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LEACHATES ANALYSIS OF GLASS FROM BLACK AND WHITE AND COLOR TELEVISION SETS

R. Kukla, T. Vítěz, P. Junga, P. Mach

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Abstract

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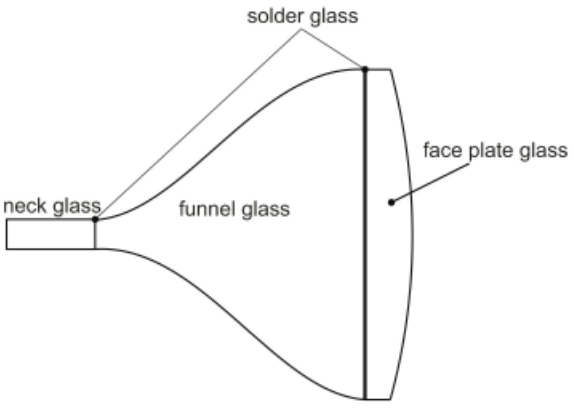
The aim of work was to determine the content of selected elements in the glass from color and black and white television (TV) sets. The amount of back taken TV sets in the Czech Republic increases annualy, which is associated with higher production of the waste glass. Currently there is 1.4 television sets for each household and the number of it should increase in future, because of higher standard of living and new technologies used. Waste glass treatment or landfilling may present, because of composition of the waste glass threat to the environment. One of the indicators of the polution from waste glass is leachate analysis, which can show us the content of hazardous substances in the waste glass, which can be released to the environment. A qualitative analysis of leachate samples was carried out by UV-VIS spectrophotometer. The results showed concentration of potencionaly hazardous substances contained in leachate samples. This was especially content of aluminum, cadmium, chromium, copper, molybdenum, nickel, lead, tin and zinc. Results of analyzes of the aqueous extract of glass were confronted with the limits specified in the currently valid legislation. Based on the results there is clear that in the case of landfilling of the glass from television sets, there is possibility of the contamination of landfill leachate by the elements, which are presented in the glass.

glass, glass screen, heavy metals, leachate

In the Czech Republic there is currently by the Czech Statistical Office (CSO) 1.4 television sets for each household. Number of households in the Czech Republic is 4.8 million, this means that the total number of TVs is 6.7 million. A cathode ray tube (CRT) represents 80% of this number. All of these TVs will be once phased out and processed. With an average weight of TV 23.5 kg and mass fraction of glass 60% it represents $75.5766 \cdot 10^3$ kg of glass screen for processing. A cathode ray tube glass unit is composed of three different parts, each doing a different job and needing to be of a different glass composition. A typical structure is shown in Fig. 1.

The viewing section known as screen, panel or face plate is made of glass which typically contains a high level of barium oxide but no lead oxide, because this discolours glass is under Xray radiation. Both the funnel glass and the neck glass contain lead oxide to shield against Xray radiation released by the high anode voltage. The funnel section contains up to 25% lead oxide. The neck section, housing the electron gun, has up to 40% lead oxide (Yang *et al.*, 1993, Kim *et al.*, 2001). The three glass components are joined together using a low melting temperature solder glass that also contains high



1: *Main glass components of a typical cathode ray tube*

I: *Typical compositions of CRT glass*

Oxide	Face plate glass	Funnel glass	Neck glass
	[%]	[%]	[%]
SiO_2	60.70	54.10	38.00
Al_2O_3	1.70	1.80	0.90
Na_2O	7.50	6.20	2.00
K_2O	6.90	8.20	16.50
CaO	0.10	3.50	0.10
MgO	1.04	1.50	0.52
BaO	9.90	0.80	0.70
SrO	8.60	0.70	4.80
ZnO	0.20	-	0.20
PbO	0.01	22.00	35.00
ZrO_2	2.50	0.30	-
Sb_2O_3	0.45	0.50	1.10
Fe_2O_3	0.05	0.02	0.03
TiO_2	0.55	0.07	0.02
NiO	0.012	-	-
CoO	0.003	-	-

levels of lead oxide up to 60% (Akai *et al.*, 2009). Glasses made by different manufacturers will be of a different composition, especially the face plate glass. Analysis of compositional data derived from the recent papers (Poon, 2008; Nnorom *et al.*, 2011; Babu *et al.*, 2007; Chen *et al.*, 2006) shows the average compositions of the glass Tab. I.

The main environmental concern about CRT glass is the amount of lead oxide and, to a lesser extent, the barium and strontium oxides it contains. The other major constituents of CRT glass are silicon (60 %), sodium (10 %), potassium (8 %), aluminium (2 %) and calcium (1 %) oxides (Chen *et al.*, 2006; Jang and Townsed, 2003). These are relatively inert and need not be removed from the glass to render it suitable for other applications. In fact, these oxides are common constituents of most commercial glasses such as container glass and flat glass.

MATERIAL AND METHODS

Screen glass obtained by removing the ten TVs were divided into a face plate glass and funnel glass separately for color and black and white TV. Individual samples of the glas were then crushed in a laboratory Retsch crusher type BB51 (Germany). After crushing the glass samples were carried out by sieve analysis according to CSN EN 933-1, Tests for geometrical properties of aggregates – Part 1: Determination of particle size distribution – Sieving method, so that for the leachate only grain size ≤ 4 mm has been available.

Preparation of aqueous leachate

Aqueous leachate was prepared from the analytical sample of the waste glass. Prior to leachate preparation determination of dry matter in a separate analytical sample have been done. For the determination of dry matter the muffle furnace LMH 07/12 have been used, for determining the mass of the sample analytical laboratory balances Radwag AS 220 / X, with an accuracy of 0.0001 g have been used. Dry matter of sample was determined at 105 ° C ± 5 ° C according to ČSN EN 14346 Characterization of waste – Calculation of dry matter by determination of dry residue or water content and the proportion of dry matter was calculated by thesimilarity relation:

$$DR = \frac{M_D}{M_W} \times 100, \quad [\%] \tag{1}$$

where:
DR ... dry matter [%];
M_D.... weight of the dried analytical sample [g];
M_W... weighed wet analytical sample [g].

Waste extraction with distilled water was carried out. Into a glass vessel of volume 250 ml solid sample was weighed with total mass M corresponding to 90 g ± 5 g of dry matter of MD. The leaching liquid (distilled water) was added, the temperature of leaching liquid used for extracting ranged between 15 °C and 25 °C throughout extraction. The amount of leaching fluid was determined by the relation:

$$L = \frac{(100 - MC)}{100} \times M_D, \quad \left[dm^3 \right] \tag{2}$$

where:
L..... amount of added leaching liquid [dm^3],
MC .. water content [%];
M_D.... weight of the dried analytical sample [g].

Closed glass vesels with samples have been attached to the shaker (Heidolph REAX 20/4). Extraction was carried out with continuous rotation of the glass vessels with sample and water by the way head – heel with the speed of 5 to 10 revolutions per minute for 24 hours. After extraction we have allowed solids in suspension to settle for 20 minutes. Subsequently, the leachate have been centrifuged on the centrifuge (SIGMA 1-6P) and pre-filtered through a filter with a larger porosity (paper filter) so that it can be subsequently filtered through a membrane filter with pore size of 0.45 μm. The obtained filtrate was subjected to analysis. At each sample pH were measured after filtration using a portable pH meter WTW (Germany). Filtrates were analyzed using methods for the analysis of wastewater. Analysis of an aqueous leachate obtained mass concentration in the extract contained the monitored substances. For the analysis portable spectrophotometer HACH DR 2800, operating at a wavelength 340–900 nm has been used. This spectrophotometer worked with cuvette tests for individual monitored susbstances contained in aqueous leachate. Range of each cuvette tests for individual saples of monitored substances were as follows, aluminium 0,02–0,5 $mg \cdot dm^{-3}$, cadmium 0,02–0,3 $mg \cdot dm^{-3}$,

chromium 0,03–1 mg·dm^{-3}, copper 0,1–8 mg·dm^{-3}, molybdenum 3–300 mg·dm^{-3}, nickel 0,1–6 mg·dm^{-3}, lead 0,1–2 mg·dm^{-3}, tin 0,1–2 mg·dm^{-3} and zinc 0,2–6 mg·dm^{-3}. Three replicate analyses were done for all of the metals and the relative standard deviation was calculated.

RESULTS AND DISCUSSION

The mean value of pH of the leachate of the CRT glass is showed in Tab. II. It corresponds with other authors. The mean dry matter content of the CRT the glass from black and white TV sets and from colour TV sets is showed in Tab. II.

The result of chemical properties of the leachate from samples of CRT glass of black and white TV sets and colour TV sets are presented in Tab. III and IV.

Our monitored parameters of leachate were compared with allowable indicators for depositing in landfills, according to the Decree 383/2001 Coll., as amended the results are shown in Tab. V.

Dismantling of Cathode Ray Tubes (CRTs) represents a pressing environmental problem. Dismantled CRTs are generally used in the production of new CRTs in close-circuit recycling scheme, but in Europe, due to the technological changes towards flat panels, CRT technology is becoming obsolete, so new applications must be found (Geskin *et al.*, 2002; Nnorom *et al.*, 2011). On the other hand, new legislation, such as the European Directive on Waste Electric and Electronic Equipment (WEEE), will require increased recycling and recovery rate, while landfilling should be more and more a residual option. CRTs contain mainly two types of glass (funnel and panel), welded together with a lead frit (Geskin *et al.*, 2002). In color equipments, the funnel contains a significant quantity of PbO (18 %–20% in weight), and present a carbon coating on the inside. The panel, instead, is characterized by high levels of BaO (9 %–11% in weight) and SrO (8 %–10% in weight) and it is coated with a matrix of thousands of tiny phosphor dots, constituted by chemicals which emit light when excited by a stream of electrons. Furthermore, a significant presence of other elements characterizes CRT glass, this must be reduced or dischared in case of landfilling of glass. To protect the environment it is necessary to exactly know the

II: *Dry matter and pH of samples of CRT glass from TV sets*

indicator type of sample	pH	Dry matter
	[-]	[%]
Funnel glass, black and white CRTs	7.99	99.96
Face plate glass, black and white CRTs	9.98	99.97
Funnel glass, colour CRTs	7.95	99.93
Face plate glass, colour CRTs	9.77	99.96

III: *Results of analysis of leachate of CRT glass from black and white TV sets, (median ± standard deviation based on median)*

indicator type of sample	Al	Cd	Cr	Cu	Mo
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Funnel glass	> 0.500*	< 0.020*	0.249 ± 0.023	> 1.000	8.28 ± 0.953
Face plate glass	> 0.500*	< 0.020*	0.214 ± 0.025	> 1.000	6.12 ± 0.704

indicator type of sample	Ni	Pb	Sn	Zn
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Funnel glass	0.602 ± 0.049	0.301 ± 0.035	0.422 ± 0.045	0.859 ± 0.064
Face plate glass	0.559 ± 0.046	0.337 ± 0.038	< 0.100*	0.938 ± 0.069

* out of range the cuvette test

IV: *Results of analysis of leachate of CRT glass from colour TV sets, (median ± standard deviation based on median)*

indicator type of sample	Al	Cd	Cr	Cu	Mo
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Funnel glass	> 0.500*	< 0.020*	0.121 ± 0.011	> 1.000*	14.50 ± 1.668
Face plate glass	> 0.500*	< 0.020*	0.214 ± 0.019	> 1.000*	8.06 ± 0.927

indicator type of sample	Ni	Pb	Sn	Zn
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Funnel glass	1.070 ± 0.088	1.070 ± 0.123	< 0.100*	0.859 ± 0.071
Face plate glass	0.622 ± 0.051	0.324 ± 0.037	0.432 ± 0.046	0.938 ± 0.077

* out of range the cuvette test

V: *Comparison of leachate parameters with the values set in the legislation*

Indicator	Al	Cd	Cr	Cu	Mo
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Limits according to Decree 383/2001 Coll., as amended					
Leach class I	NS	0.004	0.05	0.2	0.05
Leach class IIa	NS	0.5	7	10	3
Leach class IIb	NS	0.1	1	5	1
Leach class III	NS	0.5	7	10	3
Color TV sets					
Funnel glass	> 0.500*	< 0.020*	0.121	> 1.000*	14.50
Face plate glass	> 0.500*	< 0.020*	0.266	> 1.000*	8.06
B&W TV sets					
Funnel glass	> 0.500*	< 0.020*	0.249	> 1.000*	8.28
Face plate glass	> 0.500*	< 0.020*	0.214	> 1.000*	6.12

NS – not specified, * out of range the cuvette test

Indicator	Ni	Pb	Sn	Zn
	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}	mg·dm^{-3}
Limits according to Decree 383/2001 Coll., as amended				
Leach class I	0.04	0.05	NS	NS
Leach class IIa	4	5	NS	NS
Leach class IIb	1	1	NS	NS
Leach class III	4	5	NS	NS
Color TV sets				
Funnel glass	1.070	1.070	< 0.100*	0.489
Face plate glass	0.622	0.324	0.432	1.160
B&W TV sets				
Funnel glass	0.602	0.301	0.422	0.859
Face plate glass	0.559	0.337	< 0.100*	0.938

NS – not specified, * out of range the cuvette test

composition of the glass, or leachates, which can be unlaced in landfills. Our analysis suggests a possible release of heavy metals leach into the environment, which may be linked to groundwater contamination.

SUMMARY

Waste from electrical and electronic equipment is improperly handling a serious risk to the environment. One of the wastes that falls into this category is glass used in televisions and monitors. These materials are often deposited in landfills. Due to the processes occurring in landfills may be leaching of hazardous substances in glass and luminophore, which covers the glass. Leachate can contain high content of aluminum, cadmium, chromium, copper, molybdenum, nickel, lead, tin and zinc. In leachates of all investigated samples the limit concentration for the leach class I have been exceeded. For the leach class IIb limits for molybdenum have been exceeded for all samples and for samples of funnel glass for color television limits for nickel and lead have been exceeded. Parameters of leach class IIa and III have been acomplished in all leachate samples monitored. Our analysis pointed to the possibility of contamination of leachate from landfills, which should be cause by improper disposal of glass from televisions or monitors.

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Address

Dr. Ing. Radovan Kukla, Ing. Tomáš Vítěz, Ph.D., Ing. Petr Junga, Ph.D., Ing. Pavel Mach, Ústav zemědělské, potravinářské a environmentální techniky, Mendelova univerzita v Brně, Zemědělská 1, 613 00 Brno, Česká republika, e-mail: vitez@mendelu.cz