

# Image Recovery of Worn-Off Hallmarks on Silver and Gold Objects

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## **Abstract**

Hallmarks on silver objects can reveal much about the history of the piece. The name of the silversmith, the date of manufacture, the quality of the metal alloy, as well as other information can be determined from the study of the hallmarks. Because silver requires polishing to maintain its lustrous metallic surface, hallmarks tend to be worn away over time resulting in the loss of important historical information. Utilizing Scanning Acoustic Microscopy, an image of these vanished or illegible marks can be recovered. Two imaging modes are presented: time resolved surface wave imaging of the near surface deformation in the silver and direct reflection from the silver back surface through the remnant deformed silver. The contrast in these images is caused by variations in the ultrasonic velocities in the silver, density changes, and acoustic attenuation due to the deformed silver microstructure. This technique is non-destructive and non-contact.

**Keywords:** hallmarks, silver, scanning acoustic microscopy, ultrasonic imaging, acoustic imaging

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## **Introduction**

The use of hallmarks on silver has a long history dating back to the 4th century AD. They represent 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 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.

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

The complete 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 the Netherlands, 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 (See Figure 1).

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 the historic, monetary, and intrinsic value of the objects are directly linked to the ability to discern the hallmarks. Silver's susceptibility to tarnishing means that it must 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 sufficient residual 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. The highly polished silver surface provides a nearly ideal medium for the utilization of acoustic imaging techniques.

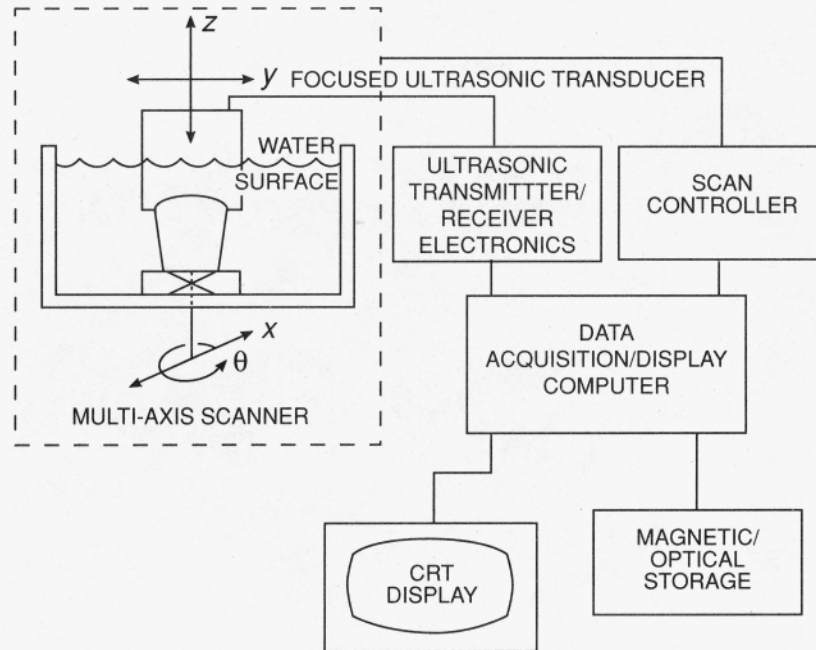


*Figure 1: Typical set of English hallmarks indicating that the object is made of sterling quality silver, made by Hester Bateman in London in the year 1787, and that a duty has been paid on the piece.*

Other methods have been successfully employed to images worn-off information from metal. Recovery of filed-off serial numbers from firearms is a well-established procedure in law enforcement forensic laboratories. Unfortunately, all of these techniques are destructive to the metal to some extent. The most common technique involves polishing the area to be imaged 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 and gold works of art.

## **Ultrasonic Imaging Systems and Scanning Acoustic Microscopes**

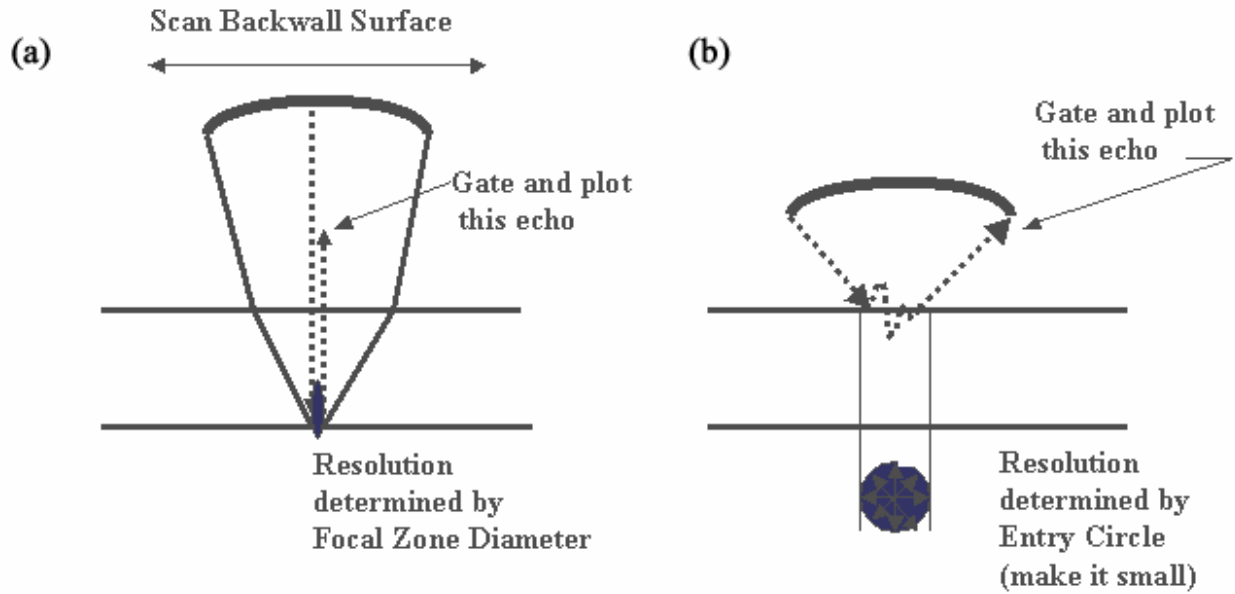
The ultrasonic imaging technologies for visualizing the surfaces and interiors of opaque solids are well established (Gilmore, 1999). Between 1929 and 1931, Sokolov and Mulhauser independently proposed the use of ultrasonic waves to form images of the interior of materials for materials characterization and nondestructive evaluation (NDE). During the 1930s all 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 focused 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



**Figure 2:** Schematic of an ultrasonic imaging system, higher frequencies and higher image magnification would make the same schematic an acoustic microscope.

oxide on sapphire transducers, C-Scan data acquisition, and microwave electronics to create very small ultrasonic images at GHz frequencies. These images rivaled 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 21<sup>st</sup> 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).

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 (See Figure 2).



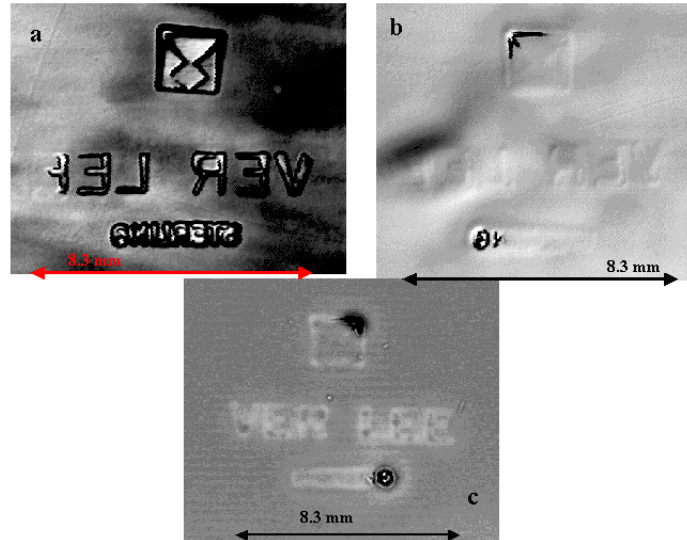
**Figure 3:** Schematic showing (a) Back surface reflection imaging (or back-wall imaging) and (b) mode converted surface wave imaging.

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

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 (See Figure 3a), (2) Back-wall or back surface imaging where an acoustic beam is focused through the full thickness of the silver and on the back surface containing the hallmark deformation (See Figure 3b). 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.

## Experimental Results

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 kelvins (K). 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  $893\text{ }^{\circ}\text{C} = 1166\text{ K}$  the stress anneal temperature would fall at approximately  $0.4 \times 1166 = 466\text{ K}$  or approximately  $93\text{ }^{\circ}\text{C}$  above the boiling point of water ( $100\text{ }^{\circ}\text{C}$  or  $373\text{ K}$ ). Room temperature is typically approximated at  $300\text{ K}$  and ambient temperature in the middle latitudes is



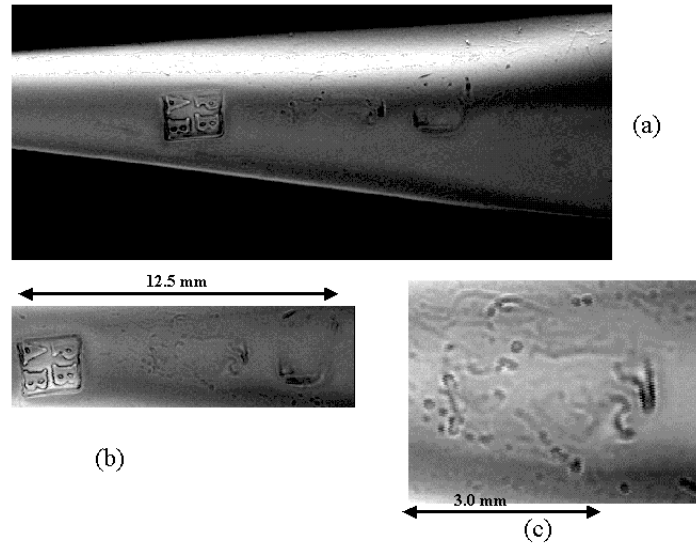
**Figure 4:** Three ultrasonic images of the sterling silver coupons. (a) A 50 MHz F/2 back-wall image of the original hallmark. (b) A 50 MHz F/2 back-wall image of the residual deformation remaining in a similar coupon where the hallmark has been polished away. (c) A 20 MHz F/1 surface wave image of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

between  $-40\text{ }^{\circ}\text{C}$  and  $54\text{ Deg }^{\circ}\text{C}$  (233 K and 327 K). Since the lowest critical temperature for sterling silver (466 K) is well above these temperatures, 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.

A second consideration in imaging residual deformation is to determine the acoustic properties of the subject material and any possible anisotropy 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 anisotropy 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  $C_{11} = 1.239\text{ Mbar}$ ,  $C_{12} = 0.939\text{ Mbar}$ , and  $C_{44} = 0.461\text{ Mbar}$  (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 the equality of  $[C_{11} - C_{12}] / 2.0$  to  $C_{44}$ . Clearly  $1.239 - 0.939 / 2.0 = 0.150$  and is not equal to  $0.461$  so silver possesses considerable anisotropy. 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. 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. Sterling silver proved to have a longitudinal velocity of  $3.89\text{ mm/microsecond}$ , a transverse velocity of  $1.73\text{ mm/microsecond}$ , and a surface wave velocity of  $1.63\text{ mm/microsecond}$ .

### *Sterling Silver Coupons*

Initial experimentation was conducted on two blank sterling silver (92.5% silver) coupons measuring approximately  $25\text{ mm} \times 25\text{ mm} \times 3\text{ mm}$ . 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. Approximately  $0.075\text{ mm}$  was removed from the struck surface of one of the coupons with a Struers Prepamatic rotary lapping machine. This was done to approximate the slow removal of the silver surface in much the same manner as years of polishing. The struck surface of the second coupon was polished in the same manner until essentially all of the hallmarks were removed. Once the marks were completely removed from surface the



**Figure 5:** Ultrasonic images of the handle of a sterling silver spoon wrought by Peter and Ann Bateman dating from 1792. The initials of the makers are clear but much of the remaining hallmarks have been removed or were improperly struck; (c) shows the isolation, magnification and partial recovery of a figure thought to be a lion.

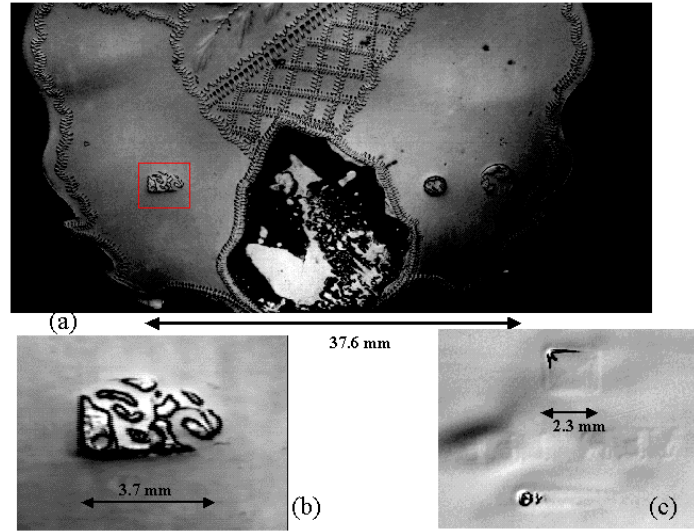
coupon was placed in a container with some keys and the container vibrated to produce scratches on the silver to simulate the surface on a genuine aged art object. The three ultrasonic images shown in Figure 4 illustrate the detail ultrasonic imaging can produce on both intact hallmarks and the deformation remaining after removal by polishing. Figure 4a shows a 50 MHz F/2 back wall image of a coupon that still retains almost all of the hallmarks placed on it. Figure 4b 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. Figure 4c shows a 20 MHz F/1 surface wave image of the same deformation in 4b 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.

### *Sterling Silver Spoon Handle*

Figure 5 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 Figure 5a the makers' initials are clear but much of the remaining hallmarks have been removed or were improperly struck. Figure 5b 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 Figure 5c 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.

### *Sterling Silver Fish Knife Blade*

Figure 6 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



**Figure 6:** Ultrasonic back-wall image of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark is isolated and magnified for comparison to the back-wall image of the coupon. No deformation appears to extend from the fish knife hallmark, suggesting that it is (1) incomplete, (2) improperly struck, (3) unstable over 100 years of the temperature environment it encountered, or (4) an annealing process has removed the residual deformation.

hallmark, suggesting that it has either been improperly struck by the silversmith or the residual deformation has been ‘relieved’ during an annealing process. The annealing process could have occurred during the manufacture or that the heat from the process of soldering the handle to the blade was sufficient to cause a localized annealing of the hallmarks since they are placed quite close to the attached handle.

A literature search has 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 residual 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 retained. An exception to this procedure will be discussed later on.

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 retrieved with the acoustic imaging technique. The coupon was then annealed in an oven at 700 degrees centigrade for twelve minutes and subjected to the imaging procedure. After only one annealing, the residual deformation has been ‘relaxed’ and the hallmarks can no longer be imaged. Regrettably, this means that the acoustic imaging technique will not work on pre-1789 French silver objects.

## Gold

Gold exhibits similar physical properties to silver such 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 degrees Celsius for 14 karat to 261 degrees Celsius for 24 karat and its degree of anisotropy is identical to silver. Together, these characteristics indicate that gold would behave in a similar manner as silver during acoustic imaging. To test this theory two gold coupons (22 and 18 karat), with the same dimensions as the silver coupons, were hallmarked and the marks polished off as described earlier.

The 22 karat 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 18 karat coupon (75.0% gold) with only a barely perceptible image of the hallmarks recovered.

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 14 karat (58.3% gold), that has been alloyed with an increasing quantity of copper will exhibit some plastic deformation making it possible to recover the hallmarks using the acoustic imaging technique.

## Discussion

A total of twenty-six 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, ie 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 5 years in age. Repeat images show results in 2002 that reproduce the results shown in the initial 1998 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.

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 (See Figure 6) 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 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 witness mark is visible the silversmith may wish to remove it; this procedure is called 'setting back the hallmark'. The silversmith can 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. This local annealing effect could 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.



## Conclusion

The success rate for acoustic imaging of worn-off hallmarks on the twenty-six objects in this project has been approximately ten percent. While this initially appears to be fairly unsuccessful, the project has succeeded in producing images one hundred percent of the time where residual 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 then 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 18 karat or higher. 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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## Disclaimer

The contents of this paper are solely the responsibility of the authors and do not necessarily represent the official position or policies of the National Park Service, the National Center for Preservation Technology and Training or the General Electric Company.

## Supplier

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

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