

## NAWTEC V

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**Electrical and Electronic Plastics Waste Co-Combustion  
with Municipal Solid Waste for Energy Recovery**

February 1997

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# Electrical and electronic plastics waste co-combustion

*with Municipal Solid Waste for energy recovery*

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A technical  
paper from:

**APME**  
ASSOCIATION OF PLASTICS

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Co-combustion tests of E+E plastics waste with municipal solid waste (MSW) in a MSW combustion pilot plant (TAMARA) at the Forschungszentrum Karlsruhe (FZK) in Germany have clearly shown that this recovery route is environmentally sound. These tests have demonstrated that medium to high amounts (3-12 wt %) of plastics waste from end of life E+E equipment can be safely added to today's municipal solid waste to generate useful energy. The major conclusions of this test programme can be summarised as follows:

- *The high heat value of added plastics waste has a very beneficial effect on the required inert character of the grate ash residue. Higher burnout is caused by a more intensive combustion*
- *Clean gas emissions recorded for the PCDD/Fs comfortably achieved the lowest regulatory limits as required by the German BImSch V 17th*
- *Controlled MSW combustion has again confirmed that it is an effective "dioxin sink" with a destruction efficiency of > 90%*
- *Installed European municipal solid waste combustor (MSWC) capacity will allow energy recovery of significant amounts of specified E+E plastics waste without affecting investigated operational limits*
- *Higher levels of halogens in the raw gas will not cause higher emissions, as today's wet, dry or semi dry control systems are well capable of handling such levels*
- *E+E waste fractions should be treated for efficient metal separation prior to combustion. Heavy metal amounts in the E+E plastics waste then conform to the range of typical municipal solid waste combusted today*
- *Higher amounts of halogens: E+E waste containing bromine (Br) and chlorine (Cl) did not increase the presence of dioxins and furans. Increased Br content will only shift the Br/Cl homologue ratio for PXDD/Fs and not cause any catalytic effect*
- *A detailed analytical characterisation of the plastics waste has shown that the major portion of heavy metals in E+E waste is not due to the plastics, but comes from a poor level of metal separation.*

### 1. INTRODUCTION

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The recovery or disposal of end-of-life electrical and electronic (E+E) equipment is receiving considerable attention from industry organisations such as APME in order to supply factual information which can be used in the development of a clear industry strategy(1,2,3). It is hoped that such information will persuade EU member states to define the best management practices for this waste stream.

One of the difficulties regarding the recovery or disposal of E+E waste is a lack of data regarding its behaviour when incinerated (4,5,6,7). This lack of data has led to unfounded conclusions by some parties that plastic wastes contain harmful halogenated species which are difficult to treat and remove, and when incinerated contribute to the emission of halogenated species and are responsible for the major portion of emissions.

APME has a comprehensive testing programme investigating the impact of plastics on municipal solid waste (MSW) incineration. APME's previous work has demonstrated the positive, beneficial effects of mixed waste plastics in the MSW energy recovery process as well as studying halogen behaviour during the combustion of packaging plastics waste and construction foam from the building industry. The current study was designed to evaluate the incineration of MSW containing typical levels of electrical and electronic (E+E) plastic waste, as well as MSW containing E+E waste in amounts up to 12%. Parameters investigated included characterisation of the base MSW feedstock, different E+E waste streams and the incineration parameters related to the base feedstock containing 3, 6 or 12% added-E+E waste. The incineration parameters included combustion efficiency, halogen content and emissions from heavy metal content and emissions from trace levels of halogenated organics. In addition, the types and quantities of plastic waste materials used in today's E+E equipment were simulated in order to approximate the composition of future waste streams.

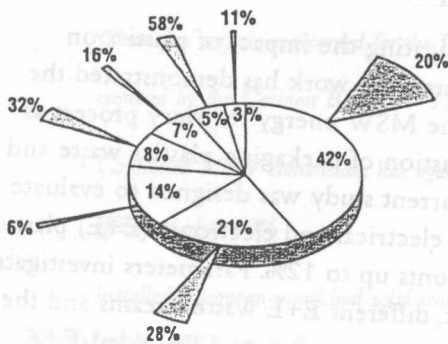
The materials investigated were representative samples from the major market sectors of consumer, commercial and industrial goods. They were of reasonable size (several hundred tonnes) and came from commercial operations in Germany, The Netherlands and Sweden. Today other countries do not have sufficient collection, dismantling and treatment capacities to provide large, representative samples.

**E+E MARKET  
INFORMATION:  
CONSUMPTION**

**2. E+E MARKET INFORMATION:  
CONSUMPTION**

Typical E+E market information is available from a SOFRES study commissioned by APME (8). Plastics consumption in 1992 for this sector was estimated at 1.15 million tonnes in Europe, representing 16 % of the total E+E equipment by weight. The following sector share and the weight% of plastics in each sector is given as:

Figure 1:  
TOTAL E+E SECTOR MARKET ANALYSIS Source: APME(8)



Sector	Sector share %	plastics wt %
Large appliances	42	20
Brown goods	21	28
Electrical equipment materials	14	6
Small domestic appliances	8	32
Data processing	7	16
Telecommunications	5	58
Office equipment	3	11

For a better understanding, the E+E waste sector can be sub-divided into consumer, industrial and commercial goods. Within the consumer sector, a further division is commonly made into brown or white goods. The white goods sector contains refrigerators, freezers, washing machines etc. which are not part of this study. These are usually collected in schemes separate from other consumer equipment. Shredder or recycling operators do not commonly mix white goods shredder residues with those of brown goods (TVs, videos and audio equipment). For an accurate comparison of ESR

(electrical shredder residue) compositions, a clear understanding of the source of the waste was needed.

The following examples are given to explain and illustrate the very different types of equipment which are considered:

Figure 2.  
EXAMPLES OF MAJOR E+E MARKET SECTORS

- |            |   |
|------------|---|
| Consumer   | (1) small appliances e.g. hairdryers, toasters, heaters, irons, toothbrushes      |
|            | (2) medium sized appliances e.g. VCRs, coffee & kitchen machines, vacuum cleaners |
|            | (3) larger size units e.g. PCs, TVs, Hi-fi equipment                              |
| Commercial | (4) electronics medium size parts e.g. PCs, fax machines                          |
| Industrial | (5) electrical switch gear equipment  |
|            | (6) electronic instrumentation and control systems.                               |

**3. ELECTRICAL + ELECTRONIC  
EQUIPMENT PLASTICS WASTE**

**3.1. E +E EQUIPMENT IN MSW**

At the present time very little E+E equipment waste is combusted in MSW combustors (MSWC).

The increasing European MSWC capacity (34 MMt in 1992) designed for energy recovery and efficient flue gas cleaning is sufficient to combust certain fractions of special E+E equipment waste streams. If it is assumed that 5-10 wt% of the MSW feed comprised suitable E+E equipment waste then all of today's E+E plastics waste could be handled by existing MSWC capacity. This demonstrates the potential importance of MSWC as a recovery route.

Efforts by APME to define the E+E content in MSW in Germany resulted in a figure of about 1 wt% within the residual MSW (equivalent to 140 kg/year per person).

The recycling of plastics, paper, glass and metals reduces the commonly accepted value of 300 kg MSW/person/year to a figure of 140 kg of which around 1 kg/person/year can be attributed to E+E waste (9). As older equipment is replaced and taken out of stock this figure is likely to increase.

### 3.2 SOURCE SEPARATED E+E MATERIALS

Electronic and electrical equipment is sometimes collected by local authorities, but the information on E+E waste categories is rather scarce. Similarly the number of pilot projects to collect E+E waste in Europe is also limited (10, 11). Very little is known about the polymer composition in different types of equipment. Nevertheless the total amount of source separated E+E equipment is growing rapidly although as yet the waste amounts are still unclear. For these trials, it was therefore necessary to get E+E waste for TAMARA, the MSW combustion pilot plant of the FZK in Karlsruhe, from larger scale commercial operations. A very detailed identification and classification of the different E+E articles has been made for countries like Germany by the Zentralverband Elektrotechnik-und Elektronikindustrie e.V. (ZVEI) (12) and France by the Fédération des Industries Electriques et Electroniques (FIEE) (13), with reports on material stream identification by article from Institut für Umwelttechnologie und Umweltanalytik e.V. (IUTA) (14) and the company Schleswig (15).

Three medium sized suppliers of E+E plastics waste streams in Germany were asked to provide pretreated E&E waste. The pretreatment was not done specially for TAMARA, but was typical of commercial operations by the following companies:

IUTA	Consumer waste
(EGR) Elektro-Geräte Recycling GmbH	Commercial/small industrial waste
SCHLESWAG	Industrial (low, medium, high voltage) waste

## 4. E + E POLYMERIC MATERIALS USED FOR THE CO-COMBUSTION TESTS

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### 4.1. WASTE MATERIALS FROM DIFFERENT MARKET SECTORS

#### IUTA: CONSUMER

The Institute for Environment Technology and Environmental Analysis (IUTA) has dismantled 1400 items of E+E equipment from the cities of Essen (20%) and Duisburg (80%) in Germany. All equipment was dismantled manually to get a better overview of the material streams. 15 % (210 t) of the input was plastics. Two thirds of these 210 tonnes were unidentified composites or polymer blends. From this unidentified amount of 140 tonnes, samples were taken according to the German specification guideline for shredder residue Länderarbeitsgemeinschaft (LAGA) specification PN 2/78.

The sampling was done over a period of two years in 1993/94 and resulted in 12 tonnes of E+E plastic waste. A 1000 kg sample for the TAMARA tests was collected from the 12 tonnes according to the same German guideline LAGA specification PN 2/78.

#### EGR: COMMERCIAL

The Electrical Equipment Recycling Company (EGR) collects E+E equipment from the Rhein-Ruhr area in Germany. EGR has an annual capacity of 2500 tonnes for E+E equipment waste treatment. Most of the industrial and commercial equipment is dismantled manually. From an amount of 144 tonnes which included TVs, audio equipment, radios, vacuum cleaners, and PCs (including housings, screens, printers and photocopiers), 15 % were plastics. A certain portion is suitable for mechanical recycling, and the remainder has to be disposed of by alternative means. Representative amounts of 100 tonnes E+E equipment were collected during 1992 and treated similarly to the shredder residue from IUTA. From the recovered 10 tonnes of plastics, 1 tonne was blended and shipped to TAMARA.

**E + E POLYMERIC MATERIALS USED FOR THE CO-COMBUSTION TESTS**

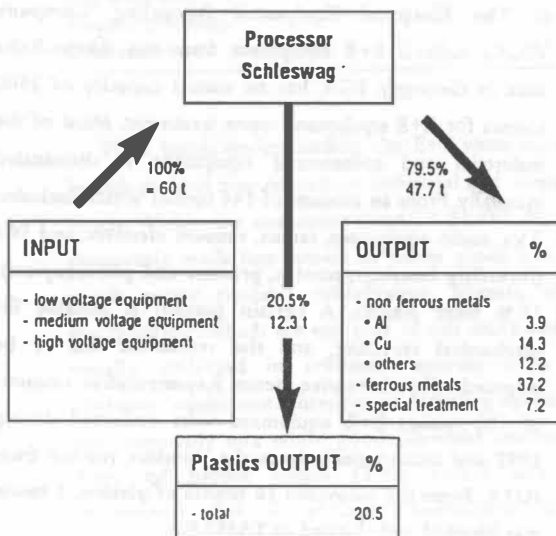
**SCHLESWAG: INDUSTRIAL**

The third source came from the company Schleswag Recycling GmbH in Brunsbüttel in the north of Germany. This operation consists of two stages. The first is dismantling and separation into the following fractions: metal housing, printed circuit boards, cables, plastic housing and screens. The second operation consists of a conventional shredding and separation phase with the following fractions being produced: iron, aluminum, plastics, thermoset plastics with fibres and metal granulate. Members of ZVEI supplied 60 tonnes of old E+E equipment resulting in 3.9 tonnes of materials to be specially treated, 26.7 tonnes of valuable metals and 29.7 tonnes (50 %) of a mixture which can only be thermally treated. The first coarse shredded fraction comprises about 25 wt% of plastics. This coarse material was shredded a second time on one of the four mechanical separation lines resulting in a fines fraction. This was the material evaluated at TAMARA.

This fraction of fines still contains high amounts of inert substances (>35 % wt) with very small metal parts barely observable to the naked eye. This amount of fillers and

**Figure 3**  
**E+E INDUSTRIAL EQUIPMENT PROCESSING**

**E+E INDUSTRIAL GOODS PROCESSING AT SCHLESWAG**  
Material composition and amount for trials



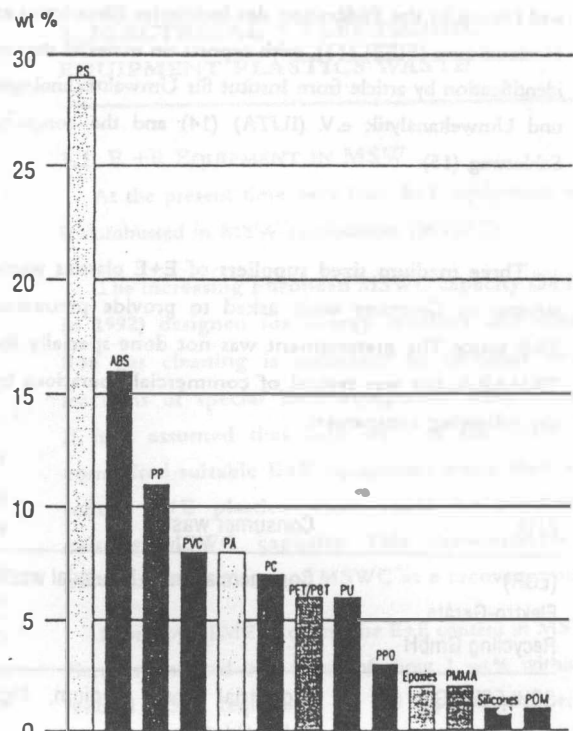
fibers is significant, contributing to high amounts of ash. The total mass balance data is very well described in (15).

**4.2. PLASTIC MATERIALS FROM TODAY'S E+E EQUIPMENT**

A simulation of the types and quantities of plastics materials used in current E&E equipment was made to approximate the composition of future waste streams arising from the disposal of such equipment. The composition of an average E&E polymer mixture in Europe supplied by APME members was simulated by blending together materials typical of those sold in the market today. The materials can be separated into two categories by burning characteristics, horizontal burning or flame retarded. The ratio between these two classes is 66 % to 34 % respectively.

The overall composition assumed for today's European market agrees very closely with the SOFRES report (8) and is given as follows:

**Figure 4:**  
**POLYMER COMPOSITION FOR TODAY'S E+E EQUIPMENT.**





The products requested from the APME member companies should be typical of normal commercial grades with respect to composition. 3 tonnes of these materials were blended at an outside commercial facility and then shipped to TAMARA.

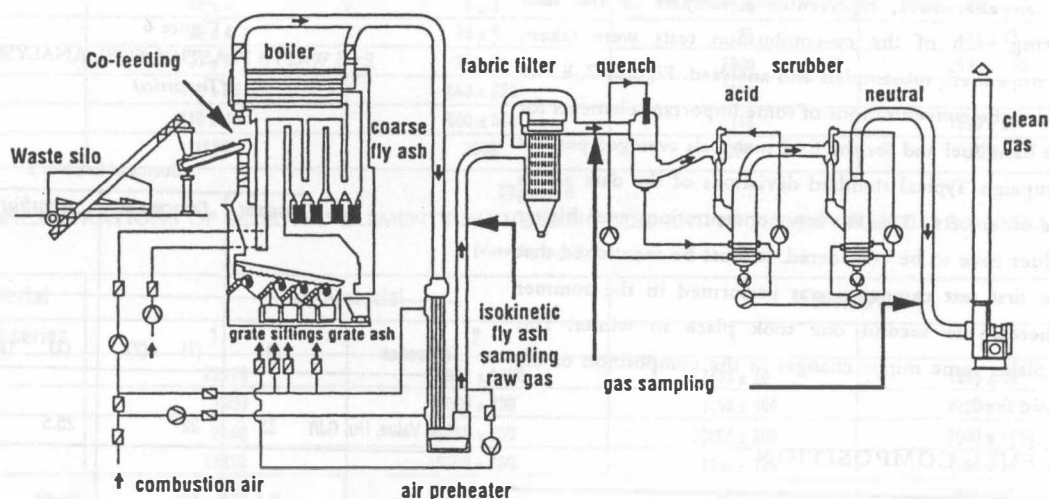
#### 4.3. E+E MATERIALS PRETREATMENT

Thermal recovery of large E+E type equipment involves a thorough pretreatment process. The operational steps may vary from company to company although most use the following sequence: dismantling

#### 5. TEST INCINERATOR TAMARA

The Karlsruhe test incinerator TAMARA is a mass burner with a nominal throughput of 250 kg/h of preconditioned waste (16). The pilot plant has been described in detail in an earlier APME TEC report (17). A schematic drawing of this incinerator is given in Fig. 5. The design of the combustion chamber can be changed from the original counter current into one of parallel flow geometry by the installation of variable roof elements. The first test trials were conducted using the

Figure 5  
SCHEMATIC DRAWING OF THE KARLSRUHE TEST INCINERATOR TAMARA FOR MUNICIPAL SOLID WASTE



to remove hazardous compounds or parts, coarse shredding, ferrous and non-ferrous metal removal, followed by a second size reduction and air separation. For the TAMARA experiments shredding is necessary to get sufficiently homogenized good quality fuel but also to obtain sufficiently small pieces to be able to feed into the chute of the furnace.

All E+E streams tested went through some type of shredder. Hazardous components such as mercury and PCBs were removed after dismantling.

parallel flow design whereas during the second campaign only two roof elements were installed forming a middle flow configuration. In the first case the residence time of acid gases and alkaline fly ashes is extended and as a consequence the fly ashes will contain higher amounts of e.g. chlorides or bromides.

Dust removal is performed by means of a fabric filter consisting of PTFE fabric tubes coated with a GORETEX® membrane. This filter is operated at a temperature of approx. 200°C. For flue gas cleaning a two-stage wet scrubbing system is installed.

The impact of the E+E waste plastic materials on the scrubbing system is not covered here but in the original

## FUEL COMPOSITION

FZK report or in (17). The majority of measurements have been done on the raw gas to understand the effect of E+E plastics waste on the combustion process. It is widely known that clean gas concentrations do not relate to the combustion conditions. They show the effect of the emission reduction system.

The basic fuel burnt in TAMARA is a shredded and sieved household waste which is enriched by 25 % of a pelletised RDF (Refuse Derived Fuel). The mean Cl and heavy metal content is slightly lower than that of typical Central European household waste.

The E+E materials were rather inhomogeneous, except the new E+E materials, and a thorough mixing in Karlsruhe of the large amounts proved to be impossible. As an alternative, representative samples of the feed during each of the co-combustion tests were taken, homogenised, subsampled and analysed. Figures 7, 8 and 9 give the concentrations of some important elements for the basic fuel and for the E+E materials averaged per test campaign. Typical standard deviations of the data are in the order of  $\pm 10\%$ . For low concentrations even higher values have to be considered. It must be mentioned that the first test campaign was performed in the summer whereas the second one took place in winter. This explains some minor changes in the composition of the basic feed.

## 6. FUEL COMPOSITION

### 6.1. STANDARD FUEL ANALYSIS

For reference comparative reasons, analysis of the various E+E plastic waste was carried out by both FZK and GfA, Gesellschaft für Arbeitsplatz - und Umweltanalytik mbH (Munster). Some key items of standard fuel characterisation: heat value, ash, etc. are shown in Figure 6. A more detailed fuel analysis overview is shown in Figures 7 and 8. Aspects more important for E+E plastics waste, such as the analysis for metals and for dioxin and furan content, are covered later.

Special importance was given to the elemental analysis of bromine and chlorine contents. Bromine analysis was performed by four different parties all

experienced in this field. The ratio of antimony to bromine is a very good indicator of the accuracy of bromine content analysis.

The range of bromine content covered was quite large, from a very low level of around 0.4 wt% up to 4 wt%. The consumer type equipment had a low level of about 0.4 wt%. The commercial material could be assumed to be more representative for the commercial/industrial E+E plastics as there is more flame retardant product used. The ratio of bromine to antimony on a weight for weight basis ranged from about 2 to 7. This is in line with the experience of formulating flame retardant products by addition of bromine plus antimony to gain beneficial synergistic effects.

Figure 6  
E+E WASTE PLASTICS FUEL ANALYSIS  
(Test series)

	Source of E+E waste					
	Consumer		Commercial		Industrial	
Test series	(1)	(1)	(2)	(1)	(2)	
Heat Value, Hu, GJ/t	35	32		25.5		35
Ash, wt%	3-5	3-5		35-40		6.5
Bromine, wt%	0.4	4.1	1.5	1.3	0.6	0.9
Chlorine, wt%	0.4	2.3	1.1	0.7	0.2	3.5
Antimony, wt%	0.2	1.3	0.2	0.35	0.2	0.3

A comparative fuel analysis is shown in the following table where all elements in the E+E plastics waste are compared to the basic fuel of the TAMARA runs. The results of the analysis are from FZK and may differ slightly from earlier data measured by GfA.

Figure 7  
CONCENTRATIONS OF SELECTED ELEMENTS IN THE BASIC FEED AND IN THE DIFFERENT E+E MATERIALS  
(data in mg/kg)

material	basic fuel	basic fuel	consumer	Today's polymer market mix
test series	1	2	1	2
Cl	5800 ± 230	6150 ± 300	3895	38550 ± 2000
K	9500 ± 500	7100 ± 800	1050	2150 ± 400
Ca	34000 ± 2500	32000 ± 5000	1200	7000 ± 1500
Ti	1120 ± 140	1420 ± 240	1730	4550 ± 620
V	46 ± 18	47 ± 12	36	900 ± 15
Cr	109 ± 12	150 ± 30	63	53 ± 8
Fe	5800 ± 900	6400 ± 650	1700	287 ± 36
Ni	69 ± 13	56 ± 13	88	30 ± 1
Cu	109 ± 22	112 ± 36	1900	137 ± 55
Zn	470 ± 30	430 ± 70	620	292 ± 18
As	17 ± 4	25 ± 11	9	47 ± 2
Br	62 ± 13	34 ± 10	4290	8600 ± 1000
Rb	22 ± 3	17 ± 2	30	20 ± 3
Sr	130 ± 19	108 ± 17	18	79 ± 17
Mo	7 ± 2	7 ± 1	2	4 ± 1
Cd	10 ± 3	9 ± 3	240	41 ± 6
Sn	26 ± 4	24 ± 5	85	18 ± 15
Sb	31 ± 8	26 ± 4	2000	2630 ± 110
Ba	410 ± 75	660 ± 320	250	-
Pb	410 ± 40	600 ± 350	146	1890 ± 50
P	1880	2080	250	1200

Figure 8  
CONCENTRATIONS OF SELECTED ELEMENTS IN THE BASIC FEED AND IN THE DIFFERENT E+E MATERIALS  
(data in mg/kg)

material	commercial		industrial	
	1	2	1	2
Cl	22970	10990 ± 1400	7435 ± 10	1865 ± 30
K	1500	3080 ± 230	1350 ± 100	2700 ± 170
Ca	2500	2550 ± 750	50000 ± 300	73900 ± 1100
Ti	18350	15200 ± 300	3350 ± 120	1500 ± 180
V	155	880 ± 30	149 ± 11	900 ± 15
Cr	164	250 ± 25	384 ± 1	140 ± 50
Fe	950	440 ± 120	3250 ± 300	2830 ± 260
Ni	780	550 ± 90	170 ± 50	200 ± 40
Cu	1140	82 ± 32	105000 ± 5000	77500 ± 6500
Zn	3350	1540 ± 320	5100 ± 800	4720 ± 70
As	38	29 ± 3	46 ± 1	45 ± 1
Br	41100	15000 ± 900	12550 ± 250	5750 ± 300
Rb	51	55 ± 30	21 ± 7	51 ± 9
Sr	36	22 ± 5	215 ± 8	222 ± 23
Mo	36	13 ± 4	35 ± 4	15 ± 8
Cd	124	123 ± 44	94 ± 7	29 ± 4
Sn	880	63 ± 39	2130 ± 10	1230 ± 230
Sb	13200	1950 ± 430	3500 ± 400	2200 ± 300
Ba	590	n.m.*	580 ± 15	571 ± 13
Pb	152	96 ± 19	2050 ± 320	1890 ± 50
		n.m.*	n.m.*	8150

**FUEL  
COMPOSITION**

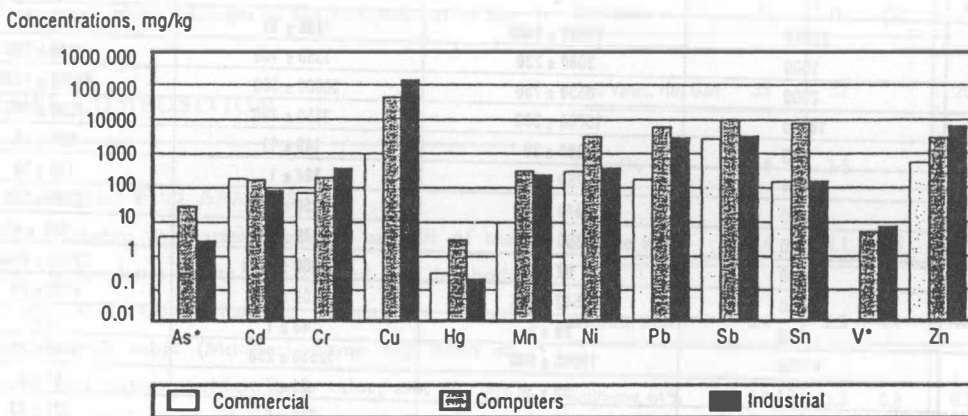
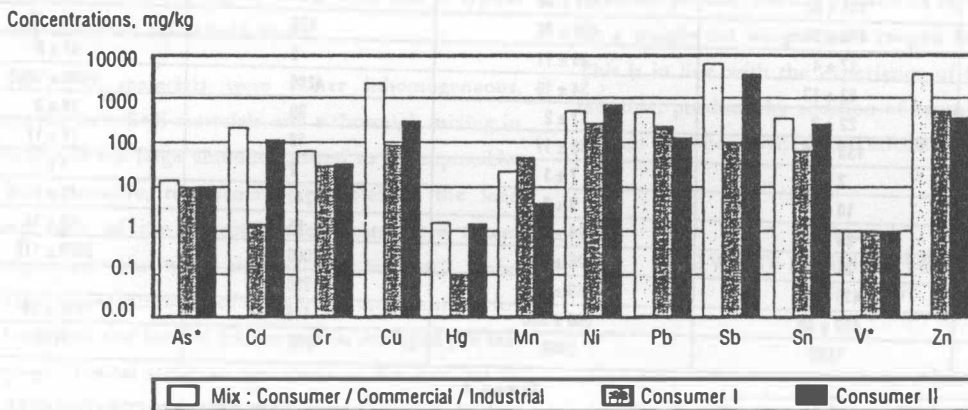
**6.2 METAL ANALYSIS OF USED PLASTICS FROM  
VARIOUS E+E SECTORS**

The broad range of metals of E+E plastics waste can be seen in Figure 9. The range is rather wide and could vary by more than several orders of magnitude.

materials (ferrous and non-ferrous metals, glass, polymer > 2 mm and rest < 2 mm) were removed. This prepreparation step made sure that residual metal content related only to the polymer. Analytical techniques have been described in earlier APME reports (18).

**Figure 9  
COMPARISON OF E+E WASTE METAL CONTENT**

\*Detection limits : As = 10 mg/kg, V = 1mg/kg



All samples were analysed for metal content by the same laboratory using the same test procedure. Prior to the polymer milling and grinding to reach a sufficiently small particle size for elemental analysis, the different

The samples representative for the computer sector came from Sweden, and represent today's personal computer (PC) market quality for all 4 equipment units: monitors, processing units, printers and keyboards.

The average data are representative of a broad market mix. The second sample from the consumer sector is representative of a small section of the market, mainly TVs and audio-visual equipment. Prior to analysis, the elemental metallic parts were removed as far as possible by hand. Differences in results between the two laboratories for elements primarily found in the polymer were acceptable. Larger differences are seen for e.g. copper, which is influenced mainly by separation of the metal. The high level of metallic content originates from wire.

The type and quality of pretreatment of the E+E plastics waste have a major influence on the amounts of metals left in the polymer/metal mixture. Low levels of elemental metals are achieved by a well run magnetic or eddy current separation. High levels of metal content are the result of a poor physical separation. Earlier results in the literature (1) claiming very high contents of metals in the polymer phase may have resulted from poor separation techniques to remove ferrous and non-ferrous metals.

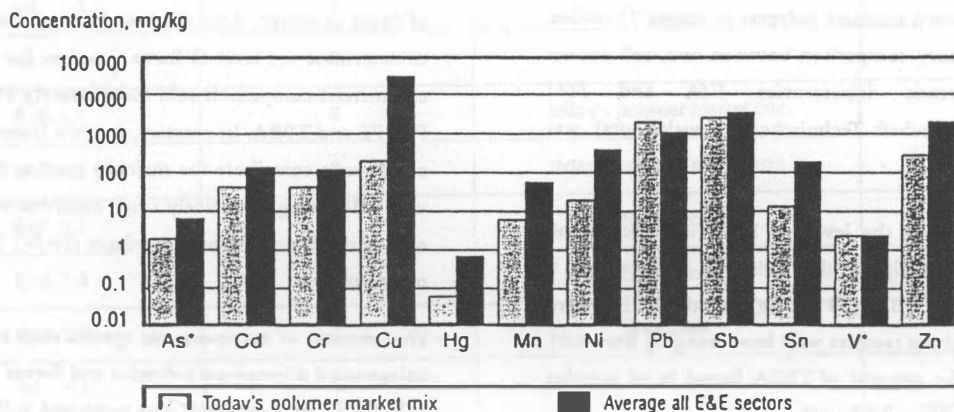
### 6.3. PLASTIC MATERIALS FROM TODAY'S E+E EQUIPMENT

The plastics studied above were from current E+E waste, i.e. from 'old' E+E equipment. They do not

represent the materials used in E+E equipment being sold today. There have been many changes in materials, colorants and additives, and it is important to understand the composition of today's materials, which will make up the E+E waste of the future.

The new plastic materials were sampled and analysed in a similar way to the previous samples from commercial operations. It is interesting to compare the new and older materials from the point of view of levels of metallic elements, as well as the numbers and types of metal found. The total amount of heavy metals was significantly less with a maximum of 0.4 wt%. There were only two major metal elements, lead and antimony, found in today's plastic materials mix; with roughly equal concentration levels of 0.2 wt%. Other heavy metals such as arsenic, cadmium, cobalt, mercury, nickel, titanium, vanadium and tin are at very low concentrations compared to the levels previously found in the commercial waste samples. It is reasonable to conclude that recovered plastics in the future will not be the source of high levels of metals. The fact that these metal elements are found in the commercial samples was due to incomplete recovery during the metal separation processes.

Figure 10  
METALS COMPOSITION COMPARISON OF OLDER VS. CURRENT POLYMERIC MATERIALS



#### 6.4. FLAME RETARDANT ANALYSIS

The range of different flame retardant materials in today's E+E market sector is quite broad and cannot be covered here. Major elemental components like aluminum (Al), bromine (Br), chlorine (Cl), magnesium (Mg) and phosphorous (P) have been looked at in more detail. Each flame retardant class gives rise to specific questions in the context of combustion. The more volatile elements were examined with respect to air and water emissions, whereas the less volatile elements should be judged on their behavior in the solid residue (grate ash). Results from leaching tests are still not subject of a common regulatory understanding (19) and have therefore been omitted.

In order to judge the destruction efficiency of the TAMARA facility, the levels of brominated flame retardant compounds in the polymer matrix were determined in a similar way to the levels of brominated dioxins and furans. It is important that waste management routes for E+E equipment should particularly address this aspect of complete destruction of all organo-halogen compounds.

Chemical analysis of the flame retardant content of mixtures of E+E waste polymers is not standardised today by any European or national standardisation body.

Analysis of typical flame retardant compounds such as polybrominated diphenylethers (PBDPEs), tetra-bromo-bisphenol A (TBBA) and polybrominated biphenyls (PBBs) has been accurately demonstrated only in single polymers or known constant polymer mixtures. Therefore an inter-laboratory comparison between two well known certified German laboratories GfA and ITU (Ingenieurgesellschaft Technischer Umweltschutz) was initiated.

In most samples the levels of PBBs were below the detection limit. Only in the industrial sample was a significant level of PBBs (50 mg/kg) found. PBDPEs were detected in all three samples with levels ranging from 0.01 to 2.0 wt%. The amount of TBBA found in all samples ranged from 0.01 to 0.60 wt%.

The accuracy of these results is satisfactory considering the fact that both laboratories had different methods of sample pretreatment, e.g. solvent extraction techniques. Calibration was done with solutions of available native congeners of the compound classes to be analysed.

Comparing the validated bromine content from four laboratories with the bromine content of the three flame retardant compounds, the following conclusions can be drawn: in addition to PBB, PBDPE and TBBA, all polymer samples contained significant levels of other brominated flame retardant compounds in the polymer matrix and the levels of the three flame retardants which could be identified ranged from 5% to 50% in the various samples.

#### 6.5. CONCLUSIONS

A detailed analytical characterisation of the plastics waste has shown that :

- Analysis of halogen levels found that the level of bromine ranged from as low as 0.4 wt % for the consumer sector, to as high as 4 % by weight for industrial high voltage applications. Ratios of Br to antimony (Sb) were between 2 and 7, which is in agreement with typical industry formulations for flame retardancy. The chlorine level ranged very widely from as low as 0,2 % to several % by weight
- The bromine level is directly linked to the amount of flame retardant. Analytical work was carried out to determine the level of flame retardant for three commercial compounds sold today namely, PBB, PBDPE and TBBA. In practice, the two latter compounds contribute the majority market share, with PBB being a relatively small contributor and other Brominated Flame Retardants (Fr-Br) from older products
- The amounts of micro-organic species such as halogenated dibenzo-para-dioxins and furans (PXDD/F) were analysed, and compared with the

limits of the German ordinances. Although the range of levels found was quite large, the average content value met the German regulations

- These levels of halogenated dioxins and furans in existing (old) end of life E+E equipment suggests that mechanical recycling of plastics waste as an option for these articles should be considered carefully. In such cases, combustion or chemical treatment of these older articles which ensures total and safe destruction of dioxins and furans are proven options.

## 7. TEST PROGRAMME

The TAMARA test programme lasted about two weeks. Two test runs were conducted per day, each lasting four hours. On the first and on the last day of each week, two reference tests were performed which burnt only the basic fuel. The test programme is detailed in Figure 11. During the first week of tests, the combustion chamber was in a parallel flow geometry and in the second week, a middle flow system was installed. The combustion temperature was kept at approx. 900°C in the first and approx. 930°C in the second week.

Figure 11  
E+E MATERIAL ADDITIONS DURING THE TEST PROGRAMME

code	test series	E+E material	addition in wt%
ref. 1.1	1	-	0
ref. 1.2	1	-	0
E+E.1.1	1	consumer	3
E+E.2.1	1	commercial	3
E+E.3.1	1	industrial	3
E+E.3.2	1	industrial	6
ref. 2.1	1	-	0
ref. 2.2	1	-	0
ref. 3.1	2	-	0
ref. 3.2	2	-	0
E+E.4.1	2	today's polymer market mix	6
E+E.4.2	2	today's polymer market mix	12
E+E.2.2	2	commercial	6
E+E.2.3	2	commercial	12
E+E.3.3	2	industrial	12
ref. 4.1	2	-	0

## 8. SAMPLING AND ANALYSIS

During all test trials, the raw gas was permanently monitored for the concentrations of O<sub>2</sub>, CO<sub>2</sub>, CO, HCl, SO<sub>2</sub>, NO, H<sub>2</sub>O, and NH<sub>3</sub>. Isokinetic gas sampling was performed by FZK in the raw gas upstream of the fabric filter. The fly ashes sampled here were used for all sorts of analyses. All other solid streams, the input as well as the residue streams were sampled taking care to obtain representative sampling, subsampling and sample pretreatment by following the recommendations of the International Ash Working Group (19).

Close to the position of the FZK isokinetic sampling train, the German certified analytical laboratory GfA had installed their own isokinetic probe for sampling of halogenated dibenzo-p-dioxins and dibenzofurans.

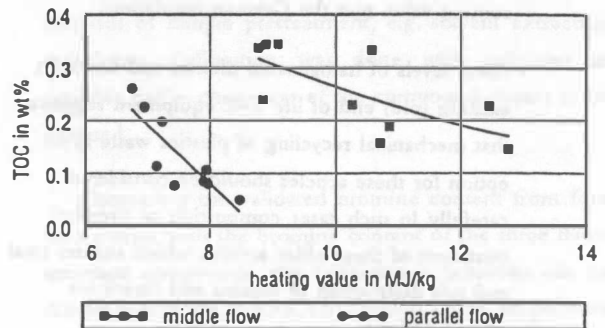
FZK conducted most of the inorganic analysis by applying total digestion to all solid samples for metal analysis. The organic samples were digested by pyrolysis followed by combustion in pure oxygen. For metal analysis, Total Reflecting X-Ray Fluorescence Analysis (TXRF) was used. Anions were analysed by means of ion chromatography. In addition, selected samples were analysed for special elements by GfA, IUTA, and other industry laboratories for comparison. In all cases different digestion and analysis methods were applied.

The clean up and the analysis of halogenated organic compounds was done by GfA following their own protocols (20). PCDD/F were analysed for comparative purposes by FZK.

## 9. COMBUSTION CONDITIONS

The combustion quality was not negatively influenced by the addition of the E+E plastic materials. As already experienced from the co-combustion of mixed post-consumer plastics waste (21), the increased heating value of the plastics improved the burnout in all residue streams. As can be seen in Fig. 12, these experiments revealed a significant reduction in the TOC of the bottom ashes. This effect is more pronounced in the parallel flow geometry of the combustion chamber due to the higher temperature at the back end of the grate.

Figure 12  
TOC IN THE BOTTOM ASHES VS.  
HEATING VALUE OF THE FEED



The burnout in the raw gas was extremely low during all test runs (CO < 5 mg/m<sup>3</sup> and TOC in the fly ashes < 700 ppm). A major difference could not be detected between the two configurations.

### 9.1. RESIDUES

An efficient metal separation prior to combustion in a MSWC plant is strongly recommended. If metal separation prior to combustion is inadequate, a substantial amount of metallic species such as Cu and Pb can be found in the grate siftings and to a minor extent in the bottom ashes. These metals are not totally oxidized inside the combustion chamber. They tend to melt down and seep through between the grate bars. This behavior may endanger the operational function of the grate. On the other hand metallic species deteriorate the bottom ash quality. Hence an efficient metal separation prior to combustion in a MSWC plant is strongly recommended. In one preliminary test run, not included in this report, a deterioration of the grate ash characteristics for a high metal content in the feed could be confirmed.

## 10. THE ROLE OF VOLATILE ELEMENTS IN MSW COMBUSTION

### 10.1. HALOGENS IN MUNICIPAL SOLID WASTE

In previous investigations (21) at TAMARA with packaging plastics and construction foam from the building industry, halogen (Cl, Br, F) behavior has been documented.

The levels of Br investigated here extend the experience to even higher Br concentrations.



The level of bromine in municipal solid waste and the chemical form in which it is introduced into the MSW is not well understood. Only very few investigations (22,23) concerning MSW composition have concentrated on this aspect. Older estimates in the literature range from 6 to 90 mg Br/kg MSW. The TAMARA feed has averaged around 200 mg/kg. APME's bromine balancing measurements calculate a feed concentration of about 30 to 60 mg Br/kg MSW (24). The contributions of bromine entering the waste can be natural bromine sources, bromine from flame retarded polymers and other bromine containing materials such as textiles.

Higher bromine levels in the feed to the combustor may influence the emission and residue disposal characteristics. The following aspects were examined during the trial:

- I. What was the bromine path through the main units : furnace and scrubber of a typical MSWC?
- II. Where did the bromine leave the MSWC: grate ash, liquid effluent and/or gaseous emission?
- III. What gaseous bromine containing compounds were formed ?

IV. How, and to what extent, did bromine act as a promoter to increase the concentration of certain chloro-bromo-organic species in the gaseous phase, as had already been proposed (25).

**ELEMENT PARTITIONING: Cl**

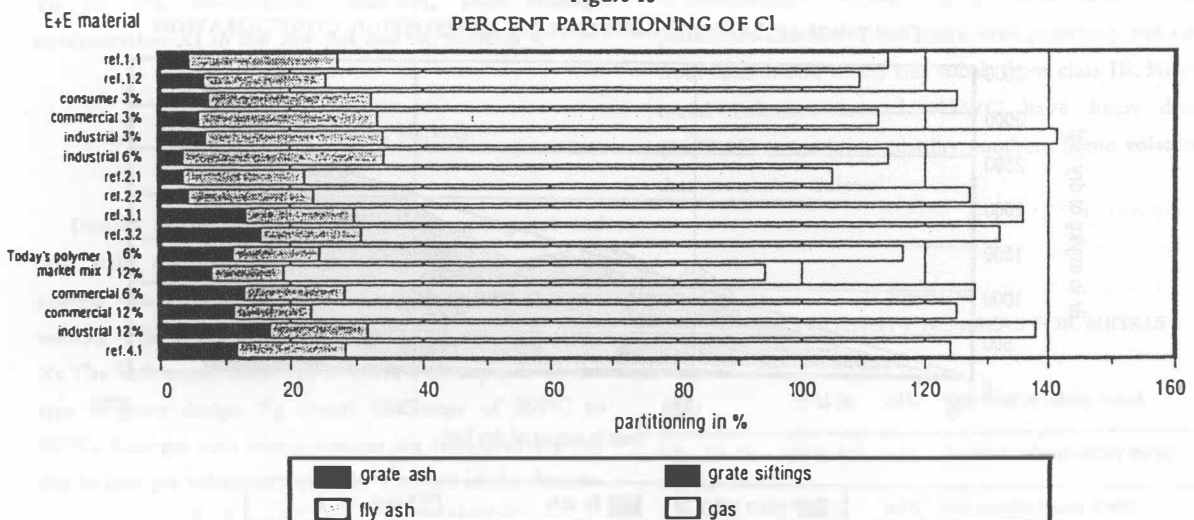
Earlier investigations had shown the distribution of Cl in the various streams for a very broad range from as low as 0.6 wt % to 3 wt %. Due to the importance of chlorine in the discussion of the formation of dioxins and furans the results from these tests are shown.

The Cl load in the feed varies between approx. 0.6 and 1,2 wt% based on output and input analysis. The comparison of the input numbers to the outputs analysed in the different compartments is shown as a percent partitioning in Fig. 13.

The Cl data show a substantial scattering and the averaged output is approx. 10 - 20 % higher than the input. This indicates errors caused during sampling, sample preparation, digestion or analysis. It is very likely that the digestion of the high volatile organic components causes most of the differences.

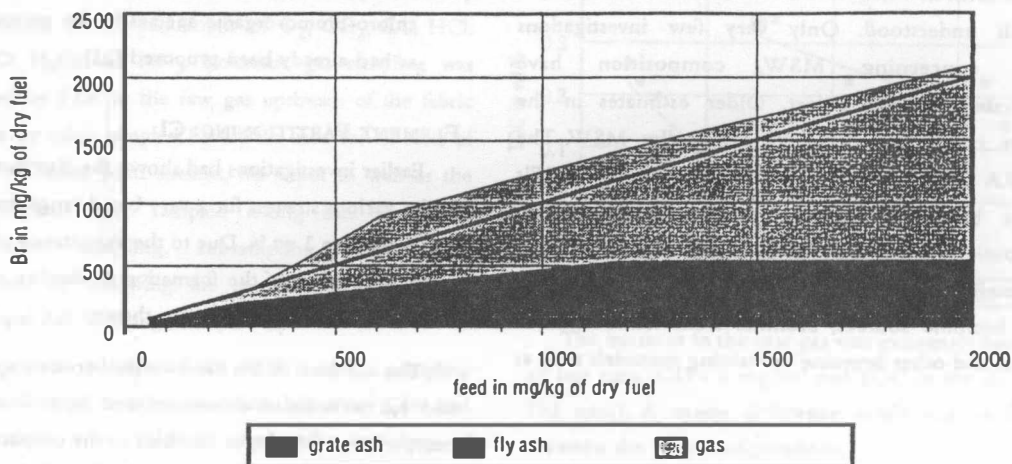
But taking into account the relative homogeneity of some of the feed materials and the analytical error of all different analyses this result can be deemed satisfactory. It is well known, from full scale incineration plants, that

Figure 13  
PERCENT PARTITIONING OF Cl



**THE ROLE OF  
VOLATILE ELEMENTS  
IN MSW COMBUSTION**

**Figure 14**  
**PARTITIONING OF Br IN THE PARALLEL FLOW COMBUSTION CONFIGURATION**



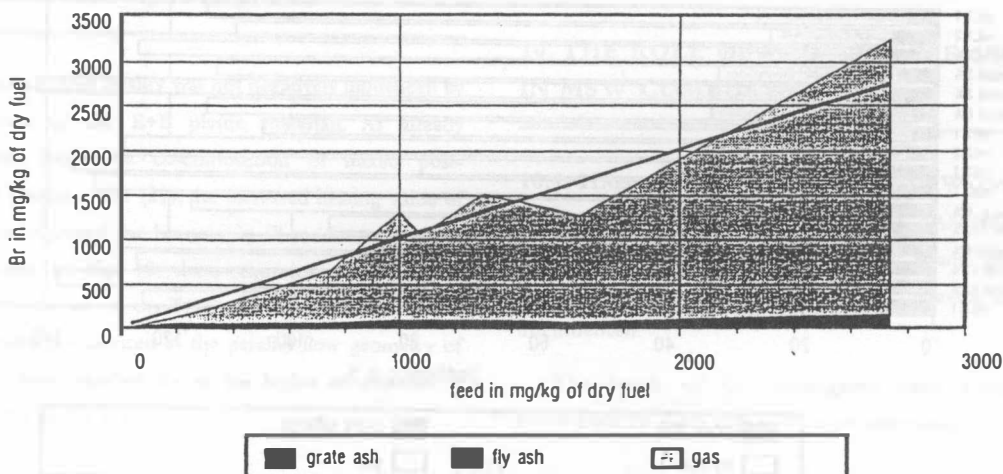
about 70 - 80 % of the total Cl inventory is found in the gas phase. This was confirmed by the tests for high Cl and very high Br concentrations.

A more detailed investigation revealed a significant difference of the partitioning depending upon the geometry of the combustion chamber. During the first test campaign the fly ashes carried a significantly higher fraction of the Cl inventory than they did in the second campaign. The probable reason was the higher residence time of the acid HCl and the alkaline fly ashes at high temperatures in the parallel flow configuration.

**ELEMENT PARTITIONING: Br**

The geometrical effect was more easily seen for the Br behaviour (Figs 14 and 15). Fig. 14 shows the sum of analysed output streams plotted against the sum of analysed input. Dry fuel is in this case the total feed, basic fuel and E+E materials without water. Again the output data were to some extent exceeding the inputs. The potential errors should be the same as those already discussed for Cl. In general the agreement of both Br balances can be deemed satisfactory. Figure 14 also indicates an increasing incorporation of Br into the fly ashes with increasing Br input. At very high input the curve seems to level off.

**Figure 15**  
**PARTITIONING OF Br IN THE MIDDLE FLOW COMBUSTION CONFIGURATION**



This might be caused by the exhausted alkalinity of the fly ashes. In almost all cases the pH of the fly ashes was in the order of 6.5 - 7, which is common in most modern large scale operations.

In the second test campaign (Fig 15) when TAMARA was operated in a middle flow combustion chamber design and even higher amounts of Br were added along with the E+E material, only smaller fractions of Br were found incorporated in the fly ashes.

The differences between the total fly ash concentrations, however, are difficult to explain purely on the basis of changes in combustion geometry.

#### 10.2. METALS IN MUNICIPAL SOLID WASTE

Two different types of metal species can be differentiated by their volatility behaviour.

Lithophilic elements stay mostly in the grate ash and do not volatilise. In this case it is the residue characteristics that are important. The others are subject to volatilisation and could cause emissions if not properly equipped.

The degree to which metals from plastics could be released to the environment through the stack depends on the levels of metals in the raw gas after the boiler. This amount is related to the following factors: metal volatility, fuel bed temperature  $T_b$ , raw gas temperature  $T_g$  in the combustion chamber, solid matter concentration  $X_s$  in the raw gas and air velocity  $v$ .

$$\text{Volatility} = F ( T_b, T_g, X_s, v \dots )$$

Due to experimental difficulties of sampling hot and high solid concentration gases, reported raw gas solid content values  $X_s$  relate mostly to the boiler exit. The air velocity  $v$  in the combustion chamber directly influences  $X_s$ . The bed temperature  $T_b$ , of a MSWC, depends on the type of grate design.  $T_g$  covers the range of 850°C to 950°C. Raw gas dust concentrations are comparatively low due to low gas velocities; typically 4 m/sec in the furnace.

Al and Mg are typical lithophilic elements and stay completely in the grate ash (17). The oxides and silicates of Al and Mg have very high boiling points and show no volatility. The concentration ranges of the MSW typically found are 0.2 to 1.0 wt % of Mg and 2 to 4 % of Al. Due to the high base load concentration in the MSW, relative small additions through the E+E plastics do not change the total concentration in the grate ash.

#### 10.3. FATE OF HEAVY METALS IN COMBUSTION

Heavy metals were examined in more detail because of the environmental concern from both the public and authorities. Heavy metals may be present in the following phases in the combustion system:

##### GAS PHASE:

1. volatilised gas
2. as an aerosol in the gas phase

##### SOLID PHASE:

3. bound to fly ash particles
4. in the solids (ash and slag)

Specific heavy metals are classified mainly by the two or three official emission classes of the waste incineration or combustion Directives. Potential critical elements from plastics are cadmium from class I, lead, antimony and zinc from class II and nickel and cobalt from class III. Heavy metal balances around MSWC have been done (26,27,28) to establish volatility numbers. Some volatility data are shown below:

Figure 16  
TYPICAL VOLATILITY NUMBERS FOR METALS

Cd	85 to 90	wt %	high volatile heavy metal
Zn, Sb, Pb	30 to 50	wt %	medium volatile heavy metal
Ni, Cu	1 to 10	wt %	low volatile heavy metal

## HALOGENATED MICRO-ORGANICS

It can be seen from Figure 16 that most of the metals in E+E type plastics waste do not show a high volatility. The most critical heavy metals from an emission directive viewpoint are Cd followed by Pb, Sb and Zn.

### ELEMENT PARTITIONING: Sb

The element antimony (Sb) is quite frequently added to improve the flame retardant behavior of E+E plastic materials. A relation of 3 - 4 to 1 is typical in flame retarded plastics for Br and Sb. This approximate value was also found in the E+E waste materials used here. Fig. 17 details the percent balances for Sb found during all of the test trials. In most cases the balances match nicely to 100 %. In two tests, during the addition of 6 and 12 wt. % of the commercial material, extremely high output numbers were found. The resultant discrepancy is most likely due to an underestimation of the input. The graph demonstrates the well known influence of increased Cl levels upon the volatilisation of Sb (21).

Estimates of the partitioning of other elements confirmed the findings of former experiments for the volatilisation of heavy metals such as Zn, As or Sb.

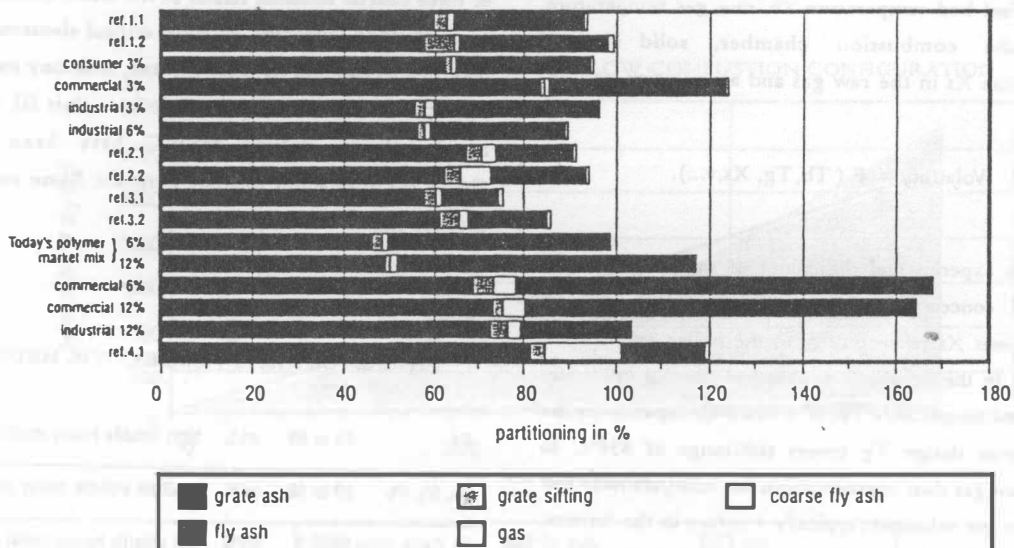
## 11. HALOGENATED MICRO-ORGANICS

Because of their persistency in the environment, halogenated micro-organics are seen as a very specific class of dangerous substances. As a consequence of the sensitive nature of this subject, specific emphasis was given to all three following aspects: their content in E+E waste, potential emissions and their degree of destruction.

### 11.1. DIOXIN AND FURAN CONTENT IN E+E WASTE

Two ordinances exist in Germany regulating the transport and handling of hazardous materials: "The German Regulations for Hazardous Materials", and a second regulating materials brought to the market in "The German Chemicals Restriction Ordinance" enacted July 16, 1994. The same 17 poly-chlorinated (PCDD/F) and 8 poly-brominated (PBDD/F) dioxins and furans are mentioned in both ordinances. Limit values are given for single congeners like the 2,3,7,8 PCDD/F as well as for groups of dioxin and furan compounds. Limits for mixed halogenated (PXDD/F) are not specified. The feed materials for the TAMARA campaigns as well as for the broad range of specific market samples were analysed.

Figure 17  
PERCENT PARTITIONING OF Sb



It is known from the literature that TV housings made out of polystyrene and containing deca-bromo-diphenyloxide as fire retardants may contain certain amounts of brominated furans/dioxins (29).

Within APME's programme to gather analytical data of polymers used in the E+E area, additional samples were analysed from typical E+E waste. In summary it was found that PXDD/F content is very broad, ranging from <1 ppb to several hundred ppb. The average value is around 20 ppb (micrograms per kg) and meets the German regulations. It can be further concluded that the amount of brominated dioxins/furans belonging to the group of 8 selected 2,3,7,8-PBDD/Fs is larger than the equivalent chlorinated group with 17 PCDD/Fs.

The level of total PXDD/Fs in old end-of-life E+E equipment still in circulation suggests that material recycling of plastics from these articles should be looked at with great care.

Disposal of these articles through methods like combustion or feedstock recycling, ensuring total and safe PXDD/F destruction, is to be preferred.

## 11.2. HALOGENATED DIOXINS AND FURANS PXDD/F IN THE RAW GAS

### 11.2.1. PCDD/F IN THE RAW GAS

A moderate increase of Cl input in the combustion chamber should not significantly influence the formation of PCDD/F. Former experiments in TAMARA did not show an effect even if the Cl load was elevated by a factor of 5 (21). This has been supported by similar tests in a German full scale MSW incinerator (24).

Two recently published studies on the relationship of PVC and PCDD/F in waste combustion also gave no indication of a significant correlation (26,27).

There is one paper claiming an increase in PCDD/F when electronic waste flame retarded by polybrominated diphenylethers is co-combusted in a MSWC plant (25).

Although the effect seems statistically insignificant such potential influences also had to be considered in our experiments. More recent investigations in Dutch incineration plants have not confirmed a correlation between Br and the total dioxin formation (28). A recently published study on the role of Br in the de novo synthesis in a model fly ash system has also not confirmed the promoting effect of Br (30).

Figure 18  
PCDD LEVELS IN THE RAW GAS

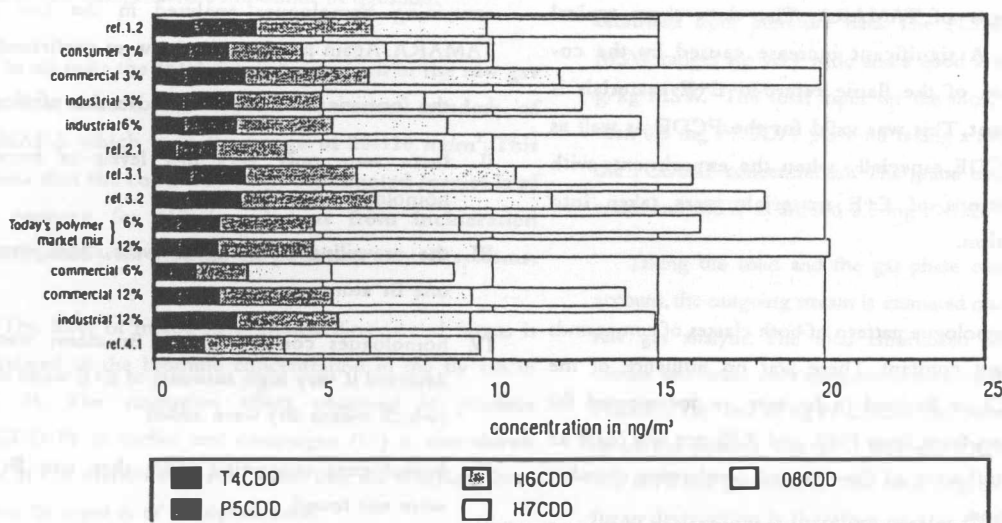
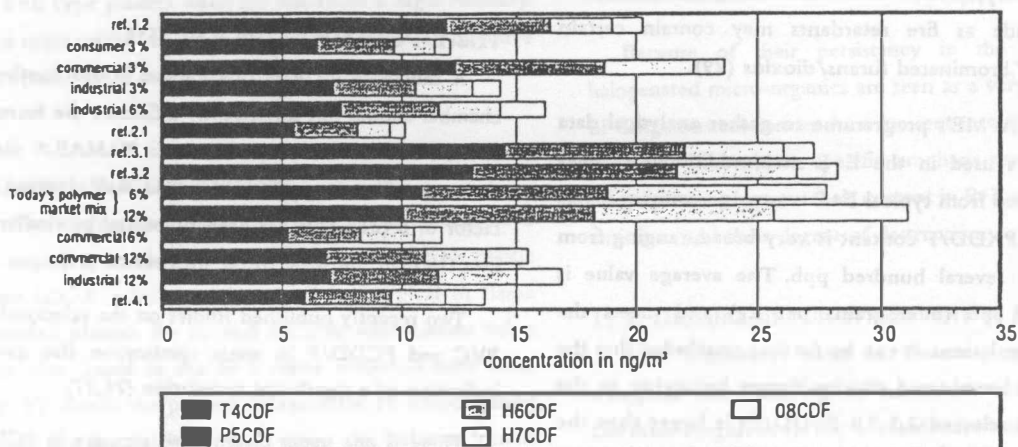


Figure 19  
PCDF LEVELS IN THE RAW GAS



The levels of PCDD and PCDF in the raw gas of TAMARA have a tendency to decrease with increasing time of operation. This has already been extensively documented and can be compared with the time behavior of large scale boilers due to dust accumulation. Hence the actual reference level of PCDD/F for certain co-combustion tests is somewhere between the initial and the final reference test results.

The PCDD and PCDF concentrations analysed by FZK and two outside laboratories were in most cases very close to each other. Figs. 18 and Fig. 19 detail the sum of homologues obtained for PCDD and PCDF in the raw gas of TAMARA. The data show typical scattering. A significant increase caused by the co-combustion of the flame retarded E+E materials is not apparent. This was valid for the PCDD as well as for the PCDF, especially when the experiments with high additions of E+E materials were taken into consideration.

The homologue pattern of both classes of compounds stayed about constant. There was no influence of the elevated Cl or Br load to be seen as documented for construction foam from PUR and XPS nor was there an observed influence of the changed combustion chamber configuration.

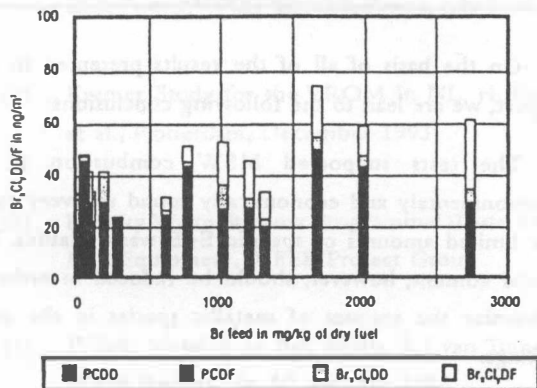
#### 11.2.2 Br CONTAINING DIOXINS AND FURANS IN THE RAW GAS

Data for PCDD and for PCDF did not show a significant influence of the elevated Br input. The situation changes as far as bromine containing dioxin and furan is concerned. According to the literature (23), brominated and mixed halogenated compounds add only a small percentage to the PCDD/F levels in MSWC. This was also confirmed by the co-combustion of XPS and PUR foams in TAMARA (17).

The analysis of brominated and mixed halogenated dibenzo-p-dioxins and dibenzofurans was also performed by GfA and ITU. Figure 20 shows the respective Br containing homologues analysed in the raw gas of TAMARA. Again previous results were confirmed:

- I. the formation of furans exceeded that of dioxins
- II. there were only very low levels of brominated homologues found
- III. the prevailing homologues were those containing one Br atom
- IV. homologues containing two Br atoms were only detected if very high amounts of E+E waste material (which means Br) were added
- V. homologues containing more than two Br atoms were not found.

Figure 20  
SUM OF HALOGENATED DIBENZO-P-DIOXINS AND  
DIBENZOFURANS



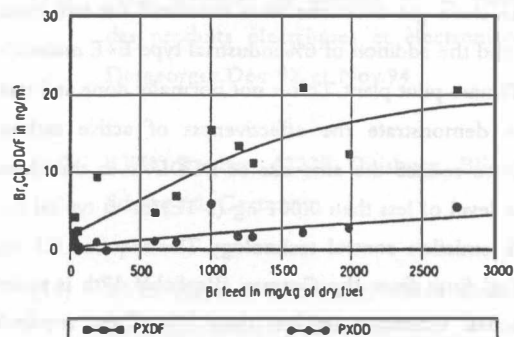
The foam tests cited above showed that the formation of Br containing dioxins and furans was limited and was responsible for approx. 20 - 30 % of the total dioxin and furan level in the raw gas if high amounts of Br were added to the feed stream. In Fig. 20 all of the analysed chlorinated and Br containing homologues are summed up for all test runs.

Fig. 20 also demonstrates that the mixed Cl/Br containing furans in these tests sometimes reached the same order of magnitude as the purely chlorinated ones. This was observed in the two tests when 12 wt. % of commercial or industrial E+E material was co-combusted. The dioxins were always lower in concentration by a factor of 3 - 4 than the furans and did not add substantially to the total sum of the halogenated compounds in question.

In all tests the total dioxin/furan load in the raw gas did not exceed the typical operation window of TAMARA which is in the range of 20-120 ng/m³. This means that the contribution of brominated species is of no concern for MSW emissions from incineration plants fitted with modern air pollution control systems.

The level of mixed halogenated dioxins and furans is correlated to the bromine concentration in the fly ash in Fig. 21. The saturation effect observed to produce PBCDD/Fs in earlier test campaigns (17) is also shown here. It can therefore be concluded that the chemical form of the Br input is of no significance.

Figure 21  
INFLUENCE OF Br CONTENT IN FLY ASH ON  
PBCDD/Fs



### 11.3. DESTRUCTION EFFICIENCY

The destruction efficiency of the TAMARA pilot plant for the halogenated dioxins and furans has been calculated to support this waste management route. A realistic scenario case has been chosen for this evaluation. The total halogenated dioxin and furan input stream from the E+E plastics waste can be estimated from the measured concentrations (see chapter 6.4). The range was very broad as indicated and a value of 2 micro g PXDD/F /kg E+E plastics waste was chosen. This concentration times the mass stream of E+E plastics waste of 15 kg/h leads to the total PXDD/F input from the plastics. For the total amount of PXDD/F, all 25 compounds from the German Dioxin Ordinance were taken into account. This resulted in a figure of about 0.030 mg PXDD/Fs per hour.

The PXDD/F mass contribution of the MSW can be estimated from literature data. The PCDD/F content in MSW ranges are very wide and a good average is 5 micro g/kg MSW. The total input for the most realistic case is then 0.5 mg PCDD/F per hour taking a medium value for the PCDD/F concentration. The grand total input of E+E waste and MSW is around 0.6 mg PXDD/F per hour.

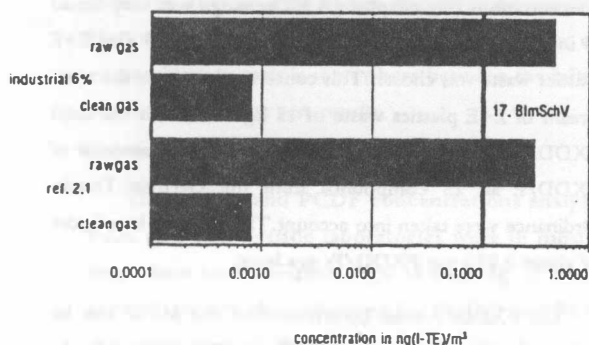
Taking the solid and the gas phase concentration into account, the outgoing stream is estimated on the basis of the raw gas analysis. The total chlorinated and halogenated dioxins and furans were measured at maximum to about 45 ng PCDD/F /m³ and 23 ng PBCDD/F /m³ respectively leading to an out flowing flux of 0.061 mg PXDD/F / h with 900 m³/h flue gas volume. The total degree of dioxin and furan destruction is therefore greater than 90 % (24).

## RECOMMENDATIONS

### 11.4. PCDD/F IN THE CLEAN GAS

The clean gas emissions were measured for two cases ref 2.1 and the addition of 6% industrial type E+E materials in the Tamara pilot plant. This is not normally done and was only to demonstrate the effectiveness of active carbon addition to reduce the amounts of PCDD/F in the clean gas. The level of less than 0.001 ng (I-TE)/m<sup>3</sup> is typical for this safe emission control technology. The required 0.1 ng (I-TE)/m<sup>3</sup> limit from the German BImSchV 17th is easily met. Actual emissions are less than 5% of the required limit in Fig. 22.

Figure 22  
E&E CO-COMBUSTION - PXDD/PXDF IN RAW AND  
PCDD/PCDF IN CLEAN GAS



### 12. RECOMMENDATIONS

On the basis of all of the results presented in this report, we are lead to the following conclusions:

The tests supported MSW combustion as an environmentally and economically sound recovery route for limited amounts of specific E+E waste plastics. The metal content, however, should be reduced in order to minimize the amount of metallic species in the grate siftings.

#### CONTRIBUTIONS:

During this project a number of people have cooperated from different companies: Elf Atochem: A. Jean, Bayer: M. Rohr, Dow Europe: F.E. Mark, Du Pont de Nemours: J.M. Falguière and representing the organisations involved: APME: R. Martin, EBFRIIP/BFRIP/EFRA: M. De Poortere, FZK: J. Vehlou, B. Bergfeld, T. Wanke, ZVEI: W. Pauli (ABB). Their dedication and efforts are appreciated.

This project was supported by the following associations: APME: the Association of Plastics Manufacturers in Europe, BFRIP: the Brominated Flame Retardant Industry Panel, EBFRIIP: their European equivalent, EFRA: the European Flame Retardant Association, FZK: Forschungszentrum Karlsruhe and FIEE: the French Electrical and Electronic producer organisation.



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