Return Harry D. Study
D-

United States Department of the Interior

NATIONAL PARK SERVICE
Statue of Liberty National Monument
Liberty Island
New York, New York 10004

IN REPLY REFER TO:

H3815

October 22, 1980

Memorandum

To: Regional Director, North Atlantic Region
Attn: Blaine Cliver, Historic Architect, Cultural Resources

From: Superintendent, Statue of Liberty N.M.

Subject: Metallurgical Study of the Statue of Liberty

– 2 mtg with Ive done HO 3/17/81

Enclosed you will find the first of three reports done for us by the Winterthur Museum. The statistical findings are a revision of those previously submitted. All of the samples tested are from the torch and were replaced with like items about seven years ago.

The torch ornaments are being retained by Winterthur pending our review of this report and should we desire additional tests for clarification.

David L. Moffitt

Enclosures
Letter fm Winterthur Museum
w/Analytical Lab Rpt (14 pages)

cc:
Edward L. Kallop, NARO.
w/enclosures

Ross Holland, WASO,
w/enclosures

Monument Files
Reading Files
Museum Curator

POWeinbaum:sm: 10-22-80

Winterthur Museum

October 8, 1980

Dr. Paul Weinbaum, Curator
Statue of Liberty National Monument
Liberty Island
New York City, New York 10004

Dear Dr. Weinbaum:

I am pleased to transmit herewith two copies of our Report A.L.#995, "Examination of Parts from the Statue of Liberty by Winterthur Museum's Energy Dispersive X-Ray Fluorescence Analyzer (XRF)", which I understand you are anxious to receive at this time.

Norman Nielsen, who has made a metallurgical study of the corrosion products, is out of town and has agreed to send a copy of his report at an early date.

We are holding the objects from the Statue until you have an opportunity to review the reports and advise us if there are additional tests that you require for clarification.

I hope that you find the information interesting and useful.

Sincerely yours,

Victor F. Hanson

Victor F. Hanson
Coordinator and Head, Scientific Research

VFH/ms

Enclosures - 2

XC: James Smith
Charles Hummel
Nancy Richards
George Reilly
Janice Carlson
Don Heller
Kate Wheeler
Norman Nielsen

WINTERTHUR ANALYTICAL LABORATORY

Report A.L.#995

Examination of Parts from the Statue of Liberty by Winterthur Museum's Energy Dispersive X-Ray Fluorescence Analyzer (XRF).

By: Victor F. Hanson Victor F. Hanson
October 8, 1980

Information Copies:

Paul Weinbaum
Paul Kinney
James Smith
Charles Hummel
Nancy Richards
Norman Nielsen
Don Heller
Kate Wheeler

INFO. COPY: Paul Weinbaum, Paul Kinney
Charles Hummel
Nancy Richards
Mary Cash
Office files (3)
James Smith
Kate Wheeler
Norman Nielsen
Don Heller

The Winterthur Museum
ANALYTICAL LABORATORY
REQUEST FOR COMPOSITIONAL INFORMATION

REQUEST NO. 995

DATE: 5/20/80

REQUESTOR: Paul Weinbaum, Paul Kinney

PURPOSE OF STUDY: (Check all applicable areas)

1. Authenticity ____
2. Conservation X
3. Addition to our library of information X
4. Art Historical information ____
5. Preparation of scientific paper ____
6. Personal interest ____
7. Technique development ____
8. Particular interest (Explain)

OBJECT OR SAMPLE INFORMATION

OBJECT DESCRIPTION: (Material, size, etc.)

Check here if non-Winterthur X

Accession Number: None

Parts from the Statue of Liberty.

(1) Tubular piece from Statue of Liberty torch.
(2) Fan ornament.
(3) Bell ornament (screw on).

Date of object: ca.1875-1876
Provenance: France
Maker: Gaget, Goutier & Co.
Owner: U.S. Government
Address: Statue of Liberty National Monumen
Liberty Island
New York, New York 10004
Telephone: 212-964-3451
212-732-1236

REPORTED BY:

APPROVED DATE: _____ BY: _____

A.L. Form #12

A.L.#995
5/20/60

Abstract

The National Park Service requested Winterthur to determine if an analytical study of the corrosion layer and the structure of the Statue of Liberty could reveal causes of the severe corrosion and make suggestions to stabilize the system to avoid catastrophic destruction.

Parts brought to the laboratory were examined by the x-ray fluorescence analyzer and by Norman Nielsen at the du Pont Experimental Station laboratories.

This report covering the Analytical Laboratory study provides the following information:

1. The compositional range of the parts examined is:

TABLE 1

Compositional Range of Parts Examined

Element	Weight %
Copper	96 - 98
Arsenic	0 - 0.2
Iron	0.2 - 0.6
Lead	0 - .7
Mercury	.05 - .8
Silver	.03 - .06
Tin	.01 - .05
Zinc	1 - 2.3

2. Compositional details are reported in Tables 2,3,4, and 5.

3. The corrosion layer scraped and analyzed was much richer in mercury and lead indicating that these elements were deposited from air-borne vapors from automobile exhausts or from industries using mercury, such as lamp works.

4. Speculations are provided to explain the origin of the trace elements found.

5. It is hoped that the compositional information supplied by this study will provide a guide for selecting electrolytically compatible materials for rivets, bolts and other fastening devices to be used in future repairs.

A.L.#995
5/20/80

BACKGROUND

On May 20, 1980, Dr. Paul Weinbaum and Paul Kinney of the National Park Service's Statue of Liberty National Monument brought to the Winterthur Museum Laboratory parts of the Statue of Liberty that were available for a metallurgical examination. This was shortly after the notorious ascent by two well publicized activists. Winterthur was selected for making this study in part as a result of a prior study of the Liberty Bell, also for the National Park Service and reported in the American Scientist, November-December 1976, Volume 64, Number 6, "The Liberty Bell: Composition of the Famous Failure".

It was hoped that such a study would define the corrosion processes that appear to be causing the copper to deteriorate at an alarming rate and which might suggest measures that might be taken to stabilize the corrosion process.

Norman Nielsen, metallurgist with the du Pont Company and consultant for Winterthur's Scientific Advisory Committee, is also involved in the study and will report his findings independently.

Don Heller, Winterthur's metals conservator, will also report his findings independently.

A.L.#995
5/20/80

I. Analytical Equipment

Winterthur's Energy Dispersive X-Ray Fluorescence Analyzer (XRFA) employs Fe^{55}, Cd^{109}, and Am^{241} as x-ray sources to excite the atoms of the various chemical elements near the surface of the object being examined. Each of the excited elements emits new x-rays having energies characteristic of that excited element. These fluorescence x-rays are absorbed in a lithium-doped silicon detector refrigerated by liquid nitrogen. This detector, which "sees" a circular area about 15 mm. in diameter, produces electrical pulses of amplitudes proportional to the excitation energy. These pulses are sorted electronically and accumulated in a magnetic memory bank having 512 storage "bins", each with a capacity of one million counts. These data are fed into a computer and processed so that a teletype printer produces a hard copy of the weight percent of 15 preselected elements.

II. Limitations of Measuring Corrosion Products

Because of their absorption in the airpath during measurement, x-rays from low atomic number elements such as carbon, nitrogen, oxygen, fluorine, sulfur, and chlorine, some of which appear in corrosion products, are not detected by this analysis system. In fact, the instrument "sees through" most thin layers of oxides, sulfides, and chlorides seeing only the elements heavier than potassium in or under the corrosion layer.

This feature reveals important information related to the surface layer that would not be found if the composition of that surface layer had to be weight averaged with the substrate of the corrosion layer by the measuring system.

The measurement is made directly on the object without requiring a sample to be removed. It is truly non-destructive since the x-rays employed are weak and do not alter the object in any way.

III. Analysis Procedure

Selected areas on the object, which had been removed from the Statue several years ago, were analyzed by placing that area above the excitor source-detector port of the system which had been previously standardized by the procedure described in Chapter 15, "Museum Objects", X-Ray Spectrometry, Herglotz/Birks, editors, New York, 1978. After 5,000 pulse counts from the copper peak channel had been accumulated, the data were transferred to the computer where they were processed channel by channel and the compositional data were then printed out in summary form.

IV. Data Presentation

The summary includes a Sequence Number which identifies the analysis. It also includes the year, day of the year, time, and a brief description of the analyzed area. In the following discussion of the various elements tabulated, reference will be made to Seq. Numbers such as B1891 which was made on the 143 rd day of 1980 at 3:54 p.m. (Refer to Table 2.)

V. Discussion

1. Antimony - Antimony found in the range of .02 - .035% is probably an impurity in the copper that could not be removed by the refining process then in use. B1894 is a measurement made at a soldered area showing 44% lead which frequently contains antimony, especially if the lead was reclaimed, since antimony is used to harden or strengthen lead structures.

2. Arsenic - Arsenic occurs naturally with some copper ores and is difficult to remove quantitatively. It might serve to help identify the source of the copper used in the various parts of the Statue if this is of interest to historians.

3. Bismuth
4. Cadmium
5. Cobalt

These elements are present in such low amounts that no relevant comment can be made to account for their presence.

6. Copper - Copper at 95 to 98% purity level is normal for the period. It is soft and ductile so that it can be easily shaped by conventional rolling and forging methods.

   The precision or reproducibility of measurement can be judged by comparing B1891 to B1880 which are the same black area measured 48 hours apart. Also B1890 and B1874 are this same area after scraping down to bare copper measured 48 hours apart. It is interesting to note that the thin corrosion layer appears to be invisible to the analyzer whereas analysis of the "scrapings" B1878 are actually close to that of the substrate B1889.

7. Gold - None found.

8. Iron - The iron content of the copper varies from about 0.3 to 0.5%, generally. B1892 shows about 2% iron on the gusset insert of the anthemium where it had been riveted or bolted to another part of the Statue.

   No iron was detected in the B1878 scraping which is strange and should be rechecked. This might be an error due to the very small sample (25 mg.) employed.

9. Lead - Lead appears generally from .3 to .7% except for the solder in B1892 and B1894.

   The lead concentration in the scrapings B1878 is about three times that of the substrate B1890, indicating that volatile lead compounds had been deposited on the surface, perhaps from automobile exhaust gases. This possibility might be of interest to environmentalists.

   The lead content of the black area B1889 is much higher than on the green area B1891 due probably to black lead sulfide.

10. Manganese - None Found.

11. Mercury - Mercury in concentrations of .04 to over 1% was surprisingly

found except at the soldered part B1894. Mercury on the solder was obscured by the contiguous element lead which appeared to be 44% in the solder.

Mercury vapor condensing on copper forms a true alloy (amalgam) that is quite stable but removable by heat (400° C.).

The concentration of mercury in the scraping is about three times that of the substrate indicating that it is definitely on the surface and not dispersed throughout the structure.

Perhaps environmentalists interested in protecting the citizenry from exposure to mercury vapor should seek out a fluorescent lamp manufacturer in the area.

12. Nickel - None Found.

13. Silver - Silver appeared in concentrations (.02 - .07%) typical of that found in copper smelted by methods in use in the mid-19th century.

14. Tin - The tin in concentrations of .02 to .03% was probably due to bronze scrap that got into the melts. This tin concentration is too low to have much effect on the hardness of the copper. Perhaps its effect on corrosion should be investigated.

15. Zinc - Zinc in concentrations as high as 2% was either added to harden the copper or was added accidentally with brass scrap.

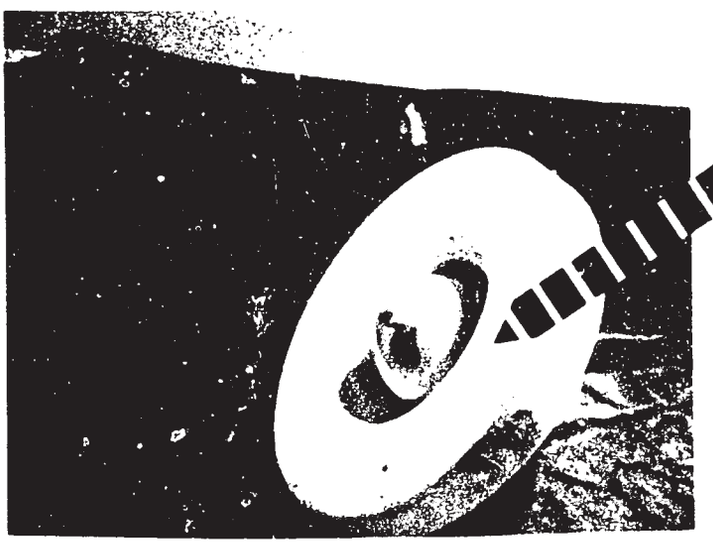
Statue of Liberty Test Parts

Winterthur Museum Analytical Laboratory

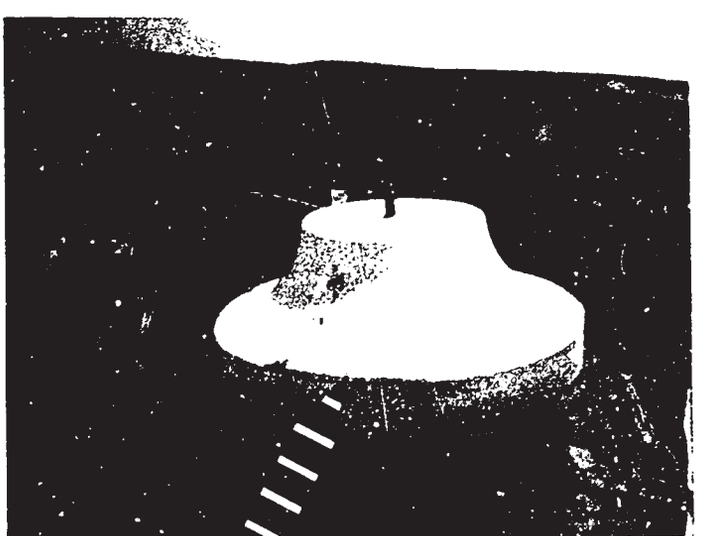
October 1980

Part - Involute

Table 3 Measurement Locations



#B1893 - Face



#B1894 - Soldered Area

TABLE 3

Statue of Liberty Corrosion Study

Part - Involute

Surface Composition at Face and Soldered Joint

THE WINTERTHUR MUSEUM
ANALYTICAL LABORATORY
BRASS SUMMARY

A.L. #	995.A7	995.A8
SED. #	#B1893	#B1894
TES. DATE	143,1989	143,1989
TES. TIME	16:10	16:22
ACCESSION #	//	//
OWNER	NAT PRK SE	NAT PRK SE
OBJECT	INVOLUTE B	N/A
DESC'N	UST	
PART	FACE	SOLDERED
MAKER	//	//
DATE	C1880	C188
PROVENCE	FRANCE	FRANCE
X	MEu-`	MEu-`
Y	ME-uBu	ME-uBu

	ELEMENT	WEIGHT %	WEIGHT %	WEIGHT %	WEIGHT %	WEIGHT %
1	ANTIMONY..	.00865	.33351			
2	ARSENIC...	.00636	.[illegible]			
3	BISMUTH...	.00010	.02328			
4	CADMIUM...	.00069	.21412			
5	COBALT....	.00000	.[illegible]			
6	COPPER....	97.63472	48.42394			
7	GOLD.....	~~.01395~~	~~.50048~~			
8	IRON.....	.21472	.43798			
9	LEAD.....	.00000	13.85630			
10	MANGANESE	.00409	.[illegible]			
11	MERCURY...	.03638	.[illegible]			
12	NICKEL....	.00000	.[illegible]			
13	SILVER....	.02675	.[illegible]			
14	TIN.....	.02191	5.62626			
15	ZINC.....	1.90217	.61142			

#B1893 - Face of Cylinder
#B1894 - Soldered Joint

STATUE OF LIBERTY TEST PARTS

Winterthur Museum Analytical Laboratory

October 1980

Part - Anthemium (Leaf)

Table 2 Measurement Locations

TABLE 4

Statue of Liberty Corrosion Study

Scraping Experiment

THE WINTERTHUR MUSEUM
ANALYTICAL LABORATORY
BRASS SUMMARY

A.L. #	995.A3	995.1.1	995.A4	995.1.5	995.1.3
SEQ. #	#81889	#81872	#81893	#81878	#81874
TEST DATE	143,1983	141,1983	143,1983	141,1983	141,1983
TEST TIME	15:29	14: 2	15:47	14:52	14:13
ACCESSION #	//		//		NOE
OWNER	NAT PRK SE	NPS	NAT PRK SE	NPS	NPS
OBJECT DESCRIPTION	TUBLR ORNA MENT	STATUE OF LIBERTY	TUBULAR OR NMT	ST OF LIB	STATUE OF LIBERTY
PART	BLK AREA	TORCH PART	SCRAPED AR	#1 SCRAPING	AREA 1 SCRAPED
MAKER	//		//		
DATE	C1870	1876	C1870		1876
PROVENCE	FRANCE	NYC	FRANCE		NYC
X	MEU-\	MEU-\	MEU-\	MEU-\	MEU-\
Y	ME-UBU	ME-UBU	ME-UBU	ME-UBU	ME-UBU

	ELEMENT	WEIGHT %	WEIGHT %	WEIGHT %	WEIGHT %	WEIGHT %
1	ANTIMONY..	.03290	.02122	.02975	.02328	.02226
2	ARSENIC...	.07115	[illegible]	.13746	[illegible]	[illegible]
3	BISMUTH...	.00017	[illegible]	[illegible]	.00341	[illegible]
4	CADMIUM...	.00000	[illegible]	[illegible]	[illegible]	[illegible]
5	COBALT....	.00004	[illegible]	[illegible]	[illegible]	[illegible]
6	COPPER....	97.35683	97.55534	97.36133	97.62494	97.06153
7	GOLD.....	~~.16621~~	~~.22543~~	~~.13971~~	~~.21009~~	~~.17515~~
8	IRON.....	.19772	.49454	.36728	[illegible]	.54445
9	LEAD.....	.28695	.38324	.21452	1.03471	.39591
10	MANGANESE	.00004	[illegible]	[illegible]	[illegible]	[illegible]
11	MERCURY...	.05262	.11232	.13449	.35784	.15338
12	NICKEL....	.00000	[illegible]	[illegible]	[illegible]	[illegible]
13	SILVER....	.06611	.05965	.06576	.13470	.06247
14	TIN:.....	.02401	.01431	.02649	.05291	.01471
15	ZINC.....	1.74533	1.13862	1.66979	[illegible]	.67231

A.L.#995
5/20/80

Table 4.

#B1889 - Black surface on Baluster.
#B1890 - Same area after scraping off corrosion layer.
#B1878 - Powdered scrapings removed from Statue (#1 scraping).

Note 1: Since the x-ray fluorescence analyzer does not respond to oxygen and sulfur elements in the corrosion layer, it shows only the metallic elements (copper and lead) in the layer.

Note 2: The high mercury (.36%) in the corrosion layer indicates that the mercury exists only at the surface layer. The mercury may have been deposited from air-borne mercury originating at a nearby factory making fluorescent lamps.

Note 3: The corrosion layer does not contain zinc which is contrary to experience related to the corrosion products of brass. The zinc corrosion products (chlorides and sulfates) are water soluble and were probably leached out.

Note 4: The arsenic, which occurs naturally in most copper ores, did not produce a stable compound in the corrosion layer.

Note 5: The high lead content of the corrosion layer may be a deposit from automobile exhaust gases.

Note 5: Silver in trace amounts is always found in copper which was produced before the advent of electrolytic refining methods.

Statue of Liberty Test Parts

Part - Tubular Ornament or Baluster

TEST LOCATIONS

(Table 4)