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Particle Induced X-ray Emission (PIXE) in Multielemental Analysis

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In this paper, we report some recent results of PIXE elemental analysis. Using PIXE technique, measurements for a collection of precious ancient Chinese artifacts have been performed with 3 MeV protons from our 9SDH-2 tandem accelerator. From the elemental determination with external-beam PIXE and vacuum-beam PIXE, the major and minor elemental contents of ancient bronzes and potsherds were obtained. The samples studied include fragments of bronze weapons of Yin-Shang and Chou dynasties (- 1600 BC), and Penghu potsherds recently recovered from deep seabed in the Penghu coast near Taiwan. Details of experimental results are given and discussed.

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I. Introduction

As is well known, a few MeV proton beam from an accelerator excites the electrons in the inner-shell of the atoms of a specimen, and characteristic x-rays are emitted in the ion-atom collision process. Detection of these x-rays and analysis of the measured PIXE spectra permit absolute determinations of the amounts of the concentration of various elements with atomic number $Z \geq 13$ in the specimen. The large atomic cross section for inner-shell ionization together with the low background radiation production make it possible to perform trace element analyses [1-7]. The mechanism and methodology of PIXE have been given in the literature [1, 2]. In recent years a large amount of PIXE works by many small accelerator group were reported at several international conference [8, 9]. Successful application areas such as materials science, semiconductor research, environmental science and archaeology have been shown.

Since a new 3 MV 9SDH-2 tandem accelerator became operational in our laboratory at the Institute of Physics, Academia Sinica in mid-1989, the machine has been dedicated to the research in the field of atomic physics and low energy nuclear physics. In 1992, several accelerator-based methods such as PIXE, RBS (Rutherford backscattering spectrometry) and NRA (nuclear reaction analysis) were developed. Among them, the PIXE technique was extensively used for elemental analysis. It has been successfully used for case studies in archaeology [3-6] and plant culture [7]. We have determined the elemental content of glazed and body parts of ancient Chinese potsherds [3], the major and trace elements of

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Chinese bronze artifacts [4], including bronze drinking vessels and helmet of Chou and Shang dynasties (16th-7th century B.C.), and a series of Chinese coins that were manufactured over a two thousand year time span [5, 6]. These studies have complemented the wealth of archaeological data obtained in this laboratory. In plant culture, we have made an application of PIXE in trace-element analysis of normal and vitrified carnations cultured in vitro [7], and found that the vitrification process is related to the amount of trace elements (K, Ca, Fe and Zn) of the plant tissue in vitro culture.

Furthermore, we have made progress in the PIXE measurement and analysis, and achieved some technical improvements on the external beam PIXE facility and used powerful GUPIX program [10] for data analysis. In this paper, we report on recent PIXE research with both in-vacuum and in-air (external beam) measurements. Investigations have been performed for the study of ancient Chinese bronze weapons (16th-7th century B.C.), and Penghu collection of ancient Chinese potsherds (A.D. 1500-1911). In the measurement, more than two PIXE spectra were obtained for each sample. From the detailed analysis, the elemental composition of the examined samples were determined.

II. Experimental

The details of the experimental setup, external-beam milliprobe and detection system for the PIXE measurement has been described elsewhere [3, 4]. A brief description is given as follows:

Samples were placed at 10 mm outside the beam exit window (a 10 μm kapton foil) and irradiated with 3 MeV protons from our 9SDH-2 pelletron tandem accelerator. The 30" beamline system was provided with a milliprobe at the end for external beam PIXE measurement. After passing through a short distance in air, the beam hits the target with a small spot of size l-2 mm in diameter. At least two spots on the sample surface were irradiated per run. Measurement of the X-rays emitted from the target surface was performed using a 30 mm^2 HpGe detector with an energy resolution of 145 eV at 5.9 keV. The detector was placed at a distance of 30 mm from the target. For measurements of bronze samples, a cobalt foil was used as absorber and inserted in front of the detector window to suppress the intense Cu K X-rays. A beam current of about 3 nA was used keeping the count rate always less than 1000 counts/sec. All PIXE spectra were recorded with conventional electronics followed by a Canberra series-95 MCA.

External beam PIXE was carried out for the studied bronze samples. For the studied potsherds, both vacuum beam PIXE and external beam PIXE were used for samples group I (small size) and group II (large size), respectively. Vacuum PIXE measurement was done using the 0" beamline for the small potsherd samples, which was set inside a 35.6 cm chamber maintaining at a vacuum of 10^{-7} Torr. The chamber was designed for X-ray measurement with a side port through which a HpGe detector arm can be placed closely to the target at 60" to the incident beam direction.

III. Samples

III-l. Ancient Chinese bronze weapons

In ancient China, the glorious bronze age appears in the Yin-Shang and Chou dynas-

ties (16th-7th century B.C.). Among vast quantities of bronze production, the manufacture of bronze weapon involve a special casting process so that the weapon produced could perform its bellicose function efficiently in the battle field. The type of ancient weapon was generally categoried into hand-held offensive and defensive, and projectiles. Closed-combat weapons normally consist of weapons with a shaft such as the dagger-axe, ji or spear. The sword and short-handled knife were used in defensive. Arrow heads, the modest-distance offensive projectiles, were bronze tipped and the crossbow mechanism was also forged from this metal. In the present analysis, we obtained [11] eighteen fragments of ancient bronze weapons including Ko (dagger axe), Mao (spearhead) and Chien (sword) of the Yin-Shang and Chou dynasties, six pieces each. For each sample, characteristic X-rays produced from the proton bombardment at two different positions on the sample surface were measured.

III-2. Penghu potsherds

Remains of a wreck on the seabed of the Penghu coast near Taiwan was found in September, 1995 by a working team in an exploration under a national project supported by the Ministry of Education [12]. It was reported that many ancient potsherds were recovered from the Chiangchun-Ao-Yu seabed, belonging to the products made in the late Ming and Ching periods (AD 1500-1911). Among these, severals were sent to this laboratory for PIXE analysis [13], including group I: five blue-and-white glazed potsherds and one white glazed potsherd (samples 175-l to 175-6), and group II: two fragments of red glazed pottery ware, and one fragment of gray corallite (samples 200-7 to 200-g). In the measurement of PIXE spectra, the beam spot was directed at the surface of glazed colors, and two measurements were made for each color.

IV. Results and discussion

IV-l. Ancient Chinese bronze weapons

The samples analyzed were a small part of the precious collection of bronzes unearthed from the ancient tombs in Ho-Nan, China, belonging to the relics in the Yin-Shang and Chou dynasties. Fig. 1 shows the typical X-ray spectra obtained from the front surface of sample Chien-5. Table I summarizes results of the PIXE analysis for fragments Ko, Mao and Chien. The values shown are the mean concentration obtained from two runs for beam impact at two different positions on the surface of the samples. In determination of elemental contents commercially available SRM 871 bronze alloy was used as standard reference material. The results confirm the samples analyzed to be a kind of Cu-Sn-Pb alloy with some trace elements Fe, Ni, Zn and Sb. We observed variations in the major contents for three different bronze weapons, and found an average ratio of content Cu:Sn:Pb = 78.6:17.1:4.2, 82.8:11.6:5.3, and 75.4:15.6:8.5 for samples Ko l-6, Mao l-6 and Chien l-6, respectively.

We note that the Cu content lies in the ranges 75-80% and SO-85% for Ko and Mao, respectively, but in a wider range 70-81% in Chien. In comparison, samples Mao have a higher value of Cu content. However, all samples were found to have low concentration in Pb (3-6%) except for samples Chien-3, Chien-4 and Chien-5. The observed Sn content is very significant. As is known nowadays, an adequate amount of Sn (12-18%) adding in the casting process make efficiently the bronze alloy hardened. From the amount of Sn content

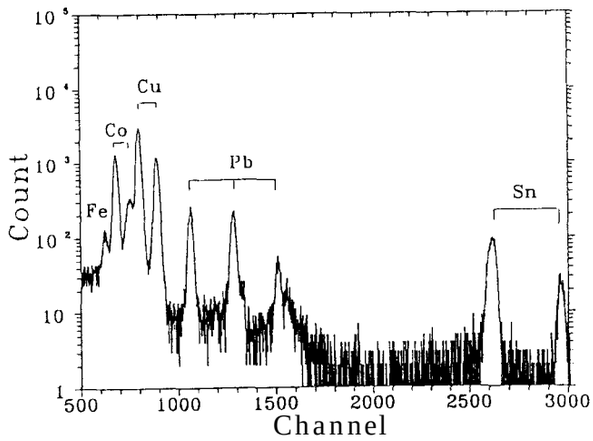

FIG. 1. PIXE spectrum from 3 MeV proton bombardment on a bronze fragment Chien-5.

TABLE I. Result of PIXE analysis of the ancient Chinese bronze weapons: Elemental composition in % by weight.

Sample		cu	Sn	Pb
Ko	1	80.6	12.6	6.56
(Dagger-axe,	2	79.2	18.1	2.64
Yin-Shang)	3	79.9	15.4	4.44
	4	76.2	20.2	3.58
	5	80.0	15.4	4.30
	6	75.7	20.8	3.48
Mao	1	84.2	10.2	5.10
(Spearhead,	2	85.1	10.8	3.71
Yin-Shang)	3	81.7	12.3	5.32
	4	80.0	13.6	5.61
	5	82.3	12.5	5.10
	6	83.4	10.1	6.49
Chien	1	75.8	18.6	5.00
(Arrowhead,	2	75.8	14.8	8.89
Chou)	3	70.9	19.5	9.05
	4	77.3	12.4	9.72
	5	71.4	14.3	13.8
	6	81.2	14.1	4.18

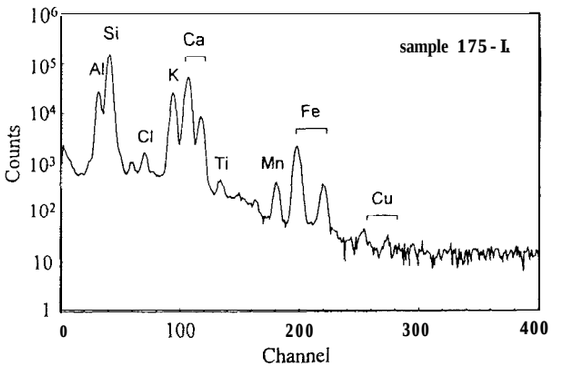

FIG. 2. PIXE spectrum from 3 MeV proton bombardment on the light blue surface of potsherd (sample, No. 175-l).

and its small variation found in the present analysis, it seems that our ancient craftmen have developed skills to some extents to control the Sn content in casting bronzes and to improve the quality of cast weapons in hardness.

IV-2. Penghu potshercls

Measurement of PIXE spectra was performed using vacuum beam PIXE for samples group I and using external beam PIXE for samples group II because of large size. Fig. 2 displays the typical PIXE spectra obtained from the light blue glaze (sample 175-l). We used SRM JB-1 as standards in determining the elemental contents. The results are listed in Tables II and III.

For group I, samples 175-l to 175-5 (underglaze blue), the contents of main elements Si, Al, and Ca (as shown in Table II) are among 62-69%, 20-28% and 2-8%, respectively. Their variations are seen to be small. Listed in Table II are also the measured minor concentrations (Mg, P, K, Ti, Mn and Fe) and ppm level of trace elements (Cl, Cr, Co, Ni, Cu and Zn). No significant change in the minor elements for these samples was observed. As was known, the ancient Chinese underglaze-blue ware often used a cobalt-blue pigment [14] with a mixture of small amounts of some metal elements such as Mn and Fe. Among the analyzed samples, there are four (samples 175-1, 175-2, 175-4 and 175-5) with a decorated pattern in two different blue colors (light blue and dark blue) on the surface. Results of measurements using beam spot directed at these two blue colors, we have observed noticeable difference in Co and Mn contents. Their contents are higher in dark blue glaze and lower in light -blue glaze. However, no appreciable variation in Fe content was found. For white-glaze, the results on the composition obtained from measurements at white color on the front and back surfaces (samples 175- 1 to 175-6) show to be in good consistence.

Recently Cheng et al [15] have reported PIXE analysis of Ching dynasty porcelains made at "Kuan" kiln. Their results on the mean concentration of main elements show a higher Si content (about 78%) and a lower Al content (about 15.9%) as compared to our measurements (65.7% in Si and 23.5% in Al). The apparent difference indicates that the Penghu potsherds studied in this work were of different origin from theirs.

TABLE II. Elemental composition of the Penghu potsherds (blue-and-white porcelain) in % by weight (composition in ppm for trace elements)

Sample	irradiated	Mg	Al	Si	P	K	Ca	Ti	Mn	Fe
175-1	light blue	2.64	24.4	66.2	0.21	0.71	5.12	0.02	0.06	0.54
175-1	dark blue	2.89	27.0	62.1	0.19	0.67	5.68	0.03	0.72	0.65
175-1	white(front)	2.51	25.2	65.4	0.04	0.50	3.72	0.02	0.05	0.38
175-1	white(back)	2.29	27.3	63.4	0.01	0.68	5.60	0.02	0.06	0.50
175-2	dark blue	3.38	27.3	63.5	0.24	0.60	3.04	0.05	1.13	0.71
175-2	light blue	3.96	27.7	63.2	0.13	0.58	3.42	0.04	0.37	0.59
175-2	white(front)	4.02	27.8	63.1	0.23	0.62	3.59	0.06	0.03	0.55
175-2	white(back)	3.34	27.8	64.0	0.23	0.67	3.10	0.05	0.04	0.69
175-3	light blue	6.02	19.6	68.6	0.09	0.68	4.19	0.02	0.08	0.62
175-3	white(front)	6.14	19.5	68.8	0.09	0.69	4.03	0.02	0.04	0.56
175-3	white(back)	4.54	19.9	70.4	0.10	0.69	3.65	0.02	0.05	0.59
175-4	light blue	4.87	20.5	65.3	0.07	0.51	8.03	0.02	0.08	0.56
175-4	dark blue	3.28	20.3	66.4	0.06	0.55	7.60	0.04	0.98	0.74
175-4	white(front)	4.32	20.5	65.4	0.12	0.54	7.61	0.03	0.54	0.76
175-4	white(back)	4.51	19.9	65.8	0.08	0.53	8.10	0.03	0.11	0.83
175-5	dark blue	2.43	22.6	64.5	0.05	0.38	7.34	0.04	1.62	0.91
175-5	white(front)	2.59	21.8	66.9	0.02	0.40	7.72	0.01	0.02	0.48
175-5	white(back)	2.70	21.1	68.0	0.06	0.44	7.00	0.02	0.02	0.54
175-6	white(front)	1.09	27.1	68.2	0	0.45	1.51	0.07	0.08	1.40
175-6	white(back)	2.70	21.8	66.3	0.01	0.43	7.80	0.01	0.05	0.77

Sample	irradiated	Cl	Cr	Co	Ni	Cu	Zn
175-1	light blue	5708	725	55	454	105	293
175-1	dark blue	4550	532	143	355	128	196
175-1	white(front)	1686	79	35 37	423	46	75 32
175-2	dark blue	5235	327	176	507	1117	248
175-2	light blue	3144	210	57	537	223	86
175-2	white(front)	4997	378	67	579	157	122
175-2	white(back)	7021	563	70	703	81	43
175-3	light blue	5242	202	38	604	73	52
175-3	white(front)	3143	178	49	695	162	71 80
175-3	white(back)	3062	289	26	663	92	339
175-4	dark blue	10112	213	157	415	51	297
175-4	white(front)	5910	478	52	489	98	302
175-4	white(back)	4277	493	64	625	51	128
175-5	dark blue	2734	186	163	539	70	139
175-5	white(front)	522	50	33	557	50	24
175-5	white(back)	1678	296	42	662	40	102
175-6	white(front)	3468	45	35	625	25	20
175-6	white(back)	321	84	24	406	18	6

TABLE III. Elemental composition of the Penghu potsherds (red pottery).

Sample	irradiated	K (%)	Ca	Ti	Mn	Fe	Cr (ppm)	Co	Ni	Cu	Zn	Rb	Sr
201-l	red(front)	6.03	10.0	4.82	0.62	9.21	24	0	27	5	41	76	18
200-l	red(back)	5.54	10.6	4.34	0.14	10.0	21	4	17	9	29	44	84
200-l	clay	5.42	10.1	4.63	0.11	10.4	16	1	8	1	29	54	24
200-2	red(front)	6.50	10.7	5.43	0.31	7.72	45	15	38	30	63	46	229
200-2	red(back)	5.66	10.3	5.05	0.39	9.22	65	24	52	60	58	48	298
200-2	clay	5.69	10.4	5.32	0.13	9.08	6	0	10	3	17	55	306
200-3	gray(front)	0.25	28.2	0.19	0.04	1.91	7.5	3.5	0	7	8	67	63
200-3	gray(back)	0.13	29.9	0.05	0.03	0.51	7	0	0	3	6	70	16
200-3	gray(side)	0.13	29.9	0.05	0.02	0.56	1	0	0	4	6	68	0

Table III lists the results of the PIXE analysis of sample group II. It is seen that, for two fragments of red pottery studied (samples 200-l and 200-2), there appears no noticeable difference between the elemental contents of the glaze and clay, except that the sample 200-2 has higher Sr trace element. The sample 200-3 is a corallite-like stone. It is manifest to have different compositions from the other two samples. As we can see it has a remarkably high Ca content (~29%) and a K content at much lower level (~0.2%). In comparison to sample group I, all three samples of group II were found to differ much in concentration of main elements (K, Ca, Ti, Mn and Fe).

V. Conclusion

From the elemental determination with PIXE, we have obtained the elemental contents of a collection of precious ancient Chinese artifacts. In the analysis of bronze weapons, the examined samples (Ko, Mao and Chien) were identified as bronze alloy with low Pb concentration. The Cu content is within 75-80% for Ko, 80-85% for Mao and 70-80% for Chien, and the Sn content lies mostly in the ranges 12-18% which is adequate amount needed to make the cast weapons with proper hardness. These findings reflect the skillful technique in casting bronzes developed in the periods of the Shang and Chou dynasties.

In the analysis of the glaze composition for the Penghu underglaze-blue potsherds, we obtained additional information on the trace elements and found an increase of the Co and Mn contents in the glaze from light blue to dark blue. This gives an evidence that certain cobalt-blue pigment was used for the glaze, and confirms that the concentration of trace elements is useful to distinguish the glaze pigments. Our results will provide the scientific basis for the study of the origin of ancient potsherds examined in this work, which are parts of precious remains recently discovered from the seabed of the Penghu coast. Further PIXE analysis of a large number of samples are clearly needed: so that accumulation of

more information on the glaze and clay composition of potsherds can be obtained, and a systematic study can be made to explore the ages production of the Penghu potsherds.

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