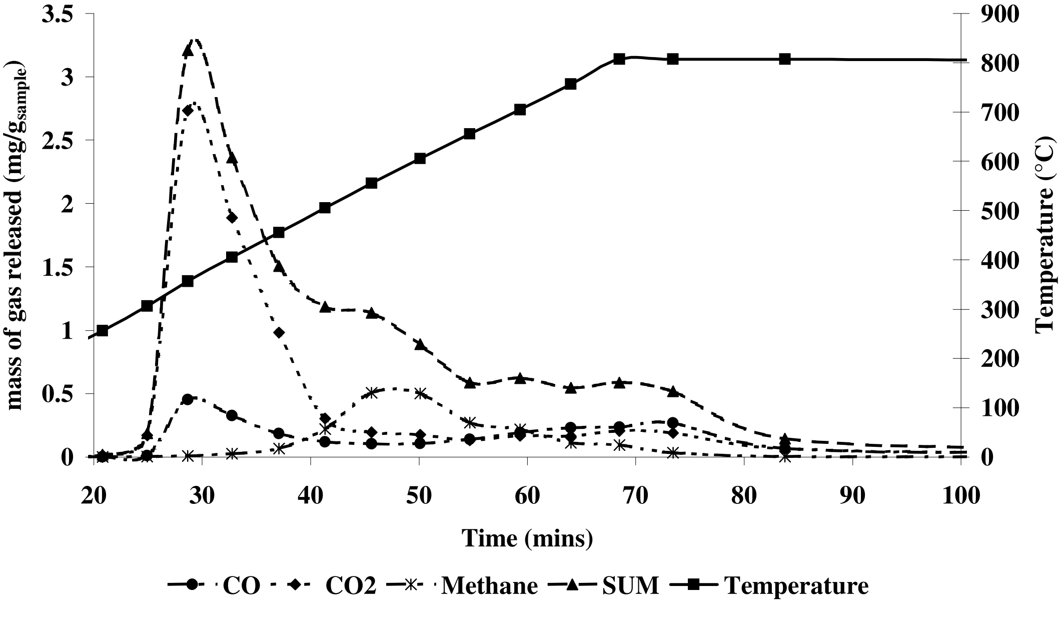


Fig. 3. Profile of the release of gases during the batch pyrolysis of television printed circuit boards

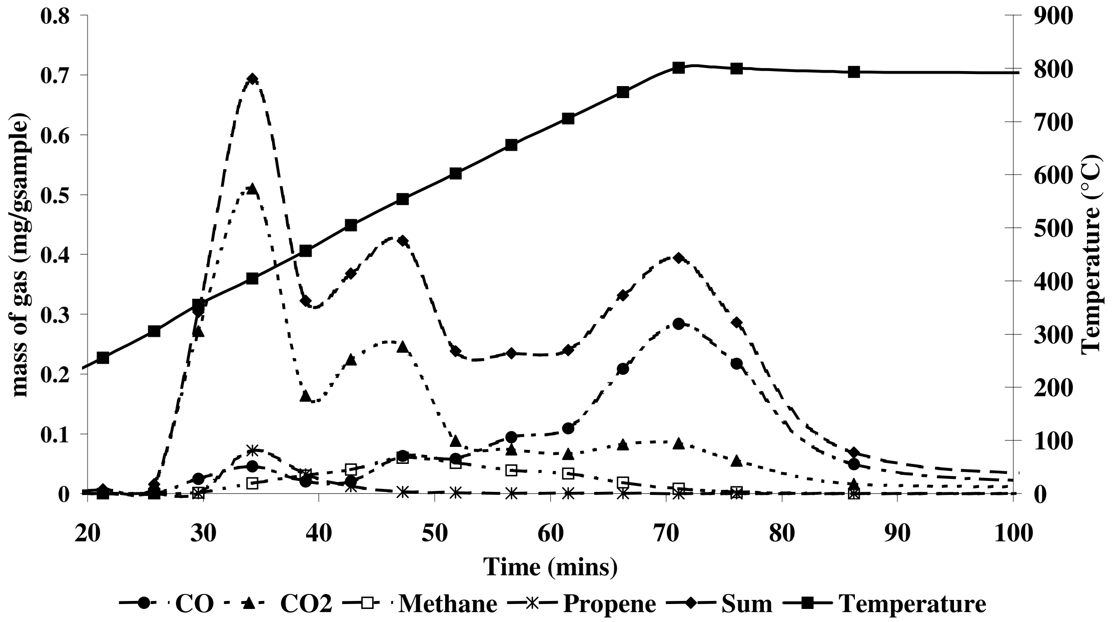


Fig. 4. Profile of the release of gases during the batch pyrolysis of mobile phone printed circuit boards

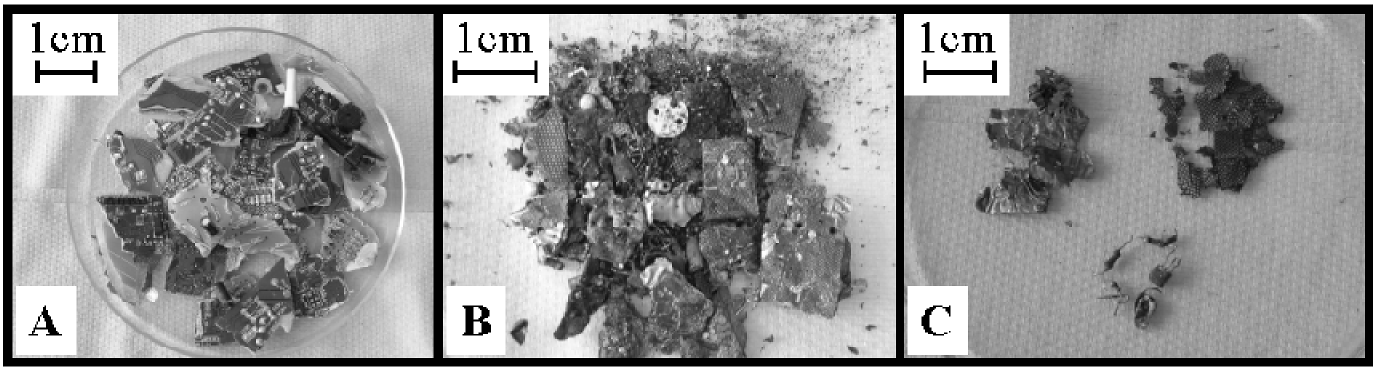


Fig. 5. Printed circuit boards before pyrolysis (A), after pyrolysis at 800°C in a fixed bed reactor (B), and after separation of the pyrolysed components (C).

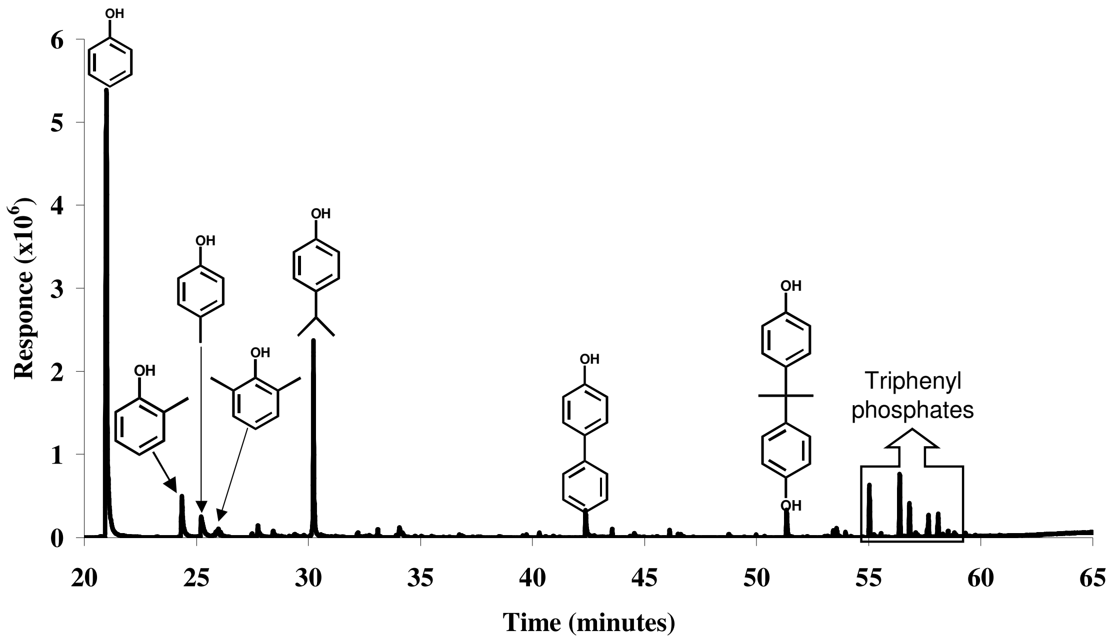


Fig. 6. An example GC-MS chromatogram of the oil resulting from the pyrolysis of printed circuit boards at 800°C in a fixed bed reactor

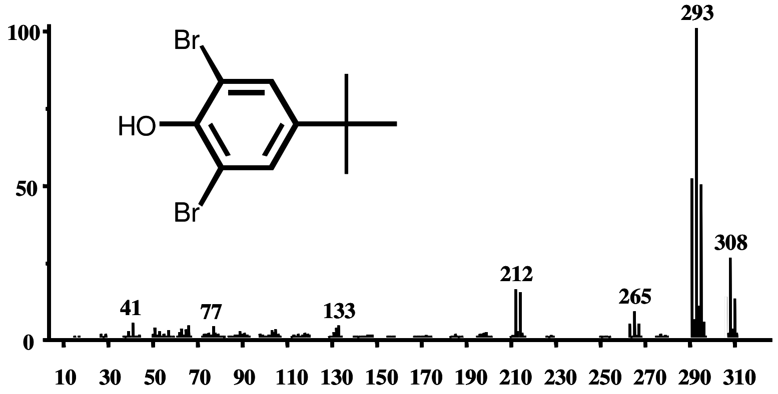


Fig. 7. Mass spectra of 2,6-dibromo-4-(1,1-dimethylethyl) Phenol

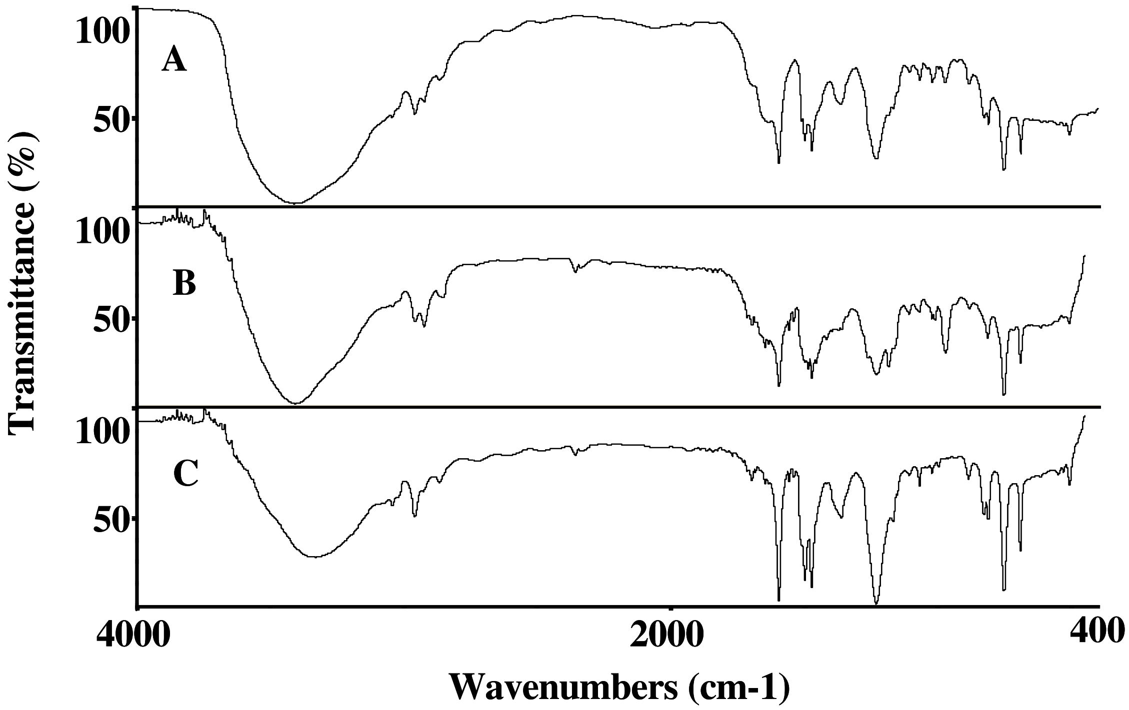


Fig. 8. FT-IR analysis of the oils produced by the pyrolysis of printed circuit boards from computers (A), televisions (B), and mobile phones (C) in a fixed bed reactor at 800°C