Distinguishing Between Legally and Illegally Produced Gold in South Africa[†]

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Abstract

The identification of gold-bearing material is essential for combating the theft of gold in South Africa. Material seized in police operations is generally a mixture of gold from different mines, and as such cannot be traced back to a single location. ICP-OES analysis of material dissolved by acid dissolution provided a database of gold compositions comprising gold from South African mines, illegal gold stolen from the mines, and commercial gold alloys and jewelery. Discrimination between legal and illegal gold was possible due to the presence of Pb, As, Sb, Sn, Se, and Te in the stolen material, elements which are not present in legally produced gold. The presence of these elements is a quick and simple way to distinguish between gold alloys based on refined gold, such as in commercially manufactured jewelery, and gold alloys containing a proportion of unrefined and therefore illegally obtained gold.

Gold lost from mining operations due to theft in South Africa makes up for a large volume of the total production value [1, 2]. Anything from the ore to the final metal product is stolen and the challenge is to develop techniques like elemental profiling to identify the original source of the gold, despite different beneficiation procedures applied by companies and criminal syndicates. The mineralogy of gold ores from the Witwatersrand mines is relatively consistent and the recovery of the gold is easily achieved with unsophisticated methods, such as panning, amalgamation, and cyanidation [3, 4].

The trace element profiles of substances such as paint [5, 6], glass [7, 8] and precious metals [9] have been used to prove a link between a sample of the material in question and samples from known provenance. There have been problems with the interpretation of the results of such profiling [10], and this has been extensively discussed and reviewed in the literature [11]. Using such a database, which is representative of the population(s), should enable the attribution of the type and source of such material on a scientific basis, without having to worry about the terms "unique" or "identification" [12], and should produce results which have more weight when presented in court [13, 14]. It has been shown that samples from the same source show significant uniformity in trace element distribution, and significant variation between different sources, leading to good discrimination between sources [15, 16].

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This discrimination is also successfully used to distinguish archeological artefacts, such as coins, with different origins [17].

For this technique, a sample of known provenance is needed for comparison, for example, gold nuggets in placer deposits are matched to known deposits, and the non-matching gold samples can indicate further exploration targets [18-20]. This issue is extremely important in the field of gold profiling. The term "gold" describes products ranging from native Au and Au alloys, to Au produced by mines for further refining, to pure refined Au and Au alloys incorporating refined Au and other metals for use in jewelery and other applications.

South Africa has a large number of gold mines, a wide range of distinct gold deposits formed through different processes in discrete geological environments [21-23], and is also the final destination for gold from all over Africa. Most of the South African gold mines exploit gold hosted in Archean alluvial fans of the Witwatersrand Basin [24-26]. However, a large amount of gold theft in South Africa does not occur from the processing plants, but actually from the ore face itself. Raw ore is processed by primitive means such as amalgamation, and then sold on to large organized syndicates, who customarily mix gold from several localities and types together. This effectively hides any elemental signature linking the stolen material to a single point of origin.

Manufacturing jewelers buy certified gold alloys from a refinery, but are then free to mix different alloys in different proportions in the finished product. The refineries themselves sell a variety of different alloys, containing different elements not only to dilute the gold, but also to alter the color and hardness of the gold, as well as casting or metallurgical properties [27-29]. For instance, Cu-rich gold is redder than Ag-rich gold, even if both contain the same amount of gold. The manufacturing jewelers are the final endpoint for illegal gold, as unscrupulous and criminal jewelers will buy illegal gold and mix it with legal alloys, further complicating the process of identifying stolen material.

Here, we report on the use of elemental profiling to distinguish between legal gold alloys and illegally processed gold, which represents gold stolen from mining operations. The identification of such illegal gold provides a legal mechanism for the seizure of such material.

Methodology and Materials

To investigate the compositional variation of gold that has been processed or refined to different degrees, a large number of samples were collected, consisting of the following:

- Alloy—61 commercially available jewelery and other Au alloys;
- Jewelery—71 pieces of jewelery, typical of jewelery recovered by pawn shops which would be the type of gold jewelery sold to the refineries as jewelery scrap. This group contains gold-plated or coated brass, which has a very low effective Au content;
- Bullion—477 bars of mine bullion from 23 different African gold mines, all produced via the carbon-in-pulp (CIP) method; and
- Suspect–249 samples of gold-containing material seized during police action, considered to be of "suspect" or illegal origin, including material recovered from slag in crucibles where pieces of copper and brazing rods were being melted together with gold-bearing material.

Samples were prepared in duplicate by drilling, using a new drill bit for each sample. 0.1 g of sample was then placed in an acid-cleaned 50-mL glass beaker. Ten milliliters of concentrated ultra-pure aqua regia was added and then heated on a hot plate under reflux until the sample was dissolved. The solution was then transferred quantitatively to an acid-cleaned 100-mL volumetric flask, using milli-Q water (conductivity of 18 million ohm/cm), and made up to 100 mL.

The samples were then analyzed on a Spectro Vision ICP-OES. The analytical lines and calibration samples used are listed in Table 1. Standards were prepared from multi-element and single-element liquid SRMs, with concentrations of 0.5, 1, and 10 ppm. These were prepared in 100-mL volumetric flasks with 10 mL ultra-pure aqua regia and made up with milli-Q water to the 100 mL mark. The acids were chemically pure grade (CP), supplied by ACE Chemicals (Johannesburg, South Africa). Standards were prepared from traceable (to NIST) standard reference materials (CPI Peak Performance) supplied by CPI International (Santa Rosa, CA). During calibration, the instrument was rinsed with 10% aqua regia inbetween samples. The aqua regia was prepared by distilling hydrochloric and nitric acid with a Milestone (Shelton, Conneticut) DuoPUR sub-boiling distillation system.

Table 1. Spectral lines and standards used for ICP-OES analysis of gold

| Element | Line(s) | Standards Used for Calibration | | | | | |
|---------|--------------------|--|--|--|--|--|--|
| As | 189.042 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element s | | | | | |
| | 242.795 | | | | | | |
| | 267.595 | 0.5 ppm PGM standard: 1 ppm PGM standard: 10 ppm PGM standard: 100 ppm | | | | | |
| Au | 274.825 | 0.5 ppm PGM standard; 1 ppm PGM standard; 10 ppm PGM standard; 100 ppm Au + 100 ppm Cu + 100 ppm Ni + 50 ppm Pb standard; 1000 ppm Au + 250 ppm Cu standard | | | | | |
| | 201.200 | | | | | | |
| | 174.050 | | | | | | |
| Be | 313.042 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| Bi | 190.241 | 0.5 ppm Bi–Sn–Te std; 1 ppm Bi–Sn–Te std; 10 ppm Bi–Sn–Te std | | | | | |
| Ca | 396.847 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| | 226.502 | | | | | | |
| Cd | 228.802 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| Co | 228.616 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| Cr | 205.552 283.563 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| | 324.754 | | | | | | |
| Cu | | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std; 100 ppm Au + 100 ppm Cu + 100 ppm Ni + 50 ppm Pb standard; 1000 ppm Au + 250 ppm Cu standard | | | | | |
| | 224.700 | | | | | | |
| Fe | 259.941 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| Ir | 263.971 | 0.5 ppm CPI PGM standard; 1 ppm CPI PGM standard; 10 ppm CPI PGM standard | | | | | |
| Li | 670.780 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |
| Mg | 279.553 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | | |

| Element | Line(s) | Standards Used for Calibration | | | | |
|---------|--------------------|---|--|--|--|--|
| Mn | 257.611 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element s | | | | |
| Mo | 202.030 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| Ni | 231.604 341.476 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std; 100 ppm Au + 100 ppm Cu + 100 ppm Ni + 50 ppm Pb standard | | | | |
| Pb | 220.353 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std; 100 ppm Au + 100 ppm Cu + 100 ppm Ni + 50 ppm Pb standard | | | | |
| Pd | 340.458 360.955 | 0.5 ppm CPI PGM standard; 1 ppm CPI PGM standard; 10 ppm CPI PGM standard | | | | |
| Pt | 265.945 | 0.5 ppm CPI PGM standard; 1 ppm CPI PGM standard; 10 ppm CPI PGM standard | | | | |
| Rh | 343.489 | 0.5 ppm CPI PGM standard; 1 ppm CPI PGM standard; 10 ppm CPI PGM standard | | | | |
| Ru | 240.272 | 0.5 ppm CPI PGM standard; 1 ppm CPI PGM standard; 10 ppm CPI PGM standard | | | | |
| Sb | 206.833 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| Se | 196.090 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| Sn | 189.991 147.516 | 0.5 ppm Bi–Sn–Te std; 1 ppm Bi–Sn–Te std; 10 ppm Bi–Sn–Te std | | | | |
| Sr | 407.771 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| Те | 214.281 238.578 | 0.5 ppm Bi–Sn–Te std; 1 ppm Bi–Sn–Te std; 10 ppm Bi–Sn–Te std | | | | |
| Ti | 334.941 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std I Multi-element std—10 ppm, 50 ppm, 100 ppm | | | | |
| T1 | 190.864 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| V | 292.464 292.402 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |
| Zn | 206.191 | 0.5 ppm CPI multi-element std; 1 ppm CPI multi-element std; 10 ppm CPI multi-element std | | | | |

Results and Discussion

Variation in Manufactured (Legal) Gold Alloys

Analysis of commercially available gold alloys and of manufactured jewelery items shows that many elements are present in quantities close to, or below, the ICP-OES detection limit in these matrices under the analytical conditions chosen. Elements such as As, Ca, Fe, Mg, Sb, Sn, Se, Te, Ti, Pb, and Bi are present either in extremely low quantities or in quantities below the detection limit of the instrumentation used. Sufficient analytes are present in measurable quantities to allow discrimination between gold samples of different provenance.

Commercial gold alloys are available in set gold concentrations, which can clearly be seen in Fig. 1, where the Au and Cu contents of the jewelery samples, the alloys and the mine bullion are compared. Clusters of jewelery samples and alloy samples occur at 9 karat (37.5 wt %), 14 karat (58.33 wt %), 18 karat (75 wt %), and 22 karat (92.5 wt %) Au. The alloys are considerably less variable than the jewelery, which often has a lower gold content than the alloys from which it is supposedly made, or consists of base metal which is plated or coated. This may also be the result of dilution during the melting of the alloys prior to the casting of

the manufactured article, and the recycling of scrap jewelery, which would include solder and other diluents. Cu is the most commonly used diluent in commercial alloys, as Cu is present in high quantities (35–50 wt %) in most 9 karat gold, and 5–20 wt % in 18 karat gold.

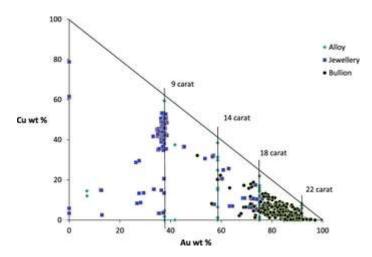


Figure 1. Comparison between the Au and Cu contents of commercial jewelery alloys, manufactured jewelery, and mine bullion. The majority of the Au alloys are 9 and 18 karat, as are most of the jewelery samples, but many jewelery samples do not plot on commercially available values, reflecting mixes of alloys created by the jewelers. Mine bullion is significantly higher in Au content than most jewelery alloys.

Another element common to all jewelery alloys and manufactured jewelery is Zn, which is present in concentrations of up to 20 wt %. Zn is added to gold alloys to improve hardness, to aid in casting and as a diluent [30]. The concentration of Zn in the gold alloys and in the manufactured jewelery is similar. Ni, Co, and Pd are present in some commercial alloys, but not in all. The manufactured jewelery can contain not only these three elements, but also As, Cd, Pt, and Rh. As and Cd are mainly from solders used in older jewelery, while Pt and Rh were used in older jewelery when they were relatively inexpensive. When detected, these elements can be present in relatively high concentrations, up to 20 wt % of the total abundance.

Comparing the manufactured jewelery to the commercial jewelery alloys, several comments can be made. Firstly, the commercial alloys are much more consistent in their composition than the manufactured items. Secondly, the older manufactured jewelery contains elements that are no longer commonly used as alloying elements or in solders. Thus, the collected dataset can be considered to contain historical samples as well as contemporary samples and so is not biased toward modern compositions.

Distinguishing Jewelery from Gold Bullion

Gold bullion, as supplied by mining companies to the refinery, has undergone significant processing using the CIP extraction method [31, 32]. Comparing the commercial gold alloys and manufactured jewelery data to the mine bullion data in Fig. 1, it is immediately apparent that the mine bullion reaches generally 70 wt % or more Au. At the same time, the Cu content is generally lower than that of the refined alloys. Extending the comparison to include Zn, the other element found in almost all jewelery, the Zn and Cu content is generally higher than mine bullion, with only a few jewelery alloys close in composition with some bullion.

It is possible to consider the relative abundance of other elements sometimes present in jewelery, namely Cd, Pd, Pt, Ni, and Co, in terms of the ratios between these minor constituents. Jewelery and mine bullion have comparable Pd/Cd ratios, but mine bullion has very different Pd/Pt and Pd/Co ratios, owing to the low concentrations of Pt and Co in this type of gold. High Cd/Pd ratios are indicative of jewelery, as is the presence of Co. It is thus possible to use these elements to distinguish between manufactured jewelery and mine bullion. These elements are not consistently present, however, and cannot be relied upon for a clear and easy method.

For forensic purposes, a simpler discrimination scheme is preferred, it is possible to characterize the source of gold solely on elements that are present in mine bullion, but not in refined gold. The element of interest is thus Pb, which is present in all natural gold deposits. Other discriminating elements are As, Sb, Sn, Se, and Te, which are undesirable in refined gold and are removed during the final refining process.

Pb was not detected in any of the jewelery items, but is present in the mine bullion in concentrations mostly in the range of 300–5000 ppm. Lead is usually found in gold ores and due to the beneficiation process will become alloyed with the gold in the mine bullion. The presence of Pb in high concentrations in most bullion samples means that analytical methods of lower sensitivity, such as handheld XRF spectrometers, can be used to easily identify suspect gold-bearing material. For the analytical procedure used in this study, with a detection limit of 1 ppm for Pb, the use of the Pb content of the analyzed samples was 100% successful in discriminating between jewelery alloys and mine bullion.

The other elements of interest are present in only some of the gold deposits. Tin is present in some bullion. Antimony is present in two samples of mine bullion from greenstone gold deposits in Murchison and Barberton [23], and As, Se, and Te are present in occasional samples. The dataset of mine bullion used in this study is heavily slanted toward gold hosted in sedimentary deposits of the Witwatersrand, so it is likely that these elements will be present in higher concentrations in deposits from other parts of the world. The presence of any of these elements is sufficient to classify the gold-bearing material as semiprocessed and not refined.

During this study, it was noted that many of the elements of interest are likely to be present at levels below the detection limit of the ICP-OES. Although the use of Pb, As, Te, Se, Sn, and Sb is sufficient for the purposes of differentiating jewelery from bullion, some mine bullion samples of high gold purity do not have levels of these elements measurable by ICP-OES. A more sensitive method of analysis such as ICP-MS should be considered to improve the discrimination achieved from trace element profiling of gold.

Identifying the Presence of Illegal Gold in Suspect Material

During the course of operations directed at combatting the illegal gold trade, numerous suspect samples of gold have been seized by the SAPS and given to the FSL for analysis and evaluation. Two hundred and forty-nine such suspect samples have been analyzed for this study and can be used to test the ability to empirically determine the source of the gold-bearing material and its legality according to South African law.

In Fig. 2, the results of a comparison between the various samples on the basis of Au and Cu is shown, with the majority of jewelery and the mine bullion quite distinctly separated by

their Au and Cu contents, with the suspect gold samples from criminal investigations mainly in-between these two extremes. The suspect material covers a much broader range of Au values than either the mine bullion or the jewelery and has Au contents ranging between 0 and 95 wt %.

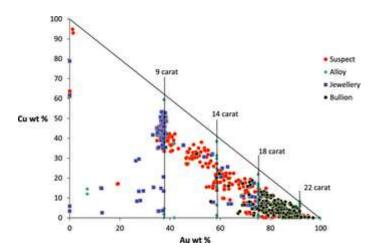


Figure 2. Comparison between seized gold (suspect; in red) and gold from known sources (alloys, jewelery, and bullion), based on Au and Cu content. The commercially produced alloys (in green) show the groupings according to karat value. Pieces of brass and copper, and Au-free jewelery (possibly Au-coated jewelery with a negligible Au content), are shown against the *y*-axis. It can be seen that the suspect samples have much greater variation than the normal jewelery.

The suspect Au values are not clustered together like the jewelery values and extend to lower Au values than the bullion. This spread, together with observations made at the crime scene where pieces of copper and brazing rods were being melted together with scrap jewelery and mine bullion, leads to the conclusion that the suspect samples include material that is not jewelery in origin. This conclusion cannot be considered definitive solely on the basis of the Au/Cu ratio in the samples. However, if the suspect samples are in fact illegally processed gold, then it is apparent that the original high gold content of the stolen mine gold, as represented by the bullion, has been diluted by adding copper-bearing material, as well as scrap jewelery. This is very evident as most of the suspect samples plot between 80 and 40 wt %, in an attempt to simulate the range expected for jewelery scrap.

To provide information on the differences in trace components between the suspect samples and legal sources of gold, a principal component analysis (PCA) was conducted on the dataset. Au and Cu were excluded from this analysis, as these components are responsible for more than 90% of the variance in the gold samples. The results of this analysis are presented in Fig. 3 and Table 2. The first five components are responsible for 95% of the variance, each component corresponding primarily to a single analyte: Component 1 (29% of variance) is dominated by Zn; Component 2 (19% of variance) by Pd; Component 3 (18% of variance) by Ni; Component 4 (15% of variance) to Pt, and Component 5 (14%) by Fe. However, all of these elements are commonly found in jewelery, alloys, and the suspect material, so plots of these components (Fig. 3) do little to discriminate the suspect material from legal jewelery and alloys. Component 6 (2% of variance), corresponding to Pb, and Component 7 (2% of variance), corresponding to Sn, are of more use in the current study.

Table 2. Results of principal component analysis on entire dataset

| | Comp. 1 | Comp. 2 | Comp. 3 | Comp. 4 | Comp. 5 | Comp. 6 | Comp. 7 |
|-------------------------|---------|---------|---------|---------|---------|---------|---------|
| Standard deviation: | 3.19 | 2.61 | 2.51 | 2.27 | 2.20 | 0.91 | 0.90 |
| Proportion of variance: | 0.29 | 0.19 | 0.18 | 0.15 | 0.14 | 0.02 | 0.02 |
| Cumulative proportion: | 0.29 | 0.48 | 0.66 | 0.81 | 0.95 | 0.97 | 0.99 |
| Loadings | | | | | | | |
| % Fe | -0.12 | | 0.44 | | -0.89 | | |
| % Ni | -0.20 | 0.18 | 0.85 | | 0.45 | | |
| % Pb | | | | | | 0.97 | -0.14 |
| % Pd | 0.21 | -0.95 | 0.23 | | | | |
| % Pt | | | | -1.00 | | | |
| % Sb | | | | | | -0.14 | -0.99 |
| % Sn | | | | | | 0.21 | |
| % Zn | 0.95 | 0.26 | 0.18 | | | | |

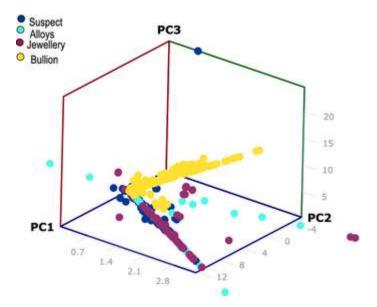


Figure 3. 3D projection of the first three principal components from Table 2.

Pb and Sn show the best utility for discriminating between stolen mine gold, jewelery, and alloys. Pb is distinctive of unrefined gold, which does not contain significant quantities of Sn, and jewelery does not contain Pb or Sn (with the exception of a few very specialist alloys used in electronic components which would not normally be found as scrap). The presence of Sn can be attributed to the use of brazing rods (commonly used brazing rods are Cu: Zn alloy with Sn added) for diluting the stolen mine bullion. This is confirmed by the presence of some of the suspect material of this composition. Other samples consisted of brass or pure copper.

Ternary plots, in which three components can be compared in a 2D projection, were used to produce a clearer discrimination using Au, Cu, and the seven elements identified by PCA. In Fig. 4, the relative proportions of Au, Cu, and Zn are shown for the complete dataset. Two mixing lines, for a combination of brass and gold and a composition of industrial copper and gold, are also plotted, as these materials are often used to dilute stolen gold. The mine bullion contains little Cu and even less Zn and is clustered around the Au apex. The commercial

alloys, made for a variety of uses, show a large variation in all three elements. The jewelery clearly shows the karat alloys, with or without zinc, with variation due to dilution by other alloying elements, predominantly in the 9 karat range. The suspect material follows the brass dilution trend for the majority of samples, with the remainder showing a Cu dilution trend and a few in-between. The only conclusion to be drawn from the combination of the observations made at the crime scene when the suspect material was collected, and the distribution of the suspect samples, as shown in Fig. 4, is that the suspect material is consistent with mine bullion which has been diluted to varying degrees with copper or brass to produce a gold alloy between 9 and 18 karat which could be passed off as jewelery scrap.

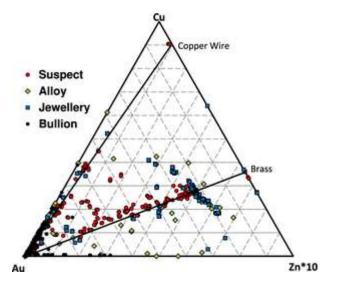


Figure 4. Relative proportions of Au, Cu, and Zn $(\times 10)$ (wt %) plotted for the complete dataset. Brass (6.5% Zn, 93.5% Cu) is used to define a lower mixing line, and industrial Cu (99% Cu, 1% Zn) is used to define an upper mixing line. These lines thus represent possible compositions that can be created by diluting gold-bearing material with either brazing rods (brass) or copper wire.

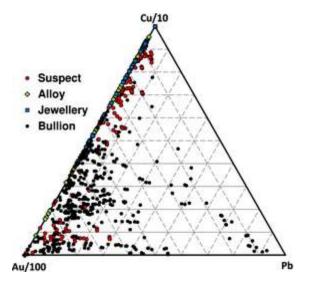


Figure 5. Relative proportions of Au, Cu, and Pb (wt %) plotted for the complete dataset. The alloys and jewelery contain no Pb, but most of the suspect material and bullion contains measurable amounts of Pb, and plots away from the Au/Cu axis.

In Fig. 5, there is a clear distinction made between alloys and jewelery, and the majority of the mine bullion, with the mine bullion being restricted in its Cu content. The suspect samples show a range of Cu content from mine bullion to Cu metal, but the majority show the presence of Pb, showing that there is a component present in these samples which corresponds to gold with an unrefined origin, similar to the bullion which is the unrefined gold extracted by the mines.

Figure 6 shows a plot of Cu, Pb, and Sn which clearly shows that the majority of the suspect material plots near the Cu apex and shows the presence of Sn in significant amounts. This corresponds to dilution of unrefined gold with either copper or brass, and Sn-bearing brazing rods. At low concentrations of Cu, the relative proportions of Sn in mine bullion increases, where detected, and this accounts for the tail of bullion and suspect material toward the Pb apex. The suspect material corresponds to diluted mine bullion.

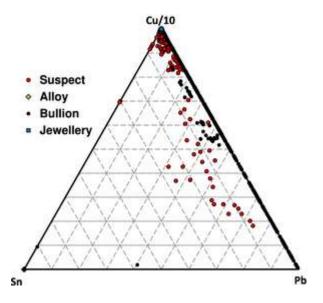


Figure 6. Relative proportions of Cu, Pb, and Sn (wt %) plotted for the complete dataset. The alloys and jewelery contain no Pb and plot at the Cu apex. Most bullion contains no Sn, but significant amounts of Sn are present in the suspect samples, clearly marking these as originating from a different process.

Conclusions

- 1. It is possible to distinguish between legal alloys derived from refined metals, such as jewelery, and unrefined, semiprocessed gold in the form of mine bullion, based on the presence of major and trace elements in the gold.
- 2. Other elements commonly associated with native gold, such as As, Se, Sb, Sn, and Te, can be used to identify gold bullion, if these elements are present at levels high enough for detection. None of these elements normally occurs in jewelery.
- 3. Elements present in relatively large amounts in gold, such as Cu, Zn, Pb, and Sn, can be used to distinguish between jewelery and unrefined gold (mine bullion and gold recovered illegally by artisanal means). The compositions of jewelery and unrefined gold are sufficiently different to allow easy discrimination between the two forms of gold on the basis of their Pb content. Jewelery alloys are made from refined metals and contain no Pb, whereas mine bullion as produced by the carbon-in-pulp (CIP) method of cyanide leaching still contains significant Pb.
- 4. Samples of gold seized during police operations include some samples that are most likely stolen mine gold, but generally show a unique geochemical signature. High

levels of Sn, the presence of Hg, along with low but measurable levels of Pb, are likely to indicate crude processing and beneficiation through mercury amalgamation and low-temperature smelting. These elements are sufficient to identify the seized material as illegal according to South African law.

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References

- 1. Gastrow P. Theft from South-African mines and refineries—B: the illicit market for gold and platinum. *ISS Monograph Series* 2001;54:1–72.
- 2. Coetzee B, Horn R. Theft of precious metals from South African mines and refineries. *ISS Monograph Series* 2007;133:1–122.
- 3. Feather CE, Koen GM. The mineralogy of the Witwatersrand reefs. *Miner Sci Eng* 1975;7:189–224.
- 4. Lloyd PJD. Maximizing the recovery of gold from Witwatersrand ores. *Miner Sci Eng* 1978;10:208–21.
- 5. Hobbs A, Almirall JR. Trace elemental analysis of automotive paints by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). *Anal Bioanal Chem* 2003;376:1265–71.
- 6. Alemayehu A, Wibetoe G, Beauchemin D. Solid sampling electrothermal vaporization inductively coupled plasma optical emission spectrometry for discrimination of automotive paint samples in forensic analysis. *J Anal Atom Spectrom* 2012;27:1928–34.
- 7. Montero S, Hobbs A, French T, Almirall JR. Elemental profiling of glass fragments by ICP-MS as evidence of association: analysis of a case. *J Forensic Sci* 2003;48:1101–7.
- 8. Trejos T, Koons R, Weis P, Becker S, Berman T, Dalpe C, et al. Forensic analysis of glass by μ-XRF, SN-ICP-MS, LA-ICP-MS and LA-ICP-OES: evaluation of the performance of different criteria for comparing elemental composition. *J Anal Atom Spectrom* 2013;28:1270–82.
- 9. Watling RJ, Herbert HK, Delev D, Abell ID. Gold fingerprinting by laser ablation inductively coupled plasma mass spectrometry. *Spectrochim Acta B* 1994;49:205–19. 10. Committee on Scientific Assessment of Bullet Lead Elemental Composition Comparison. Forensic analysis: weighing bullet lead evidence. Washington, DC: National Research Council, 2004.
- 11. Barton MM, Miskelly GM. The use and limits of compositional analysis for discrimination and classification of samples. *Chem New Zealand* 2006;70:3–6.
- 12. Cole SA. Forensics without uniqueness, conclusions without individualization: the new epistemology of forensic identification. *Law Prob Risk* 2009;8:233–55.
- 13. Kaasa SO, Peterson T, Morris EK, Thompson WC. Statistical inference and forensic evidence: evaluating a bullet lead match. *Law Human Behav* 2007;31:433–47.
- 14. Saks MJ, Koehler JJ. The coming paradigm shift in forensic identification science. *Science* 2005;309(5736):892–5.
- 15. Sie SH, Murao S, Suter GF. Trace-element distribution in native gold. *Nucl Instrum Meth B* 1996;109:633–8.

- 16. Keegan E, Richter S, Kelly I, Wong H, Gadd P, Kuehn H, et al. The provenance of Australian uranium ore concentrates by elemental and isotopic analysis. *Appl Geochem* 2008;23:765–77.
- 17. Bugoi R, Constantinescu B, Constantin F, Catana D, Plostinaru D, Sasianu A. Archaeometrical studies of Greek and Roman silver coins. *J Radioanal Nucl Chem* 1999;242:777–81.
- 18. Leake RC, Chapman RJ, Bland DJ, Condliffe E, Styles MT. Microchemical characterization of alluvial gold from Scotland. *Trans Inst Min Metall B* 1997;106:B85–98.
- 19. Outridge PM, Doherty W, Gregoire DC. Determination of trace elemental signatures in placer gold by laser-ablation inductively-coupled plasma-mass spectrometry as a potential aid for gold exploration. *J Geochem Explor* 1998;60:229–40.
- 20. Mortenson JK, Chapman R, LeBarge W, Jackson L. Application of placer and lode gold geochemistry to gold exploration in western Yukon. In: Emond DS, Lewis LL, Bradshaw GD, editors. Yukon Exploration and Geology 2004: Yukon Geological Survey, 2005;205–212.
- 21. South Africa Mineral Economics Directorate. South Africa's Mineral Industry 2005/2006. 23rd rev. edn. Pretoria, South Africa: Republic of South Africa Minerals and Energy Department, 2006;1–173.
- 22. Robb LJ, Robb VM. Gold in the Witwatersrand basin. In: Wilson MGC, Anhaeusser CR, editors. The mineral resources of South Africa. Cape Town, South Africa: Council for Geosciences, 1998;294–349.
- 23. Ward JHW, Wilson MGC. Gold outside the Witwatersrand basin. In: Wilson MGC, Anhaeusser CR, editors. The mineral resources of South Africa. Cape Town, South Africa: Council for Geosciences, 1998;350–86.
- 24. Goldfarb RJ, Groves DI, Gardoll S. Orogenic gold and geologic time: a global synthesis. *Ore Geol Rev* 2001;18:1–75.
- 25. Hallbauer DK, Barton JM Jr. The fossil gold placers of the Witwatersrand: a review of their mineralogy, geochemistry and genesis. *Gold Bull* 1987;20:68–79.
- 26. Frimmel HE. Detrital origin of hydrothermal Witwatersrand gold—a review. *Terra Nova* 1997;9:192–7.
- 27. Ott D. Optimising gold alloys for the manufacturing process. *Gold Technol* 2002;34:37–44.
- 28. Rapson WS. The metallurgy of the coloured carat gold alloys. *Gold Bull* 1990;23:125–31.
- 29. Raub CJ, Ott D. Developments in modern gold jewellery alloys. In: Gafner G, King RP, editors. GOLD 100: Proceedings of the International Conference on Gold: Vol. 3: Industrial Uses of Gold. Johannesburg, South Africa: South African Institute of Mining and Metallurgy, 1986;65–72.
- 30. Raub CJ, Ott D. Gold casting alloys. The effect of zinc additions on their behaviour. *Gold Bull* 1983;16:46–51.
- 31. Fleming CA. Hydrometallurgy of precious metals recovery. *Hydrometallurgy* 1992;30:127–62.
- 32. Laxen PA, Becker GSM, Rubin R. Developments in the application of carbon-in-pulp to the recovery of gold from South African ores. *J South African Inst Min Metall* 1994;94:189–203.