Los Angeles Jewelry Mart
Sampling and Survey Project (2003)
Data Analysis and Summary

1. Introduction

Between May and August, 2003 the University of California, Riverside conducted a study of activities being conducted at the Los Angeles Jewelry Mart (LAJM) consisting of both field sampling and written informational surveys. The LAJM is a district of buildings covering approximately 16 square blocks in downtown Los Angeles housing roughly 1500 individual jewelry related businesses. UC-Riverside has produced a report entitled "Sampling of Wastestreams at the Los Angeles Jewelry Mart" that provided the purpose and methodologies for sampling as well as the raw data from laboratory analysis of samples taken during this study (attached). This report summarizes the data collected by UC-Riverside. Samples were analyzed by both a third party contract laboratory, Anachem, as well as by DTSC's Hazardous Materials Lab (HML). The overall goal of this project was to better quantify the types and proper handling of jewelry manufacturing wastes.

2. Data Quality

Anachem conducted quality assurance (QA) testing using Matrix Spike and Matrix Spike Duplicates on 30 samples for all California regulated metals (CAM 17) and gold as a measure of how accurate the analysis is. QA recovery rates are generally considered to be out of range if they are more or less than 30% of the expected values. Of the roughly 500 analytes that were analyzed for quality assurance, 30 of them were more than 30% off of the expected recovery rate. Table 1 (below) summarizes the analyte and frequency at which the recovery rates were outside of expected norms. The more conductive precious metals; gold, silver and copper appeared to be more susceptible to being out of the range of norm than other metals, although barium and nickel had multiple instances of non-conformance. Arsenic, cadmium, molybdenum, antimony, selenium, thallium and vanadium had no instances of Matrix Spikes being out of norms.

Of the 30 instances where the Matrix Spike recovery was outside of norms, only 3 of the samples would have indicated the presence of a hazardous waste. All 3 of these samples were Soluble Threshold Limit Concentrations (STLC) results for copper, and all of those samples that were out of range were at least an order of magnitude higher than the STLC level. In one of these cases, HML did the same analysis on the same type of waste stream from the same tenant, and found that concentration to be only 30.3% of the concentration found in the sample with questionable recovery rate. It is worth noting that the Matrix Spike percent recovery in this instance was reported as

29.7%. The other two samples in question did not have similar analysis done by HML as a point of comparison. Given the above discussion of the accuracy of the laboratory analysis, it does not appear that the variations in quality assurance data should have any effect on the validity and usefulness of other data gathered during this project.

TABLE 1: SAMPLE ACCURACY DATA

Analyte	Number of times <30% below expected recovery	Number of times >30% above expected recovery
Ag- Silver	6	1
Au- Gold	5	1
Ba- Barium	2	0
Be- Beryllium	1	0
Co- Cobalt	1	0
Cr- Chromium	1	0
Cu- Copper	6 [1]	0
Ni- Nickel	2	1
Pb- Lead	1	0
Zn- Zinc	1	1
Hg- Mercury	0	1

[1] Three of these Matrix Spike samples had the non-spiked samples indicating that the waste met hazardous waste criteria according to STLC.

Work conducted by HML showed the same trends as those noted in the Anachem body of work. HML data show matrix spike and matrix spike duplicate results outside of expected norms for silver, gold, copper, barium, nickel and zinc with silver, gold, copper and barium being the most deviant from expected values.

Data quality may be questioned for reproducibility based on two factors: unknown spike amounts added by Anachem may bias results by including only low quantities of spiked elements which are more easily reproduced, and HML spikes varied from the actual quantities of elements in samples on such a level that any variance noted is possibly more reflective of sample variability rather than variability between spikes.

Anachem also reported the relative percent difference (RPD) between the matrix spike and matrix spike duplicate results as a measure of how precise the results are. This is similar to reporting a standard deviation or the range in which the reader can be sure that actual value should lay. RPD values are generally considered out of range if they exceed 20% of the expected value. For the 30 samples that were analyzed (570 analytes), twelve of the analytes have values that were out of range. Table 2 (below) shows the number of samples where the RPD was outside of the expected range. None of the occurrences of the RPD being exceeded were in samples that would also

meet hazardous waste criteria. As when measuring accuracy, the data for precision was out of range most often with the precious metals silver and gold.

TABLE 2: SAMPLE PRECISION DATA

Analyte	Number of instances where RPD exceeds 20%
Ag- Silver	4
Au- Gold	4
Co- Cobalt	1
Cu- Copper	1
Mo- Molybdenum	1
Zn- Zinc	1

Three of the analytes were out of range for both accuracy and precision. None of the samples in question demonstrated concentrations above hazardous waste levels. Two (2) of the analytes were gold which has no regulatory level, and the third was silver.

The analysis of silver in samples presents a unique potential problem. Laboratory sample preparation techniques for analysis of metals generally involve the addition of hydrochloric acid to act as a reflux agent. This addition of chloride ions will cause a reaction with the silver ions to form silver chloride which in turn precipitates out of solution and is not measured in the analysis. This precipitation will have the most effect in samples having high silver content. It does not appear that any anomalies potentially caused by this would have any effect on the overall classification of a waste because those wastes which had elevated levels of silver were generally found to exceed hazardous waste criteria for other metals such as copper, nickel and/or zinc.

3. Waste Stream Analysis

GENERAL OVERVIEW

Individual sample data was entered into a database and sorted by waste stream. Analysis was conducted on various waste streams for metals (both TCLP and WET procedures), pH, cyanide concentration, flash point, and fish bioassay. Because the number of facilities that had each waste stream varied, the number of individual samples and the statistical relevance of this analysis varies. Table 3 (below) provides a summary of each waste stream, the number of samples that were analyzed, the number of analyzed samples that exceeded regulatory levels, and the analytes for which the concentrations of the analytes would be considered hazardous waste.

Table 3: Waste stream findings summary

Waste stream (waste number in UCR report)	No. of samples analyzed	No. of samples exceeding regulatory levels	Analyte(s) for which samples are hazardous
Investment slurry/sludge (1)	81	2	Copper, Nickel
Pickling solution w/sodium bisulfate/sodium sulfate dilutions (2)	35	17	Cadmium Nickel, Zinc, pH
Spent ultrasonic bath solution (3)	52	11	Copper, Chrome, Silver,
Spent HF or other acids (4)	12	6	pH, Cadmium, Chrome, Copper, Nickel, Lead, Zinc
Spent ultrasonic bath solutions w/ammonium phosphate or hydrogen peroxide (5)	6	0	None
Grinding dust (6)	6	6	Cadmium, Copper, Nickel, Zinc
Solvents: Acetone, methylene chloride, etc. (7)	N/A	N/A	Not sampled
Aqueous cleaners, soaps, detergents, etc. (8)	N/A	N/A	Not sampled
Cyanide bombing solutions (9)	8	3	Cyanide, Copper
Magnetic tumbler solutions w/soap and chelators (10)	30	22	Chrome, Nickel, Silver, Selenium
Automated mass finishing solutions w/soap and chelators (11)	N/A	N/A	Not sampled
Polishing dust (12)	56	56	Copper, Nickel, Silver, Zinc, Arsenic, Cadmium, Selenium, Barium[1]
Pickling with acid solutions like trisodium phosphate (13)	N/A	N/A	Not sampled
Electroplating acidic or basic solutions (14, 14.1-.7))	27	13	pH, cyanide, various metals (depends on type of solution)
Building wastewater influent to onsite treatment system (15, 15.1-.3))	37	8	Cyanide[2]
Sludge from building waste water onsite treatment system (16)	48	4	Copper, Nickel
Waste oil from drying machine (20)	3	0	None
Platinum divestment remover solution (21)	4	4	Arsenic, Barium, Beryllium, Cadmium, Chromium, Copper, Nickel, Lead,

Waste stream (waste number in UCR report)	No. of samples analyzed	No. of samples exceeding regulatory levels	Analyte(s) for which samples are hazardous
			Thallium, Vanadium, Zinc, Antimony, Selenium, pH
Combined magnetic tumbler and ultrasonic bath solution (22)	4	4	pH, Copper
Combined wastewater from two tanks (23)	4	4	Nickel
Combined wastewater from two tanks (24)	4	4	pH, Chrome, Copper, Nickel
Sandblasting compound (25)	4	0	None
Boric Acid Flux (26)	3	0	None
Caustic soda solution (27)	N/A	N/A	Not sampled
4% cyanide pickling solution (28)	3	2	Silver
Pickling rinse (29)	3	0	None
Ceramic tumbling solution(30)	3	0	None
Metallic ball bearing tumbling solution (31)	3	0	none
Waste water (32)	4	2	Copper
Combined magnetic tumbler and ultrasonic bath solution (33)	8	3	Copper
Burnt polishing dust from recycler (34)	8	8	Copper, Nickel, Zinc, Barium [3]
Fresh cyanide bombing (35)[4]	3	3	Copper

[1] The average concentration of gold in this waste was 44,391 mg/kg
[2] The average concentration of cyanide in this waste was 0.581 mg/l
[3] The average concentration of gold in this waste was 32,973 mg/kg
[4] Fresh cyanide bombing solution is a solution that was just used; it has not had any time to oxidize, be diluted or otherwise changed.

Most samples were taken in duplicate or triplicate for the same waste generation point. The taking of multiple samples from each waste stream allows for determination of the precision of analysis for each analyte, as well as statistical analysis of the data as a whole. Where multiple samples were taken from a single waste generation point, a determination was made as to whether conclusions regarding that set of samples could be made within a 90% upper confidence limit (UCL). The UCL is a measure of how sure the reader can be that the samples are within a “normal” range or distribution. UCLs were determined by adding the standard deviation (a statistical measure of how alike sample values are) to the average (or mean) of the sample values (for a one-sided UCL such as was calculated in this case). When the calculated 90% UCL of an analyte exceeds the hazardous waste

regulatory levels, it can be said with confidence that the waste meets hazardous waste criteria.

FISH BIOASSAY

The results of the fish bioassay tests were not very useful. The fish bioassay is a test that provides a measure of toxicity which is expressed as an LC_{50} or lethal concentration- the concentration of chemical at which 50% of the test fish died. Generally, the test is conducted at various dilutions (100% chemical, 75% chemical-25% water, 50% chemical-50% water, etc.) which allows for an LC_{50} to be calculated using multiple data points and straight line plotting. The tests conducted for this project were run at 100% solution and not at any other dilution. It is very difficult to determine any information regarding an LC_{50} because an LC_{50} is difficult to calculate without multiple dilutions, unless the 100% solution killed only some of the test fish. Data from a 100% strength sample will generally yield a line that is a straight line that never crosses the 50% mark, and thus can not be used to determine the LC_{50}. It may be assumed that those samples that failed to kill fish at 100% strength (i.e., have a 0% kill rate) would fail to kill fish at any lower concentrations. This assumption is difficult to apply to the results of this project because multiple samples of similar waste streams gave conflicting results.

Of the 25 samples taken from the influent to the basement wastewater treatment units, 13 were determined to have a 0% fish kill rate. These 13 samples came from all 7 of the basement treatment units sampled. Only one building (448 S. Hill Street) had all samples returning 0% kill rates, with the other 6 units reporting kill rates at both 0% and 100%, indicating that the waste entering the basement treatment units fluctuates. The data can only demonstrate the absence of a hazardous waste (via the 0% kill rate assumption) during the sampling period. Since only one basement unit had three consecutive 0% kill rates, it can not be determined with any certainty if the waste water that entered the basement treatment units is hazardous or not. Thus, the regulatory status of the basement treatment units remains in question when based solely on this data. Other wastes analyzed using the fish bioassay included the water in the basement treatment units and two wastewater treatment tanks located in a tenant space used to do some rudimentary treatment prior to discharge to the building wastewater system. All of the data collected demonstrated a 0% fish kill rate for these waste streams.

4. Process Wastes and Areas of Generation
BUFFING, POLISHING, AND GRINDING DUSTS

Of the waste streams generated by jewelry manufacturers, buffing and polishing dust remained one of the largest regulatory questions until this project. It was expected that the dust would contain large concentrations of gold, but what other constituents were present, and in what quantities, was unknown. Analysis of 56 dust samples taken from 15 different manufacturing locations has shown that other metals are also present in large quantities. As expected, every sample analyzed contained gold, and in high concentrations. The average concentration of gold in the dust was 44,391 mg/kg. On a rough equivalency scale, this would mean that 4.5% of the dust consists of gold. Other metals that were prevalent in the dust included copper and nickel. Copper was found in every sample, and above hazardous waste regulatory levels in every sample. The average concentration of copper in the dust was 23,781 mg/kg (roughly 2.5% of the total dust) which is 10 times the level at which copper containing dust is would be classified as hazardous waste. Nickel was found in all but one dust sample, and above hazardous waste regulatory levels in half of all samples. Silver, barium and zinc were also present in every sample analyzed, while arsenic and cadmium were present in over half of the samples. The concentrations of each of these metals was generally less than double the concentration that would classify the waste as hazardous for that metal. All individual samples that were found to be above hazardous waste levels were within the 90% UCL for the waste which was sampled. Table 4 summarizes the polishing dust contents.

Table 4: Polishing Dust Metals

Analyte	# dust samples containing detectable amount	# of samples above regulatory levels	% of all dust samples above regulatory levels
Ag- Silver	56	10	18%
As- Arsenic	30	10	18%
Au- Gold	56	N/A	N/A

Ba- Barium	56	2	4%
Be- Beryllium	1	0	0
Cd- Cadmium	33	4	7%
Co- Cobalt	13	0	0
Cr- Chromium	9	0	0
Cu- Copper	56	56	100%
Hg- Mercury	0	0	0
Mo- Molybdenum	21	0	0
Ni- Nickel	55	27	48%
Pb- Lead	9	0	0
Sb- Antimony	15	0	0
Se- Selenium	9	3	5%
Tl- Thallium	0	0	0
V- Vanadium	23	0	0
Zn- Zinc	56	17	30%

An additional process that generates dust and other similar wastes is grinding. The analytical results from wastes identified as grinding showed tendencies similar to those exhibited by the polishing dusts. Wastes identified as grinding wastes were taken from 2 manufacturing locations and were found to exceed regulatory levels for copper, chromium, nickel, and zinc in more than half of the samples analyzed. There were many less samples taken of this the grinding waste stream than of the polishing dust, and thus the statistical significance of the data is more subject to question. Another similar waste stream is burnt polishing dust. As with the grinding wastes, regulatory levels were exceeded for copper, nickel and zinc, and for this waste stream also for barium.

Only 2 of the 17 written surveys indicated the disposal practices of the business with respect to grinding and polishing dusts. Both of these surveys indicated that the dusts were sent to a recycler for disposal. Thirteen (13) of the 17 facilities indicated that they conducted polishing activities, and 14 of the 17 did some grinding. The disposal practices of these facilities were not indicated in the surveys.

INVESTMENT WASTE

The investment stage of jewelry manufacturing is the stage in which the piece of jewelry is designed and cast using the metal desired. Generally, a wax model of the piece of jewelry is made and affixed to a “tree” and a mold or cast (known as investment) is poured around the wax tree and model. After hardening, the next

step is to remove the wax by burning it out of the mold, leaving a “hole” into which the molten metal can then be poured. This is known as the lost wax casting technique. Once the molten metal has cooled, the excess investment (mold) must be removed to retrieve the jewelry piece(s). This step is known as divestment or knockout. The piece of jewelry must then be cleaned to remove any excess investment cast that may be stuck to it. Wastes generated during the investment stage of jewelry manufacturing include sludge and slurry from mold removal as well as various cleaning solutions used to remove residual investment from cast parts. Investment sludge and slurry were analyzed for their metal content and were found to have detectable levels of barium, chromium, copper, nickel and zinc. Of these constituents, only copper and nickel exceeded regulatory levels in the liquid or solid fraction of investment waste. Samples were obtained from 9 different manufacturing locations. In 81 samples analyzed, copper was found to exceed regulatory levels only twice (at 2 different locations), while nickel exceeded the regulatory level only once. None of the samples that exceeded hazardous waste levels were part of a sampling set that met the 90% UCL, indicating that the waste stream can not be confidently classified as hazardous waste based on these samples. Silver and gold were detected and were more prevalent in the solid fraction of the waste, but no analyte was found to exceed Total Threshold Limit Concentration (TTLC) regulatory levels.

Investment casting also requires cleaning. Multiple cleaning processes are used, including pickling with sodium bisulfate solutions, immersion in ultrasonic baths, dipping in acid solutions and immersion in ultrasonic baths utilizing ammonia phosphate or hydrogen peroxide. Surveys indicated that 11 of the 17 manufacturers did casting, knockout, and generated divestment waste from tree cleaning. Nine (9) of the facilities reported putting the investment sludge and slurry down the drain to the basement treatment unit, while one facility placed it in the trash. Ten (10) facilities were noted as using ultrasonic baths, and all 10 indicated that the spent solutions were poured down the drain for disposal.

Analysis of the sodium-based pickling solutions showed that the solutions are generally hazardous due to pH. Ten (10) facilities were sampled for this waste stream. Sixty three (63) percent of the sodium-based pickling solutions were outside of regulatory limits for pH (less than or equal to 2, or greater than or equal to 12.5), with an average pH of all of the acid solutions being 2.15, and the average pH of all of the basic solutions being 10.5. These samples came from 8 of the 10

facilities sampled. In addition to generally being corrosive, many of the pickling solutions were found to have levels of cadmium, copper, lead, chromium, nickel and zinc above regulatory levels. Most prevalent were copper (above regulatory levels in 43% of samples and at 5 of the 10 facilities sampled), cadmium (31% of samples/3 of 10 facilities), nickel (28% of samples /3 of 10 facilities) and zinc (27% of samples /5 of 10 facilities). Chromium and lead were above regulatory levels in 15% of the samples. The 90% UCL for all of the analytes in this waste stream was found to be above hazardous waste levels.

Ultrasonic cleaning solutions were sampled from 14 facilities and tested positive for pH above upper or below lower regulatory limits only once in 55 samples collected, with average acidic and basic pHs of 4.8 and 10.1 respectively. Like the spent sodium-based pickling solutions, the ultrasonic cleaners occasionally can be classified as hazardous waste based on metal content. Elevated levels of copper (above regulatory levels in 23% of samples but only at 3 of 14 facilities sampled), chromium (6% of samples /2 of 14 facilities), lead (2% of samples /1 of 14 facilities) and silver (4% of samples /2 of 14 facilities) were found in ultrasonic solutions. The solutions sampled from 11 of the 14 facilities did not exhibit any hazardous waste criteria. The 90% UCL for all of the analytes in this waste stream was found to be above hazardous waste levels.

Acidic cleaning solutions were sampled from 2 locations and were found to be either strong acids that were hazardous due to pH or weak acids that were pH near normal (pH=7). Overall, the acid solutions exceeded regulatory levels for cadmium, chromium, copper, nickel, lead and zinc at both sampling locations and within the 90% UCLs. In the vast majority of instances where elevated metals levels were noted, the pH of the solution was also found to be hazardous. Only one acidic cleaning solution with a pH above 2 was found to have any metal analyte present above regulatory levels (lead). From the limited data, it may be worth noting that the more weakly acidic the solution, the less likely it is to contain elevated levels of metals. The levels of fluorides, found in hydrofluoric acid were not measured in this waste stream, although fluoride salts have an established regulatory level.

Ultrasonic baths that use peroxides or ammonium phosphate cleaners were found to be moderately basic (pH= 9.8), and contain only elevated levels of copper. This waste stream was sampled only from one facility. The 90%

UCL for copper did exceed the regulatory level for copper in this waste stream.

Investment remover specifically identified as being used for platinum jewelry was evaluated apart from other solutions. Investment used to cast platinum must withstand a higher temperature during casting than the investment used to cast gold, and thus has a different formulation. Platinum investment removal solutions taken from one facility were found to be strong bases (average pH=12.7) that contained elevated levels of metals. In a very limited sample size, all samples exceeded the regulatory thresholds for each of the following metals: arsenic, barium, beryllium, cadmium, chromium, copper, nickel, lead, selenium, antimony, thallium, vanadium and zinc. The 90% UCL for all of the analytes in this waste stream was found to be above hazardous waste levels. Molybdenum and cobalt were present, but not found above regulatory levels.

CLEANING AND FINISHING

The surveys conducted indicated that 15 of the 17 businesses visited conducted some sort of cleaning activities, but did not identify specifically how the cleaning was conducted. Sample data shows that no solvent cleaners were sampled or analyzed. The waste stream identified as aqueous cleaners also showed no data collection, although the written surveys include ultrasonic cleaning solutions as a subcategory of this larger cleaning group. No information was collected on the written surveys with respect to these waste streams. The main body of data and survey information focused on the removing of fire scale and oxidation from cast pieces. The written surveys indicated that all businesses that remove fire scale or oxidation were also generating tumbling media or tumbling media mixed with cleaners such as soap or chelating agents. In these instances, all of the facilities surveyed noted that the waste was being disposed of to the drain to the basement water treatment unit. According to the surveys, 2 facilities conducted cyanide bombing as a cleaning activity although samples were obtained from only one location.

<u>Magnetic Tumbling</u>

Data from the sampling of tumbling media fell into four categories: magnetic tumbling with soaps, combined magnetic tumbling and ultrasonic baths, ceramic tumbling, and metallic ball bearing tumbling. Only one facility was sampled for both the ceramic tumbling and the metallic ball bearing tumbling

media. Both of these waste streams were analyzed for metal content and pH. Neither media displayed any hazardous characteristics due to the presence of metals or pH. The pHs of these media was generally neutral to slightly basic (7.7 and 9.2, respectively). Silver, gold, copper, nickel and zinc were present in all samples analyzed for both of these wastes, but none of the samples contained concentrations of these metals in quantities high enough for them to be classified as hazardous waste.

Magnetic tumbling with soap solutions were sampled from 10 facilities and analyzed for metals and pH. Twenty seven (27) of the 35 solutions tested for pH were found to be on the acidic end of the scale, with an average pH of 4.2. None of these solutions were found to be above upper or below lower regulatory thresholds for corrosivity based on pH. The average pH of the basic solutions tested was found to be 9.3. When looking at the metals in this solution, more than half of the samples analyzed indicated that elevated levels of chromium were present (22 of 48, 46% of samples/from 6 of the 10 facilities). Also present at hazardous levels were nickel (16% of samples/3 of 10 facilities), selenium (5% of samples/1 of 10 facilities) and silver (5% of samples/1 of 10 facilities). The 90% UCL for these analytes in this waste stream were found to be above hazardous waste levels. All metals analyzed for, except thallium, were found in this media, although, with the exception of those listed above, none of the other metals were found at hazardous waste levels. The average concentration of gold in this media was found to be only 40.25 mg/l when analyzed using the WET procedure. As noted with other acidic waste streams, the more acidic the solution was, the more likely a detectable amount of metal was present in solution and the more likely the amount of metal present would be above or near hazardous waste levels.

Like the magnetic tumbling media, the combined waste from magnetic tumbling and ultrasonic cleaning was sampled at only one facility and analyzed for metal content and pH. As seen with the magnetic tumbling media, the pH of these solutions was either very acidic or slightly basic, and the acid solutions were more likely to test positive for corrosivity. Only 2 metals were found in this media exceeding regulatory levels: copper and silver. Copper was found above regulatory levels in all 4 of the samples, silver in one. The 90% UCL for these analytes in this waste stream were found to be above hazardous waste levels. Gold, chromium, nickel and zinc were generally present in the waste, but not at levels that would cause the waste to be classified as hazardous. The average concentration of gold in this media was found to be 106.1 mg/l using the WET procedure.

Cyanide Bombing Solutions

A cleaning option used by a few jewelry manufacturers is cyanide bombing. This process generally utilizes mixing a heated cyanide solution (potassium or sodium cyanide) with hydrogen peroxide. The chemical reaction of the resultant mixture removes scale and oxidation from gold. A cyanide bombing solution was sampled from only one facility and tested for pH, cyanide content and metals. The average pH of a cyanide bombing solution was found to be 10.3, and none of the samples tested as hazardous for pH. The amount of cyanide in the solution was also measured, and was found to average 917 mg/l. This is roughly equivalent to a 0.09% cyanide solution. This solution is generally started with a 3-4% cyanide solution, so approximately 97% of the cyanide was consumed in these samples. All 3 of the cyanide bombing samples were found to have cyanide in them. When analyzed for metals, only one sample provided a result which would classify the waste as hazardous. This sample contained an elevated level of copper. The presence of silver, gold, cadmium, chromium, zinc, molybdenum, nickel, arsenic, antimony and barium was also determined, although all at levels below regulatory thresholds.

A fresh cyanide bombing solution was also tested just after a bombing event had occurred. The same facility that was sampled for the cyanide bombing solution discussed above “staged” a cyanide bombing event so that a fresh solution could be tested just after use. The pH of this solution was similar (10.2) to that of other cyanide bombing solutions (10.3) sampled, but the concentration of cyanide was considerably lower (30 mg/l as compared to 917 mg/l). The reason for this is unknown, but may be explained by more careful measurement of chemicals during preparation or an increased interaction period between chemicals resulting in more complete cyanide destruction.

Other Jewelry Manufacturing Wastes

Cyanide Pickling

A method used to clean plated gold is to use a 4% cyanide solution as a pickling solution. This process is generally used to strip excess silver or gold from a previously plated surface prior to re-plating (generally cosmetic or very fine pieces) as well as to remove fire scale or oxidation. Only one facility was sampled for this waste stream. In these solutions, the pH was found to be moderately basic, which is consistent with most cyanide solutions. The amount of cyanide in the rinse waters was not analyzed. The amount of

cyanide in the pickling solution is known to be 4% (roughly 40,000 mg/l) as it is purchased pre-mixed at that concentration. The pickling solution was found to have elevated levels of silver, above those that classify the waste as hazardous. Other metals present in both the pickling solution and the rinse waters, but at concentrations below regulatory levels, include gold and zinc. Rinse waters contained lower levels of barium, copper and nickel, while the pickling solution had low levels of cobalt and molybdenum.

Sandblasting

Sandblasting is not a preferred method of cleaning jewelry because of the "softness" of most precious metals. Soft metals may be pitted by the "sand" during the process leaving a less than desired finish. When used, sandblasting is generally used to remove investment from cast parts. The samples analyzed from sandblasting did not meet any hazardous waste criteria. Amounts of silver, gold, cadmium, copper, nickel, lead and zinc were found in samples analyzed, but all were below regulatory levels. This waste stream was sampled at only one location.

Boric Acid Flux

Jewelry may be dipped in boric acid solutions containing alcohol as a means to prepare the piece for soldering. During the dipping process, the part is coated with the boric acid solution. The part is then heated to evaporate the alcohol component, leaving a coating that aids in the adhesion of solder. The boric acid solution from one facility was tested for pH and metals content. The average pH of the samples was found to be 3.0, but none of the limited samples were found to be hazardous waste. The metals analysis showed amounts of zinc, nickel, cobalt, copper, chromium, and barium, but all at concentrations below regulatory levels.

5. Building Waste Water Treatment Unit

Influent to the basement treatment units was analyzed because it is believed that many wastes are being poured down tenant's drains and treated in these units. Entering this project, the proper regulatory status of these units was unknown, since it had never been determined which, if any, hazardous wastes from the tenant spaces the units were receiving. The surveys indicated that almost all of the wastes generated by individual tenants in the buildings are being poured down drains to these units, the exception being the buffing and grinding dusts. Seven (7)

basement treatment units were sampled. The influent wastes to the unit were analyzed for metals, pH and cyanide. The metals analysis showed the presence of silver, gold, barium, chromium, copper, molybdenum, nickel, lead, and zinc. All of these metals were present at concentrations below regulatory levels. The average concentration of gold in these samples was 0.51 mg/l (roughly 0.06 troy oz. of gold per gallon). The pH of the incoming solution never exceeded hazardous waste criteria. Cyanide was detected in 11 of the 25 samples analyzed, with an average concentration in the influent of 0.845 mg/l. The values ranged from 0.027 mg/l to 2.26 mg/l with a median value of 0.56 mg/l. It should be pointed out that these samples were obtained at the point at which commingled and possibly diluted wastes entered the treatment unit, and this may account for the presence of many metals, albeit at levels below hazardous waste criteria.

The sludge that is captured and removed from the bottom of the water treatment unit was also analyzed at 7 buildings. Of the 54 samples analyzed, only one sample contained detectable levels of cyanide. The concentration of cyanide in the sludge was found to be 15.4 mg/kg. The sludge at each building was also analyzed for metals concentrations. Both a TTLC and STLC value were obtained. TTLC values were all found to be below regulatory levels. STLC values were exceeded for copper (4 of 54 samples/3 of 7 buildings sampled) and nickel (1 of 54 samples/1 of 7 buildings sampled). The 90% UCL for these analytes in this waste stream was found to be above hazardous waste levels.

Waste water from two tanks in a tenant operated wastewater treatment unit was also analyzed. The tenant operated wastewater treatment unit was located in an electroplating operation, and treated process and rinse waters prior to discharging wastes to the building's wastewater unit via the drain. The results of this analysis were very similar to those found in the influent to the basement treatment unit. A measure of pH found 4 of the 8 samples to be below lower regulatory limits (all on the acidic side), and the average cyanide concentration was measured at 1.06 mg/l. Cyanide was found in all 8 samples analyzed and the median concentration of cyanide was 1.5 mg/l. Metals found in the holding tanks were similar to those found in active influent sampling, except that in the holding tanks nickel, copper and chromium samples were found to be above regulatory levels.

6. Conclusions

The intent of this study was to assist in the classification of wastes generated by “normal” jewelry manufacturing activities. The data collected during the sampling of jewelry manufacturing waste streams indicates that the majority of the wastes generated by manufacturing activities will qualify as hazardous wastes. The conclusions presented in this report are drawn from small sample sets, and as such should be recognized as potentially limited in their statistical significance, although almost all samples were within the 90% UCL even for the small sample sets. This information allows DTSC to say with 90% confidence that the conclusions drawn are statistically valid and reflective of the conditions of the locations sampled.

The quality control performed on the data indicates valid accuracy and precision with respect to the data presented. Variances in accuracy and precision were most commonly seen with the more conductive precious metals: silver, gold and copper. The results for gold are presented for informational purposes only as no regulatory levels have been established. Data for silver may be skewed to a value lower than actual silver concentrations due to the precipitation of silver out of solutions before analysis. The precipitation of silver from solution is generally due to the addition of sample preparation acids which react with the silver to form silver chloride which then fall out of solution and are not included in the analysis. Limits on data for silver and copper are valid, and are often reinforced by more valid data on other constituents such as nickel and zinc, which are often present at hazardous levels in the same waste streams as those that contain elevated levels of copper or silver.

Within the jewelry manufacturing process there are four general steps: Investment/casting, ornamentation, cleaning, and polishing/finishing. Not all manufacturers conduct all four processes. Electroplating is an affiliated process used by some jewelers.

Within the investment/casting part of manufacturing the cleaning process used to remove excess investment from cast parts appears to be the process that generates the most hazardous wastes. Investment and casting were found to generate very little waste, although the potential silica exposure from dry investment removal was not examined in this study. Gross investment removal does not appear to generate a hazardous waste. Cleaners used to remove excess investment from cast parts, be it ultrasonic cleaning, acid pickling or sodium-based pickling, generally exhibited hazardous waste characteristics. As a group, both the pH and presence of metals such as copper, chrome, zinc, lead, nickel and cadmium led to these wastes being identified as hazardous wastes. The least hazardous cleaner appeared to be the sodium-based ultrasonic solutions which were within regulatory levels for pH, and exceeded regulatory levels only for copper content. It should be

noted that this waste stream had a limited sample size when compared to the other waste streams. An additional factor that must be considered is the fact that the majority of facilities sampled that utilized standard ultrasonic cleaning solutions did not have any samples which exceeded hazardous waste levels.

Jewelry cleaning is used in this report to represent those steps taken to remove oxidation or fire scale from pieces. This process generally includes either physical tumbling with various media or chemicals or cyanide bombing. Tumbling activities that utilize chemicals generally can be classified as generating hazardous wastes based on the concentrations of metals, specifically copper and chromium. It should be noted that wastes generated from tumbling with physical media such as ceramic or metallic balls would not be classified as hazardous according to the data collected. A limited sample size of these two processes should be considered. Cyanide bombing solutions may be considered hazardous, as a group, based on cyanide content. It appears that most of the cyanide is consumed in the bombing process and that the remaining levels, while hazardous, would not be likely to produce cyanide gas clouds.

The final step in jewelry manufacturing is polishing. Polishing dusts were found to be hazardous for many different metal constituents. It should be noted that all of the written surveys indicated that this waste stream was collected and sent to a recycler in lieu of being disposed of to the drain or as a hazardous waste. Questions remain as to if this waste is properly transported to recycling facilities as anecdotal information points to shipments via common carriers such USPS, FedEx or UPS rather than registered hazardous waste transporters. Additional concerns regarding this waste include the fact that the final destination of the dust is precious metal reclamation, but under state law the dust must be sent to a primary smelter or permitted secondary smelter to qualify for the reduced transportation and handling standards.

Overall, it appears that the fact that gold and other jewelry metals are alloyed is the key contributor to the classification of wastes generated by jewelry manufacturing as hazardous wastes. The presence of copper, zinc and nickel in gold alloys means that any steps to work the gold will result in the generation of these metals in the process.

The data obtained from the basement treatment units is less conclusive than other data. The primary reason for this is that the data from the fish bioassay testing can not be used to draw any firm conclusions. When examined in light of each individual waste which may enter the system and the statements collected during the surveys that indicates that these wastes are disposed of to the basement treatment units, it appears that the basement treatment units are receiving hazardous wastes from various tenant spaces, but that at the

time of treatment in the unit the wastes no longer exhibit the characteristics of hazardous waste due to commingling or dilution.

The information collected from written surveys of jewelry manufacturing activities indicates that, with the exception of polishing dusts, the majority of these wastes are being improperly disposed of to jewelry mart building basement waste water treatment units. The basement treatment units are, in turn, receiving and treating hazardous wastes, and further generating sludge that may qualify as hazardous wastes. As discussed above, it does not appear that the polishing dusts are being disposed of in accordance with law either.