CHARACTERIZATION OF LEAD LEACHABILITY FROM CATHODE RAY TUBES USING THE TOXICITY CHARACTERISTIC LEACHING PROCEDURE

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Timothy G. Townsend, Principal Investigator
Stephen Musson
Yong-Chul Jang
Il-Hyun Chung

State University System of Florida
FLORIDA CENTER
FOR SOLID AND HAZARDOUS WASTE MANAGEMENT
2207 NW 13 Street, Suite D
Gainesville, FL 32609

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Principal Investigator
Timothy G. Townsend
Assistant Professor
Department of Environmental Engineering Sciences
University of Florida

Graduate Research Assistant
Stephen Musson
Department of Environmental Engineering Sciences
University of Florida

Graduate Research Assistant
Yong Chul Jang
Department of Environmental Engineering Sciences
University of Florida

Visiting Professor
Il-Hyun Chung
Department of Environmental Engineering
Mokpo National University, Republic of Korea

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FINAL REPORT

PROJECT TITLE: Characterization of Lead Leachability from Cathode Ray Tubes Using the Toxicity Characteristic Leaching Procedure

PRINCIPAL INVESTIGATORS: Timothy G. Townsend

AFFILIATION: Department of Environmental Engineering Sciences, University of Florida

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ABSTRACT

One of the emerging issues facing environmental policy makers and waste management professionals today is the management of discarded electronic devices. Examples of discarded electronic devices include televisions, computers, and communications equipment. Currently many thousands of tons of these materials are being discarded as part of the solid waste stream. With the introduction of low-cost, readily available personal computers and the looming replacement of standard-definition television with high-definition television, this practice will likely escalate. This presents a problem from an environmental protection viewpoint (heavy metals may leach from these components, either in the landfill or in the ash from an incinerator), as well as an opportunity to recover valuable resources.

Cathode ray tubes (CRTs) in televisions and computer monitors are one of the most common components of discarded electronics in the solid waste stream. CRTs present a disposal problem because of their growing magnitude in municipal solid waste (MSW) and their role as a major source of lead in MSW. Using the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP), lead leachability from CRTs was studied.

A total of 36 CRTs were processed and analyzed. CRT samples produced an average concentration of 18.5 mg/L lead. This exceeds the regulatory limit of 5.0 mg/L. Several factors affected the TCLP lead concentrations of each CRT. These included the location of the glass in the CRT (face plate, funnel, neck), the particle size used in the tests, and the CRT type. The most significant quantities of lead were contained in the funnel portion of the CRTs at an average lead concentration of 75.3 mg/L. The major source of lead in the funnel is the frit seal of color CRTs. Monochrome CRTs did not leach lead greater than hazardous levels. The results of the testing should provide useful information for the regulatory and waste management community for developing policies for managing discarded CRTs.

1.0 INTRODUCTION

An issue of expanding prominence in the United States is the disposal of computers and electronic equipment. Rapid technology advancements have made the advanced 486 powered computer of the early 1990's an archaic adding machine today. Additionally, the future transition from analog to digital high definition televisions will result in the massive disposal of televisions. As rapidly as new electronics are created, old electronics require disposal. According to recent statistics, the computer and electronics industry is the largest manufacturing employer in the United States. It comprises 11 percent of the gross domestic product and is growing at an annual rate of 4 percent (MCC 1996). Thus the management of discarded electronics is an issue of concern to today's solid waste management professionals.

Cathode Ray Tubes (CRTs) in televisions and computer monitors are one example of discarded electronics now recognized as a disposal problem. Management of discarded electronics, including CRTs, takes place through the traditional methods of municipal solid waste (MSW) management: landfilling and incineration. When disposed in landfills, increased concentrations of heavy metals in landfill leachate may occur. When discarded electronics are disposed at waste-to-energy facilities, the heavy metals become concentrated in the ash, limiting disposal and reuse options.

The management options and requirements for solid wastes in the U.S. depend largely on whether the solid waste is characterized as hazardous. The Toxicity Characteristic Leaching Procedure (TCLP) is a method of determining whether a solid is hazardous from leaching of hazardous pollutants (40 CFR Part 261). CRTs have been anecdotally referred to as failing the TCLP for lead (Porter 1998, Feinbaum 1998, Dillon 1998), but this information is not available in the scientific literature. While a number of problems have been cited with the TCLP in regard to its true representation of environmental conditions (EPA Science Advisory Board, 1999), the test has been found in recent work to leach many heavy metals (including lead) in a similar manner as domestic landfill leachate (Hopper et al. 1998), the intended result of the test.

This paper reports the results of a study examining lead leachability from CRTs using the TCLP. Regardless of whether the test truly reflects environmental conditions encountered by CRTs upon disposal, the classification as hazardous does have an impact on how CRTs may be managed in the current U.S. regulatory environment. If CRTs are truly a hazardous waste as often anecdotally cited, regulators would have additional options to require removal from the waste stream. Regulations to encourage their reuse and recycling, such as the universal waste rule, could be applied (40 CFR Part 273).

2.0 BACKGROUND

2.1 LEAD IN MSW

Lead is widespread throughout MSW in the United States. It accounted for 213,652 tons of waste in 1986 and is projected to rise to over 281,000 tons by 2000 (EPA 1989). It is found in both the combustible and non-combustible portions of MSW. The primary sources of lead in MSW projected for 1995 are shown in Figure 1.

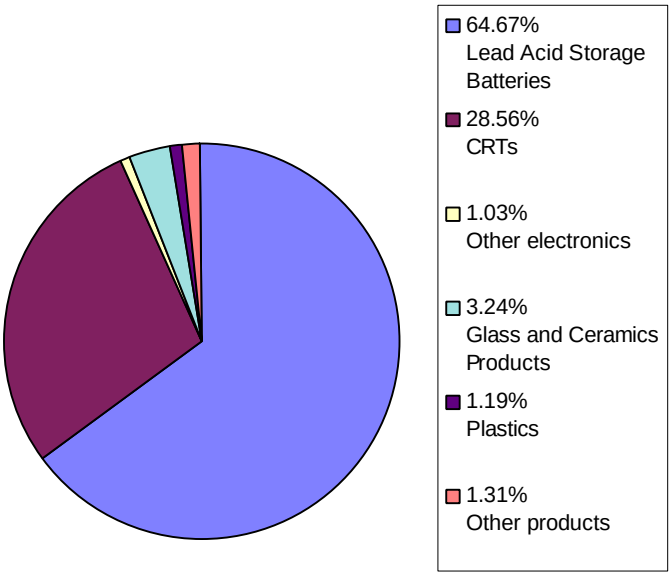

Figure 2.1: Lead in MSW for 1995 (EPA 1989)

Lead-acid batteries far outweigh any other source of lead in MSW. These batteries are used primarily for starting, lighting, and ignition for automotive products. Approximately 138,000 tons of lead in batteries were discarded in 1986. It is projected that this number will reach 182,000 tons by the year 2000 and remain the number one source of lead in MSW (EPA 1989). This category is the only category for which recycling in significant amounts occurs. The EPA (1989) estimated that up to 700,000 tons lead (or five times as much) would have entered the MSW stream without this recycling effort.

Consumer electronics include television sets, personal computers, radios, and VCRs. Consumer electronics were the number four source of lead in MSW in 1970. However, by 1975 they were the number two source and accounted for 27 percent of lead discards in MSW in 1986. They are projected to make 30 percent of lead discards by 2000 (EPA 1989). Figure 2 shows the contribution of lead from cathode ray tubes if lead acid batteries were removed from MSW. CRTs are the major component of televisions and computer monitors.

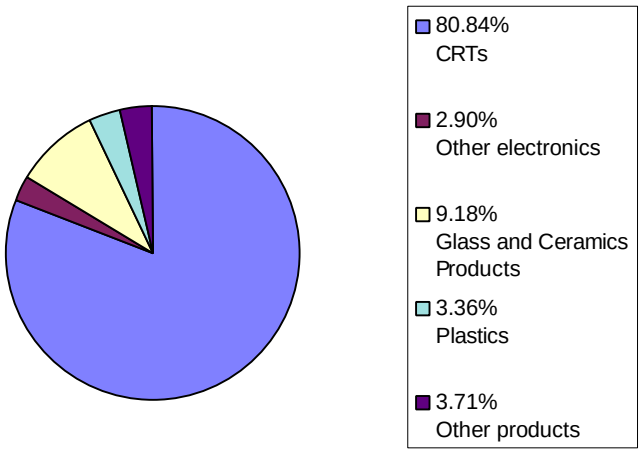

Figure 2.2 MSW Lead Sources Other than Batteries

Lead in glass and ceramic products includes glass containers for food and beverages, glass and ceramic tableware, cookware, mirrors, optical appliances, and other uses. Lead is a component in glazes and enamels used on glass containers. Lead is also used as a colorant in some designs. This was the number three source of lead in MSW for 1986 and is expected to grow slightly through the year 2000 (EPA 1989).

Plastics have come into increased usage from the early 1970s until today. In 1970 plastics were not among the leading sources of lead in MSW, but by 1986 ranked fourth among sources of lead. Although the amount of lead contributed by plastics is expected to grow through the year 2000, its percentage of the total is expected to remain near one percent (EPA 1989).

Other sources of lead in MSW include soldered cans, pigments, light bulbs, collapsible tubes, brass and bronze products, foil wrappers, used oil, and rubber products. Soldered cans, pigments, collapsible tubes, brass and bronze products, and used oil contributions are expected to decline through the year 2000. Only rubber products and light bulbs are expected to increase in their contributions. All of these sources will remain at minute levels in comparison with the previous categories (EPA 1989).

2.2 CRT OPERATION

Cathode-ray tubes are the technology used in most televisions and computer display screens. A CRT uses high voltages to accelerate electrons toward a luminescent material called a "phosphor" that is deposited on the faceplate (Figure 1.3). The phosphor converts the kinetic energy of the electrons into light. In a color CRT, the phosphors are patterned in dots or stripes of red, green, and blue phosphors.

The electrons are emitted from three cathodes in the electron gun assembly and pass through an apertured metal "shadow mask" during their passage to the phosphor. The shadow mask absorbs the electrons from each cathode that are directed at the wrong color phosphor. Pictures are created by first focusing the electron beams into tiny spots, which are moved by deflecting the electron beams electromagnetically so that the spots move across the phosphor surface in a left-to-right and top-to-bottom motion.

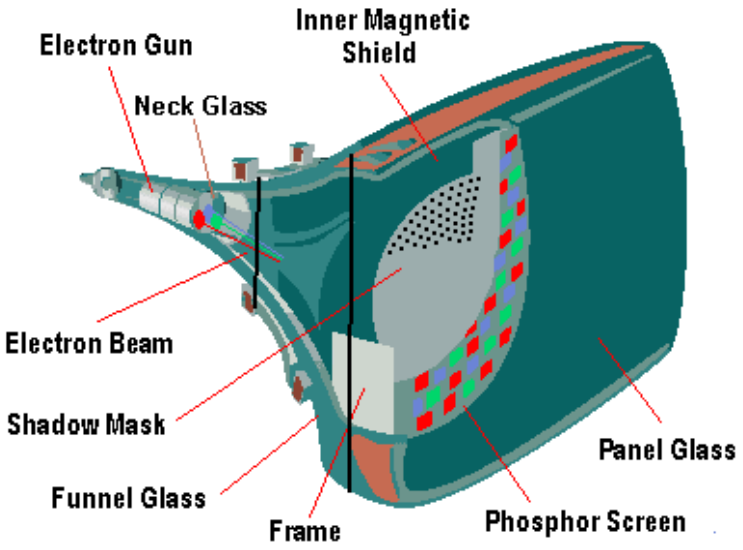

Figure 1.3 CRT Parts

The electron guns require high vacuum to achieve long life and the bulb envelope must have sound mechanical integrity to resist the force of atmospheric pressure. The high voltages used to accelerate the electrons must be insulated from the external surfaces of the tube and the envelope must have excellent electrical insulating properties. The decelerating electrons produce X-rays and the envelope must also be a good X-ray absorber.

A CRT display is composed of a glass panel, a cathode ray tube, a casing, various connecting wiring, shielding, and a deflection yoke. A tube ranges in weight from 8 to 70 pounds depending upon its size. The internal composition of the color CRT requires an envelope that can be opened for deposition of the patterned phosphor screen and other materials. The two halves of the envelope are mated with the shadow mask and sealed together with a low temperature frit (a solder glass with organic binders) in a high temperature bake process called Lehr bake. The monochrome tubes for direct view or projection can be made from one-piece bulbs without resorting to the frit glass seal (Morrell et al. 1974).

Although there are several issues of environmental concern in the manufacture of CRT displays, the primary issues concern disposal of end-of-life CRTs and the use of lead in the components. The lead content of the CRT is predominantly confined to the neck and funnel of the CRT. The industry uses both a no-lead and a 2% to 3% lead faceplate composition with a trend toward increasing the use of the no-lead composition. Approximate lead content is shown in Table 2.1.

2.3 MAGNITUDE OF DISCARDED CRT STREAM

In 1998 when referring to discarded CRTs, Porter wrote that the “volume of material involved is mind boggling.” In 1996, there were over 300 million CRTs (TVs and monitors) in North America. In that same year, forty-two million CRTs were sold in the U.S. and seventy-nine million computers were retired (Porter 1998). The annual growth rate for computer sales is

Table 2.1 Lead Content in CRT Glass Components by Mass (Froning 1999, MCC 1996)

Glass	Color CRT	Monochrome CRT
Panel	0% – 3%	0% – 3%
Funnel	24%	4%
Neck	30%	30%
Frit	70%	N/A

around 15 percent and it is estimated that for every three computers now purchased, two will become obsolete. That ratio is expected to be 2:1 by 2005 (Matthews et al. 1997).

An exploding industry is the computer recycling and resale market. While recycling of computers is still economically limited, the number of recycling companies has increased as the life span of computers shorten and computer discards increase. Greater tax incentives and a larger supply of computers have made the donation of computers to charities and schools more popular among corporations and individuals. Additionally, more companies have developed which repair and resell computers. These older computers are often sent to other countries where they are considered quite advanced. In the July 1997 revision of its 1991 study, Carnegie Mellon University suggested that 150 million computers would be recycled by 2005. The original study had predicted most of these to be landfilled.

A further factor is the storage of electronics, most notably computers. One study estimated that 75% of all computers are placed in storage. Many electronics disposal companies point out the owner's emotional attachment to the computer. Beyond the standard word processing and games, many people place personal information on their computers or use the computers for important projects. Personal attachments can be so great, that people have been known to bring their decommissioned work computers home (Goldberg 1998).

Owners may also hold on to their computers due to economic shock. People cannot bring themselves to throw away something they believe still has value. Yet, computers may lose 80 percent of their initial value within the first year (Goldberg 1998). Simply put, people cannot believe that a machine that cost $3000 when they bought it is worth only $100 just four years later. So they place it in storage looking for a better option. This is not limited to individuals, but includes businesses and institutions as well.

The final option for disposal is the least favorable, placing CRTs in MSW. This includes landfilling and incineration. While cathode ray tubes (CRTs) in particular represent about one third of electronics tonnage, their lead content may represent as much as 80 percent of the toxic metals in discarded electronics. When disposed in landfills, increased concentrations of heavy metals in landfill leachate may result. When discarded electronics are disposed at waste-to-energy facilities, the heavy metals become concentrated in the ash, limiting disposal and reuse options.

No matter the disposal option one fact is definite, the amount of discarded electronics, including CRTs will increase. The tonnage of CRTs generated annually will increase as more personal computers are purchased for household use. The tonnage of analog televisions sent for repair and resale will drop as broadcasters switch to high-definition TV broadcasts between 1998 and 2006. Three decades of CRTs stored in attics and basements will be "cleaned out" as consumers abandon the notion they still have value once standard definition TV transmissions are discontinued.

3.0 METHODOLOGY

3.1 PHASE I

Over 10 weeks, televisions and computer monitors were collected from individual donations, electronics repair facilities, an electronics manufacturer, and institutional electronics disposal. No division between televisions and monitors was made. Televisions tend to be kept longer than monitors and are a larger proportion of the older age groups. However, the construction of a CRT does not differ between a television and a monitor, thus no distinction was necessary.

During initial research, no significant differences in construction of CRTs, based on age were discovered. To detect any changes in lead levels with age, three categories were developed: 1988 and earlier, 1989 to 1993, and 1994 to 1998. This divided the CRTs into five-year groups, with 12 CRTs in each group. These age brackets were based on availability of CRTs. CRTs older than 1984, although available, were rare. The five-year increments provided adequate division while preventing any one time frame from being difficult to find. The earliest time frame was expanded to include any CRT manufactured during or before 1988.

A goal was to obtain a variety of CRT manufacturers in the sample population. It was not possible to determine the CRT manufacturer and year until the monitor was disassembled. Thus, approximately 80 CRTs were collected to achieve a mix of CRT manufacturers in the differing groups. The final sample distribution contained thirteen CRTs in the 1988 and before age group, eleven in the 1989-1993 age group, and 12 in the 1994-1998 age group. The goal of this process was to generalize CRTs as a whole, not to single out any one manufacturer.

In addition to these considerations, interest existed in which parts of the CRT leached the most lead. If the faceplates leached minimal lead, then the face section of the CRT could possibly be sent to a conventional glass recycling facility rather than a more costly leaded glass recycling operation. To measure the differences in the CRT lead concentrations, each CRT was divided into three sections. The sections consisted of the neck, the funnel and the faceplate.

After carefully releasing the vacuum by breaking the glass seal at the cathode connection point, the sections were scored using a diamond tipped rotary cutting tool. The neck was scored two to three centimeters below the point it flared. The funnel was scored between the frit seal (color monitors) or support frame (monochrome) and faceplate. The score was tapped with a screwdriver and hammer to cause the CRT to break along the scored lines. The mass of the complete CRT, the neck, and the funnel were recorded. The mass of the faceplate was computed by subtracting the funnel and neck mass from the total mass.

Once divided, each section was reduced in size as required by EPA SW846 method 1311, the Toxicity Characteristic Leaching Procedure. The TCLP is the test prescribed by the U.S. EPA to determine whether a solid waste is hazardous by the toxicity characteristic. Each division of a tube was tested separately (i.e. the neck, funnel, and faceplate were analyzed individually). A sample of glass, from 200 to 500 grams, was placed in a stainless steel bowl. The glass was covered by a cloth for protection from airborne glass, and manually crushed with a standard hammer. Intermittently, the glass was separated through a 9.5-mm sieve and the remaining large

fraction returned to the bowl for further crushing. The remainder of the glass (that not crushed) was saved. For the face and funnel fractions, the remaining material mass was often large (relative to the amount crushed the test). The rest of method 1311 was completed and the leachate was digested and analyzed for lead using SW846 methods 3010A and 7420.

3.2 PHASE II

During Phase I testing, variability in leachate lead concentrations was noticed between samples of identical manufacturer and model. The cause of this was believed to be differences in particle size composition of the samples and possible heterogeneity of the CRT glass. Differences in particle size would result in varying surface area composition of the samples changing the amount of lead leaching from the CRT glass. This factor is detailed in many CRT industry opinions concerning the use of the Toxicity Characteristic Leaching Procedure. The heterogeneity issue was raised because of the different lead concentration of the frit (relative to the funnel) and its possible impact of the funnel TCLP lead results.

Three CRTs from Phase I were selected for additional testing in phase II. The three CRTs chosen had three different funnel lead concentrations (high, moderate, and low levels) measured in Phase I. The portions of the funnels not crushed in Phase I (a much greater mass than used in phase I) were crushed and sieved into two size fractions: 4.75 mm to 9.5 mm and 4.75 mm and smaller. This ensured that the samples continued to meet the requirements of the leaching procedure. For each of the three CRTs used, three samples of the large fraction and three samples of the small fractions were extracted and analyzed to check repeatability. This produced six lead leachate measurements per CRT.

3.3 PHASE III

Phase III was conducted to further investigate the variability encountered in phases I and II. One CRT from Phase I was selected to investigate the effect of sample size on the variability of lead leaching as well as to determine whether the minimum of 100g mass per sample required by TCLP was appropriate to represent lead leaching in CRTs. The crushed CRT funnel was carefully mixed in the fume hood with a stainless steel scoop in a stainless steel bowl for 10 minutes. Three different masses of the sample were chosen, 40g, 70g, and 100g. Masses greater than 100g were not possible due to the volume limitations of the extractor bottles. Three samples of each mass were extracted and analyzed using the same solid to liquid ratio (1:20 by mass) for a total of nine samples.

To determine whether the lead frit largely affected TCLP results of color CRTs, an additional CRT was obtained. Two samples from the funnel of the CRT were taken. The first sample contained only glass of the funnel section, excluding any frit from the sample. The second sample included the frit within the sample glass. Figure 3.2 illustrates the samples taken. Two extractions were performed on each sample for a total of 4 measurements.

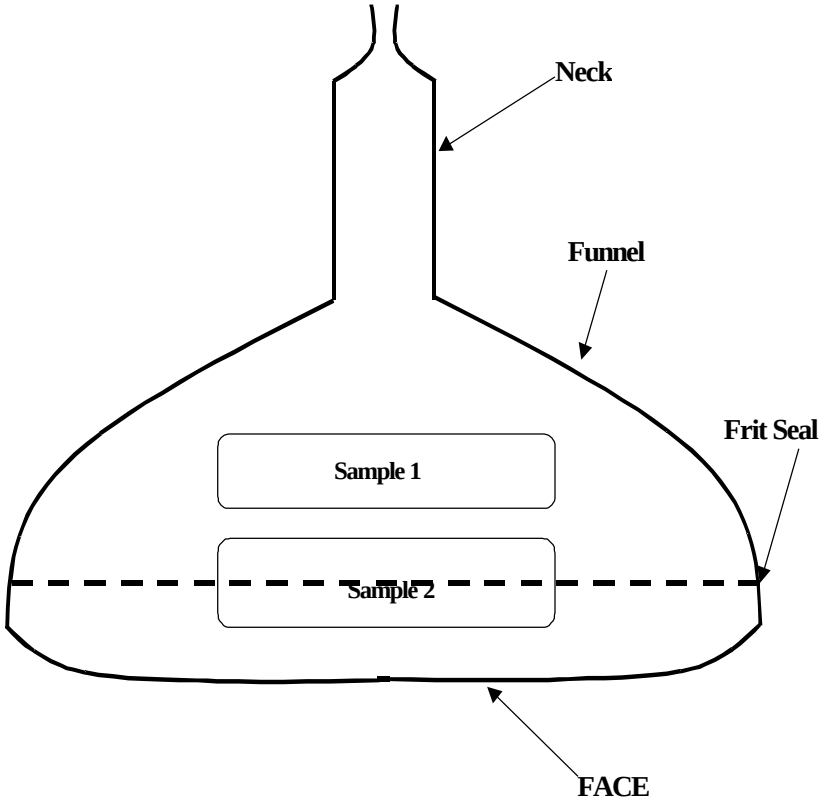

Figure 3.2 Phase III Sample Locations

4.0 RESULTS AND DISCUSSION

4.1 PHASE I RESULTS

Phase I of the study represented the bulk of the work conducted, and involved the measurement of TCLP lead concentrations from CRTs as a function of glass location on the CRT. A total of 36 CRTs were processed and analyzed. CRT screen size ranged from 18 cm (8 inches) to 63 cm (27 inches). As seen in Figure 3.1 each tube was divided into three sections, the neck, the funnel, and the face. The average glass composition of the CRTs was 4.9% neck, 25.2% funnel, and 69.9% face.

The pH of the leaching solution, an important controlling factor in the leaching of heavy metals from wastes, was measured every time a TCLP was performed. The leaching behavior of lead is typically characterized as demonstrating the greatest amount of leaching at low pH values, with a minimum leachability being observed at pH values in the range of 9 to 10, and an increased degree of leachability at pH values above 10 (Van der Sloot et al. 1997). The change in pH occurring during the TCLP was found to be small. The initial pH of all TCLP extraction solutions was 4.93±0.05, and the final pH ranged from 4.8 to 5.2.

The concentration of lead was measured in TCLP extracts from three fractions for every CRT. Table 4.1 presents the lead concentrations for all samples analyzed. The highest concentrations of lead measured were from the funnel fractions. The average lead concentration in the funnel TCLP extracts was 75.3 mg/L. This compares to an average concentration of lead in the leachate of 8.6 mg/l for the neck fractions. Based upon the values for lead content listed in Table 2.1, the funnel fractions were expected to leach less lead than the neck fractions. While this was true for the monochrome CRTs, this was true for only 4 out of the 30 color CRTs. The reasons for this observation will be discussed later. No lead was detected from the face of the CRTs excluding one sample that leached lead at a concentration of 8.0 mg/L, resulting in an average concentration of 0.22 mg/L.

A weighted average TCLP lead concentration was determined for each CRT using the measured fraction weight and the measured TCLP lead concentration of each fraction. The results of these calculations are presented in Table 4.2. The average CRT TCLP lead concentration was 18.5 mg/L. This concentration exceeds the regulatory limit of 5.0 mg/L for TCLP lead (40 CFR Part 261). It is less than the 75.3 mg/l average for the funnel fraction because of the large mass of face plate glass in each CRT that did not contribute any lead. The 99% confidence interval for the weighted average TCLP lead concentration for all CRTs was 9.1 mg/L to 28.0 mg/L.

Table 4.2 also provides average TCLP lead concentrations for different categories among the sample group. These categories include color CRTs only, monochrome CRTs only, CRTs by age group, and color CRTs by age group.

Table 4.1 Summary of TCLP Leachable Lead Concentrations for All Samples

					Leachable Lead Concentration (mg/l)			
Maker	**TV/ Mon**	**Color/ Mono**	**Year Man.**	**Tube Maker**	**Neck**	**Funnel**	**Face**	**Weighted Average**
Acer	MON	C	93	Panasonic	9.5	347.3	<1.0	57.2
Digital	MON	M	90	Clinton	4.2	<1.0	<1.0	<1.0
Elite	MON	C	92	Chunghwa	9.7	81.2	<1.0	19.3
Emerson	TV	C	84	Goldstar	6.5	6.6	<1.0	1.5
Gateway	MON	C	93	Toshiba	9.0	9.2	<1.0	3.2
Gateway	MON	C	92	Toshiba	12.8	174.5	<1.0	54.1
Hp	MON	M	84	Matsushita	<1.0	<1.0	<1.0	<1.0
Hp	MON	M	85	Matsushita	1.7	<1.0	<1.0	<1.0
IBM	MON	C	87	Matsushita	9.5	38.4	<1.0	9.4
IBM	MON	C	89	Panasonic	9.5	142.9	<1.0	41.5
IBM	MON	M	92	Phillips	1.1	<1.0	<1.0	<1.0
Imtec	MON	C	89	Samsung	8.2	200.6	<1.0	60.8
Imtec	MON	C	89	Hitachi	13.6	403.6	<1.0	85.6
Memorex	MON	C	97	Toshiba	10.1	103.0	<1.0	21.3
Memorex	MON	C	97	Kch	12.7	49.4	<1.0	15.4
Memorex	MON	C	98	Samsung	7.0	25.7	<1.0	6.1
Memorex	MON	C	98	Chunghwa	10.9	7.8	<1.0	2.3
Memorex	MON	C	97	Toshiba	8.4	34.9	<1.0	9.1
Memorex	MON	C	98	Samsung	7.1	7.1	<1.0	2.2
Memorex	MON	C	97	Chunghwa	8.3	35.3	<1.0	10.6
NEC	MON	C	87	NEC	11.3	50.3	<1.0	10.7
Orion	TV	C	96	Orion	9.1	132.5	<1.0	33.1
Panasonic	TV	C	84	Matsushita	22.4	11.8	<1.0	3.5
Quasar	TV	C	84	Quasar	13.6	182.4	<1.0	43.5
Samsung	MON	M	89	Samsung	<1.0	<1.0	<1.0	<1.0
Seiko	MON	C	87	NEC	9.1	100.0	8.0	26.6
Sharp	TV	C	94	Sharp	8.7	16.4	<1.0	4.4
Sharp	TV	C	84	Sharp	7.9	6.0	<1.0	1.5
Tandy	MON	C	85	Sharp	17.6	116.1	<1.0	35.2
Techmedia	MON	C	95	Samsung	<1.0	20.1	<1.0	6.9
Teknika	TV	M	86	Phillips	1.6	<1.0	<1.0	<1.0
Ttx	MON	C	91	Chunghwa	7.5	10.0	<1.0	2.8
Zenith	TV	C	94	Zenith	18.3	198.8	<1.0	54.5
Zenith	TV	C	94	Zenith	15.8	7.1	<1.0	1.6
Zenith	TV	C	77	Zenith	<1.0	97.7	<1.0	21.9
Zenith	MON	C	85	Toshiba	7.5	92.1	<1.0	21.5
Averages					8.6	75.3	0.2	18.5

Table 4.2 Summary of Results by CRT Characteristic

Category	Number of Samples	Number Exceeding Regulatory Limits	Average Leachable Lead Concentrations[1] (mg/l)
All CRTs Tested	36	21	18.5
Televisions	10	4	16.5
Computer Monitors	26	17	19.3
CRTs – 1988 and before	13	7	13.5
Color CRTs – 1988 and before	*10*	*7*	*17.5*
CRTs – 1989 to 1993	11	6	29.5
Color CRTs – 1989 to 1993	*8*	*6*	*40.6*
CRTs – 1994 to 1998	12	8	13.9
Color CRTs – 1994 to 1998	*12*	*8*	*13.9*
Color CRTs	30	21	22.2
Monochrome CRTs	6	0	0.03

[1] As measured by the EPA Method 1311, Toxicity Characteristic Leaching Procedure

4.2 PHASE II RESULTS

Results of the phase I work demonstrated concentrations of TCLP lead greater than the 5.0 mg/l regulatory standard for a majority of the monitors. The range of TCLP lead concentrations, even for distinct locations of the CRT (namely the funnel), was more variable than originally expected. This variability was especially noted for some CRTs of the same manufacture of the same year. For example, for two Zenith CRTs manufactured in 1994, the funnel section of one leached 7 mg/l while the other leached nearly 200 mg/l. Phase II was conducted to further explore this variability. The factors that were looked at were particle size and sample heterogeneity.

The results of the Phase II are presented in Table 4.3. Three CRT funnel samples from phase I, each representing a different magnitude of lead leachability were re-tested in triplicate. Unlike the phase I study, however, the entire funnel fraction was first size-reduced before selecting a sample. In the phase I study, only enough larger glass pieces needed for the mass to conduct the TCLP were crushed to less than 9.5 mm. Also in phase II, the three samples were sieved into two different size fraction (4.5 mm to 9.5 m, less than 4.5 mm), each with approximately equal mass. As seen in Table 4.3, all three samples leached more lead from samples with the small particle size as compared to the larger particle size. It is noted that the two CRTs with lower concentrations in the phase I testing (sample 25 and 35), were found to

have higher concentrations in phase II. It is also noted that the variability (as described by relative standard deviation) observed in the triplicate analyses was largest in the larger size samples.

Table 4.3 Phase II Experimental Results

Sample	Large Fraction (mg/L)	Small Fraction (mg/L)	Phase I Result (mg/L)
#25	149.2 (57.2%)	198.2 (53.4%)	81.2
#26	209.8 (40.1%)	439.7 (20.9%)	403.6
#35	44.7 (73.8%)	171.5 (35.9%)	7.1

[1] As measured by the EPA Method 1311, Toxicity Characteristic Leaching Procedure
Values in parentheses are relative standard deviations of triplicate measurements.

4.3 PHASE III RESULTS

The phase II results again showed variability in analytical results even among triplicate measurements. The results did demonstrate that particle size does play a role in the amount of lead that leaches, but results were still variable even for samples sieved to more uniform particle size fractions. This suggests that even for particles of the *same* size, lead leaching is still variable. Phase III was conducted to explore this further. An additional sample from phase I was selected, sieved into the two fractions, and mixed extensively (beyond that conducted in phase II). TCLP tests were then conducted for different masses (40g, 70g, 100g each in triplicate) of CRT glass, while still maintaining a 20-to-1 liquid-to-solid ratio. The results of this analysis are presented in Table 4.3.

Table 4.4 Phase III Experimental Results

Mass	Small Fractions Concentration (mg/L)	Large Fractions Concentration (mg/L)
40 g	448.5 (20.3%)[1]*	122.1 (43.1%)
70 g	377.7 (10.3%)	168.7 (30.3%)
100 g	421.1 (3.1%)	105.0 (35.2%)

[1]Relative standard deviations of triplicate analyses.

Phase III showed similar results as phase II, with larger particle sizes leaching less lead and with larger variability. For the small particle size samples, more mass used in the test resulted in smaller variability. This trend was less clear for the larger particle size. These results, along

with the phase I and II results, lead to the conclusion that some particles have much greater concentrations of lead than others, so that very large numbers of particles must be present to achieve low sample variability.

The most obvious source of particles with much greater levels of leachable lead is the CRT frit. As mentioned in Table 2.1, the frit contains by far the largest fraction of lead in the CRT. A simple experiment that was also conducted in phase III was collecting sections of the funnel glass with and without the frit. The results of this analysis are presented in Table 4. While only for two samples from one color CRT, the results do confirm the suspicions that the frit section of the funnel does contribute by far much larger concentrations of leachable lead.

Table 4.5 TCLP Lead Comparison of Funnel Glass With and Without Frit

Sample	Extraction #1	Extraction #2
#1 (without Frit)	10.8	13.3
#2 (with Frit)	492.0	574.8

4.4 DISCUSSION

4.4.1 Statistical Analysis

ANOVA analysis of the three age groups (1988 and before, 1989-1993, 1993-1998) yielded an F value of 3.23 and a p-value of 0.0385. Based on the statistical analysis, there was a significant difference between the color CRTs from 1989-1993 and the other two age groups (only color CRTs). However, no significant changes in CRT construction were found during these years. Instead, the difference is more likely due to variability in the sample composition, such as frit content of the samples.

4.4.2 Differences in Color and Monochrome CRTs

Twenty-one of thirty color CRTs exceeded 5.0 mg/L of TCLP lead with an average TCLP lead concentration of 22.2 mg/L. For color CRTs, the 99% confidence interval was 12.6 to 31.9 mg/L. No monochrome CRTs exceeded the 5.0 mg/l regulatory limit, with an average TCLP lead concentration of 0.03 mg/L. For monochrome CRTs, the 99% confidence interval was 0.02 to 0.05 mg/L. The difference between color and monochrome CRTs can be explained by the difference in manufacture of each type. Color CRTs utilize the leaded frit seal between the funnel and the face. There is no such seal with a monochrome CRT. The amount of lead used in the funnel is also greater in color CRTs compared to monochrome CRTs. The major contributor to lead in monochrome CRTs is the neck.

The difference between color and monochrome CRTs may allow monochrome CRTs to be treated through conventional waste disposal means. Although nine of the thirty color CRTs were less than regulatory levels, this is likely a result of the lack of frit in the funnel samples analyzed

for those CRTs during the phase I tests. As a reminder, the phase I funnel samples were produced from random pieces of CRT funnel glass generated during the initial CRT destruction (not from the entire funnel). Thus the chance of having very little frit in the sample was greater than if a representative crushed sample of the entire funnel was sampled. Results from phase II and phase III analysis demonstrated that funnel samples collected from the entire crushed funnel (including the frit) always exceeded 5 mg/l. Therefore, a conclusion of this research is that representative samples of glass from color CRTs will exceed the 5 mg/l TCLP regulatory limit.

5.0 CONCLUSIONS

Cathode ray tubes (CRTs) are often referred to as being a hazardous waste because of the leaded glass they are constructed of. This fact, however, is not well documented in the scientific literature. A study was conducted to determine the validity of this claim and to produce such documentation. A total of 36 CRTs were tested for lead leachability using the U.S. EPA's toxicity characteristic leaching procedure (TCLP). In initial testing, twenty-one of the thirty color CRTs exceeded the 5 mg/l of lead regulatory limit for characterization as a hazardous waste. None of the six monochrome CRTs exceeded this limit. Follow-up testing demonstrated that by far the largest concentration of leachable lead is from the frit seal between the funnel and the face panel. The amount is large enough that if a representative glass sample from a color CRT is tested with the TCLP, it will in almost all cases exceed 5 mg/l of lead.

The authors do not attempt to draw conclusions beyond those stated above in regard to the implications of the lead leaching from CRTs. The fact that the TCLP test may not represent the true condition of CRTs upon disposal was not an issue of discussion in this research. That is left to the reader. However, it is recognized that the TCLP is a currently required regulatory test, and that color CRTs do exceed the limit for lead. It is also recognized that the magnitude of CRTs being disposed will increase in the future, and that the appropriate management of these devices needs to be addressed. The fact that color CRTs do exceed the hazardous waste characteristic level for lead using the TCLP does open possibility for inclusion of CRTs in regulatory programs such as the Universal Waste Rule.

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APPENDIX A - QA/QC DATA

1. Laboratory Blanks

Sample Name	Concentration (mg/L)
Blank #1 11-21-98	BDL[1]
Blank #2 11-21-98	BDL[1]
Blank #3 11-21-98	BDL[1]
Blank #4 11-21-98	BDL[1]
Blank #5 11-21-98	BDL[1]
Blank #6 11-21-98	BDL[1]
Blank #7 11-21-98	BDL[1]
Blank #8 11-21-98	BDL[1]
Blank #9 11-21-98	BDL[1]
Blank #10 11-21-98	BDL[1]
Blank #11 11-21-98	BDL[1]
Blank #12 11-21-98	BDL[1]
Lab Analysis Blank 5-20-99	BDL[2]
Lab Analysis Blank 6-24-99	BDL[2]
Blank 5-12-99	BDL[2]
Blank 6-17-99	BDL[2]

1 Detection Limit of 1.0 mg/L
2 Detection Limit of Lead: 0.5 mg/L

2. Replicates

Sample	Leachable lead (mg/L)	Replicate Leachable Lead (mg/L)	Replicate percentage of original
1	132.54	120.84	0.91
4	198.88	198.16	1.00
8	6.58	6.46	0.98
10	174.52	141.8	0.81
13	5.99	6.69	1.12
18	0.000	0.000	N/A
22	11.840	11.680	0.99
23	200.600	200.400	1.00
25	81.220	83.920	1.03
28	9.990	10.340	1.04
31	49.370	50.140	1.02
34	34.850	32.410	0.93

3. Matrix Spike Recovery

Sample Name	Sample Concentration (mg/L)	Spike Added (mg/L)	Spike Response (mg/L)	Spike Recovery (%)
#1R Funnel 11-21-99	71.42	50.00	119.46	98.4
#4R Funnel 11-21-98	202.00	50.00	263.60	104.6
#8R Funnel 11-21-98	7.83	50.00	56.62	97.9
#10R Funnel 11-21-98	279.92	50.00	340.52	103.2
#13R Funnel 11-21-98	6.75	50.00	54.62	96.2
#18R Funnel 11-21-98	0.00	50.00	49.43	98.9
#23R Funnel 11-21-98	219.40	50.00	250.72	93.1
#25R Funnel 11-21-98	121.40	50.00	185.14	108.0
#28R Funnel 11-21-98	12.56	50.00	55.08	88.0
#31R Funnel 11-21-98	46.56	50.00	81.74	84.7
#34R Funnel 11-21-98	33.26	50.00	85.23	102.4
Blank #4 11-21-98	0.00	50.00	47.13	94.3
Blank #7 11-21-98	0.00	50.00	47.28	94.6
Blank #11 11-21-98	0.00	50.00	38.08	76.2
35-3S 5-12-99	140.50	50.00	180.00	94.5
Blank 5-12-99	0.00	50.00	55.00	110.0
Blank 6-17-99	0.00	20.00	16.38	81.9