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

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SENS®

SWICO recycling

SLRS

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Summary

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

In practice however, distinguishing between PCB-containing and PCB-free capacitors is difficult even for qualified personnel, as well as time and cost intensive, and therefore rarely done. As a consequence, the large majority of capacitors (> 2.5 cm) are removed from all WEEE categories, collected as PCB-containing capacitors and treated as hazardous waste. As a result, their disposal in a high-temperature incinerator is not only expensive, but also excludes the potential for material recycling of non-hazardous capacitors, largely due to a lack of a method of identification.

Thus, this investigation on "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 guarantee a safe and sustainable disposal of small capacitors. Especially, the occurrence of toxic and environmentally hazardous substances in small capacitors from electrical and electronic equipments is determined, and the consequences of a potential release of PCB emissions are estimated. The results shall provide a basis for decision-making, to reassess the treatment requirements for small capacitors and revise them as necessary.

For this study, capacitors from ten different product categories and types have been collected from different dismantling and recycling companies. The random samples collected totalled 1'482 kg of capacitors, 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 samples and, subsequently, further compounds or substance classes, were identified by means of a GC/MS Full Scan Analysis in the extracts. In the next step, a GC-ECD / FID Fingerprint Analysis and the quantification of the main components were performed exclusively on the capacitors from microwave ovens. 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 therefore quite demanding. The results of PCB measurements by three different, certified laboratories specialised in PCB analyses shows significant errors and uncertainties persist. In case of high concentrations, the PCB content of the same sample varies by approximately a factor 10. Main error sources are possibly "extraction methods" and "separation of congeners".

Table 1 PCB contents [mg/kg] as sum of 6 PCB congeners and its multiplication by LAGA Factor 5[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	Capacitive ballasts in FL* luminaries	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	–	–

* FL: fluorescent lamps

Small capacitors from capacitive ballasts in luminaries of fluorescent lamps (FL) and a typical mixture of large household appliances contain significant amounts of PCB's. About 6 – 60 % or 1 – 4 %, respectively of capacitors in these electrical and electronic equipment still contain PCB. The PCB emission potential of these two device categories in 2006 was 400 – 4'300 kg, and thus exceeded 95% of the total PCB load from waste electrical and electronic equipment. Small capacitors from information technology and consumer electronics (IT/CE) (> 2.5 cm) and small household appliances also contain a minor PCB contamination. However, in 2006, this fraction was fairly low, at approx. 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 in the atmosphere from Switzerland is estimated at 2'000 – 8'000 kg/a.

In the small capacitors from cooling and freezing appliances and IT/CE (< 2.5 cm), as well as uninterruptible power supply systems (UPS), no PCB's were found, and their annual PCB emission potential can be considered as negligible. Small capacitors from microwave devices are basically PCB-free. In these samples 18% biphenyls and 0.2% phthalates were identified.

Diverse naphthalenes, phthalates and substituted biphenyls were identified as PCB-substitutes. The origin of the phthalates is uncertain, as they might originate from plasticized PVC sheets or cable sheathings. They are present in almost all the samples. But generally, we may say that, except for chlorinated naphthalenes, only substance groups significantly less persistent than PCB's were identified.

Polar and oxidizing electrolytes were virtually undetected with the chosen extraction methods, and mainly hydrophobic dielectrics were identified. However, we must bear in mind that electrolytes are comparatively reactive and therefore disintegrate very quickly. Therefore, with regard to the amounts and the types of electrolytes in capacitors from WEEE, the present study does not allow assertions.

Based 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, in order to increase the controlled disposal of capacitive ballasts in FL luminaries, primarily from the B2B channel. The capacitors from capacitive 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 changed. Diffuse emissions of probably 10-20 t per year of predominantly environmentally hazardous substances can, thus, be avoided.
- When determining PCB's in mixtures from capacitors, the chemical analysis requires utmost attention. Control and quality assurance measures should be applied to the extraction of PCB's and the separation of congeners.
- In a follow-up project, PCB substitutes and electrolytes will be analysed more specifically and quantitatively, according to the origin of the capacitors and with regard to the category of the devices.
- As the share of PCB-containing capacitors, used dielectrics and the composition of electrolytes will evolve with time, such analyses should be repeated in a few years (e.g. in 2010), in order to ensure safe and reasonable handling of small capacitors from electrical and electronic equipments.

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

1 Initial Situation and Target

1.1 Capacitors and Environment

Small capacitors are passive electrical components and found in many electro technical devices. In electrical and electronic equipment, they serve as energy and charge storage devices, frequency dependent impedances, converters or sensors. A capacitor consists of two electrically conducting surfaces, i.e. the electrodes, mostly separated by a small gap. The gap is filled with an isolating dielectric, which may be solid or liquid. In case one of the electrodes is formed by a conducting liquid, it is referred to an electrolytic capacitor. The dielectric in an electrolytic capacitor is aluminium oxide (Al_2O_3) or tantalum oxide (Ta_2O_5) which is generated in a chemical reaction between electrodes and electrolytes. Common designs are roller-type capacitors (i.e. paper sheet, plastic sheet, metal paper and electrolytic capacitors), mass capacitors (i.e. ceramic and electrolytic capacitors) and layered capacitors (Hentschel 2000).

Due to the electrically 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 prohibited in 1986. Internationally, the production and application of PCB's was banned, first in open systems in 1978 and then completely 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, their environmental hazard cannot be excluded. In Al capacitors, organic carbonic acids – heavily toxic and corrosive (Baumann 2005) – are frequently used as electrolytes. These electrically conductive substances 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)[2]. The Swiss regulations make a distinction 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 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 ‚other wastes which are subject to control' (Waste Code: 16 02 16 [ak]).

Annex 2 of the European WEEE Directive (EU 2002) stipulates the removal from equipment and a separate disposal of PCB-containing capacitors and electrolyte capacitors (height > 25 mm; diameter > 25 mm or proportionally similar volumes) containing environmentally relevant substances. The European Waste Catalogue also classifies these capacitors as hazardous waste. However, for PCB-free capacitors the WEEE Directive does not stipulate any binding regulation.

The Swiss system operators SENS and SWICO, responsible for the disposal of electrical and electronic equipments, also require treatment of small capacitors in accordance with Swiss and European standards. Based on the definition in Annex 2 of the WEEE Directive, all the PCB-containing and electrolyte capacitors should be removed from the equipment and disposed of separately.
However, in practice, a differentiation between PCB-containing and PCB-free capacitors is difficult even for qualified personnel and prohibitively cost and time intensive, and therefore rarely done. A handy manual (KTAG 2004) for identifying PCB-free capacitors is incomplete and contains uncertainties. Therefore in practice, almost all capacitors are removed from every equipment category, assigned to the PCB-containing capacitors and treated as hazardous waste (Waste Code: 16 02 09 [S]), in agreement with the VeVA Waste Catalogue (VEVA a 2005; VEVA b 2005).

1.3 Previous Analyses

Of the many PCB analyses of small capacitors only the most important publications, especially with reference to the Swiss context are cited below.
In 1988, small capacitors from a total of 2'400 appliances, differentiated according to 17 categories, were analysed for their PCB contents. PCB-containing capacitors were found in an average of 20 % of the appliances (0–70%) (Barghoorn 1988, cited in BUWAL 2004).
A study in 2003 on the average material composition of small electrical and electronic waste equipment revealed that the average PCB concentration was 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 in today's obsolete equipment and on the other hand, that the PCB content in capacitors from various equipment categories or components varies substantially and can partly be very low. In capacitors from small equipment (IT/CE and SHA), very low values were determined, while in capacitors from large household appliances (LHA) high PCB values were measured (samples were not representative).

1.4 Objectives

The present study should provide additional knowledge in order to guarantee a safe and sustainable handling of small capacitors. Particularly, the potential quantities of hazardous substances in small capacitors from electrical and electronic equipments are to be identified and assessed. The results shall serve as a decision-making basis, in order to review the treatment requirements for small capacitors and, if needed, to revise them. The following aims have been defined in detail:

1. Differentiated sampling among various categories and types of equipment and representative sampling of small capacitors from electrical and electronic equipment.
2. Analysis of the PCB content in small capacitors from various categories and types of equipment.
3. Extension of the analyses to identify compounds or substance classes in the above samples (identification of possible PCB substitutes and electrolytes).
4. Formulation of measures and recommendations regarding the handling of small capacitors from waste electrical and electronic equipment, based on the results.

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

2 Sampling and Sample Preparation

2.1 Sampling

A sample of capacitors from various categories and types of equipment was collected from dismantling facilities of 13 recycling plants. The analysed categories or types of equipment and the amount of capacitors removed are shown in Table 2.

The capacitors were removed from the equipment between June and August 2006, and the total amount of all random samples was 1'482 kg, which corresponds to about 1.2 % of all capacitors removed from WEEE in 2006 in Switzerland. The various recycling companies represent different collection areas and consumer segments.

The capacitor sample size was selected to be equivalent to be at least 1% of the annually processed quantity. Table 3 shows the sample size in relation to the yearly processed quantities in the respective categories (2006). The estimates on the share of capacitors within an equipment category are based on random sample analyses or batch tests. For cooling and freezing appliances and IT/CE equipment, more than one per cent of the annual quantity could be sampled, for LHA's 0.7%, FL luminaries 0.5% and SHA's merely 0.2%. The quantity of processed uninterruptible power supply (UPS) systems is not accounted for in the material flow compilation of SENS and SWICO. Hence, there are no indications about the processed quantities.

It is assumed that a large part of the FL luminaries is not collected by the collective systems and is ending directly as scrap metal. According to the Swiss Lighting Recycling Foundation (SLRS) about 1.5 million FL luminaries were sold in 2006. Assuming an average weight of 3.7 kg per FL luminary (see Annex C), this would correspond to a total weight of 5'570 t. However, in the same period, only 420 t luminaries (FL luminaries and other luminaries) were processed within the collective systems.

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	Capacitive ballasts in FL luminaries[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 sampling campaigns: June – August 2006 (38 kg) and June – July 2007 (61 kg)

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

Fig. 2 Splitting and reduction of samples by means of „coning and quartering" 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	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[4]	10'673	26	**0.2**
FL luminaries	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.[5]	n.d.	n.d.	**n.d.**

[4] 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
[5] n.d.: no data available

The capacitor samples collected separately for each equipment category were visually screened for their category (plausibility check) and for the presence of interfering materials / items. It may be assumed that the separation according to the equipment categories was done reliably. Annex B presents the supplied or coarsely shredded capacitors, respectively. The number of capacitors, the manufacturers or other product data were collected only for sample Nr 6 "capacitive ballasts in FL luminaries" Considering the very high quantities (about 30'000 small capacitors), such cost and time consuming compilations for all other samples was not undertaken.

2.2 Sample Preparation

The shredding of the collected small capacitors occurred in a fine shredder (sieve 12 mm or 8 mm, respectively, for the IT/CE sample < 1cm). After every batch, the shredder was dry cleaned and eventual residues removed with toluene. As a further measure to avoid carryover, a forerun of about 10 % of the input was practised in every case and not used for the sample concerned.

After shredding, the sampled quantity was reduced to about 2 kg by means of conical heap method (coning and quartering). Further preparations and analyses were done in the laboratory.

3 Laboratory Analyses

3.1 Procedure

Neither are standardised preparation and identification methods for the handling of shredded small capacitors established, nor are laboratories experienced in specialised analysis of PCB in a 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 the appropriate homogenisation, sub-sampling and extraction method.

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

3.2 PCB Analysis

The preparation of the heterogeneous samples, the separation of the congeners and the identification were handled differently by the three analytical laboratories. Table 4 illustrates the essential differences. Measuring inaccuracies are estimated 20 – 25 % or 20 – 30 % respectively by the laboratories. The results of the analyses are shown in Table 5, with the figures rounded off within < 1 %. In case of high PCB contents, the values of the different laboratories vary significantly, sometimes even by a factor of 10.

Table 4 Differences in the preparation of 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[6] 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	Capacitive ballasts in FL luminaries[7]	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	–	–

[6] Ballschmiter congeners 28, 52, 101, 138, 153, 180

[7] 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 were identified in the extracts with a GC-MS Full Scan Analysis. The results are compiled in Table 6. These are qualitative analyses using 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 most of these substance classes contained 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	Capacitive ballasts in FL luminaries	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 cya-nide, butoxyethoxy-ethyl acetate, biphenyls, chlorinated naphtha-lene, phthalates
10	UPS	hydrocarbons

3.4 GC-ECD / FID Fingerprint Analysis

Sample N° 4 "microwave devices" was subject to a more sophisticated analysis, in order to allow more precise statements on the dielectrics and electrolytes used after the PCB prohibition. The samples were prepared so as to allow individual identifications and quantification within the substance classes. 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 is not unambiguous and is expressed with probabilities in the laboratory report. However these are clearly technical mixtures as used in typical products for high voltage 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 used in microwave devices. The amount of phthalates is in the range of ppt (parts per thousand).

Table 7 Quantification of main components in capacitors from microwave devices (sample Nº 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 results from the different laboratories on the same sample vary by approx. a factor 10 for the PCB content in sample N° 1 "mixture of large household appliances" and N° 6 "capacitive ballasts in FL luminaries". Such a spread is unacceptable even with a matrix as complex as shredded old capacitors. An investigation was therefore initiated to clarify the causes for these differences and find out which results were the most reliable. However, even an experienced PCB analyst could not find a concluding answer to these questions as, among others, the specifications for the applied methods and the quality assurance systems of the laboratories were incomplete. Potential sources for errors with conditioning and splitting of the samples 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 they are multiplied with the LAGA-factor according to the standards. All in all, we must assume that the actual PCB contents are situated in the middle of the ranges given by Table 5. The values derived for interpretation were calculated based on these ranges. For the conclusions, the analytical uncertainties are, however, 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 content of 30 % in PCB-containing capacitors (KTAG 1998) and an average weight for the capacitors according to the corresponding device category, we come to the absolute and relative 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 of the average share of PCB-containing capacitors is significant for all the device categories. Moreover, both studies reveal, plausibly, that the highest shares of PCB-containing capacitors originate from device categories averaging the longest service life.

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[8] [%]
Large Household Appliances (LHA), Small Household Appliances (SHA)						
1	LHA mixture	150	2'767	14–152	0.5–5.5	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	Capacitive ballasts in FL luminaries	120	825	67–681	8.1–82.5	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	11–20	0.4–0.6	
10	UPS	500	534	< 1	< 0.1	–

[8] 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[9] [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

[9] The amount of capacitors per category has been estimated on the total; the amount of FL luminaries, however, is very uncertain.

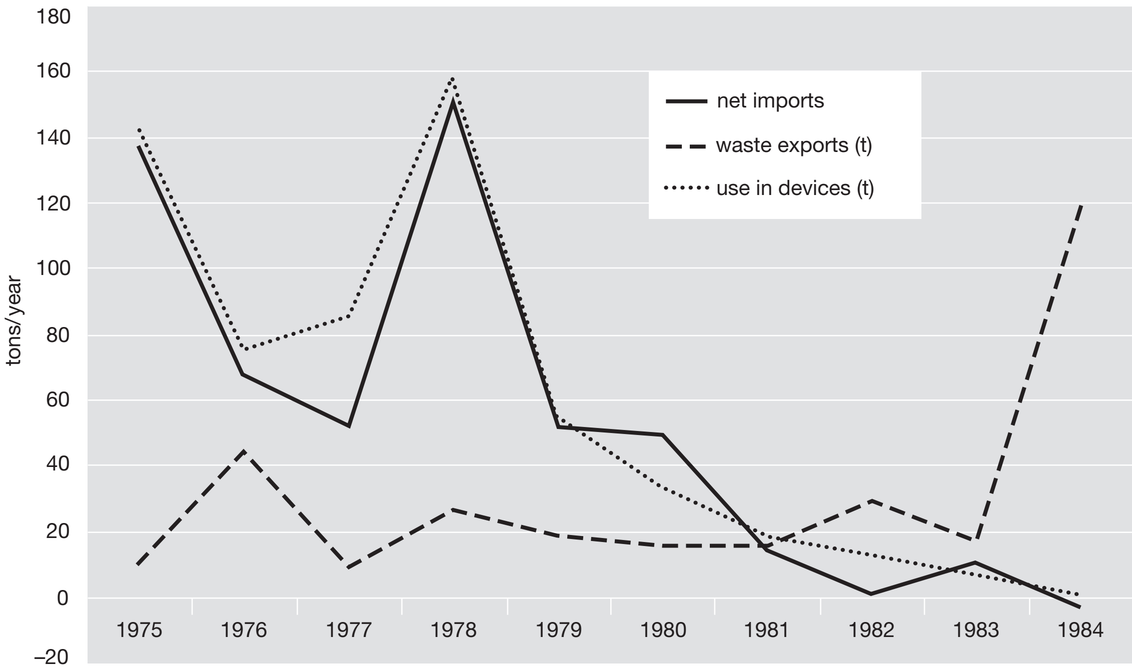
4.2 Annual PCB Flows

Annual PCB flows from small capacitors in electrical and electronic equipments were derived from the measured PCB contents and annual massflow statistics of processed devices. The amount of capacitors per category is estimated since the companies are not differentiating them according to the categories in the statistical data. The ranges of the annual PCB flows shown in Table 9 result 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 capacitive ballasts in FL luminaries (330 – 3'330 kg/a). 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. The total annual flow of 500 – 4'400 kg/a from WEEE is to be related with flows in the environment and earlier consumption data.

According to a study by the Swiss Federal Office for the Environment (BUWAL 1994), the total yearly atmospheric PCB deposition is estimated to be 2'000 – 8'000 kg/a. For a major part, this deposition emanates from the remobilisation of already present environmental contaminations. Capacitive ballasts in FL luminaries, 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 the BUWAL 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.

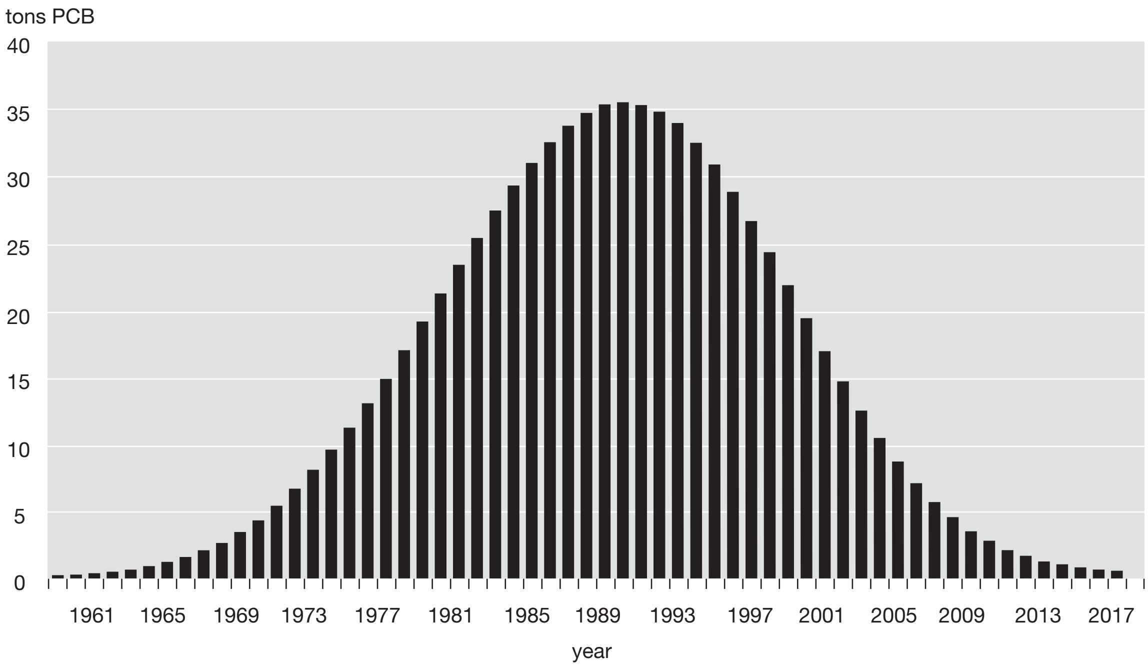
Based upon official statistical enquiries, net imports, consumption figures and waste exports of PCB for Switzerland in 1975-1984 are presented in Fig. 3. The total consumption in the course of these 10 years ranged around 600 t. However, imported small capacitors are not included in the statistical data (BUWAL 1994). In the same study, the consumption of PCB's in capacitive ballasts in FL luminaries has been derived from conditions in Germany. Thus, a yearly total averaging of 50 t was supposedly used in the period of 1959–1980 exclusively for this purpose. Taking into account the fact that in this study at hand nearly 50% of the capacitors from capacitive ballasts in FL luminaries originate from the sample between 1960 and 1980 (see Annex C), the calculated flow of 0.3 – 3 t/a is very small – an indication that the largest share of FL luminaries is being disposed of uncontrolled together with 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; PCB's in 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 of PCB in the year 2006 from old washing machines and FL luminaries is rated at 9'700 kg, with over 99 % coming from capacitive ballasts in FL luminaries. By considering the relative rejection rates, the annual emission potential was calculated for the period from 1960 to 2020 (see Fig. 4).

Fig. 4: Annual potential level of PCB emissions in tons, from capacitive ballasts in FL luminaries 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[10] 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[11]	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						

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

Regarding the PCB substitutes, a series of substance groups was found which are also in literature mentioned as dielectrics. The phthalates, present in almost all the samples, are of uncertain origin, as they may also be derived from softened PVC sheets or cable sheaths. The results reflect a typical pattern of a universally applicable substance group, such as PCB's, after its prohibition. A multitude of different substitutes is being used after the prohibition, which complicates the assessment of the hazard potential of small capacitors in WEEE.

In general it may be said, that except for chlorinated naphthalenes, only substance groups obviously less persistent than PCB's are found. There are, though, also substance groups with potentially environmentally hazardous or chronically toxic properties. However, based on these analyses, a risk assessment is not possible, as more differentiated assessment strategies would have to be selected.

4.4 Electrolytes

As a result of the extraction methods used, polar and oxidising electrolytes were barely registered; with mainly hydrophobic dielectrics being identified. We must bear in mind that electrolytes are comparatively more 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 in Switzerland already more than 99% of PCB capacitors from WEEE were disposed of.
- Small capacitors from capacitive ballasts in FL luminaries and typical mixtures of large household appliances still contain significant amounts of PCB's. About 6–60% or 1–4%, respectively, of these capacitors still contain PCB's. For the two device categories the PCB emission potential in 2006 represents about 400–4'300kg/a.
- In lesser quantities, small capacitors from IT/CE (> 2.5cm) show also a PCB flow. In 2006, the PCB flow adds up 40–60 kg/a, reaching about 1% of the estimated total PCB flow from WEEE.
- Also small capacitors in end-of-life small household appliances hold PCB in small amounts. At about 20kg/a in 2006, the PCB emission potential is negligible.
- 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 (UPS). 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 substances 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, in general, as hazardous for environment and health. Namely small capacitors from large household appliances (N° 1 and 2), small household appliances (N° 3), FL luminaries (N° 6), IT/CE (N° 8, 9) are concerned.
- Analysing shredded small capacitors of highly varying matrices is demanding. Error sources and uncertainties are obviously important. The PCB content of the same sample, notably with high concentrations, is varying by approx. a factor 10 between the three specialised laboratories. The essential sources of error are to be looked for among the extraction methods and the splitting of congeners.

5.2 Recommendations

- All appropriate measures should be taken immediately, in order to increase the controlled disposal of capacitive ballasts in FL luminaries, primarily from the B2B channel. The capacitors from capacitive ballasts must thereby be removed systematically, also if solidly welded in. Thereby, several dozen tons of PCB spill to the environment can be avoided.
- Regarding the removal of capacitors from electrical and electronic equipments, the regulations and guidelines of the system operators SENS and SWICO should not be changed. Fugitive emissions of probably 10–20 t per year of predominantly environmentally hazardous substances can, thus, be avoided.
- When determining PCB's in mixtures from capacitors, the chemical analysis requires utmost attention. Control and quality assurance measures should be applied to the extraction of PCB's and the separation of congeners. The values with PCB contents in old capacitor mixtures found in literature are to be interpreted with the appropriated precautions. Current imprecision 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 will be analysed more specifically and quantitatively, according to the origin of the capacitors and with regard to the category of the devices. The results of such a follow-up project shall enable risk estimations and cost-utility considerations for the removal of capacitors.
- As the share of PCB-containing capacitors, the dielectrics used and the composition of electrolytes will evolve over time, the analyses should be repeated in a few years (e.g. in 2010), in order to ensure safe and sustainable 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. Gallen.

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 luminaries 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. Gallen 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 uninterruptuble 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)

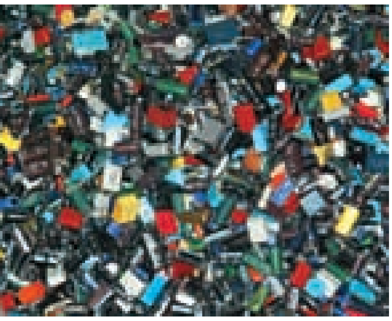
3 Small household appliances (SHA), mixed, without microwave devices

4 Microwave devices (SHA)

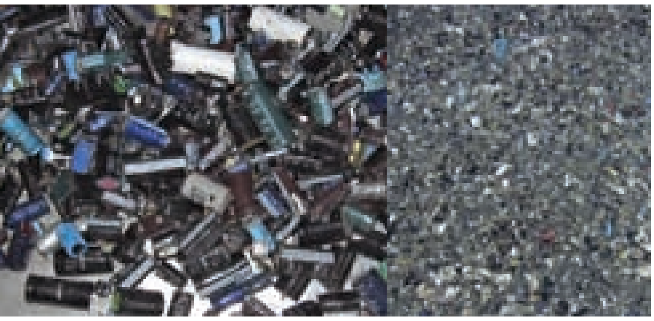
5 Cooling and freezing appliances

6 Capacitive ballasts in FL luminaries

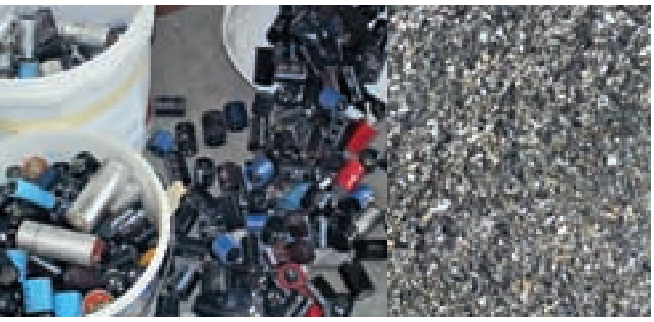
IT (Information Technology) / CE (Consumer Electronics) / UPS (uninterruptible power supply systems)



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 FL Luminaries”

In the table below, quantities and weights of the analysed capacitors from capacitive ballasts in FL luminaries are compiled:

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

Company	Quantity capacitors	Weight Capacitors [kg]	Average Weight [kg]	Weight FL Luminaries [kg]	Share Capacitors FL Luminaries [%]
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 capacitive 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 capacitive ballasts in FL luminaries

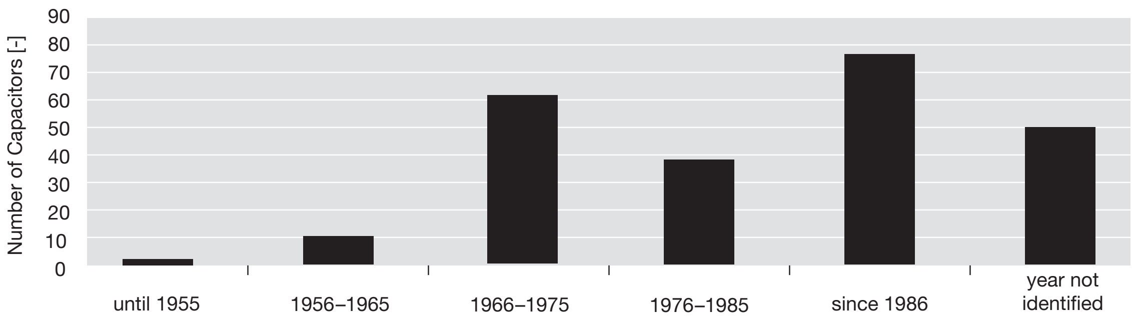


Fig. 6 Distribution of the weights of the analysed capacitors from capacitive ballasts in FL luminaries