

Elemental Compositions of Over Two Dozen Cell Phones

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Research In Motion

Twenty-nine different cell phones have been disassembled, ground up, dissolved and analyzed for elemental content, mainly for information about the metals present in the phones, but also for some metalloids and non-metals. The following elements were detected in some or all of the phones: Be, Mg, Ti, V, Mn, Fe, Co, Ni, Cu, Zn, As, Nb, Ag, Sn, Sb, Ba, Ta, W, Au and Pb. The following elements were not detected: Se, Cd, In, Te, Pt, Tl or Bi. The paper will discuss the method used and propose possible sources in the telephones for certain elements of interest and the reasons for the interest in some of the elements.

Introduction

Over the course of the last decade cell phones have been collected and analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES, commonly referred to as just ICP). Part of this was out of curiosity, for environmental compliance testing, to answer questions about conflict minerals, to answer internal company questions about reclamation value and to provide information for customer inquiries about all of the preceding. Currently there are various flavors of the RoHS directive that affect lead, cadmium, mercury, chromium and bromine in one way or another. Conflict minerals typically include the elements tantalum, tin, gold and tungsten. However, most people are unaware that one of the major minerals containing tantalum, coltan, contains a mixture of tantalum and niobium. Therefore expect to see niobium on conflict mineral lists sooner rather than later. The main metals of interest from an economic recovery point of view are of course the noble metals. Depending on the reference¹, these can include: ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, mercury and rhenium. For the manufacture of electronics, this is usually restricted to palladium, silver, platinum and gold.

The ICP/OES instrument measures characteristic atomic emission spectra. Dissolved, liquid samples are nebulized and the resulting fine aerosols are transported to the plasma torch. A radio-frequency inductively coupled plasma (ICP) is produced at the tip of the torch which atomizes and excites the analytes. The excited atoms emit UV-visible radiation. The spectra are dispersed by a grating polychromator, and the intensities of the spectra are monitored at specific wavelengths by a CCD detector. Currents from the detector are processed and controlled by a computer system. The identification is done via the presence of characteristic emission lines of a specific element, and the quantification is done via the intensity of the emission line.

No attempt was made to test for all elements of the periodic table. Noble gases and radioactive elements were not expected to be present for reasons of unreactivity and safety, respectively. Group one elements, which usually form salts, were also not tested for. No elements definitively considered to be non-metals, for instance halogens, were tested for either. Mercury, which is a significant element in the present context, was not tested for as ICP is not the proper instrument for this element.

The lanthanide series of elements were also not tested for. This of course is going to change immediately because of the looming shortage of these elements in the short to medium term because of China's decision to decrease exports of these elements to keep them for domestic industry and consumption for internal needs². Testing will be necessary to aid in determining where they are used and also because it is possible that the United States government will request information on their usage from cell phone manufacturers and the rest of the electronics manufacturing industry, although calls for this do not appear in recent legislation related to this topic³.

The "elements of life" C, H, O, N, P and S were also not tested for. Certainly the first four and sulfur would be found in the plastics used to make electronic products. Twenty-nine elements were selected for testing. All are metals except arsenic, antimony, selenium and tellurium. In hindsight one structural element that should have been tested for is aluminum.

Method

No special procedures were used in the handling of the cell phones. Gloves were not used, as the pedigree of the phones was not always known, so taking precautions at such a late date seemed pointless. Each phone after disassembly was divided into three portions – a) LCD module; b) main printed circuit board assembly (PCBA) and c) outer plastics, objects attached to it and anything that was not part of groups a and b. The materials were then cut up into 1 cm x 1cm pieces using a cross-sectioning saw. Previous work⁴ has shown this method not to be a source of significant contamination.

The pieces were then slowly feed into a Retsch ZM 200 grinder for further reduction of size. The grinder was carefully cleaned before being used for each different phone. Sixteen (16) ml of HCl acid was slowly poured into each beaker containing 0.5 g of the portion of cell phone to be tested. After allowing to sit for 5 min, while swirling gently, 4 ml of HNO₃ acid was added. Acids were added separately to prevent conversion of Sn to SnO₂ or Sb to Sb₂O₃. The mixture was digested on a hot plate for 1 hour and then evaporated until the solution volume was approximately 2 mL. After cooling down, 16 mL of HCl acid was added slowly and carefully to the solution. The solution was then made up to a known volume in a 50 mL centrifuge tube and then a portion was extracted from this mother solution and further diluted as required for testing individual elements.⁵

To analyse Nb and Ta, 10 ml of hydrofluoric acid acid was added to a 0.1 g portion of a cell phone to be tested. The mixture was digested on a hot plate for 1 hour and then evaporated until the solution volume was approximately 2 mL. After cooling down, the solution was then made up to a known volume in a 50 mL centrifuge tube. No further dilution was necessary due to the low concentrations of the analyzed elements.

Two Perkin Elmer ICPs were used. Most of the work was carried out using a Perkin Elmer Optima 2000 model, but more recent work was done using a Perkin Elmer Optima 7300DV. Typical ICP parameters used were:

Gas used		Argon
Plasma view		Axial
Plasma aerosol type		Wet
Gas flow	Plasma	15 L/min
	Nebulizer	0.7 L/min
	Auxiliary plasma	0.4 L/min
Power		1450 W
Sample flow rate		1.5 mL/min
Source equilibration delay		15 sec
Wash time with automatic sampler		60 sec

Results

Figure 1 shows the average amount of the elements in the twenty-nine phones tested. Iron and copper were the only elements present in amounts of up to almost 15 grams each. The next most abundant elements were nickel, magnesium and tin. Vanadium, arsenic and niobium were usually present in the range of 0.01 grams or less.

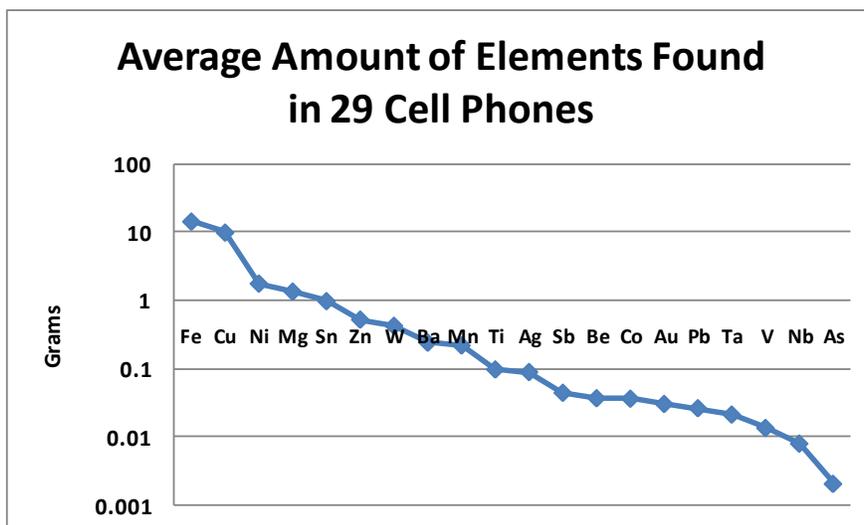


Figure 1 Average Abundance of the Elements Tested for in 29 Phones

The following elements were not detected: Se, Cd, In, Te, Pt or Tl. It was good news that cadmium was never detected, as this metal is restricted under RoHS and other directives and legislation in various jurisdictions. Thallium is also very toxic and was not expected to be present. Small amounts of selenium, and platinum were expected. Selenium is used in some semiconductors. Platinum has on occasion been used as a surface finish, although rarely because of its expense. It also is used for other purposes because of its high electrical conductivity and resistance to corrosion.

Bismuth has found use as a surface finish too. Significant concentrations of bismuth in the presence of tin and lead together are bad as there is a ternary alloy of the three metals that melts at 96°C. However, in the portions of the electronic industry that must comply with RoHS, there are very few components that have a tin/lead surface finish that have not been purged. As a result, there is a resurgence in components with tin/bismuth finishes. In part this is due to lower melting temperatures and in part due to attempts to decrease the possibility of tin whiskers or tin pest. However, there are some movements to ban/restrict the use of bismuth. Presumably this is due to the fact that the primary source of bismuth is as a by-product of lead mining. However, since no more than one percent of the lead that is mined is for the electronic industry⁶, restricting bismuth will in no way decrease the amount of lead mined. There has also been voiced some concern about the dissolution of bismuth compounds, but if this were a real issue, it seems to be refuted by the decades safe use of an over-the-counter product called PeptoBismol™, which is essentially bismuth subsalicylate. This product is ingested and passes into the stomach where the pH is less than 3.

It can be argued that iron is the structural basis of any significant civilization over the past two millennia⁷. It certainly seems to be the bedrock element for many of the cell phones as well. Concentrations of iron as high as 40 grams to as low as 1.7 grams were found. It is interesting to note that some of the higher amounts have been found in some of the more recently manufactured phones, at a time when manufacturers are aiming for lighter phones. It is presumed additions have been to toughen the phones.

Copper usage was found in a narrower range of 6 to 16 grams, with a more or less steady increase over the years. See **Figure 2**. It was assumed that gradual increase in copper was due to the increasing complexity of the circuit boards themselves. However, by examining the amount of copper coming from the main PCBAs, this does not appear to be the case. The additional copper is coming from the LCD assemblies and from the electronic components that are attached to the plastic housing rather than soldered to the PCBs. The comparison between total copper and copper from the PCBAs is shown in **Figure 3**.

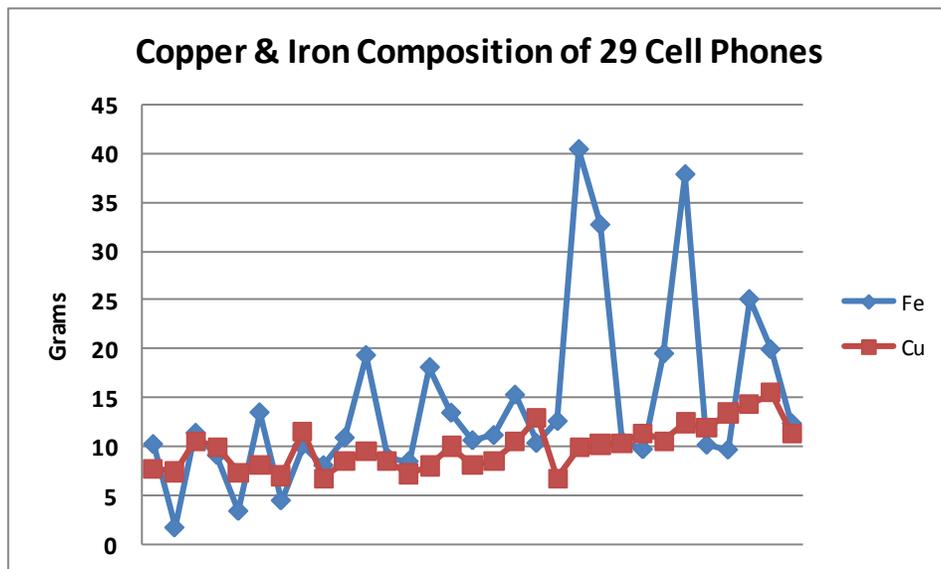


Figure 2 Iron and Copper in the Cell Phones

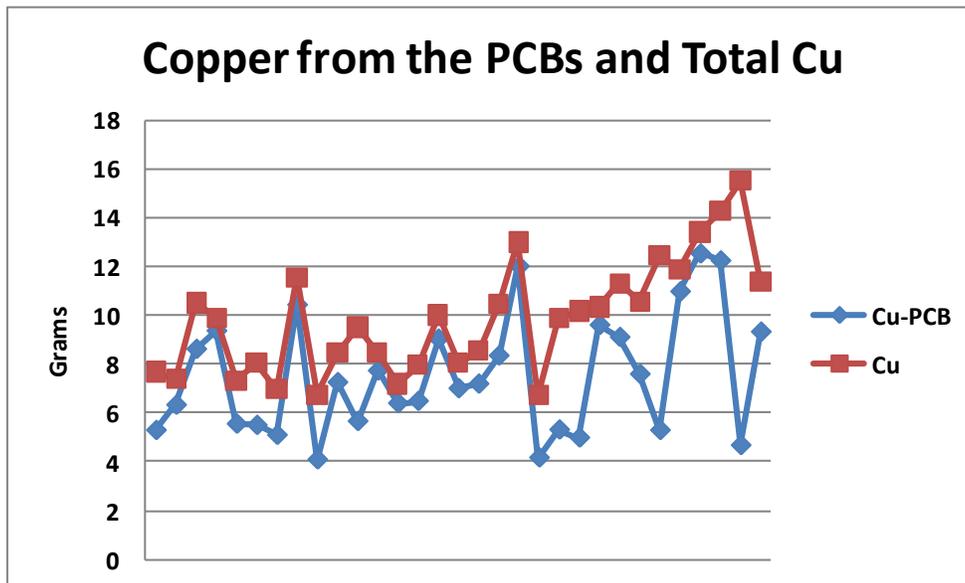


Figure 3 Comparison Between Copper from the Whole Device and from the Main PCBA

Two other fundamental metals of our modern society are nickel and zinc. It is interesting to note that the highest use of nickel is in some of the more recent phones, at a time when there are restrictions on the use of nickel that may come in contact with human skin⁸. It is estimated⁹ that 10-15% of women and 1-2% of men have a skin sensitivity to nickel. As a result, the EU has issued a directive that essentially disallows the use of nickel on the outside of cell phones and other common, portable electronics. The high nickel concentrations are quite likely due to the presence of German silver RF cans. The concentration results for zinc are fairly consistent, except for one cell phone model. The reason for this is not known. See Figure 4.

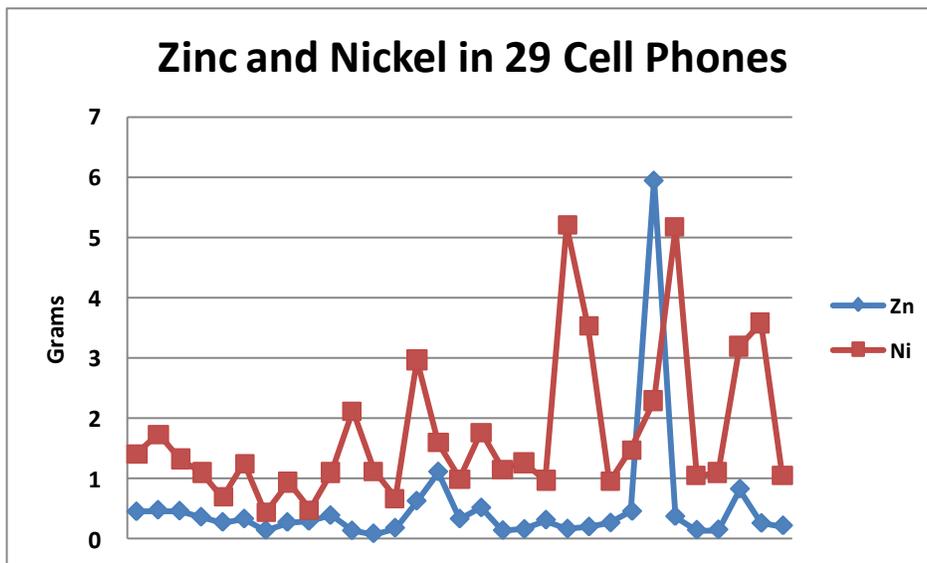


Figure 4 Zinc and Nickel in Cell Phones

Silver and gold are two metals used since antiquity. They are beautiful, found in native form, are relatively rare yet not exceedingly so and are easy to work because of their malleable and ductile natures. The latter two properties, plus their good electrical conductivity and solubility in tin based solders, have made them elements often used in the electronics industry. However, it was expected that with the rise in the price of gold from \$275 ten years ago¹⁰ to over \$1,800 a troy ounce at the time this is being written, that the amount of gold found in cell phones would have decreased over the decade. With an average amount of 0.03 grams of gold per cell phone and assuming a price of \$1800 per ounce or \$57.88/g, each cell phone is “worth” around \$1.70 just for the gold content. Assuming 0.1 grams of silver at a price of \$1.31 per gram adds another \$0.13. Of course this must be weighed against the cost of disassembly and extraction. **Figure 5** shows that the amount of silver used is about three times as high as the amount of gold. There also has been a very gradual increase in the amount, just like gold and copper.

The first two cell phones of **Figure 6** were produced using tin/lead solder and the rest were made with lead free solders. Because about one gram of the 63/37 tin/lead eutectic solder was replaced by lead free solder with 95% tin (ignoring density differences) this would require about an additional 0.3 grams of tin, which would in part explain the higher tin content seen for the lead free phones. During one period of time the tin concentrations were not measured. The tin results that were collected are shown in Figure 6.

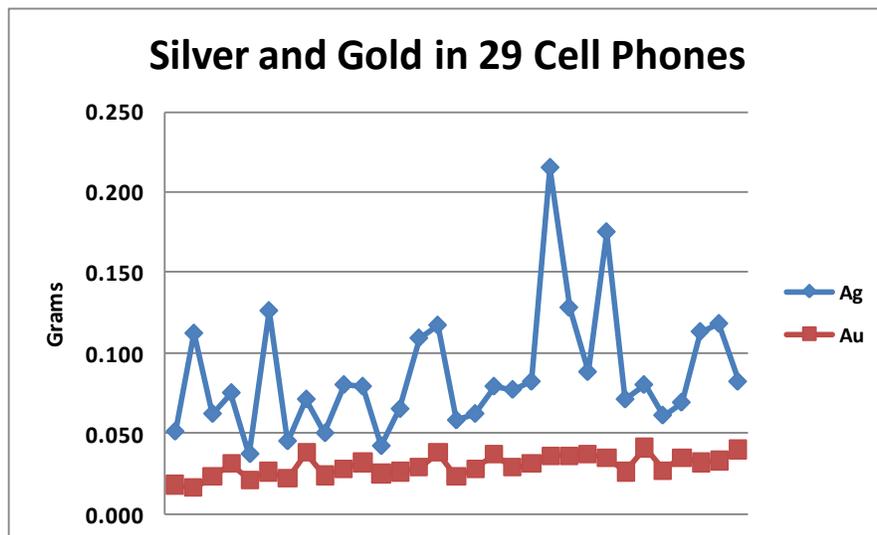


Figure 5 Gold and Silver used in Cell Phones

Tin is of course one of the elements that potentially comes from “blood minerals”, most often from the Democratic Republic of the Congo¹¹. Blood minerals are like blood diamonds, in that they are materials that are mined illegally and the monetary proceeds are used to fund violent warlords who perpetrate rape, murder and genocide on various areas in Sub-Saharan Africa. However, unlike tantalum and niobium which are only mined in a few locations, the sources for tungsten, tin and gold are relatively more widespread and the resulting ability to track these latter three metals to their source will be that much harder.

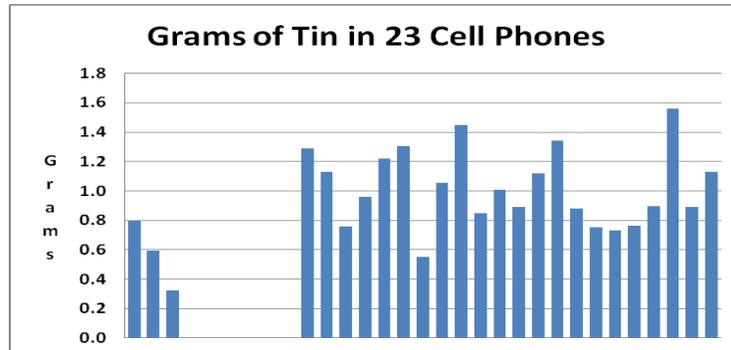


Figure 6 The Amount of Tin In Cell Phones

Tantalum, along with tin, tungsten and gold, are listed as the four blood mineral elements. The first three come from the parent ores coltan, cassiterite and wolfram, respectively. Gold is found in its elemental form. What is often not known is that tantalum and niobium are usually found together, so niobium is essentially in the same “bucket”. Figure 7 shows the amounts of tantalum and niobium used. Tantalum is obviously used in tantalum capacitors, but is also found in filters and a few other components. The spikes in the concentration are most likely due to phones that have a larger number of tantalum capacitors than the others. Niobium may be present because of manufacturers not using high purity tantalum. For tantalum the amounts used range from zero to 0.08 grams with an average of 0.022 grams. To produce ten million cell phones with that average amount would require 22 kilograms of pure tantalum. This equates to about 31 kilograms of coltan. Due to the variable nature of the amount of iron and tantalum present in the form of oxides, one cannot be specific about the exact amount of coltan that would be required for an exact amount of pure metal.

Information for some RIM phones was collected specifically about tantalum and then compared with the analytical results. In most cases the analytical results for those phones shown in this paper are low compared to the elemental sum from the information in the component supplier data sheets. Work is continuing on this challenge.

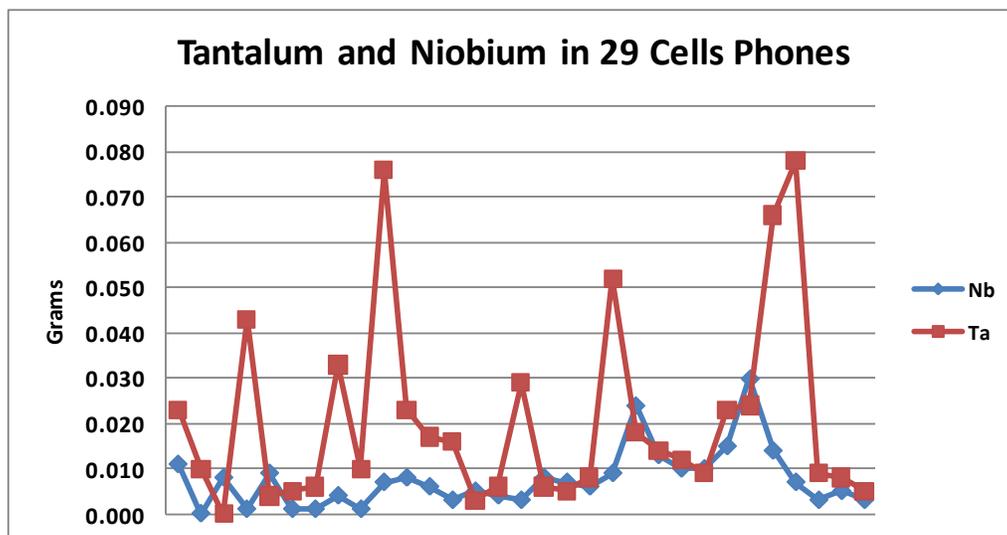


Figure 7 Tantalum and Niobium in Cell Phones

The last element of the four elements targeted that might come from illegal mining in the DRC is tungsten. It is interesting to note that this element gets the least amount of coverage for its possible DRC sourcing and yet it is present in much larger

quantities than niobium and tantalum. In fact it is present at about three times the amount of niobium, tantalum, gold and silver combined. The main use of tungsten appears to be as the off center weight on the end of the shaft of the small motor that acts as the vibrator in cell phones. The reason for this use is the high density of tungsten (19.25 g/cc), about 1.7 x that of lead.

The difference in the amount of tungsten found for the first third of the cell phones examined and the latter two thirds is due to a change in analytical technique rather than a sudden increase in the use of this element. Also, where available, comparing environmental certificates of compliance where the manufacturer gave more information than just what was required for RoHS and REACH, allowed the researchers to see that the amounts of tungsten found analytically were too low.

The vibrator was separated from the PCBA and digested with a 4:1 solution of HCl:HNO₃ acids until only W was left. An X-ray fluorescence spectrometer (XRF) was used for checking for the presence of other metals in the remaining part of the vibrator. When the XRF showed that only W and no other metals were left, the digestion process was considered completed. The solution was evaporated to approximately 2 mL. After cooling down, 16 mL of HCl acid was added slowly and carefully to the solution. The solution was then made up to a known volume using a 50 mL centrifuge tube and analyzed by ICP. The small portion of vibrator which was not possible to dissolve in acids was weighed using an analytical balance and this amount was used for final calculations of tungsten.

Manganese is an element with comparable concentrations. In older style plated through hole tantalum capacitors, manganese was used to form the cathode material.^{11a} It is also an important additive for stainless steel and for corrosion-resistant aluminum^{11b}. The concentration values of manganese and tungsten are shown together in **Figure 8** simply because they are found in comparable quantities. Nothing should be inferred from this pairing.

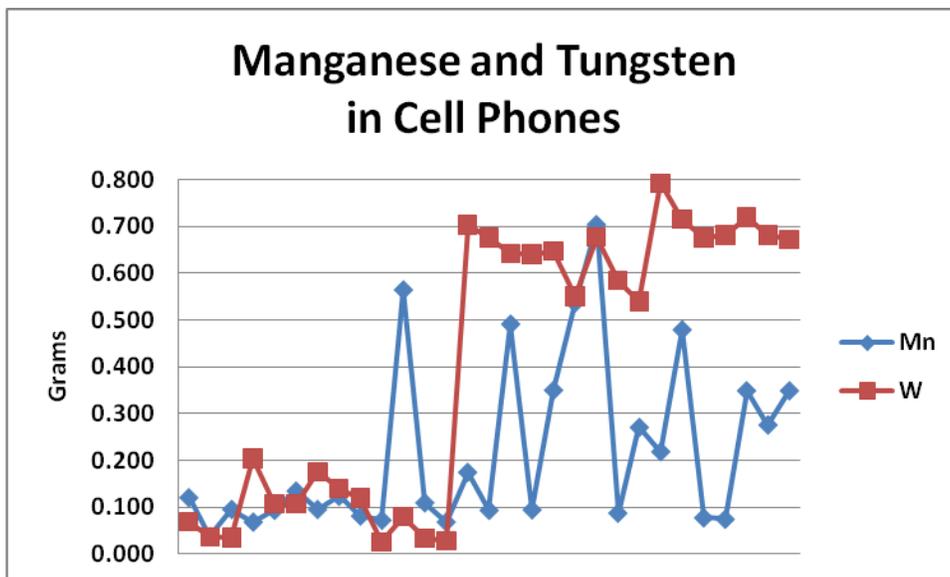


Figure 8 The Amounts of Tungsten and Manganese Used in Cell Phones

The next element of interest was beryllium. A principle use of beryllium in the electronics industry is as an additive to copper for spring contacts. Two common component types taking advantage of this characteristic are: 1) the copper gaskets around the doors of equipment that can generate and/or are sensitive to RF and 2) spring conductors connecting PCBAs with LCDs or keyboards. The potential issue with beryllium is that during its manufacture and even more likely in uncontrolled disassembly, there can be the formation of air borne beryllium containing dust that can be breathed in by unprotected workers. This can lead to a terrible industrial malady called berylliosis¹⁴. Less than 0.01 grams was detected in each phone (**Figure 9**). In several cases no beryllium was found. It is not known if this was because there was none, it was below the detection limit of the equipment (which is not the same as zero) or if there were interferences that affected the end result.

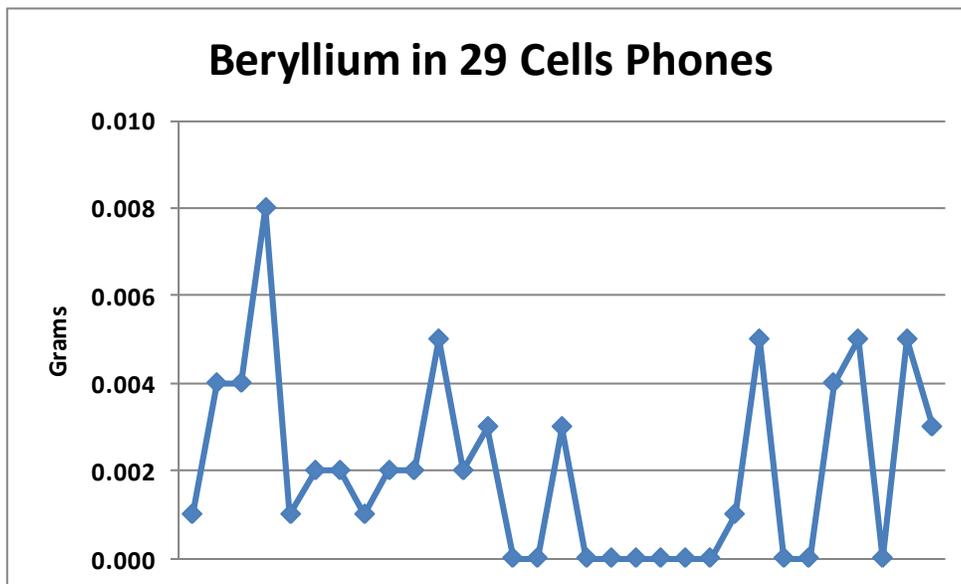


Figure 9 Grams of Beryllium Found in Cell Phones

One of the antimony oxides (Sb_2O_3) has been used as a flame retardant in some industries. However, there is some confusion in our industry because of the way antimony concentrations are sometimes reported in environmental certificates of compliance. Historically antimony concentrations have been determined gravimetrically as the oxide Sb_2O_3 . Even today, although elemental antimony concentrations are usually determined by modern analytical instruments like atomic absorption spectrometers (AA) and inductively coupled plasma optical emission spectrometers (ICP-OES), the results are often quoted in terms of Sb_2O_3 , irrespective of the fact that there was none of this oxide present in the sample being tested. A significant new use for antimony is the development of a new generation of memory devices which will replace flash drive memory devices presently used in computers, mobile phones and USB memory devices. These new memory devices – known as phase-change devices – use an alloy of germanium, antimony and tellurium ($Ge_2Sb_2Te_5$) known as “GST”. In June 2010, Samsung Electronics started mass-producing these phase-change devices from GST for use in mobile phones and laptops. These devices are up to 30 times faster than normal flash memory.¹⁵

Although lead is highly restricted by the RoHS directive, there are a number of exemptions of use to manufacturers of electronic equipment. These include:

- Lead as a machining additive for steel, aluminum and copper
- High lead solder for die attach
- Lead in glasses and ceramics
- Lead in flip chip solder balls

This means that it is quite likely that any electronic device, whether it is “lead free” or not will have some lead in it. Only one of the 29 cell phones had no lead detected. Most had between one and twelve milligrams. Others had 18, 22, 29, 84, 230 and 255 milligrams of lead. See **Figure 10**. All but the one with 255 mg were lead free products. Those with 18, 22 and 29 milligrams were recent RIM products where each individual component had been tested for RoHS compliance. So even though the concentration in homogeneous materials that are mechanical separable would be higher than, for example, 29 ppm, the values were not above 1000 ppm, the maximum allowed where no exemption is called out. It is interesting to note that the amount of lead found in some of the newest phones was higher than that found for most of the earlier ones. No explanation is available at this time for the two lead values over 200 mg. It is possible that someone made a mistake and the phones in question were really not lead free. No mention is made here of the possible manufacturers.

The Oko Institute at one point suggested that arsenic should be banned from electronics but information supplied by the electronics industry allowed the institute to give a different opinion in its final report¹⁶. Every cell phone in the world has at

least one irreplaceable gallium arsenide IC, so all of them should have had detectable arsenic. Gallium arsenide is an excellent insulating substrate, has high carrier mobility, which gives better transistor transconductance; can handle higher power levels and gives good isolation. Most had between 0.002 and 0.010 grams. Ten phones had no detectable arsenic. This measured absence points out again that the complex nature of the elemental mixture of a cell phone can lead to complex reactions that can interfere with a complete analysis of the device in question.

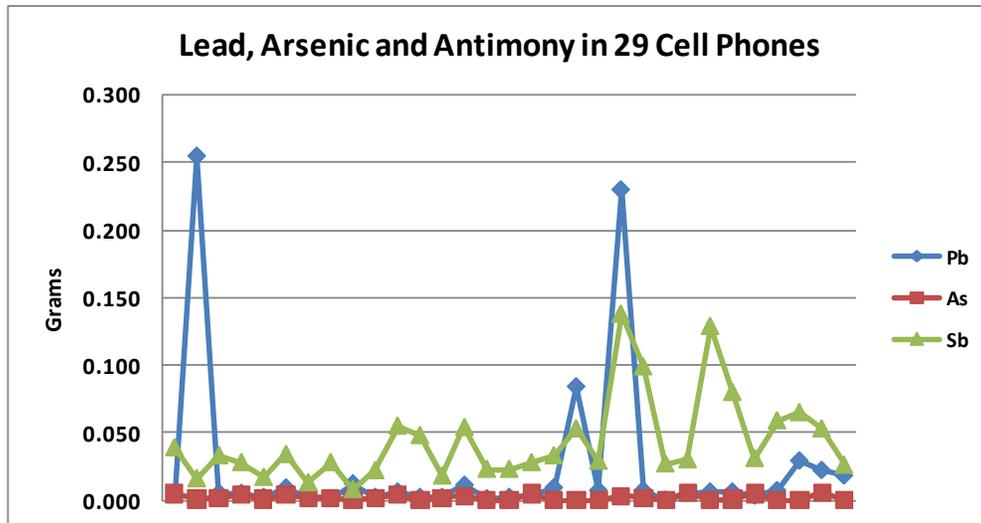


Figure 10 Concentrations of Lead, Antimony and Arsenic

Figure 11 shows the concentration of magnesium in 23 of the 29 phones. Concentrations were not determined for the other six. Note that the y-axis scale is logarithmic to account for the widely varying concentrations. Four of the cellphones had magnesium-based shields where between 5 and 11 grams of magnesium was used. Excluding these four and those where the magnesium concentration was not determined, the amount found was 0.030 +/-0.015 grams. Once the concentrations get to this level, one has to wonder whether the metal was intentionally added or was an impurity, short of having information definitively stating an element was added for a certain purpose.

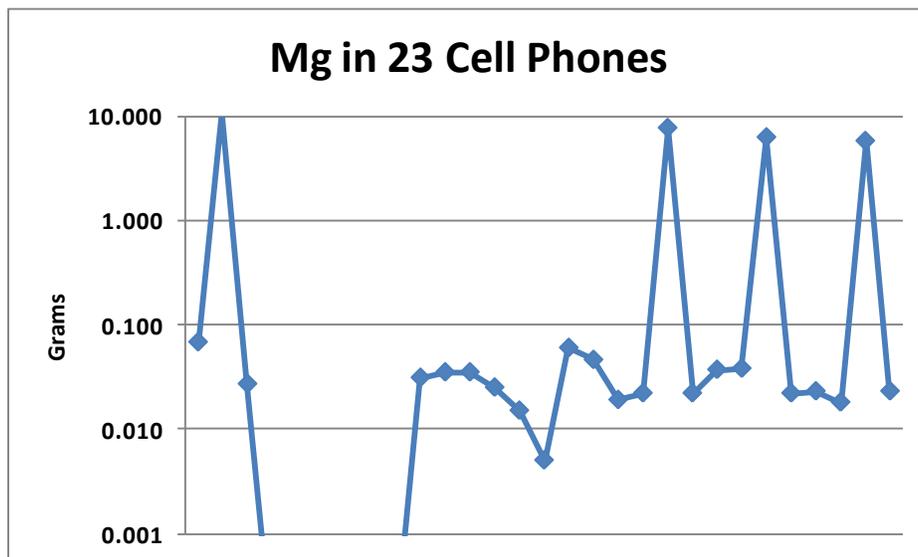


Figure 11 Magnesium in 23 of the 29 Cell Phones Tested

Cobalt has many uses in electronics¹⁷, the most well known is in magnetic recording media, which of course is not germane for the devices in question. However, other uses in cell phones are possible. IC connections are usually made with aluminium, but higher temperatures have seen a transition to Pt/Si and CoSi is another possibility for this purpose. Cobalt is also used to aid the diffusion of gold into substrates. Hard gold contacts contain up to 15% cobalt. Note that the low

concentrations of vanadium more or less follow the concentration plot of cobalt. It is therefore tempting to suggest that the vanadium is present only as an impurity in the cobalt. However, vanadium is also used as a doping agent, is in some refractory materials that may or may not end up in electronics and is present in rare earth vanadate magnets.¹⁸ Vanadium also stabilizes the beta form of titanium.¹⁹ See **Figure 12**.

Titanium has been used as a barrier coating in some ICs. Probably one of the bigger uses is the barium titanate piezoelectric materials used in acoustic devices.²⁰ The concentrations of both barium and titanium are shown in **Figure 13**. There does appear to be a correlation. If the gram amounts are divided by the atomic weight of each element to determine the number of moles of each element, then the ratios are usually quite close to 1:1 (**Figure 14**), which essentially confirms that these elements are present as BaTiO₃.

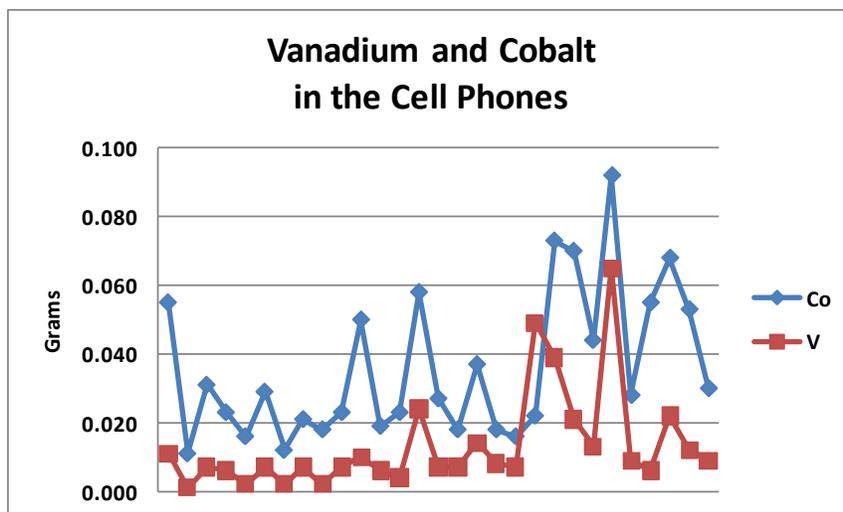


Figure 12 Concentrations of Two of the Transition Elements - V and Co

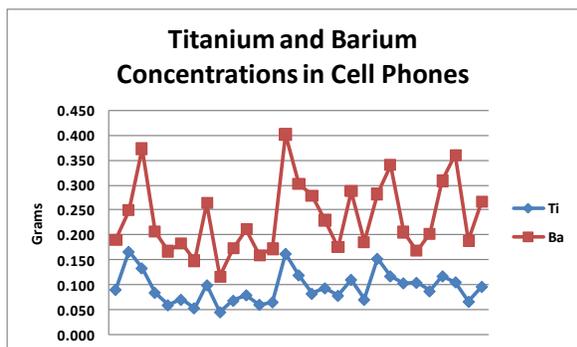


Figure 13 Concentrations of Titanium & Barium

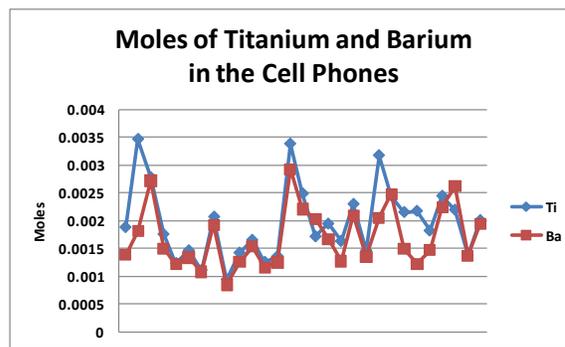


Figure 14 Moles of Titanium & Barium

Conclusions

Although laborious and requiring hundred thousand dollar equipment, it is possible to measure elemental composition of electronic devices. It is acknowledged that the work could be done with an AA instead of an ICP, however the cost of the individual elemental lamps and the labor involved in making the lamp changes for each element would be onerous at best. The question still remains how accurate are the results for any analytical technique. There are possibilities for very complex reactions among all the elements present and the dissolving acids. There is no guarantee that these are all broken down, even in the 8000°C argon plasma flame. Without complete elemental disclosure of every component of every subassembly from all suppliers, there will be no way to know for sure of the level of accuracy of the results. Certainly more work can easily be done on the accuracy and precision of the results.

In this work it has been shown that for the cell phone collection examined; there is a continuing, slow rise in the use of copper, gold and silver, irrespective of the rising cost of the latter two.

The elements that potentially are coming from illegal mines in the DRC are certainly present. Tantalum was found in all but one. Tin was found in all those tested and gold and especially tungsten were found in every cell phone, where tested. How exactly the industry will deal with the dilemma of tracking the source of these elements when their ultimate source may be buried in six to ten layers of a supply chain must be worked out in the coming months. One suggestion has been to “follow the money”, not the ore itself.

Although cadmium was not found, lead certainly was, although usually in small amounts that can probably be tied to the RoHS exemptions. Two cases were mentioned where this might not be the case.

Additional testing is most likely going to be necessary to detail the end use of the lanthanide elements.

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Why?

- **Curiosity**
- **Environmental compliance testing**
- **To answer questions about conflict minerals**
- **To answer internal company questions about reclamation value**
- **To provide information for customer inquiries about all of the preceding**
- **Rare earth elements (next round)**



Why?

- **Enviro compliance – RoHS, REACH, Canadian Chemical Management Plan**
- **Conflict minerals – rape, pillage, slave labor**
- **Rare earth elements – China controls 95% of the market**



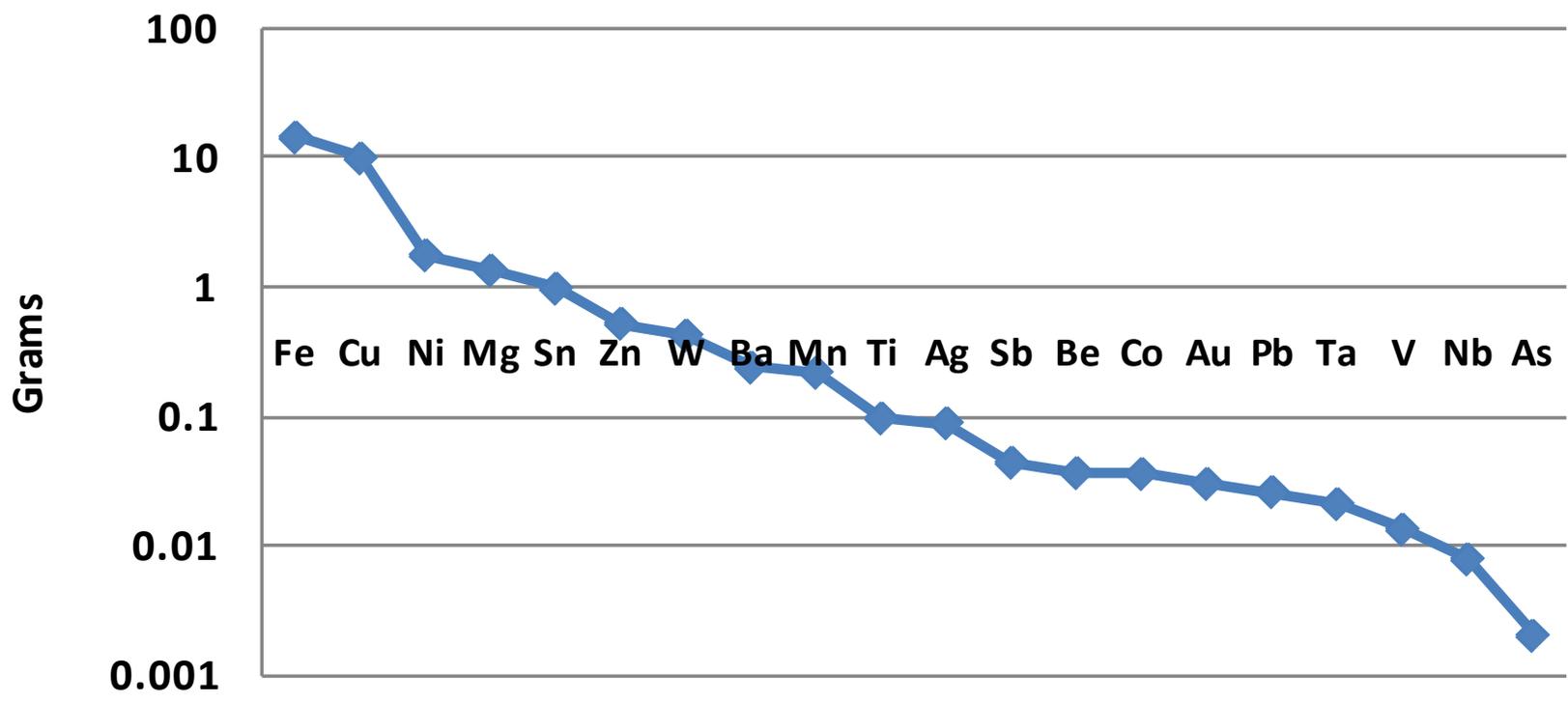
Equipment used

- Retsch ZM 200 grinder
- Perkin Elmer Optima 2000
- Perkin Elmer Optima 7300V



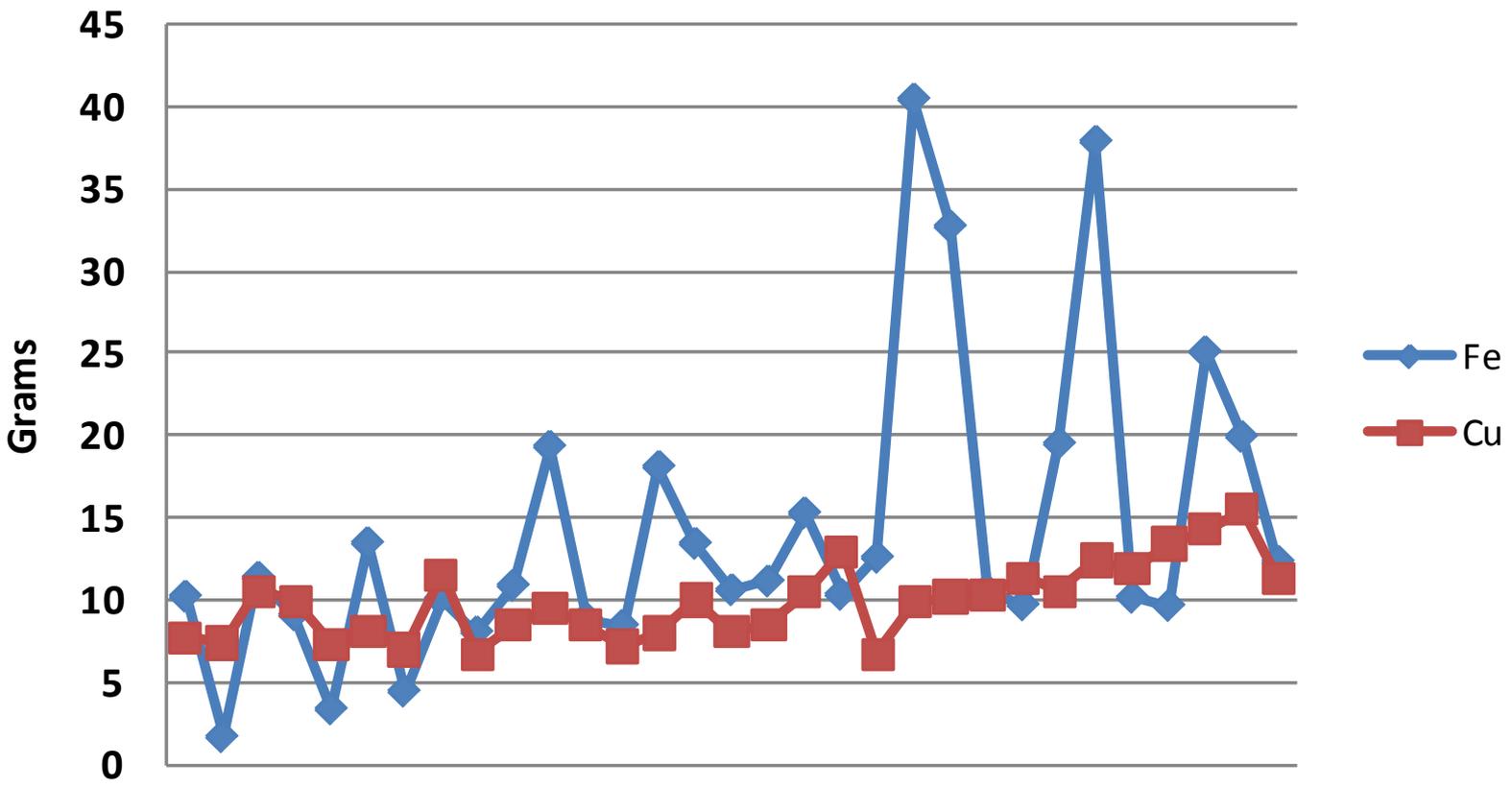


Average Amount of Elements Found in 29 Cell Phones



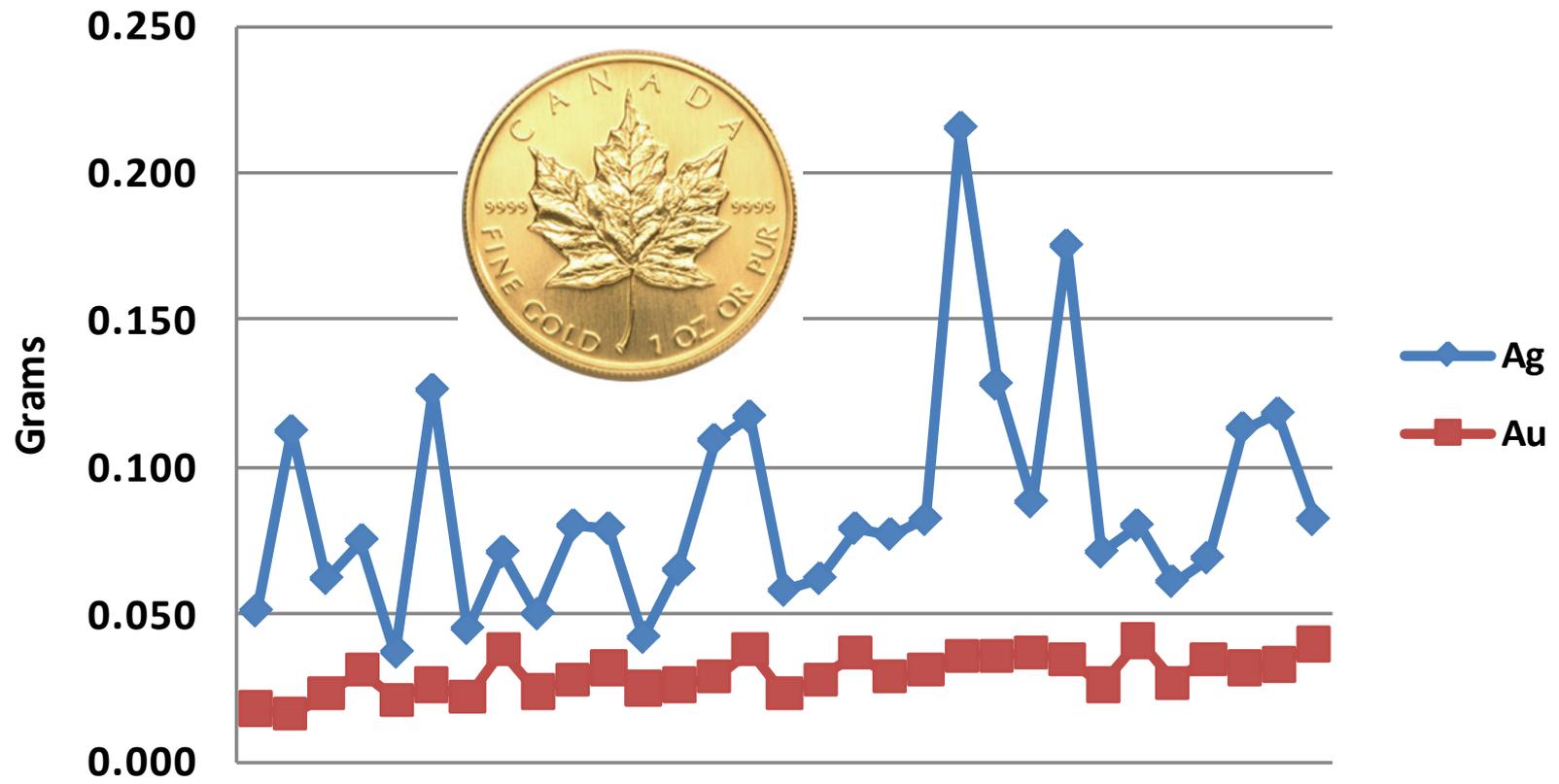


Copper & Iron Composition of 29 Cell Phones





Silver and Gold in 29 Cell Phones



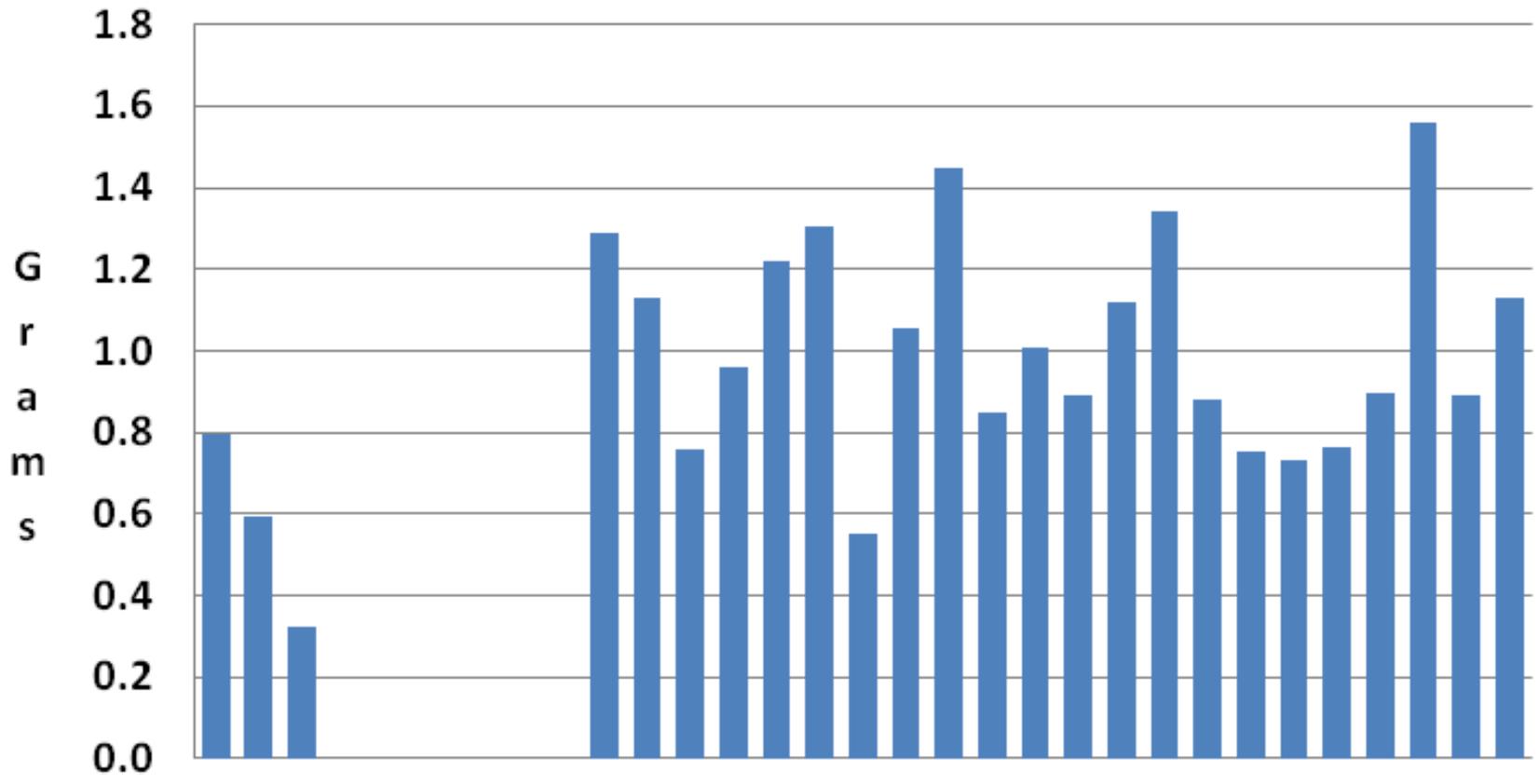


Cost of Silver and Gold

- **Gold has risen for \$35/troy ounce to \$275 to \$1722 (Monex, Nov 1, 2011)**
- **Silver is at \$34.32 (same source)**
- **Assuming each current phone contains 0.03 grams of gold and 0.1 grams of silver this equates to:**
- **$\$1.66 + \$0.11 \approx \$1.77/\text{phone}$**

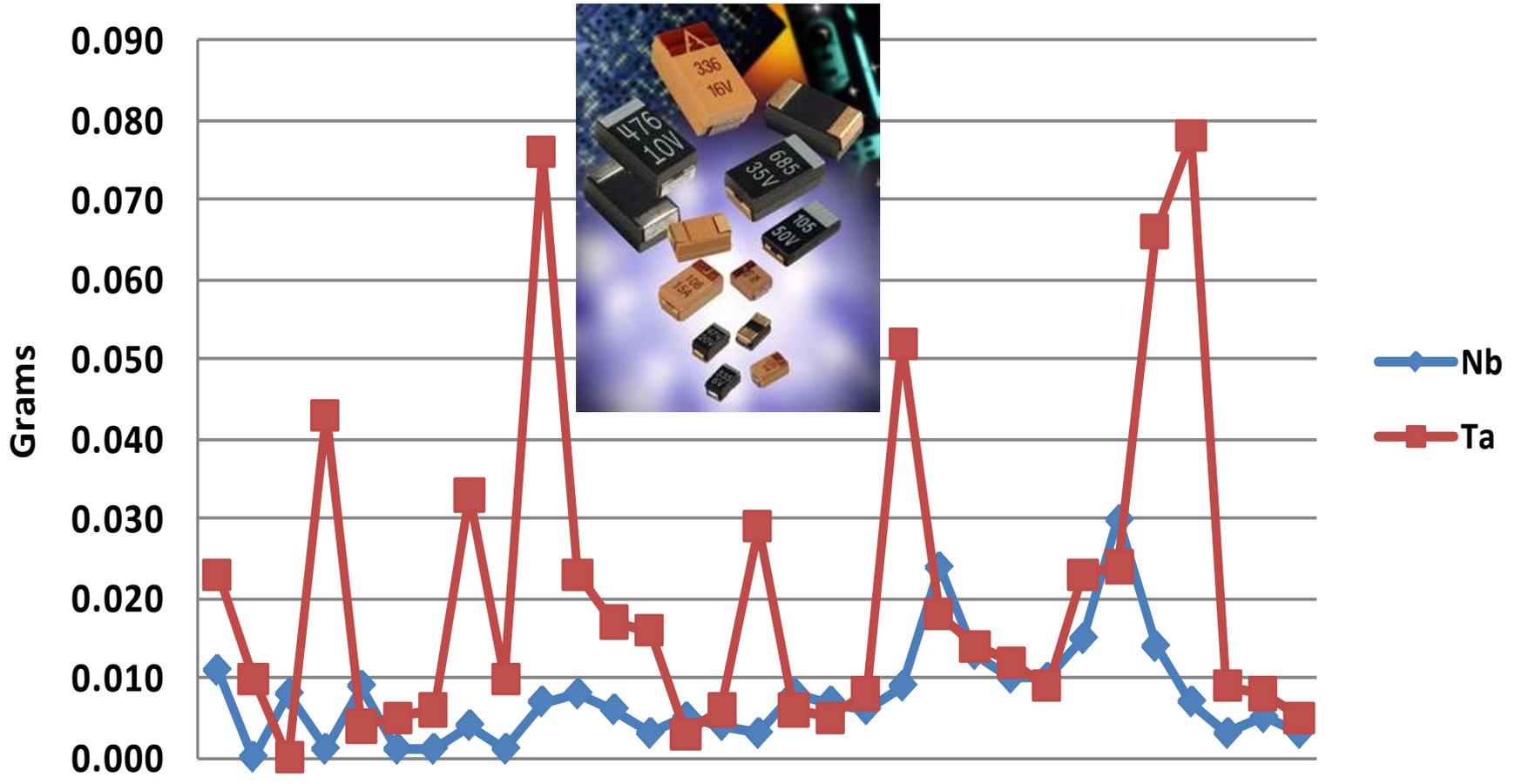


Grams of Tin in 23 Cell Phones



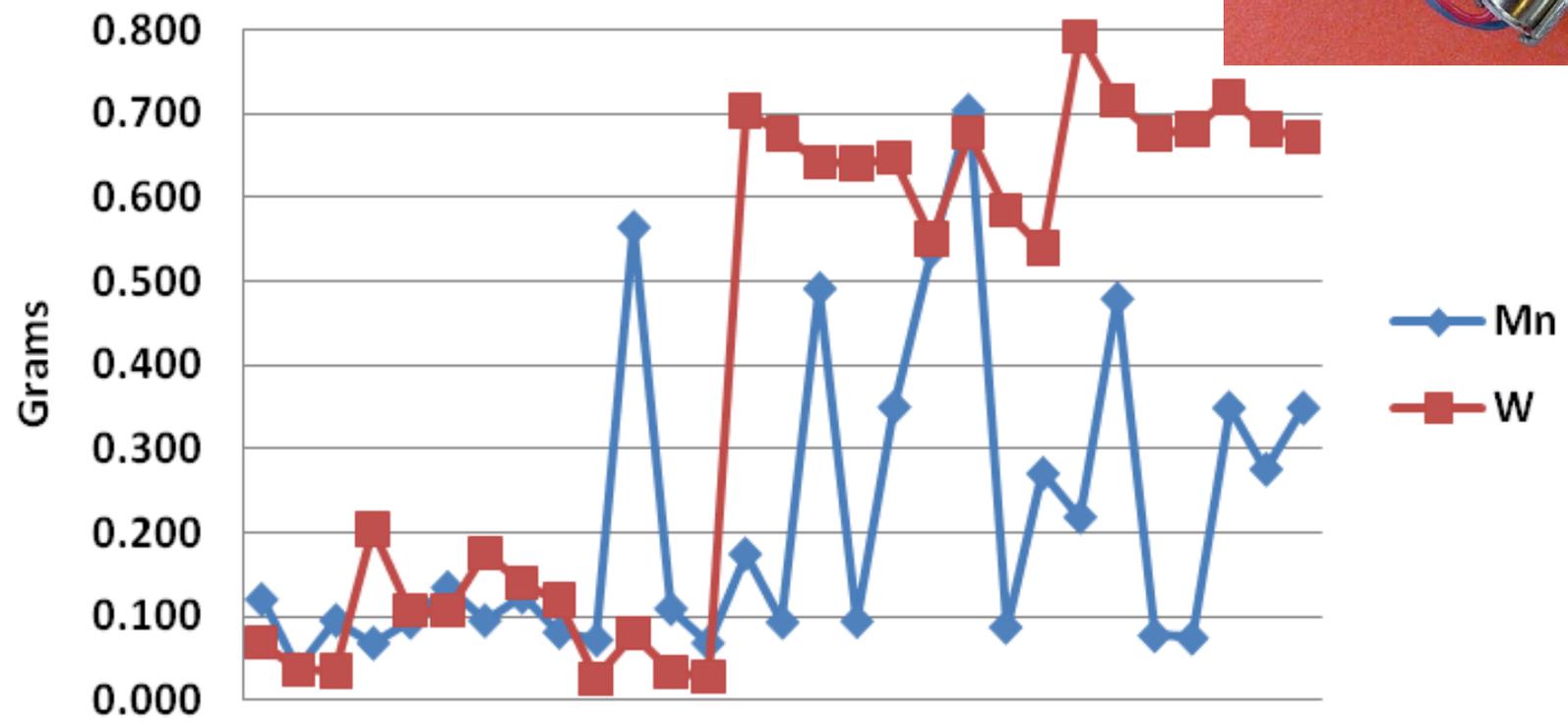
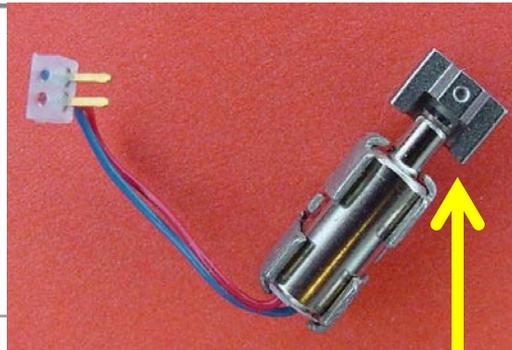


Tantalum and Niobium in 29 Cells Phones





Manganese and Tungsten in Cell Phones



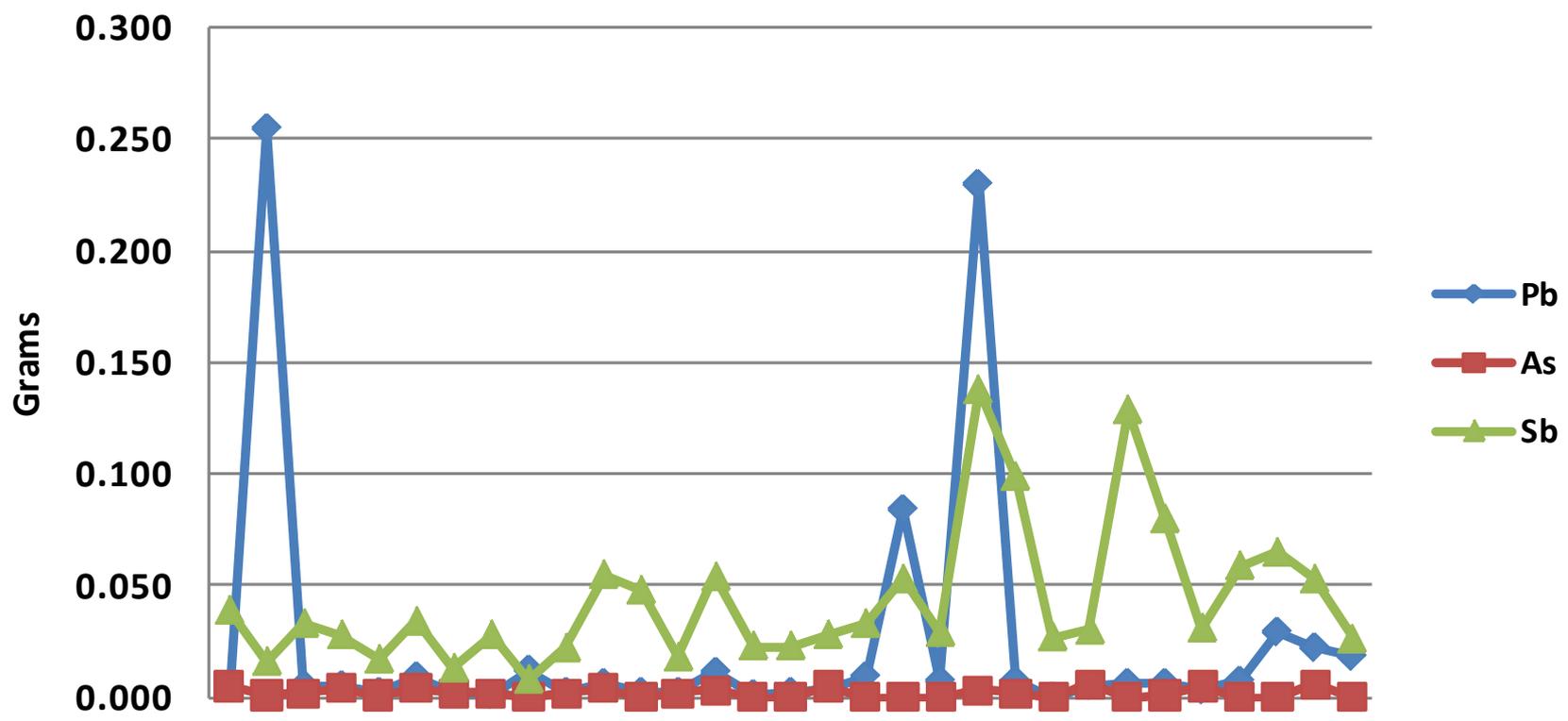
Why use tungsten?



- **Density!**
 - Beryllium = 1.85 g/cc
 - Aluminum = 2.70 g/cc
 - Titanium = 4.54 g/cc
 - Iron = 7.87 g/cc
 - Copper = 8.96 g/cc
 - Lead = 11.34 g/cc
 - **Tungsten = 19.25 g/cc**

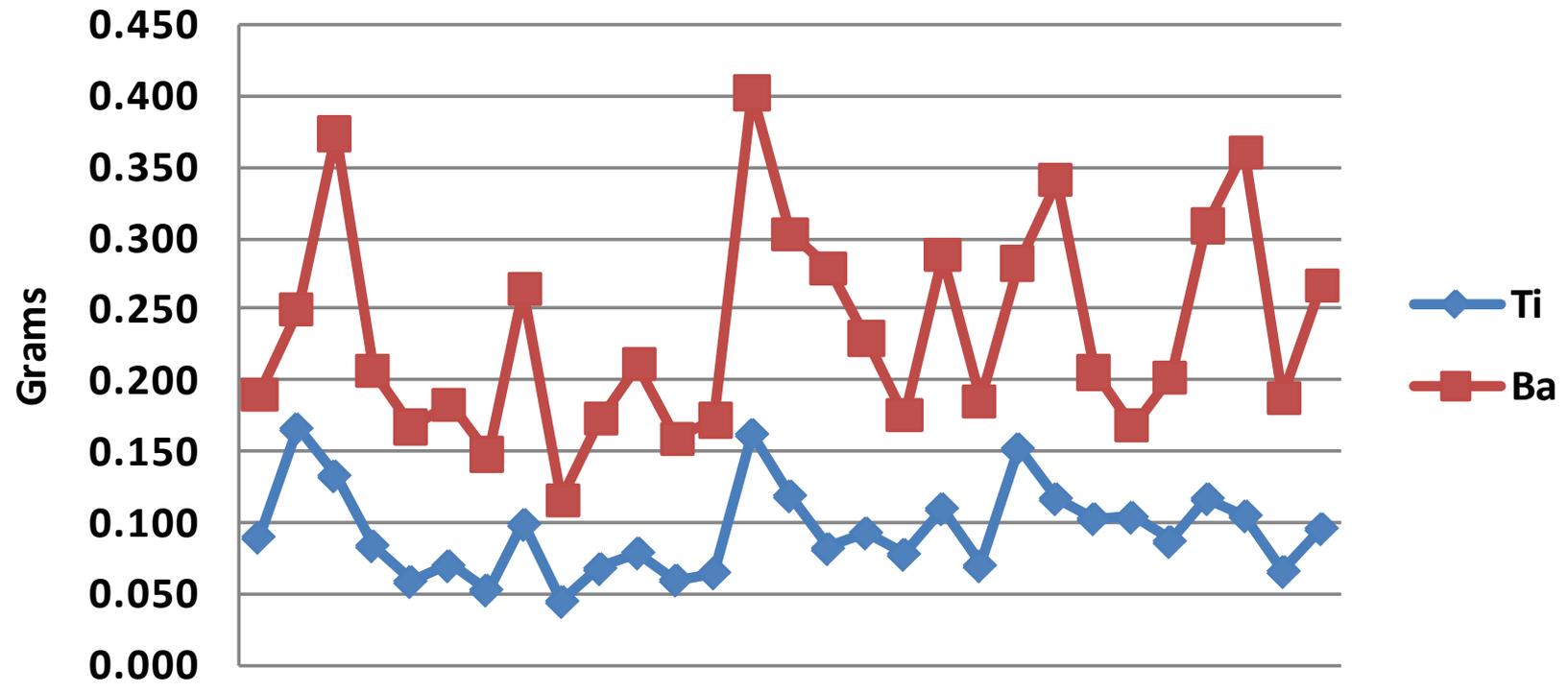


Lead, Arsenic and Antimony in 29 Cell Phones





Titanium and Barium Concentrations in Cell Phones

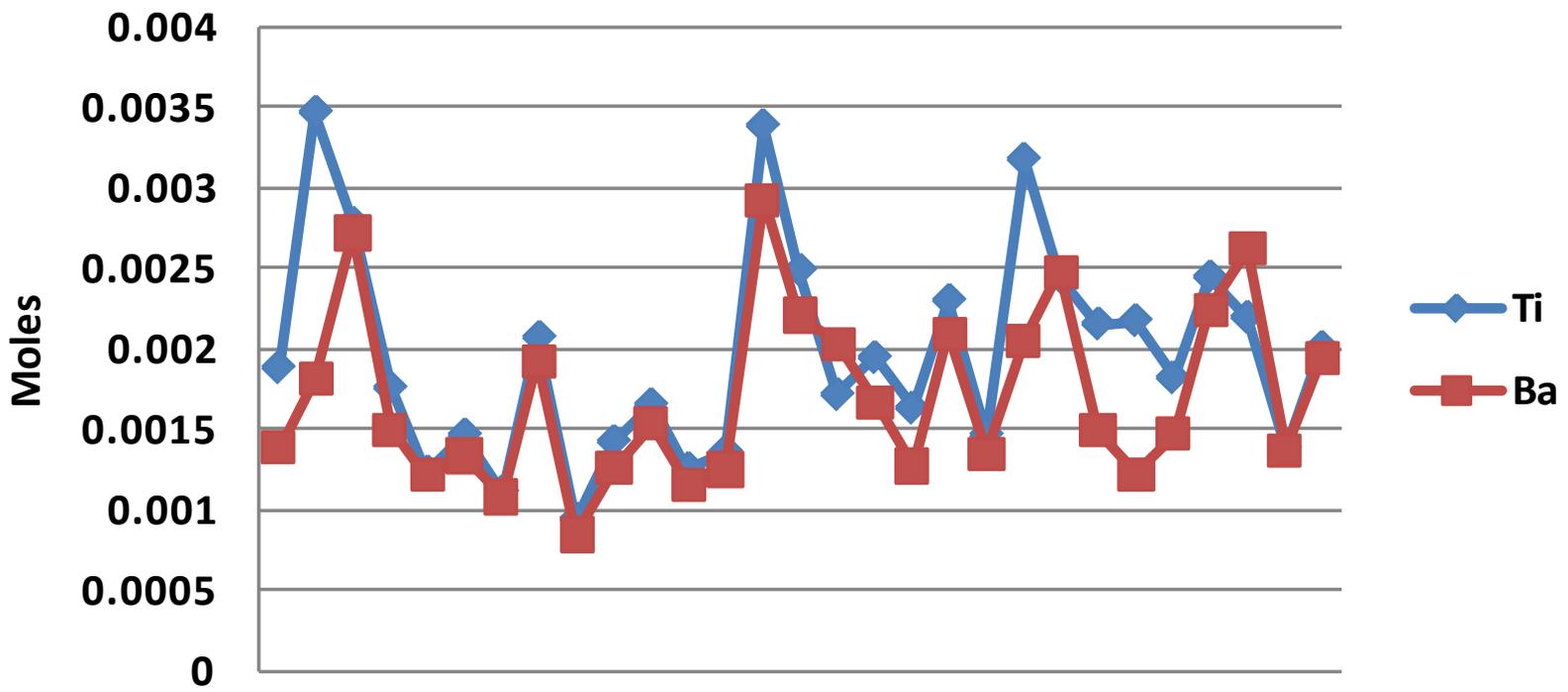




- **Did you notice anything about the previous graph?**



Moles of Titanium and Barium in the Cell Phones





Conclusions

- **Elemental (generally metallic) analysis of cell phones can be carried out by ICP-OES**
- **Questions remain about accuracy**
- **There a slow increase in the use of copper, silver and gold.**
- **There is very little vanadium, niobium and arsenic.**
- **Demands for analytical results WILL increase.**



Questions?