FINAL REPORT

Non-Destructive Imaging Of Worn-off Hallmarks and Engravings From Metal Objects of Art Using Scanning Acoustic Microscopy

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TABLE OF CONTENTS

EXECUTIVE SUMMARY 2

PART 1 INTRODUCTION 3
1.1 Historical Development of Acoustic Imaging 5

PART 2 METHODS AND MATERIALS 7
2.1 Theoretical Background 7
2.1.1 Stress Annealing 7
2.1.2 Anisotropy 8
2.2 Coupling Fluid 9
2.3 Acoustic Transducers 10
2.4 The Scanning Acoustic Microscope 11
2.5 Initial Experimentation 11
2.5.1 Sterling Silver Coupons 11
2.5.2 Gold Coupons 13
2.6 Objects Scanned 14

PART 3 RESULTS 16
3.1 Sterling Silver Spoon Handle 16
3.2 Sterling Silver Fish Knife Blade 17
3.3 Dessert Knife 20
3.4 Apostle Spoon 20
3.5 Sterling Silver Fork 21
3.6 American Silver Dime 22
3.7 English Teaspoon 23

PART 4 DISCUSSION 23

PART 5 CONCLUSIONS 25

PART 6 ACKNOWLEDGMENTS 26

PART 7 REFERENCES 26

PLATES 28

EXECUTIVE SUMMARY

The goal of this project was to determine if worn-off or illegible hallmarks on silver and gold works of art could be imaged using scanning acoustic imaging techniques. The project was quite successful, up to a point, and represents the first time acoustic images have been made of remnant deformation in silver and gold objects of art.

This imaging technique utilizes the residual plastic deformation left in the metal after the hallmarks or engravings have been struck to form a sonogram image representing the differences in the acoustic response of the struck area and the surrounding metal. Theoretically, this should be possible based on the calculated degree of anisotropy and the stress annealing temperature of both silver and gold. In practice, these residual stresses in gold of the historical alloys of 18K-22K (75%-92% gold) could not be imaged while silver, of various experimental alloys, did yield good images.

Numerous combinations of coupling fluids, lens geometries, and sound frequencies were tried in both surface-wave and back-wall imaging modes. In the end, FC-40 (an inert fluorocarbon liquid) used in the surface-wave imaging mode with an input frequency of 20 MHz through an F/1 lens produced the best results. These then are the recommended materials and parameters for imaging worn-off marks on silver and gold when using a scanning acoustic microscope.

Hallmarks and engravings from a total of twenty-six silver, two gold, and one copper alloy (bronze) objects were imaged during the two-year course of the project. Multiple images were made of the marks on these objects so that well over one hundred images were made during the project. The silver objects ranged in age from the 17th to the 20th centuries, the gold objects were modern coupons, and the one bronze object was a coin dating from the 1790's. The silver content of the objects ranged from 80-95% silver while the gold objects were of 18K and 22K. The silver objects examined came from the collections of the Nelson-Atkins Museum of Art, private collections, and from purchases from dealers.

Imaging of worn-off or illegible hallmarks and engravings was successful one hundred percent of the time when residual flow was still present in the metal. Searches of the available literature on hallmarking techniques and consultations with silversmiths and the Superintendent Assayer of the Worshipful Company of Goldsmiths in London revealed that heat was probably used during most of the final cleaning and shaping processes of silver objects after the hallmarks were applied. It now appears that in most cases the heat was sufficient to anneal the metal, thus eliminating the residual plastic flow. In these situations there was nothing to image except metal grain structure. Unfortunately, there are no visual clues on the surface of the metal to indicate whether the requisite plastic flow is still present in the subsurface.

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 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 fomalized 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 (Jackson, 1921).

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 to1681 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 (Figure 1).

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 a duty has been paid on the finished 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. Silver's susceptibility 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 may be completely worn away, there may still be sufficient residual plastic deformation within the metal from the original act of striking the surface to create an image of the vanished 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. As a general rule, the surface roughness of the material to be imaged should be less than one-third the wavelength of the input acoustic frequency to provide sufficient returned energy to produce an image; when the surface roughness exceeds this parameter there is too much surface scattering of the acoustic signal to produce a meaningful image.

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 (Table 1). 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.

Table 1. (compiled from Treptow, 1978)

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

1.1 Historical Development of Acoustic Imaging

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 1930's 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 1950's. 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 1970's 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 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 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 recent literature search has found only three references to the use of acoustic microscopy for evaluating 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 the 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 (Figure 2).

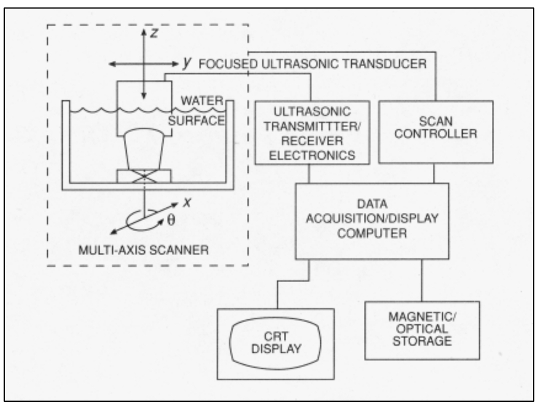

Figure 2. *Schematic of an ultrasonic imaging system; higher frequencies and higher image magnification would make the same schematic an acoustic microscope.*

The contrast changes in acoustic images are produced by variations of elasticity, density, and acoustic attenuation within the material being imaged. When the hallmark is applied by striking the surface of the metal, a localized change in the silver's physical properties occurs. Some of these properties that are altered include yield strength, tensile strength, hardness, and ductility. Any or all of these changes effects the acoustic attenuation of the insonified signal directly under and in near proximity to the struck area (Figure 3).

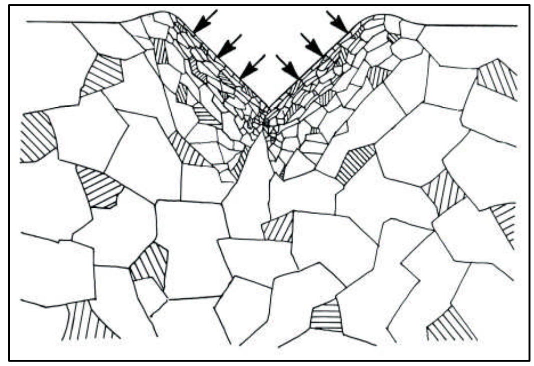

Figure 3. *Cross-sectional view of deformation in stamped hallmark. Slip lines, twinning bands, and smaller grain size result where metal absorbs stamping compression (shown by arrows). From Treptow, 1978.*

In the specific case of imaging worn hallmarks, it has been demonstrated that images of the residual deformation in the metal from the stamping process can be obtained by two methods: (1) Backwall 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 (Figure 4a); (2) Surface wave imaging of the surface containing the hallmark deformation (Figure 4b). In other words, surface waves are used to produce images of the entry surface, i.e., the struck surface, whereas backwall images are obtained from the surface opposite to the struck surface.

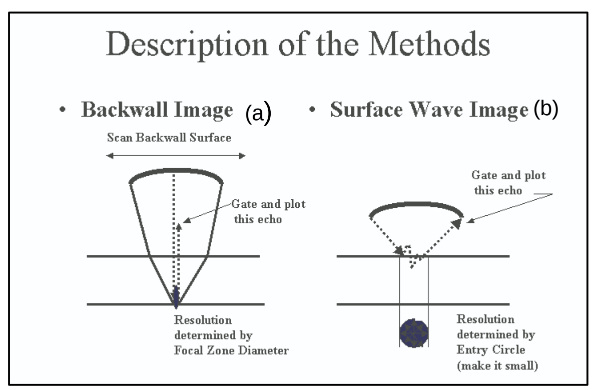

Figure 4. *Schematic showing (a) back surface reflection imaging (or backwall imaging) and (b) mode converted surface wave imaging.*

Only that part of the reflected signal that corresponds with the surface of interest is used to create the image; this process is referred to as 'gating' (Figure 5). Correctly choosing the proper reflection to gate and process requires experimentation and experience on the part of the operator to obtain a properly resolved image.

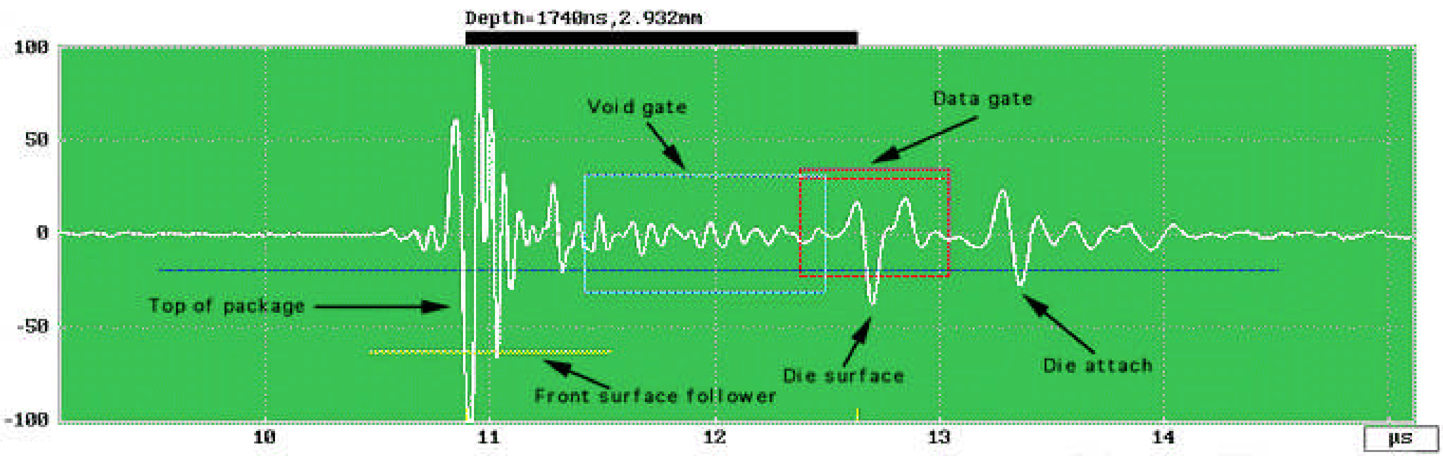

Figure 5. *A typical acoustic pulse showing a 'gate' around that portion of the pulse to be processed to form an image. (source of image unknown)*

2. Methods and Materials

2.1 Theoretical Background

2.1.1 Stress Annealing

A first step in determining if the amount of residual deformation in silver or any other material is sufficient 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 temperature is generally considered to be approximately 4/10ths (0.4) of the absolute melting temperature as expressed in degrees Kelvin (^{o}K) (Callister, 2003). The highest temperature below the melting point affecting the retention of the deformation is less exact, but is in the range of temperatures at which recrystallization occurs. Here the grain boundaries in the silver migrate and the microstructure entirely recrystallizes. Any residual plastic flow remaining from striking a hallmark would begin to relax at the stress annealing temperature and could totally disappear during recrystallization. Since the melting point (Mp) of sterling silver is 893^{o}C (1166^{o}K) the stress annealing temperature would be approximately 0.4 x 1166^{o}K = 466^{o}K, or approximately 93^{o} above the boiling point of water (100^{o}C or 373^{o}K). Room temperature is typically approximated at 300^{o}K; since the lowest critical temperature for sterling silver (466^{o}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 given in Table 2.

Table 2. Approximate 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

** from Smith, 1978; all other melting point figures are from Lide, 2002; other figures were calculated

2.1.2 Anisotropy

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 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 the Zener Anisotropy Ratio [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 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. Anisotropy for other metals is shown in Table 3. 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 do with the small size of the silver grains since, even at 50 MHz, the grains are too small to provide any backscatter amplitude.

Table 3. Estimation Of The Degree Of Anisotropy 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	1.239	0.939	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. All data are from Simmons and Wang, 1971.

2.2 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 4).

Distilled water at ambient room temperature was initially used to produce back-wall acoustic images of the hallmarks. While this produced reasonable images it was felt that the image resolution could be improved by processing surface wave information from the metal. A search was made for a liquid with a relatively slow acoustic velocity transmission and that met certain health and safety considerations. A line of perfluoro liquids called Fluorinert®, manufactured by 3M Specialty Materials met the health and safety criteria and are non-corrosive when in contact with precious metals. They contain no hydrogen or chlorine making them un-reactive to most metals and they are environmentally safe, non-toxic, have a low volatility, and have an acoustic transmission velocity of about one half that of water.

After initial experimentation with various Fluorinert® liquids it was determined that FC-40 was best suited to the imaging requirements. This coupling liquid had the least attenuation of the acoustic signal while its acoustic properties best matched the transducer lenses available at the time (Table 5).

Table 4. Relative Acoustic Velocities Of Some Coupling Fluids

COUPLING FLUID	TEMPERATURE (DEGREES C)	VELOCITY (MM/μSEC)	ABSORPTION (S^2/M)
Distilled Water	25	1.495	22.0
Distilled Water	60	1.550	10.2
Acetone	30	1.158	54.0
Ethanol	30	1.127	48.5
Methanol	30	1.088	30.2
FC-40	25	0.656	Not available

Table 5. Acoustic Properties Of Select Fluorinert® Liquids

COUPLING LIQUID	ACOUSTIC VELOCITY (MM/μSEC)	DENSITY (G/ML)	VISCOSITY (CENTISTOKES)
FC-40	0.656	1.87	2.2
FC-70	0.687	1.93	14.0
FC-72	0.512	1.68	0.4
FC-77	0.505	1.78	0.8
FC-84	0.542	1.73	0.55
Distilled Water	1.495	1.00	1.0

The propagation of longitudinal sound waves in water is approximately 1.48 mm/μsec versus 0.656 mm/μsec in the FC-40. This slower acoustic velocity translates into a smaller angle of incidence for the generation of surface waves in silver allowing for the use of standard transducers for the imaging instead of requiring custom-made transducers if water was the coupling medium (Table 6).

For this work FC-40 was used to make surface wave images in the sterling silver objects discussed here. The images acquired in this work were all made by immersing the silver objects in FC-40 for surface wave imaging and in distilled water for back-wall imaging.

2.3 Acoustic Transducers

After some initial testing it was determined that the best (highest resolution) images for back-wall imaging was obtained with a Panametrics Type V390 50 MHz F/2 transducer with 0.5" focal length, 0.25" aperture opening, and a 1.5" diameter quartz buffer-rod. For surface wave imaging a Panametrics polymer film 20 MHz F/1 transducer with 0.4" focal length and 0.4" aperture opening was used. These transducers were already available at the facilities where all imaging took place.

With the hopes that the resolution of the surface wave images could be further improved, a custom designed transducer was purchased. It was a Panametrics PZ25 33 MHz PVDF film transducer with 0.25" focal length and 0.25" aperture opening. It was felt that the shorter fluid path of this transducer would allow for higher frequency returns (improved resolution) but the frequency of the returned signals still did not exceed much more than 7.5MHz. This was only a slight improvement over the 20 MHz F/1 transducer originally used and did not produce visually superior images.

Table 6. Acoustic Velocities And Angle Of Incidence To Generate Surface Waves In Sterling Silver And Gold*

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

*All figures were experimentally derived

2.4 The Scanning Acoustic Microscope

The microscope utilized for all experimentation is owned by General Electric Research and Development and located in Schenectady, New York. The scanner is an Anorad ruling engine design. The electronics were developed by General Electric and have a bandwidth of 100 kHz to 100 MHz with 70 dB of available gain. The dynamic range of this system is 40 dB and its output data is digitized at 8-bits. The display software is called Winview and was also developed by General Electric.

2.5 Initial Experimentation

2.5.1 Sterling Silver Coupons

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 then polished with various grades of diamond paste on a Struers Prepamatic rotary lapping machine 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. The polishing was done at the premises of Honeywell Federal Manufacturing and Technologies in Kansas City, Missouri.

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 Figure 6 illustrate the detail ultrasonic imaging can produce on both intact hallmarks and the deformation remaining after removal by polishing. Figure 6a shows a 50 MHz F/2 back wall image of a coupon that still retains almost all of the hallmarks placed on it as struck. Figure 6b shows a 50 MHz F/2 back-wall image of the residual deformation in the coupon where almost all of the original hallmarks have been polished away. Figure 6c shows a 20 MHz F/1 surface wave image of the same deformation as figure 6b 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.

In order to prove that this imaging technique was not unique to the apparatus at General Electric, another research facility that employs acoustic microscopy, Honeywell Federal Manufacturing and Development in Kansas City, Missouri, was asked to replicate the experimental procedure used on the test coupon. The images compared quite favorably to the images produced by General Electric so it is felt that the imaging procedure is applicable for use on other acoustic microscopes. See Plate No. 31.

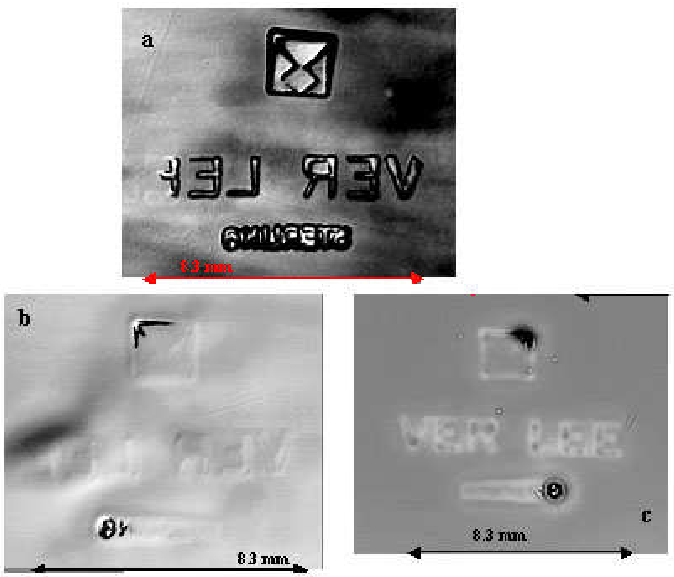

Figure 6. *Three ultrasonic images of a sterling silver test coupon. (a) A 50 MHz F/2 back-wall image of the original hallmark. (b) A 50 MHz F/2 back-wall image of the residual deformation remaining in the coupon after the hallmark has been polished away. (c) A 20 MHz F/1 surface wave image of the same deformation in 6b except imaged from the surface containing the deformation*

2.5.2 Gold Coupons

Coupons of 18K and 22K gold, measuring approximately 25 mm x 25 mm x 3 mm, were purchased and stamped with hallmarks by an experienced silversmith. These alloys were chosen because the earliest historical European standard for gold work was 19.2 carats (80%). In later years additional standards were established but it was felt that 18K and 22K would represent the alloys that would be most often encountered in works of art.

Once the hallmarks had been placed on the coupons they were polished off as previously described. Surface wave imaging of the gold coupons was done only with FC-40 as the coupling medium; no back-wall imaging was done. Converted surface waves were captured but surprisingly, either no images or barely perceptible images of the polished-off hallmarks were recovered (Figure 7). A possible explanation for these results can be accounted for by 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 deformation to image. It is proposed that a lower purity gold, such as 14K (58.3%), that has been alloyed with an increasing quantity of copper will exhibit some plastic deformation making it possible to recover hallmarks using the acoustic imaging technique. No further experimentation with gold was done because of the lack of results on these two coupons.

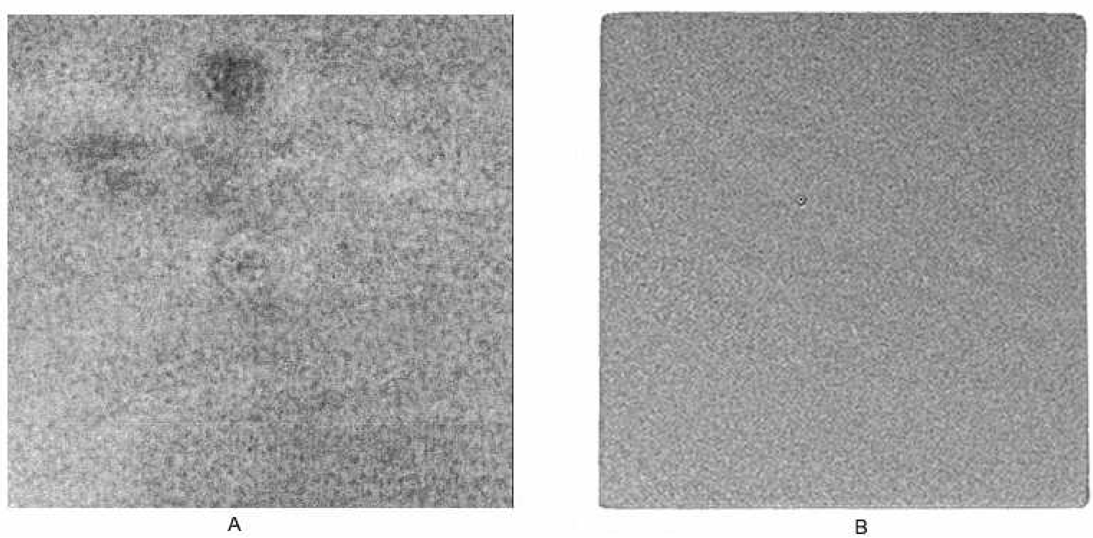

Figure 7. *Acoustic images: (A) an 18K gold coupon and (B) a 22K gold coupon*

2.6 Objects Scanned

A total of twenty-nine silver objects were scanned (Table 7). Objects were selected to cover a broad range of ages and to represent silverwork from several countries. It was assumed that not all objects were "sterling" silver as alloy standards varied from country to country and changed through the course of time. For example, the English silver standard was changed from sterling (92.5%) to Britannia (95%) for the period 1697-1719. However, the Britannia standard was never abolished leaving the silversmith free to produce wares that were marked with the sterling standard but could in fact be of the higher silver alloy. It should be remembered that the alloy standards provided for minimum silver content but not a maximum silver content (Jackson, 1921).

Other countries established their own standards, which, again, varied over time. Imaging of American silver objects was initially avoided, as their silver content could not be verified without additional testing. Standards for American silver were not formally codified until 1906, which meant that silver could be called 'sterling' without meeting the generally accepted 92.5% silver content. In fact, there are examples of American 'sterling silver' that contain no silver at all. In the end, these variations in the silver content proved to have no effect on the ability to image the residual deformation in the silver.

Objects chosen for imaging were limited to a fairly small size for two considerations. First was the quantity of the coupling fluid available. After the coupling fluid, FC-40, was chosen only a small quantity, approximately two liters, was purchased due to the very high cost of the material and for fear that it could quickly evaporate if there were no mechanism to prevent it from doing so. Secondly, it was much more difficult than initially thought to find silver objects with worn-off hallmarks that the owners were willing to lend for the experiments. Insurance considerations prevented certain pieces from leaving the Nelson-Atkins Museum and private owners were hesitant to loan their silver to the project without additional insurance. In the end, only five pieces from the Nelson-Atkins Museum were tested, with the rest coming from loans from silver dealers, private owners, or purchases.

Table 7. Objects Scanned For Hallmark Recovery Project

OBJECT	DATE	OWNER	ORIGIN	PLATE NO.
Sterling silver test coupon	Modern	Purchased		1, 2 & 31
Sterling silver test coupon (annealed)	Modern	Purchased		Figure 12B
Teaspoon (Bateman)	1792	NAMA no. 72-45/4B	English	3
Spoon (Christina)	Early 20th c	C. Nelson	American	4
Teaspoon (salt)	1780	Purchased	English	5
Teaspoon (Paul)	Unknown	P. Benson	Unknown	6
Teaspoon (EW)	1790's (?)	Purchased	English (?)	7
Teaspoon (MH)	Unknown	Purchased	Unknown	8
Teaspoon (JRD)	Unknown	Purchased	Unknown	9
Teaspoon (1 Mono)	Unknown	Purchased	Unknown	10
Paten cover	1569	NAMA no. 52-16B	English	11
Dessert knife	1800-1810	NAMA no. 76-34/12C	French	12
Fish knife	1875-1925	NAMA no. F83-76/10	French	13
Spoon (Churchman)	Unknown	M. Churchman	English	14
Fork (Belgium)	18th c.	W. Wilkinson	Belgium	15
Spoon (Apostle)	1603	J. Shredds	English	16
Spoon (Apostle)	1603?	J. Shredds	English	17
Fork (Barbados)	Colonial	W. Wilkinson	Barbados	18
Spoon (Rattail)	1716	J. Shredds	English	19
U.S. Silver Dime	1840's	G. MacCurdy	American	20 & 21
French coin	1790's	K. Garland	French	22
Spoon (BH)	18th c	J. Weidman	Scottish	23
Spoon (George III)	1790	W. Wilkinson	English	24
22K gold coupon	Modern	Purchased		25
18K gold coupon	Modern	Purchased		26
Nichols Silver Coupon A	Modern	Purchased		27
Nichols Silver Coupon B	Modern	Purchased		27
Trivet	1787	NAMA no. 71-45/1	English	28
Fork (Monogram)	1808	W. Wilkinson	English	29
Spoon (1809)	Unknown	W. Wilkinson	French Caribbean	30

3.0 RESULTS

To eliminate duplicate discussions of the results of scanning all the individual objects, only a few of the results that illustrate a particular point will be presented here. Acoustic images of all of the objects can be found in the attached plates.

3.1 Sterling Silver Spoon Handle

Figure 8 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 8a the makers' initials are clear but much of the remaining hallmarks have been removed. Figure 8b shows isolation, magnification, and partial recovery one of the hallmarks believed to be that of a lion. The image of the "lion" shown in Figure 8c 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).

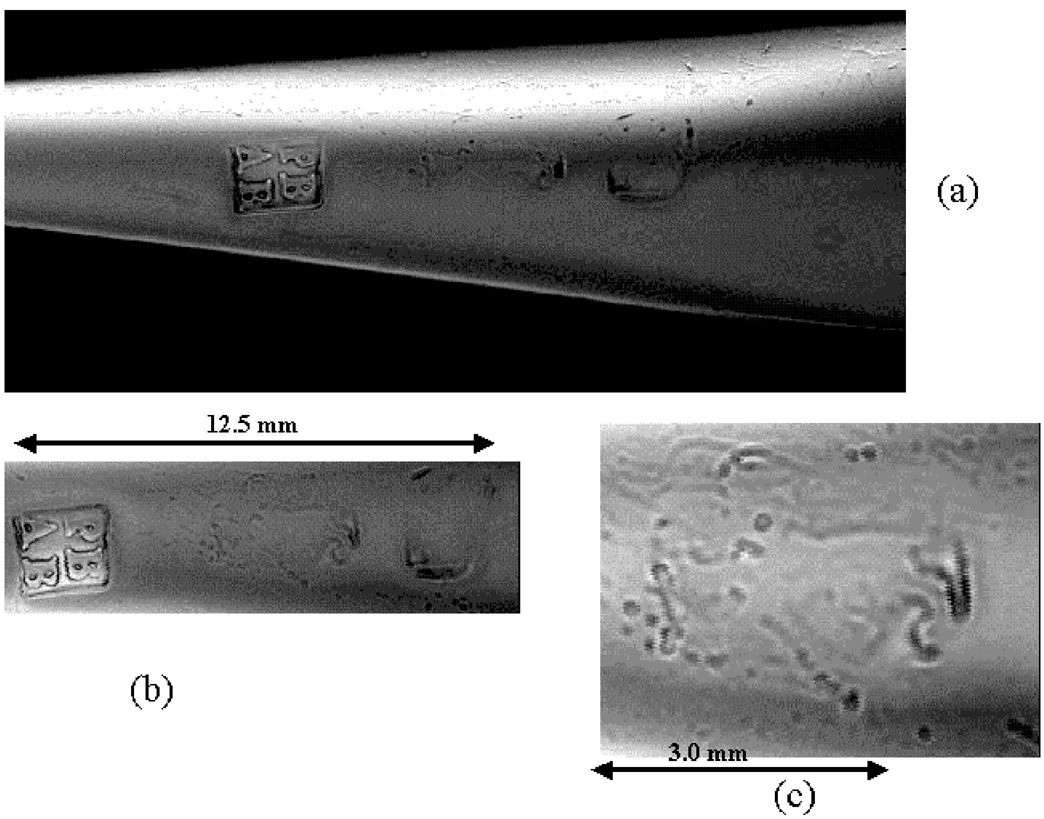

Figure 8. *(a) Ultrasonic images of the handle of a sterling silver teaspoon wrought by Peter and Ann Bateman dating from 1792. (b) The initials of the makers are clear but much of the remaining hallmarks have been removed. (c) Shows the isolation, magnification, and partial recovery of a figure thought to be a lion.*

Subsequent imaging processing comparisons with a visible hallmark from another 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 top of 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 (Figure 9).

Figure 9. *A recovered acoustic image of a worn-off lion hallmark overlaying a digital image of an identical hallmark from the same set of teaspoons.*

Figure 10 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 10. *Recovered acoustic images of the date letter 'r' overlaying a digital image of a visible 'r' hallmark from the same set of teaspoons.*

3.2 Sterling Silver Fish Knife Blade

Figure 11 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 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 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 contrast 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.

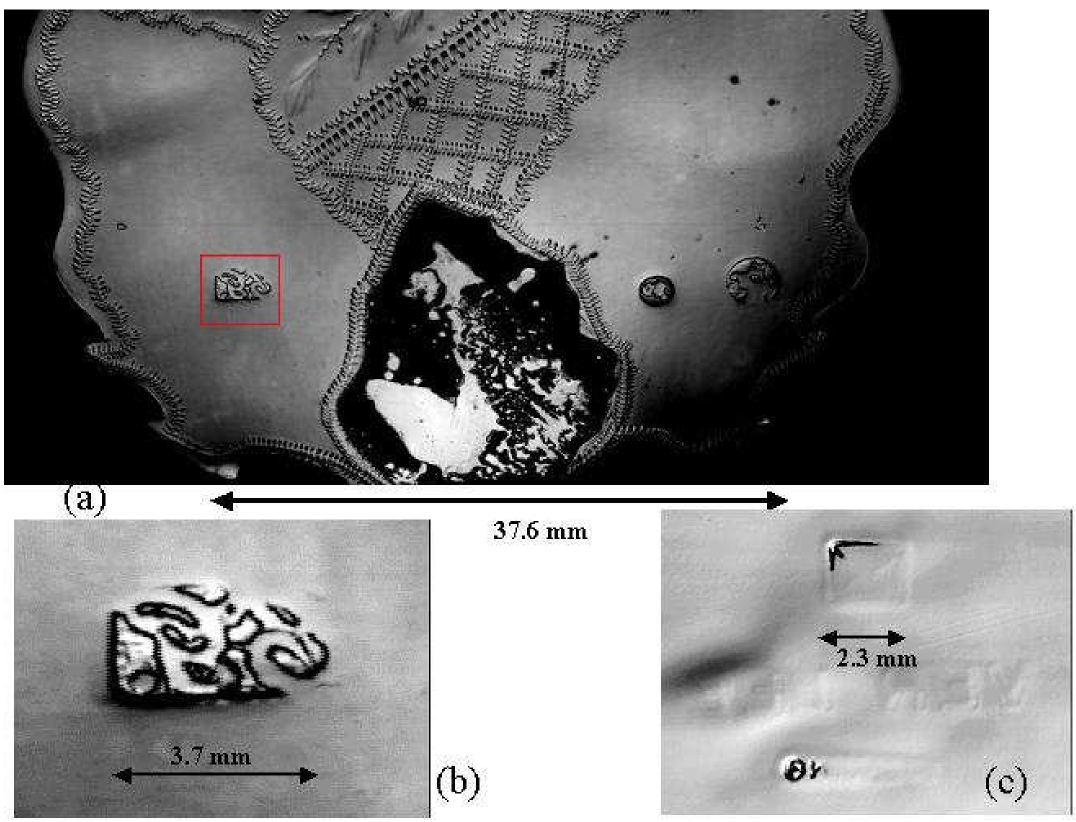

Figure 11. *Ultrasonic back-wall image of the sterling silver blade of a French fish knife dated approximately 1875 to 1925. One hallmark is isolated (b) and magnified for comparison to the back-wall image of the coupon (c). No deformation appears to extend from the fish knife hallmark.*

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 ºC 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 (Figure 12). Incidentally, the dark area in Figure 12 B shows an enrichment in copper compared to the lighter colored more silver rich area around it. (See also the SEM-EDX analysis on Plate 32)

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).

By chance, Figure 11 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 coating that were not visually apparent but were quite obvious in the acoustic image.

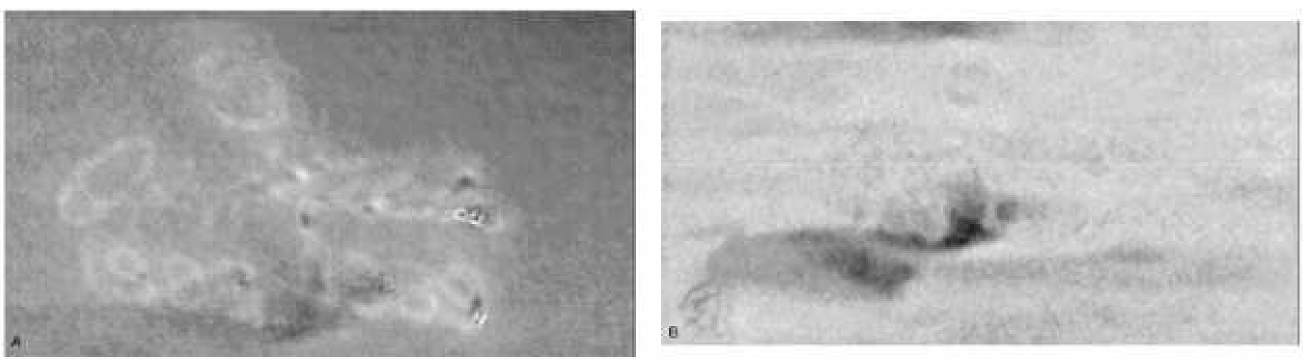

Figure 12. *Effects of annealing on sterling silver. (A) A recovered acoustic image of polished-off hallmarks on a sterling silver coupon before annealing. (B) The same area after annealing the coupon.*

3.3 Dessert Knife

Acoustic images of a steel bladed silver French dessert knife dating from the beginning of the nineteenth century are illustrated in Figure 13. The partially worn-off maker's name is 'engraved' on the steel blade and appears to be an ideal candidate for the recovery of an engraving using the acoustic imaging method. The direct reflection image in (a) clearly shows the maker's name with the central section completely worn away; Figure 13b is a surface wave image of the same area. No

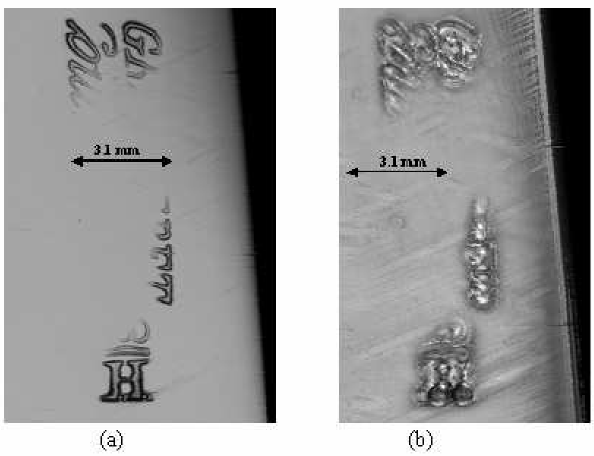

Figure 13. *Silver dessert knife with a steel blade. (a) Direct reflection acoustic image. (b) Surface wave acoustic image of the same area.*

remnant reformation is seen in (b) because the maker's name has not been applied to the blade by stamping but probably by etching or through the mechanical removal of metal. In either case, there is no subsurface deformation so acoustical methods cannot recover the missing inscription.

This object serves as a reminder that inscriptions can be created by several means and only those created by stamping the metal produce a subsurface deformation that can be recovered by acoustical imaging; the process of removing metal does not create the requisite deformations.

3.4 Apostle Spoon

Figure 14 is an acoustic image of the hallmarks on a silver Apostle spoon supposedly dating from 1503. The date letter "F" was visible and clearly readable but the other mark could not be discerned. A series of acoustic images were made of the hallmarked area by focusing the sound at progressively deeper intervals into the metal. Unfortunately, none of the images were able to resolve the illegible mark but some unexpected information was gained. In Figure 14 it can be seen that (1) there is a noticeable bulge in the handle where the hallmark has been applied and (2) there is a well defined join line just to the right of the letter "F" where it appears that the handle was either broken and repaired or that two individual handles have been joined to form one complete handle. In either case, the placement of the hallmarks is rather odd. It should also be noted that this join and bulge are not apparent in a visual inspection of the spoon.

An experienced dealer was able to immediately determine that the spoon was a forgery based on stylistic grounds while the acoustic image provides hard evidence of the deceit.

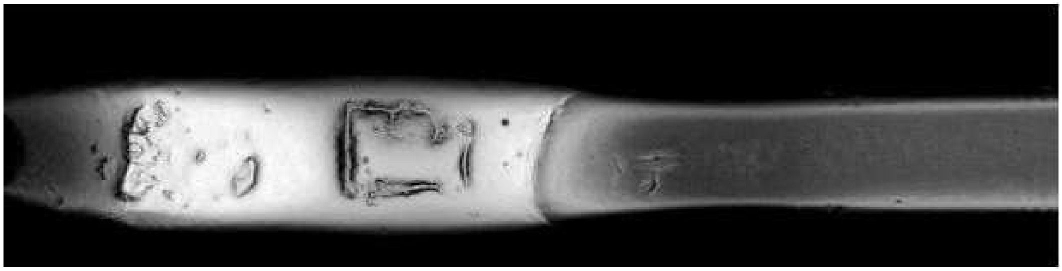

***Figure 14*.** *Acoustic image of the hallmarks on a silver Apostle Spoon supposedly dating from 1503.*

3.5 Monogram 1808 Silver Fork

Figure 15a is an acoustic image of a purposely-removed hallmark from an English 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 the acoustic image presented here, the hallmark is difficult to decipher. At best it can only be recognized that there was a hallmark present at some time in the past (Figure 15b). The interpretation of this

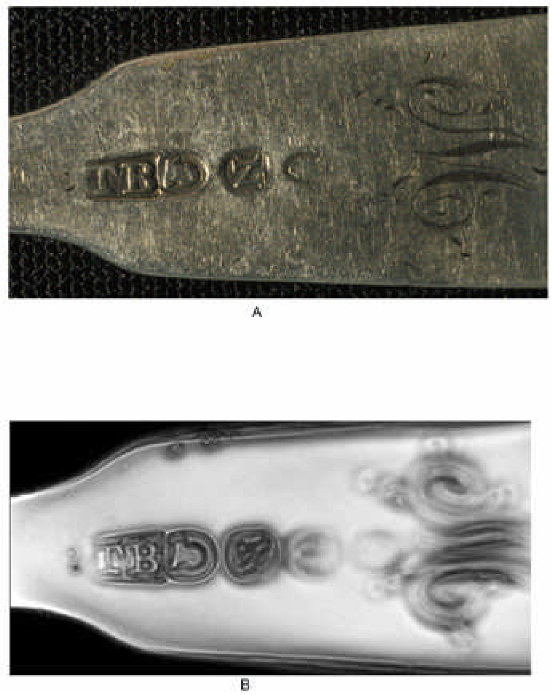

Figure 15. *Silver fork with a hallmark deliberately removed. (A) Photograph of the visible hallmarks on the fork. (B) An acoustic image of the hallmarks showing that a fifth mark was present at one time. The now-missing hallmark has been interpreted as a lion.*

being the lion hallmark was based on a much clearer computer image at the time the image was acquired.

Image processing using Adobe Photoshop CS was used to try to enhance the image of this recovered hallmark. Various filters were applied to the original acoustic image to bring out any residual information that could be present in the acoustic image and it is now possible to positively identify the hallmark as that of a lion, as was expected (Figure 16).

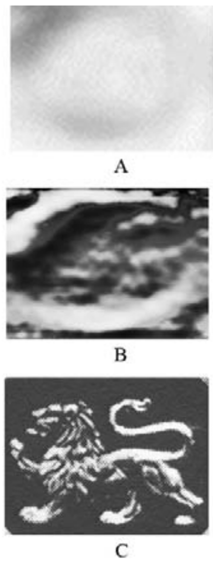

Figure 16. *A. Original acoustic image of removed hallmark from the spoon in Figure 15a. B. Photo-enhanced image of the same hallmark indicating a worn image of a lion. C. Photograph of a lion hallmark for comparison with B.*

The use of photo-enhancement software greatly improved (in some cases) the quality of the acoustic images to the extent that positive identifications of images of worn-off hallmarks could be made by non-experts. Subsequently, all of the acoustic images acquired during the course of this investigation were re-examined and these enhanced images are included in the Plates.

3.6 American Silver Dime

One important application of the acoustic imaging technique involves the potential ability to image worn-off inscriptions on coins. Coins are commonly encountered on archaeological excavations and can provide critical assistance in dating and determining the history of the site.

Two coins, one copper alloy and the other one silver (Figure 17), were imaged to try and recover the date stamped on them. In neither case was this successful but different previously illegible markings on the coins were seen in the acoustic images. In this case, the ability to image the markings probably depended on whether or not there was a design on the opposite side in the corresponding position. Since both sides of the coins were struck at the same time there is a mixing of the subsurface deformations that the acoustic signal could not resolve. Even though the dates of the coins could not be directly ascertained, the images of the other markings were sufficient to allow an expert to make an informed identification of both coins.

In the case of the dime illustrated in Figure 17A the surface wave image reveals the word 'one' which is not visible in the direct reflection image Figure 17B.

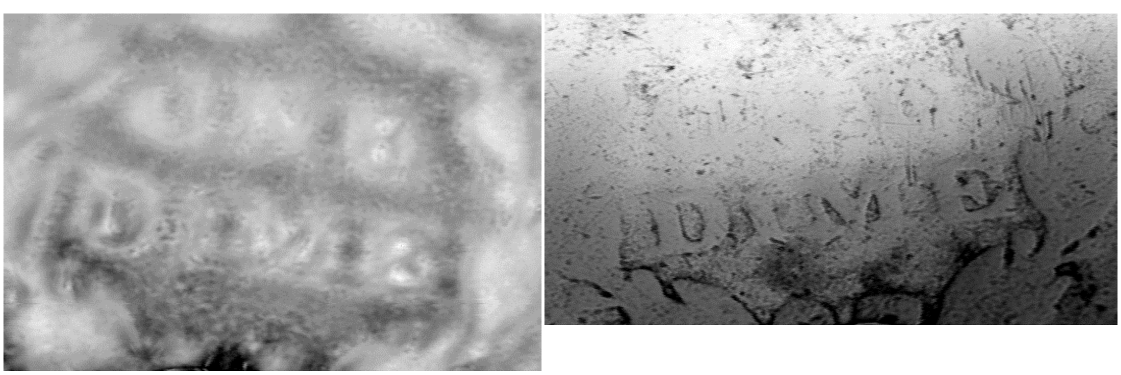

Figure 17. *American silver dime dating from the 1840's. (A) Surface wave acoustic image made in FC-40 as the coupling medium. (B) Same image except water was used as the coupling medium for the direct reflection image*

3.7 "EW" English Teaspoon

The teaspoon had a partially readable maker's mark with the first initial being a "T", the second initial too worn too be read, and two other illegible hallmarks present on the reverse of the handle (Figure 18).

Figure 18. *Photograph of a teaspoon with one partially readable hallmark and two illegible hallmarks.*

The acoustic images revealed that the two illegible hallmarks were probably the date mark and the mark for sterling silver, a lion, but both images lacked the resolution to make a definitive interpretation of the marks (Figure 19).

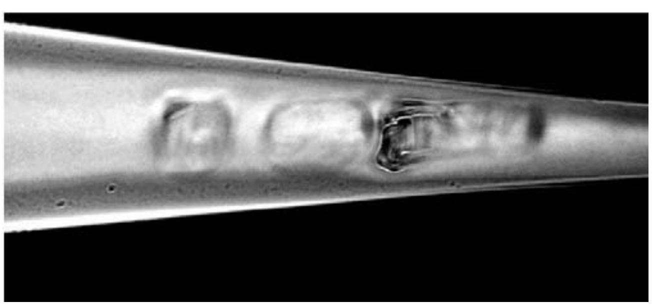

Figure 19. *Acoustic image of the "EW" teaspoon with illegible hallmarks and a partial hallmark.*

Image processing using PhotoShop CS clarified the acoustic image to the extent that the previously unidentified teaspoon could now be identified as being made by Thomas Wallis (initials TW) and the date mark as the letter "h" for the year 1783/84. The third hallmark was not distinct but resembles the mark for sterling quality metal; i.e. the lion passant. (See Figure 20.)

Figure 20. *Image processed acoustic image with the date letter "h" and the maker's initials "TW" outlined for clarity. The third hallmark is still illegible but resembles the lion passant mark for sterling quality metal.*

4. DISCUSSION

A total of twenty-nine silver, gold, and bronze 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 seven 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 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 (Figure11) 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 (193^{o} C) 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.

As mentioned earlier, it was not possible to experiment with silver objects of greater value than flatware due to insurance restrictions. It is possible that objects that are of a size that would allow for the hallmarks to be fully struck without alteration of the shape of the piece after the marks have been applied would be more amenable to the imaging technique. For example, the shape of a plate or vessel would have been fully developed before the hallmarks were applied (except in France) such that only a final cleaning would have been required to complete the piece and it is not envisioned that cleaning, even in a hot acid bath to remove fire scale, would be sufficient to remove the subsurface deformation of the hallmarking process. It is quite regrettable that this could not have been proven by experimentation on antique silver objects.

Surface wave images of two antique coins suggest that downward or compressive deformation, i.e., a dent, is more readily defined than the up welling 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.

5. CONCLUSIONS

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 a fairly unsuccessful, the project has succeeded in producing images one hundred per cent of the time where remnant plastic deformation exists. Subsequent imaging processing of the images utilizing a standard software program further clarified about fifty percent of the acquired images. 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.

Images of removed or worn-off engravings may be recoverable depending on their method of removal. The inscription would have to have been applied by chasing, i.e. by hammering the lines into the metal as opposed to removal of the metal with a scribe. Then they would have to be 'removed' by either filling them with silver solder or by being polished away. If the inscription was 'removed' by either hammering or by stoning then the acoustic method cannot be used for their recovery.

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.

Acoustic imaging of archaeological artifacts, e.g. coins, has great potential to be a valuable aid in dating and re-constructing the history of excavated sites. The only caveat being that the objects must have a very smooth surface to permit successful imaging.

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