PCB's in Small Capacitors from Waste Electrical and Electronic Equipments

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SENS®

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Summary

In 2006, 121 t small capacitors from 96'400 t waste electrical and electronic equipments (WEEE) were separated and disposed of in Switzerland (SENS-SWICO 2007). The Swiss legislative regulations make a distinction between the disposal routes for PCB-containing and PCB-free capacitors. PCB-containing capacitors must be eliminated in high-temperature incinerators, while there are no specific requirements regarding the disposal of PCB-free capacitors. The treatment requirements of the Swiss system operators SENS and SWICO for the disposal of WEEE rule the treatment of small capacitors in accordance with Swiss and European standards.

In practice, distinguishing between PCB-containing and PCB-free capacitors is difficult – even for qualified personnel – time and cost intensive, and therefore rarely done. As a consequence, as good as all the capacitors (> 2.5 cm) are removed from all WEEE categories, then attributed to the PCB-containing capacitors and treated as hazardous waste. Accordingly, the prescribed disposal in a high-temperature incinerator involves great expenses and excludes at the same time a potential material recycling of non-hazardous capacitors, due to lacking knowledge.

The investigation into "PCB's in small capacitors from waste electrical and electronic equipments" by the technical control bodies of SENS and SWICO aims at extending the knowledge, in order to grant a safe and wise handling of small capacitors. Especially the occurrence of unhealthy and environmentally hazardous substances in small capacitors from electrical and electronic equipments needs to be elicited, and the sequels of a potential diffuse release are to be estimated. The results shall provide a basis for decision-making, so as to verify the treatment requirements for small capacitors and, were necessary, revise them.

In dismantling plants and at work places of diverse recycling companies, capacitors from ten different product categories and types had been collected. The capacitor random samples totalled 1'482 kg, hence equal to about 1.2 % of all the capacitors removed from WEEE in 2006.

As a first step, the PCB content was determined in all ten bulk samples and, subsequently, further compounds or substance classes, respectively, were identified by means of a GC/MS full scan analysis in the extracts. Afterwards, a GC-ECD / FID fingerprint analysis and the quantification of the main components were performed exclusively on the capacitors from microwave systems. Table 1 summarises the detected PCB content.

No standardised processing and identification methods are currently available for the analysis of the diverse and heterogeneous matrices of shredded small capacitors. PCB determinations in such heterogeneous samples are most demanding. The results of PCB measurements by three different, certified laboratories specialised in PCB analyses show that considerable error sources and uncertainties are persisting. Namely in case of high concentrations around factor 10, the PCB content of the same bulk sample varies sensibly. Main error sources need to be looked for within the items "extraction methods" and "separation of congeners".

Table 1 PCB contents [mg/kg] as sum of 6 PCB congeners and its multiplication by factor 5 following LAGA[1]

N°	Origin of the Capacitors	PCB Content [mg/kg]		
		Laboratory 1	Laboratory 2	Laboratory 3
Large Household Appliances (LHA), Small Household Appliances (SHA)				
1	LHA mixture	16'450	1'490	3'110
2	Dishwashers	224	172	–
3	SHA mixture, except for microwave devices	439	353	–
4	Microwave devices	11	–	–
5	Cooling and freezing appliances	<5	–	–
6	Ballasts in fluorescent tube lamps	247'690	24'260	68'600
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply)				
7	IT/CE: capacitors < 1 cm	<5	–	–
8	IT/CE: capacitors 1-2.5 cm	55	54	–
9	IT/CE: capacitors > 2.5 cm	1'905	1'081	1'590
10	UPS	<5	–	–

Small capacitors from ballasts in fluorescent tube lamps and a typical mixture of large household appliances embody, as ever, relevant amounts of PCB's. These capacitors in electrical and electronic equipments still include about 6 – 60 % or 1 – 4 % PCB, respectively. Regarding 2006, the PCB emission potential of these two device categories approached 400 – 4'300 kg/a and thus exceeded 95% of the total PCB flow from waste electrical and electronic equipments. Small capacitors from information technology and consumer electronics (IT/CE) (> 2.5 cm) and small household appliances are also featuring a minor PCB flow. In 2006, the latter were low and approximated 40 – 60 kg/a or 20 kg/a, respectively. According to a study by the Swiss Federal Office for the Environment (BUWAL 1994), the annual total deposition of PCB's from the atmosphere is estimated at 2'000 – 8'000 kg/a.

In the small capacitors from cooling and freezing appliances, IT/CE (< 2.5 cm), including uninterruptible power supply systems (UPS), no PCB's have been found, and their annual PCB emission potential may be neglected. Small capacitors from microwave devices are as good as PCB-free, however, 18% biphenyls and 0.2% phthalates were identified in the samples.

Diverse naphthalenes, phthalates and substituted biphenyls were identified as substitutes. The origin of the phthalates is uncertain, as they might come from plasticized PVC sheets or cable sheathings, and they are present in almost all the samples. But generally, we may say that, excepting chlorinated naphthalenes, solely substance groups were found, which are significantly lesser persistent than PCB's.

Polar and oxidizing electrolytes are, virtually, not seized with the chosen extraction methods and mainly hydrophobic dielectrics were identified. Additionally, we must assume that electrolytes are, by way of comparison, reactive and therefore also disintegrating themselves very quickly. With regard to the amounts and the types of electrolytes in capacitors from old equipments, the present study does not allow assertions.

Basing on the results and findings of these analyses, the following suggestions for handling small capacitors are formulated:

- All the appropriate measures should be taken immediately, so as to increase the controlled disposal of ballasts in fluorescent tube lamps, primarily from the B2B channel. The capacitors from ballasts must thereby be removed systematically.
- Regarding the removal of capacitors from electrical and electronic equipments, the regulations and guidelines of the system operators SENS and SWICO should not be subject to a noticeable change. Diffuse emissions of probably 10-20 t per year by predominantly environmentally hazardous substances can, thus, be avoided.
- When determining PCB's in mixtures from old capacitors, the chemical analysis requires utmost attention. Control and quality assurance measures should have been applied to the extraction of PCB's and the separation of congeners.
- In a follow-up project, PCB substitutes and electrolytes are set to be analysed more specifically and quantitatively, according to the origin of the capacitors and with regard to the category of the devices.
- Basing upon the fact that the share of PCB-containing capacitors, dielectrics and the composition of electrolytes will evolve with the time, the analyses shall be repeated in a few years (in 2010, for instance), in order to secure a safe and wise handling of small capacitors from electrical and electronic equipments.

[1] Guidelines of LAGA (Länderarbeitsgemeinschaft Abfall, Germany) for the determination of the PCB-content in heterogenous matrices

1 Initial Situation and Target

1.1 Capacitors and Environment

Small capacitors are passive electrical building elements and found in many electrotechnical devices. In electrical and electronic equipments, they serve as energy and charge-coupled memory, frequency depending resistances, converters or sensors. A capacitor consists of two electro-conducting surfaces, mostly at small intervals, i.e. the electrodes. Between them, there is always an area with isolating properties, the dielectric, which may be solid or liquid. The case of one of the electrodes formed by a conducting liquid refers to an electrolyte capacitor. The dielectric is found in the aluminium oxide (Al_2O_3) or tantalum oxide (Ta_2O_5) of the electrolyte capacitor, generated as a chemical reaction between electrodes and electrolytes. Most current designs are winding capacitors (i.e. paper sheet, synthetic sheet, metal paper systems), mass capacitors (i.e. ceramic and electrolyte capacitors) and layer capacitors (Hentschel 2000).

Due to the electrical insulating property, difficult inflammability, chemical and thermal stability of polychlorinated biphenyls (PCB's), these chemical chlorine compounds were often used as dielectrics in paper capacitors. As a consequence of their hazardous impacts on human health (BAG 2006) and their extraordinary stability, the production and application of PCB's in Switzerland was generally prohibited in 1986. On an international level, the production and application of PCB's was banned, first in open systems in 1978 and then broadly prohibited in 1986 (UNEP 1999). Various non-conductive oils, mainly without halogens, were used as substitutes for PCB's. But as these substitutes must also have a certain thermal and electrical stability, the environmental hazard cannot be excluded. In Al capacitors, organic carbonic acids – heavily toxic and corrosive (Baumann 2005) – are frequently used as electrolytes. These electro-conductive matters are often mixed with additives and solvents.

1.2 Legal Provisions and System Regulations

In 2006, 121 t small capacitors from 96'400 t electrical and electronic waste equipments were removed and disposed of separately in Switzerland (SENS-SWICO 2007) . The Swiss legal provisions differentiate on principle between the disposal routes for PCB-containing and PCB-free capacitors. According to the Swiss Ordinance on the Return, Acceptance and Disposal of Electrical and Electronic Equipments (VREG), Art. 6 Abs. 1 lit. a (VREG 1998), "especially contaminated components such as PCB-containing capacitors must be disposed of separately". The guidance on the VREG (BUWAL 2000) stipulates high-temperature incineration for PCB-containing capacitors.

Specific requirements for the disposal of PCB-free capacitors are not defined in the Swiss legislation, unless their classification as "heavily contaminated components" can be justified. According to the VeVA Waste Catalogue (Ordinance on the Handling of Waste), PCB-free capacitors are assigned to the other wastes which are subject to control (Waste Code: 16 02 16 [ak]).

In Annex 2 (EU 2002) of the European WEEE Directive, the removal from equipments and a separate disposal of PCB-containing capacitors and electrolyte capacitors with environmentally relevant matters (height > 25 mm; diameter > 25 mm or proportionally similar volumes) are stipulated. Following the European Waste Catalogue, these capacitors are also ranked as hazardous waste.

The Treatment Requirements of the Swiss system operators SENS and SWICO on the disposal of electrical and electronic equipments are ruling the handling of small capacitors in accordance with Swiss and European standards. Basing on the definition in Annex 2 of the WEEE Directive, all the PCB-containing and electrolyte capacitors shall be removed from the equipments and disposed of separately.

In practice, a differentiation between PCB-containing and PCB-free capacitors is difficult – also for qualified personnel – cost and time intensive, and therefore rarely done. Available auxiliary documents for identifying

PCB-free capacitors (KTAG 2004) show uncertainties and lacks. That is why in practice, almost all the capacitors are removed from every category of equipment, assigned to the PCB-containing capacitors and treated as hazardous waste (Waste Code: 16 02 09 [S]), in agreement with the VeVA Waste Catalogue (VEVAa 2005; VEVAb 2005).

1.3 Previous Analyses

In 1988, small capacitors from totally 2’400 equipments, differentiated following 17 categories, were analysed for their PCB contents in Switzerland. PCB-containing capacitors were found in averagely 20 % of the equipments (Barghoorn 1988, cited in BUWAL 2004).

Analyses from 2003 on the average composition of small electrical and electronic waste equipments reveal that the average PCB concentration is 13 mg/kg (± 4 mg/kg) (BUWAL 2004) (Morf, Tremp et al. 2007).

Furthermore, unpublished results from random sample analyses by the technical control bodies of SENS and SWICO in 2005 are available (see Annex A). These analyses confirm that on the one hand, PCB’s are still present today in old equipments and on the other hand, that the PCB content of capacitors from diverse categories of equipments or components varies much and can, partly, be very low. In capacitors from small waste equipments (IT/CE and SHA), low values were determined, while in opposition, high PCB values were measured in capacitors from large household appliances (LHA). Actually, it is a matter of non representative random samples.

1.4 Objectives

Within the present study, additional findings shall allow to secure a safe and wise handling of small capacitors. Quite particularly, the potential of health and environmentally hazardous substances in small capacitors from electrical and electronic equipments is to be found and assessed. The results shall serve as a decision-making basis, in order to check the treatment requirements for small capacitors and, if needed, to revise them. The following aims have been defined in detail:

1. Differentiated sampling following diverse categories and types of equipments and representative sampling of small capacitors from electrical and electronic equipments.
2. Analysis of the PCB content in small capacitors from diverse categories and types of equipments.
3. Extension of the analyses to identifying compounds or substance classes, respectively, in the single specimen extracts (identification of possible PCB substitutes and electrolytes).
4. Formulation of measures and suggestions regarding the handling of small capacitors from old electrical and electronic equipments, basing on the results.

[2] Amount of disposed of small capacitors from waste electrical and electronic equipments in Switzerland: 2005: 130 t, 2004: 121 t; 2003: 109 t

2 Sampling and Sample Preparation

2.1 Sampling

In dismantling plants and at the work places of diverse recycling companies, who are currently discharging pollutants, capacitors from diverse categories and types of equipments were collected. The analysed categories or types of equipments, respectively, and the amount of removed capacitors are shown on Table 2.

The capacitors were removed from the equipments between June and August 2006, and the amount of random samples was 1'482 kg, which corresponds to about 1.2 % of all the capacitors removed in 2006 from equipments. The various recycling companies represent differing trading areas and customer segments.

The amount of capacitor samples was chosen in a way to have, the relative quantity of sampled equipments correspond in each case to at least 1 % of the yearly total of processed units. Table 3 composes the sampled share of the yearly processed equipments following their respective categories. The estimations on the share of capacitors within a category of equipments are based upon random sample analyses or batch tests. With regard to cooling and freezing appliances and IT/CE's, more than one per cent of the yearly total could be sampled, as for LHA's, they reached 0.7 %, lamps 0.5 % and SHA's merely 0.2 %, due to the temporally limited sampling. The quantity of processed uninterruptible power supply systems has not been accounted in the material flow compilation of SENS and SWICO. Hence, there are no indications about the processed amounts.

It is assumed that a large part of the fluorescent tube lamps is not being registered by the collective systems and ending directly in the scrap metal. According to the Swiss Lighting Recycling Foundation (SLRS) about 1.5 million fluorescent tube lamps were sold in 2006. By supposing an average weight of 3.7 kg per fluorescent tube lamp (see Annex C), it would correspond to a material amount of 5'570 t. In 2006, only 420 t lamps (fluorescent tube and other lamps) were processed within the collective systems, however, a much higher waste volume is expected.

Table 2 Amount of capacitor random samples following the category or type of equipment

N°	Origin of Capacitors	WEEE Category	Amount of Capacitors	
			[kg]	[%]
Large Household Appliances (LHA), Small Household Appliances (SHA)				
1	LHA mixture	1	415	28.0
2	Dishwashers	1	22	1.5
3	SHA mixture, without microwave devices	2	13	0.9
4	Microwave devices	1	50	3.4
5	Cooling and freezing appliances	1	148	10.0
6	Ballasts in fluorescent tube lamps[3]	5	99	6.7
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)				
7	IT/CE: capacitors < 1 cm	3, 4	21	1.4
8	IT/CE: capacitors 1-2.5 cm	3, 4	322	21.7
9	IT/CE: capacitors > 2.5 cm	3, 4	125	8.4
10	UPS (uninterruptible power supply systems)	–	267	18.0
Total			1'482	100.0

[3] Two separate samplings – campaigns: June – August 2006 (38 kg) and June – July 2007 (61 kg)

Fig. 1 Shredder for the reduction of the capacitors (type: Vecoplan VAZ 105/120, 18.5 kW, approx. 550 kg/h) and 8 mm sieve used for IT/CE < 1cm (bulk sample N° 7)

Fig. 2 Splitting and reduction of samples by means of splitting the angle of repose of the shredded material

Table 3 Share of sampled equipments from the total amount of processed units in the collective systems SENS, SWICO and SLRS in 2006

Category of Equipment	Bulk Sample N°	Amount of Capacitor Samples [kg]	Share of Capacitors (Estimation) [kg/t]	Processed Total 2006 [t]	Amount of Sampled Equipments [t]	Sample Share/ Amount 2006 [%]
LHA	1, 2	437	2.5	24’709	175	**0.7**
SHA	3, 4	63	2.4[1]	10’673	26	**0.2**
Fluorescent tube lamps	6	99	32	420	2	**0.7**
Cooling and freezing appliances	5	148	0.1	14’929	1’480	**9.9**
IT/CE	7, 8, 9	468	0.8	41’713	585	**1.4**
UPS	10	267	n.d.[2]	n.d.	n.d.	**n.d.**

[1] determined from estimated shares of capacitors in SHA’s (0.8 kg/t) and microwave devices (5 kg/t); in Switzerland, microwave devices are assigned to SHA’s, in the EU, they are considered as large WEEE equipments, category 1
[2] n.d.: no data available

The capacitor samples collected according to the categories of equipments were checked visually for their belonging to the respective categories of equipments and for the eventual presence of interfering matters. It may be assumed that the separation according to the categories of equipments was performed reliably. Annex B presents the supplied or coarsely shredded capacitors, respectively. The number of capacitors, the manufacturers or other product data were seized for bulk sample “ballasts in fluorescent tube lamps” only. Considering the very high quantities (about 30’000 small capacitors), such cost and time consuming compilations had to be abandoned for the other samples.

2.2 Sample Preparation

The crushing of the collected small capacitors occurred in a fine shredder (sieve 12 mm or 8 mm, respectively, for bulk sample IT/CE < 1 cm). After every passage, the shredder was dry cleaned and eventual residues removed with toluene. As a further measure to avoid transmissions, a forerun of about 10 % of the input was practised in every case and not used for the sample concerned.
After shredding, the amount of samples was reduced to about 2 kg by means of splitting the angle of repose of the shredded material in a structured way. Further preparations and analyses were practiced in the laboratory.

3 Laboratory Analyses

3.1 Procedure

No standardised preparation and identification methods are yet ruling the handling of shredded small capacitors. Neither do relevant analytical experiences by PCB specialised laboratories exist on this heterogeneous mixture of oily metal, plastic and paper particles of varying size. To verify the results, three different certified laboratories specialised in PCB analyses were therefore commissioned to test certain samples. They were free to choose appropriate homogenisation, sample splitting and extraction method.

In a first step, the PCB content was determined after the preparation in all ten bulk samples (see paragraph 3.2). Secondly, further compounds or substance classes, respectively, were identified by means of a GC-MS full scan analysis (see paragraph 3.3). Further tests were performed on capacitors from microwave devices, as findings about the use of PCB substitutes and, perhaps, of electrolytes were expected (see paragraph 3.4). Such high-tension capacitors have a relatively uniform design; they often include significant amounts of liquids and should not hold any PCB's, as the first devices of this kind were introduced on the market only after the PCB prohibition. A GC-ECD / FID fingerprint analysis and a quantification of the main components were practiced.

3.2 PCB Analysis

The preparation of the heterogeneous samples, the division of the congeners and the identification were diversely performed by the three analytical laboratories. Table 4 illustrates the essential differences. Measurement errors are evaluated up to 20 – 25 % or 20 – 30 % by the laboratories. The results of the analyses are shown in Table 5, with the figures ranging within < 1%. In case of high PCB contents, the values of the different laboratories vary significantly and may come up to factor 10.

Table 4 Differences in the preparation of bulk samples

Amount of extract	7– 30 g; 0.2 g; 5 g
Homogenisation	disk vibratory mill, ultra-centrifugal mill
Extraction solvent	Soxhlet extraction with n-hexane; ultrasound extraction with cyclohexane / acetone / or cyclohexane / ethyl acetate
Control of extraction efficiency	none / insufficient
Extract evaporation	highly variable

Table 5 PCB contents [mg/kg] as sum of 6 PCB congeners[5] and its multiplication by factor 5 following LAGA; results of the tests in the three analytical laboratories

N°	Origin of Capacitors	PCB Content [mg/kg]		
		Laboratory 1	Laboratory 2	Laboratory 3
Large Household Appliances (LHA), Small Household Appliances (SHA)				
1	LHA mixture	16’450	1’490	3’110
2	Dishwashers	224	172	–
3	SHA mixture, without microwave devices	439	353	–
4	Microwave devices	11	–	–
5	Cooling and freezing appliances	<5	–	–
6	Ballasts in fluorescent tube lamps[6]	247’690	24’260	68’600
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)				
7	IT/CE: capacitors < 1 cm	<5	–	–
8	IT/CE: capacitors 1–2.5 cm	55	54	–
9	IT/CE: capacitors > 2.5 cm	1’905	1’081	1’590
10	UPS (uninterruptible power supply systems)	<5	–	–

[5] die Ballschmiter Kongenere 28, 52, 101, 138, 153, 180

[6] In the specimen from the 2nd sampling campaign in June – July 2007, a PCB content of 84’300 mg / kg was determined (laboratory 3); to calculate the total, the Ballschmiter numbers 28, 52, 101, 138, 153 and 180 were added up and multiplied by factor 4.3 (following AHR and ALTLV).

3.3 GC-MS Full Scan Analysis

Further compound or substance classes, respectively, were identified in the extracts with a GC-MS full scan analysis. The results are compiled in Table 6. They refer to qualitative analyses consisting in spectral comparisons with MS library spectra (NIST05). A detailed verification of the results was not done. The analyses revealed a multitude of compounds and substance classes and that these latter contain a great number of totally different compounds.

Table 6 Identified individual substances and substance classes in the capacitor samples

N°	Origin of Capacitors	Possible Compounds / Substance Classes
Large Household Appliances (LHA), Small Household Appliances (SHA)		
1	LHA mixture	naphthalene, hydrocarbons, chlorinated naphthalene, phthalates
2	Dishwashers	naphthalene, hydrocarbons, biphenyls, chlorinated naphthalene, phthalates
3	SHA mixture, without microwave devices	hydrocarbons, methyl-naphthalene, chlorinated naphthalene
4	Microwave devices	biphenyls (for ex. ethyl methyl), phthalates
5	Cooling and freezing appliances	naphthalene, benzyl-methylbenzene, hydrocarbons, biphenyls, triphenyl phosphate, phthalates, phosphoric acid ester
6	Ballasts in fluorescent tube lamps	phthalates
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)		
7	IT / CE: capacitors < 1 cm	hydroxybutyric acid, chloro-butyrophenon, phthalates, fatty acid, fatty acid ester, hexabrome benzene
8	IT / CE: capacitors 1–2.5 cm	dimethylacetamide, hydroxybenzoic acid, benzyl alcohol, dimehyl-benzyl alcohol, dibenzoyloxy-heptane-diamide, benzoic acid ester, chlorinated naphthalene, carbonic acids, fatty acid ester, hexab-rome benzene, phthalates, phosphoric acid ester
9	IT / CE: capacitors > 2.5 cm	Dimethyl acetamide, hydroxybutyric acid, methyl pirrolidon, benzoic acid chlorethyl ester, benzoic acid ester, tetrabutyl ammonium cyani-de, butoxyethoxy-ethyl acetate, biphenyls, chlorinated naphthalene, phthalates
10	UPS	hydrocarbons

3.4 GC-ECD / FID Fingerprint Analysis

Bulk sample N° 4 "microwave devices" was submitted to a differentiated analysis, in order to enable, as much as possible, more precise statements on the di-electrodes and electrolytes used after the PCB prohibition. The samples were prepared so as to allow individual identifications within the substance classes, including quantification. Table 7 displays the results.

Two significant substance groups could be traced with a fingerprint measure by GC-ECD / FID: a technical mixture of alkylated biphenyls and a technical mixture of phthalates within DINP and DIDP range (di-isononyl phthalate and di-isodecyl phthalate). The identification of individual substances was not obvious and led to probabilities in the laboratory report. But these are clearly technical mixtures as used in typical products for high-tension capacitors in microwave ovens (see paragraph 4.3). With that, the results of the GC-MS full scan analysis could be asserted. The quantification of these main components revealed that especially a very high amount of substituted biphenyls (18%) is found in capacitors from microwave devices. In opposition, the amount of phthalates is situated in the per thousand range.

Table 7 Quantification of main components in capacitors from microwave devices (bulk sample N° 4)

Substance Group	[mg/kg]
Sum of biphenyls: (substituted by 4 methyl groups at most)	180'000
Sum of DINP (di-isononyl phthalates) and DIDP (di-isodecyl phthalates)	2'150

4 Discussion on the Results

4.1 Uncertainties with the Sample Preparation

The varying results from the different laboratories on the same bulk sample for the PCB content approximate factor 10 with regard to N° 1 "mixture of large household appliances" and N° 6 "ballasts in fluorescent tube lamps". Even with a complex matrix, such as shredded old capacitors, this is, on principle, not acceptable. An overall survey was therefore set to clarify the causes of the differences and find out which results were the most reliable. Even an experienced PCB analyst could not find a concluding answer to the two questions as, among others, gaps occurred in the specifications for methods and quality assurance systems of the laboratories. Potential sources of error with reconditioning and splitting were identified in the three laboratories. Insufficient extraction yield may have caused the low values, while too high values can result from the unsatisfactory splitting of congeners, if, according to the standard, they are multiplied with the factor following LAGA. All in all, we must assume that the real PCB contents are situated in the middle of the ranges given by Table 5. The values derived for interpretation were calculated on the basis of these ranges. Anyway, for deriving conclusions, the analytical uncertainties are of minor significance.

For plausibility considerations and comparisons with analyses dating back about 20 years (BUWAL 1994), the number of PCB-containing capacitors was estimated from the PCB contents in Table 5. By assuming a PCB share of 40 % in PCB-containing capacitors (KTAG 1998) and an average weight for small capacitors reckoned according to the corresponding device category, we come to the absolute and percentual shares from the measured PCB contents of Table 8. It is a rough estimate, as these assumptions are not sufficiently secured statistically. In spite of this reservation, these results allow a comparison with studies performed in 1988 (BUWAL 1994). The decrease is significant for all the device categories. Moreover, both studies reveal that the highest shares in PCB-containing capacitors originate from device categories averaging the longest service life. Also this result is plausible.

Table 8 Calculated number of PCB-containing capacitors, compared with 1988

N°	Origin of Capacitors	Average Weight [g]	Number of Capacitors, Random Sample [–]	Number of PCB-Containing Capacitors [–]	Share [%]	Comparison BUWAL 1994[7] [%]
Large Household Appliances (LHA), Small Household Appliances (SHA)						
1	LHA mixture	150	2’767	10–114	0.4–4.1	8.4
2	Dishwashers	150	147	< 1	< 0.1	4.2
3	SHA mixture, without microwave devices	80	163	< 1	< 0.1	1.4
4	Microwave devices	225	222	< 1	< 0.1	–
5	Cooling and freezing appliances	100	1’480	< 1	< 0.1	0.5
6	Ballasts in fluorescent tube lamps	120	825	51–511	6.2–61.9	68.5
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)						
7	IT / CE: capacitors < 1 cm	10	2’100	< 1	< 0.1	2.5
8	IT / CE: capacitors 1–2.5 cm	20	16’100	3	< 0.1	
9	IT / CE: capacitors > 2.5 cm	40	3’125	8–15	0.3–0.5	
10	UPS	500	534	< 1	< 0.1	–

[7] Specimens of 1988, share calculated from subcategories

Table 9: Estimation of the PCB flows 2006 from small capacitors in diverse categories of waste electrical and electronic equipments

Device Category	Capacitors 2006[8] [t]	PCB Content [mg/kg]	PCB Flows 2006 [kg/a]
LHA	62	1'500–16'500	Ca. 90–1'020
SHA	51	350–440	Ca. 20
Fluorescent tube lamps	13	24'500–250'000	Ca. 330–3'330
Cooling and freezing appliances	1.5	5	0
IT/CE	33	1'080–1'900	Ca. 40–60
Total			Ca. 500–4'400

[8] The amount of capacitors per category has been estimated on the total; the amount of fluorescent tube lamps, however, is very uncertain.

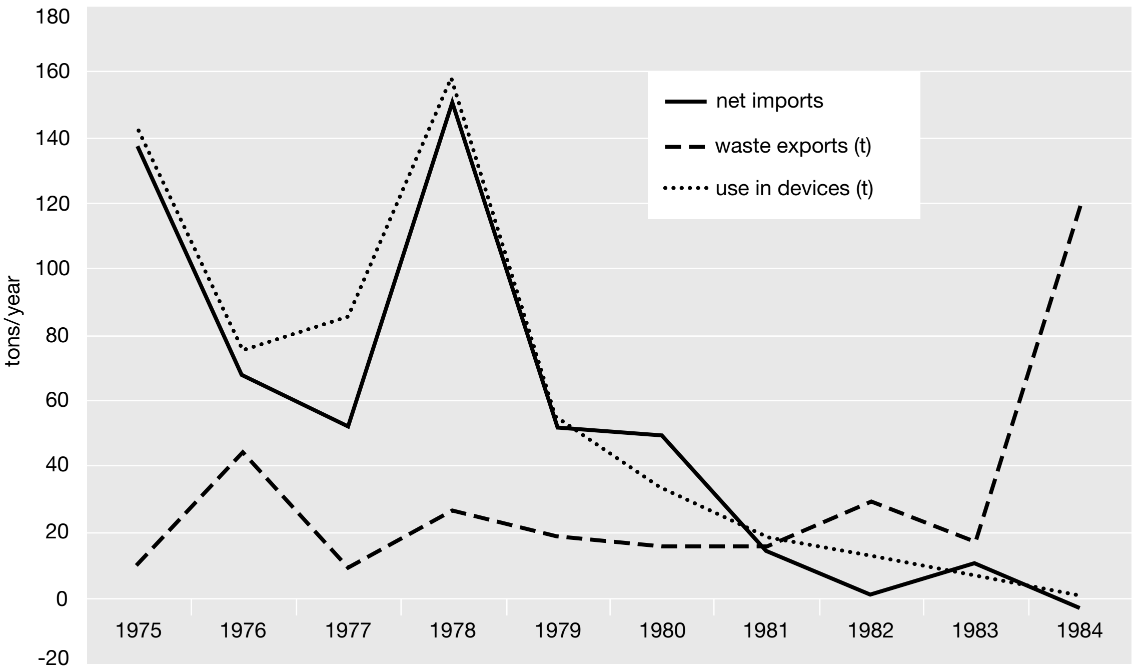
4.2 Annual PCB Flows

PCB values measured and yearly amounts of processed devices and capacitors allow the estimate of PCB flows from small capacitors in electrical and electronic equipments. Most notably, the amount of capacitors per category is evaluated, as the companies are not differentiating them according to the categories. The ranges shown in Table 9 come from the analytical uncertainties (see paragraph 4.1). Obviously, > 95 % of the PCB flow originates from large household appliances (90–1'020 kg/a) and ballasts in fluorescent tube lamps (330–3'330 kg/a). This annual flow of 500–4'400 kg/a from WEEE is to be related with flows in the environment and earlier consumption data. Distinctly lower PCB flows result from small household appliances, IT and CE. With regard to the very small PCB concentrations in capacitors from cooling and freezing appliances, this flow is insignificant. In Table 9, the annual PCB flows 2006 are compiled.

According to a study by the Swiss Federal Office for the Environment (BUWAL 1994), the total yearly atmospheric PCB deposition is rated 2'000–8'000 kg/a. For a major part, this deposition emanates from the remobilisation of already present environmental contaminations. Ballasts from fluorescent tube lamps, contaminated oils from motors, transformers and switches, contaminated floors in scrap treatment plants and former PCB users are cited as primary anthropogenic sources for a possible new entry. In this study, small capacitors from household appliances are considered as insignificant sources, and the load due to waste electronic equipment (IT/CE) is rated as minor.

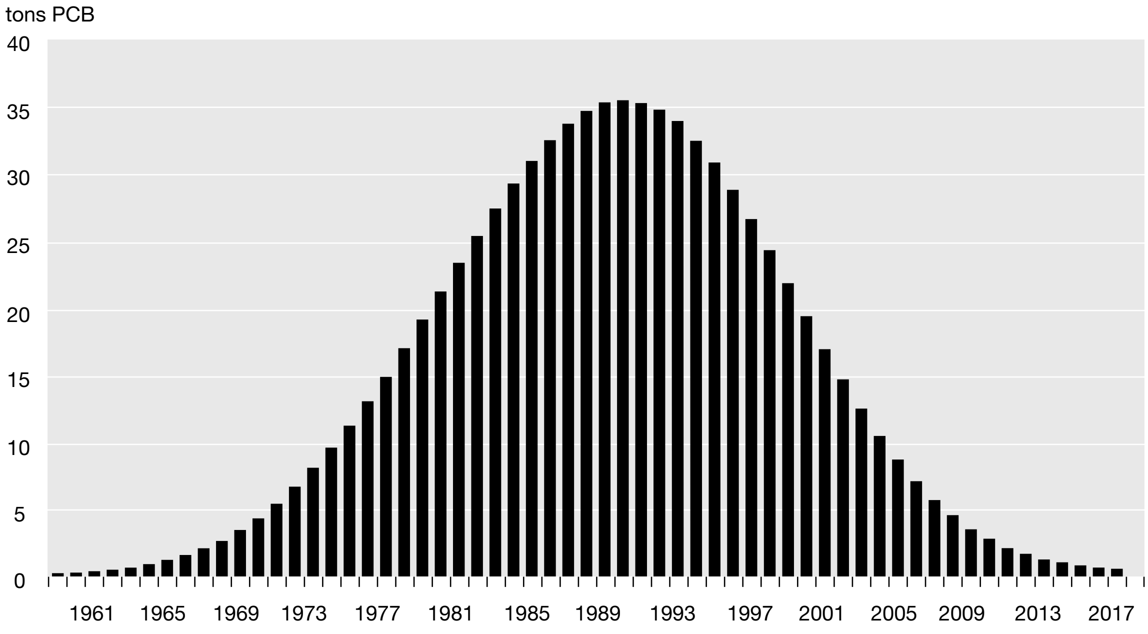
Basing upon official statistical enquiries, net imports, consumption figures and waste exports of PCB for Switzerland in 1975-1984 are registered in Fig. 3. The total consumption in the course of these 10 years ranged around 600 t. The latter are not including the imported small capacitors (BUWAL 1994). In this same study, the consumption of PCB's in ballasts in fluorescent tube lamps has been derived from German conditions. Thus, a yearly total averaging 50 t was supposedly used in the time span 1959–1980 for this purpose exclusively. In fluorescent tube lamps disposed of under control, approximate 5 % of the former consumption are supposed to be dealt with about 50 years later. Taking into account the fact that nearly 50 % of the capacitors in ballasts originate from the bulk sample between 1960 and 1980 (see Annex C), the calculated flow of 0.3–3 t/a is very small – a further indication that the largest share of fluorescent tube lamps is being disposed of uncontrolledly with the metal scrap. On 29.7.1983, the production of PCB-containing small capacitors was stopped (BUWAL 1994).

Fig. 3 Import and use of PCB's in Switzerland; small capacitors imported in devices are not covered by the statistical data (BUWAL 1994)



According to a PCB mass balance for Austria by the Umweltbundesamt (Austrian Federal Environment Agency UBA-AU 1996), the whole PCB inventory 1995 in closed systems amounted to 481–571 t. As rendered by this study, an essential share of the estimated stock inventory of 47–56 % is to be derived from small capacitors in devices and electronics. The annual emission potential in the year 2006 from old washing machines and fluorescent tube lamps is rated at 9'700 kg, with over 99 % of the capacitors coming from ballasts in fluorescent tube lamps. By considering the relative rejection rates, the annual emission potential was calculated from 1960 to 2020 (see Fig. 4).

Fig. 4: Annual potential level of PCB emissions in tons, from small capacitors in fluorescent tube lamps and washing machines – projections for Austria (UBA-AU 1996); error range 20 %



We may assume that the situation in Switzerland does not differ much from that in Austria. By converting the total annual flow 2006 in Austria proportionally to the Swiss population figure, we reach a PCB flow of approx. 8'500 kg/a from WEEE in Switzerland. Compared with Swiss consumption figures, circumstances abroad and former examinations, and in spite of the analytical uncertainties, the flows derived from the analyses are plausible.

4.3 PCB Substitutes

All matters and groups of substances identified qualitatively with the screening methods described under paragraph 3.3, are presented in Table 10. In most of the cases, larger groups of substances with a great number of individual matters are found, and these latter can vary considerably from each other. Interpretations must therefore be made with great reservations. As far as it is known, the substances are subdivided according to their functions in capacitors and labelled with the EU Classification Risk Phrases for Hazardous Substances. As a first priority, the official classification of hazardous matters was founded upon the Directive (1967/548/EWG). A list of the hazardous matters with their respective classification is given in Annex II of the present Directive. Hazard classifications for substances not included in this list can be found in safety data sheets from manufacturers or other databases, such as the IUCLID[9] Chemical Data Sheet.

Table 10: Overview of identified substance groups following capacitor samples with the marking of hazardous materials

Identified Substances and Substance Groups	Marking of Hazardous Materials		1 LHA MIxture	2 Dishwashers	3 SHA MIxture	4 Microwaves	5 Cooling and freezing appliances	6 Fluorescent Tube Lamps	7 IT / CE < 1 cm	8 IT / CE 1 – 2.5 cm	7 IT / CE > 2.5 cm	10 UPS Systems
	Official Annex II 67/548/CE	Other Sources										
Electrolytes, Solvents and Other Additives												
N,N, dimethylacetamide,	R20/21, 36, 40, 61									X	X	
(2-)hydroxybenzoic acid		R22, 37/38, 41								X		
Benzyl alcohol	R20, 22									X		
Dimethylbenzyl alcohol		R22, 36/37/38								X		
PCB Substitutes (Dielectrics)												
Naphthalene	R22, 40, 50/53		X	X	X					X	X	
Chlorinated naphtalene		R20/21/22, 36/37/38	X	X	X					X	X	
Dibutyl phtalates	R40, 50, 61, 62		X	X	X	X	X		X	X	X	
Diethyl phtalates			X	X	X	X	X		X	X	X	
Diethylhexyl phathalates	R40, 60, 61		X	X	X	X	X		X	X	X	
1,1-diphenyl ethan						X						
2,2'-dimethyl biphenyl						X						
Biphenyl, substituted (alkyled) biphenyls				X		X[10]	X				X	
Diverse hydrocarbons			X	X	X		X					X
Matters with Unknown Function												
(1-)methyl naphthalene		R22, 36/37/38, 42/43, 51/53			X							
Triphenyl phosphate		R50/53					X					
Hexabrom-benzene		R20/21/22/22, 36/37/38							X	X		
1,11-dibromoundecane						X						

[9] International Uniform Chemical Information Database
[10] Quantitative value: 18 % referring to capacitor weight

Regarding the PCB substitutes, a series of substance groups was found, also referred to, in literature, as dielectrics. As to the phthalates, present in almost all the samples, their origin is uncertain, as they may also be derived from softened PVC sheets or cable coatings. The results reflect a typical pattern of the situation after the prohibition of a universally appliable substance group, such as PCB's. A multitude of different substitutes is being used specifically, and that complicates the assessment of the hazard potential of small capacitors in WEEE.

It may be said, in general, that except for chlorinated naphtalenes, only substance groups obviously less persistent than PCB's are found. Referring to the environmentally hazardous or chronically toxic properties, there are, though, also substance groups featuring hazard potential properties. On the basis of these analyses, a risk assessment is, however, not possible, as more differentiated assessment strategies would have to be selected.

4.4 Electrolytes

With the chosen extraction methods, polar and oxidising electrolytes are, practically, not registered; mainly hydrophobic dielectrics were identified. We must assume that the electrolytes are, by a way of comparison, reactive and therefore degrading very quickly. According to the identifications in Table 10, the utmost probability resides in hydroxybenzoic acid as electrolyte. Based on the present study no statement can be made following the amounts and types of electrolytes in capacitors from WEEE. Due to the reactivity of electrolytes, the assumption arises that this design requires diverse additives like, for instance, corrosion protection additives which might have an environmental hazard potential.

5 Final Conclusions and Measures

5.1 Final Conclusions

From the results of the investigations into PCB content and further substances in small capacitors from electrical and electronic equipments, the following conclusions may be drawn:

- It may be assumed that already more than 99% of the PCB capacitors from WEEE, respectively, were disposed of.
- Small capacitors from ballasts in fluorescent tube lamps and typical mixtures of large household appliances are, as before, including relevant amounts of PCB's. About 6–60 % or 1–4 %, respectively, of these capacitors still contain PCB's. For the two device categories of 2006, the PCB emission potential represents about 400–4'300 kg/a.
- In lesser quantities, small capacitors from IT/CE (> 2.5 cm) show also a PCB flow. In 2006, the PCB flow adds up 40–60 kg/a, reaching about 1 % of the estimated total flow from electrical and electronic equipments.
- Also small capacitors in waste small household appliances hold PCB in small amounts. With about 20 kg/a, the PCB emission potential of 2006 is irrelevant.
- No PCB's could be traced in small capacitors from cooling and freezing appliances, IT/CE (< 2.5 cm), and from uninterruptible power supply systems. Their annual emission potential is also negligible.
- Small capacitors from microwave devices are as good as PCB-free. 18 % biphenyls and 0.2 % phthalates were identified in the samples.
- A GC-MS full scan analysis for identifying compounds and substance classes in the extracts revealed the presence of a large number of matters in most of the samples. Some of the identified compounds must be classified as environmentally hazardous or harmful to health. Simultaneously, most of the samples show increased PCB values and are to be considered, holistically, as hazardous for environment and health. Namely small capacitors from large household appliances (N° 1 and 2), small household appliances (N° 3), lamps (N° 6), IT/CE (N° 8, 9) are concerned.
- Analysing shredded small capacitors of highly varying designs is fastidious. Error sources and uncertainties are obviously important. The PCB content of the same bulk sample is varying much between the three specialised laboratories, notably with high concentrations around factor 10. The essential sources of error are to be looked for among the extraction methods and the splitting of congeners.

5.2 Recommendations

- All the appropriate measures must be taken at once to increase the controlled disposal of ballasts in fluorescent tube lamps, mainly from the B2B channel. It implies that capacitors are consequently removed from ballasts, also if solidly welded. Thereby, several dozen tons PCB's can be kept away from the environment.
- The Regulations and Directives of the system operators SENS and SWICO do not need to be modified regarding the removal of capacitors from electrical and electronic equipments. For the capacitors and the dimensional criterion, the rules in Annex II of the WEEE Directive also make sense. By way of precaution, they allow to avoid probably 10–20 tons per year of predominantly environmentally hazardous matters.
- When analysing PCB's in mixtures of old capacitors, the analytical methods require special attention. Control and quality assuring measures are essential with regard to the extraction of PCB's and the splitting of congeners. The values with PCB contents in old capacitor mixtures found in literature are to be interpreted with the appropriated precautions. Current imprecisions of ± 20–30 % may be exceeded considerably within this demanding matrix, especially in case of high concentrations.
- In a follow-up project, PCB substitutes and electrolytes are to be studied more specifically and quantitatively, following the origin of the capacitors and their category of devices. The results of the said follow-up project shall enable risk estimations and cost-utility considerations for the removal of capacitors.
- Due to the fact that the share of PCB-containing capacitors, the dielectrics used and the composition of the electrolytes are changing with time, the investigations should be repeated in a few years (follow-up analyses in 2010, for example), so as to grant a safe, wise handling of small capacitors from electrical and electronic equipments.

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Annex A: Summarized Results of the Analyses 2005 by Technical Control Bodies of SENS and SWICO

In 2005, the technical control bodies of SENS and SWICO studied the case of polychlorinated biphenyls (PCB's) in small capacitors. The study focussed on the sampling of eight varying types of small capacitors from electrical and electronic equipments, their preparation and analysis of PCB's and total chlorine concentration. Additionally, the composition of three capacitors from uninterruptible power supply systems (UPS) was examined by Empa St. Gall.

By means of a gas chromatograph with electron capture detector (ECD), the PCB's were determined, according to DIN 51'527, and rated by projection basing on factor 5 following LAGA. The total chlorine content was appraised according to DIN EN ISO 10'304.

It appears from the analyses that the PCB content of capacitors from printed wiring boards, power supply units, uninterruptible power supply systems, small household appliances (SHA) and lamps was situated under the detection limit (< 5 mg/kg) or approximating, for electrolyte capacitors, 6 mg/kg. Capacitors from large household appliances (LHA) reached a PCB content of 3'623 mg/kg.

By determining the total chlorine content, the chlorine in PVC was taken into account. Consequently, the results are undifferentiated and cannot be used for further interpretations.

The analyses performed by Empa St. Gall on the composition of three capacitors from uninterruptible power supply systems (see Table 12) did not reveal the presence of particularly toxic matters. As dielectrics in paper capacitors which, previously to 1984, often consisted of PCB's, the following substitutes could be identified:

Capacitors A: glycol derivate, totally absorbed by paper
Capacitors B: low volatile mineral oil, consistence resembling petroleum jelly
Capacitors C: dioctyl phtalate, diphenyl ethane and dimethyl diphenyl, thin fluid consistence

Table 11 PCB and total chlorine content of diverse capacitor types from waste electrical and electronic equipment

Device Categories / Components	Amount	Weight [g]	PCB's [mg/kg]	Total Chlorine [%]
Printed wiring boards, mid-size	200	2'580	< 5	1.20
Printed wiring boards, large	50	3'340	< 5	0.36
Power supply, small	400	2'040	< 5	0.68
Power supply, mid-size – large	40	760	< 5	0.51
UPS, mixed	50	600	< 5	0.92
Large electrical equipments	35	4'270	3'623	0.81
Elektrolyte capacitors	24	2'950	6	0.38
Small household appliances and lamps	25	2'709,5	< 5	0.10

Table 12 Composition of three capacitors from uninterruptible power supply systems (Empa St. Gallen, 2005)

Text	Capacitors A	Capacitors B	Capacitors C
Total weight, g	750	344	139
Aluminium casing, weight in g	110	60	41
Aluminium casing, share in %	15	17	29
Aluminium sheet, weight in g	330	105	31
Aluminium sheet, share in %	44	31	22
Plastic material etc., weight in g	320	140	40
Plastic material etc., share in %	43	41	29
Oil etc., weight in g	0	35	30
Oil etc., share in %	0	10	22

Annex B: Pictures of Supplied, Precrushed Capacitor Samples

Large Household Appliances (LHA), Small Household Appliances (SHA) and Cooling and Freezing Appliances

1 Large household appliances (LHA), mixed

2 Dishwashers (LHA)

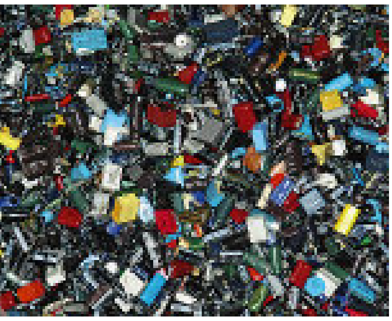
3 Small household appliances (SHA), mixed, without microwave devices

4 Microwave devices (SHA)

5 Cooling and freezing appliances

6 Ballasts in fluorescent tube lamps

IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)



Information technology and consumer electronics (IT/CE): capacitors < 1 cm

Information technology and consumer electronics (IT/CE): capacitors 1–2.5 cm

Information technology and consumer electronics (IT/CE): capacitors > 2.5 cm

Uninterruptible power supply systems (UPS)

Annex C: Characterization of the Bulk Sample "Capacitors from Ballasts in Fluorescent tube lamps"

In the table below, quantities and weights of the analysed capacitors from fluorescent tube lamps or ballasts for fluorescent tubes, respectively, are compiled:

Table 13 Sampling of capacitors from lamps; quantities and weights (campaign June – July 2007)

Company	Quantity apacitors	Weight Capacitors [kg]	Average Weight [kg]	Weight Lamps [kg]	Share Capacitors in Lamps [%]
Company 1	55	6.5	0.118	291	2.2
Company 2	318	38.0	0.119	880	4.3
Company 3	134	16.1	0.120	713	2.2
Total	**507**	**60.6**	**0.120**	**1884**	**3.2**

Compared to a previous study by the Cantonal Laboratory Aargau (Kantonales Labor Aargau), the average weight of the capacitors (0.120 g) is lower by about 65 %. Such a difference is probably due to a higher share of more recent and, thus, capacitors lighter in weight (see Fig. 5 and Fig. 6).

From the 507 collected capacitors, 239 (47 %) were individually characterized with the name of the manufacturer, model / type, production date, weight and specific declarations. But considering the state of the capacitors (damages, painting), not all of them could be categorised unambiguously. On the whole, 124 of the 507 examined capacitors (24 %) were designated as PCB-free. The average service life of capacitors from ballasts varies between 20 and 30 years (Kuhn and Arnet 2000). It may therefore be assumed that a significant share of PCB-containing capacitors is still in use.

Fig. 5 Distribution of the years of manufacture for the analysed capacitors from ballasts in fluorescent tube lamps

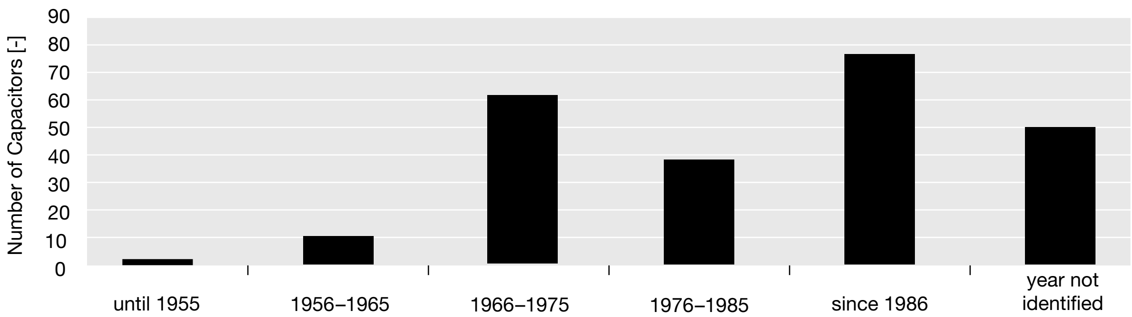
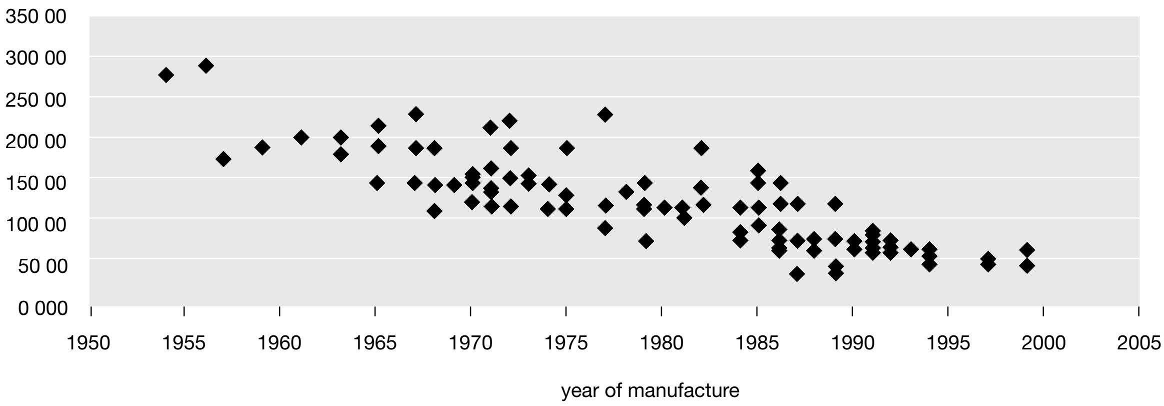


Fig. 6 Distribution of the weights of the analysed capacitors from ballasts in fluorescent tube lamps




+ Unterhaltung