Photon Activation for Archaeological Analysis at Idaho State University

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Using photon activation analysis (PAA), ppm concentrations of elements in two obsidian rock samples were determined and compared to a powdered obsidian NIST (National Institute of Standards and Technology) standard. The tests were conducted in an effort to develop new analytical methods for the analysis of archaeological artifacts using non-destructive, whole artifact methods. Resultant spectra and plots identified the varying isotopic concentrations highlighting PAA's ability to detect elemental concentrations comparable to techniques such as neutron activation analysis and x-ray florescence demonstrating the future potential for PAA analysis in archaeology, museum studies, and materials analysis.

I. Introduction

Archaeological research is interdisciplinary and has a long history of interaction with the fields of chemistry, physics, and biology. It is this character that has led to the use of methods and techniques of geo and radiochemistry to interpret human cultural history though the development of dating techniques, the analysis of residues and pigments, and through isotopic and elemental analyses to provenience the sources of artifacts and raw materials. Geochemistry has been an intimate part of archaeology since the early 1800s when chemist Martin Klaproth studied the chemical composition of Roman glass and Sir Humphry Davy analyzed the pigments from Rome and Pompeii. Damour, a French mineralogist in the mid 1800s, emphasized the necessity for archaeologists to call upon those trained in other disciplines such as geology and chemistry to aide them in giving meaning to the past, which included his research on geochemical analyses of Celtic Jade axes (Ref. 1). Over 100 years after these early pioneers created what is now called archaeometry, the interface between archaeology, chemistry, and physics is fundamental to the field and little modern research is conducted without this collaboration (Refs. 2-8).

From dating techniques to provenience studies to the characterization of archaeological and museum materials, radiochemistry is a key interdisciplinary area. Radiochemistry and other nuclear techniques are the application of the phenomenon of radioactive decay and techniques common to nuclear physics to solve problems in the field of chemistry and related fields (Ref. 9). Nuclear methods are used to create and analyze the decay chains of various radionuclides. In other words, these nuclear methods are used to initiate the transmutation of isotopes into a state of radioactivity, which in return can be monitored as they decay back to a stable state. The radionuclide or daughter element produced through these various activities can be used to determine the original element or parent and its relative abundance (Ref. 9). In the past the preferred radiochemical techniques/methods used in the analysis of archeological materials were

dominated by Neutron Activation Analysis (NAA), X-ray florescence (XRF), and in more recent years Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Refs 6, 10-16).

NAA has been used to analyze a suite of materials from pigments to obsidian, ceramics, cherts and stucco (Ref. 6 and 16-17), and has been shown to be highly effective for trace element analysis of archaeological materials. While technically non-destructive (ref. 6), NAA is only non-destructive for archaeological materials when the samples consist of beads, small coins, or similar. In all other cases, small samples must be removed from the artifact for analysis (Ref. 16). Furthermore, the fact that the samples are considered radioactive for months to years, renders it effectively a destructive technique since the artifact cannot be returned to a museum or landowners in a reasonable time frame (Ref. 6 and 16). XRF is an excellent technique for non-destructive analysis and has been widely used for the analysis of homogenous materials, such as obsidian, or in the analysis of surface decorations and pigments/paints on pieces of art, ceramics, and other sources (Ref. 6). ICP-MS analysis, particularly with laser ablation, is a rapidly growing area of inexpensive analysis but much like NAA, it suffers from the need to destructively sample artifacts and museum specimens. XRF on the other hand, while non-destructive, is basically an analysis of the surface of an artifact, regardless of the heterogeneity of the sample. To compliment NAA, XRF, and ICP-MS, a completely non-destructive means of whole-artifact characterization is needed to fill the analytical and technical problems with these other techniques: Photon Activation Analysis (PAA) has the potential to solve exactly these problems (Ref. 18-20).

Photon activation analysis, as in Neutron Activation Analysis, is used to transmutate unknown nuclides to a radioactive state, creating a decay chain that can then be used to identify the isotopic composition of an object (Ref. 9). In PAA, a photon enters the nucleus of an atom and (predominantly) causes a neutron to be emitted from the nucleus via (γ,n) reactions. The resultant isotope releases one or more beta-decayed gamma rays at specific energies as the nucleus decays to its ground state, thus allowing the isotope to be identified through gamma spectrometry. Other reactions occur in smaller percentages, such as a proton being emitted from the nucleus (γ,p), two neutrons being emitted $(\gamma,2n)$, an alpha particle (γ,α), etc. In addition, photo-fission occurs if higher Z elements, such as uranium, are present in the sample (γ,f).

Determination of what isotope is actually being detected and where it originated is key in the analysis of samples by PAA, as in all other radiochemical techniques. A typical PAA process involves using an electron accelerator to create bremsstrahlung gamma radiation, followed by gamma ray identification of the activated specimen through some form of spectroscopy. Through spectroscopy the elemental concentrations can be determined. The activation process is shown in Figure 1.
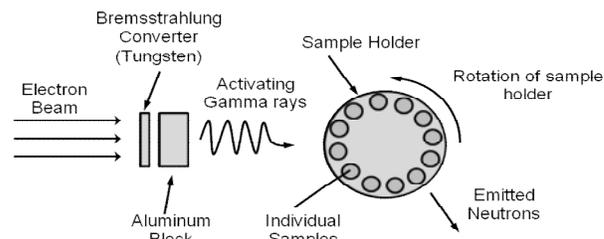

Figure 1: Schematic of photon activation analysis

One of the attractive aspects of developing PAA for archaeology is its non-destructiveness in the determination of trace element concentrations in a wide variety of materials (Ref. 18-19). The small amount of time required for analysis, the ability to determine concentrations for multiple elements all at once, and the range of identifiable isotopes, have led to its continued development at a handful of facilities across the planet. While attempts have been made to use NAA in a non-destructive way, it is time consuming and expensive (Ref. 1). Even laser ablation, which is usually used in connection with ICP-MS, leaves a scar on the artifact being sampled. In addition, photon activation has the ability to penetrate the entire depth of the artifact, which creates a more homogeneous representation of the sample. Other methods such as Proton Induced X-ray Emission (PIXE), XRF, and laser ablation are incapable of doing this because they sample the surface up to a few microns into the artifact and have little ability to identify and interpret the variability found in virtually all materials whether they are human constructed or naturally produced. One other advantage of photon activation over neutron activation is the amount of time the artifact remains radioactive after being activated, which is a few weeks in PAA, and years to decades in NAA depending on materials activated, energy, and irradiation time (Ref. 6 and 16).

With this in mind we have began to develop new methods in the use of PAA for analyzing culturally produced and modified materials with our current focus on igneous rocks used as tool stone. The desire to analyze tool stone is based on the knowledge that an intricate piece to comprehending the relationship between an individual's knowledge of the landscape and its resources is determined by our ability to use modern scientific knowledge to decipher prehistoric behavior. The ability to

understand the relationship between prehistoric individuals and their knowledge of and interaction with these tool stone quarries would enable archaeologists to recognize and interpret economic interaction, social organization, and political structures that existed in prehistory (Ref. 13).

II. Experimental

I.A. Samples and Standards

As a first test, samples were collected from two obsidian sources in the western US that have been intensely analyzed by NAA, XRF, and ICP-MS: Glass Butte in Oregon and Bear Gulch near West Yellowstone. The raw samples from these locations were cut into 4 x 4 x 0.4 cm tiles approximately 4 grams in mass using a rock saw equipped with a diamond edged cutting blade. The tiles were then cleaned and placed in small polypropylene sealed vials prior to being activated. As a standard for comparison and calculation, NIST standard reference material #278, a finely powdered obsidian rock obtained from Clear Lake, Newberry Crater, Oregon, was also separated into five different samples of approximately 4 grams and placed in the same type of vials used for the tiles prior to irradiation.

II.B. Irradiation

All samples were placed in a large container and positioned on a platform that rotated 38 times each minute in order to assure that all samples received an identical photon flux. While some of the samples were closer to the middle of the container during irradiation, it was assumed that attenuation was negligible. A 25MeV LINAC accelerator with a (80) μA beam current, a 4 μs pulse time, and a frequency of 100 Hz was used to accelerate electrons. The electron beam struck a target composed of tungsten and aluminum which produced bremsstrahlung gamma rays. The gamma rays struck samples in the container, thus causing activation to occur. The samples were activated for 12 hours.

II.C. Counting

The samples were analyzed for resulting activity after a period of 11-12 days after activation using a high purity germanium detector. MPA-Win software, developed by FAST Com Tec, was used to identify the peak areas, counts, and associated gamma energies (Fig. 2).

II.D. Efficiency

Detector efficiencies were measured for three different detector distances, and the detector efficiency at zero distance (where the samples were actually resting

when counted) was extrapolated from these data. These efficiency values were used to calculate concentration values for all the samples.
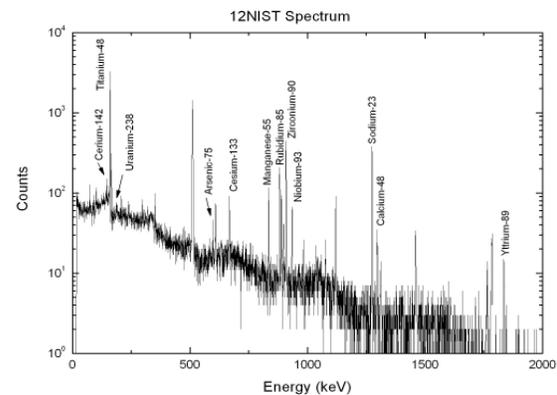

Figure 2. A typical spectrum from one of the NIST obsidian samples.

III. Results

The 12NIST sample was chosen (arbitrarily) as the standard with which to compare all other samples, including the other NIST samples. Most of the ppm values for the elements in the NIST samples were known, but some elements (zirconium, arsenic, yttrium, and niobium) not listed on the NIST sheet showed up during PAA. In order to compare 12NIST sample to all the others, the ppm values for these unknown elements needed to be estimated. The equations employed by Ni (Ref. 21) were used to accomplish this, in which a known ppm value was compared to another measured energy value within the same 12NIST sample. Using appropriate cross section and efficiency values for each energy, and assuming that the photon flux was constant, the unknown ppm values were calculated. Concentrations (in ppm) of the remaining samples were also determined using Ni's method, although the calculations were significantly easier since a given isotope had the same cross section, efficiency value, photon flux, and isotopic abundance.

Table 1 demonstrates clearly that with this preliminary experiment we have been able to achieve levels of sensitivity < 10 ppm (we have reached < 100 ppb in single element samples). Further, biplots of nearly all elements work well in distinguishing between the two natural obsidian sources, and between these and the NIST sample (Figs. 3&4 as examples).

As shown in Table 2, our current PAA values are highly correlated with NAA values, although some elements appear to show systematic bias, ranging as high as 41 percent higher. This is, presumably a product of still working out certain aspects of the method, and still

developing our quality controls to ensure standard practice. A plot of our PAA values with known NAA values clearly demonstrates that our results correlate favorably at this preliminary stage in the research with those from NAA (Fig. 5, r^2 =.99). Tests on other materials done in Japan and Europe have shown that PAA and NAA produced highly comparable results (Ref. 18, 20, 22). Moreover, the fact that the three samples are easily distinguishable and that the recorded values cluster by source indicates that we have shown photon activation analysis at the Idaho Accelerator Center to be a viable method for materials classification and analysis.

Table 1: ppm values for the elements determined in this work. GB=Glass Buttes, NIST=NIST No. 278, BG=Bear Gulch.*12NIST was used as the standard.

| Sample	Cerium (ppm)	Titanium (ppm)	Cesium (ppm)	Manganese (ppm)	Rubidium (ppm)	Yttrium (ppm)	Zirconium (ppm)	Niobium (ppm)	Sodium (ppm)	Calcium (ppm)	Uranium (ppm)
24BG	155.44	1503.39	7.51	538.25	271.85	56.2	411	129.4	46150.74	9545.65	10.69
19BG	156.96	1430.16	7.83	533.64	283.78	52.38	392.26	121.93	45043.26	7037.96	7.48
18BG	121.38	1134.79	5.66	431.67	226.8	46.32	334.53	108.05	37534.3	6246.74	4.8
17BG	158.7	1701.35	8.64	535.9	305.19	53.73	438.44	127.65	48239.9	9039.99	9.03
16BG	155.34	2252.72	6.23	463.94	248.97	41.72	341	110.12	38974.87	7426.43	5.9
46GB	53.35	1491.74	5.58	714.97	132.45	34.66	200.06	16.95	51462.98	20890.19	
37GB	43.76	1878.14	3.65	531.47	107.62	22.66	153.81	13	39615.24	14691.94	3.85
38GB	23.08	1384.55	3.07	367.3	76.07	23.13	115.58	12.18	26997.35	10009.73	
40GB	23.24	1498.91	3.72	418.96	78.86	24.41	112.02	10.74	31010.76	10870.82	
39GB	53.76	1330.75	3.91	650.56	124.29	28.34	188.54	12.15	49480.91	16633.13	3.97
*12NIST	62.2	1468.39	5.5	402.72	127.5	31.57	245.25	30.26	35905.9	7025.41	4.58
14NIST	64.81	2738.65	6.79	554.47	171.55	41.89	317.77	29.43	50999.72	9912.99	3.02
6NIST	32.6	1709.83	5.92	427.2	137.75	35.28	252.54	30.85	38987.99	8770.28	2.15
8NIST	46.39	1393.25	7.17	446.73	148.19	34.11	256.41	27.6	40653	6686.66	3.83
13NIST	55.05	2072.04	8.29	580.38	169.8	39.03	333.33	33.46	51883.07	9000.8	5.86
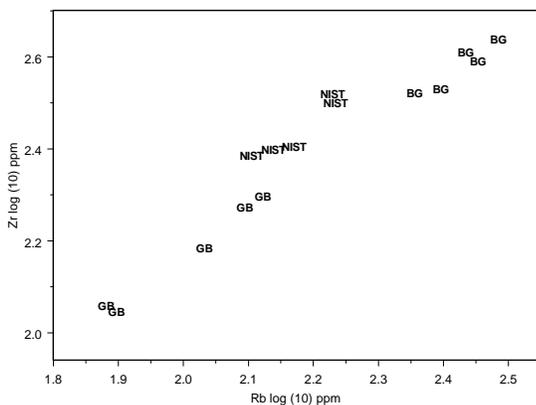
Figure 3: Bivariate plot of log(10) ppm values of zirconium by rubidium. GB=Glass Buttes, NIST=NIST No. 278, BG=Bear Gulch.
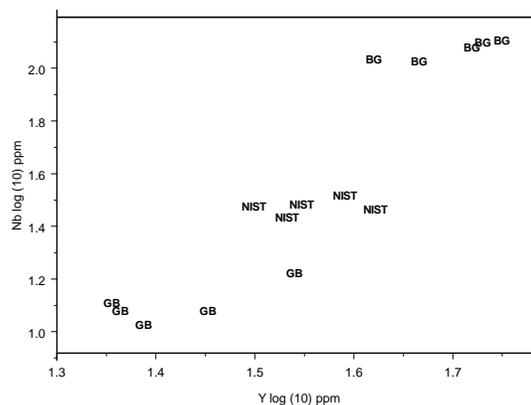

Figure 4: Bivariate plot of log(10) ppm values of niobium by yttrium. GB=Glass Buttes, NIST=NIST No. 278, BG=Bear Gulch.

Table 2: Comparison of ppm values between PAA and NAA (NAA data provided by Michael Glascock, MURR, University of Missouri) for the Bear Gulch obsidian source. Note that while the PAA values are on average 31% higher than the comparable NAA values, the measurements are correlated highly, as shown in Fig. 5).

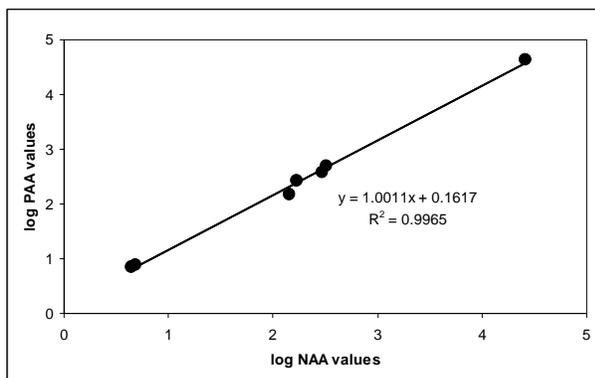| Element	NAA mean	PAA mean	%difference
Ce	145.00	149.56	3
Cs	4.43	7.17	38
Mn	320.21	500.68	36
Rb	169.59	267.32	37
Zr	296.30	383.45	23
Na	25808.78	43188.61	40
U	4.80	7.58	37

Figure 5: Plot of PAA by NAA values for seven elements identified in samples from the Bear Gulch obsidian source.

IV. Conclusions

Native American groups increasingly demand that completely non-destructive techniques be used for the analysis of items of cultural heritage. Since NAA is destructive during routine archaeological analysis because 30-100mg of materials must be drilled from the artifact for analysis, small samples must be removed for ICP analysis (Ref. 6 and 16), and because XRF, PIXE, and similar techniques only measure surface or near surface values, PAA is extremely attractive as a valuable non-destructive method of whole-artifact characterization.

Our first experiments using the LINAC at the Idaho Accelerator Center for the analysis of obsidian have been successful. Not only were a number of key elements necessary for distinguishing between obsidian sources easily determined, but a number of elements not previously reported for the NIST sample were identified and quantified.

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