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## Quantitative Elemental Analysis of Art Objects by Energy-Dispersive X-ray Fluorescence Spectroscopy

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Victor F. Hanson

*Henry Francis du Pont Winterthur Museum, Winterthur, Delaware 19735*

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Techniques have been developed for the analysis of glass and metal objects for up to 35 elements in a few minutes for aiding the curator in determining the authenticity of many museum objects. No samples are removed nor are the objects altered by the measurements. Trace elements present as impurities in older pieces and absent in modern forgeries as well as the major constituents can be measured with accuracies at least as high as wet chemical and spectrographic methods generally employed in museum laboratories. Tables of instrument response to 71 elements presented together with empirical corrections for matrix effects permit direct calculations of weight percentages within 20% of all the elements present. Employment of reference standards and the use of the principal element as an "internal standard" improve this accuracy to better than 1% of the major elements present. Charts of "peak heights" of the various spectral lines of each element plotted as a function of energy permit a rapid determination of the most probable elements that are present in a spectrum. It also aids in selecting peaks that are free of interference from other elements. Tables of peak heights and energies of the peaks of 71 elements listed in order of atomic number indicate where the spectral peaks of the various elements will be found and what their relative intensity is. Procedures are described for determining weight percent of 15 or more elements in metal and 30 or more in glass objects from spectral data. Examples of analytical results are given for typical museum objects and specially prepared samples.

INDEX HEADINGS: Nondestructive analysis; Art object analysis; Archeological object analysis; Analysis, for elements; Fluorescence; Instrumentation, x-ray; Methods, analytical; X-ray fluorescence.

### INTRODUCTION

The Henry Francis du Pont Winterthur Museum contains a collection of American decorative arts spanning the 200 years from the 17th century through the early 19th century. In a great country house surrounded by a private park of striking beauty are examples of domestic architecture, furniture, textiles, silver, pewter, ceramics, paintings, and prints, shown in almost 200 period rooms and special displays. The thousands of pieces of silver, brass, pewter, glass, and ceramics in the collection have been characterized by date, provenance, maker, style, and other attributes that can be evaluated by the faculties of the human senses. Early in 1960, Charles Montgomery and Charles Hummel of the museum and C. Lalor Burdick of the Lalor Foundation initiated a program to add chemical compositional information to the descriptive information then being provided by the curatorial staff. Results from a joint program with the Department of Chemistry of the University of Delaware, which was being funded by the Copeland-Andelot Foundation, indicated that information of considerable interest to the curatorial and conservation staffs could indeed be obtained from the chemical analysis of museum objects.

In 1966, plans submitted by staff to Henry Francis du Pont for approval of a new research building included a laboratory provided with instruments for analyzing various museum objects. Naturally there was a great concern for methods then in use that required the removal of samples for analysis.

The energy-dispersive x-ray fluorescence analyzer, which was developed in the 1960's as a qualitative analysis instrument, showed promise of being adaptable for quantitative analysis. We therefore selected this as the primary instrument when the laboratory was completed in 1969.

### I. EXPERIMENTAL

#### A. Description of the Energy-Dispersive X-ray Fluorescence Analyzer

A combination of electronic components made by the KeveX Corporation, Packard Instrument Company, and Hewlett Packard was selected since this appeared to provide the flexibility which would be required for the development of quantitative techniques applicable to a wide range of materials.

The instrument (Fig. 1) employs radioactive x-ray emitters to excite the atoms in an object which is placed

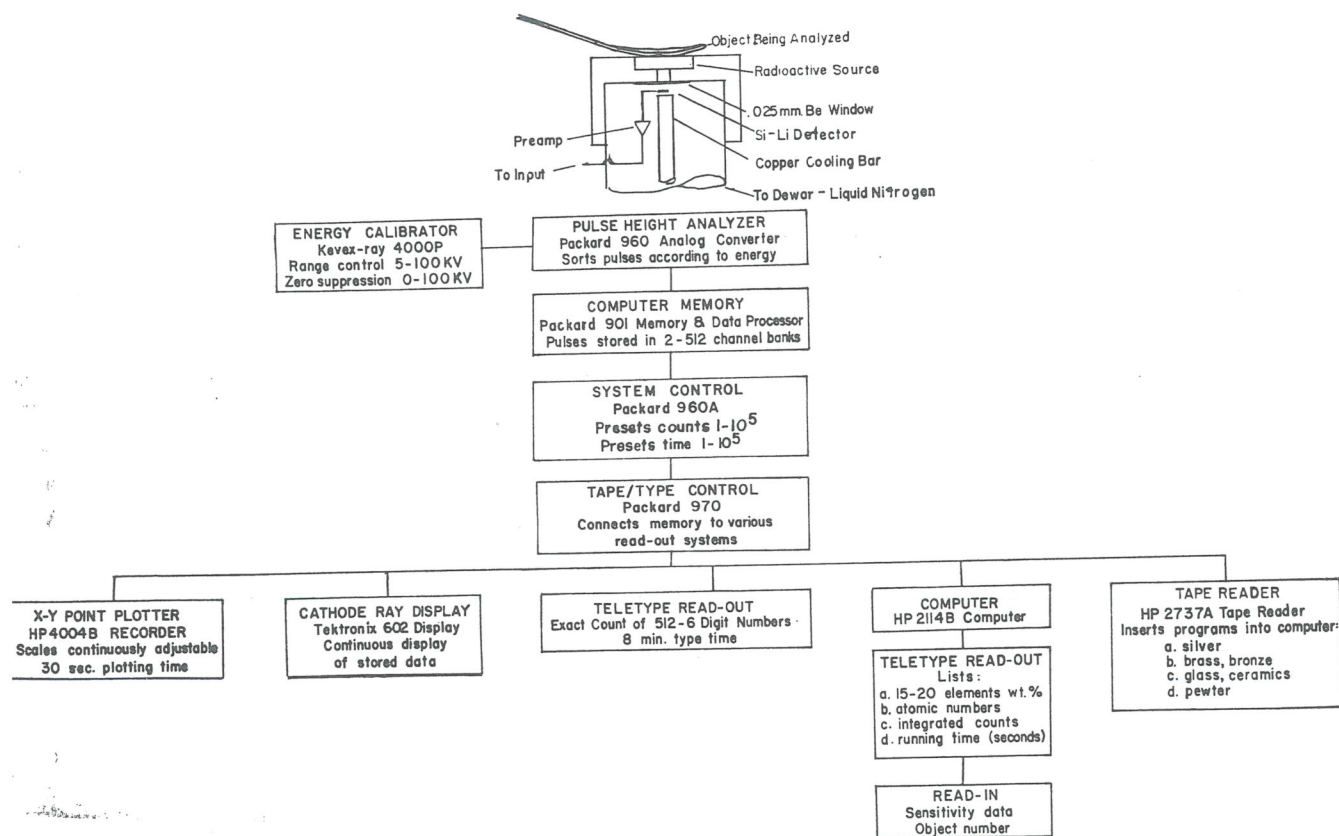


FIG. 1. Block diagram of analyzer system.

about 2 cm from the ring-shaped radiation source. The object is not altered by the measurement nor is there a radiation hazard since the sources are weak and of low penetration power. The elements in the object fluoresce at energies characteristic of those elements. X-rays from the sample pass through a 7-mm hole in the source holder, thence through a 0.025-mm beryllium window to a lithium-doped silicon detector which is maintained at liquid nitrogen temperature. The x-rays from the object produce electrical pulses proportional to the energy of those x-rays. The pulses from the detector are amplified linearly, sorted, and stored in one of two 512-channel memory banks. Each channel has a capacity of a million counts. The contents of the memory banks are continually displayed on an oscilloscope and can be printed out digitally on a teletypewriter or an X-Y plotter at any time. Since counts from all the elements present in the object are accumulated simultaneously, the typical analysis time is in the 5 to 15 min range for up to 30 or more elements.

### B. Development of Quantitative Techniques

The efficiency of the conversion of the x-rays from the radioactive source to fluorescence x-rays in the sample to electrical pulses in the detector varies with the source employed and the competition between the various elements present. For example, when elements of contiguous atomic numbers are present such as nickel, copper, and zinc in German silver, there are several internal fluorescence energy transfers so that the lower energy

fluorescence of the nickel is enhanced at the expense of the copper and zinc, as illustrated in Fig. 2, a, b, and c. This and other complications dictate that reference standards be employed if quantitative results are to be obtained.

Accordingly, we had brass and silver alloy castings made which would span the ranges of compositions that we expected to encounter. Table I lists the silver standards and Table II the brass standards which were prepared for us by Handy and Harman of Fairfield, Connecticut. The alloys, which were induction-melted, were cast in chilled copper molds to minimize segregation of the elements during the cooling cycle. The effect of segregation will be noted from the difference in composition of the chilled face at the top of the casting which was the last part to solidify. While we hoped to check our calibration by using silver coins, we found 0.67% difference in the nominal 10% copper content on the two sides of a 1944 U.S. coin because of segregation of the elements in the original cast billet. We finally adopted Ref. No. 47.4 arbitrarily as our silver reference standard. Subsequently, Dr. George Reilly of this Laboratory made 42 duplicate runs over a 2-week period on our silver reference 47.4 with the following results:

	Silver (%)	Copper (%)	Gold (%)
$\bar{X}$ (Arithmetic mean)	92.64	6.85	0.4888
$\bar{d}$ (Average deviation)	0.14	0.09	0.0207
$S$ (Standard deviation)	0.17	0.14	0.0265
Confidence limits <sup>99</sup>	0.08	0.06	0.012
Percentage	92.64 ± 0.08	6.85 ± 0.06	0.49 ± 0.01

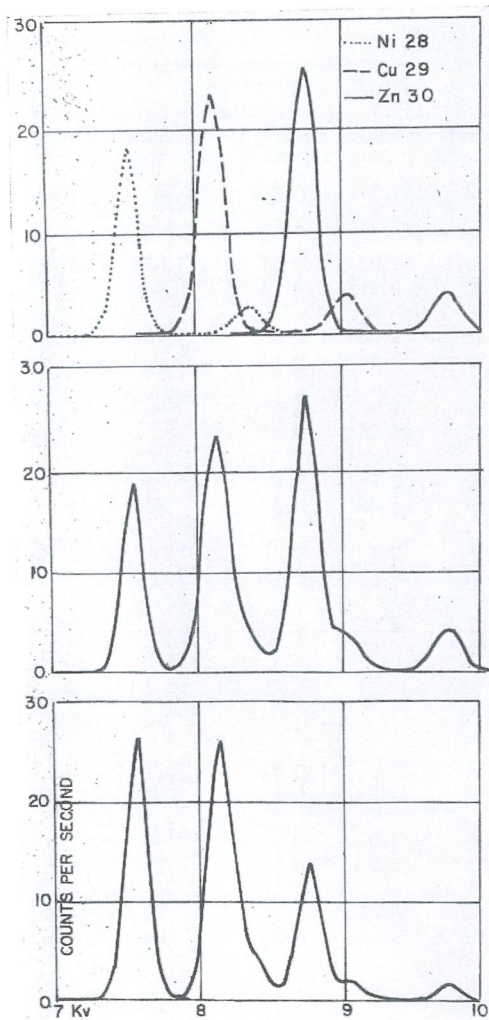


Fig. 2. Fluorescence energy transfer between elements. a (upper), spectra of nickel, copper, and zinc, atomic numbers 28, 29, and 30, each irradiated and recorded separately for 100 sec. Note the sensitivity of the instrument is highest for zinc, intermediate for copper, and lowest for nickel. b (middle), spectra of nickel, copper, and zinc each irradiated for 100 sec and the accumulated spectra plotted showing the additive effects of the overlapping peaks. The ordinates of the curves are the arithmetic sums of those shown in part a. c (lower), spectra of an alloy of 33.3% Ni, 33.3% Cu, and 33.3% Zn irradiated for 300 sec.

	Ni	Cu	Zn	Zn	Total count
Energy, kV	7.6	8.2	8.7	9.7	
Peak heights (b)	3.8	4.7	5.4	1.0	175 K
Peak heights (c)	5.3	5.2	2.7	0.4	160 K

Note that over half the radiation from zinc indicated in part b has been transferred to copper and nickel with a net loss of only 10% of the total counts. This highly efficient energy transfer process illustrates the importance of having reference standards approximately the composition of the objects being analyzed if quantitative results are to be achieved.

These results gave us confidence that quantitative results could be obtained which are as reliable as our reference standards.

It then became clear that we would frequently be more interested in trace elements than in the major elements, especially when analyzing glass and ceramic ob-

TABLE I

A. Silver series: Reference standards.<sup>a</sup>

Ref. No.	Weighed in (%)			Analyzed values, chilled side †			Analyzed values, top side		
	Ag	Cu	Au ‡	Ag	Cu	Au	Ag	Cu	Ag
47.1	92.5	7.5	0.00	92.2	7.7	0.00	93.4	6.6	0.00
47.2	92.5	7.4	0.10	92.5	7.3	0.08	93.8	6.0	0.05
47.3	92.5	7.3	0.20	92.4	7.4	0.14	93.7	5.8	0.16
47.4	92.5	7.0	0.50	92.5	7.0	0.50	93.8	5.3	0.45
47.5	90.0	10.0	0.00	88.4	12.1	0.00	89.5	11.8	0.00
47.6	95.0	5.0	0.00	94.5	5.6	0.00	95.8	4.1	0.00
47.7	85.0	15.0	0.00	81.5	18.6	0.00	87.4	12.6	0.00

<sup>a</sup> Analysis results of "Reference Standards" cast blocks. The chilled side of 47.4 was selected as the arbitrary reference standard.

B. 1944 U.S. silver half-dollar.

	Ag	Cu	Au
Specifications	90	10	0.00
Heads	90.4	9.22	0.00
Tails	89.8	9.89	0.00

TABLE II. Brass series: Reference standards.<sup>a</sup>

Ref. No.	Weighed in %			Analyzed values, chilled side			Analyzed values, top side		
	Cu	Zn	Ag	Cu	Zn	Ag	Cu	Zn	Ag
29.1	80.0	20.0	0.00	80	20.2	0.00	82.0	18.6	0.004
29.2	70.0	30.0	0.00	71.1	28.9	0.005	71.0	29.6	0.006
29.3	60.0	40.0	0.00	69.5	38.5	0.006	62.0	37.0	0.010
29.4	75.0	25.0	0.00	73.4	25.3	0.010	77.5	22.9	0.008
29.5	75.0	24.9	0.10	75.8	24.0	0.105	77.5	22.9	0.160
29.6	75.0	24.8	0.20	76.8	23.6	0.202	78.0	22.4	0.155
29.7	75.0	24.5	0.50	75.0	24.5	0.50	77.2	23.1	0.400
29.7 <sup>b</sup>				74.5	25.2	0.47			
29.7 <sup>c</sup>				75.5	25.0	0.42			

<sup>a</sup> Analysis results of "reference standards" 25- × 32- × 12-mm cast brass blocks. The chilled face of Ref. 29.7 was selected to be the arbitrary reference standard. A slice 8 mm from the chilled face was cut by a hacksaw. The analysis of the intermediate face is given in the second from the bottom row and values from 32 mg of the cuttings are given in the bottom row.

<sup>b</sup> Section 8 mm from chilled face.

<sup>c</sup> 32-mg chips from interface.

jects. Here, too, we could expect overlapping peaks from some major elements to obscure the peaks from other elements at low concentration. We could also expect internal fluorescence energy transfer from peaks of one element to lower lying absorption edges of nearby elements.

While tables of emission energies of the various elements were available<sup>1</sup> at the outset, no clues were provided as to the relative intensities of the various peaks from a single element. ASTM subsequently published an elaborate set of tables listing emission energies of 92 elements which are quite useful in exploratory work.<sup>2</sup> The intensities of the peaks are a function of the excitation source, sample geometry, and matrix effects, to name a few. We procured a few high purity samples of the elements that interested us in studies of brass and silver objects. However, after finding many "strange" peaks in old glass and metal objects which we were unable to identify, we obtained samples of the remaining elements we expected to encounter in our metal and glass studies to verify the elements responsible for the strange peaks.

TABLE III. Sensitivity data: Kevex energy-dispersive x-ray analyzer.

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts
11 Na	K $\beta_1$	1.07	89	1.07	0.001	22	1.1	0.2	51	1.04	0.01
Sodium	K $\alpha_2$	1.04	87	1.04	0.001						
12 Mg	K $\beta_1$	1.30	107	1.28	0.01	33	1.65	0.15	65	1.3	0.01
Magnesium	K $\alpha_2$	1.25	105	1.25	0.08	26	0.18	0.18			
13 Al	K $\beta_1$	1.56	134	1.60	0.01	31	1.55	0.06	78	1.5	0.01
Aluminum	K $\alpha_2$	1.49	124	1.49	0.05	28	1.4	0.14			
14 Si	K $\beta_1$	1.83	147	1.8	0.43	38	1.9	0.46	88	1.7	0.06
Silicon	K $\alpha_2$	1.74	144	1.73	0.43	35	1.75	0.23			
15 P	K $\beta_1$	2.14	175	2.10	1.6	42	2.1	0.5	42	2.1	0.5
Phosphorus	K $\alpha_2$	2.01	167	2.0	1.7	39	1.95	0.5	37	1.9	0.6
16 S	K $\beta_1$	2.46	200	2.4	0.7	48	2.4	0.17	136	2.72	0.02
Sulfur	K $\alpha_2$	2.30	194	2.30	5.8	46	2.3	0.12			
17 Cl	K $\beta_1$	2.82	240	2.88	0.5	57	2.85	0.12			
Chlorine	K $\alpha_2$	2.62	227	2.72	4.8	51	2.55	0.1	133	2.67	0.02
18 Ar	K $\beta_1$	3.19			0.1				50	3.0	0.01
Argon	K $\alpha_2$	2.96	245	2.95	0.6						
19 K	K $\beta_1$	3.59	302	3.62	0.6	74	3.7	0.12	71	3.6	0.3
Potassium	K $\alpha_2$	3.31	282	3.38	6.0	66	3.3	0.1	64	3.2	0.5
20 Ca	K $\beta_1$	4.01	339	4.06	7.5	80	4.0	0.1	80	4.0	0.5
Calcium	K $\alpha_2$	3.69	314	3.7	50.0	73	3.7	0.3	71	3.6	4.0
21 Sc	K $\beta_1$	4.46	381	4.56	4.0	89	4.45	0.4	88	4.4	1.8
Scandium	K $\alpha_2$	4.09	349	4.18	24.5	80	4.1	0.6	80	4.0	12.5
22 Ti	K $\beta_1$	4.93	409	5.0	16	100	5.0	1.0	98	4.9	8
Titanium	K $\alpha_2$	4.51	374	4.6	114	90	4.5	4.5	89	4.5	49
23 V	K $\beta_1$	5.43	456	5.6	13	111	5.5	1.3	103	5.40	11
Vanadium	K $\alpha_2$	4.94	416	5.0	87	93	4.65	6.0	93	4.65	66
	L $\gamma_1$										
	L $\beta_2$										
	L $\beta_1$										
	L $\alpha_1$	0.52									
	L $\alpha_2$	0.51									
24 Cr	K $\beta_1$	5.95	500	6.0	1.0	120	6.05	1.3	118	5.9	15
Chromium	K $\alpha_2$	5.41	450	5.5	33	109	5.45	10.4	105	5.4	99
25 Mn	K $\beta_1$	6.49				131	6.55	2.0	130	6.5	17
Manganese	K $\alpha_2$	5.90	491	5.9	7.0	119	5.95	13.3	118	5.9	104
	L $\gamma_1$										
	L $\beta_2$										
	L $\beta_1$	0.65									
	L $\alpha_1$	0.64									
26 Fe	K $\beta_1$	7.06				143	7.1	2.0	141	7.1	23
Iron	K $\alpha_2$	6.40				128	6.4	14.0	128	6.4	148
	L $\gamma_1$										
	L $\beta_2$										
	L $\beta_1$	0.72		0.72	0.001						
	L $\alpha_1$	0.70									
27 Co	K $\beta_1$	7.65				148	7.6	3.6	148	7.6	25
Cobalt	K $\alpha_2$	6.92				139	6.95	18	133	6.9	159
	L $\gamma_1$										
	L $\beta_2$										
	L $\beta_1$	0.79									
	L $\alpha_1$	0.78									
28 Ni	K $\beta_1$	8.26				167	8.30	5.0	166	8.3	33
Nickel	K $\alpha_2$	7.48				151	7.50	30.0	150	7.5	205

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Ccunts	Channel	Energy	Counts
Nickel	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	0.87		0.87	0.001						
	L <sub>α1</sub>	0.85									
29 Cu	K <sub>β1</sub>	8.9				180	8.9	7.0	180	9.0	39
Copper	K <sub>α2</sub>	8.02				163	8.15	40.0	161	8.1	243
Copper	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	0.95		0.95	0.001				50	1.1	0.2
30 Zn	K <sub>β1</sub>	9.6				194	9.6	8.7	193	9.6	44
Zinc	K <sub>α2</sub>	8.6				173	8.65	51.0	174	8.7	274
Zinc	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.03		1.03	0.001				62	1.2	0.02
	L <sub>α1</sub>	1.01									
31 Ga	K <sub>β1</sub>	10.3				208	10.3	8.9	207	10.3	45.0
Gallium	K <sub>α2</sub>	9.2				187	9.30	51.0	186	9.3	273.0
Ga <sub>2</sub> O <sub>3</sub>	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.12									
	L <sub>α1</sub>	1.10	89	1.1	0.01						
32 Ge	K <sub>β1</sub>	11.0				215	11.0	11	215	10.7	44
Germanium	K <sub>α2</sub>	9.9				193	9.9	59	193	9.95	273
Germanium	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.22							70	1.4	0.02
	L <sub>α1</sub>	1.19	111	1.13	0.10						
	L <sub>α2</sub>										
							9.2	15			
33 As	K <sub>β1</sub>	11.7				237	11.8	13.0	237	11.8	44
Arsenic	K <sub>α2</sub>	10.5				213	10.6	68.0	212	10.6	244
Arsenic	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.32		1.3	0.001				28	1.4	0.01
	L <sub>α1</sub>	1.28									
34 Se	K <sub>β1</sub>	12.5				252	12.6	11.0	252	12.6	49
Selenium	K <sub>α2</sub>	11.2				226	11.3	89.0	226	11.3	306
Selenium	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.42	127	1.5	0.01				28	1.4	0.01
	L <sub>α1</sub>	1.38	113	1.35	0.01						
35 Br	K <sub>β1</sub>	13.3				268	13.4	13.0	269	13.3	49
Bromine	K <sub>α2</sub>	11.9				240	12.0	61.0	242	12.0	254
KBr	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.53	132	1.58	0.1	33	1.7	0.50	32	1.6	0.01
	L <sub>α1</sub>	1.48	130	1.5	0.10						
37 Rb	K <sub>β1</sub>	15.0				302	15.1	21.0	300	15	47
Rubidium	K <sub>α2</sub>	13.3				270	13.5	99.0	268	13.4	274
RbCl	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.75	145	1.74	0.02	41	2.05	0.07			
	L <sub>α1</sub>	1.69	142	1.72	0.01	37	1.85	0.06			
38 Sr	K <sub>β1</sub>	15.83				319	15.9	17.0	320	16.0	48
Strontium	K <sub>α2</sub>	14.1				285	14.2	86.0	286	14.3	263
SrCl <sub>2</sub>	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	1.87	160	1.9	0.3	42	2.1	0.10	40	2.0	0.3
	L <sub>α1</sub>	1.80	156	1.8	0.4						
	L <sub>α2</sub>			1.95	0.15						
39 Y	K <sub>β1</sub>	16.7				337	16.8	32.0	340	16.8	53
Yttrium	K <sub>α2</sub>	14.9				300	15.0	142.0	303	15.0	303
Y <sub>2</sub> O <sub>3</sub>	L <sub>γ1</sub>										
	L <sub>β2</sub>										
	L <sub>β1</sub>	2.0	166	2.0	3.5	42	2.1	0.2	52	2.6	0.1
	L <sub>α1</sub>	1.9	163	1.9	1.0				46	2.3	0.1

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts
40 Zr	Kβ <sub>1</sub>	17.7				356	17.8	34.0	358	17.8	51
Zirconium	Kα <sub>2</sub>	15.7				317	15.9	162.0	319	15.9	305
Zirconium	Lγ <sub>1</sub>	2.3	192	2.3	0.5						
	Lβ <sub>2</sub>	2.2	184	2.2	0.7				50	2.5	0.4
	Lβ <sub>1</sub>	2.1	175	2.1	0.7	43	2.15	0.01			
	Lα <sub>1</sub>	2.04	170	2.0	0.1						
	Lα <sub>2</sub>										
	Peak		176	2.1	0.7						
41 Nb	Kβ <sub>1</sub>	18.6				369	18.8	30	370	18.6	48
Niobium	Kα <sub>2</sub>	16.5				328	16.7	149	328	16.6	274
Niobium	Lγ <sub>1</sub>	2.46	205	2.5	0.10	54	2.7	0.2	50	2.5	0.3
	Lβ <sub>2</sub>	2.37	198	2.4	0.50						
	Lβ <sub>1</sub>	2.25	186	2.3	0.52						
	Lα <sub>1</sub>	2.16	180	2.2	0.43				41	2.1	0.3
42 Mo	Kβ <sub>1</sub>	19.6				395	19.7	31.0	398	19.7	50
Molybdenum	Kα <sub>2</sub>	17.4				351	17.5	159.0	354	17.5	281
Molybdenum	Lγ <sub>1</sub>	2.62	218	2.6	0.7	52	2.6	0.1	59	2.9	0.03
	Lβ <sub>2</sub>	2.52	210	2.5	0.7						
	Lβ <sub>1</sub>	2.4	200	2.4	2.4				49	2.5	0.02
	Lα <sub>1</sub>	2.3	192	2.3	2.5						
	Lα <sub>2</sub>					46	2.3	0.20			
44 Ru	Kβ <sub>1</sub>	21.7				437	21.7	6.8	435	21.7	27.2
Ruthenium	Kα <sub>2</sub>	19.3				389	19.4	38.0	386	19.3	150
(NH <sub>4</sub> ) <sub>2</sub> RuCl <sub>5</sub>	Lγ <sub>1</sub>	2.96	250	3.0	0.5	59	2.9	0.02	58	2.9	0.01
	Lβ <sub>2</sub>	2.84	232	2.8	1.5	56	2.8	0.1			
	Lβ <sub>1</sub>	2.68	223	2.7	5.5				51	2.6	0.6
	Lα <sub>1</sub>	2.55	216	2.59	2.5						
	Lα <sub>2</sub>					55	2.57	0.25			
45 Rh	Kβ <sub>1</sub>	22.7				459	22.9	14.00	450	22.7	9.0
Rhodium	Kα <sub>2</sub>	20.1				407	20.3	76.00	410	20.1	71.0
(NH <sub>4</sub> ) <sub>3</sub> RhCl <sub>5</sub>	Lγ <sub>1</sub>	3.14	265	3.2	0.5	61	3.1	0.3	64	3.2	0.01
	Lβ <sub>2</sub>	3.01	250	3.0	1.5						
	Lβ <sub>1</sub>	2.83	233	2.8	3.5	57	2.9	0.02	58	2.9	0.2
	Lα <sub>1</sub>	2.70	225	2.7	5.0	55	2.7	0.2	53	2.6	0.03
	Lα <sub>2</sub>	2.69									
									461	23.1	12
46 Pd	Kβ <sub>1</sub>	23.9				480	24.0	20.0	484	24.1	15
Palladium	Kα <sub>2</sub>	21.2				426	21.3	107.0	429	21.2	82
Palladium	Lγ <sub>1</sub>	3.3	275	3.3	0.8	66	3.3	0.1	65	3.3	0.1
	Lβ <sub>2</sub>	3.17	255	3.1	2.5	63	3.1	0.1	62	3.1	0.4
	Lβ <sub>1</sub>	2.99	239	3.0	6.0				60	3.0	1.6
	Lα <sub>1</sub>	2.84	236	2.8	8.0	56	2.8	0.2	54	2.7	2.0
	Lα <sub>2</sub>										
						291	24.6	3.5	449	22.5	4.6
47 Ag	Kβ <sub>1</sub>	25.0				304	25.0	40.0	507	25.3	2.5
Silver	Kα <sub>2</sub>	22.0				247	22.1	200.0	484	22.4	15.0
Silver	Lγ <sub>1</sub>	3.52	294	3.5	1	72	3.6	0.3	70	3.5	0.1
	Lβ <sub>2</sub>	3.35	280	3.4	2	67	3.3	0.3	67	3.3	0.2
	Lβ <sub>1</sub>	3.15	255	3.1	6	64	3.2	1.0	64	3.2	1.2
	Lα <sub>1</sub>	3.0	243	2.9	10	58	2.9	1.0	61	3.1	1.3
	Lα <sub>2</sub>								416	20.8	1.5
						314	25.7	7.0	108	25.5	0.5
48 Cd	Kβ <sub>1</sub>	26.1				329	26.2	26.0	122	26.1	1.0
Cadmium	Kα <sub>2</sub>	23.0				466	23.3	128.8	471	23.2	6.0
Cadmium	Lγ <sub>1</sub>	3.7	320	3.8	0.6	74	3.7	0.9	74	3.7	0.1
	Lβ <sub>2</sub>	3.5	298	3.6	2.2	70	3.5	1.2	70	3.5	0.2
	Lβ <sub>1</sub>	3.3	284	3.4	7.0	66	3.3	0.1	65	3.3	0.5
	Lα <sub>1</sub>	3.1	269	3.2	12.0	62	3.1	0.2	61	3.1	0.7
	Lα <sub>2</sub>										
						338	26.8	4.5	136	26.8	1.0
49 In	Kβ <sub>1</sub>	27.3				351	27.6	21.0	141	27.3	1.1
Indium	Kα <sub>2</sub>	24.0				486	24.3	136.0	83	24.1	5.0
Indium	Lγ <sub>1</sub>	3.9	325	3.9	1.0	78	3.9	0.9	78	3.9	0.1
	Lβ <sub>2</sub>	3.7	308	3.7	3.0	75	3.7	0.6	74	3.7	0.1
	Lβ <sub>1</sub>	3.5	292	3.5	8.0	70	3.5	1.3	69	3.5	0.8
	Lα <sub>1</sub>	3.3	276	3.3	11.5	67	3.3	1.8	63	3.2	1.5
	Lα <sub>2</sub>										
						364	28.2	6.0	162	28.1	0.3
			347	4.1	0.2						

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd			
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts	
50 Tin	Sn	Kβ <sub>1</sub>	28.4			376	28.6	35.0	171	28.5	1.5	
		Kα <sub>2</sub>	25.0			310	25.3	173.0	104	25.2	5.0	
	Tin	Lγ <sub>1</sub>	4.1	355	4.1	0.5	82	4.1	0.3	82	4.1	0.1
		Lβ <sub>2</sub>	3.9	334	3.9	1.3	78	3.9	0.4	78	3.9	0.1
		Lβ <sub>1</sub>	3.6	314	3.75	12.0	72	3.6	0.7	72	3.7	2.0
		Lα <sub>1</sub>	3.4	383	3.5	18.0	68	3.4	0.9	67	3.4	1.5
		Lα <sub>2</sub>										
					389	29.4	7.0	185	29.2	0.4		
						24.7	4.0					
						39.2	6.0					
51 Antimony	Sb	Kβ <sub>1</sub>	29.7			404	29.8	36	403	29.8	0.9	
		Kα <sub>2</sub>	26.1			335	26.3	125	334	26.3	4.0	
	Antimony	Lγ <sub>1</sub>	4.3	366	4.4	0.5	86	4.3	0.2	93	4.7	0.1
		Lβ <sub>2</sub>	4.1	345	4.2	3.5	80	4.0	0.3	83	4.1	0.4
		Lβ <sub>1</sub>	3.8	326	3.9	14.0	78	3.8	1.3	76	3.8	1.5
		Lα <sub>1</sub>	3.6	307	3.7	19.0	72	3.6	1.8	70	3.5	1.3
		Lα <sub>2</sub>										
					415	30.7	6.0	210	30.5	0.1		
					427	31.2	27.0	238	31.2	0.2		
52 Tellurium	Te	Kβ <sub>1</sub>	31.0			335	27.6	132.0	160	27.4	3.0	
		Kα <sub>2</sub>	27.2			92	4.6	0.2	93	4.5	0.1	
	TeO <sub>2</sub>	Lγ <sub>1</sub>	4.57	385	4.5	0.5	88	4.4	0.4	83	4.2	0.5
		Lβ <sub>2</sub>	4.3	361	4.3	2.5	80	4.0	1.0	82	4.1	1.5
		Lβ <sub>1</sub>	4.03	340	4.0	8.0	74	3.7	1.5	77	3.8	0.9
		Lα <sub>1</sub>	3.77	319	3.8	12.0						
		Lα <sub>2</sub>	3.76									
					441	31.9	5.5	237	31.8	0.1		
					453	32.5	24.0	250	32.4	0.6		
53 Iodine	I	Kβ <sub>1</sub>	32.3			379	28.6	114.0	174	28.7	4.0	
		Kα <sub>2</sub>	28.3			97	4.9	0.4	98	4.9	0.3	
	Iodine	Lγ <sub>1</sub>	4.8	403	4.9	1.3	93	4.6	0.6	94	4.7	0.4
		Lβ <sub>2</sub>	4.5	375	4.5	3.8	83	4.2	1.5	82	4.1	2.0
		Lβ <sub>1</sub>	4.2	356	4.3	13	76	3.8	2.5	76	3.8	1.8
		Lα <sub>1</sub>	3.9	332	4.0	18						
		Lα <sub>2</sub>	3.9									
					469	33.2	5.0	262	33.2	0.1		
					319	35.2	23.0	303	35.1	0.8		
55 Cesium	Cs	Kβ <sub>1</sub>	35.0			235	31.1	106.0	322	31.1	3.5	
		Kα <sub>2</sub>	30.6			105	5.3	0.8	106	5.3	0.3	
	CsCl	Lγ <sub>1</sub>	5.28	444	5.3	1.0	98	4.9	1.5	98	4.9	0.6
		Lβ <sub>2</sub>	4.9	406	4.9	4.0	92	4.6	2.5	92	4.6	2.5
		Lβ <sub>1</sub>	4.6	380	4.6	15.0	83	4.2	2.5	85	4.3	2.5
		Lα <sub>1</sub>	4.3	362	4.3	20.0						
		Lα <sub>2</sub>	4.3									
					338	36.1	5.0	322	36.1	0.2		
					348	36.6	20.0	332	36.6	0.6		
56 Barium	Ba	Kβ <sub>1</sub>	36.4			261	32.3	92.0	240	32.0	3.0	
		Kα <sub>2</sub>	31.8			110	5.5	1.0	115	5.7	0.3	
	BaCO <sub>3</sub>	Lγ <sub>1</sub>	5.5	467	5.5	0.4	101	5.1	0.3	102	5.1	1.0
		Lβ <sub>2</sub>	5.2	435	5.2	5.0	95	4.7	3.0	97	4.8	6.0
		Lβ <sub>1</sub>	4.8	407	4.8	15.0	88	4.4	0.6	88	4.4	5.0
		Lα <sub>1</sub>	4.5	377	4.5	25.0						
		Lα <sub>2</sub>	4.4									
					368	37.4	4.0	353	37.6	0.2		
					357	37.8	17.0	356	38.1	0.6		
57 Lanthanum	La	Kβ <sub>1</sub>	37.80			270	33.5	83.0	268	33.6	3.0	
		Kα <sub>2</sub>	33.2			115	5.7	0.8	115	5.8	0.4	
	LaB <sub>6</sub>	Lγ <sub>1</sub>	5.79	488	5.8	3.0	107	5.4	1.5	106	5.3	1.5
		Lβ <sub>2</sub>	5.38	451	5.4	6.0	100	5.0	2.5	100	5.0	5.0
		Lβ <sub>1</sub>	5.04	425	5.1	20.0	92	4.6	3.0	91	4.6	5.0
		Lα <sub>1</sub>	4.65	389	4.7	27.0						
		Lα <sub>2</sub>	4.64									
					344	4.13	1.0	380	39.0	0.2		
					406	39.5	17.0	412	39.6	0.3		
58 Cerium	Ce	Kβ <sub>1</sub>	39.3			306	34.8	49.0	290	34.4	1.5	
		Kα <sub>2</sub>	34.3			124	6.2	0.4	123	6.2	0.3	
	Ce <sub>2</sub> O <sub>3</sub>	Lγ <sub>1</sub>	6.1	494	5.9	3.0	112	5.6	1.2	113	5.6	1.5
		Lβ <sub>2</sub>	5.6	470	5.6	7.0	106	5.3	3.0	106	5.3	8.3
		Lβ <sub>1</sub>	5.26	441	5.3	2.2	97	4.8	4.0	98	4.9	7.0
		Lα <sub>1</sub>	4.84	405	4.85	32.0						
		Lα <sub>2</sub>	4.82									
					427	40.3	3.0	412	40.6	0.5		
					291	34.6	20.0	301	35.0	2.5		



TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts
59 Pr Praseodymium Pr <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	40.7				435	41.0	12.0	420	41.2	0.2
	Kα <sub>2</sub>	35.5				333	36.2	43.0	323	36.2	2.5
	Lγ <sub>1</sub>	6.3				126	6.3	0.2	126	6.4	0.3
	Lβ <sub>2</sub>	5.85	48	5.8	1.1	118	5.8	1.0	118	5.9	2.0
	Lβ <sub>1</sub>	5.5	456	5.5	15.0	110	5.5	1.0	111	5.5	9.4
	Lα <sub>1</sub>	5.03	423	5.03	10.0	100	5.0	2.0	100	5.0	9.0
	Lα <sub>2</sub>	5.02									
						456	42.1	3.0	442	42.1	0.1
60 Nd Neodymium Nd <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	42.3				315	35.7	20.0	315	35.7	1.3
	Kα <sub>2</sub>	36.8				465	42.5	10.0	450	42.5	0.02
	Lγ <sub>1</sub>	6.6				370	37.5	20.0	352	37.0	0.06
	Lβ <sub>2</sub>	6.1				132	6.6	0.3	133	6.6	0.3
	Lβ <sub>1</sub>	5.7	472	5.7	8.3	121	6.1	0.9	121	6.0	0.3
	Lα <sub>1</sub>	5.2	440	5.2	10.0	116	5.8	3.0	115	5.7	9.0
	Lα <sub>2</sub>	5.2				105	5.2	3.0	104	5.2	9.0
						471	43.6	3.0			
62 Sm Samarium Sm <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	45.4				340	37.0	10.0	354	37.7	0.12
	Kα <sub>2</sub>	40.1				308	45.4	9.0	308	45.4	0.4
	Lγ <sub>1</sub>	7.2				202	40.1	44.0	202	40.1	2.0
	Lβ <sub>2</sub>	6.6				144	7.2	1.2	143	7.2	1.8
	Lβ <sub>1</sub>	6.2				135	6.6	3.0	131	6.6	5.0
	Lα <sub>1</sub>	5.6				124	6.2	7.0	123	6.2	19.0
	Lα <sub>2</sub>	5.6				112	5.6	8.0	111	5.6	18.0
						149	7.5	0.8	149	7.5	1.2
63 Eu Europium Eu <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	47.0				190	39.5	26.0	190	39.5	1.2
	Kα <sub>2</sub>	40.9				168	38.4	1.3			
	Lγ <sub>1</sub>	7.48				332	46.6	2.3	330	46.5	0.1
	Lβ <sub>2</sub>	6.84				343	47.1	10	141	47.1	0.40
	Lβ <sub>1</sub>	6.46				218	40.8	35	28	41.2	1.9
	Lα <sub>1</sub>	5.85	496	5.84	5.0	149	7.4	0.8	152	7.6	1.6
	Lα <sub>2</sub>	5.82				137	6.8	1.0	140	7.0	4.0
						129	6.4	7.0	130	6.5	16.0
64 Gd Gadolinium Gd <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	48.7				117	5.8	10.0	117	5.8	16.0
	Kα <sub>2</sub>	42.3							115	5.7	1.0
	Lγ <sub>1</sub>	7.8				231	41.5	60.0	437	41.8	2.2
	Lβ <sub>2</sub>	7.1				368	48.2	3.0	166	48.3	0.1
	Lβ <sub>1</sub>	6.7				412	48.6	11.5	173	48.7	0.5
	Lα <sub>1</sub>	6.0	512	6.1	2.0	302	42.0	36.1	58	42.3	1.7
	Lα <sub>2</sub>	6.03				157	7.9	1.5	157	7.8	1.0
						141	7.1	3.9	143	7.2	5.0
65 Tb Terbium Tb <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	50.4				134	6.7	6.0	135	6.8	21
	Kα <sub>2</sub>	43.7				120	6.0	10.0	121	6.1	20
	Lγ <sub>1</sub>	8.1							110	5.5	2.0
	Lβ <sub>2</sub>	7.4				287	43.3	51.0	60	43.0	2.0
	Lβ <sub>1</sub>	7.0				435	51.7	3.0	205	50.2	0.2
	Lα <sub>1</sub>	6.27				410	50.5	10.0	208	50.4	0.5
	Lα <sub>2</sub>	6.25				277	43.8	28.0	88	43.7	1.0
						162	8.1	1.4	164	8.2	1.5
66 Dy Dysprosium Dy <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	52.2				147	7.4	3.0	158	7.9	5.0
	Kα <sub>2</sub>	45.2				140	7.0	6.0	148	7.4	24.0
	Lγ <sub>1</sub>	8.4				125	6.3	10.0	140	7.0	26.0
	Lβ <sub>2</sub>	7.6							125	6.3	2.2
	Lβ <sub>1</sub>	7.2				291	44.5	47.0	90	44.5	2.0
	Lα <sub>1</sub>	6.5				441	52.1	2.0	235	51.8	0.1
	Lα <sub>2</sub>	6.46				444	52.2	8.0	241	52.2	0.4
						306	45.3	26.0	120	45.2	1.0
67 Ho Holmium Ho <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	53.9				168	8.4	1.8	169	8.5	2.0
	Kα <sub>2</sub>	46.7				152	7.6	4.0	153	7.6	5.0
	Lγ <sub>1</sub>	8.7				145	7.3	8.0	145	7.3	26.0
	Lβ <sub>2</sub>	7.6				130	6.5	12.0	130	6.5	25.0
	Lβ <sub>1</sub>	7.2							116	5.8	2.5
	Lα <sub>1</sub>	6.5				346	46.1	47.0	120	46.0	1.0
	Lα <sub>2</sub>	6.46				475	53.7	2.5	273	53.8	0.1
						277	53.4	8.0	279	53.9	0.3
68 Er Erbium Er <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	53.9				133	46.7	22	134	46.7	0.8
	Kα <sub>2</sub>	46.7				175	8.7	2.0	176	8.8	2.5
	Lγ <sub>1</sub>	8.7									
69 Tm Thulium Tm <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	53.9									
	Kα <sub>2</sub>	46.7									
	Lγ <sub>1</sub>	8.7									
70 Yt Ytterbium Yb <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	53.9									
	Kα <sub>2</sub>	46.7									
	Lγ <sub>1</sub>	8.7									
71 Lu Lutetium Lu <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	53.9									
	Kα <sub>2</sub>	46.7									
	Lγ <sub>1</sub>	8.7									

TABLE I

Elem

68  
Erbium  
Er<sub>2</sub>O<sub>3</sub>

69  
Thulium  
Tm<sub>2</sub>O<sub>3</sub>

70  
Ytterbium  
Yb<sub>2</sub>O<sub>3</sub>

71  
Lutetium  
Lu<sub>2</sub>O<sub>3</sub>

7  
Lu

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts
68 Er Erbium Er <sub>2</sub> O <sub>3</sub>	Lβ <sub>2</sub>	7.9				157	7.9	4.0	159	8.0	6.0
	Lβ <sub>1</sub>	7.5				151	7.6	11.0	151	7.5	27
	Lα <sub>1</sub>	6.7				134	6.7	14.0	135	6.7	26
	Lα <sub>2</sub>	6.6							120	6.0	2.5
						150	47.5	36.0	153	47.6	1.4
						306	55.3	2.0	309	55.5	0.1
	Kβ <sub>1</sub>	55.7				315	55.7	6.7	315	55.7	0.3
	Kα <sub>2</sub>	48.2				164	48.2	20	165	48.2	0.8
	Lγ <sub>1</sub>	9.1				183	9.1	1.5	183	9.1	2.5
	Lβ <sub>2</sub>	8.1				163	8.1	3.0	166	8.3	8.0
	Lβ <sub>1</sub>	7.8				157	7.9	12.0	157	7.9	32.0
	Lα <sub>1</sub>	6.95				139	7.0	16.0	139	6.9	30.0
Lα <sub>2</sub>	6.90							126	6.3	3.0	
					182	49.1	33.0	186	49.3	1.3	
					344	57.2	1.7	349	57.4	0.1	
					348	57.4	5.5	351	57.5	0.5	
69 Tm Thulium Tm <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	57.6				195	49.7	19.0	216	49.8	1.0
	Kα <sub>2</sub>	49.8				189	9.5	1.5	190	5.9	2.8
	Lγ <sub>1</sub>	9.4				169	8.4	6.0	170	8.5	8.0
	Lβ <sub>2</sub>	8.4				162	8.1	19.0	163	8.1	35.0
	Lβ <sub>1</sub>	8.1				144	7.2	20.0	144	7.2	34.0
	Lα <sub>1</sub>	7.2								6.4	3.0
	Lα <sub>2</sub>	7.13								50.9	2.0
						215	50.7	30.0	318	50.9	2.0
						385	59.2	1.6	385	59.2	0.2
						455	62.8	0.2	386	59.3	0.2
70 Yb Ytterbium Tb <sub>2</sub> O <sub>3</sub>	Kβ <sub>1</sub>	59.4				258	52.9	1.2	250	51.4	1.2
	Kα <sub>2</sub>	51.3				197	9.8	1.0	198	9.9	2.0
	Lγ <sub>1</sub>	9.8				174	8.7	0.9	176	8.8	6.0
	Lβ <sub>2</sub>	8.7				170	8.5	6.0	169	8.4	40.0
	Lβ <sub>1</sub>	8.4				150	7.5	5.0	149	7.4	39.0
	Lα <sub>1</sub>	7.5							134	6.7	3.0
	Lα <sub>2</sub>	7.3							249	52.4	1.4
									420	61.0	0.3
						453	62.6	0.1	428	61.4	0.2
						256	52.8	1.2	260	53.0	0.6
71 Lu Lutetium Lu <sub>2</sub> O <sub>3</sub>	Kα <sub>2</sub>	53.0				206	10.3	0.8	205	10.2	1.8
	Lγ <sub>1</sub>	10.2				181	9.0	1.0	182	9.1	6.0
	Lβ <sub>2</sub>	9.0				176	8.8	6.0	175	8.7	40.0
	Lβ <sub>1</sub>	8.7				155	7.7	4.0	154	7.7	40.0
	Lα <sub>1</sub>	7.7							136	6.8	3.0
	Lα <sub>2</sub>	7.6							285	64.5	1.0
									402	63.1	0.3
									263	63.3	0.2
									93	54.7	0.5
72 Hf Hafnium HfO <sub>2</sub>	Kβ <sub>1</sub>	63.2				107	54.6	0.1	213	10.6	1.5
	Kα <sub>2</sub>	54.6				212	10.6	0.7	186	9.3	7.0
	Lγ <sub>1</sub>	10.5				187	9.3	1.0	180	9.0	35
	Lβ <sub>2</sub>	9.3				183	9.2	7.0	159	8.0	35
	Lβ <sub>1</sub>	9.0				159	8.0	5.0	144	7.2	2.0
	Lα <sub>1</sub>	7.9									
	Lα <sub>2</sub>	7.8									
						255	52.7	1.0	420	56.0	0.75
						118	55.9	0.1	500	65.0	0.1
									308	65.1	0.2
73 Ta Tantalum Tantalum	Kβ <sub>1</sub>	65.2				121	56.5	0.1	126	56.3	0.8
	Kα <sub>2</sub>	56.3				221	11.1	0.6	220	11.0	2.0
	Lγ <sub>1</sub>	10.9				193	9.6	1.2	196	9.8	12.0
	Lβ <sub>2</sub>	9.6				189	9.5	8.0	188	9.4	50.0
	Lβ <sub>1</sub>	9.3				164	8.2	6.0	164	8.2	50.0
	Lα <sub>1</sub>	8.1							196	7.3	4.0
	Lα <sub>2</sub>	8.0							153	57.6	0.9
						242	52.1	0.2			
						257	52.8	0.2			
							59.5	0.4 <sup>a</sup>			
74 W Tungsten Tungsten	Kβ <sub>1</sub>	67.2							349	67.5	0.2
	Kα <sub>2</sub>	58.0							161	58.0	0.5
	Lγ <sub>1</sub>	11.3				227	11.3	0.6	228	11.4	2.5
	Lβ <sub>2</sub>	10.0				199	10.0	0.8	202	10.1	10.0
	Lβ <sub>1</sub>	9.7				195	9.8	8.0	195	9.7	44
	Lα <sub>1</sub>	8.4				170	8.5	6.0	164	8.5	45

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd		
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts
75 Re Rhenium NH <sub>4</sub> ReO <sub>4</sub>	Lα <sub>2</sub>	8.3							150	7.5	3.0
									189	59.5	0.7
							59.5	0.4			
	Kβ <sub>1</sub>	69.3							390	69.5	0.1
	Kα <sub>2</sub>	59.7				241	59.5	0.4	197	59.8	0.6
	Lγ <sub>1</sub>	11.7				236	11.8	0.6	236	11.8	3.0
	Lβ <sub>2</sub>	10.2				206	10.3	1.0	204	10.2	8.0
	Lβ <sub>1</sub>	10.0				202	10.1	7.0	202	10.1	40
	Lα <sub>1</sub>	8.7				174	8.7	6.0	147	8.7	45
	Lα <sub>2</sub>	8.6							154	7.7	3.0
76 Os Osmium (NH <sub>4</sub> ) <sub>2</sub> OsCl <sub>6</sub>						223	61.1	0.06	225	61.2	0.65
	Kβ <sub>1</sub>	71.4							429	71.4	0.01
	Kα <sub>2</sub>	61.5				244	62.2	0.20	230	61.5	0.2
	Lγ <sub>1</sub>	12.1				241	12.1	0.56	244	12.2	3.0
	Lβ <sub>2</sub>	10.6				210	10.5	3.0	212	10.6	8.0
	Lβ <sub>1</sub>	10.3				206	10.3	6.0	206	10.3	40.0
	Lα <sub>1</sub>	8.9				180	9.0	6.0	179	9.0	42.0
	Lα <sub>2</sub>	8.8							160	8.0	2.5
									263	63.2	0.4
									268	73.4	0.01
77 Ir Iridium (NH <sub>4</sub> ) <sub>3</sub> IrCl <sub>6</sub>	Kβ <sub>1</sub>	73.5							64	63.3	0.2
	Kα <sub>2</sub>	63.3				242	62.1	0.20	253	12.6	4.0
	Lγ <sub>1</sub>	12.5				253	12.7	0.62	218	10.9	6.0
	Lβ <sub>2</sub>	10.9				220	11.0	1.0	214	10.7	40.0
	Lβ <sub>1</sub>	10.7				217	10.9	6.5	185	9.2	45.0
	Lα <sub>1</sub>	9.2				185	9.3	6.0	164	8.2	2.0
	Lα <sub>2</sub>	9.0							98	64.9	0.3
									156	76.1	0.1
78 Pt Platinum Platinum	Kβ <sub>1</sub>	75.7							121	65.0	0.2
	Kα <sub>2</sub>	65.1				242	62.1	0.2	262	13.1	4.0
	Lγ <sub>1</sub>	12.9				258	12.9	0.7	224	11.2	6.0
	Lβ <sub>2</sub>	11.2				224	11.2	0.8	220	11.0	40
	Lβ <sub>1</sub>	11.0				217	10.9	7.2	190	9.5	43.0
	Lα <sub>1</sub>	9.5				185	9.5	7.3	175	8.5	2.0
	Lα <sub>2</sub>	9.4							138	66.9	0.4
									372	78.6	0.05
									392	78.1	0.1
									158	67.0	0.3
79 Au Gold Gold	Kβ <sub>1</sub>	78.0							271	13.4	8.0
	Kα <sub>2</sub>	67.0							230	11.5	65.0
	Lγ <sub>1</sub>	13.4				271	13.6	1.5	228	11.4	1.5
	Lβ <sub>2</sub>	11.5				231	11.6	15	195	9.7	71.0
	Lβ <sub>1</sub>	11.4				228	11.4	1.5	177	8.6	4
	Lα <sub>1</sub>	9.7				196	9.8	14.0	198	69.0	0.5
	Lα <sub>2</sub>	9.6							160	8.0	0.8
				180	2.3	2.0			287	14.3	0.4
									434	81.2	0.10
									200	69.0	0.25
80 Hg Mercury HgCl	Kβ <sub>1</sub>	80.3							279	13.9	1.5
	Kα <sub>2</sub>	68.9							238	11.9	60
	Lγ <sub>1</sub>	13.8				279	13.9	1.5	216	10.8	1.5
	Lβ <sub>2</sub>	11.9				239	11.9	0.4	200	10.0	61
	Lβ <sub>1</sub>	11.8				234	11.7	1.4	198	9.0	4
	Lα <sub>1</sub>	10.0				202	10.1	12.0	174	8.7	3.0
	Lα <sub>2</sub>	9.9							270	13.5	0.5
									285	14.2	2.5
									297	14.3	0.5
									224	71.2	0.35
81 Tl Thallium Tl <sub>2</sub> CO <sub>3</sub>	Kβ <sub>1</sub>	82.6							465	83.5	0.1
	Kα <sub>2</sub>	70.8							479	83.0	0.10
	Lγ <sub>1</sub>	14.3				289	14.5	1.5	224	71.4	0.3
	Lβ <sub>2</sub>	12.3				247	12.4	16.0	290	14.4	7.5
	Lβ <sub>1</sub>	12.2				240	12.0	1.6	246	12.3	65.0
	Lα <sub>1</sub>	10.3				207	10.4	14.0	221	11.1	1.8
	Lα <sub>2</sub>	10.1							207	10.3	65
									184	9.2	4.0
									161	8.1	0.6
									265	73.2	0.5

TABLE III. Continued

Element	Source		<sup>55</sup> Fe			<sup>241</sup> Am			<sup>109</sup> Cd				
	Line	Energy	Channel	Energy	Counts	Channel	Energy	Counts	Channel	Energy	Counts		
82 Lead	Pb	Kβ <sub>1</sub>	84.9			377			249	85.0	0.05		
		Kα <sub>2</sub>	72.8			331			77	73.3	0.20		
		Lγ <sub>1</sub>	14.8			298	14.9	2.0	299	14.8	8.0		
		Lβ <sub>2</sub>	12.6			255	12.7	20.0	250	12.6	80		
		Lβ <sub>1</sub>	12.0			248	12.4	0.3	229	11.4	2.0		
		Lα <sub>1</sub>	10.6			213	10.6	16.0	213	10.6	75		
		Lα <sub>2</sub>	10.5				9.3	0.7	184	9.2	4.0		
					200	2.4	3.5	15.9	0.2	128	75.2	0.20	
					230	2.8	0.3	15.3	0.9	306	15.3	3.2	
					310	3.7	0.1	1		277	13.8	0.3	
			358	4.3	0.1								
			130	1.56	0.15								
83 Bismuth	Bi	Kβ <sub>1</sub>	81.3			421	81.0	0.02					
		Kα <sub>2</sub>	74.8			369	78.4	0.01	89	74.4	0.01		
		Lγ <sub>1</sub>	15.2			308	15.4	1.5	307	15.3	9.2		
		Lβ <sub>2</sub>	13.0			262	13.1	1.5	262	13.1	76		
		Lβ <sub>1</sub>	13.0			263	13.1	19.0	235	11.7	2.0		
		Lα <sub>1</sub>	10.8			219	10.9	15	217	10.8	68		
		Lα <sub>2</sub>	10.7						189	9.4	3.5		
					212	2.54	1.5	128	6.4	2.0	127	6.3	12.0
					232	2.78	0.16			140	7.0	2.0	
					317	3.80	0.15			235	11.7	2.0	
			388	4.55	0.10			298	14.9	0.6			
			462	5.54	0.15			315	15.7	3.0			
90 Thorium	Th	Kβ <sub>1</sub>	105.6										
		Kα <sub>2</sub>	89.9										
		Lγ <sub>1</sub>	19.0			383	19.1	3.6	383	19.1	13		
		Lβ <sub>2</sub>	15.6			315	15.7	12	315	15.7	30		
		Lβ <sub>1</sub>	16.2			327	16.3	28	326	16.3	77		
		Lα <sub>1</sub>	13.0			261	13.1	27	261	13.1	97		
		Lα <sub>2</sub>	12.8			223	11.1	1.5	223	11.1	5.6		
							58	2.9	1.0	58	2.9	4	
							292	14.6	0.8	292	14.6	2.6	
							345	17.2	0.2	345	17.2	0.7	
92 Uranium	U	L1	11.6			393	19.7	1.5	395	19.7	4.0		
		Lα	13.6			232	11.6	1.3	232	11.6	5.5		
		Ln	15.4			272	13.6	22.0	232	13.6	98.0		
		L <sub>3</sub> -N <sub>3</sub>	15.8			308	15.4	0.6	308	15.4	2.2		
		Lβ <sub>2</sub>	16.5			316	15.8	0.6	316	15.8	2.6		
		Lβ <sub>1</sub>	17.2			330	16.5	9.0	330	16.5	28		
		Lγ <sub>5</sub>	19.5			345	17.2	12	330	17.2	53		
		Lγ <sub>1</sub>	20.2			391	19.5	0.2	391	19.5	1.0		
		Lγ <sub>3</sub>	20.8			404	20.2	3.0	404	20.2	11		
		Lγ <sub>4</sub>	21.7			416	20.8	1.3	416	20.8	4.8		
UO <sub>2</sub> (NO <sub>3</sub> ) <sub>2</sub>					434	21.7	0.2	434	21.7	1.0			
	Mα <sub>2</sub>	3.05							3.05	2.6			
				3.05	2.5								

<sup>a</sup> Source.

It then appeared necessary to prepare a systematic tabulation of the spectral data by element and by energy before any attempt was made to develop quantitative analytical methods. Accordingly, we irradiated 71 elements by each of our three sources for 1000 sec each and tabulated the peaks by energy (as determined by the internal standardization provided on the Kevelex unit) and by counts per second (as determined by a Teletype read-out from the memory storage). These data were tabulated numerically in terms of the elements in Table III and graphically as a function of energy in Fig. 3, a to i.

### C. Sensitivity Data by Element and by Energy

These data have been extremely helpful in our determination of the elements in a wide range of museum ob-

jects. The tables and graphs provide the following information:

1. The identification of the most probable elements responsible for the peaks found in a spectrum. For example, referring to Fig. 3g, Ge, Hg, Au, Yb, Re, and W appear at or near 10 kV. To be Ge there would have to be a secondary peak at 10.6 kV. To be Hg there would have to be a secondary peak at 10.6 kV. To be Au there would have to be a comparable peak at 11.9 kV, etc. If such clues are insufficient to confirm the most probable element, a confirmation by irradiating the suspected element should be made.

2. The choice of the most likely peak from one element which will be "clear" of overlap from other elements to simplify identification.

3. The minimum concentration of one element which

can be determined in the presence of the major elements in an object. For example, from Fig. 3a, Ti has a response of 5 times that of Ba, La, and Ce, all of which are found in clay-based redware at 4.6 kV. We could expect to determine 0.2% Ti in the presence of 1% of Ba.

4. Methods for determining both elements in an overlapping peak. Note example for determining arsenic in the presence of lead in the analysis of glass, brass, and bronze, in which arsenic and a major lead peak both appear at 10.6 kV (Fig. 3g).

5. Methods for making quantitative determinations by employing a major constituent as an "internal standard." These methods employ the "count per second" data of the tables to determine "count ratios" to normalize all elements to the "internal standard," permitting concentration of the various elements to be determined with fair accuracy.

These accuracies can be enhanced by adjusting the count ratios from measurements made on accurately made reference standards.

6. If reference standards are available having several elements present in known concentrations, other elements not in the standard can be estimated very closely by employing counts from nearby peaks after normalizing them from ratios of counts taken from the tables.

For example, our silver reference standard 47.4 contains 92.5% Ag, 7.0% Cu, and 0.5% Au. Concentrations of lead at 12.6 kV would be 65/80 of the equivalent gold count at 11.5 kV (Table III). Concentrations of zinc at 8.7 kV would be 243/274 of the equivalent concentrations of copper at 8.1 kV. Arsenic has the same response as copper, and so its concentrations can be determined in a direct proportion to the copper count when employing the Cd 109 source for excitation.

7. The optimum excitation source can be selected from the graphs. For example, Ag, Cd, Sn, Sb, and Ba, etc., respond strongly to the  $^{241}\text{Am}$  source (Fig. 3d) and weakly to the  $^{109}\text{Cd}$  source (Fig. 3h). Also, Mn, Fe, Ni, Co, Cu, and Zn have a better response to the  $^{109}\text{Cd}$  source (Fig. 3, f and g) than to the  $^{241}\text{Am}$  source (Fig. 3, b and c). Also, the  $^{55}\text{Fe}$  source (Fig. 3a) is required for low atomic-numbered elements such as S, Cl, K, Ca, Se, Ti, and V. In glass and ceramic analysis it is frequently necessary to employ more than one source.

It should be noted that the response data presented are a function of the strength of the excitation source; the geometry of the sample-exciter-detector system; and the span, resolution, and sensitivity of the detector system, to name a few. The data of Table III can be employed by other instrumentation conditions by measur-

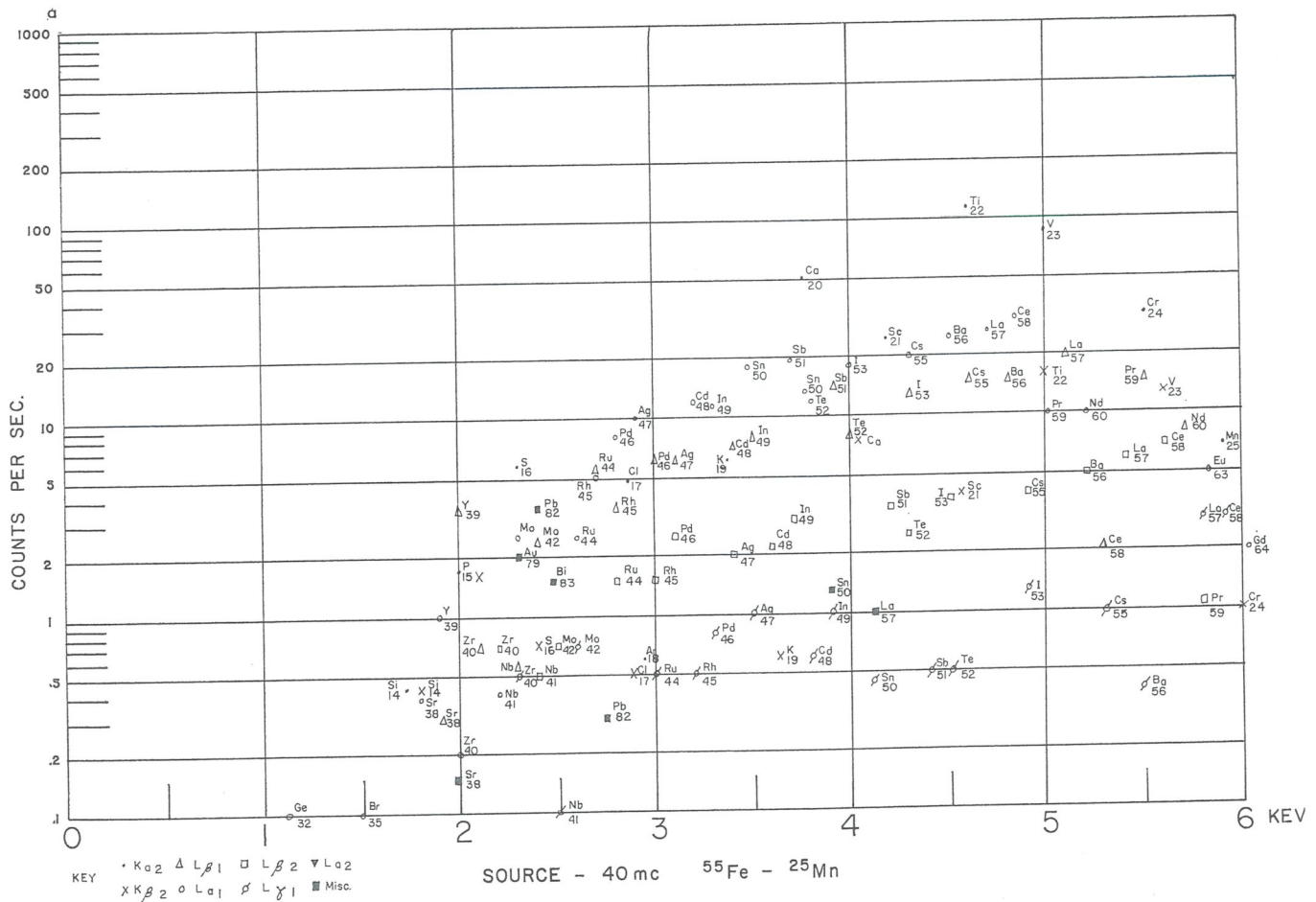


FIG. 3. Plots of instrument sensitivity in cps of the various x-ray fluorescence peaks vs energy for  $^{55}\text{Fe}$ ,  $^{109}\text{Cd}$ , and  $^{241}\text{Am}$  excitation sources. These plots make possible a rapid assignment of the most probable elements to the spectrum of an art object. The plots also indicate possible interference from other elements.

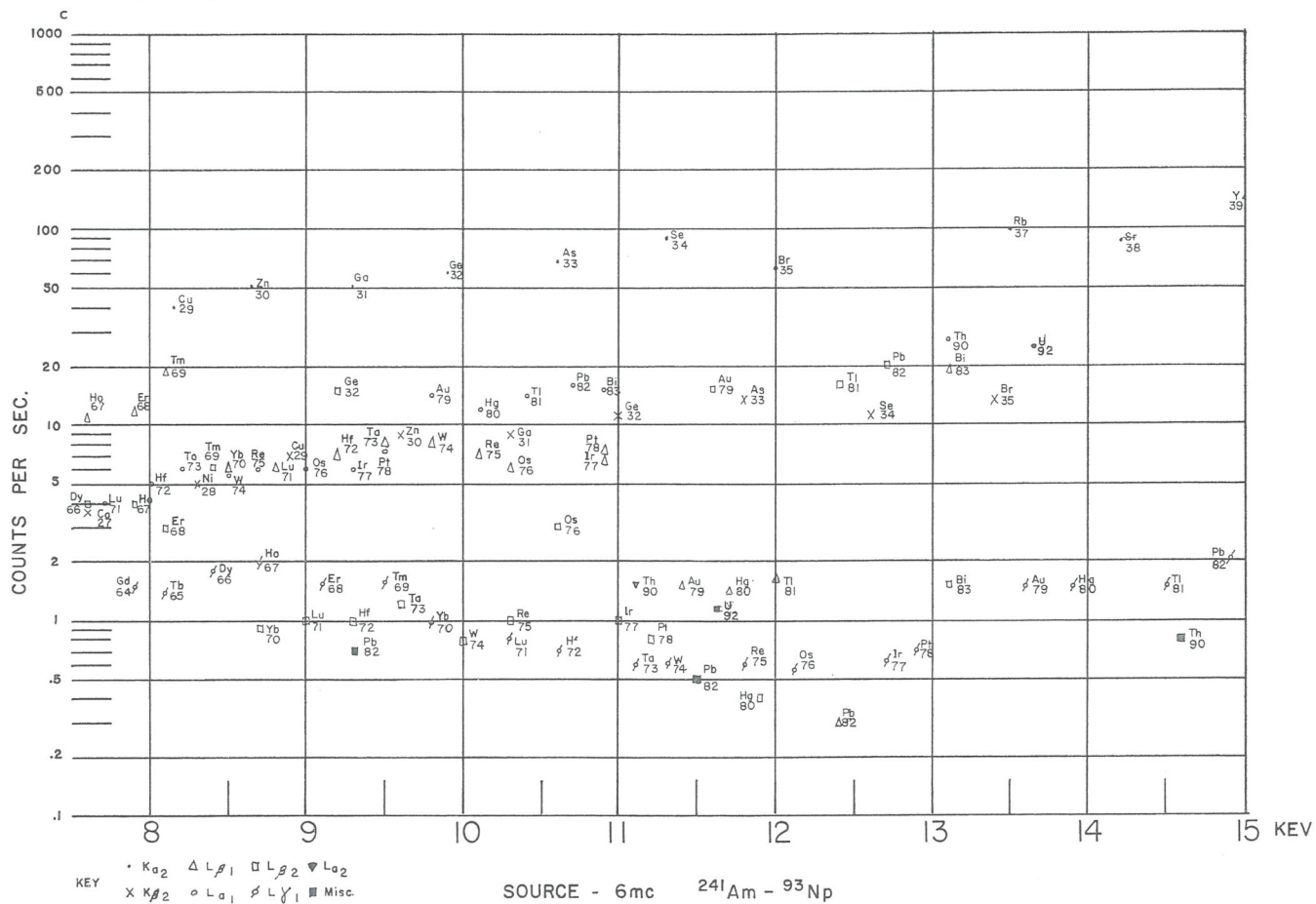
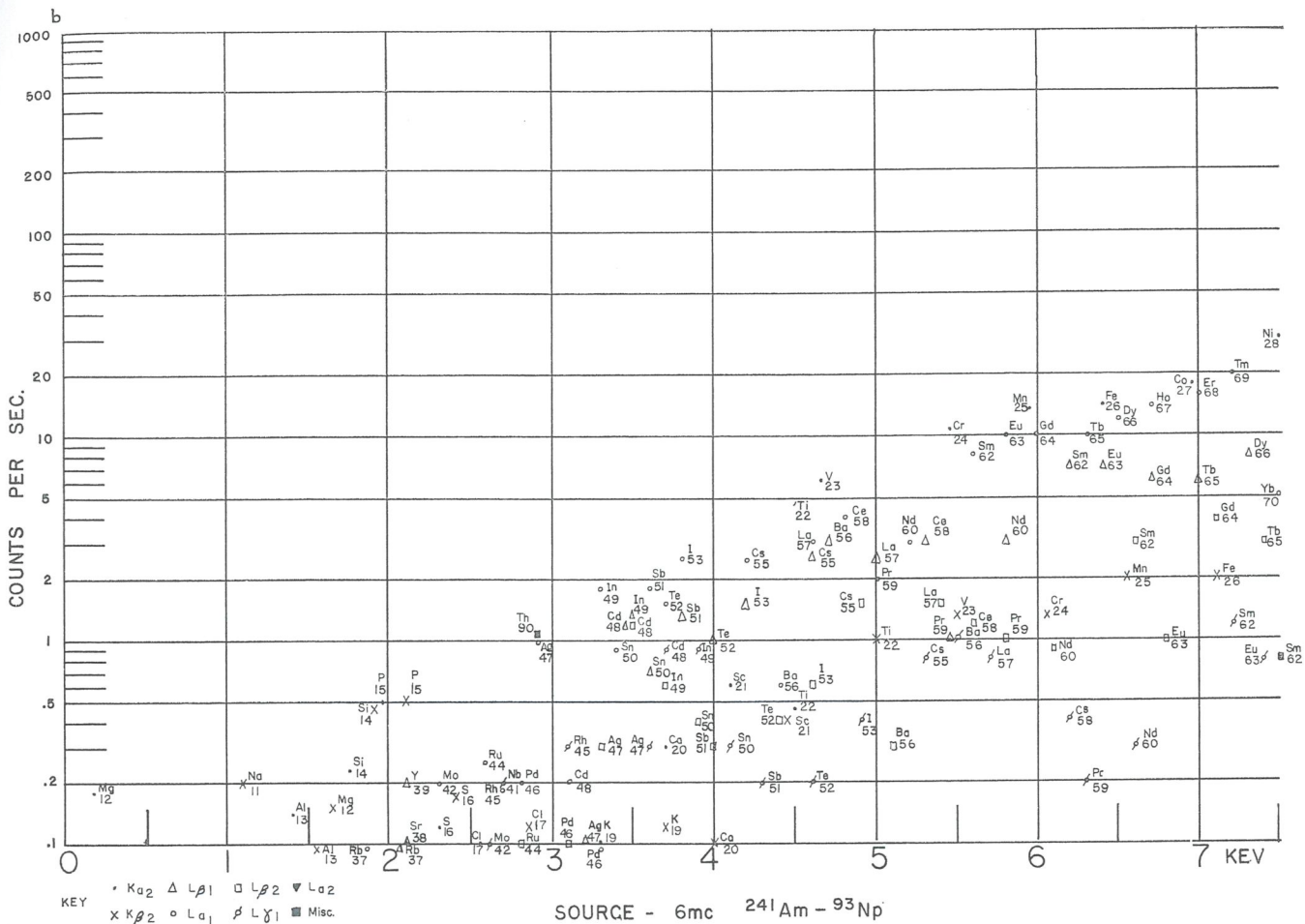


FIG. 3, b and c

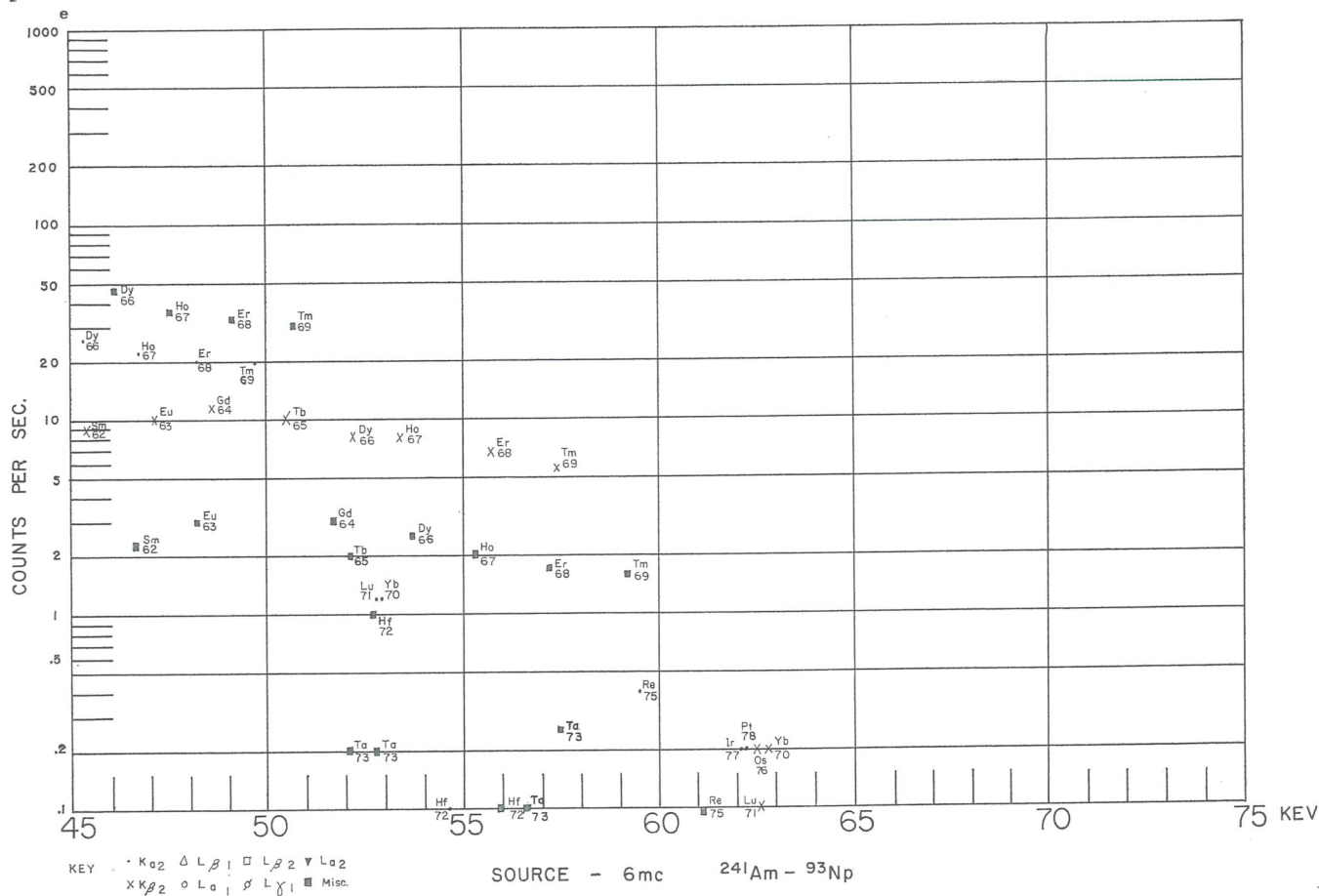
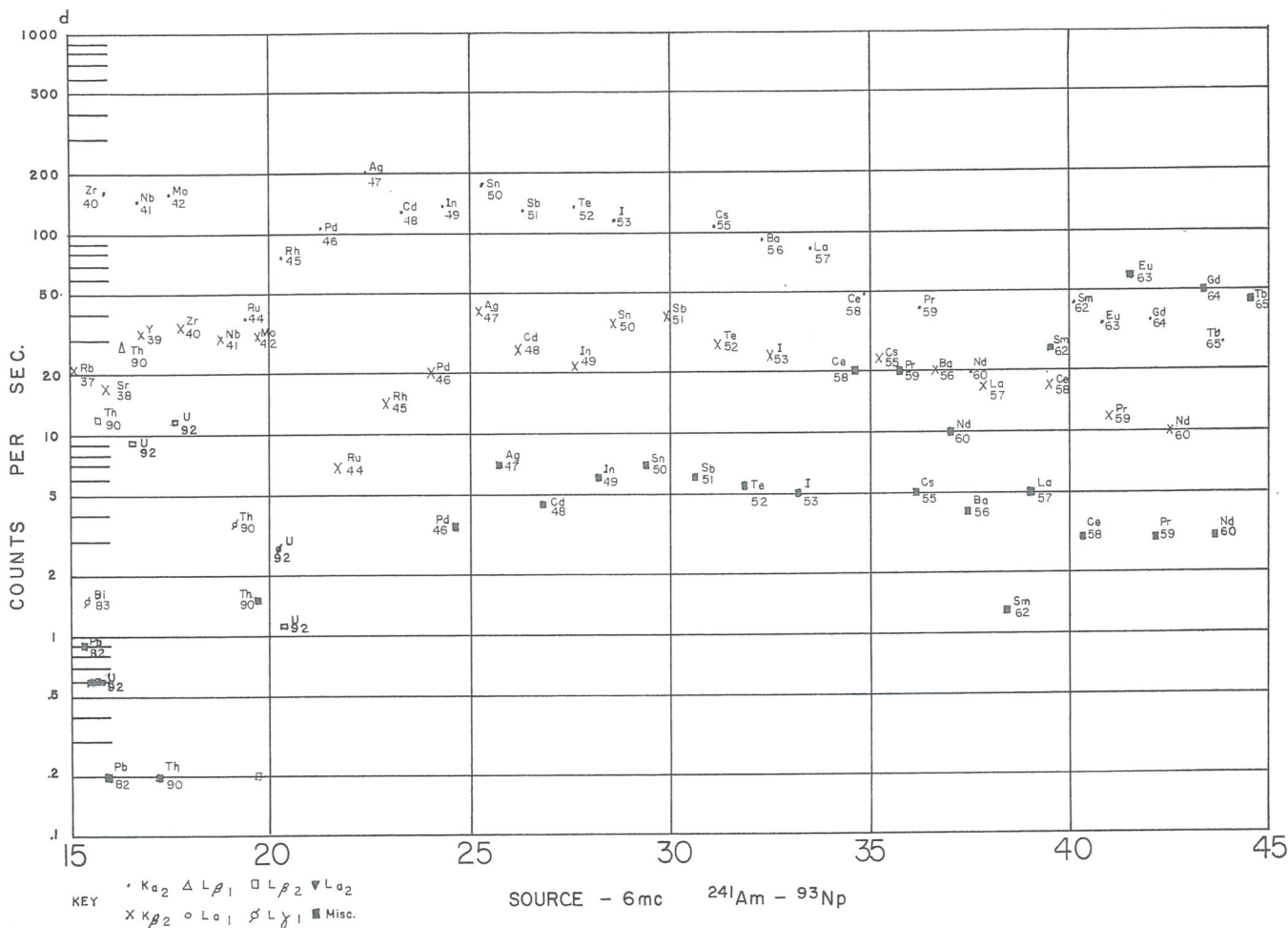
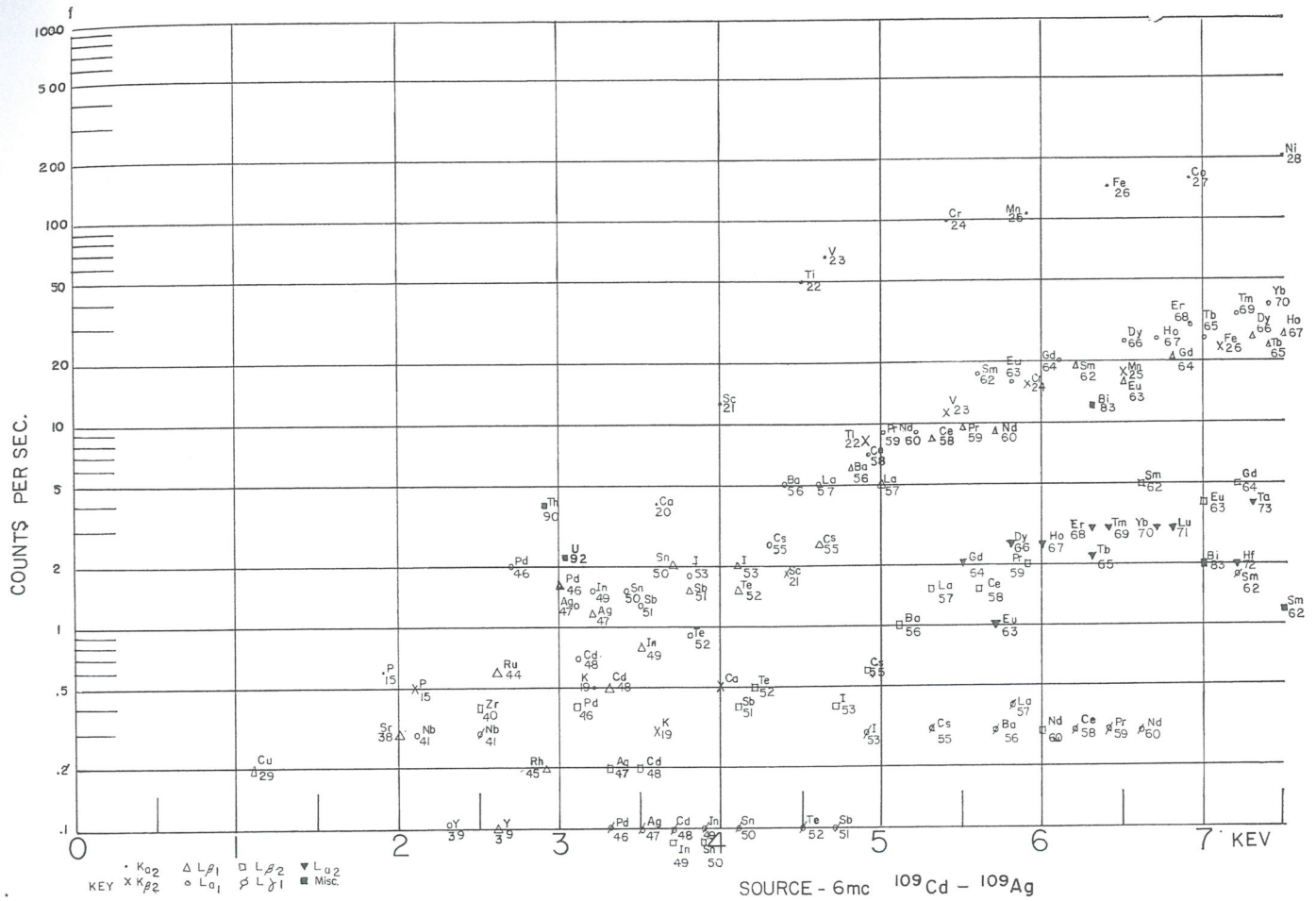
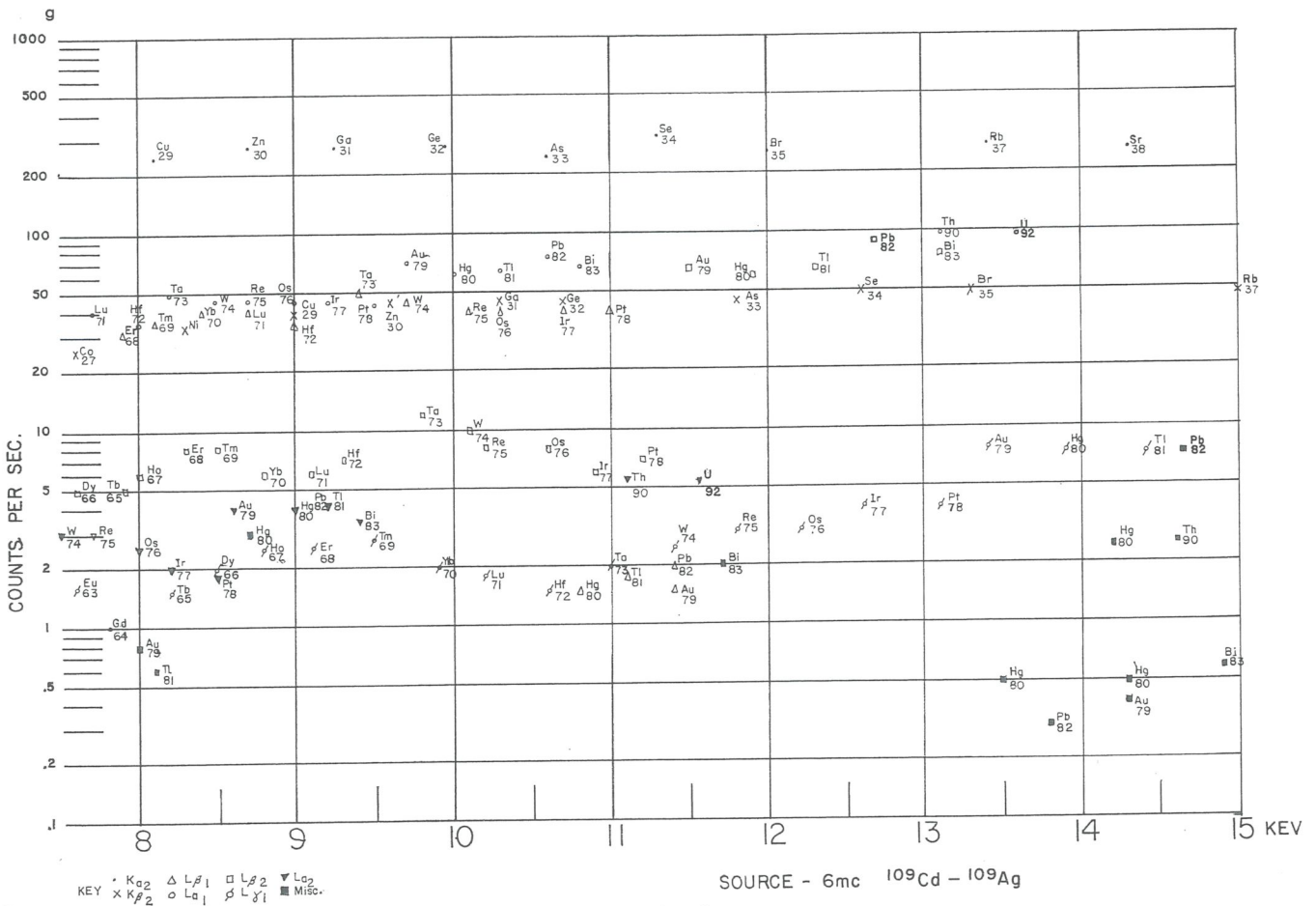


FIG. 3, d and e  
322



SOURCE - 6mc <sup>109</sup>Cd - <sup>109</sup>Ag



SOURCE - 6mc <sup>109</sup>Cd - <sup>109</sup>Ag

FIG. 3, f and g



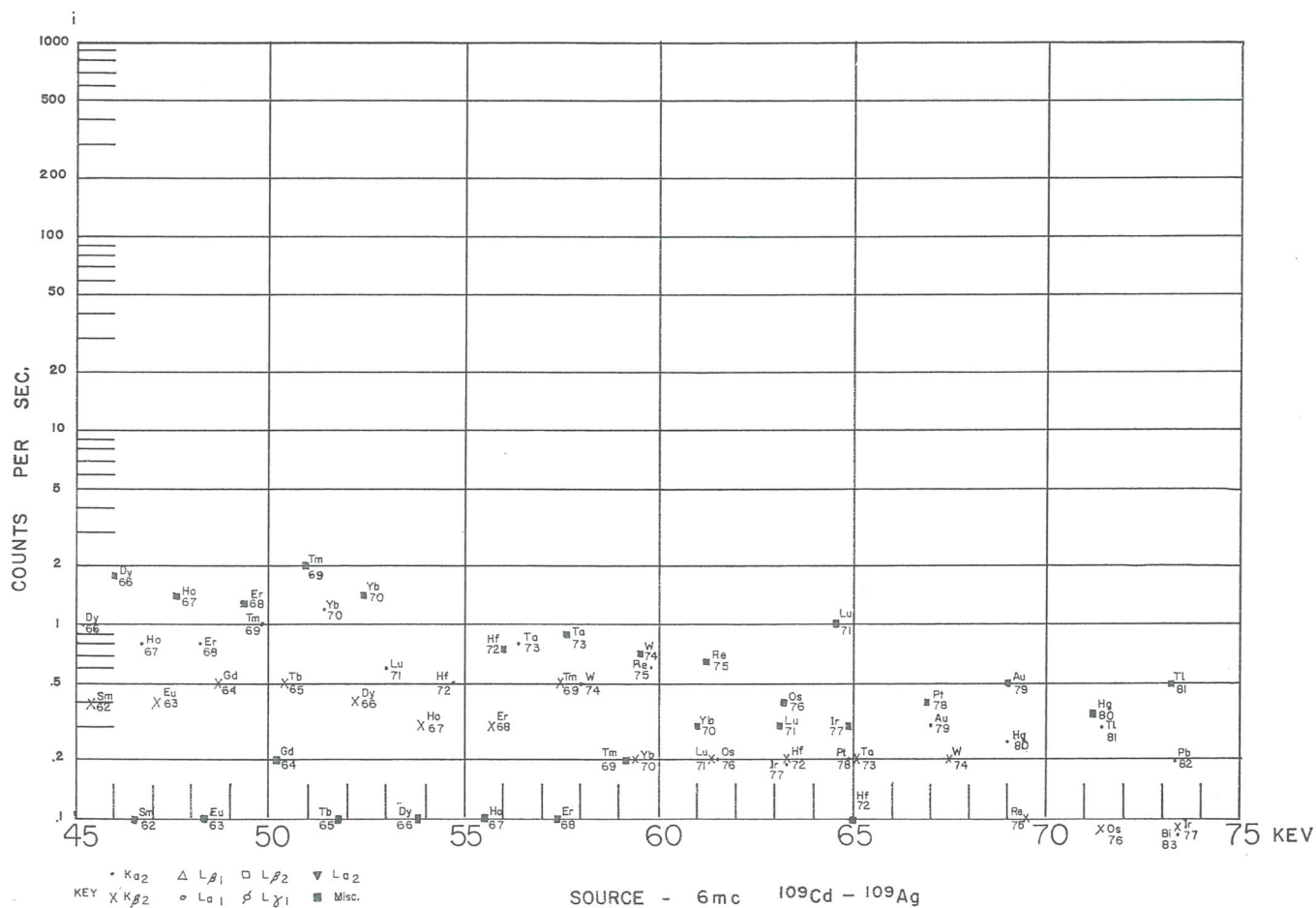
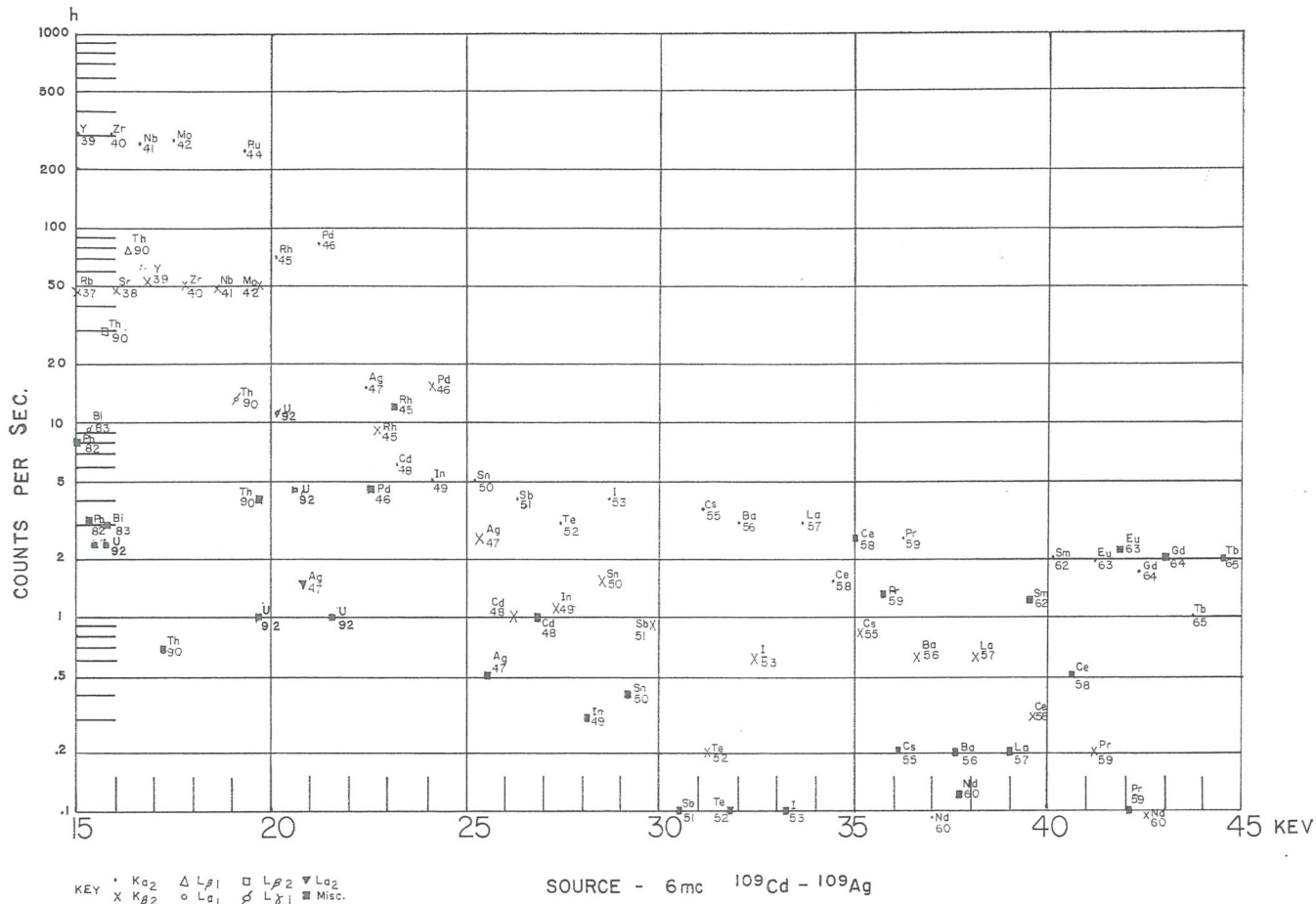


FIG. 3, h and i  
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ing a few high purity elements over the energy span of the instrument and determining the ratio of peaks from these elements to the data tabulated in Table III. This ratio can then be applied to the other elements in the table regardless of the geometry, sensitivity, and other factors listed above.

#### D. Computation of Concentrations in Weight Percent from Peak Spectra Values without Reference Standards

If we have elements  $P, Q, R, S,$  and  $T$  present with net peak counts of  $p, q, r, s,$  and  $t$ , and we choose  $P$  to be our internal reference standard, then we proceed as follows:

From Table III tabulate the counts per second for these elements at the channels selected. Call these peak values  $p', q', r', s',$  and  $t'$ . Since  $P$  has been selected as the "internal reference," then we can normalize the response of the instrument for the other elements to  $P$ . Dividing  $p'$  by  $p', q', r', s',$  and  $t'$ , we have multiplying factors for  $P, Q, R, S,$  and  $T$  of  $1, p'/q', p'/r', p'/s',$  and  $p'/t'$ , respectively. Then

$$p \times 1 + \frac{q \times p'}{q'} + \frac{r \times p'}{r'} + \frac{s \times p'}{s'} + \frac{t \times p'}{t'} = U \quad (1)$$

where  $U$  is the total count normalized to  $P$ . Percentage by weights of  $P, Q, R, S,$  and  $T$  will be:

$$\begin{aligned} \%P &= \frac{1 \times p}{0.01U} & \%Q &= \frac{q \times p}{q' \times 0.01U} \\ \%R &= \frac{r \times p}{r' \times 0.01U} \text{ etc.} \end{aligned} \quad (2)$$

#### E. Analysis Procedures for Metals from Teletype Spectra Read-Out

We find it convenient to employ a data sheet similar to Table IV.

1. Locate the channels where the peaks of elements  $P, Q, R, S,$  and  $T$  appear. This can be done to a close approximation from Table III. The exact channels are determined from the Teletypewriter read-out. Record the peak counts at these channel locations in column C of a table similar to Table IV.

2. Run a spectrum of element  $P$  for " $p$ " counts. " $p$ " will be silver for silver-based alloys, copper for brass and bronze, and tin for pewter. Tabulate the counts of the peak channel locations in column A. This will be the "baseline."

3. Subtract the counts of the baseline at these channels from values  $q, r, s,$  and  $t$  and tabulate them in column D.

These are net counts for each of the elements. Do not subtract " $p$ " since this is the internal standard.

4. Record in column B the ratios of counts calculated from Table III for the various elements at the selected channels with element  $P$  in the numerator. These fractions will normalize counts from all elements to that of element  $P$ .

5. Tabulate in column E the products of columns B and D. The sum of these values will be the "total equivalent count."

6. The weight percent of the various elements can then be tabulated in column F by dividing each value in column E by 0.01 of the total equivalent count.

7. If normalizing ratios of column B are found to be in error owing to matrix effects, they can be adjusted by analyzing similar alloys of accurately known compositions. Results of these procedures are illustrated in

TABLE IV. Effect of excitation source: Brass/bronze determinations, sample MB 180

Column description: A: baseline copper 99.9% + - counts per sec; B: ratio copper counts to element from tables; C: measured counts per sec; D: counts minus baseline except for copper ( $C - A$ ); E: product  $B \times D$ , normalizing to copper; F: calculated % of each element,  $100E/\sum E$ ; G: wt % of elements before melting and casting.

Element	kV	<sup>241</sup> Am							<sup>109</sup> Cd						
		A 279 sec	B	C 413 sec	D	E	F	G	A 60 sec	B	C 90 sec	D	E	F	G
Mn	5.9	0.39	3	0.32	0	0	0	0.07	0.27	2.3	0.20	0	0.00	0.00	0.07
Fe	6.4	0.65	2.9	0.57	0	0	0	0	0.45	1.6	0.54	0.09	0.14	0.15	0.00
Co	6.9	0.63	2.2	0.59	0	0	0	0	0.28	1.5	0.46	0.18	0.27	0.20	0.00
Ni	7.5	0.63	1.3	0.69	0.06	0.08	0	0.17	0.47	1.2	0.70	0.23	0.28	0.21	0.17
Cu	8.1	35.8	1.0	24.2	24.2	24.20	81.00	82.6	150	1.0	110	110	110	82.50	82.6
Zn	8.7	0.72	0.79	3.2	2.5	2.00	6.67	6.45	1.4	0.89	12.0	10.6	9.40	7.06	6.45
Pb + As	10.6	0.18			0.56				0.1		3.0	2.9			
As	10.6		0.59	0.76	0.08	0.05	0.16			1.0		0	0.00	0.00	0.00
Pb	12.6	0.11	2.0	0.92	0.81	1.60	5.30	7.0	0.06	3.0	3.72	3.66	11.80	8.90	7.00
Bi	13.1	0.065	2.1	0.1	0.03	0.06	0.20	0	0.01	3.2	0.21	0.20	0.72	0.54	0.00
Au	11.6	0.09	2.7	0.11	0.02	0.05	0.16	0	0.03	3.7	0.08	0.05	0.18	0.09	0.00
Ag	22.2	0.043	0.20	0.024	0.01	0.002	0.006	0	No response at following energies						
Cd	23.3	0.032	0.31	0.07	0.04	0.012	0.04	0							
In	24.3	0.046	0.29	0.21	0.16	0.05	0.16	0							
Sn	25.3	0.029	0.23	7.2	7.2	1.65	5.50	3.1							3.10
Sb	26.3	0.040	0.32	0.37	0.33	0.10	0.35	0.0							
$\sum$						29.90	99.69						132.98		

Table V for copper-based alloys, and in Tables X and XI for glass.

## II. RESULTS

### A. Analysis of Brass and Bronze "Standards"

While the ingredients of the various brass coupons were accurately weighed in, Dr. Charles Coxe of Handy Harman, knowing the metallurgical problems associated with such sample preparation, could not provide us with "certified" analysis data. We arbitrarily selected Ref. No. 29.7 as our brass "standard" and analyzed the other specially prepared brass specimens in terms of 29.7

TABLE V. Normalizing factors for copper-based alloys (copper as internal standard).

Computation techniques with overlapping peaks. Example: arsenic in presence of lead. Arsenic and lead both have strong emission lines at 10.6 kV but lead is "in the clear" at 12.6 kV. In the absence of arsenic the ratios of the lead peak at 10.6 to that at 12.6 kV are:  $^{241}\text{Am}$ :  $16/20 = 0.80$ ;  $^{109}\text{Cd}$ :  $75/80 = 0.94$ . It can be assumed, then, that arsenic accounts for that part of the peak at 10.6 kV that is greater than the above fraction of the 12.6 kV peak. Arsenic normalized for copper =  $0.59 (\text{Pb}_{10.6} - 0.8 \text{Pb}_{12.6})$  for  $^{241}\text{Am}$ ; =  $1.0 (\text{Pb}_{10.6} - 0.94 \text{Pb}_{12.6})$  for  $^{109}\text{Cd}$ . For column description, see legend to Table IV.

Element		$^{241}\text{Am}$		$^{109}\text{Cd}$	
Column:	kV	C (cps)	B (Cu/x)	C (cps)	B (Cu/x)
Mn	5.9	13.3	3.0	104	2.3
Fe	6.4	14.0	2.9	148	1.6
Co	6.9	18.0	2.2	159	1.5
Ni	7.5	30	1.3	205	1.2
Cu	8.1	40	1.0	243	1.0
Zn	8.7	51	0.79	274	0.89
As	10.6	68	0.59	244	1.0
Pb	10.6	16	2.5	75	3.2
Pb	12.6	20	2.0	80	3.0
Bi	13.1	19	2.1	76	3.2
Au	11.6	15	2.7	65	3.7
Ag	22.2	200	0.20	15	16
Cd	23.3	129	0.31	6	40
In	24.3	136	0.29	5	49
Sn	25.3	173	0.23	5	49
Sb	26.3	125	0.32	4	60

weighed-in value. Results of these measurements are listed in Table II. Typical differences appear on the two sides of the casting owing to segregation during casting.

### B. Comparisons of Results from Cadmium-109 and Americium-241 Sources on Brass and Bronze Analyses

Data of Table IV were taken with both our  $^{109}\text{Cd}$  and  $^{241}\text{Am}$  sources. Data covering 5 to 35 kV were stored in 500 channels of the 512-channel memory bank or 60 V per channel.

The instrument was set to turn off after 10 000 counts were accumulated in the peak copper channel at 8.1 kV. Time in seconds is accumulated in channel zero which we use to reduce the counts accumulated to "counts per second" for convenience of comparison to values taken from Table III.

Data were tabulated in Table IV according to the procedure outlined in "Analysis Procedures from Teletype Spectra Read-Out" to provide the reader with a feel for the quantities actually measured on bronze sample MB 180 employing sources  $^{109}\text{Cd}$  and  $^{241}\text{Am}$ . It is important to note that elements appearing above 22.2 kV do not appear with the  $^{109}\text{Cd}$  source because of low instrument response and because there is a silver artifact in the 20- to 22-kV region due to Compton backscatter from the silver radiation produced by the  $^{109}\text{Cd}$  source. Because of these factors we chose to employ the  $^{241}\text{Am}$  source for copper-based alloys although tin and silver in the 3.7 kV and 3.1 kV, respectively, could be employed with the  $^{109}\text{Cd}$  source if  $^{241}\text{Am}$  source is not available.

Summary results from five brass and bronze samples based on these same procedures are given in Table VI. These include measurements made from 20-mg filings taken from MB 180 and HH 29.7. While we do not have a "certified" assay of these bronzes, we have listed the components added to make up the melt as reported by the founder (column G). Since significant differences in composition of the chilled bottom faces and the top faces of the castings exist (Table II), we were surprised to find such a close agreement between our analyses based on Table III and samples MB 180, MB 181, and MB 249

TABLE VI. Summary brass analyses: Prepared test samples,  $^{241}\text{Am}$  source.

Sample:	MB 180					MB 181		MB 249		HH 29.5		HH 29.3		HH 29.7		
	A. Copper 100%	B. Cu x	G. As cast	F. Solid	F. Chips, 20 mg	G. As cast	F. Us	G. As cast	F. Us	G. As cast	F.	G. As cast	F.	G. As cast	F. Solid	F. Chips 20 mg
Mn	0.39	3	0.07	0	0.07	0	0	0	0							
Fe	0.65	2.9	0.00	0	0	0.03	0	1.96	4.3							
Co	0.63	2.2	0.00	0	0	0	0	0	0							
Ni	0.63	1.3	0.17	0	0	0.11	0	0	0							
Cu	35.8	1.0	82.6	81.00	85.0	88.5	82.0	87.2	90.0	75	73.5	60	59.5	75	72.0	71.4
Zn	0.72	0.79	6.45	6.67	3.8	3.0	3.2	5.3	5.7	24.9	25.2	40	40.0	24.5	26.1	23.8
Pb + As		0.18														
As	0.00	0.59	0.16		0		0									
Pb	0.11	2.0	7.0	5.3	6.6	0.44	0.60	0.09	0.06	0	0.3	0	0.5	0	0.4	0.3
Bi	0.06	2.1	0.0	0.20	0.0	0	0.04	0	0							
Au	0.09	2.7	0.0	0.30	0.0	0	0.00	0	0	0	0.05	0	0.05	0	0.08	0.3
Ag	0.043	0.20	0	0.006	0.0	0	0.05	0	0	0.1	0.14	0	0.02	0.5	0.60	0.53
Cd	0.032	0.31	0	0.04	0	0	0.08	0	0.01							
In	0.046	0.29	0	0.16	0	0	0.41	0	0.01							
Sn	0.029	0.23	3.1	5.5	4.1	7.75	11.3	0.18	0.43	0	0.03	0	0.00	0	0.05	0.70
Sb	0.040	0.32	0.0	0.35	0	0	0.12	0	0							

TABLE VII. Analysis results: Six Paul Revere tankards, Massachusetts, 1768.

Analysis of eight parts from each of six tankards made by Paul Revere in the period 1768-1771, shown in Fig. 4. The difference in the copper content of the "bottom of body" and the "side of body," which are both the same piece of metal, is due to an acid dip made by the silversmith to remove oxides and copper at the surface just prior to the final polishing. The silver-rich surface has been removed from the side of the body by repeated polishings whereas the infrequent polishing of the bottom left it in its silver-rich condition. Abrasive-containing silver polishes cut through this layer in a few minutes. While we have only tabulated values of Ag, Cu, Au, and Pb in this table, we actually recorded a total of 14 elements. It was interesting to note that several parts of the various tankards have essentially the same composition, indicating that they were probably made from the same melt. Furthermore, one might conclude that he mixed his alloys in small batches, judging by the many differences in analysis. The variability of composition of the parts on the same piece is typical of American-made pieces.

Accession Number	Bottom of body				Side of body				Base rim				Lid			
	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb
57.859.1	93.8	5.4	0.19	0.26	94.0	5.5	0.15	0.22 <sup>a</sup>	94.5	4.7	0.09	0.20	94.6	4.5	0.13	0.28
.2	93.6	5.4	0.04	0.26	92.9	6.0	0.04	0.31	92.9	6.5	0.15	0.26	90.7	8.5	0.15	0.31
.3	93.3	6.0	0.18	0.33	86.5	12.7	0.12	0.30	93.3	6.2	0.16	0.21	93.4	6.1	0.14	0.22
.4	93.9	5.4	0.08	0.20	92.9	6.6	0.09	0.17	93.1	6.3	0.17	0.23	94.3	3.8	0.16	0.20
.5	93.4	6.0	0.13	0.22	91.4	8.0	0.17	0.24	92.8	6.9	0.12	0.18	94.0	5.4	0.16	0.23 <sup>a</sup>
.6	93.1	6.4	0.14	0.32	88.7	10.5	0.10	0.37	93.3	5.5	0.13	0.22 <sup>a</sup>	93.8	5.6	0.17	0.27 <sup>a</sup>

Accession Number	Handle face				Handle side				Finial				Hinge			
	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb	Ag	Cu	Au	Pb
57.859.1	93.4	6.1	0.15	0.20	90.0	9.2	0.13	0.27	94.2	5.2	0.16	0.29	92.7	6.8	0.03	0.14
.2	94.3	5.2	0.16	0.29	93.8	5.7	0.17	0.20 <sup>a</sup>	92.1	6.5	0.32	0.35	85.4	12.0	0.11	0.27
.3	91.2	7.4	0.13	0.21	90.5	8.5	0.18	0.28	94.5	4.9	0.13	0.10	91.4	8.1	0.07	0.14
.4	94.1	5.4	0.19	0.19 <sup>a</sup>	91.0	8.1	0.20	0.16	93.8	5.7	0.19	0.24 <sup>a</sup>	90.1	8.7	0.05	0.17
.5	93.1	6.4	0.18	0.17	93.5	5.7	0.21	0.24 <sup>a</sup>	93.9	5.7	0.15	0.11	90.2	9.2	0.15	0.19
.6	94.4	5.2	0.16	0.21	89.2	9.5	0.09	0.22	91.3	7.0	0.28	0.35	92.5	6.8	0.08	0.30

<sup>a</sup> Certified values. The seven parts designated postscript "a" are of the same composition, indicating that they were probably all cast from the same melt. Other parts can also be grouped together based on homologous compositions.

which were taken from intermediate sections of the original castings. The <sup>109</sup>Cd source provides high signal-to-noise or baseline ratio to the elements below 12 kV and hence closer agreement than from the <sup>241</sup>Am source.

Since silver appears as an impurity in old brass and bronze, it is important to be able to detect it in the 0.05% to the 0.5% level to detect forgeries. We therefore employ the <sup>109</sup>Cd source for the elements listed up to 15 kV and the <sup>241</sup>Am source from 15 to 45 kV. The <sup>241</sup>Am source is free from the silver artifact.

We also adjust the multiplier factor of column B to "fit" our reference standards, thereby increasing the accuracy considerably as judged by a closer fit to many objects which have been analyzed by other methods.

We have recently prepared a computer program which provides a better baseline correction for small samples (5 to 25 mg) so that there is a very close agreement with the analysis of the parent block from which the filings were obtained. Details of this work will be reported after these preliminary results are confirmed.

### C. Computer Read-Out

In mid-1971 we obtained a Hewlett-Packard 2114B computer with our HP 7620A chromatograph with the intent of adapting this computer to our x-ray fluorescence equipment. While Hewlett-Packard said that it was impossible at that time to operate this computer on line without going through an intermediate tape punching and reading operation, P. H. Gaither of our Scientific Advisory Committee not only took the necessary few steps to operate it on line but also to develop programs to make the computations and to provide direct read-outs of weight percent of 15 elements in the silver,

brass, and pewter programs, and 35 elements in our glass program. There is really no limit to the number of elements which can be determined in any one analysis. There is, however, a practical limit mostly because of the clerical requirements if too many elements are included in the analysis.

The computer read-out has enabled us to analyze 15 elements and characterize over 2000 silver objects of American origin and about 100 of British origin during the past year. We can now distinguish the origin and authenticity of most pieces with a high level of confidence on the basis of silver, copper, and minor element content. Table VII shows typical results from six tankards made by Paul Revere in 1768 (Fig. 4). Only 4 elements are listed in this table although 15 were determined. We also analyzed in one afternoon a group of 24 15th century Italian bronze objects in a joint study with the National Gallery of Art and the Louvre and showed that 3 of these objects had 15 elements present in identical concentration and, even though they had been separated for over 100 years, they were indeed poured from the same batch of metal. Furthermore, 1 piece was a medallion of a 15th century pope and was signed by the sculptor. Details of this work, which would be the envy of Ripley's "Believe It or Not" creation, will be published soon.

### D. Operational Procedures for Computer Read-Out for Metal Objects Employing "Reference Standards"

1. Choose the element which is to provide the baseline correction. This is generally the principal element or one whose secondary peak overlaps an important element peak.

Alloy	Principal element	Baseline	Source
Sterling silver	Silver	Silver	<sup>109</sup> Cd
Silver solder			
Pewter	Tin	Tin	<sup>109</sup> Cd
Brass	Copper	Copper	<sup>241</sup> Am
Bronze			
German silver			

The <sup>109</sup>Cd source actually produces silver x-rays which are a result of a nuclear transformation. These x-rays not only excite the elements in the object being analyzed but also enter the detector by a direct backscattering process, or by the Compton backscatter, so that a silver artifact always appears when employing the <sup>109</sup>Cd source. When analyzing pewter, the 22.3 kV backscatter peak is more prominent than the tin peak which appears with the secondary silver peak near 25 kV. We employ tin to produce the baseline when analyzing pewter since this compensates for the 25 kV silver artifact which appears in the tin peak.

This same principle applies in separating the secondary copper peak from the principal zinc peak when analyzing brass. We have standardized our procedure to accumulate data from pure copper for the baseline and from the copper in the brass or bronze object until a count of 10 000 is reached in the 8.1 kV copper peak. This requires about 5 min. Here the copper baseline is made to equal the principal copper peak from the object so that the overlap of copper and zinc at 8.7 kV is resolved, leaving only counts from the zinc.

2. Choose the element which is to serve as the "internal standard." Counts from the appropriate peaks of all the elements are "ratioed" to this element.

3. Locate the channels where the elements of interest appear. This can be done to a first approximation from Table III and precisely located from the Teletype read-out.



FIG. 4. A beautiful set of six tankards in the Winterthur Collection made by Paul Revere in 1768 provided us with an excellent opportunity to characterize Revere's alloy-making practice as noted in Table VII. Photograph courtesy of The Henry Francis du Pont Winterthur Museum.

TABLE VIII. Computerized analysis of metals.

Accompanying notes:

a. Arsenic, which frequently appears with lead in glass and bronze, is determined as follows. From Table I, lead counts in the absence of arsenic

kV	Counts	
	<sup>241</sup> Am	<sup>109</sup> Cd
10.6	16	75
12.6	20	80
Ratio 10.6/12.6	0.80	0.94

Since arsenic appears at the 10.6 kV peak, its net count will be: arsenic normalized to copper:

Source	
<sup>241</sup> Am	As count = 0.59 (Pb <sub>10.6</sub> - 0.80 Pb <sub>12.6</sub> )
<sup>109</sup> Cd	As count = 1.0 (Pb <sub>10.6</sub> - 0.94 Pb <sub>12.6</sub> )

b. Since the Compton backscatter peak (CBS) at 20.8 kV builds up at the expense of the principal silver peak at 22.3 kV, errors occurring in analyzing small samples (5 to 100 mg) can be reduced by adding three times the 20.8 kV peak to the 22.3 kV silver peak.

Alloy:	Silver	Pewter	Brass, bronze
Source:	<sup>109</sup> Cd	<sup>109</sup> Cd	<sup>241</sup> Am
Baseline:	Ag	Sn	Cu
"Internal reference":	Ag	Sn	Cu
Range, kV:	5-35	5-35	5-35
Peak count baseline element:	2000	2000	10 000
Number of channels (30 kV):	500	500	500
Normalizing factor:	K <sub>Ag</sub>	K <sub>Sn</sub>	K <sub>Cu</sub>

Item	Element	Z	Channel	kV			
1	Mn	25	12	5.9	0.120	0.015	1.0
2	Fe	26	22	6.4	0.100	0.01	0.8
3	Co	27	30	6.9	0.100	0.01	0.3
4	Ni	28	40	7.5	0.070	0.02	0.3
5	Cu	29	50	8.1	0.175	0.071	1.0
6	Zn	30	59	8.6	0.120	0.043	0.64
7	As	33	92	10.6	0.040	0.015	0.40
							(a)
8	Ag	47	286	22.3	1.0	0.00	0.11
	Ag		263	20.8	(b)		
	(CBS)						
9	Cd	48	303	23.3	1.0	0.00	0.10
10	Sn	50	338	25.3	1.1	1.0	0.097
11	Sb	51	357	26.3	1.2	1.2	0.09
12	Au	79	105	11.6	0.13	0.01	1.40
13	Hg	80	114	13.9	0.12	0.01	1.45
14	Pb	82	127	20.0	0.10	0.052	1.60
15	Bi	83	134	13.1	0.09	0.035	1.65

4. Include two channels from each side of these "peak" channels so that a "shift" of the peak channel will not "lose" the peak value. A peak shift of one channel in 24 h is not uncommon. The sum of the counts of the peak and the adjacent four channels provides the "gross count" for each element.

5. Establish the gross count of the same five channels from the baseline for each element. Deduct these from item 4, giving a "net count."

6. The product of these net counts and the normalizing factors ( $K$ ) of Table VIII gives the "weight equivalent count" for each element.

7. The weight percent of each element is in the ratio of weight equivalent count to 0.01 times the sum of weight equivalent counts of all the elements being analyzed.

Each morning we make a baseline run and a run from our reference standard. If there is a channel shift of the principal peaks or a change in response to the principal elements, we compensate the " $K$ " (normalizing factor of Table VIII) and the channel number for these changes in the computer. This adjustment takes only a few minutes.

In a few cases where we checked the reference standards of other laboratories, we made several determinations over an extended period and averaged the results to achieve a high level of accuracy. Such duplicate analyses are seldom justified in our routine work.

Table VII is given as an example of our silver analysis study. Four of the 15 elements determined are tabulated for 8 parts each of a 6-tankard set made by Paul Revere in 1768.

It appears that Mr. Revere made up his castings in 2 units per lot. The items marked with a superior "a" are near enough alike chemically to have been made from the same batch of molten silver. From these measurements we might even be able to say that his tankard department was geared up to make two tankards at a time.

A characteristic of American-made holloware silver (coffee pots, tea services, tankards, etc.) is the variability of composition of the various parts in a piece. British-made silver has a smaller variability between parts of a piece, and none of them has yet been found to contain less than the 92.5% minimum of silver. Because of the stringent enforcement of the minimum silver requirement, the British silversmith played it safe so that 94 to 95% silver is common and 92.5% is the exception. Most American silversmiths, on the other hand, exercised little if any control over the composition of their alloys.

Fig. 5 shows a British-made tankard whose body was replaced and touchmarked "J.R." for Joseph Richardson, famous Philadelphia silversmith. The composition of the various parts and of the silver solder used on this tankard is listed in Table IX.

#### E. Analysis of Glass and Ceramics

Museum laboratories employ a wide range of instruments and techniques for the analysis of glass and ceramic objects. These range from wet chemical methods to emission spectroscopy and atomic absorption, to name a few. No one method provides a complete analysis. Furthermore, few curators will permit samples of sufficient size for reasonable analytical accuracy to be removed. Since none of these limitations applied to energy-dispersive x-ray fluorescence analysis, we de-

cidated to try to segregate 48 glass objects into two sets. Some were authentic Massachusetts-made Sandwich 3-mold blown glass and some were forgeries. It was no surprise to find that the 38 detectable elements in each of the 48 objects varied considerably and no order could be established.

Some order was restored, however, when the curator separated the objects into two sets based on other information which he had withheld up to this time. The analytical procedure was as follows:

1. Thirty-five elements at peak locations determined from Table III were listed in a table similar to Table XII.

2. An "element finder mask" (Fig. 6) in which the locations of the elements of item 1 were underlined to facilitate locating the peaks without having to examine 512 6-digit numbers.

3. A baseline was established for each of our sources by irradiating a piece of high purity silica for 500 sec. Counts at the peak locations were tabulated in column A.

4. The object was irradiated for 500 sec, and the gross counts were tabulated in column B.

5. The concentrations of the various elements were calculated from the count data of Table III after subtracting the baseline counts.

While we later learned of the errors in absolute concentrations due to matrix effect, the results still were usable because they were consistent between pieces.



FIG. 5. Example of a British-made tankard which had been "up-graded" to help fill the demand for higher priced "American antiques." A former owner, apparently in attempting to remove the marks which distinguished it as being British-made, ruined the body and replaced it with 20th century sterling silver which lacked impurities characteristic of old silver, as shown in Table IX. Photograph courtesy of The Henry Francis du Pont Winterthur Museum.

TABLE IX. The Winterthur Museum Analytical Laboratory silver analysis data report: "J. Richardson" tankard, accession number 64.52.

Analysis of parts of a tankard (Fig. 5) bearing the J.R. touchmark of Joseph Richardson, famous 18th century Philadelphia silversmith. All parts except the body are high in silver, typical of early British pieces. The body, lacking traces of gold, is strictly 20th century silver of compositions 92.5% Ag, 7.5% Cu. One theory is that a previous owner, wishing to upgrade an otherwise good British tankard to take advantage of the higher prices being paid for American antiques, goofed when he attempted to remove the inscription and the original maker's mark. He made a new body from 20th century sterling silver, which is free of the gold impurity of old silver. Furthermore, he employed a 20th century silver solder to bond the bottom of the handle to the new body. This solder lacks the 0.2 to 1.0% lead which is present as an impurity in old solders. Furthermore, his copy of Richardson's touchmark was not too carefully made so that the forgery was detected several years ago. This piece is part of Winterthur's "Study Collection," which includes odd pieces for training graduate students in residence to be wary.

Part	Ag	Mn	Fe	Co	Ni	Cu	Pb	Zn	Au
Lid	92.8	0.00	0.03	0.04	0.02	6.5	0.32	0.07	0.13
Base rim	93.8	0.03	0.02	0.05	0.02	5.5	0.31	0.07	0.11
Side	92.5	0.02	0.04	0.06	0.01	7.4	0.01	0.06	0.00
Handle	91.7	0.06	0.03	0.04	0.03	7.4	0.37	0.14	0.16
Top of hinge	94.7	0.02	0.07	0.04	0.01	4.6	0.20	0.09	0.12
Bottom of hinge	94.6	0.03	0.13	0.05	0.01	4.6	0.24	0.09	0.13
Underside	94.7	0.08	0.06	0.05	0.01	4.5	0.31	0.07	0.14
Solders									
Bottom to rim	84.7	0.04	0.06	0.05	0.05	11.6	0.43	3.0	0.09
Top of handle to side	77.8	0.11	0.10	0.12	0.10	13.8	0.17	7.6	0.02
Bottom of handle to side	89.3	0.14	0.14	0.13	0.09	6.3	0.09	3.5	0.10

ELEMENT CHANNEL FINDER 5-35 Kv.		El.Chan'l.	
000000	000500	000003	000014
000008	000214	000312	000492
000016	000805	000812	000841
000024	000586	000674	000628
000032	000879	000879	000827
000040	000739	000738	000701
000048	000422	000591	000517
000056	000429	000479	000412
000064	000312	000320	000336
000072	000241	000284	000244
000080	000229	000202	000189
000088	000212	000210	000224
000096	000155	000154	000142
000104	000127	000122	000110
000112	000124	000128	000124
000120	000117	000133	000112
000128	000140	000133	000155
000136	000124	000164	000172
000144	000138	000109	000095
000152	000177	000160	000106
000160	000096	000105	000142
000168	000121	000082	000076
000176	000190	000205	000263
000184	000108	000111	000144
000192	000316	000302	000247
000200	000383	000137	000154
000208	000296	000239	000178
000216	000063	000055	000057
000224	000062	000093	000091
000232	000074	000076	000073
000240	000079	000080	000080
000248	000070	000069	000058
000256	000073	000058	000066
000264	000076	000061	000085
000272	000067	000070	000067
000280	000095	000134	000162
000288	000213	000126	000118
000296	000092	000093	000144
000304	000290	000231	000209
000312	000081	000112	000173
000320	000509	000473	000468
000328	000095	000102	000133
000336	000460	000528	000514
000344	000124	000097	000076
000352	000334	000433	000468
000360	000255	000176	000123
000368	000124	000194	000256
000376	000334	000288	000238
000384	000075	000067	000071
000392	000172	000085	000067
000400	000082	000085	000067
000408	000076	000077	000105
000416	000133	000102	000106
000424	000124	000182	000214
000432	000418	000466	000483
000440	000149	000112	000112
000448	000319	000341	000349
000456	000441	000386	000281
000464	000133	000154	000183
000472	000338	000376	000402
000480	000252	000170	000139
000488	000243	000309	000370
000496	000474	000532	000525
000504	000203	000178	000151

FIG. 6. A mask made from an 8 1/2 x 11" transparent plastic "sheet protector" underlining the location of the principal peaks of the elements in the 5 to 35 kV range facilitates the location of 31 peaks without having to examine all the 512 6-digit numbers tabulated for one analysis. A teletype read-out from NBS Glass 610 has been slipped into the mask as an illustration. The left-hand column designates every 8th channel. The other 8 columns are count data from the 8 intermediate channels. It will be noted that some of the peaks shifted a channel after the mask was made. The true peaks can be seen

The following features were noted between the authentic and forgery pieces:

Element	Authentic	Forgery
Ti	50-200 ppm	0
Pb	25-30%	20-22%
Mn, Fe, Co, Cu	Variable	Variable

The silica sand at Sandwich apparently contains traces of ilmenite whereas "Brand X" acid-treated their sand to remove these black titanium-containing particles.

The results of this and other glass studies will be reported elsewhere.

### F. NBS Test Glasses

The National Bureau of Standards in cooperation with Robert Brill of the Corning Museum of Glass made some test glasses 610, 612, 614, and 616 containing 61 elements at concentration levels of 500, 50, 1, and 0.02 ppm. These have been used at many laboratories throughout the world to check their analytical methods. These glasses gave us an opportunity to have reference standards for comparing glasses, glazes, and ceramic bodies.

In a few scouting experiments we have used these glasses to measure the composition of component objects such as porcelain, glazed redware, and stoneware. While we don't yet know how to relate instrument readings to a heterogeneous glazed ceramic object, we have obtained significant descriptive information about several porcelain pieces that is of considerable value. This work on ceramics is in progress and will be reported when definitive results are obtained.

The NBS glasses did provide a badly needed refer-

at a glance in spite of this shift. Since our computer cannot exercise this judgement, we add the counts from the adjoining 2 channels to the peak channel count.

TABLE X. NBS 610, 612, 614 glass, 20 June 1972,  $^{109}\text{Cd}$  source, 5 to 35 kV, 500 sec.

Analysis results of NBS 612 glass having 61 elements at its 50 ppm level. The  $^{109}\text{Cd}$  source is employed for elements Mn through Mo, and Au, Pb, and Bi. The  $^{241}\text{Am}$  source provides more favorable signal-to-baseline sensitivity for these elements than does the  $^{241}\text{Am}$  source shown in Table XI. Analytical results in column M are based on computations employing Table III and corrections from Fig. 7. Column N analytical results are direct ratios from NBS 610 glass. Column description: A: NBS 614 glass, counts/500 sec, baseline; B: NBS 610 glass, counts/500 sec; C: NBS 610 glass, net counts (B - A); D: NBS 610 glass, concentrations, ppm; E: NBS 610 glass, total net counts normalized to 500 ppm/500 sec; F: NBS 610 glass, net counts normalized to 500 ppm/sec; G: peak counts for elements from Table I; H:  $G \times 0.005$  (cps/500 ppm); I: ratio of measured counts per sec from NBS glass to column H; this column indicates fluorescence enhancement of glass matrix over pure elements; the value for gold is suspect; J: NBS 612 glass, counts/500 sec; K: NBS 612 glass minus baseline (614 glass) counts/500 sec; L: NBS 612 glass concentrations, ppm reported by NBS; M: concentrations calculated from basic data of Table III; N: concentrations calculated from ratios of counts: (counts NBS 612  $\times$  ppm 610)/(counts NBS 610).

Element	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
Mn	25	44	75	31	485 <sup>a</sup>	32	0.064	54	0.027	2.4	50	6	40 <sup>a</sup>	102	69
Fe	26	52	93	41	460 <sup>a</sup>	43	0.086	74	0.037	2.3	57	5	51 <sup>a</sup>	56	56
Co	27	40	93	53	390 <sup>a</sup>	68	0.136	93	0.047	2.9	48	7	35 <sup>a</sup>	54	52
Ni	28	45	113	68	500	68	0.135	117	0.058	2.6	61	16	38 <sup>a</sup>	83	64
Cu	29	60	179	119	444 <sup>a</sup>	134	0.268	150	0.075	3.6	71	11	37 <sup>a</sup>	38	41
Zn	30	37	191	154	433 <sup>a</sup>	178	0.356	172	0.086	4.2	58	21	50	55	59
As	33			131	500	131	0.260	158	0.079	3.4		15	50	63	57
Rb	37	42	535	493	425 <sup>a</sup>	500	1.00	200	0.10	10.0	78	36	32 <sup>a</sup>	33	32
Y	39	41	744	703	500	703	1.41	256	0.128	11.0	110	69	59	49	49
Zr	40	61	900	839	500	839	1.68	250	0.125	13.5	138	77	50	46	43
Nb	41	45	961	916	500	916	1.83	210	0.105	17.5	128	83	50	45	45
Mo	42	57	929	872	500	872	1.74	230	0.115	15.1	141	84	50	48	48
Au	79	37	97	60	25 <sup>a</sup>	1200	2.40	42	0.021	100	58	21	5 <sup>a</sup>		3
Pb	82	48	198	150	426 <sup>a</sup>	176	0.34	53	0.027	12.6	69	21	39 <sup>a</sup>	63	59
Bi	83	38	370	332	500	332	0.66	41	0.021	31.0	78	40	50	63	60

<sup>a</sup> Certified values.

ence for our glass study. The magnitude of the matrix effect was determined in which the instrument response is enhanced many-fold when elements are contained in a glass matrix than when they are separately excited. These enhancements are shown in columns H and I of Table X in which 610 glass was excited by our  $^{109}\text{Cd}$  source. The enhancement factors are plotted as a function of atomic numbers in Fig. 7.

In Tables X and XI we have demonstrated that excellent analytical results can be obtained at low element concentrations in a similar glass matrix. We could achieve even closer agreement empirically if we were sure of the actual composition of the noncertified elements in the sample.

We have now computerized our glass analyses, which enables us to determine 15 elements with our  $^{109}\text{Cd}$  source and 20 others with our  $^{241}\text{Am}$  source in about 20 min total elapsed time. These determinations are made by having the computer compare the number of counts associated with the various elements to those of the NBS 610 glass and employing the NBS 614 glass as a baseline. We cannot determine the low atomic number major elements such as Si, Na, Mg, Al, and O, and so we report only the elements above calcium.

### G. Analysis of Brill's Synthetic Ancient Glasses A, B, C, and D

In 1968 Dr. Robert H. Brill, Director of Research at the Corning Museum of Glass, prepared four glass samples designated A, B, C, and D containing related concentrations of elements detected in ancient glass found in archeological sites throughout the world. He sent duplicate samples to over 20 laboratories active in analyzing archeological objects. The results from 16

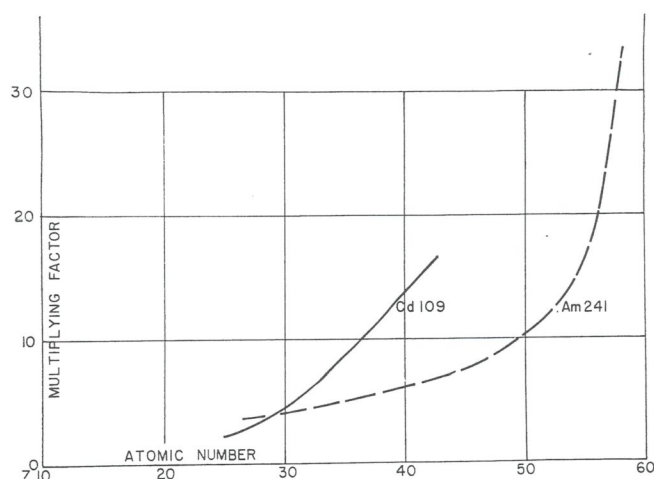


FIG. 7. Correction factors for matrix effect in glass. The NBS 610, 612, and 614 glasses have 61 elements in the 500, 50, and 1 ppm concentration levels. These elements in a glass matrix produce fluorescence radiations in greater proportion than when irradiating the pure elements by themselves. This "matrix effect" creates from 5 to 35 times as many counts than would be predicted for any one element from Table III. To determine weight per cent the counts per second values in the tables should be normalized by multiplying by the appropriate "multiplying factor."

laboratories were appraised and the most probable values were derived by a statistical analysis and reported to Dr. Brill by E. Plumet, Directeur des Recherches, Glaverbel, Gilly, Belgium, in 1970.

We analyzed these glasses and calculated the concentrations of the 19 elements reported to Dr. Brill. Plumet reported the weight percentages as oxides from



TABLE XI. NBS glass 610, 612, 614, <sup>241</sup>Am source, 5 to 35 kV, 500 sec, 15 June 1972

Analysis results of NBS test glass 612 having 61 elements at the 50 ppm level based on NBS glass 610 having the same 61 elements at the 500 ppm level. Elements above niobium ( $z = 41$ ) require the <sup>241</sup>Am source. Note that copper and zinc do not appear because of the high baseline at low energies. These elements are readily detected by employing the <sup>109</sup>Cd source (see Table X). Column O analytical results of NBS 612 glass are based on Table III with correction from Fig. 7. Column P analytical results are based on a direct ratio of the counts obtained from NBS 610 glass. Composition on basis of interpolation. Column description: Z: atomic number; A: channel number of fluorescence peak; B: kV energy of fluorescence peak; C: counts per 500 sec from 614 glass (1 ppm) for baseline; D: counts per 500 sec from 610 glass (500 ppm); E: net counts: column D-column C; F: parts per million in 610 glass; G: net counts normalized to 500 ppm; H: counts per sec per 500 ppm (column G/500); I: counts per sec from Table III; J: counts per sec from Table III normalized to 500 ppm and 60 V/channel span (column I  $\times$  0.0005  $\times$  30/25); K: counts per sec measured in 610 glass divided by prediction (column H/column J); L: counts per sec from NBS 612 glass (50 ppm); M: net counts from NBS 610 glass (column M-column C); N: concentrations reported by NBS; O: concentrations calculated by using curve; P: concentrations calculated from counts and concentrations in 610 glass (500  $\times$  column H/column D).

Element	Z	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P
Nb	41	192	16.7	39	316	277	500	277	0.55	149	0.089	6.2	76	37	50	83	66
Mo	42	207	17.5	43	324	281	500	281	0.56	159	0.094	6.0	75	32	50	66	57
Ag	47	285	22.3	43	290	247	254	490	0.98	200	0.120	8.2	77	34	22	45	35
Cd	48	302	23.3	39	324	285	500	285	0.57	129	0.078	7.3	81	42	50	81	73
In	49	320	24.3	56	509	453	500	453	0.90	136	0.082	11.0	107	51	50	87	56
Sn	50	333	25.3	57	528	471	500	471	0.94	173	0.105	9.0	92	35	50	45	37
Sb	51	353	26.5	46	533	487	500	487	0.97	125	0.075	13.0	117	71	50	120	73
Te	52	374	27.5	45	364	319	500	359	0.62	132	0.080	7.9	70	25	50	37	39
Cs	55	434	31.1	27	483	451	500	456	0.91	106	0.064	14.0	83	56	50	78	61
Ba	56	454	32.3	40	479	439	500	439	0.88	92	0.055	16	93	53	41	74	60
La	57	476	33.5	31	500	469	500	469	0.94	83	0.050	18.8	74	43	36	55	46
Ce	58	497	34.8	34	532	498	500	498	1.00	49	0.03	33	95	61	39	76	61
Cu	29	51	8.1	533	591	58	444	58	0.116	40	0.024	4.8	531	-2	37.7	0	0
Zn	30	60	8.7	329	391	62	433	62	0.12	51	0.031	3.9	306	-23	50	0	0
Rb	37	139	13.5	60	196	136	425	136	0.27	99	0.06	4.5	74	14	31.4	53	51

TABLE XII. Analysis results: Brill's synthetic ancient glass.

Column description: Z: atomic number; El: element; kV: energy of measured peak; A: percent of element reported by National Bureau of Standards, 610 glass B:

Elements	Irradiation time (sec)	Source	kV span
19-23	500	<sup>55</sup> Fe	1-6
24-30, 82, 83	500	<sup>109</sup> Cd	5-15
38-56	500	<sup>241</sup> Am	10-35

C: net counts calculated for 1% concentration level in NBS 610 glass; D: net counts calculated for 1% of values for elements from Table III; E: concentration of elements in NBS glass based on Brill glass A as standard; F: concentration of elements in Brill glasses reported by Glaverbel, S.A. Laboratoire Central, Gilly, Belgium, to Robert H. Brill of the Corning Museum of Glass in 1970; G: counts expected from 1% element concentration based on Brill's glass A; H: concentration based on linear extrapolations from NBS 610 glass; I: concentration based on linear interpolation from Table III data; J: concentration based on linear interpolation from Brill glass A.

Z	El	kV	A	B	C	D	E	Brill's glass A					Brill's glass B				
								B	F	G	H	I	B	F	G	H	J
19	K	3.3	0.046	70	1550	30	0.2	780	2.3	326	0.5	26	285	0.91	313	0.18	0.87
20	Ca	3.8	8.1	4600	568	250	8.07	2150	3.8	570	3.8	8.6	3540	6.3	562	6.23	6.21
22	Ti	4.4	0.0440	90	2045	560	0.054	800	0.48	1687	0.82	1.43	130	0.06	2167	0.06	0.078
23	V	5.0	0.050	140	2800	450	0.002	170	0.003	57K	0.06	0.38	75	0.016	4687	0.027	0.001
24	Cr	5.4	0.050	9	180	500	0.0005	13	0.0007	18K	0.07	0.026	0	0.0034	0	0	0
25	Mn	5.8	0.050	10	200	520	0.071	130	0.92	141	0.71	0.25	40	0.21	190	0.29	0.28
26	Fe	6.4	0.046	35	761	740	0.12	220	0.75	293	0.29	0.29	100	0.24	417	0.13	0.34
27	Co	7.1	0.040	34	850	800	0.068	60	0.12	500	0.071	0.075	25	0.028	893	0.029	0.05
28	Ni	7.6	0.045	47	1044	1000	0.066	17	0.024	708	0.017	0.017	54	0.027	2000	0.052	0.07
29	Cu	8.0	0.045	73	1622	1220	0.10	675	0.97	696	0.41	0.55	1900	2.1	905	1.17	2.7
30	Zn	8.7	0.043	71	1651	1380	0.043	50	0.03	1667	0.03	0.036	175	0.16	1094	0.11	0.10
82	Pb	12.7	0.043	80	1860	400	0.062	90	0.07	1286	0.048	0.22	640	0.37	1730	0.35	0.49
83	Bi	13.3	0.050	160	3200	350	0.029	5	0.0009	5555	0.0015	0.014	34	0.0045	7555	0.010	0.006
38	Sr	14.2	0.050	325	6500	430	0.053	550	0.09	6111	0.084	1.28	110	0.009	12.2K	0.017	0.02
40	Zr	15.8	0.050	180	3600	810	0.0056	100	0.0031	32K	0.028	0.12	100	0.018	5555	0.028	0.003
47	Ag	22.3	0.029	200	6896	1000	0.0060	60	0.0018	33K	0.008	0.06	90	0.009	10K	0.013	0.003
50	Sn	25.3	0.050	430	8600	860	0.052	1800	0.22	8182	0.21	2.1	360	0.03	12K	0.042	0.04
51	Sb	26.4	0.050	400	8000	630	0.044	11.7K	1.3	9000	1.4	18.6	3000	0.34	8823	0.37	0.33
56	Ba	32.2	0.050	400	8000	460	0.056	3450	0.48	7190	0.43	7.5	730	0.12	6083	0.091	0.10

TABLE XII. Continued

Z	El	kV	Brill's glass C					Brill's glass D				
			B	F	G	H	J	B	F	G	H	J
19	K	3.3	325	2.3	141	0.21	1.0	2000	9.6	292	1.8	8.6
20	Ca	3.8	830	3.1	230	1.45	1.46	4980	11.2	444	8.7	8.7
22	Ti	4.4	2280	0.49	4653	1.1	1.4	330	0.24	1375	0.16	0.20
23	V	5.0		0.003				85	0.008	10.6K	0.03	0.0015
24	Cr	5.4	40	0.0007	57K	0.22	0.002	0	0.0017	0	0	0
25	Mn	5.8	40			0.02	0.03	50	0.44	114	0.25	0.36
26	Fe	6.4	80	0.23	348	0.11	0.27	86	0.34	253	0.11	0.29
27	Co	7.1	60	0.13	462	0.07	0.12	1	0.017	59	0.001	0.002
28	Ni	7.6	47	0.024	1958	0.045	0.06	21	0.047	447	0.02	0.03
29	Cu	8.0	415	0.94	441	0.25	0.60	190	0.32	594	0.11	0.27
30	Zn	8.7	55	0.03	1833	0.03	0.03	60	0.08	750	0.04	0.04
82	Pb	12.7	10600	34.2	310	5.7	8.2	250	0.25	1000	0.13	0.20
83	Bi	13.3		0.009				15	0.0022	6818	0.004	0.003
38	Sr	14.2	310	0.09	3444	0.05	0.05	250	0.04	6250	0.04	0.04
40	Zr	15.8	80	0.0037	21.6K	0.02	0.003	80	0.009	8889	0.02	0.003
47	Ag	22.3	10	0.0018	5555	0.0014	0.003	60	0.0046	13K	0.008	0.002
50	Sn	25.3	220	0.17	1294	0.03	0.027	850	0.10	8500	0.10	0.10
51	Sb	26.4	0	0	0	0	0	5700	0.72	7917	0.71	0.63
56	Ba	32.2	12.3K	10.7	1150	1.5	1.7	2200	0.29	7586	0.27	0.30

which we calculated the percentages of the elements, as shown in column F of Table XII.

We calculated the number of counts that one would expect from a 1% concentration of each of these elements by interpolation or extrapolation from the following: (1) 1% of the counts reported for individual elements in Table III (column I for glass A); (2) extrapolation to 1% from the 500 ppm level in NBS glass 610 (column H); (3) interpolation or extrapolation of the counts in Brill's glass A (column J). The agreement between the results based on NBS 610 extrapolation and on the Brill glass A is remarkably close in Brill's glasses B and D. The agreement with data derived from Table III was not as good.

The agreement with glass C, which is similar to glass A except for 500 times the lead and 200 times the barium concentrations, is quite good with the trace elements, but we missed by a factor of 4 in extrapolating from 400 ppm for lead to 34% and from 500 ppm of barium to 10.7%. This problem can be resolved by making up a reference glass similar to glass C to employ with high lead glasses and glazes. We might even use Brill's glass C for this purpose. We consider the agreement between the nonlead glasses A, B, D, and NBS 610 to be excellent.

### III. DISCUSSION

#### A. Interpretation of Analysis Results

The analytical results from each silver object analyzed are recorded on "McBee"-type cards designed for the purpose by Dr. George Reilly of this laboratory. Each part of a complex piece is analyzed and reported separately. This is expected to permit scholars interested in the shop practices of the early silversmiths to discover if they made their own castings, trim, and solder, or if certain shops specialized and supplied certain parts to the trade. It also characterizes certain silversmiths by their practices so that "new finds" attributed to these craftsmen can be appraised on the basis of comparative data which we have on file.

We can express confidence in the minimum age of brass or bronze objects on the basis of trace impurities. This could cause some embarrassment to importers of shiploads of ancient oriental art objects if someone elects to check them.

### IV. FUTURE WORK

We expect to complete the analysis of the remaining 2000-odd silver and pewter objects during 1972-73. We will then tackle the more difficult problem of characterizing glass objects. We see possibilities of characterizing ceramic objects in sufficient detail to establish their place of origin. This is expected to take a few years more.

### ACKNOWLEDGMENTS

The cooperation of the Winterthur staff in the studies which led to the preparation of this article has been superb and to them I say, "Many thanks!" George Reilly, our Museum Scientist, has contributed many ideas and has been very helpful in programming our computer. P. H. Gaither, of our Scientific Advisory Committee, made up the interface between the analyzer and the computer and developed the computer programs which are very flexible and versatile. Charles Coxe of Handy and Harman was very helpful in making up our metal reference standards. Without Miss Catherine Wheeler's editorial assistance I might have abandoned this project. To them—many thanks!

1. *American Institute of Physics Handbook*. (McGraw-Hill, New York, 1963), 2nd ed.
2. G. G. Johnson, Jr., and E. W. White, *X-Ray Emission Wavelengths and KEV Tables for Nondiffractive Analysis* (ASTM Data Series DS 46) (American Society for Testing and Materials, Philadelphia, 1970).
3. R. S. Frankel and O. W. Aitken, *Appl. Spectrosc.* **24**, 557 (1970).
4. A. L. Heath, R. S. Frankel, R. J. Gehrlee, and J. Barstow. *Proc. Anal. Instr.* **9**, F-2 (1971).

*feature author*



Victor Hanson, Coordinating Scientist of the Henry Francis du Pont Winterthur Museum, received a B.S. in Physics from the California Institute of Technology

in 1926 after which he did research in geophysics, chemical process development, and "talking movies" for years in California before joining the E. I. du Pont Nemours Company at Niagara Falls in 1934. There he founded and supervised the physical laboratory and obtained several patents on instruments and processes. One of these, described in A.C.S. Anal. Ed., Vol. 1941, "Ultraviolet Photometer for Quantitative Measurements of Small Traces of Solvent Vapors in Air," is still employed in checking air pollution.

He coordinated the instrument development work for the Hanford Engineer Works original atomic energy project which du Pont designed and built for the government in 1943. He served as the first Instrumentation Department Superintendent at that plant through 1944 and 1945.

He established and directed the following instrumentation-oriented corporate laboratories for du Pont:

1945 Applied Physics Section

1950 Instrument Development for the A.I. Savannah River Plant

1954 Radiation Physics Laboratory

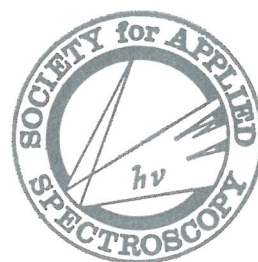
1959 Engineering Physics Laboratory

He presented an invited paper at the Stockholm Instrumentation Conference in 1949; was Chairman of the Gordon Conferences on Instrumentation in 1949 and 1950; organized and chaired the session, "Applications of New Analytical Techniques to Process Control," at the 1959 National A.C.S. meeting at Atlanta; and has been trustee and Chairman of the Instrumentation Research Committee of the University of Delaware Instrumentation Research Foundation for a number of years.

He vacationed in Greece for 3 weeks after retirement from du Pont in 1969, after which he organized a museum laboratory in which he undertook the developments reported in this article as a part time postretirement job.

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