Article: Image recovery of worn-off hallmarks on silver and gold objects
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IMAGE RECOVERY OF WORN-OFF HALLMARKS ON SILVER AND GOLD OBJECTS

Paul L. Benson and Robert S. Gilmore

1. Introduction

The use of hallmarks on silver has a long history dating back to the fourth century AD and represents the oldest known form of consumer protection. A series or system of five marks has been found on Byzantine silver dating from this period though their interpretation is still not completely resolved (Dodd, 1961).

Hallmarking of European silver probably originated in France in the 13th century and spread from there to other countries. The first hallmarks represented a guarantee of the silver or gold content of the metal alloy or their place of manufacture. For example, the alloy that is today universally recognized as 'sterling silver' (92.5% silver) originated in an English statute of 1300 and was based on the alloy of the English silver coinage in use at that time. The English gold alloy standard was based on an existing alloy standard known as the "touch of Paris" or 19.2 carats/ 80% gold (Hare, 1978). In contrast to these long established standards the American standards were not formalized until 1906.

Over time, additional hallmarks were placed on silver and gold objects to denote various aspects of the manufacturing process such as the maker's name, the location of the assay office where the alloy was tested, the year of manufacture, tax implications, and commemorative events (Fig. 1).

As hallmarks were a form of consumer protection there were strict penalties for their misuse. For example, a metalsmith could have his substandard wares seized, he could be fined, jailed, maimed, banished, or even put to death (Jackson 1921).

The history of European hallmarking of silver and gold is far from complete as some historical records have been lost through time. For example, the London guildhall records prior to 1681 were lost in a fire at the Assay Office and, in Holland, records were destroyed when the guild system was abolished in 1807. As the history and standards of hallmarking silver and gold objects from various countries is complex, it should be consulted on an individual basis (Wyler, 1937; Jackson, 1921).

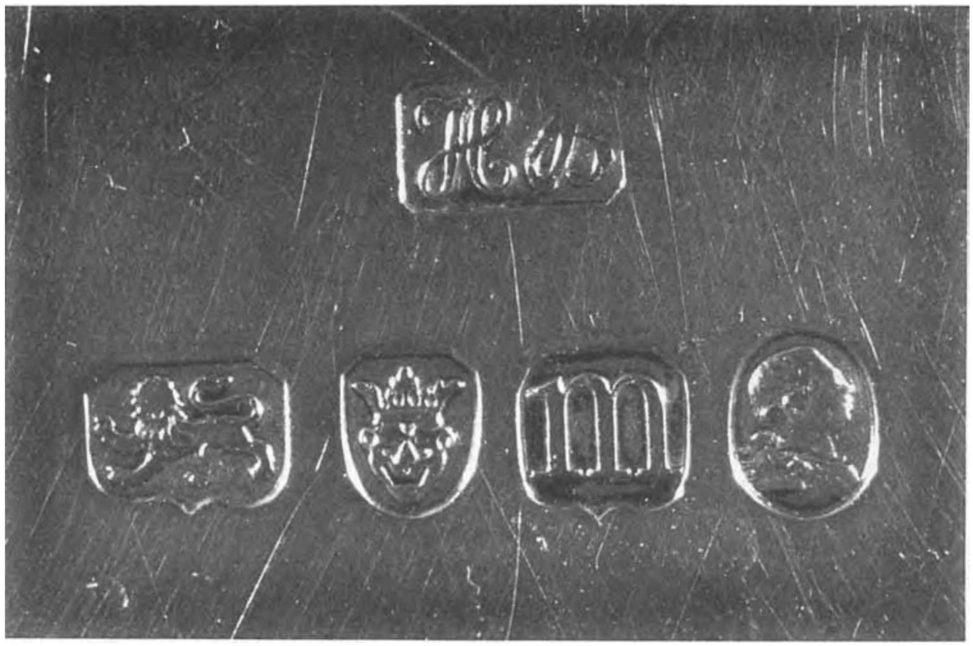


Figure 1. Typical set of English hallmarks indicating that the object is made of sterling quality silver, made by Hester Bateman in London in the year 1787, and that a duty has been paid on the piece.

Hallmarks on silver and gold objects can fix these pieces in history by providing direct evidence of the maker, the place and date of manufacture, and the quality of the metal alloy at a particular time. To some extent then, the historic, monetary, and intrinsic value of the objects are directly linked to the ability to discern the hallmarks. The susceptibility of silver to tarnishing means that it must to be polished regularly to maintain its desired bright metallic surface finish. The polishing process removes a thin layer of silver metal so that over time the hallmarks will be gradually reduced to the point where they are either illegible or completely worn away, resulting in the loss of valuable historic information. The ability to read the original marks would greatly aid in placing these objects back into their rightful place in history.

Even though the hallmark can be completely worn away there may still be remnant plastic deformation within the metal from the act of striking the surface to create the hallmark. This residual deformation can be characterized in the form of an acoustic response when the surface is insonified with a focused acoustic beam; the amplitude of the response is then used to create an image on a computer screen. A highly polished metal surface provides a nearly ideal medium for the utilization of acoustic imaging techniques.

Other methods have been successfully employed to image worn-off information from metal. For example, recovery of filed-off serial numbers from firearms is a well-established procedure in law enforcement forensic laboratories (Fig. 2).

METHODS OF RECOVERING OBLITERATED SERIAL NUMBERS FROM FIREARMS

Chemical and Electrolytic Methods- etching by chemical or electrolytic process
- Acid Etching- Fry's reagent, nitric acid, ferric chloride, Restora-A-Gel
- Electro polishing
- Electro etching with a DC current

Ultrasonic Cavitation- etching by action of water in state of cavitation
- Dental De-Scaler

Magnetic Particle Method- application of magnetic particles to magnetized specimen
- Magnaflux

Heat Treatment Methods- gradual heating of metal surface
- Heat Tinting
- Heat Etching

Cold-Frost Method- application of extreme cold to produce frost on the surface
- Dry Ice

Radiography
- X-rays and Gamma rays

Liquid Penetrant Method- application of a liquid and a fluorescing developer
- Crack Location

Electroplating- application of a metallic coating on the surface
- Copper or nickel plating

Figure 2. Various methods that have been proposed to recover obliterated serial numbers from firearms (after Treptow 1978).

Unfortunately, most of these techniques are destructive to the metal to some extent. The most common technique involves polishing the area to be imaged and then etching the surface with an acid to bring out the latent serial numbers; needless to say, the use of this technique would not be tolerated on works of art. The newly developed acoustic imaging procedure is non-contact and does not harm the metal in any way. It is the only known non-destructive technique that has the potential to recover lost information from silver, gold, and other metallic works of art.

2. Ultrasonic Imaging Systems and Scanning Acoustic Microscopes

2.1 History

The ultrasonic imaging technologies for visualizing the surfaces and interiors of opaque solids are well established (Gilmore, 1999). Between 1929 and 1931, Sokolov and Mulhauser independently proposed the use of ultrasonic waves to form images of the interior of materials for materials characterization and non-destructive evaluation (NDE). During the 1930s efforts to develop ultrasonic images involved the development of acoustic amplitude sensitive screens that displayed visible contrast in proportion to the acoustic amplitude incident on the screen. These image converter screens (such as the Pohlmann Cell and the Sokolov Tube) had such poor sensitivity and resolution that little use was made of them other than as curiosities. Pulse-echo and pulse-transmission C-Scan images, using both focussed and unfocused ultrasonic beams, were introduced in the early 1950s. The primary use was for industrial NDE.

These initial C-Scan images were displayed on photographic or voltage sensitive paper and were acquired by scanning a single transducer back and forth over the subject material. The image was built up line by line. By the early 1970s ultrasonic C-Scan inspections of both the surfaces and interior volumes of industrial materials were in general use and C-Scan images had been produced as high as 50 MHz in frequency. In the early 1970s work at Stanford University under the direction of C. F. Quate (Lemons and Quate, 1979) combined zinc oxide on sapphire transducers, C-Scan data acquisition, and microwave electronics to create very small ultrasonic images at GHz frequencies. These images rivalled optical microscopy in resolution, detail, and field of view; therefore, the devices that made them were called Scanning Acoustic Microscopes. The GHz frequencies, low depths of penetration, and very small fields of view limited the industrial usefulness of scanning acoustic microscopy except for microelectronic assemblies. However, the near optical resolution of the acoustic microscope images provided a new emphasis and enthusiasm for ultrasonic imaging in general. This renewed effort combined with the collateral advances in the computational power, storage, and display capabilities of small computers resulted in three decades of rapid progress in ultrasonic imaging devices, methods and applications.

By the start of the 21st century ultrasonic imaging methods were well established to characterize material microstructures, bonds, defects (flaws, voids, cracking, porosity, layer delaminations), coating delaminations, elastic modulus and density variations, heat-affected zones in welds and other fusion processes, stress distributions in isotropic materials, and in vitro carious lesions.

Materials examined include ceramics, composites, glass, metals and alloys, polymers, plastics, semiconductors, electronic components, geological materials, coffee and soybeans, bone, teeth, soft biological tissue, and organic compounds. However, a literature search has found only three references to acoustic microscopy and metal or ceramic art objects (Stravoudis, 1989; Benson, 1991; Ouahman, 1995).

2.2 Description of the Acoustic Microscope

Several texts are available that clearly describe ultrasonic imaging and acoustic microscopy (Lemons and Quate, 1979; Briggs, 1982; Gilmore, 1999); therefore, the characteristics and operation of the systems will only be summarized here. A typical transducer used for acoustic imaging consists of a piezoelectric layer cut to a specified frequency and bonded to a plano-concave lens to focus the ultrasonic beam. For high frequency operation the lens is usually fabricated from single crystal sapphire or fused quartz. Alternatively, eliminating the lens and spherically curving the piezoelectric layer itself can also focus the ultrasonic beam. In the case of pulse-echo C-Scan data acquisition, the transducer acts as both the transmitter and receiver of the acoustic energy. A short electrical pulse is applied to the piezoelectric layer to create the acoustic pulse and return acoustic echoes interact with the layer to create electrical signals. The object to be scanned is placed at the focal point of the ultrasonic beam. What makes an acoustic microscope unique is the ability to place the focal point of the acoustic energy either on the surface of the object or subsurface in the object's interior. Again, as with all C-Scan type data acquisition, the image is acquired by raster scanning the ultrasonic beam and acquiring echo amplitudes at an increment along the scan lines equal to the line-to-line spacing (Fig. 3).

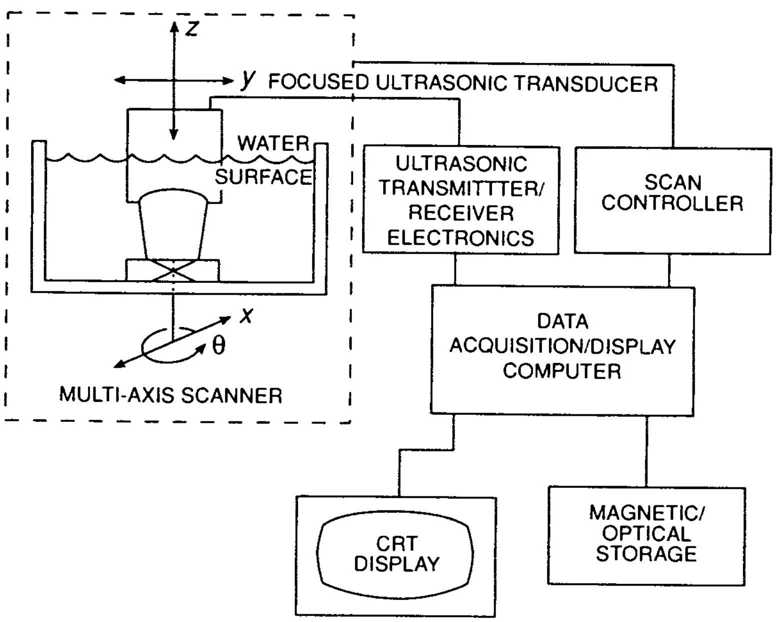


Figure 3. Schematic of an ultrasonic imaging system; higher frequencies and higher image magnification would make the same schematic an acoustic microscope.

2.3 Coupling Fluid

For frequencies much above 1 MHz, acoustic waves are rapidly attenuated in air so it is necessary to utilize a coupling fluid between the transducer and object to be imaged. The acoustic properties of the coupling fluid are a significant factor in determining the resolution that can be achieved by the acoustic imaging system. The most widely used fluid is water but other fluids have acoustic properties (namely a higher or lower velocity) that make them superior to water particularly when surface wave imaging is used (Table 1).

Table 1. Relative Acoustic Velocities of Some Coupling Media

COUPLER	TEMPERATURE	VELOCITY	ABSORPTION	COEFFICIENT
Water	25	1495	22.0	1.0
Water	60	1550	10.2	1.4
Acetone	30	1158	54.0	0.8
Ethanol	30	1127	48.5	0.8
Methanol	30	1088	30.2	1.1
FC-40	25	656	Not available	Not available

(table is modified after Lemons and Quate, 1979)

For this work Fluorinert FC-40 (an inert and environmentally friendly fluorocarbon fluid with a velocity less than half that of water) was used to make surface wave images in the sterling silver and gold objects discussed here. Usually, the object is submerged in the fluid while being scanned but some systems use pumped fluid columns essentially squirted at the surface being scanned. The images acquired in this work were all made by immersing the objects in FC-40 or water.

2.4 Acoustic Transducer

The choice of the coupling fluid was also based on how surface waves are produced in water versus FC-40 and the availability of existing acoustic transducers. When using water as a coupling fluid the angle of incidence needed to generate surface waves in silver is greater than 65° and transducers with this geometry would have to be custom-made. By using the FC-40 with its slower acoustic properties the angle of incidence needed to generate surface waves in silver is approximately 24° and 29°-35° in gold. Transducers with these geometries are readily available (Table 2). Note that it is not possible to generate surface waves in gold using water as the coupling fluid as the angle of incidence is greater than 90°.

Table 2. Acoustic Velocities and Angle of Incidence to Generate Surface Waves in Sterling Silver and Gold

	Sterling Silver	18K Gold	22K	Water	FC-40
Longitudinal velocity	3.89 mm/sec	3.55 mm/sec	3.39 mm/sec	1.48	0.656
Shear velocity	1.73	1.46	1.31	0	0
Rayleigh velocity	1.63	1.33	1.15	Frequency dependent	Frequency dependent
Angle of incidence to generate surface waves	FC-40 = 23.7° Water = 65.3°	FC-40 = 29° Water = >90°	FC-40 = 35° Water = >90°		

Back-surface imaging was done at 50 MHz using a Panametrics type V390 F/2 transducer with a 1.5" diameter quartz buffer-rod and a 0.25" diameter beam focussed at 0.5" in water. Surface wave imaging was done at 20 MHz using a Panametrics F/1 polymer film transducer with a 0.4" diameter beam focussed at 0.4" in the FC-40.

3. Methods of Creating an Acoustic Image

The contrast changes in acoustic images are produced by variations of elasticity, density, and acoustic attenuation within the material to be imaged. In the specific case of imaging worn hallmarks, this paper will demonstrate that images of the residual deformation in the metal from the stamping process can be obtained by two methods: (1) Surface wave imaging of the surface containing the hallmark deformation (Fig. 4a), (2) Back-wall or back surface imaging where an acoustic beam is focussed through the full thickness of the metal and on the back surface containing the hallmark deformation (Fig. 4b). In other words, surface waves are used to produce images of the entry surface, i.e., the struck surface, where back-wall images are obtained from the surface opposite to the struck surface.

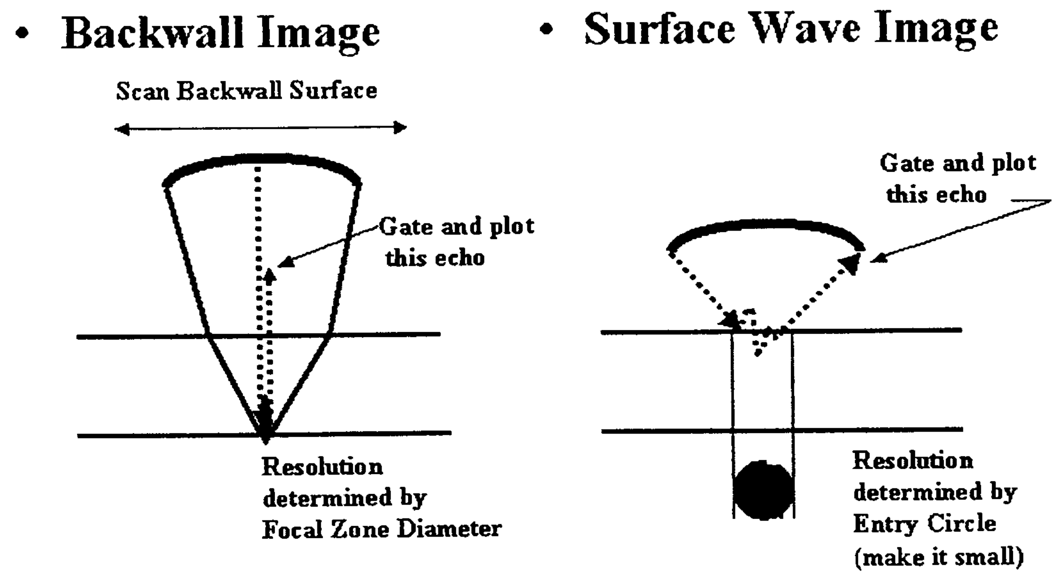


Figure 4. Schematic showing (a) back surface reflection imaging (or back-wall imaging) and (b) mode converted surface wave imaging.

4. Factors in Determining Suitability for Acoustic Imaging

4.1 Stress Annealing Temperatures

A first step in determining if residual deformation in silver or any other material is a candidate for acoustic imaging is to determine the stability of this deformation over time. The lowest temperature that might affect this stability is the residual stress annealing temperature. This is generally considered to be approximately 4/10ths (0.4) of the absolute melting temperature as expressed in degrees Kelvin (K) (Callister 2003). The highest temperature below the melting point affecting the retention of the deformation is less exact, but is the range in temperature at which recrystallization occurs. Here the grain boundaries in the silver migrate and the microstructure entirely recrystallizes. Any residual plastic flow remaining from a hallmark would begin to relax at the stress anneal temperature and could totally disappear during recrystallization. Since the melting point (Mp) of sterling silver is 893°C = 1166 K the stress anneal temperature would fall at approximately 0.4 x 1166 K = 466 K or approximately 93° C above the boiling point of water (100° C or 373 K). Room temperature is typically approximated at 300 K and since the lowest critical temperature for sterling silver (466 K) is well above this temperature, it seems reasonable to expect the residual deformation produced by a hallmark stamp to be relatively stable over a few hundred years of time, even if repeatedly washed in hot water. Stress annealing temperatures for other metals are shown in Table 3.

Table 3. Stress Annealing Temperatures for Various Metals

METAL		MELTING POINT (MP) IN DEG. CELSIUS	STRESS ANNEALING TEMPERATURE IN DEG. CELSIUS	RATIO OF MAX. AMBIENT TEMPERATURE TO MP IN DEG. KELVIN*
Gold	24K	1063	261	0.24
	22K	1003	237	0.25
	18K	905	198	0.27
	14K	845	173	0.28
Silver	pure	962	221	0.25
	sterling	863	193	0.27
Copper		1082	269	0.23
Lead		327	-33	0.50
Bronze	10% tin	1005	238	0.25
	20% tin	890	192	0.27
Brass	10% zinc	1040	252	0.24
	20% zinc	995	234	0.25
Iron		1538	451	0.18
Steel		1515	442	0.18

*At ratios less than 0.40 the plastic flow surrounding the hallmarks should be stable at temperatures up to the stress annealing temperature

** Gold alloy melting point data from Smith 1978; remaining melting point data from Lide 2002; all other figures have been calculated.

4.2 Anisotrophy

A second consideration in imaging residual deformation is to determine the acoustic properties of the subject material and any possible anisotrophy of the material. Unless the deformation process produces micro-fractures there is no reason to anticipate that a truly isotropic material would be rendered anisotropic by plastic deformation. Anisotropic materials, however, should undergo considerable change during deformation, since a local deformation would significantly rearrange that microstructure. It seemed appropriate to estimate the anisotrophy in silver to determine if ultrasonic backscatter from the silver microstructure itself might be used to track the deformation underlying hallmarks. The three elastic constants for single crystal silver (cubic system) are C11 = 1.239 Mbar, C12 = 0.939 Mbar, and C44 = 0.461 Mbar (Simmons and Wang, 1971). Isotropic materials have only two independent elastic constants instead of the three required to describe the cubic system. A typical test for isotropy (again within the cubic system) is given by the Zener anisotrophy ratio of [C11 – C12] / 2.0 to C44 (Chung and Buessem 1968). Clearly 1.239 – 0.939 / 2.0 = 0.150 and is not equal to 0.461 so silver possesses considerable anisotrophy. Therefore, ultrasonic backscatter from the silver grains should be able to track the modifications in the microstructure caused by the plastic flow in the silver around the hallmarks. Anisotrophy for other metals are shown in Table 4.

Table 4. Estimation of Degree of Anisotrophy of Various Metals

METAL	C11	C12	C44	RATIO OF C11-C12/2.0 TO C44*
Gold	1.923	1.631	0.420	0.15
Silver	1.240	0.937	0.461	0.15
Copper	1.684	1.214	0.755	0.24
Lead	0.495	0.423	0.149	0.05
Brass-4% zinc	1.633	1.177	0.744	0.23
9% zinc	1.571	1.137	0.723	0.22
17% zinc	1.499	1.098	0.715	0.20
Iron	2.314	1.346	1.164	0.49

*If this ratio is less than C44 then the metal exhibits anisotropy (from Chung and Buessem, 1968)

Having established this possibility one should immediately state that backscatter imaging of the silver microstructure has not proven effective to date for displaying residual deformation in the silver. The probable explanation for this has to due with the small size of the silver grains so that even at 50 MHz the grains are too small to provide any backscatter amplitude.

5. Experimentation

5.1 Sterling Silver Coupon

Initial experimentation was conducted on a blank sterling silver (92.5% silver) coupon measuring approximately 25 mm x 25 mm x 3 mm. An experienced silversmith then placed three different hallmarks on one surface. A silversmith was employed to produce the hallmarks thinking that he would strike the silver with approximately the same force used by silversmiths for the past several hundred years so that the marks would be neither too deep nor too shallow. The struck surface of the coupon was polished with a Struers Prepamatic rotary lapping machine operating at thirty Newtons force at 150 RPMs counter-revolution. The lapping machine used a nine-micron diamond polishing abrasive compound to polish away the surface until the hallmark was no longer visible; approximately 0.3 mm of silver was removed. This was done to approximate the slow removal of the silver surface in much the same manner as years of polishing. Once the marks were completely removed from the surface the coupon was placed in a container with some keys and the container vibrated to produce scratches on the silver to simulate the surface on a genuine aged silver object. The three ultrasonic images shown in Fig. 5 illustrate the detail ultrasonic imaging can produce on both intact hallmarks and the deformation remaining after removal by polishing. Fig. 5a shows a 50 MHz F/2 back wall image of a coupon that still retains almost all of the hallmarks placed on it. Fig. 5b shows a 50 MHz F/2 back-wall image of the residual deformation in a similar coupon where almost all of the original hallmarks have been polished away. Fig. 5c shows a 20 MHz F/1 surface wave image of the same deformation in Fig. 5b except viewed from the surface containing the residual deformation. Both back-wall images were acquired using water to couple the ultrasonic beam into the part. The surface wave image used FC-40 in order to mode convert a longitudinal wave in the fluid into a surface wave on the silver coupon's surface.

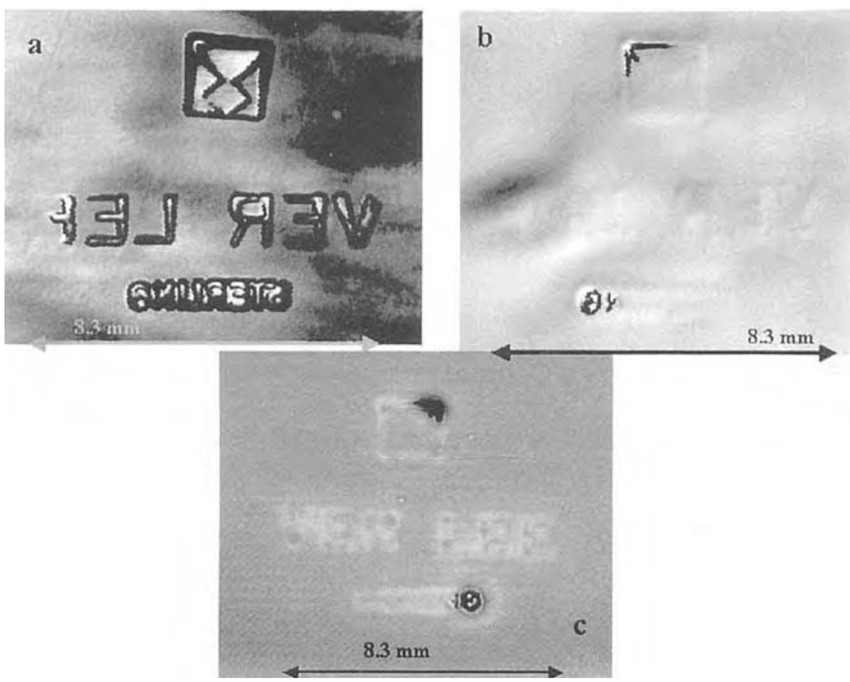


Figure 5. Three ultrasonic images of the sterling silver coupons. (a) A 50 MHz F/2 back-wall image of the original hallmark. (b) A 50 MHz F/2 back-wall image of the residual deformation remaining in a similar coupon where the hallmark has been polished away. (c) A 20 MHz F/1 surface wave image of the same deformation in 4b except imaged from the surface containing the deformation.

5.2 Sterling Silver Spoon Handle

Fig. 6 shows a set of surface wave images of a sterling silver spoon wrought by Peter and Ann Bateman dating from 1792. This teaspoon, one from a set of eight, was chosen because its four hallmarks varied from perfectly readable to completely polished away. Also, the four hallmarks are legible on the other spoons from this set, making it easier to target the desired image quality. In Fig. 6a the makers' initials are clear but much of the remaining hallmarks have been removed. Fig. 6b shows the isolation, magnification, and partial recovery of one of the hallmarks believed to be that of a lion. The image of the "lion" shown in Fig. 6c is the best result of a series of trials where the focus of the transducer was changed slightly for each trial. The importance of even very small changes in the system focus has been repeatedly demonstrated in the course of this work. To the untrained eye the figure of the lion is not clear in the acoustic image but to an expert it is readily discernable (Wilkes, 2001).

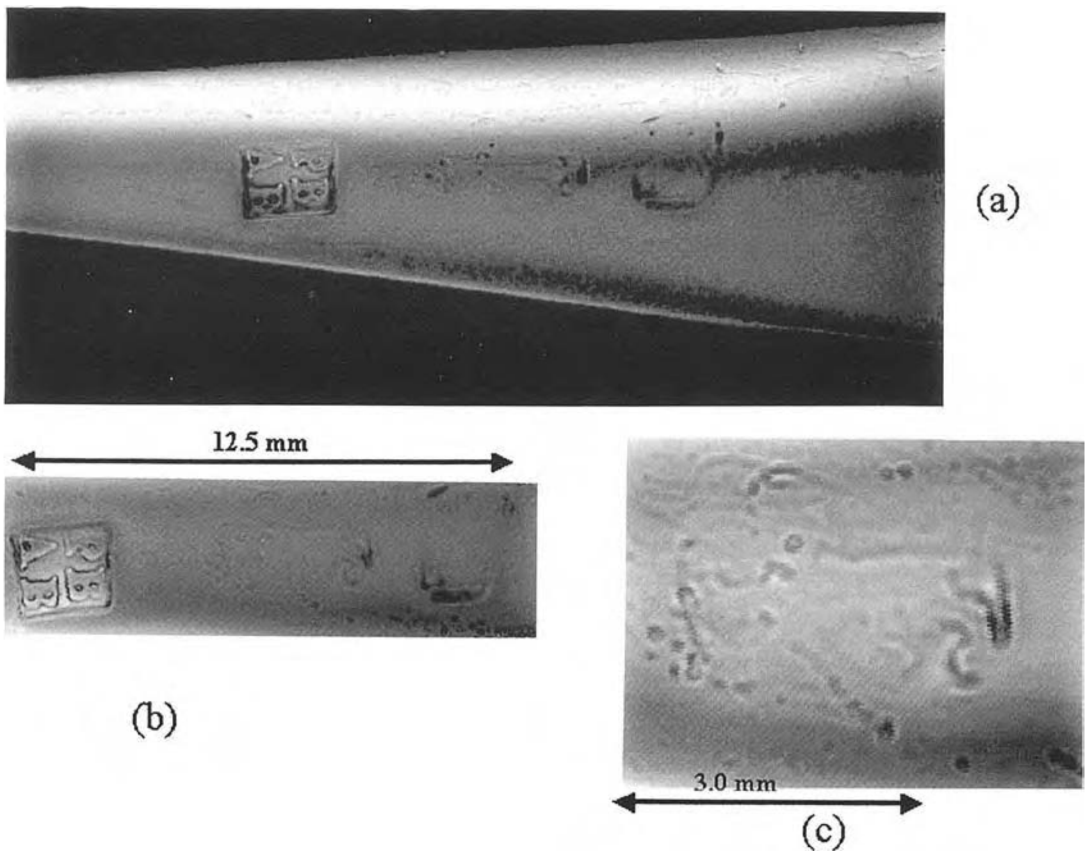


Figure 6. (a) Ultrasonic images of the handle of a sterling silver teaspoon wrought by Peter and Ann Bateman dating from 1792. (b) The initials of the makers are clear but much of the remaining hallmarks have been removed. (c) Shows the isolation, magnification and partial recovery of a figure thought to be a lion. (Nelson-Atkins Museum of Art, No. 72-45/4B)

Subsequent image processing comparisons with a visible hallmark from a teaspoon from this same set of spoons has confirmed that the recovered image of the lion mark is identical to the visible hallmark. A series of six acoustic images of the worn-off lion hallmark were adjusted for size and overlaid on a digital image of the visible lion hallmark. The acoustic images were made by adjusting the focal spot of the sound waves either a little higher or a little lower in the metal. With only a two hundred nanosecond difference in the travel time of the sound waves from the first acoustic image to the sixth one there was a surprising difference in the quality of the images (200-nanosecond travel time converts to an actual distance difference of 0.0026 inch). The composite acoustic images had near perfect registration on the visible hallmark which demonstrates that the illegible hallmark was struck with the same die as the visible hallmark on the teaspoon from this set of teaspoons (Fig. 7).

Figure 7. A recovered acoustic image of a worn-off lion hallmark overlaying a digital image of an identical hallmark from the same set of teaspoons.

Fig. 8 shows the best results of a series of trials on recovering the date letter 'r'. Here, a series of three acoustic images of the letter 'r' were adjusted for size and orientation then overlain on top of a digital image of the corresponding hallmark from another teaspoon from the same set. Again, there is near perfect registration of the recovered acoustic image on the visible hallmark. This demonstrates that the recovered hallmark image is actually the letter 'r' and that it was struck with the same die as the visible hallmark on the other teaspoon.

Figure 8. Recovered acoustic images of the date letter 'r' overlaying a digital image of a visible 'r' hallmark from the same set of teaspoons.

5.3 Sterling Silver Fish Knife Blade

Fig. 9 is intended to show the lack of subsurface deformation where one would naturally assume that it should be present. Shown is a set of ultrasonic back-wall images of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark has been isolated and magnified (b) for comparison to the back-wall image of the deformation in the test coupon (c). Clearly no deformation appears to extend from the fish knife hallmark, suggesting that it has either been improperly struck by the silversmith, it has been worn away through the subsurface deformation zone, or the residual deformation has been 'relieved' during an annealing process. The annealing process could have occurred during manufacture, or the heat from the process of soldering the handle to the blade may have been sufficient to cause a localized annealing of the hallmarks since they are placed quite close to the attached handle.

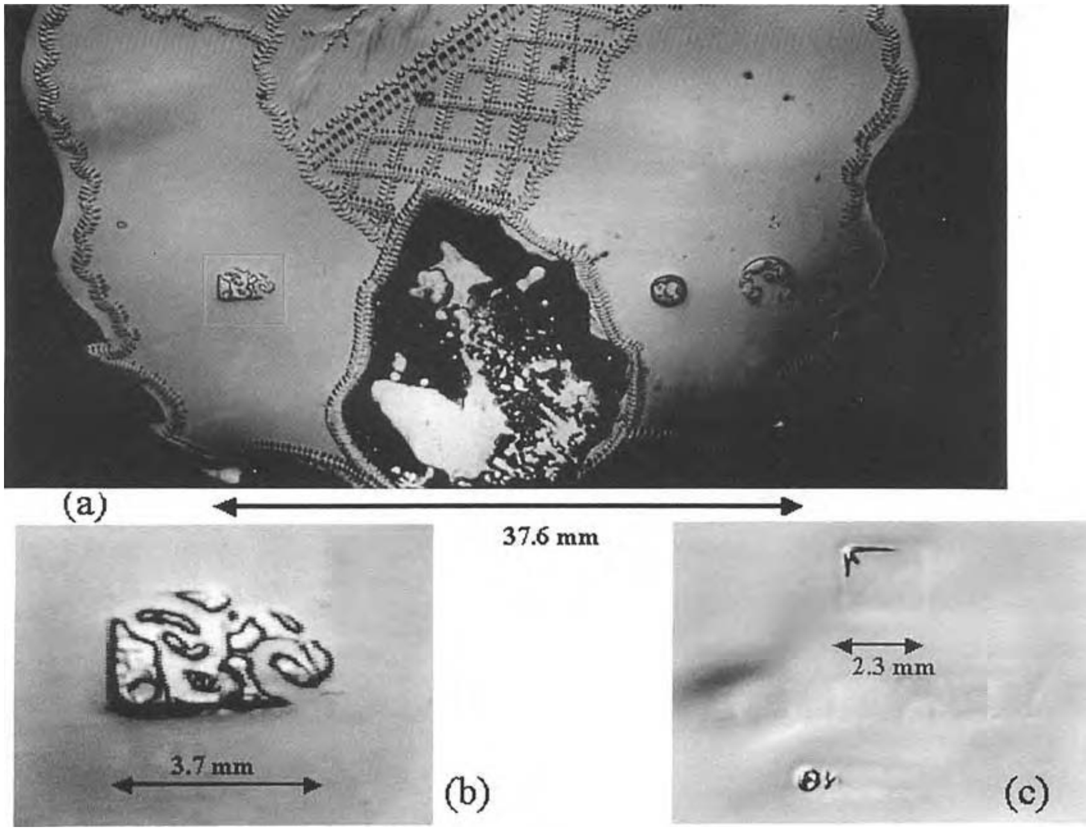


Figure 9. Ultrasonic back-wall image of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark is isolated (b) and magnified for comparison to the back-wall image of the coupon (c). No deformation appears to extend from the fish knife hallmark.(Nelson-Atkins Museum of Art, no. F83-76/10)

A literature search found that three of the four hallmarks applied on French silver manufactured prior to 1789 were actually applied to the roughed–out silver sheet before the object was completed. The finished object would therefore have been subjected to multiple annealing steps during its manufacture thereby relieving the metal of any remnant deformation from the hallmarking procedure (Bimbenet-Privat and de Fontaines, 1995). This is in comparison to the English system of applying the hallmarks only after the object had been completed or nearly completed, thus the residual plastic deformation in the metal would be expected to be retained. An exception to this procedure will be discussed later.

To confirm the historical accounts of the French hallmarking procedures a sterling silver coupon was stamped with several hallmarks as described earlier. Again, the marks were polished off and images of these hallmarks were produced with the acoustic imaging technique.

The coupon was then annealed in an oven at 700° C for twelve minutes and then subjected to the imaging procedure. After only one annealing the remnant deformation has been 'relaxed' and the hallmarks can no longer be imaged (Fig. 10). Regrettably, this means that the acoustic imaging technique will not work on pre-1789 French silver objects (after this date the French hallmarking procedures were changed).

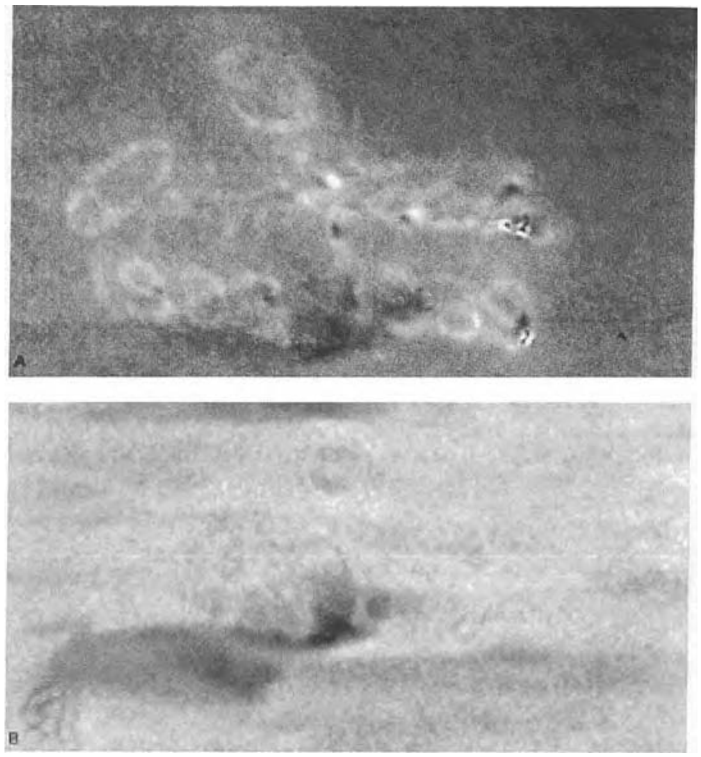


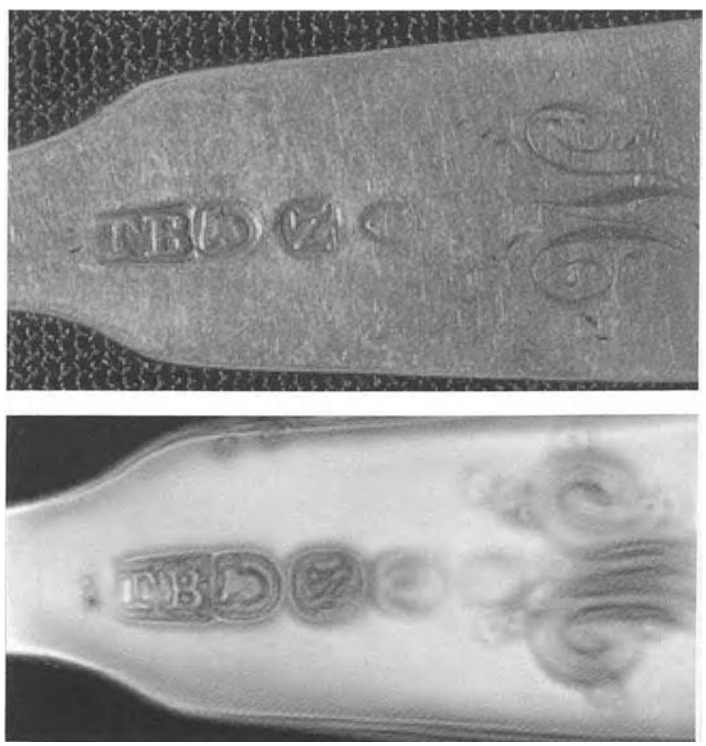
Figure 10. Effects of annealing on sterling silver. (a) A recovered acoustic image of polished-off hallmarks on a sterling silver coupon before annealing. (b) The same area after annealing the coupon.

By chance, Fig. 9 also shows additional information recovered by acoustic imaging concerning the quality of the solder join of the handle to the blade. The light colored spots inside the attachment area represent gaps/flaws in the solder join. These areas have a different acoustic response than the surrounding well-soldered metal so they are readily visible.

Another interesting chance image was obtained from a 16th century paten cover (not illustrated) during the course of imaging the hallmarks. In this case, flaws or bubbles in the cellulose nitrate coating that were not visually apparent but were quite obvious in the acoustic image.

5.4 Sterling Silver Desert Fork

Fig. 11(b) is an acoustic image of a purposely-removed hallmark from an English desert fork by Thomas Barker dating from 1808. At some period during the spoon's lifetime an owner decided to add the monogram "M" to the back of the handle. In order to accommodate this addition the lion hallmark was removed. Traditionally, there have been four ways of removing hallmarks and engravings. If the marks were shallow they could simply be polished away. Deeper marks could be hammered out with a subsequent thinning of the metal. They could also be filled with silver solder and finished to seamlessly blend with the surrounding metal. Finally, they could be filled by a process know as 'stoning'. In this case the surface of the silver is literally rubbed with a stone, pushing the surrounding metal into the indentations of the hallmarks or engravings. Marks removed by hammering and stoning cannot be recovered by acoustic methods but marks erased by polishing and filling should be recoverable. In the case of the lion hallmark, its recovery probably meant that the hallmark was simply polished away. Note that in Fig. 11(a) the hallmark is very difficult to decipher; at best it can only be recognized that it is present where none was visible on the fork. The interpretation of the mark representing a lion was based on a much clearer computer image at the time the work was done.



A

B

Figure 11. Silver fork with a hallmark deliberately removed. (a) Photograph of the visible hallmarks on the fork. (b) An acoustic image of the hallmarks showing that a fifth mark was present at one time. The now missing hallmark has been interpreted as a lion.(Private collection)

5.5 Gold Coupons

The physical properties of gold suggest that it should also be a good candidate for acoustic imaging techniques. The residual stress annealing temperature for various alloys of gold varies from 173° C for 14K to 261° C for 24K and its degree of anisotrophy is nearly identical to silver. Together, these characteristics indicate that gold should behave in a similar manner as silver during acoustic imaging. To test this theory two gold coupons, one 22K and the other 18K, of the same dimensions as the silver coupons, were hallmarked and the marks polished off as described earlier.

The 22K coupon (91.66% gold) was placed in the FC-40 coupling fluid and insonified with the 20 MHz pulsed signal through an F/1 lens. A converted surface wave was captured but surprisingly, no images of the polished-off hallmarks were recovered. The experiment was repeated with the 18K coupon (75.0% gold) with only a barely perceptible image of the hallmarks recovered (Fig. 12).

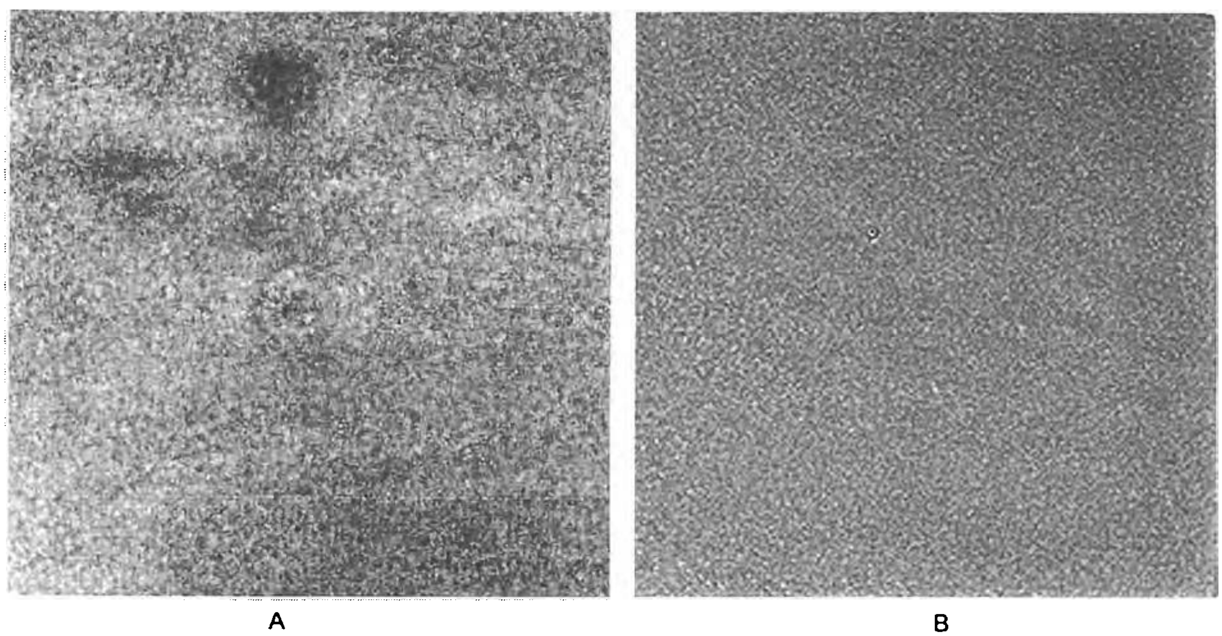


Figure 12. Surface wave acoustic images of gold coupons. (a) 18K gold coupon shows just a hint of residual deformation; (b) 22K gold coupon shows no residual deformation from the hallmarks.

The explanation for these results can be found in one of the physical properties of gold, its malleability. High purity gold is extremely malleable and does not produce plastic flow when struck during the hallmarking process. Instead, the metal simply pushes aside and wells-up around the hallmark leaving no subsurface deformation to image. It is proposed that a lower purity of gold, such as 14K (58.3% gold) will exhibit some plastic deformation due to the copper content, making it possible to recover the hallmarks using the acoustic imaging technique.

6. Discussion

A total of twenty-nine silver and gold objects from widely varying time periods have been subjected to the acoustic imaging techniques. Objects imaged included spoons, forks, knives, coins, a paten cover, a trivet, and coupon blanks. Results from the modern sterling silver blanks have been very encouraging. The hallmarks were placed on the blanks in the early summer of 1997 by an experienced silversmith. These hallmarks were well and truly struck, i.e. their original existence is well documented. After the hallmarks were removed by polishing, ultrasonic imaging produced clearly decipherable images of the remnant deformation on the surface of the silver. Both surface wave imaging and back-wall imaging were clearly effective at displaying residual deformation in the silver. Where only part of the hallmark was removed, the imaging methods are able to show remnant deformation extending out from the remnant surface dents in the surface. The blanks are now approaching five years in age. Repeat images show results in 2002 that reproduce the results shown in the initial 1997 images. However, despite the clear anisotropy in silver, backscatter imaging of the silver microstructure has not yet proven effective. Neither the silver microstructure itself nor deformation of that microstructure has been shown by backscatter imaging at the 20 MHz or 50 MHz frequencies used to date. The failure of the backscatter imaging is confusing since both the back-surface reflection images and the surface wave images clearly indicate that the acoustic properties of the silver showed significant changes at the hallmark locations. The small size of the silver grains may be one factor in the inability to produce backscatter images. More work clearly needs to be done to fully understand this.

Work to recover partially obliterated hallmarks on antique silver objects has been less encouraging than the work on the coupons. But in these cases one cannot be certain that the hallmarks were properly struck in their original condition. The silver blade of the French fish knife (Fig. 9) demonstrates this case in point. The fish knife is ideally configured for back-wall imaging and yet no remnant deformation could be shown to extend from the dented marks remaining on the blade. Several different scenarios could account for this. First of all, the hallmark could have been improperly struck so that the entire mark was never there in the first place. It is also possible that the heat from the soldering attachment of the handle annealed the silver thus removing the residual deformation of the hallmark. Use and/or polishing may have partially removed the residual subsurface deformation or repeated washing in boiling water over an extended period of years partially annealed the silver. This last possibility is most unlikely as the theoretical stress annealing temperature of sterling silver is well above the boiling point of water.

One other scenario based on the hallmarking procedure itself may also be possible. When a hallmark is applied to a thin piece of silver a 'witness mark' may appear on the reverse side of the silver from where the mark was struck. This witness mark is a raised area with the same shape as the hallmark. If this mark is visible the silversmith may wish to remove it; this procedure is called 'setting back the hallmark'. The silversmith may simply hammer the witness marks flat or can apply localized heat to that area first to make the hammering process easier and less likely to cause any damage to the surrounding metal. In the case of flatware, the hallmarks were frequently applied to the back of the handles before they had been wrought to their final shape. This allowed the assay office to place their marks completely on the silver and still allow the metalsmith the freedom to produce a slender handle that in the final shape would not provide sufficient space for the hallmarks; the final shaping would have certainly involved heating the metal. This local annealing effect would then diminish the ability to produce an image of the hallmark using acoustic methods.

Surface wave images of two antique coins (not illustrated) suggest that downward or compressive deformation (i.e., a dent) is more readily defined than the upwelling of material. Efforts to image the originally upraised patterns of the years in which coins were struck have not yet been successful. This suggests that the deformation under dents is more readily detected than bulges. Also, since both sides of a coin are struck at the same time there will be some mixing of subsurface deformations making it more difficult to separate individual elements of the design (e.g., the date).

7. Conclusion

The success rate for acoustic imaging of worn-off hallmarks on the twenty-nine objects in this project has been approximately ten per cent. While this initially appears to be fairly unsuccessful, the project has succeeded in producing images one hundred per cent of the time where remnant plastic deformation exists. When the deformation no longer exists either through being poorly struck, being annealed out, or completely worn/polished through the zone of deformation, acoustic methods cannot produce an image. Unfortunately, there are no visual clues on the surface of the metal that will permit speculation on the success or failure of the acoustic imaging technique. Each object will have to be imaged individually to determine if there is any residual deformation to be found.

Worn hallmarks on objects manufactured from high purity gold cannot be imaged with the acoustic methods as described here. The historical standards for objects made of gold have been 18K or greater. It is suggested that at this purity gold is too malleable to produce plastic flow when struck in the hallmarking process. As the quantity of alloying metal in gold increases (corresponding to a decrease in the purity of the gold) the chances for the acoustic recovery of worn hallmarks and inscriptions should increase but this has not yet been proven experimentally.

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Materials

FC-40 Fluorinert Brand Electronic Liquid: a perfluoro liquid containing no hydrogen or chloride: 3M Specialty Materials, 3M Center, St. Paul, Minnesota 55144-1000 USA. (651-737-6501).

Acoustic Transducers: Panametrics, 221 Crescent St., Waltham, MA 02453 USA. (781-899-2719)

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