Going for the Gold: Authentification of Coins and Precious Metals

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Richard Haddock, CoinSecure Inc., Palo Alto, CA

Welcome

Topics

- Why use XRF for precious metals and coins?
  - Comparison with other techniques
  - XRF from Handheld to Benchtop: does size matter?
- Going for the gold
  - Use of HH-XRF for precious metal identification and quantification
    - Where it works
    - Where it is limited
  - Use of HH-XRF for authentication of "ancient" and recent collector coins
    - Where it works
    - Where it is limited
- Conclusion
  - We get the gold, but there is *no golden bullet* for this application

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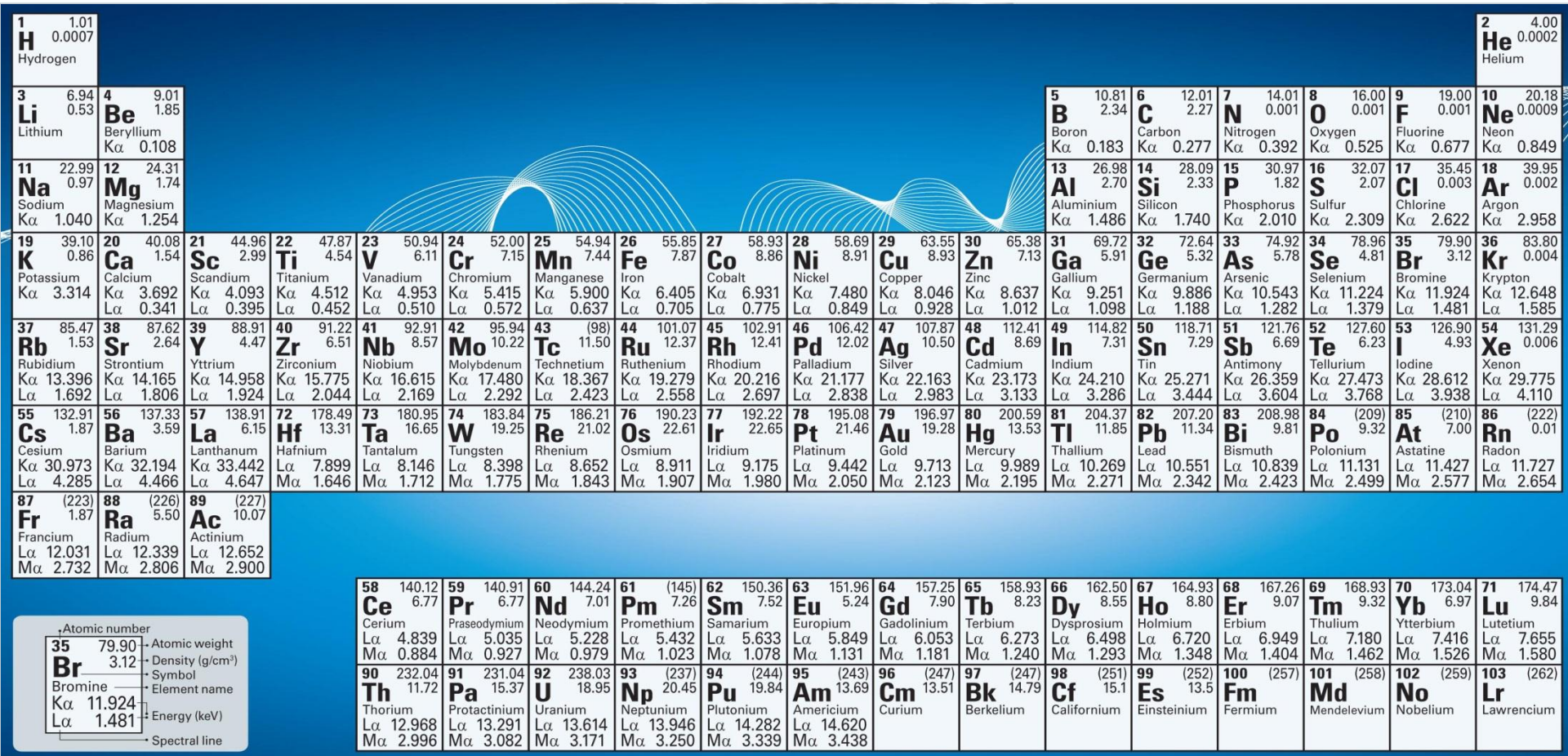
Global Product Manager HH-XRF
Bruker

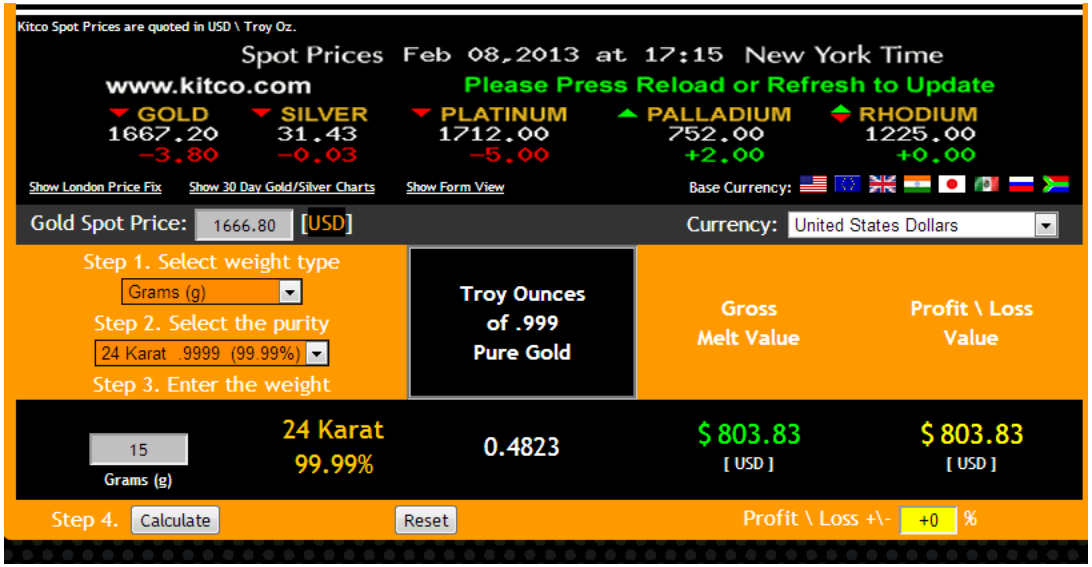
Richard Haddock
President
CoinSecure Inc.

Why use XRF for precious metals and coins?



First steps in any precious metal test

- Weighing the sample: g or ounce
- Locate stamps and identifying marks
- Conversion
  - 28.3495231 grams per ounce
  - 14.175 grams per half ounce
- Find gold price and gold scrap price (scrap price is below gold price)



Hallmarking Built-in Grade

Much of the gold jewelry manufactured before 1980 is slightly below its marked karat value. For example, jewelry marked 18K would actually be between 17K and 17.5K. In 1980, the laws changed regarding the marking and purity of gold jewelry (Europe).

Hallmark Symbol	Other mark variations	Carat Rating	Gold Purity
375	9ct 9k, 9kt	9ct	37.5%
585	14ct, 14k, 14kt	14ct	58.3%
750	18ct, 18k, 18kt	18ct	75.0%
916	22, 22ct, 22k, 22kt	22ct	91.6%
990 999	999, 999.9	24ct	100%

Calculation Example

- Nice "older" gold chain 35 g
  - No readable markings
  - 14K (58.3%) 1093 melt value
  - 18k (75%) 1406 melt value
  - 17k (70.8%) 1328 melt value
  - 19K (79.2%) 1485 melt value

- The more accurate the concentration is known, the more money you make

SOURCE http://www.silverrecyclers.com/Calculators/gold_calculator.aspx

Analysis Techniques (1)

Acid Tests / Scratch Tests

- A set of acidic solutions is used to “dissolve” the scratched-off material from a “touch” stone (different solutions for gold and platinum)
  - Qualitative test tells you if the scratched-off material was 14K, 18K etc.
  - Comparison with “scratch” from known material
- PROs
  - Low cost and easy to obtain
  - Very efficient by experienced users
- CONs
  - Not an exact value (approximate)
    - 4K “intervals” affect price
  - Can be fooled
  - Somehow destructive, consumables

© Van Dijk Toetsstenen

Analysis Techniques (2)

Electronic Gold Testers

- Electrochemical principle with either consumable probe or gel
- Can determine karat value and distinguish different gold grades (white, pink etc.) 6-24K
- PROs
  - Portable, fast 2-5 sec
  - Mid-range pricing < 1K $
- CONs
  - +/- 0.5 K
  - Can be fooled
  - Consumables

The ultimate and reference method

- The accepted reference method for precious metal analysis is fire assay
- Time-tested art/method since medieval times
- Fully destructive with an accuracy of 1 to 10000 in metal
- **ASTM E1335 - 08 Standard Test Methods for Determination of Gold in Bullion by Fire Assay Cupellation Analysis**
- Gravimetric determination of the gold
  - Ir and Ru are also deliberately doped in jewelry as their melting points are over 2500° C and cannot be detected by fire assay or acid tests.
  - More weight, more $$$

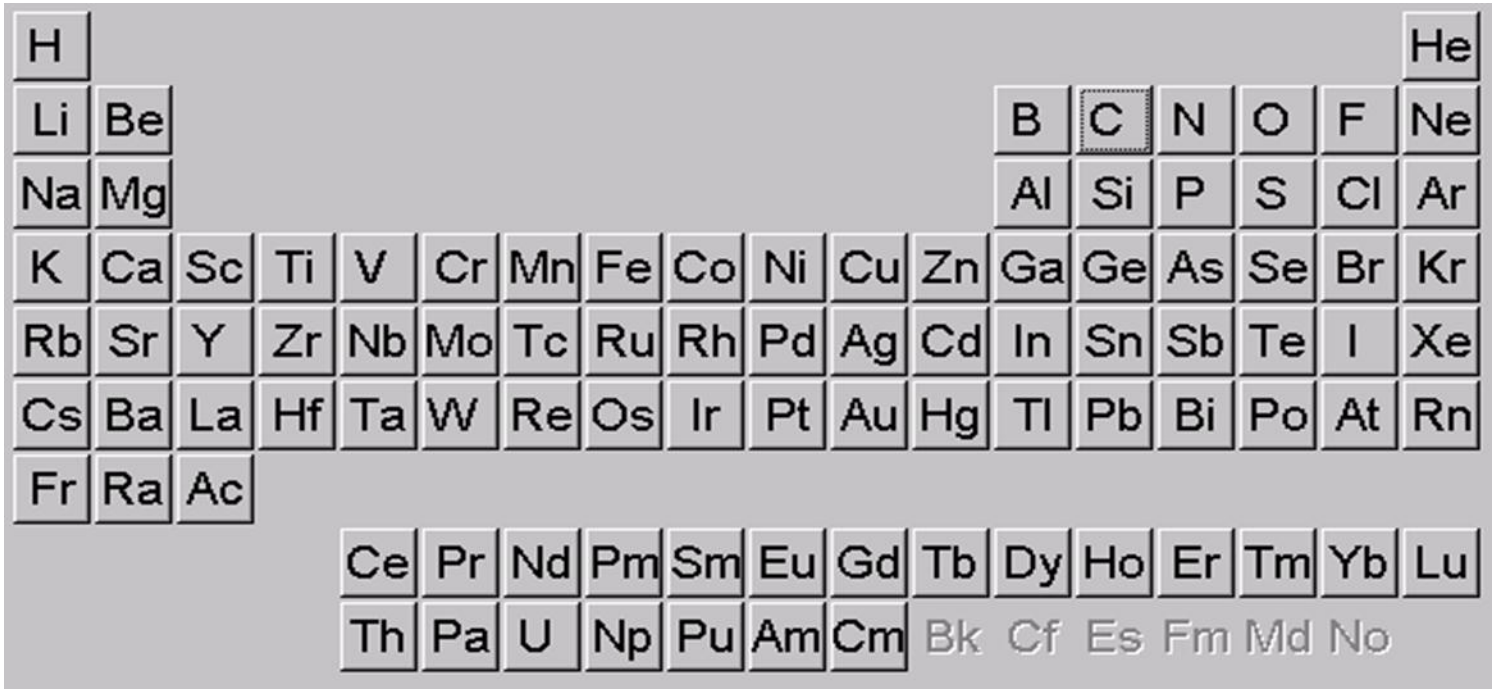
Why XRF?

- Non-destructive for the sample
- No consumables
- Portable to handheld
- Simple to use: One click or trigger pull to get results in % and KARAT
- Accuracy comparable to fire assay, e.g. within 1/8 of a fire assay value(*)
- Most analyses can be done within seconds
- Measures all elements in the sample

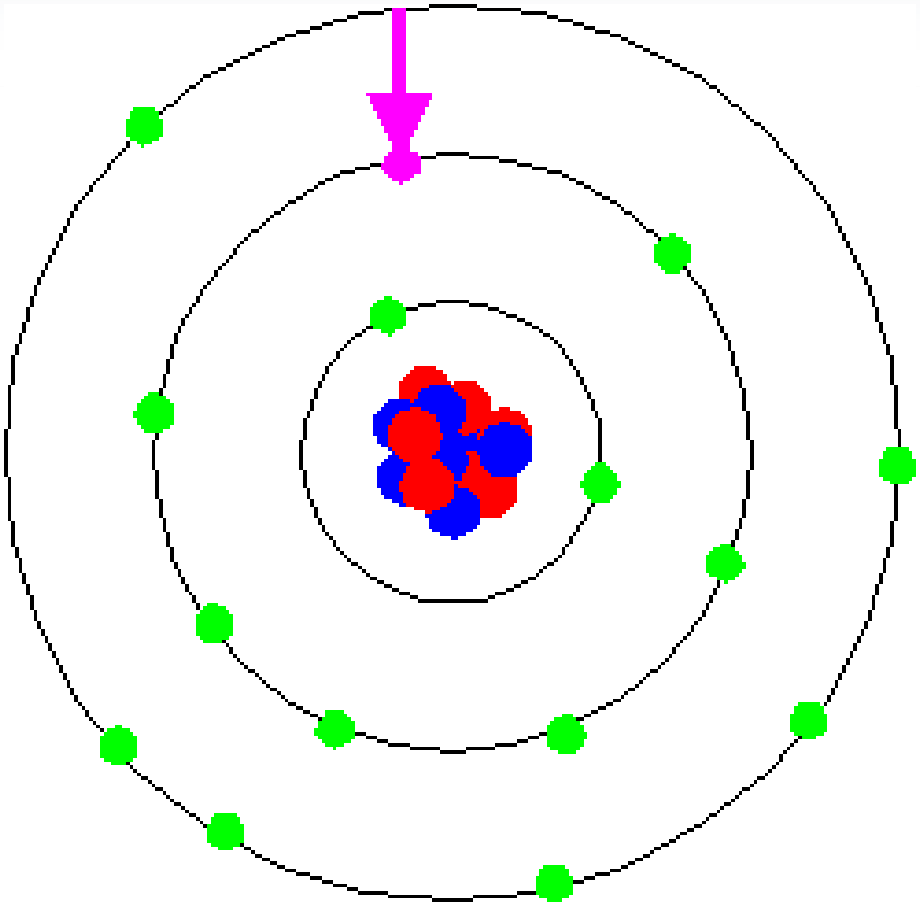
XRF: X-ray Fluorescence Analysis or X-ray Spectrometry

XRF is the method for:

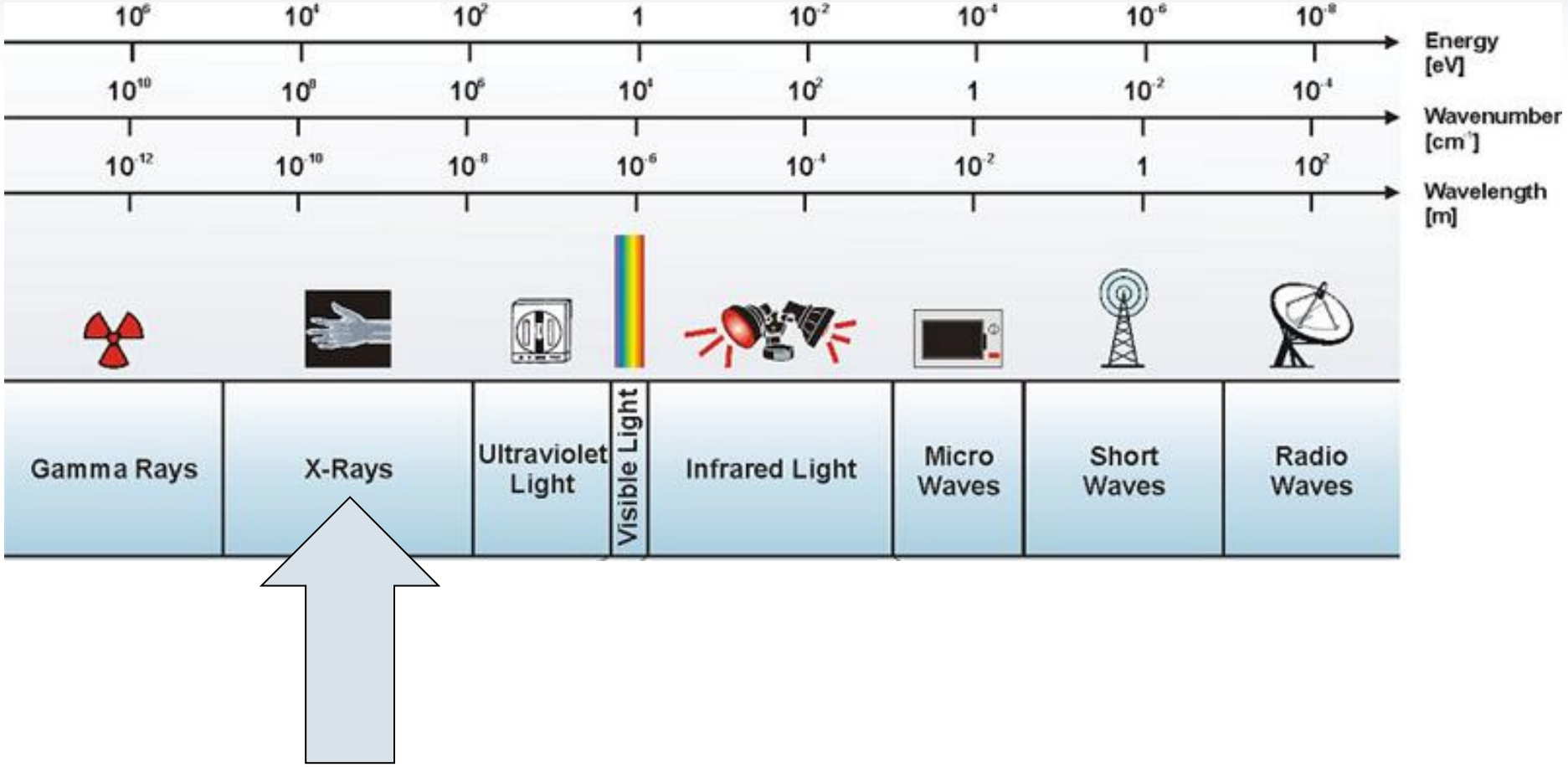
doing qualitative and quantitative analysis of elemental composition by excitation of atoms and detection of their characteristic X-rays



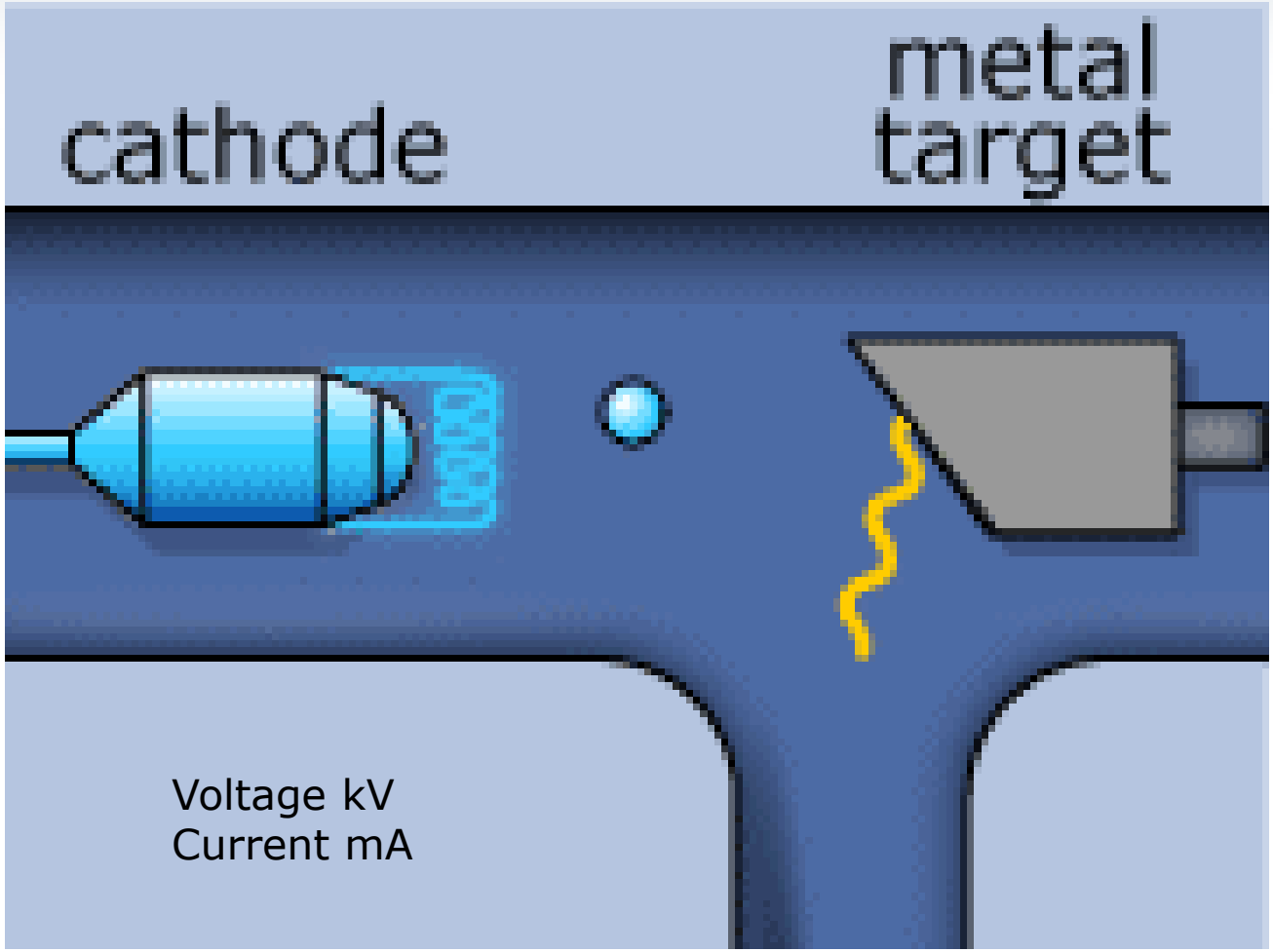
How Characteristic X-rays are Generated in an Atom



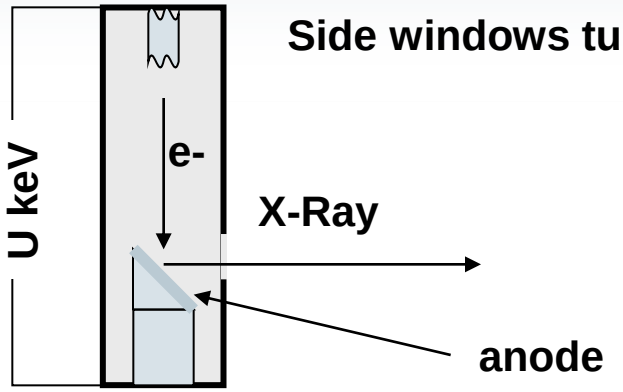
Where X-rays Fit Into the Energy Spectrum

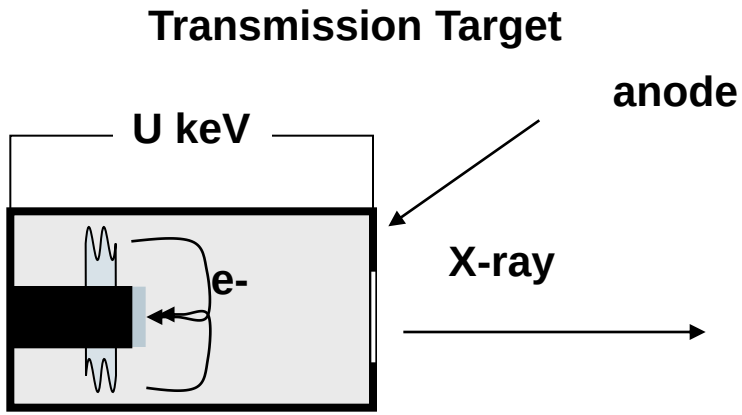


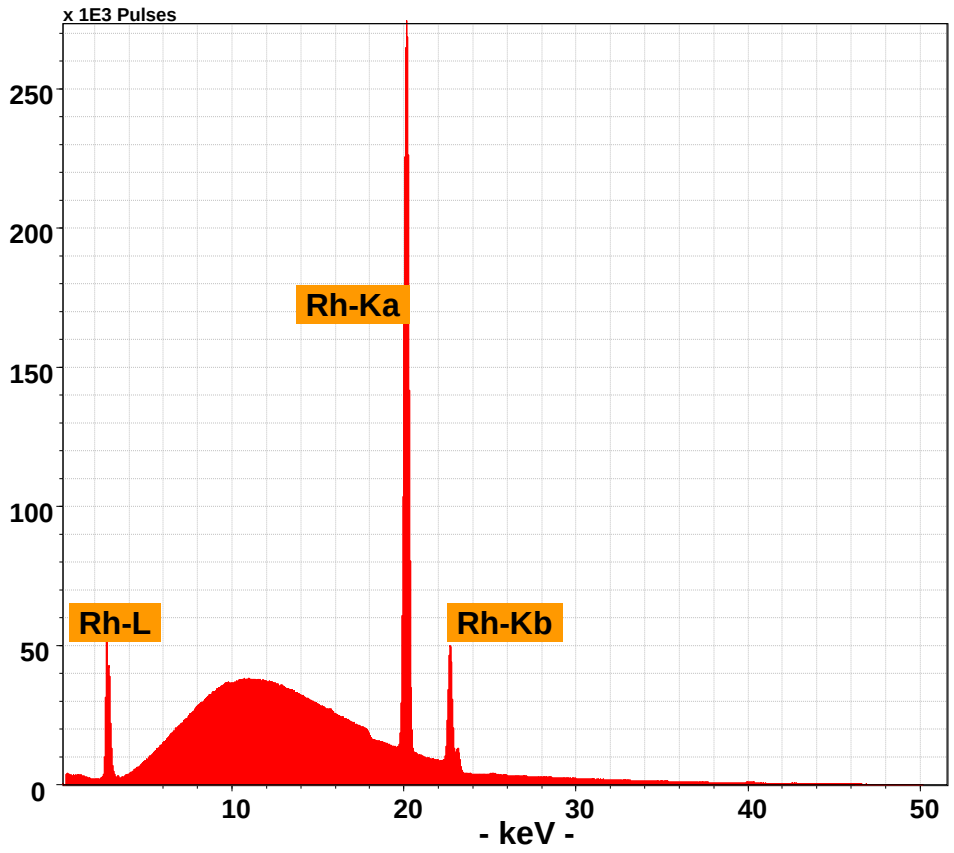
Generation of X-rays in an X-ray Tube



X-ray Production on Demand

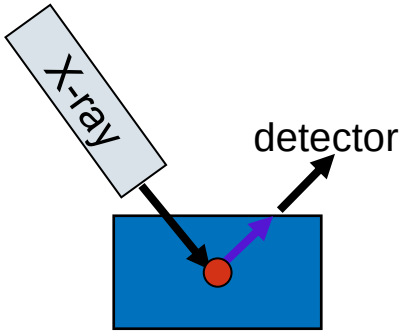


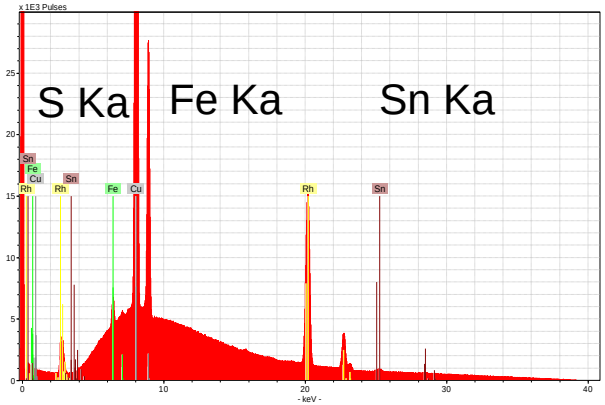




Absorption in the sample and from the sample

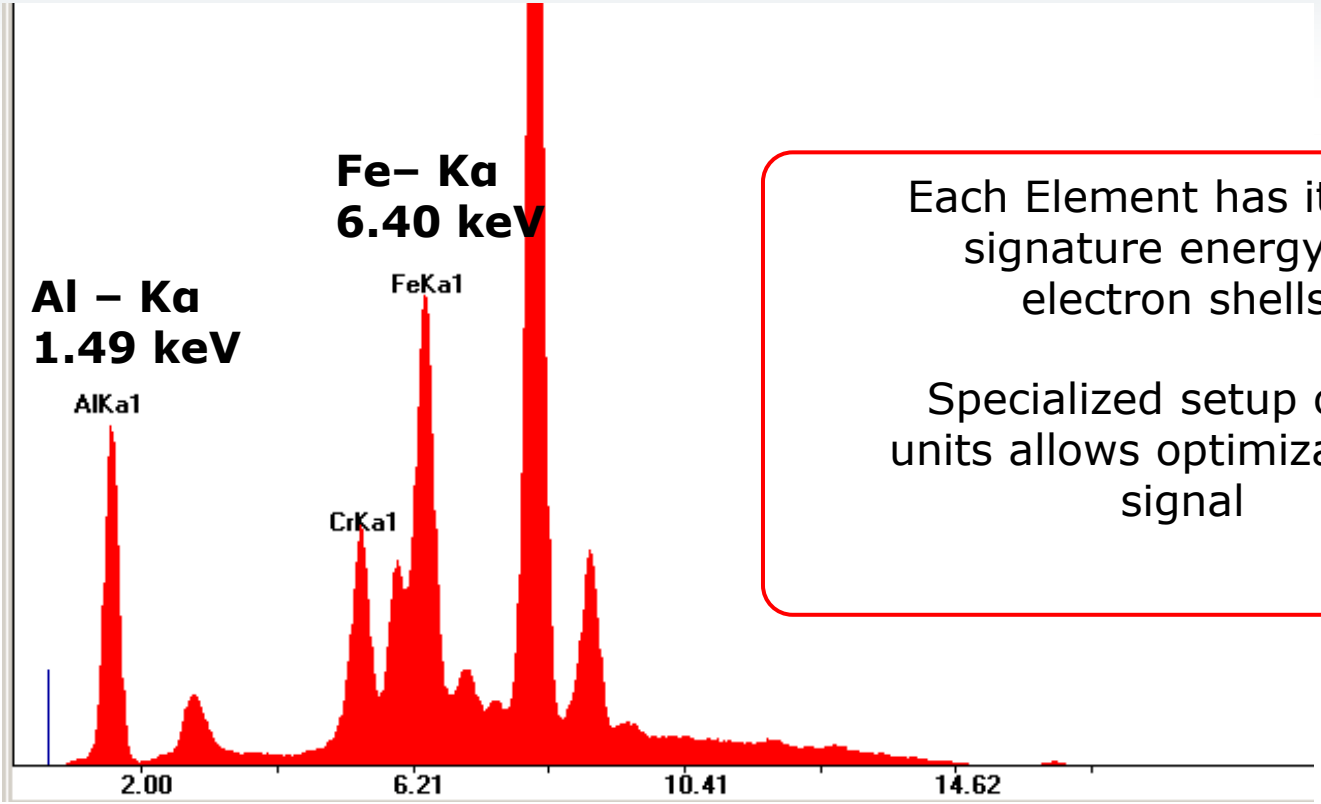
absorption: responsible for the information depth.
“depth from which a photon produced within the sample can leave the sample and reach the detector”





wood (45°)	ceramic (45°)	metal (45°)
polypropylene	SiO_2	Cu
S Ka 45 µm	S Ka 3 µm	S Ka 0.5 µm
Fe Ka 1200 µm	Fe Ka 50 µm	Fe Ka 8 µm
Sn Ka 29000 µm	Sn Ka 2600 µm	Sn Ka 45 µm

Example of XRF Spectrum



Each Element has its own signature energy for electron shells.

Specialized setup of the units allows optimization of signal

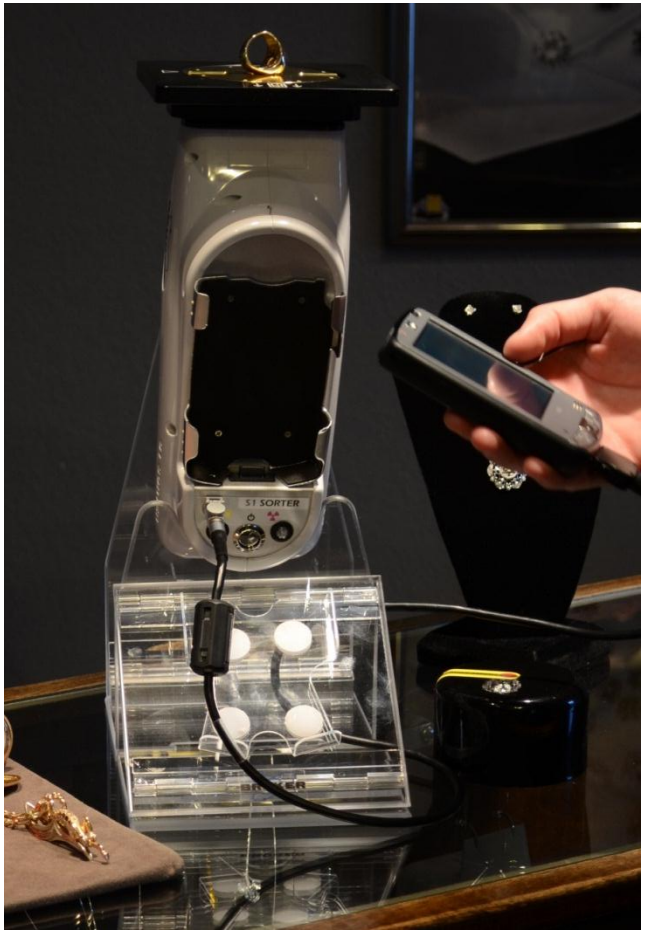
X-ray energy tells you WHAT element it came from

Number of X-rays tells you HOW much is present

Instrumentation (handheld)

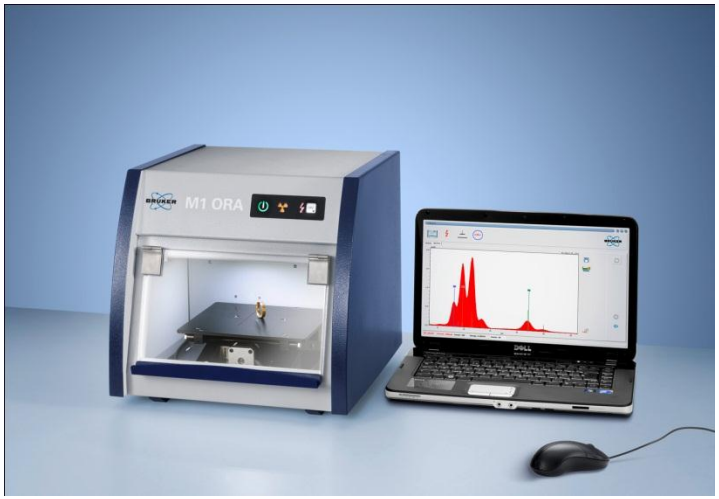
- Around 1.4 kg weighing instrument, easy to transport

Handheld or stationary use



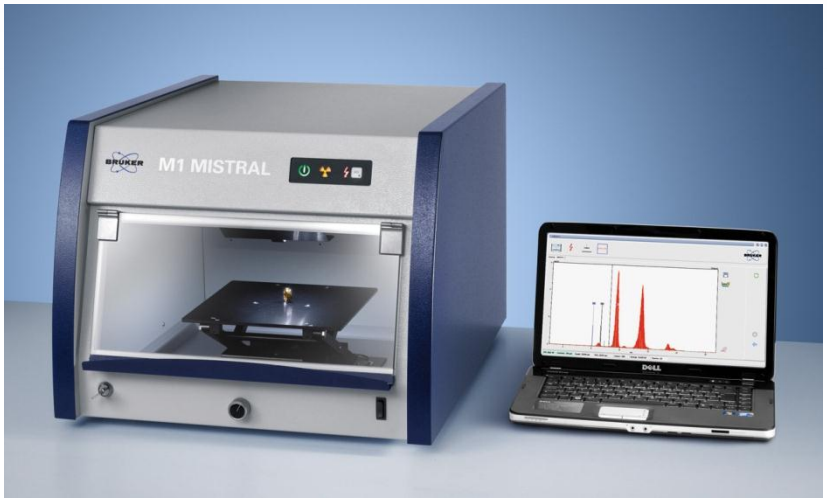
Micro-XRF benchtop units

M1 Ora



Small unit for jewelry analysis

M1 Mistral^{SDD}

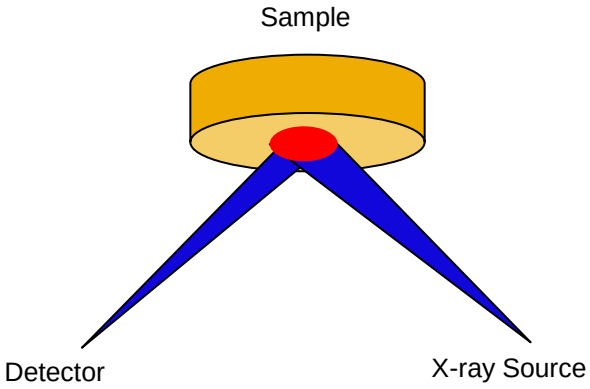


Larger unit for unknowns, platings

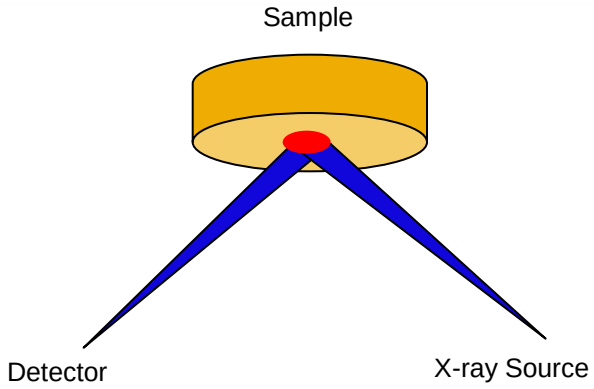
- Measurement on air.
- Spot size down to 0.1 mm.
- Measurement from top
- Quantification standard based, standardless, coating thickness

HH-XRF vs Micro-XRF
Beam Size Comparison

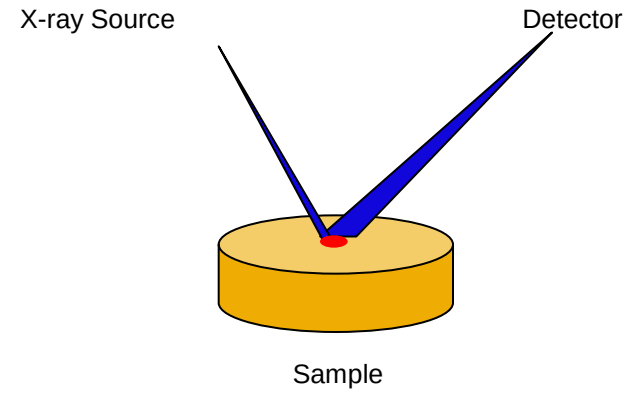
S1 SORTER (~6mm^2)



S1 TITAN (3x2mm)



M1 Ora / Mistral (~0.07mm^2)



Use of HH-XRF for precious metal identification and quantification

- HH-XRF can be used to identify the "GRADE" of the metal as well as the KARAT reading
- More importantly it can determine the concentrations of the all elements in the object.
  - This allows to detect elements such as Ir and Ru which cannot be detected by the fire assay for settlement analysis
  - Unusual alloys such as dental alloys (containing Hg)
  - Palladium jewelry can be distinguished from Pt
  - XRF is useful also for silver alloys which vary much more nationally than other precious metals

Courtesy 123 Precious Metal Refining, LLC

Gold Accuracy and repeatability

S1 TITAN		Stdev absolut (1s) for 10 measurements			
Grade	Content	Au	RelStdevAu	Ag	Cu
22 karat	91.60%	0.06%	0.06%	0.04%	0.05%
18 karat	75.20%	0.11%	0.15%	0.08%	0.03%
13 karat	53.80%	0.10%	0.19%	0.08%	0.07%
10 karat	41.50%	0.10%	0.23%	0.07%	0.07%

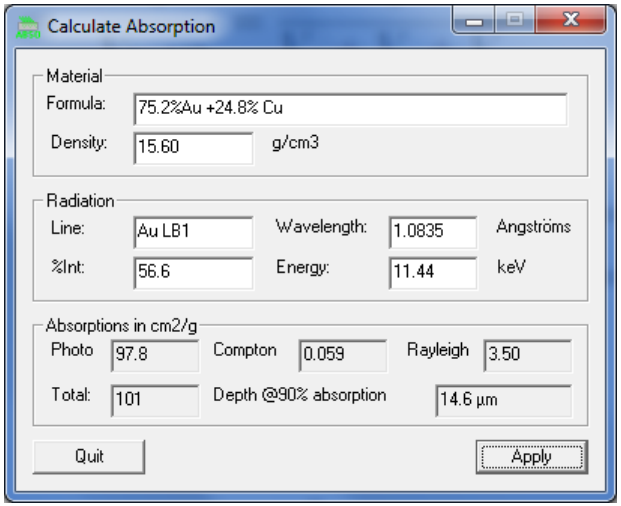
NOTE: you need to balance speed with precision. Average over the sample does not necessarily be a better analysis

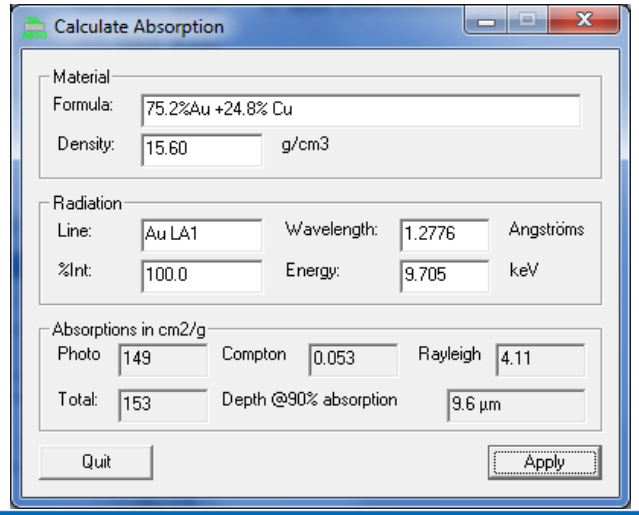
Small objects not covering the spot are normalized to 100% using Bruker's unique small sample intensity scaling which includes full FP matrix correction.

Size and power does not matter!
The layer is defined by the sample!

The analytical lines (emissions) from the sample pose some challenges:

- Au Ka1 68.803 KeV K abs (excitation potential) 80.725 KeV
- Au Kb1 77.984 KeV
- Au La 9.713 KeV L1 abs (excitation potential) 14.535 KeV
- Au Lb 11.442 KeV
- Au Lγ 13.381 KeV
- Au Ma.. 2.123 KeV M1 abs 3.148 KeV





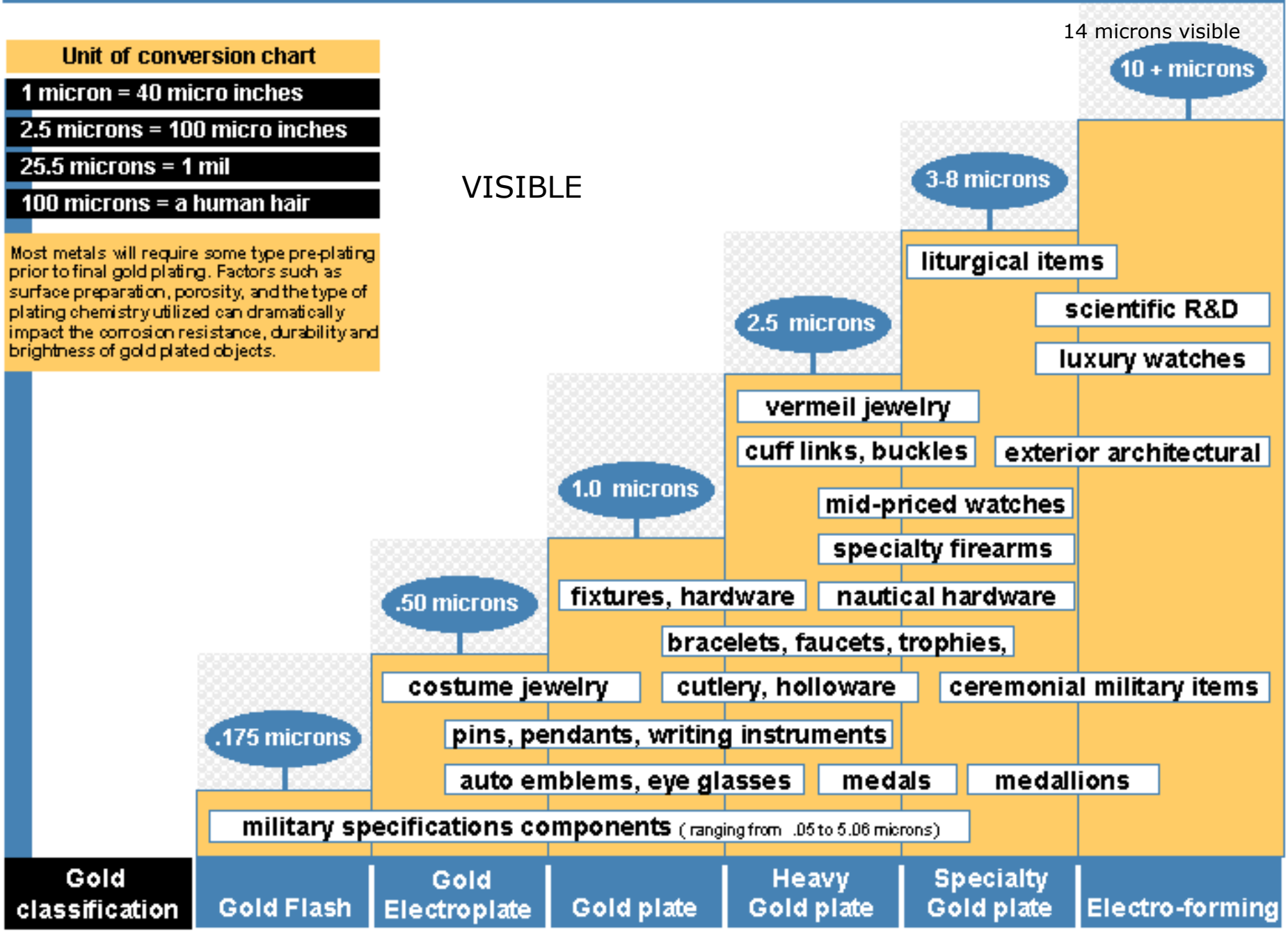
18K gold

The GOLDEN cent

- What happens if we measure a coated sample?
  - If the gold layer is smaller than the layer we analyze (which is governed by physics), we read a mix of base and the gold layer.

- This is a flash gold coating measured to be .25 micron

Thickness diagram for decorative gold plating – Copyright 2004 Metal Arts Specialties



What is plated…

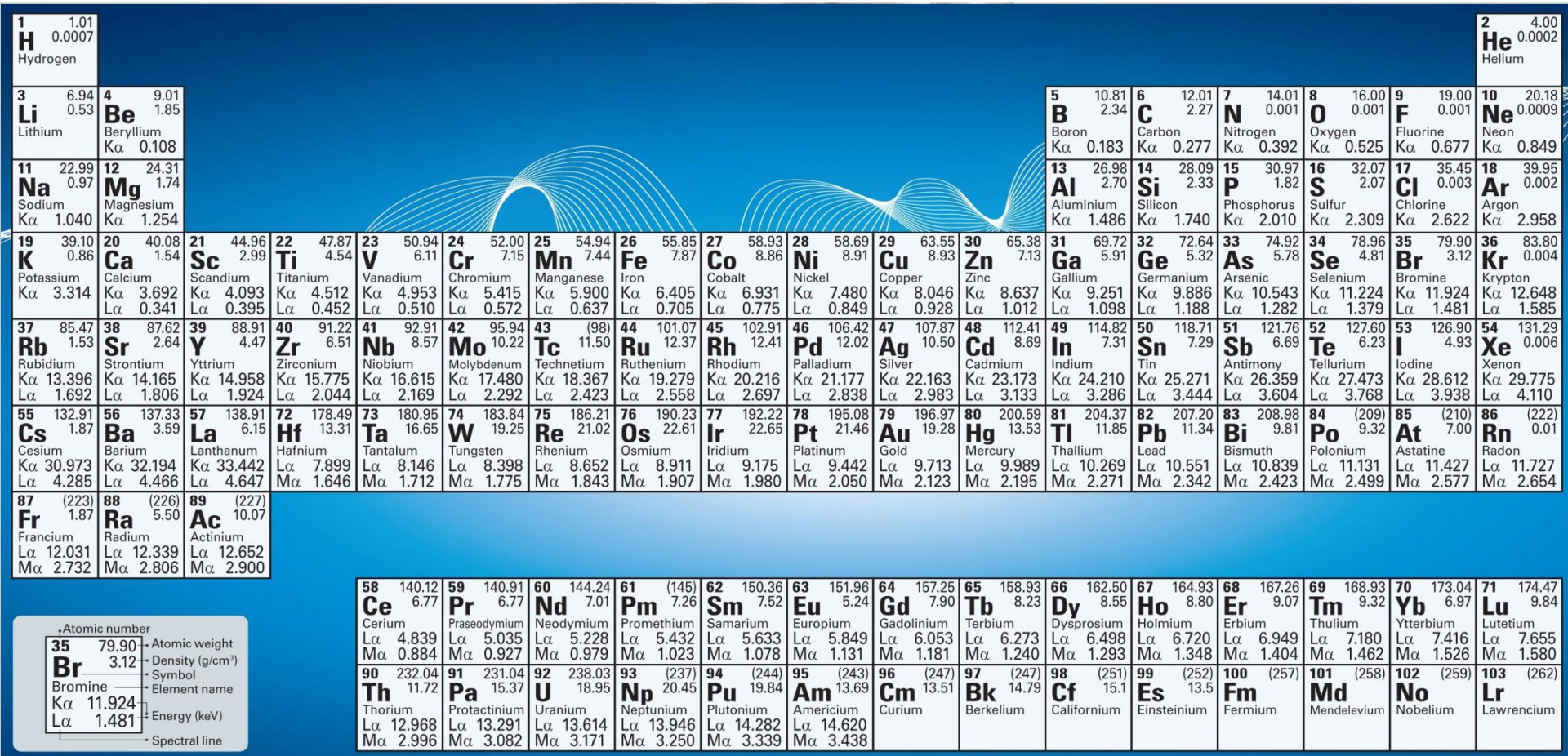
- Decorative gold plating on antique pieces, bathroom fittings or furniture articles is mostly flash gold typically 22-24K and in the range of 0.2-0.5 microns and can be spotted by the "LOW" Karat reading and high "other" metal content (e.g. Pb in brass)
- It is possible that 22K plating has been applied to 18K articles and needs verification "upgrading" the 18K to 19-20K. This is done to upgrade non-HALMARKED materials and to trick acid tests! The plating can be in the range of 2-6 microns and used in jewelry, watch and eyewear industries (requires Ni bonding layer)
  - This can be spotted again by unusual Karat grade and by studying the spectra: the ratio between the Au emission lines will be "off" from its theoretical ratio
  - Measure more spots and look for variations indicating coating
- Hard "electroformed" materials with coating in excess of 14 microns (if Au LB) is measured or 10 microns (for Au La1) appear solid

Faked! Lose 72 K in one deal!

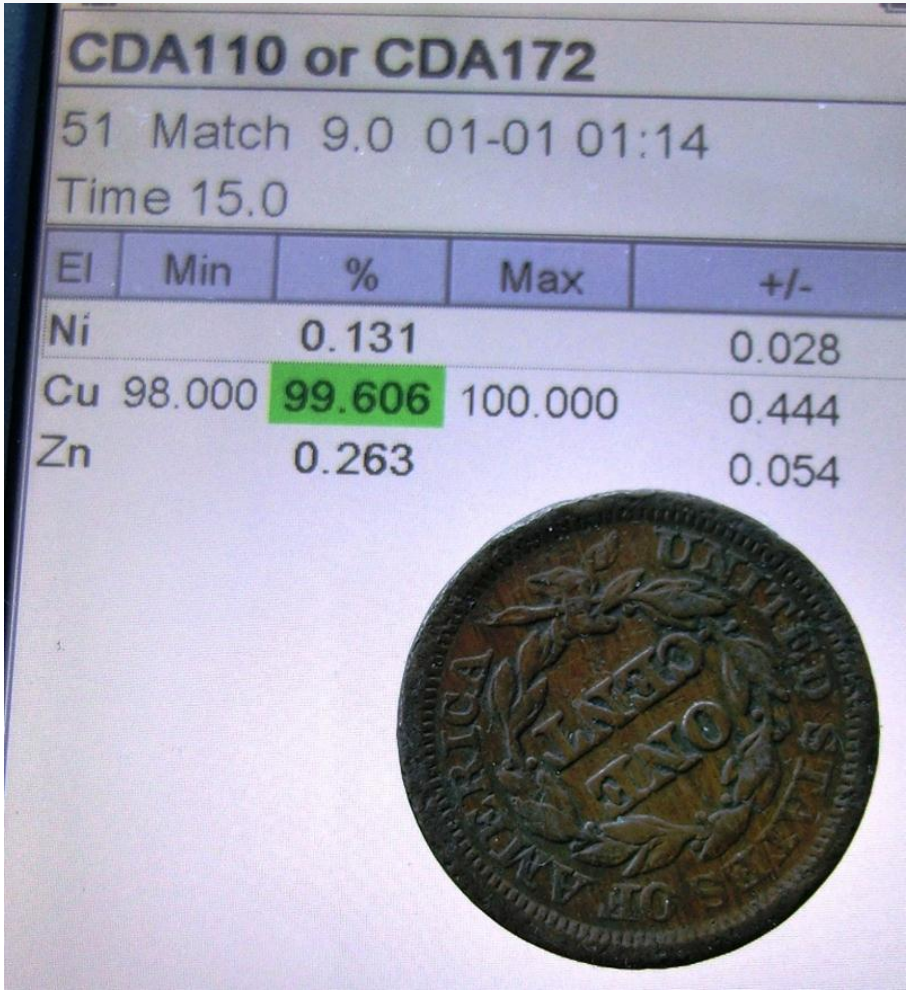
- W coated with thick Au is undetectable by all mentioned techniques!
- One gold dealer discovered that four of the 3-inch-by-1-inch gold bars he bought — worth about $72,000 retail — were counterfeit (Sept 23rd 2012). He was tricked by the "respectable" markings and correct weight and dimensions.
- Only drilling or most accurate density measurements (by fluid displacement) will help here
- If it sounds too good to be true, it is either stolen or fake!

Be aware of the ORIGINAL , enables to spot the fake!

COINS


1 1.01 H 0.0007 Hydrogen
2 4.00 He 0.0002 Helium
3 6.94 Li 0.53 Lithium
4 9.01 Be 1.85 Beryllium Kα 0.108
5 10.81 B 2.34 Boron Kα 0.183
6 12.01 C 2.27 Carbon Kα 0.277
7 14.01 N 0.001 Nitrogen Kα 0.392
8 16.00 O 0.001 Oxygen Kα 0.525
9 19.00 F 0.001 Fluorine Kα 0.677
10 20.18 Ne 0.0009 Neon Kα 0.849
11 22.99 Na 0.97 Sodium Kα 1.040
12 24.31 Mg 1.74 Magnesium Kα 1.254
13 26.98 Al 2.70 Aluminium Kα 1.486
14 28.09 Si 2.33 Silicon Kα 1.740
15 30.97 P 1.82 Phosphorus Kα 2.010
16 32.07 S 2.07 Sulfur Kα 2.309
17 35.45 Cl 0.003 Chlorine Kα 2.622
18 39.95 Ar 0.002 Argon Kα 2.958
19 39.10 K 0.86 Potassium Kα 3.314
20 40.08 Ca 1.54 Calcium Kα 3.692 Lα 0.341
21 44.96 Sc 2.99 Scandium Kα 4.093 Lα 0.395
22 47.87 Ti 4.54 Titanium Kα 4.512 Lα 0.452
23 50.94 V 6.11 Vanadium Kα 4.953 Lα 0.510
24 52.00 Cr 7.15 Chromium Kα 5.415 Lα 0.572
25 54.94 Mn 7.44 Manganese Kα 5.900 Lα 0.637
26 55.85 Fe 7.87 Iron Kα 6.405 Lα 0.705
27 58.93 Co 8.86 Cobalt Kα 6.931 Lα 0.775
28 58.69 Ni 8.91 Nickel Kα 7.480 Lα 0.849
29 63.55 Cu 8.93 Copper Kα 8.046 Lα 0.928
30 65.38 Zn 7.13 Zinc Kα 8.637 Lα 1.012
31 69.72 Ga 5.91 Gallium Kα 9.251 Lα 1.098
32 72.64 Ge 5.32 Germanium Kα 9.886 Lα 1.188
33 74.92 As 5.78 Arsenic Kα 10.543 Lα 1.282
34 78.96 Se 4.81 Selenium Kα 11.224 Lα 1.379
35 79.90 Br 3.12 Bromine Kα 11.924 Lα 1.481
36 83.80 Kr 0.004 Krypton Kα 12.648 Lα 1.585
37 85.47 Rb 1.53 Rubidium Kα 13.396 Lα 1.692
38 87.62 Sr 2.64 Strontium Kα 14.165 Lα 1.806
39 88.91 Y 4.47 Yttrium Kα 14.958 Lα 1.924
40 91.22 Zr 6.51 Zirconium Kα 15.775 Lα 2.044
41 92.91 Nb 8.57 Niobium Kα 16.615 Lα 2.169
42 95.94 Mo 10.22 Molybdenum Kα 17.480 Lα 2.292
43 (98) Tc 11.50 Technetium Kα 18.367 Lα 2.423
44 101.07 Ru 12.37 Ruthenium Kα 19.279 Lα 2.558
45 102.91 Rh 12.41 Rhodium Kα 20.216 Lα 2.697
46 106.42 Pd 12.02 Palladium Kα 21.177 Lα 2.838
47 107.87 Ag 10.50 Silver Kα 22.163 Lα 2.983
48 112.41 Cd 8.69 Cadmium Kα 23.173 Lα 3.133
49 114.82 In 7.31 Indium Kα 24.210 Lα 3.286
50 118.71 Sn 7.29 Tin Kα 25.271 Lα 3.444
51 121.76 Sb 6.69 Antimony Kα 26.359 Lα 3.604
52 127.60 Te 6.23 Tellurium Kα 27.473 Lα 3.768
53 126.90 I 4.93 Iodine Kα 28.612 Lα 3.938
54 131.29 Xe 0.006 Xenon Kα 29.775 Lα 4.110
55 132.91 Cs 1.87 Cesium Kα 30.973 Lα 4.285
56 137.33 Ba 3.59 Barium Kα 32.194 Lα 4.466
57 138.91 La 6.15 Lanthanum Kα 33.442 Lα 4.647
72 178.49 Hf 13.31 Hafnium Lα 7.899 Mα 1.646
73 180.95 Ta 16.65 Tantalum Lα 8.146 Mα 1.712
74 183.84 W 19.25 Tungsten Lα 8.398 Mα 1.775
75 186.21 Re 21.02 Rhenium Lα 8.652 Mα 1.843
76 190.23 Os 22.61 Osmium Lα 8.911 Mα 1.907
77 192.22 Ir 22.65 Iridium Lα 9.175 Mα 1.980
78 195.08 Pt 21.46 Platinum Lα 9.442 Mα 2.050
79 196.97 Au 19.28 Gold Lα 9.713 Mα 2.123
80 200.59 Hg 13.53 Mercury Lα 9.989 Mα 2.195
81 204.37 Tl 11.85 Thallium Lα 10.269 Mα 2.271
82 207.20 Pb 11.34 Lead Lα 10.551 Mα 2.342
83 208.98 Bi 9.81 Bismuth Lα 10.839 Mα 2.423
84 (209) Po 9.32 Polonium Lα 11.131 Mα 2.499
85 (210) At 7.00 Astatine Lα 11.427 Mα 2.577
86 (222) Rn 0.01 Radon Lα 11.727 Mα 2.654
87 (223) Fr 1.87 Francium Lα 12.031 Mα 2.732
88 (226) Ra 5.50 Radium Lα 12.339 Mα 2.806
89 (227) Ac 10.07 Actinium Lα 12.652 Mα 2.900
58 140.12 Ce 6.77 Cerium Lα 4.839 Mα 0.884
59 140.91 Pr 6.77 Praseodymium Lα 5.035 Mα 0.927
60 144.24 Nd 7.01 Neodymium Lα 5.228 Mα 0.979
61 (145) Pm 7.26 Promethium Lα 5.432 Mα 1.023
62 150.36 Sm 7.52 Samarium Lα 5.633 Mα 1.078
63 151.96 Eu 5.24 Europium Lα 5.849 Mα 1.131
64 157.25 Gd 7.90 Gadolinium Lα 6.053 Mα 1.181
65 158.93 Tb 8.23 Terbium Lα 6.273 Mα 1.240
66 162.50 Dy 8.55 Dysprosium Lα 6.498 Mα 1.293
67 164.93 Ho 8.80 Holmium Lα 6.720 Mα 1.348
68 167.26 Er 9.07 Erbium Lα 6.949 Mα 1.404
69 168.93 Tm 9.32 Thulium Lα 7.180 Mα 1.462
70 173.04 Yb 6.97 Ytterbium Lα 7.416 Mα 1.526
71 174.47 Lu 9.84 Lutetium Lα 7.655 Mα 1.580
90 232.04 Th 11.72 Thorium Lα 12.968 Mα 2.996
91 231.04 Pa 15.37 Protactinium Lα 13.291 Mα 3.082
92 238.03 U 18.95 Uranium Lα 13.614 Mα 3.171
93 (237) Np 20.45 Neptunium Lα 13.946 Mα 3.250
94 (244) Pu 19.84 Plutonium Lα 14.282 Mα 3.339
95 (243) Am 13.69 Americium Lα 14.620 Mα 3.438
96 (247) Cm 13.51 Curium
97 (247) Bk 14.79 Berkelium
98 (251) Cf 15.1 Californium
99 (252) Es 13.5 Einsteinium
100 (257) Fm Fermium
101 (258) Md Mendelevium
102 (259) No Nobelium
103 (262) Lr Lawrencium
Atomic number
35 79.90 Br 3.12 Bromine Kα 11.924 Lα 1.481
Atomic weight
Density (g/cm³)
Symbol
Element name
Energy (keV)
Spectral line

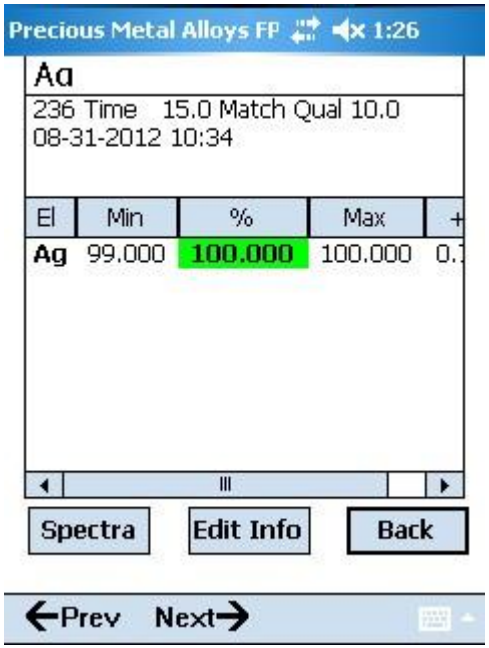
At one point pennies were Cu

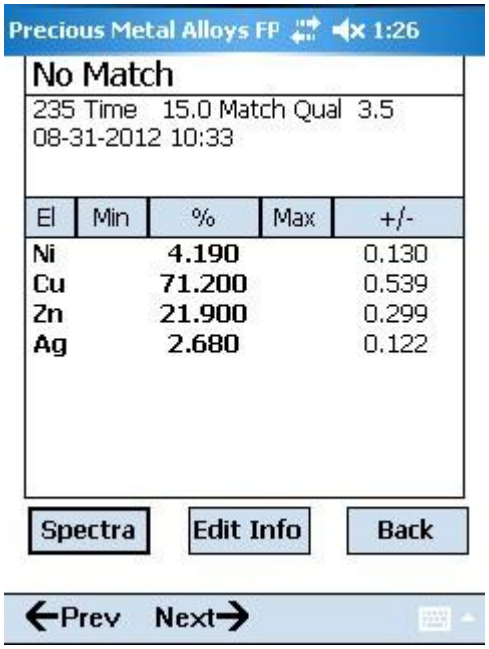


Collector coins: another area of concern and use of HH-XRF

Silver content:

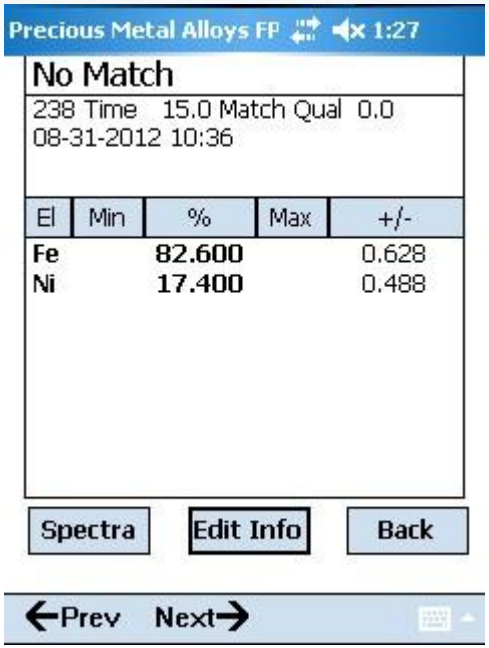
if it ain't 5 9's, it's not fine silver

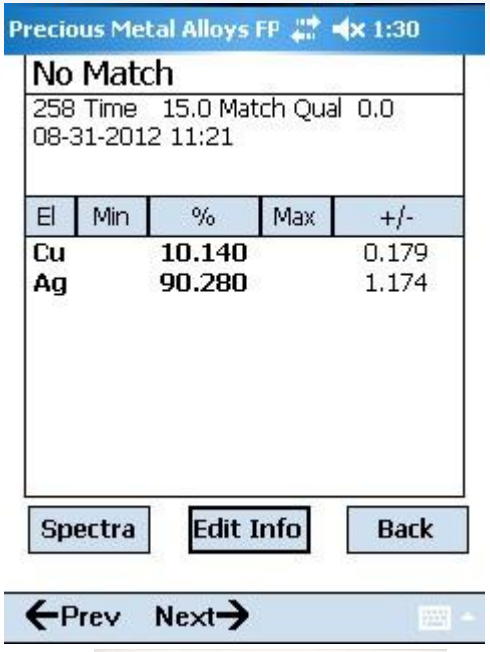




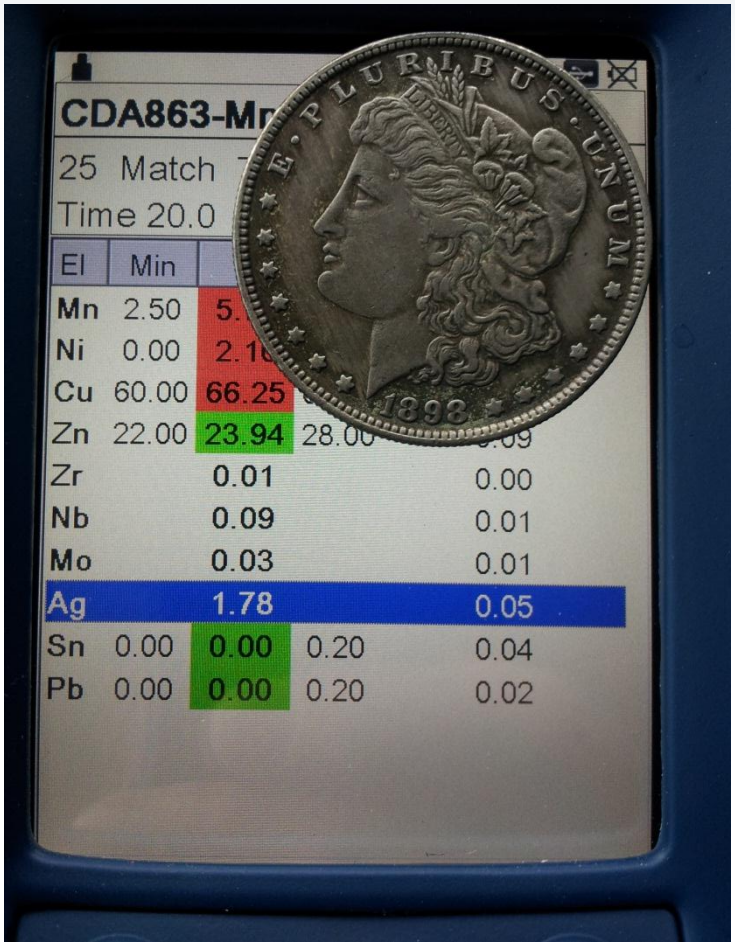
Fake Morgan vs “boxed” Real Morgan

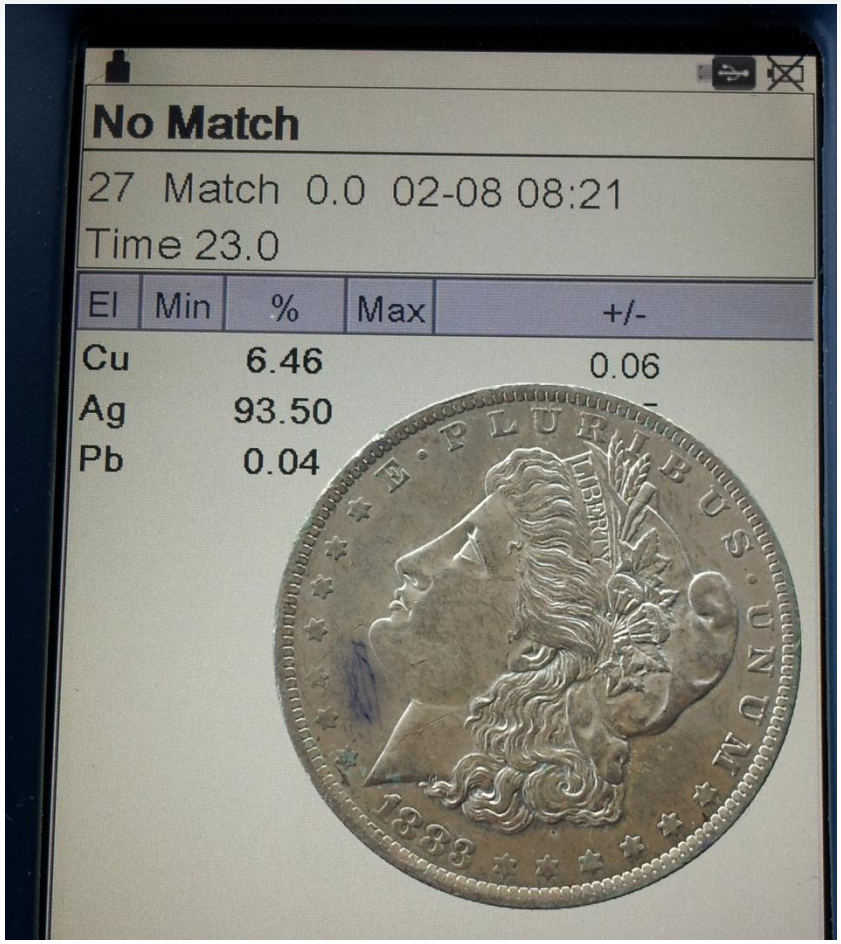
Diameter: 38.1 millimeters
Weight: 26.73 grams
Composition: .900 silver, .100 copper Edge: Reeded
Net Weight: .77344 ounce pure silver.





More Morgans

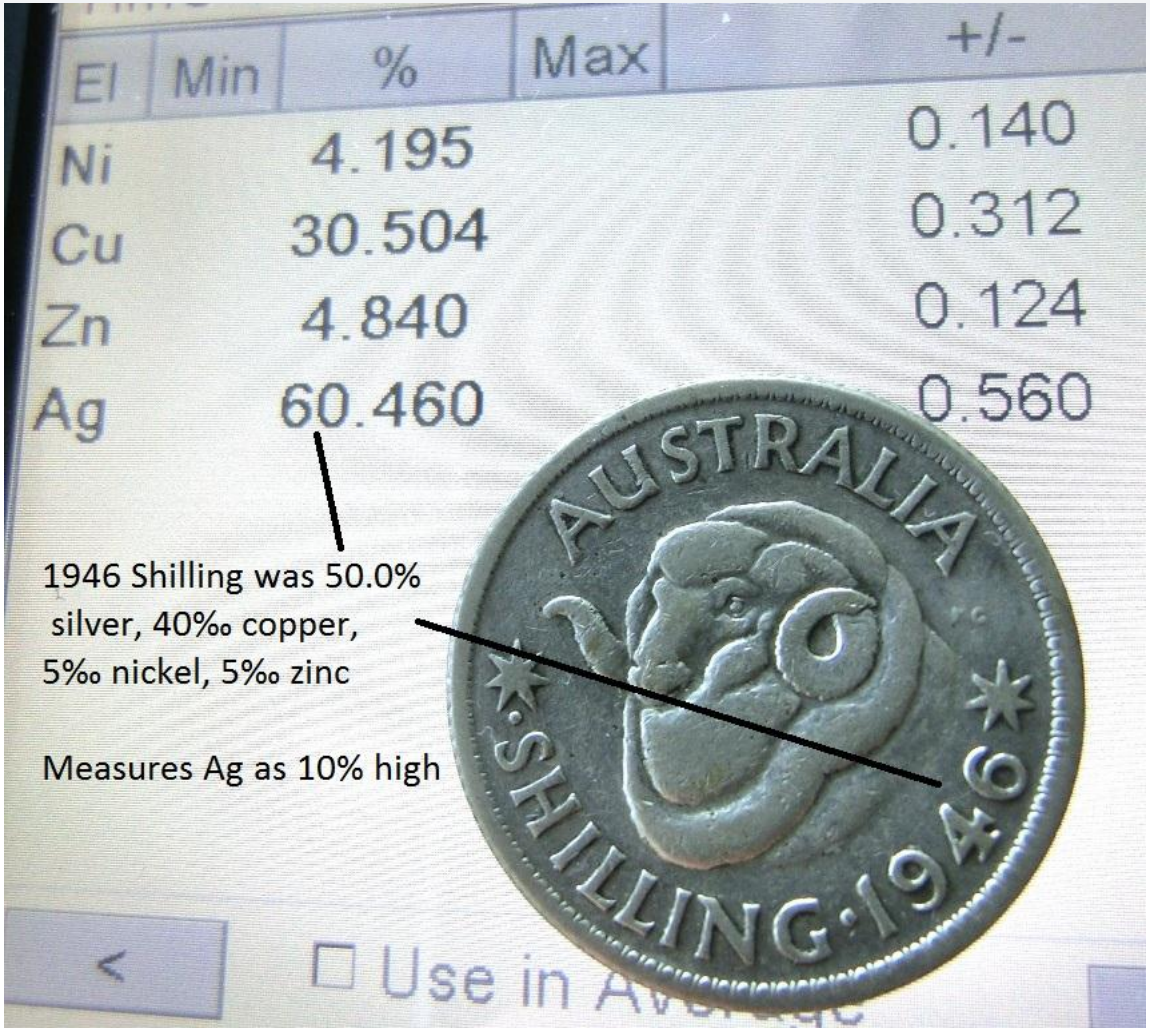




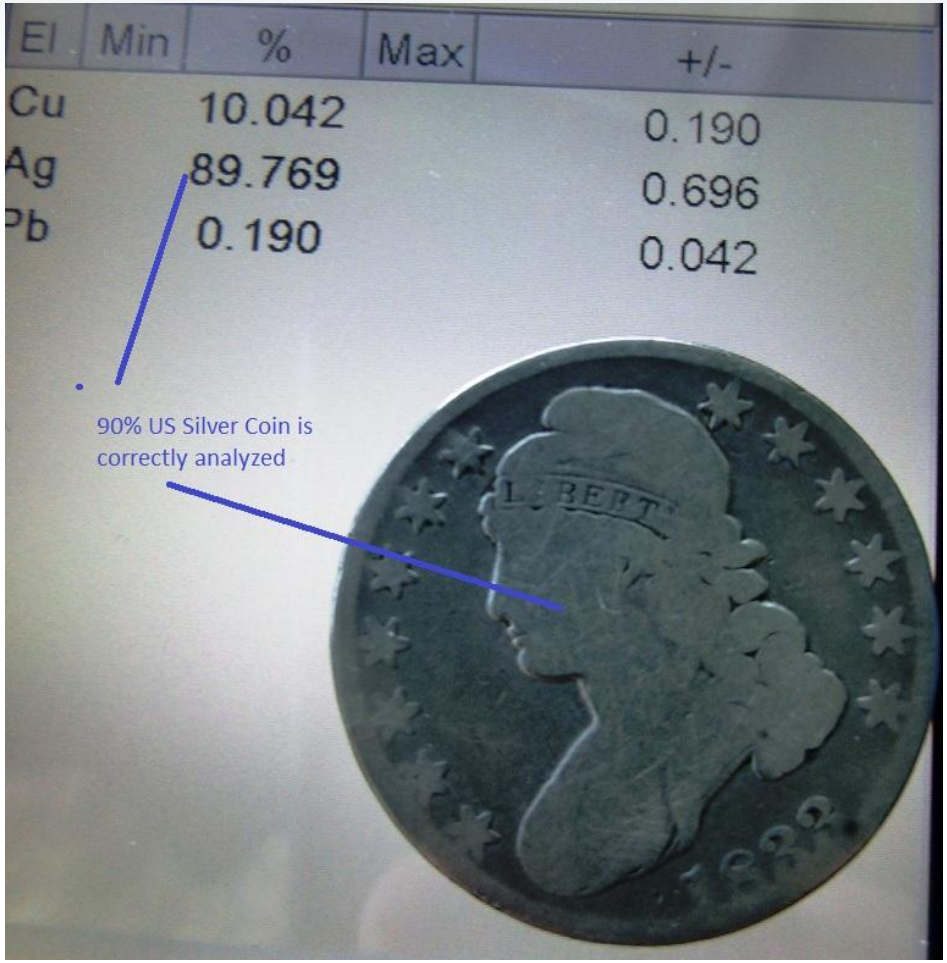
COINs (Mx) reading higher in Ag? Instrument issue?

COINs (Mx) reading higher in Ag? Instrument issue?

Also this Australian (1946) coins reads strangely high



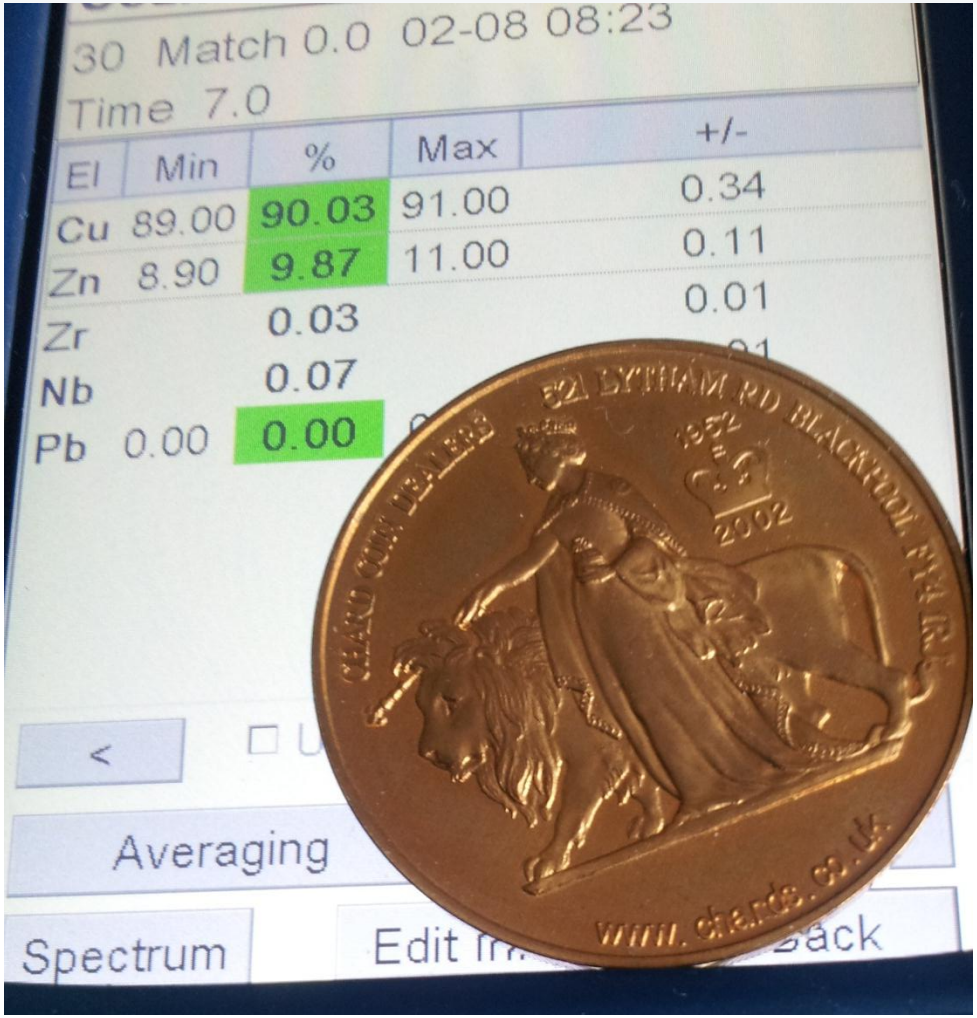
US coin read correct



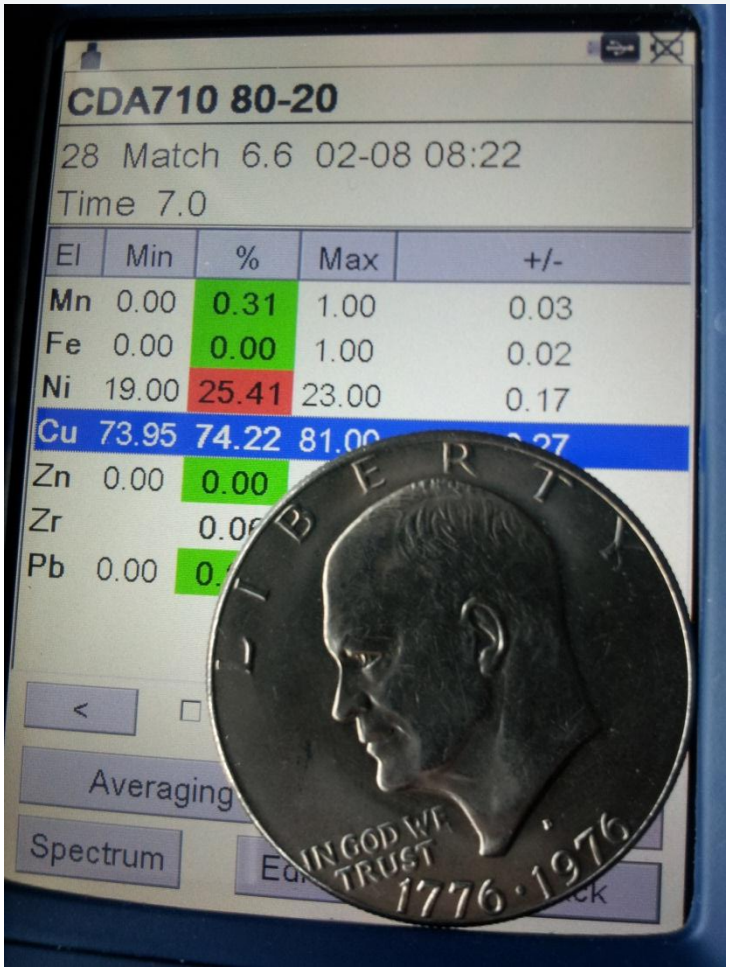
What happened here

- Once we “removed” the surface layer of some of those coins and measured again, we got the correct / expected concentration
- The coins were ACID washed, removing the Cu and Zn
  - Due to analyzed layer, we read Ag “higher” since it is depleted in the removed elements

HM Pb-free coins



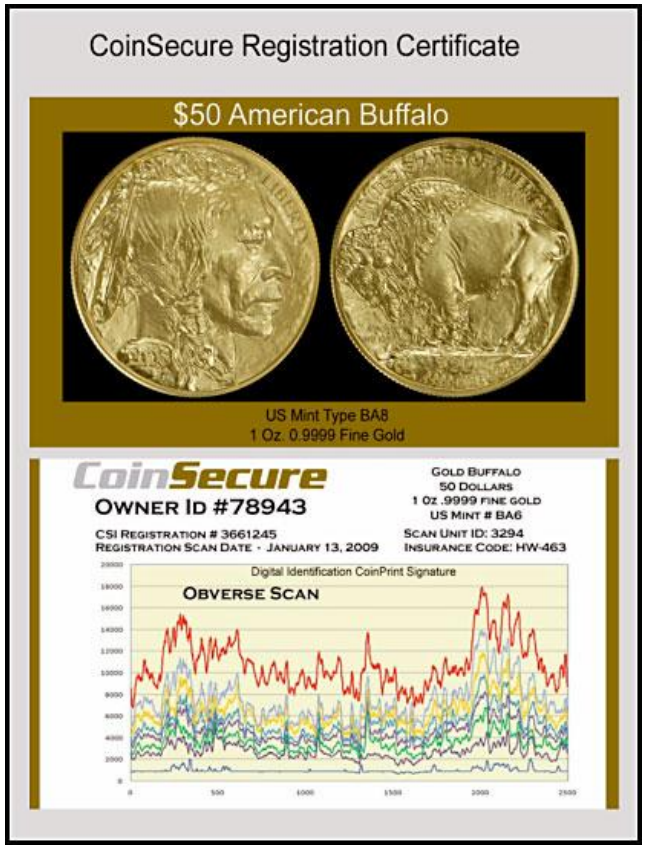
Coated: Ni layer



XRF is only one fingerprint

- The **CP16 CoinAnalyzer™--** a desktop coin identification system, can find unique characteristics within seemingly identical coins and record these characteristics as a file to serialize the coin. ***This gives each coin an individual identity that is permanently linked to the physical coin attributes.***
- In less than 5 seconds, the CP16 can analyze a coin, finding the unique characteristics of that coin and storing them in a ***CoinPrint™*** **ID file** similar to a fingerprint file. An individualized **serial number** is added to this identification record.

CoinSecure



Conclusion

- HH-XRF and the smaller spot size micro-XRF are great tools for the larger scale buyer of precious metal scrap or "… buy gold" establishments as they are for any refiner
- With pricing of well below $20K USD, HH-XRF allows for more conclusive and accurate ID, which will result in higher margins, paying for the analyzer possible in just a few deals!
  - Recall our 4-Karat difference and the ability to spot older jewelry…
- Investigating the raw data (spectral fingerprint) enables to spot plating as long as the analyzed layer is thicker than the plating. Using the "tramp" elements such as Cu and Ni enable to spot them as well, BUT the HH-XRF is NOT the tool to unequivocally test and measure layers.
- Micro-XRF is designed for layer analysis but is limited by the same physics
- One technique alone is not enough to counter today's counterfeiters, which take advantage of the high prices and eBay-based trades
- Authenticated coins (boxes) from trusted companies are enabling peace of mind and creating value for buyer, seller and collector

Q&A

Any Questions?

Please type any questions you may have for our speakers in the Q&A panel and click Send.

Thank you!