Supporting information

Potential and recycling strategies for LCD panels from WEEE

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1. S1 Use of indium

Indium has a wide range of applications in electronic equipment as a semi-conductive material and is also found in metals and alloys, as well as in specialty products [1]. Between 50% and 70% of available indium is used to produce transparent electro-conductive thin films, named indium tin oxide (ITO) films [2,3]. About 20 to 30% is used for semi-conductors, applied in LED and solar panels (CIGS)[3].

ITO as a main application of indium is an In-Sn compound and consists of indium oxide and tin oxide. The transparent ITO layer is a fundamental component in liquid crystal displays (LCD), which are applied in almost all screen devices like computer monitors, notebooks, mobile phones, television sets, etc. [4,5].

The worldwide reserves of indium amount to around 16,000 t [6]. In 2014, the main producers were China, with over 50% of the worldwide mine output, followed by Korea, Japan and Canada [7]. Indium mostly originates as a by-product of the mineral sphalerite, which is a zinc-sulfide ore. The indium concentration in this ore is only between 10 and 20 mg/kg [8]. In 2011, 1,220 t indium was primary mined worldwide, from which 660 t indium was refined [3]. In recent years, the output of refined indium increased to 800 t in 2013 and 820 t in 2014 [7].

In 2011, about 360 t (~55 %) of this virgin indium went into ITO production. Interestingly, this process needed in total about 1,500 t indium. The difference is explained by new scrap recycling, which circulates back 1,140 t to the beginning of the ITO production process. Approximately 170 t indium is stocked in this highly efficient recycling cycle, which takes about one month to complete, resulting in a significant flow over a whole year. Nevertheless, ITO production is related to high a loss of about 300 t. Further processing of the semi-finished products account for an additional loss of 20 t. [3]

2. S2 Current recycling practice

Currently, recycling of indium from EOL devices is not yet carried out on an industrial scale [4,32,37,41]. Practical recycling of indium is conducted in the production of semi-finished and intermediate products only. Quantitatively relevant recycling from new scrap takes place in the production of “ITO targets” and “electr. semi-conductors” (cf. figure 1 in main text).

2.1. ITO targets

The processes used for the production of ITO targets are highly inefficient. Only 10% of the ITO is successfully applied on the substrate, while about 20% is lost on the surfaces of tools and working chamber linings. 70% is transferred to a residual material, which is subsequently recycled with high efficiencies (>90 %). Other new scrap from the further processing of ITO targets is also assumed to be recycled in the same process. [7,36,37]

The recycling processes for sputtering and etching residues are mainly based on hydrometallurgical approaches. Solvent extraction is the most commonly used method for the purification of indium in process metallurgy. Initially introduced in zinc refineries, it is used to recover indium from sulfate solutions [22,38]. Besides this highly solvent consuming process, electrolytic refining can be applied subsequently [39].

Alternative methodologies have been tested in recent years. One example is the recovery of indium from pure indium oxide using vacuum carbon reduction, which represents a vacuum metallurgy approach. Here, indium could be selectively recovered by using coke coal as a reducing agent [26].

2.2. Electr. semi-conductors

The production of semiconductors and electrical components used for laser diodes, solar cells and LED are also associated with high losses. Here, only 30% of the indium used is applied to end products.

About 50% is lost completely in the production of solar panels. In the production of LED and laser diodes, over 23% is lost, while 47% constitutes new scrap which can be recycled. Here, the same recovery efficiencies were assumed as for the recycling of ITO targets as most probably the same recycling processes were used. [7]

3. S3 Share polarizer foils and glass substrate in LCD panels

Table 1: Share of the main components polarizer foils and glass substrate in LCD panels from various screen devices

Equipment type	UNU key	Number of samples [-]	Share polarizer foil [%]	Share glass substrate incl. ITO and organics [%]
Mobile phone	0306-01	11	21.3 ± 3.5	78.6 ± 3.2
Smartphone	0306-02	27	18.3 ± 10	81.7 ± 10
Notebook	0303-01	18	13.9 ± 3	86 ± 3
PC Monitor	0309-01	11	15.6 ± 1.6	83.3 ± 1.6
LCD TV	0408-01	9	20.6 ± 3.5	79 ± 3.1
Tablet	0303-02	26	23.6 ± 7.6	76.4 ± 7.6

4. S4 Indium and tin mass fractions in LCD panels

Table 2: Indium in ppm and mg/m² and tin in ppm as average including standard deviation for various investigated screen devices

Equipment type	UNU key	Number of samples [-]	Indium [ppm]	Indium [mg/m²]	Tin [ppm]
Mobile phone	0306-01	11	330 ± 198	817 ± 612	24 ± 12
Smartphone	0306-02	27	25 ± 20	56 ± 50	2 ± 3
Notebook	0303-01	18	134 ± 95	558 ± 372	11 ± 4
PC Monitor	0309-01	11	172 ± 24	689 ± 81	10 ± 1
LCD TV	0408-01	9	166 ± 66	642 ± 293	18 ± 7
Tablet	0303-02	26	176 ± 93	438 ± 367	16 ± 10

Note: ppm describes the relative share of indium to the mass of the LCD panel, while mg/m² relates to an indium mass as a function of a normalized cross sectional area

5. S5 Indium in ppm vs. screen size

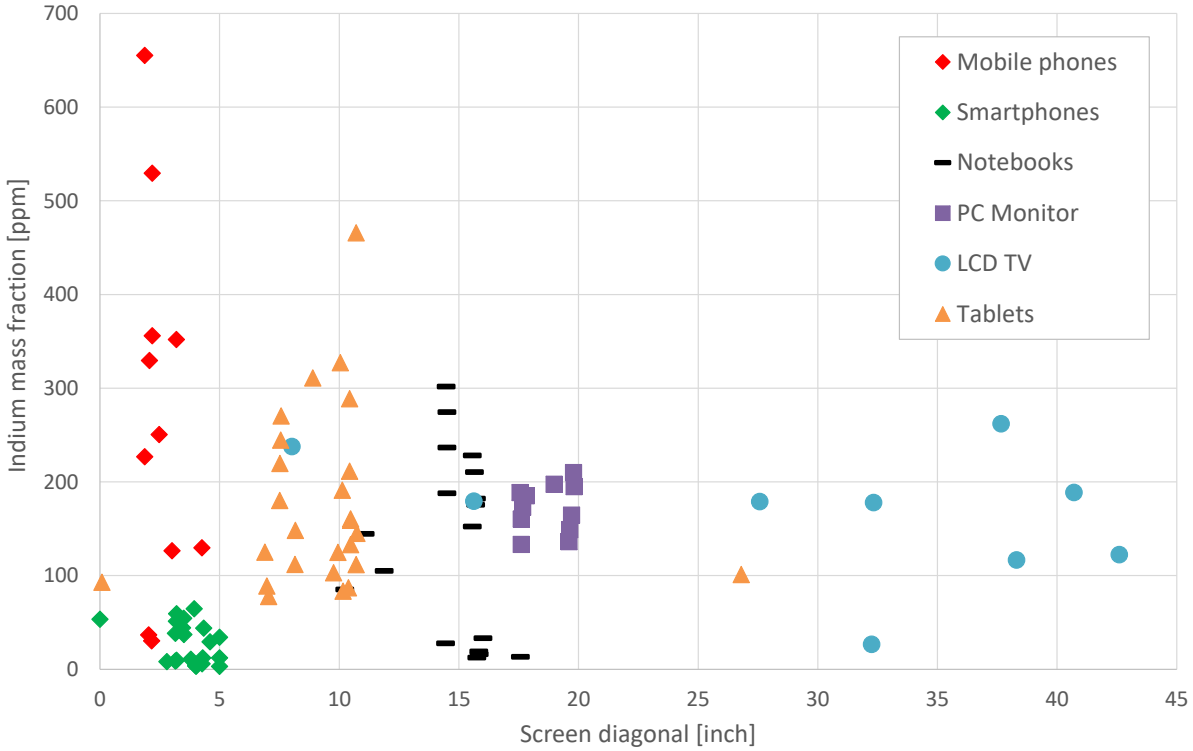

Figure 1: Indium mass fraction vs screen size (diagonal)

6. S6 Indium in mg/m² vs. screen size

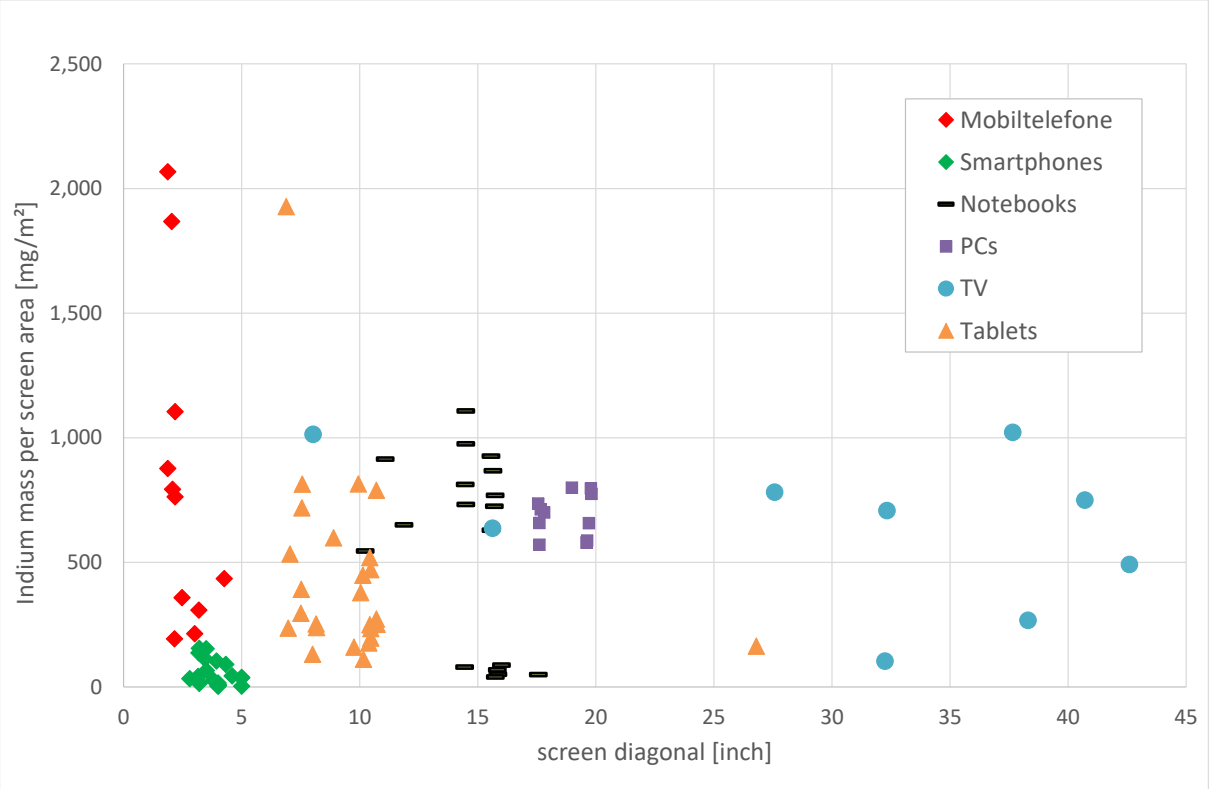

Figure 2: Indium mass in mg per screen are in m² versus the screen size in inch

7. S7 Time trend in the application of Indium

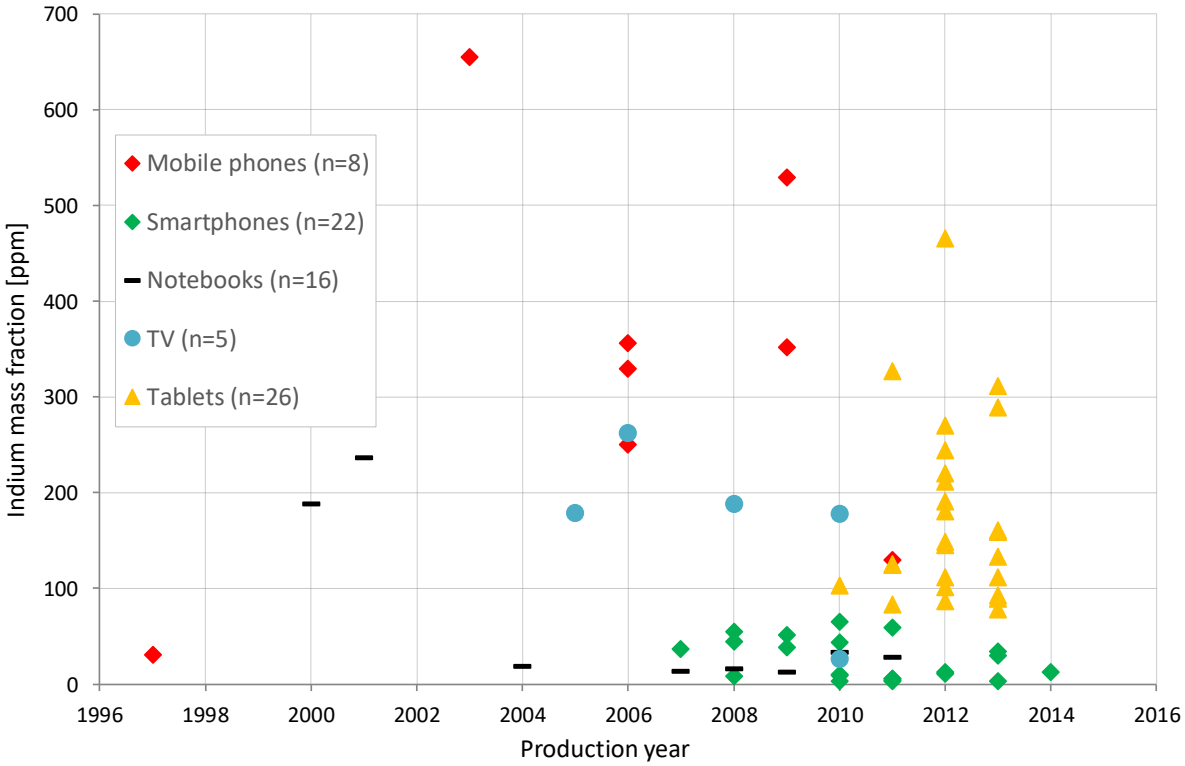

Figure 3: Indium mass fraction vs production year of panels from various screen devices investigated

8. S8 Share of investigated LCD panels in which toxic heavy metals+ Sr were qualitatively determined

Not all elements were detected in all equipment types nor in all panels investigated in any relevant equipment group. Table 3 shows the share of LCD panels in which toxic heavy metals + Sr were determined. Each screen device investigated is depicted separately.

Table 3: Share of LCD panels investigated in which toxic heavy metals + Sr were qualitatively determined for each equipment type (0 % = element not found in any LCD investigated; 100 % element present in all LCD panels investigated in this equipment type)

Equipment type / Element	**Mobile phones n=27**	**Smartphones n=27**	**Tablets n=26**	**Notebooks n=18**	**PC monitor n=10**	**LCD TV n=5**
	0306-01	0306-02	0303-02	0303-01	0309-01	0408-01
	all values in %					
As	23	7	0	78	90	20
Sb	92	70	88	72	100	60
Sr	100	100	100	100	100	100
Pb	0	4	0	11	0	0
Cr	0	0	0	0	0	0

9. S9 Mass fractions of toxic heavy metals + Sr

9.1. LCD from mobile phones (0306-01)

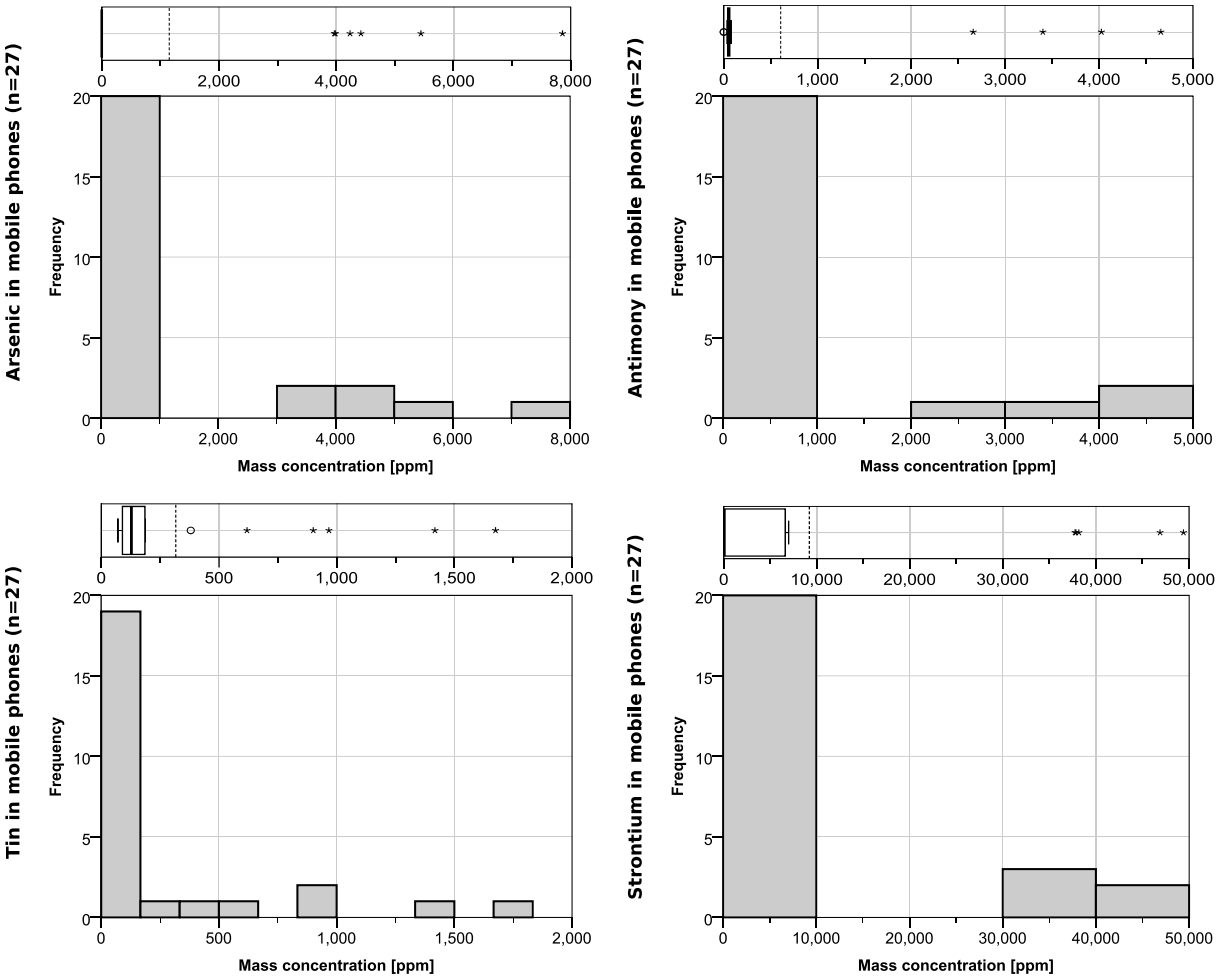

Figure 4: Arsenic, antimony, tin and strontium in mobile phone LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

9.2. LCD from smartphones (0306-02)

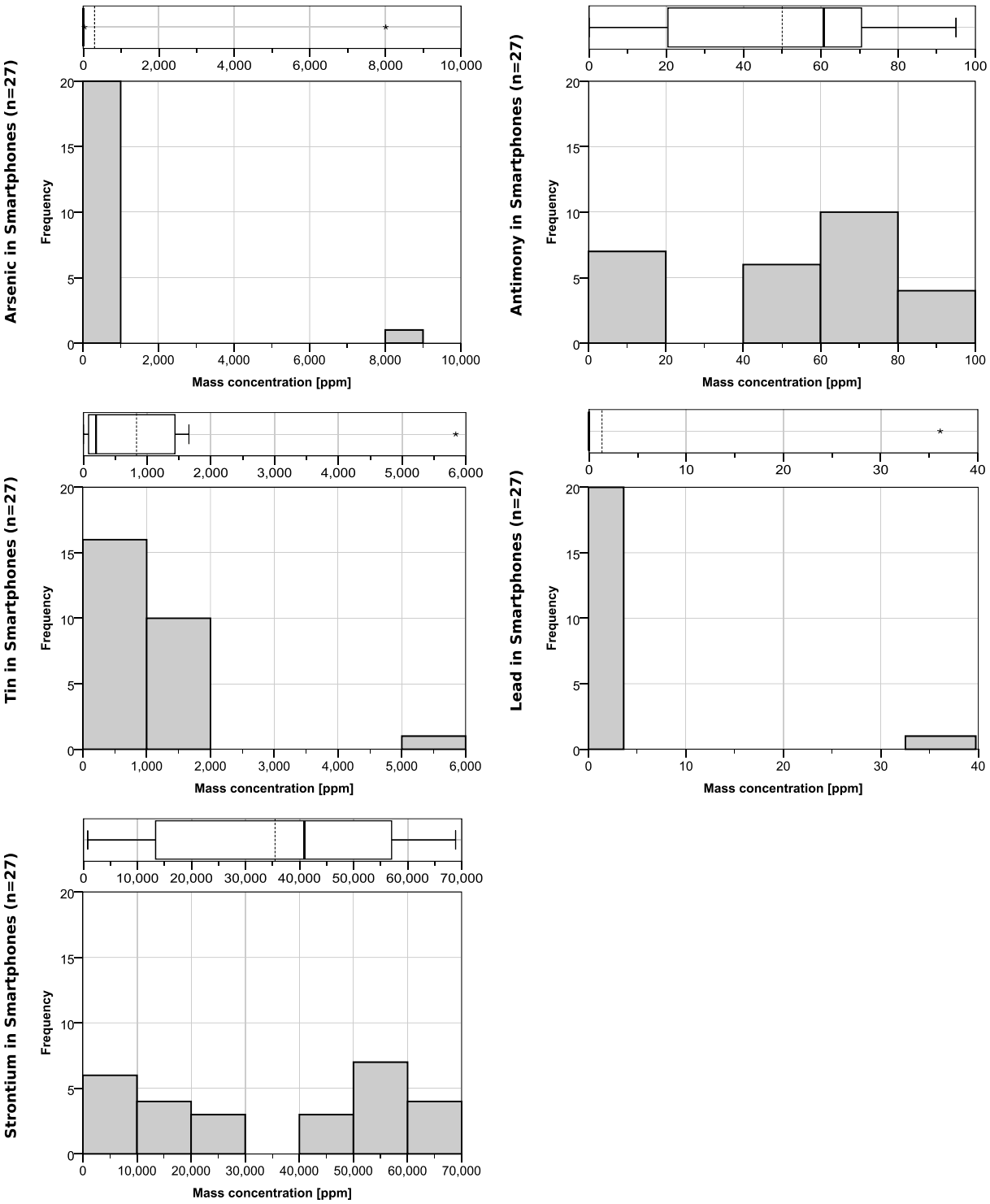

Figure 5: Arsenic, antimony, tin, lead and strontium in smartphone LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

9.3. LCD from tablets (0303-02)

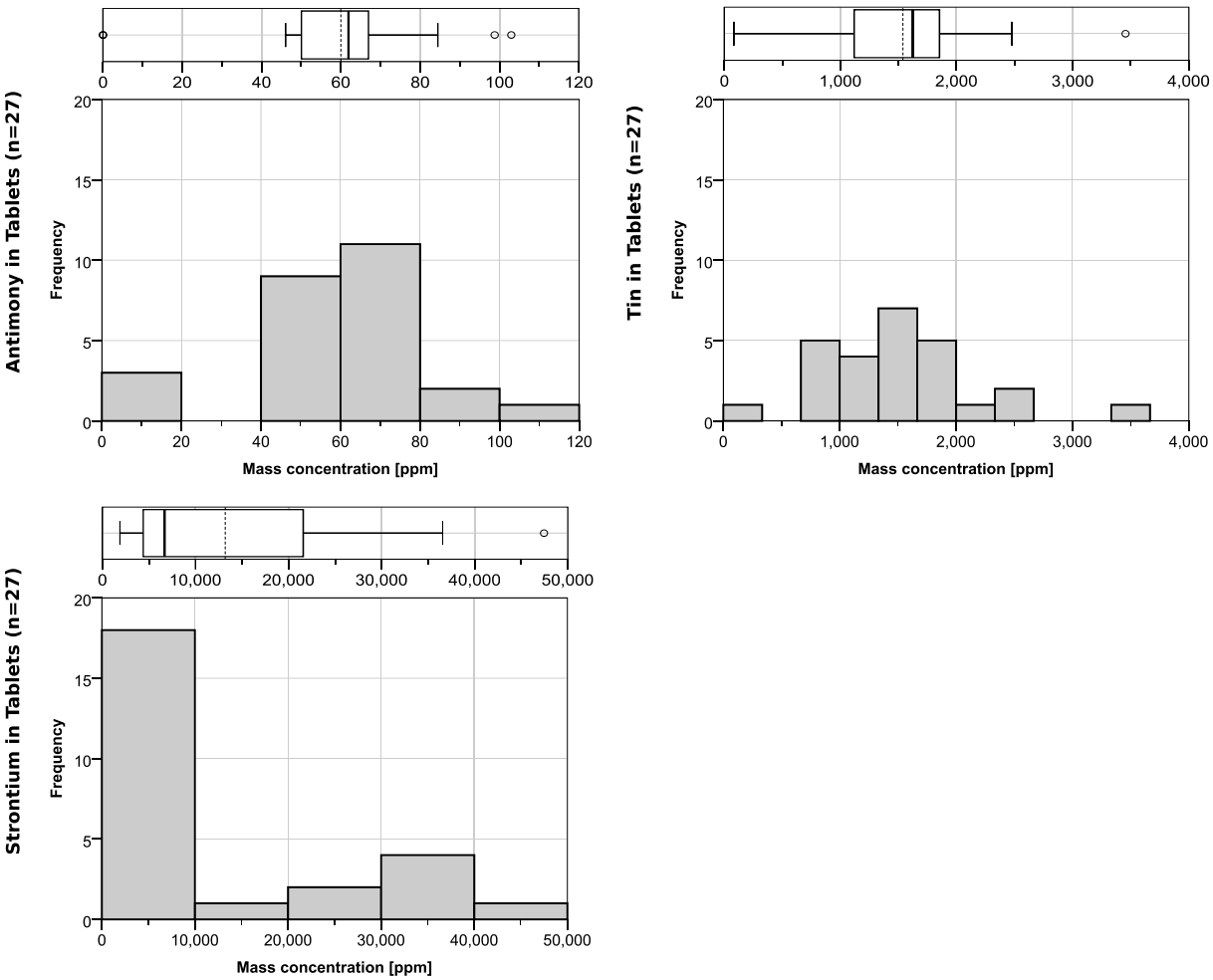

Figure 6: Antimony, tin and strontium in Tablet LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

9.4. LCD from notebooks (0303-01)

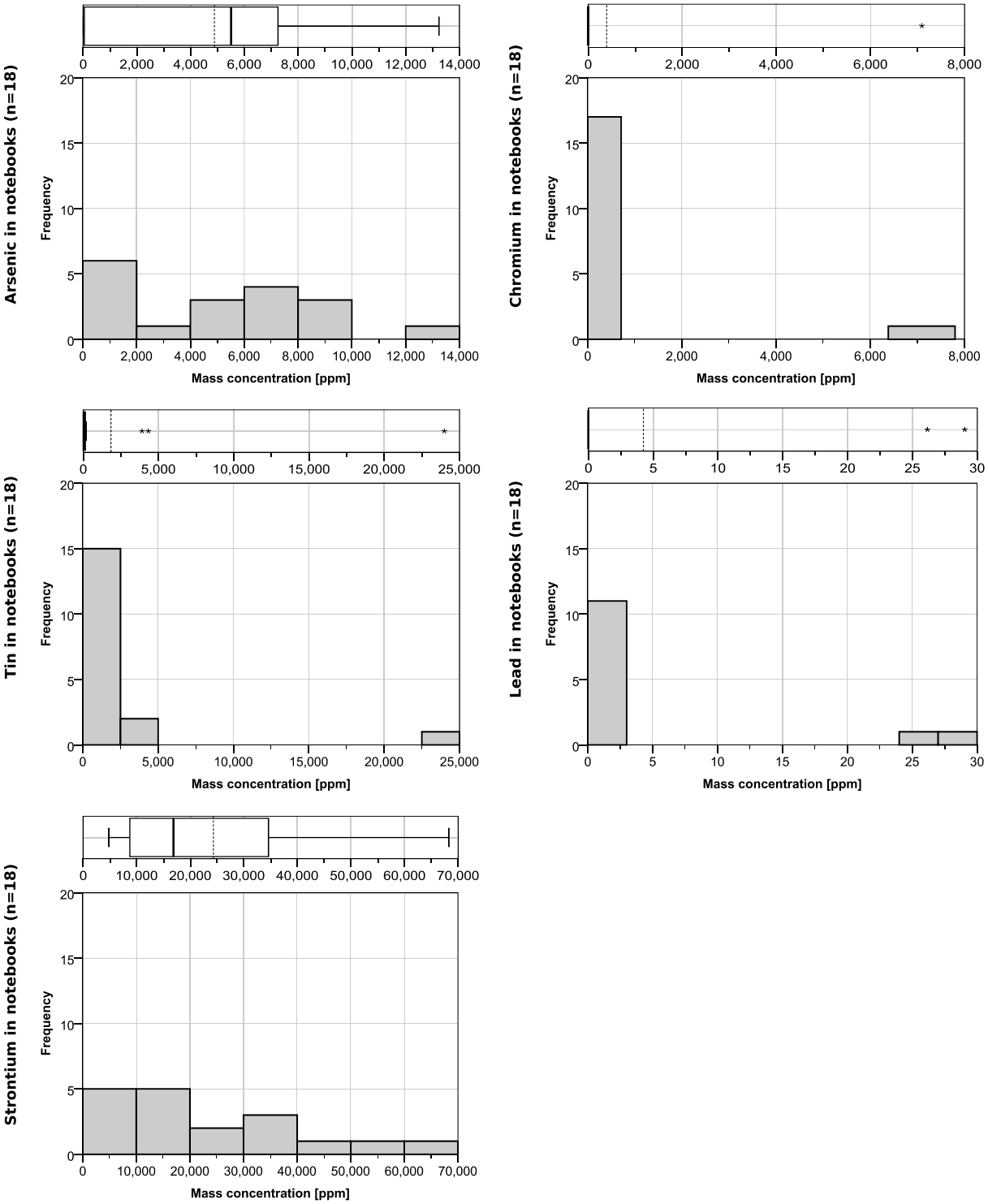

Figure 7: Arsenic, chromium, lead, tin and strontium in notebook LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

9.5. LCD from PC monitors (0309-01)

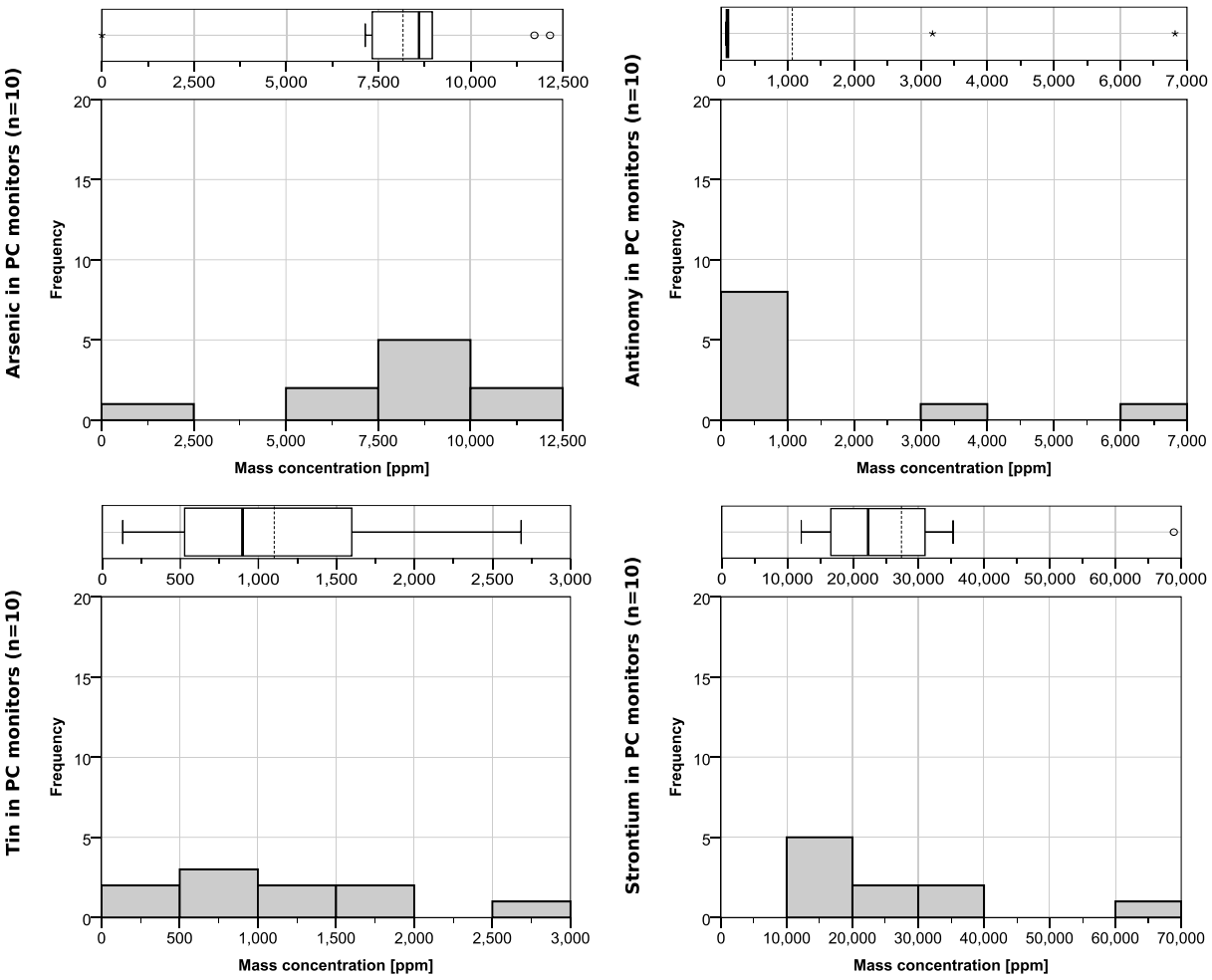

Figure 8: Arsenic, antimony, tin and strontium in PC monitor LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

9.6. LCD from TV (0408-01)

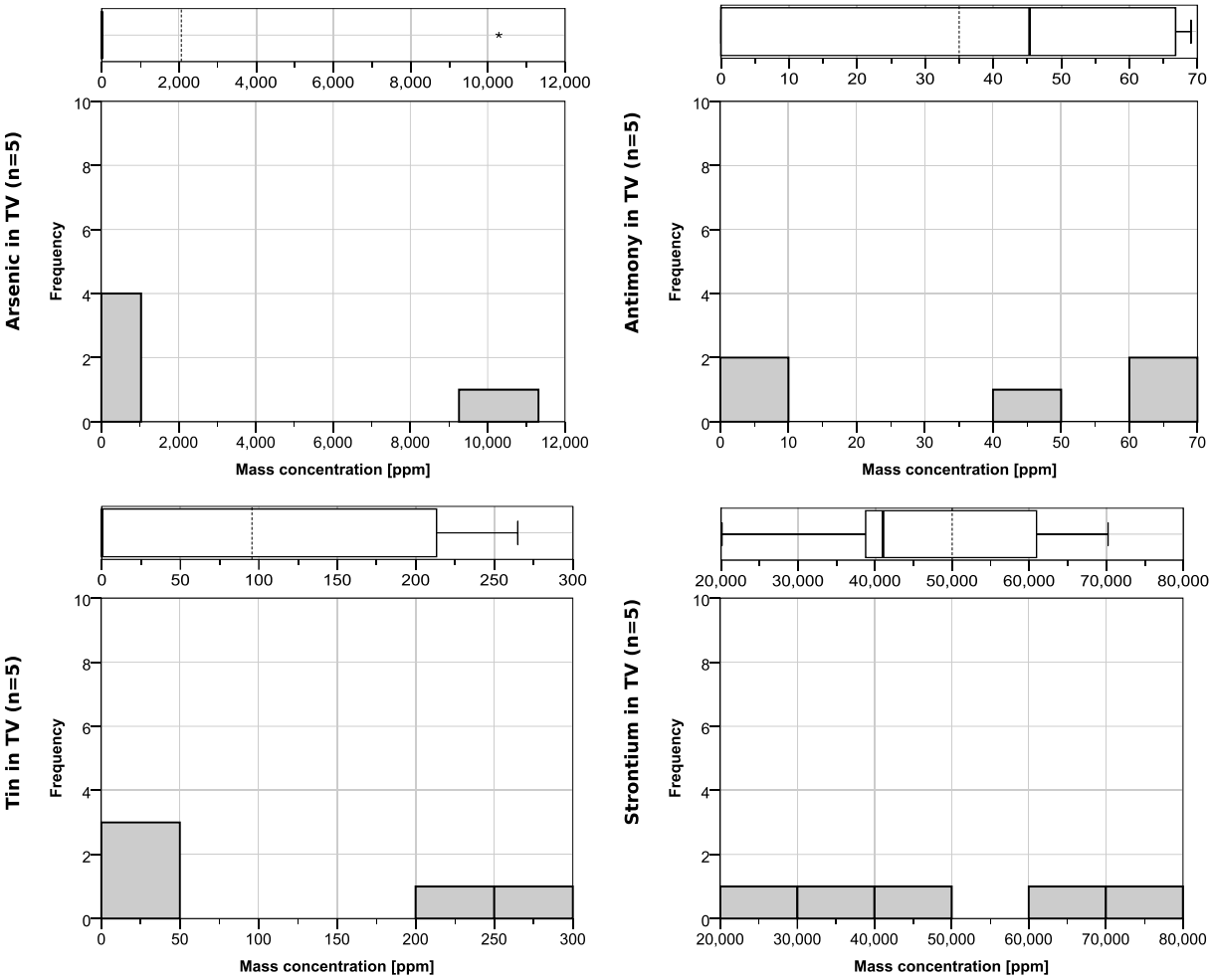

Figure 9: Arsenic, antimony, tin and strontium in PC monitor LCD. Top: boxplot with interquartile range (25/75 %); whiskers 1.5 IQR; asterisk = extremum; circle = outlier; dashed line = arithmetic mean; below: histogram

10. S10 Toxic heavy metals + Sr in panel glass versus manufacturing date

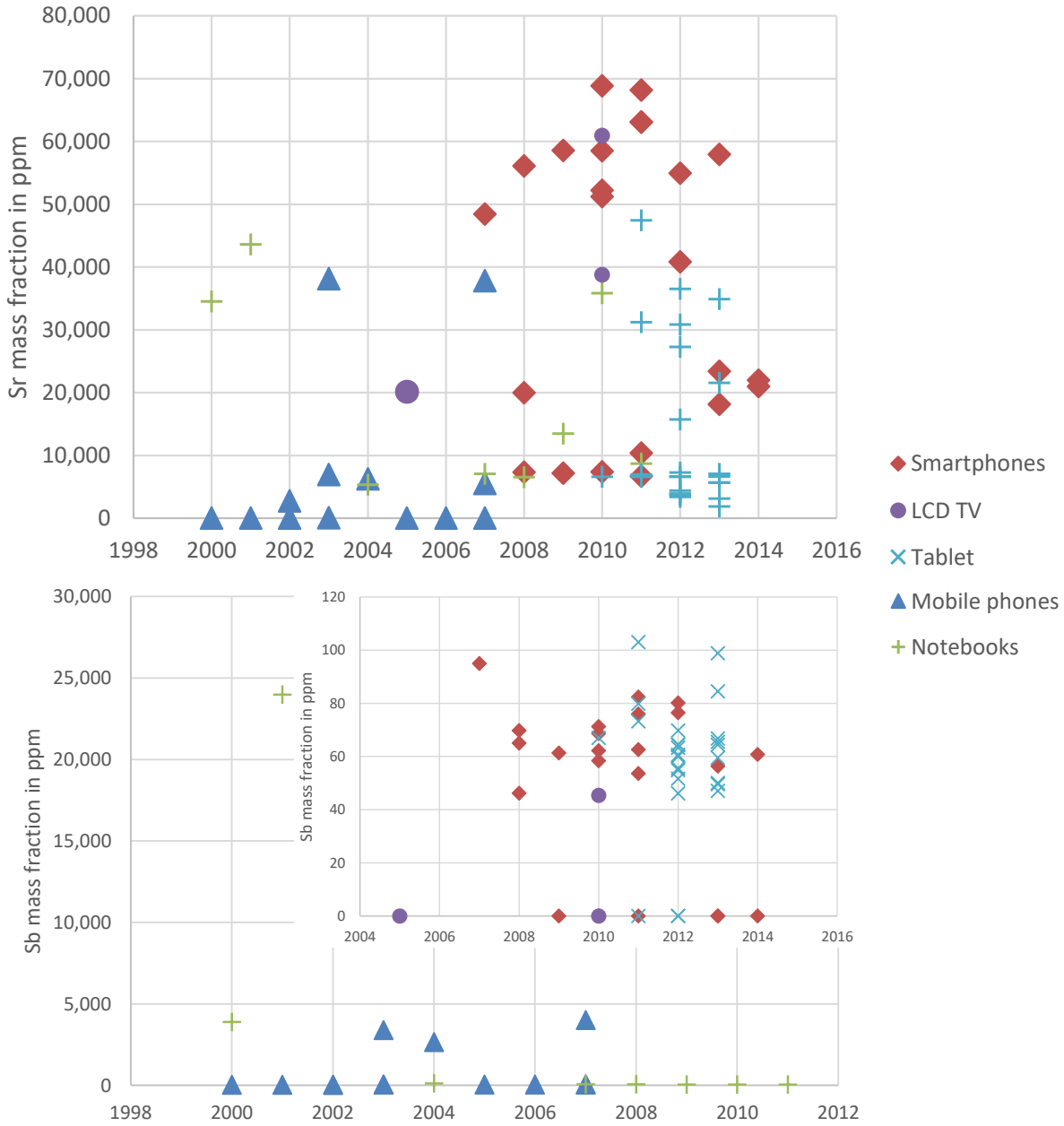

Figure 10: Mass fractions of Sr and Sb in ppm versus manufacturing date of various investigated screen devices

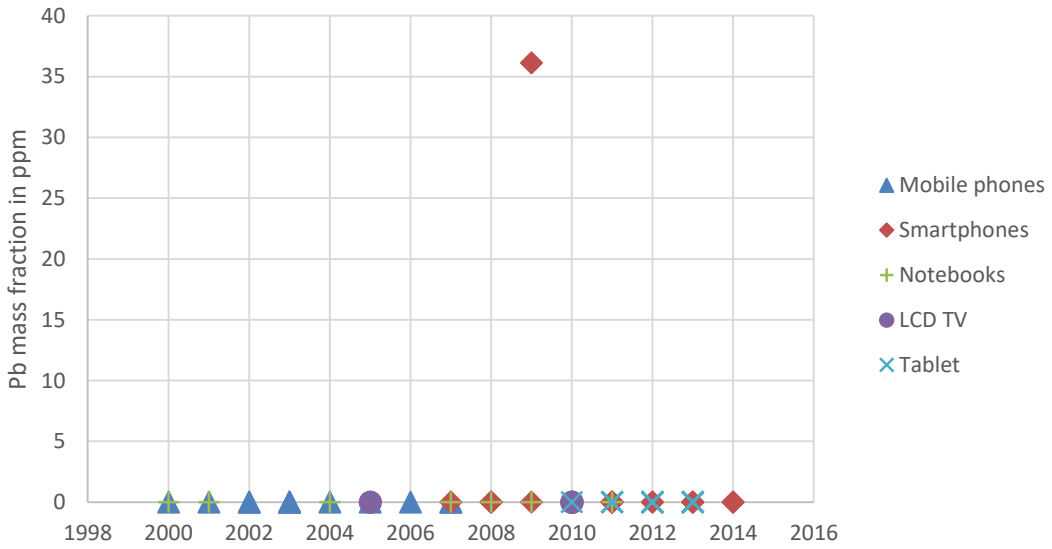

Figure 11: Mass fractions of Pb in ppm versus manufacturing date of various investigated screen devices

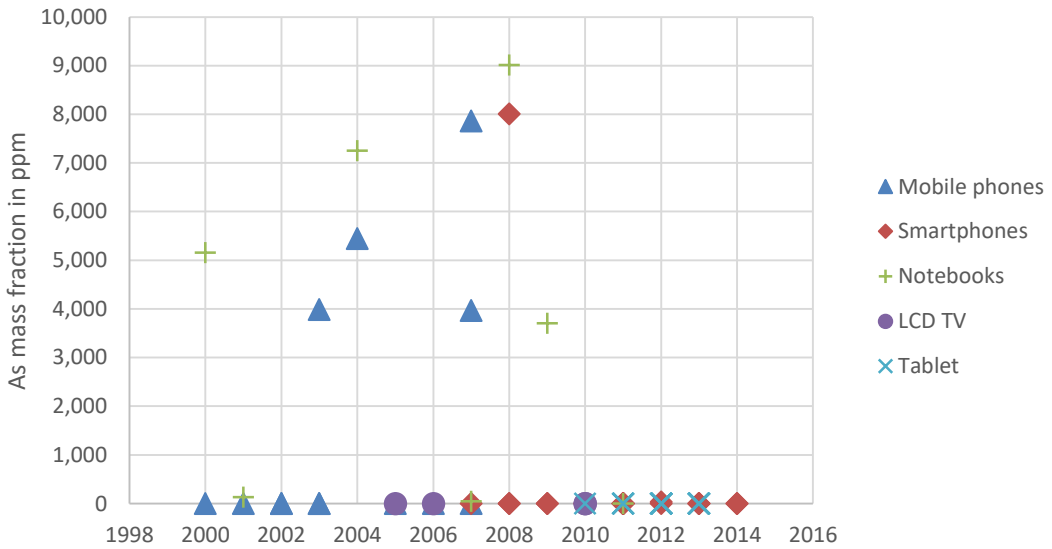

Figure 12: Mass fractions of As in ppm versus manufacturing date of various investigated screen devices

Note: No graph was drawn for Cr, as this substance was not determined in the samples investigated. PC monitors are also not depicted, as no data about the manufacturing dates were available.

11. S11 Validation of chemical analyses

Generally, chemical analyses carry the risk of systematic errors. Therefore, the methodologies used have to be verified and described in a transparent and comprehensible way. This applies to both the wet chemical analyses with an ICP and to non-destructive approaches with an XRF.

11.1. Indium in ICP vs AAS

In order to verify the data for the chemical composition of LCD panels from measurements made with an ICP-OES, parallel chemical analyses with an AAS have been carried out. Figure 13 shows exemplarily the results for 10 mobile phones and 10 tablet samples for both measurement devices used.

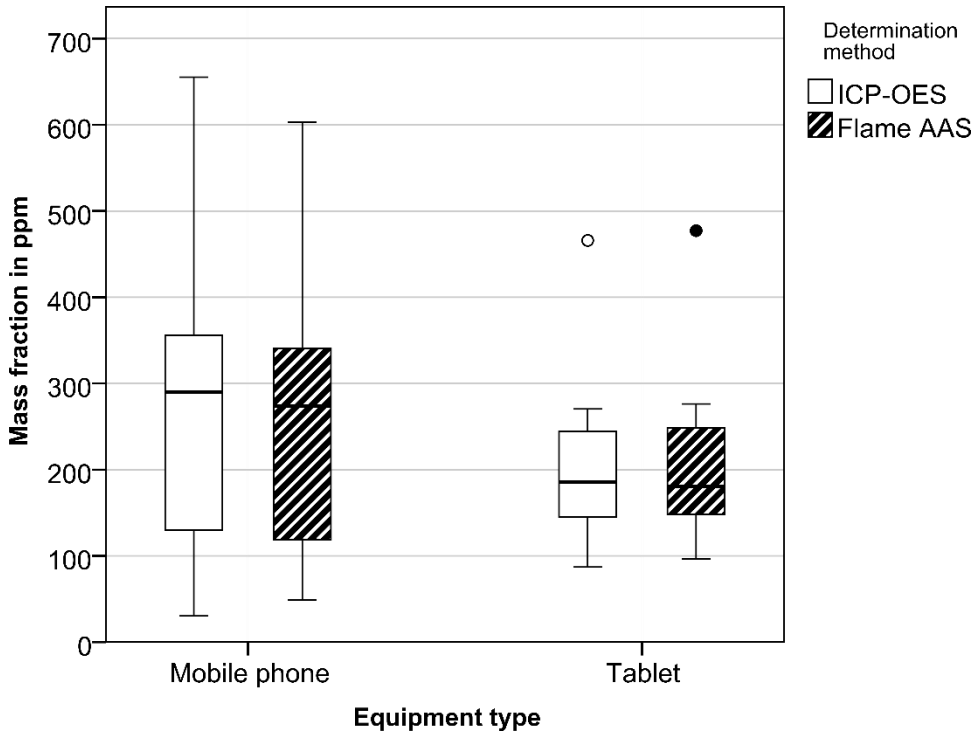

Figure 13: Exemplary comparison of indium mass fractions determined in LCD panels from mobile phones (n=10) and tablets (n=10) measured with ICP-OES and flame AAS depicted as boxplot with median, interquartile range (IQR) (25/75 %) and whiskers 1.5 IQR (circle: outlier >1.5 IQR)

The results show that both determination methodologies provide similar values. Therefore, the results are expected to be reliable.

11.2. Determination of toxic heavy metals + Sr

Chemical analysis with an XRF device is usually related to higher systematical errors. In particular automatic systems with an internal calculation based on proprietary algorithms can provide reliable results for common elements but may have limits with regard to trace materials. The error of each measurement directly calculated by the software of the measuring device usually gives first information about the result quality. These errors vary greatly for single toxic heavy metals + Sr in LCD panels determined with the XRF technique. Figure 14 shows the mean and average errors for Sr, Cr, As, Sb and Pb.

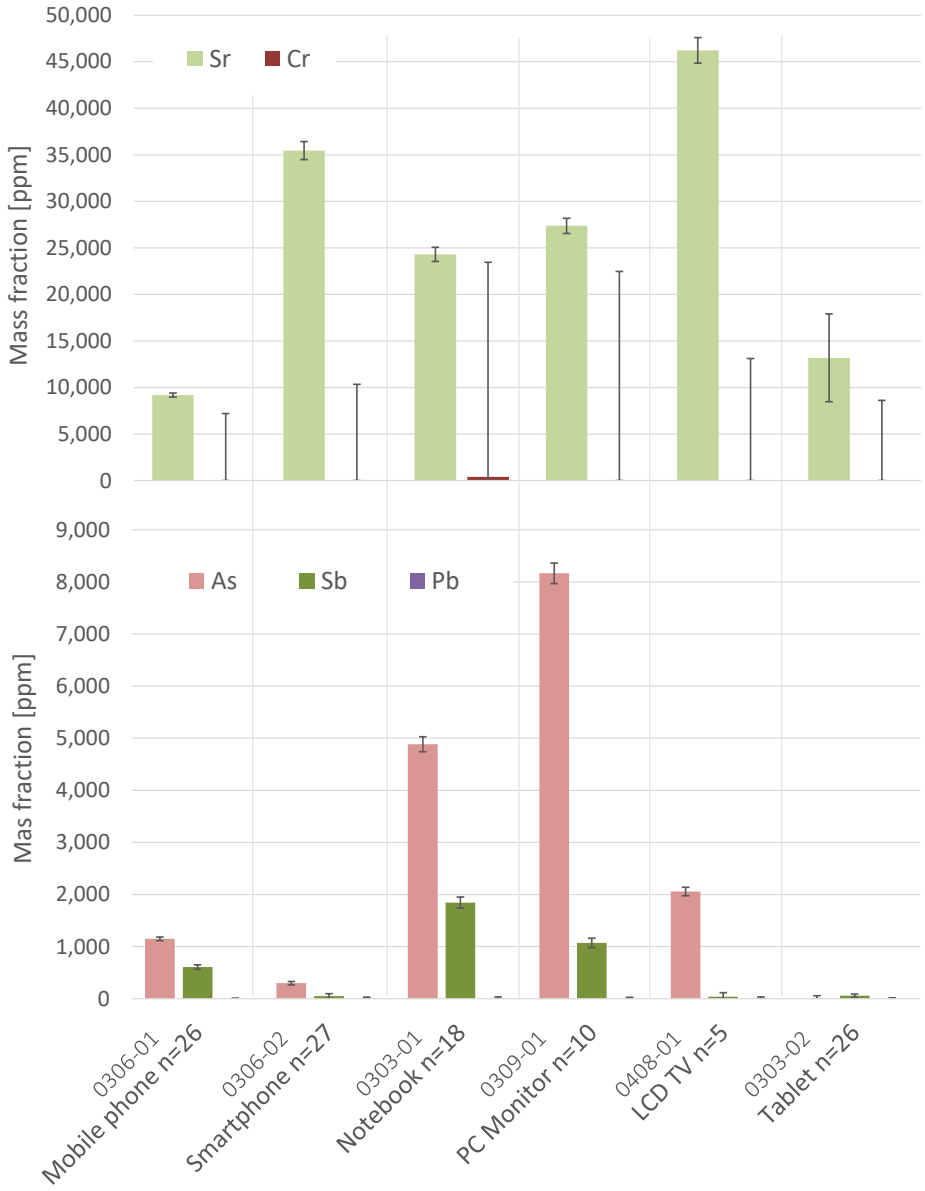

Figure 14: Average values and errors for the chemical analyses of applied toxic heavy metals + Sr in all LCD panels investigated in various equipment types

The results for Sr, As, Sb and Pb are related to very low errors. Therefore, these results are expected to be reliable. In contrast, the results for chromium are related to very high errors, ranging from 0.6 to almost 2.5% in the equipment types investigated. Furthermore, traces of Cr were found in the composite separation test for smartphones and tablets. Consequently, the presence or absence of Cr in the samples is not verified.

12. S12 Example of an FT-IR spectrum

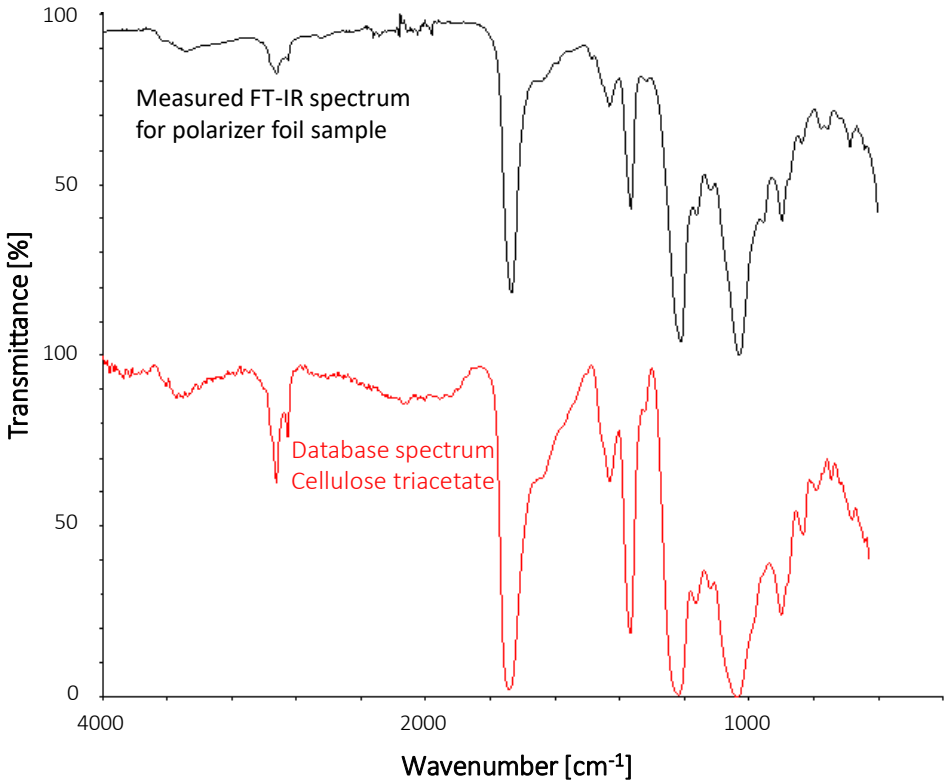

Figure 15: Example of an FT-IR spectrum recorded for a polarizer foil (upper graph) plotted versus a database spectrum Cellulose triacetate (lower graph)

13. S13 Calculation scheme for LCD panels and indium, polarizer foils and glass substrate masses

Table 4: LCD panels and related indium, polarizer foil and glass substrate masses calculation for mobile phones, smartphones, tablet, notebooks, PC monitors and LCD TV for Germany / worldwide in 2013

2013		Mobile Phone		Smartphone		Notebook		Flat Screen Monitor		LCD TV		Tablet	
		Average	StDev	Average	StDev	Average	StDev	Average	StDev	Average	StDev	Average	StDev
General	UNU key	306-01		306-02		303-01, 303-03		309		408-01		303-02	
Germany	Put on market	Number equipment put-on-market [pieces]	4,300,000		22,400,000		5,000,000		2,000,000		7,620,000		5,688,000	
		Mass equipment put-on-market [Mg]	419	213	2,717	544	13,356	2,352	10,767	427	102,706	74,213	2,923	1,018
		Masses LCD panels POM [Mg]	37	25	386	272	1,206	264	1,031	102	9,146	7,373	589	446
		Masses foils [Mg]	8	3	71	44	168	36	161	16	1883	919	139	75
		Masses glass [Mg]	29.33	10.33	315.18	130.31	1037.86	131.55	858.00	50.52	7255.65	3065.93	449.60	192.68
		Indium mass POM [Mg]	0.01	0.01	0.01	0.01	0.16	0.07	0.18	0.02	1.51	0.91	0.10	0.07
	Collection for recycling	Masses equipment collected for recycling purposes [Mg]	1,088		1,209		246		1,142		1,582		8	
		Number equipment collected for recycling purposes [pieces]	11,163,587	5,673,263	996,511	199,614	91,921	16,186	212,087	8,419	117,397	84,828	16,410	5,715
		Masses collected LCD panels [Mg]	97	41	17	12	22	3	109	10	141	50	2	1
		Masses collected foils [Mg]	21	6	3	2	3	1	17	2	29	8	0.40	0
		Masses collected glass [Mg]	76.1	17.81	14	5.59	19	1.57	91	4.98	112	22.15	1.30	0.50
		Indium mass collected [Mg]	0.03	0.02	0.0005	0.00	0.00	0.00	0.02	0.00	0.02	0.01	0.00030	0.00
World wide	Put on market	Number equipment put-on-market [pieces]	818,934,080		989,846,780		181,000,000		697,000,000		220,100,000		219,900,000	
		Mass equipment put-on-market [Mg]	79,805	40,556	120,068	24,051	483,475	85,134	3,752,183	148,947	2,966,618	2,143,597	112,993	39,354
		Masses LCD panels POM [Mg]	7,103	4,714	17,050	12,022	43,661	9,567	359,186	35,577	264,185	212,953	22,764	17,255
		Masses foils POM [Mg]	1,511	627	3,122	1,949	6,082	1,312	56,034	5,575	54,399	26,558	5,382	2,901
		Masses glass POM [Mg]	5,585.6	1,967.7	13,927.5	5,758.6	37,570.7	4,761.9	299,011.6	17,604.6	209,575.8	88,557.8	17,381.8	7,449.0
		Indium mass POM [Mg]	2.3	1.5	3.0	2.4	5.8	2.7	61.8	7.4	43.7	26.3	4.0	2.6

14. S14 Put-on-market and recycling potential of polarizer foils and glass substrate from LCD panels

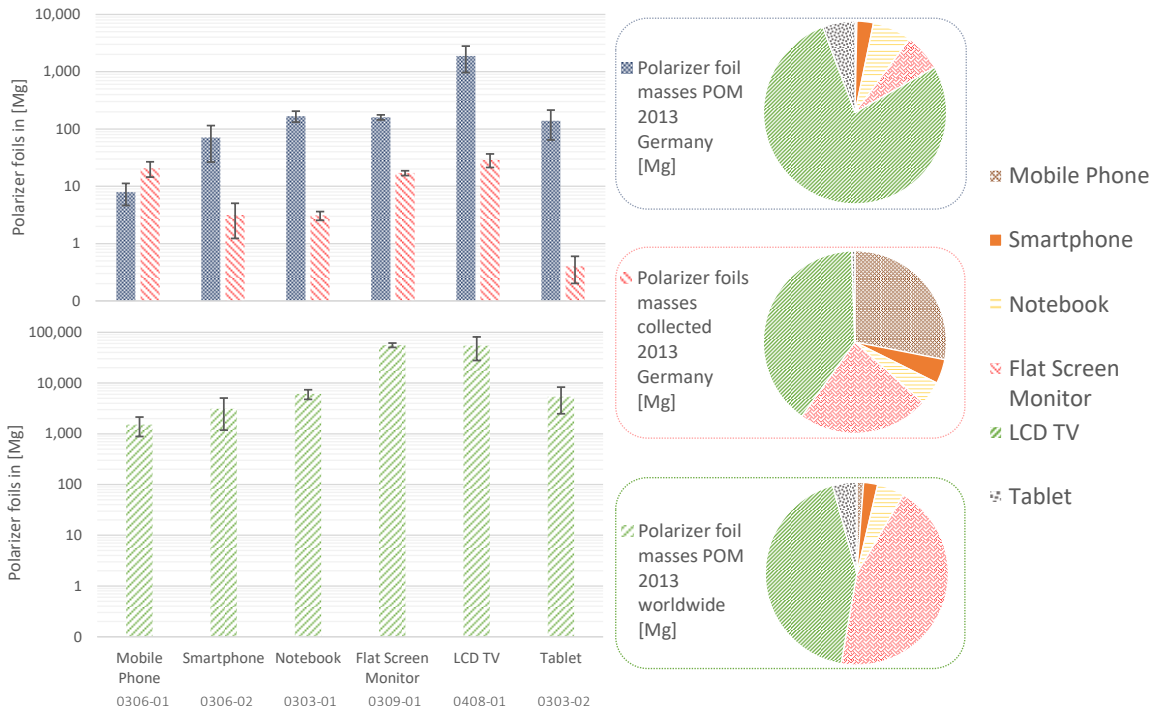

Figure 16: Total polarizer foils potential from LCD panels in various put-on-market devices (Germany / worldwide) versus devices collected for recycling purposes in Germany in 2013

Figure 17: Total indium potential from LCD panels in various put-on-market devices (Germany / worldwide) versus devices collected for recycling purposes in Germany in 2013

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