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Application of Charged Particle Activation Analysis (CPAA) in archaeology

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***Abstract* – Charged Particle Activation is a nuclear technique used in material science for analysis, and as an essential technique in the production of radioisotopes in nuclear medicine. It is less known in archaeology. After a systematic study, we have found that proton and deuteron activations offer some unique analytical possibilities, unknown to other methods, in archaeology. With its extremely high sensitivity for some elements like Ca, Ti, Fe, Sr and Sb, proton activation can be very useful in developing new markers for provenance studies (eg: Fe and Ti, in knowing the origin of sand used by Romans for making glass), and verification of homogenisation of added ingredients like Ca and Sb in glass. Similarly, deuteron activation, through carbon analysis, can help in understanding various problems like the supply of quality fuel, proper maintenance, furnace accidents etc. faced by the ancient glass industry.**

Keywords: **Proton activation analysis, Deuteron activation analysis, glass analysis, pottery and mortar analysis, nuclear reactions, radioactive measurements, gamma-ray spectroscopy.**

I. INTRODUCTION

The common methods of analysis of archaeological glass, pottery and other materials are by XRF, ICP-OES, ICP-MS and EPMA. A method like ICP-OES requires sample dissolution leading to possible contamination of the archaeological specimen. For many elements, XRF, EPMA do not offer high sensitivity. As alternative, nuclear techniques like PIXE, PIGE and NAA are available, but they also have certain limitations. One nuclear method which is relatively unknown in archaeology is Charged Particle Activation Analysis (CPAA).

CPAA is possible with protons, deuterons, Helium-3 and alpha particles[1-5]. Among them, proton activation analysis (PAA) is the most popular technique for medium Z elements [6]. Our CEMHTI laboratory specialises in the analysis of high-tech materials by charged particle activation using all four different particles and also other methods like PIXE, PIGE, RBS, NRA and NAA.

Recently, we have made a detailed investigation of the usefulness of PAA in archaeology and found that 14 medium Z elements can be successfully determined with 12 MeV protons [7-8]. Among them, results for some elements like Ca, Ti, Fe, Sr and Sb can be obtained with high precision and accuracy (see below), indicating they have good potential to serve as special "markers" in provenance studies. Application of PAA in archaeology by other research groups is also known [9-13].

Further, we have developed low energy Deutron Activation Analysis (DAA) for the analysis of light elements (C, Na, Mg and Al) in archaeological glass and pottery [14-17], with special emphasis on carbon analysis.

This report is a review summarising various possibilities offered by PAA and DAA for analytical purposes in archaeology.

It must be mentioned that Charged Particle Activation is extensively used today in nuclear medicine for diagnosis and therapy. The PET (Positron Emission Tomography) scanning nuclides like C-11, N-13, F-18, Cu-64 and Ga-68 are produced by this technique [18].

II. EXPERIMENTAL

A. Samples and standards

The glass and other samples (pottery, mortar etc.) were collected from *Moguntiacum* (Mainz), a military town under Roman rule, and its surounding areas.

Additionally, Moldavite meteorite, Libyan glass etc. were analysed. As standards, pure metallic foils (Mg, Al, Fe, Ti, Cu etc.), glassy carbon, compounds of metals (NaCl, Sb_2O_3, GaAs etc.) were used, depending on the element.

B. Irradiations and counting

The energy requirements for PAA and DAA are quite different. So, two different types of accelerators, namely

a cyclotron for 12 MeV PAA and a pelletron for 2 MeV DAA were used. Both accelerators are available at CNRS-CEMHTI. (Currently, cyclotron is shut down).

While preparing the samples for PAA, a 10 μm Nb foil (purity: 99.9%, supplier: Goodfellow, UK) was placed in front of the archaeological sample and they were wrapped together in a commercially available 12 μm Al foil (Fig.1). The gamma-ray peak of 263 keV from Mo-93m produced by Nb was used as a flux monitor, in addition to conventional charge measurements (as µC) on the target. (We find, '*precise*' proton flux, required for provenance studies (see below), is provided by radioactivity measurements of flux monitors (as counts/s/end of irradiation) than charge measurements (as µC) on targets). After slight energy loss (0.3 MeV) in Al and Nb foils, the energy of protons striking the archaeological specimen will be about 11.7 MeV. For standards also, same procedure was followed with Nb flux monitor.

Fig. 1: Sample mounting on target holder for PAA, using Nb foil as flux monitor.

The nuclear reactions suitable for 12 MeV PAA are given in Table 1, including that on Nb flux monitor. The irradiations were performed at 200-300 nA for PAA and lasted from 30 to 40 min.

The nuclear reactions suitable for DAA are given in Table 2. In DAA, because of very low energy (2.0 MeV) of deuterons, flux monitors cannot be used as they will absorb the total energy of deuterons without leaving any rest energy to interact with the archaeological target. So, charge measurement, as µC, is the only possibility for analysis in DAA. For irradiations, 20-30 nA current was used and they lasted 10 min. each [15-17].

After irradiation, the counting was done with 26% HPGe detector in a separate low-background room and the same detector and counting arrangement was used both for PAA and DAA. (In DAA, the time required for transferring the irradiated sample / standard from accelerator to the counting room was 6-8 min).

The counting procedures followed for PAA and DAA are also quite different. As the half-life of the radioactive nuclides produced from 14 elements in PAA are very different, a minimum of 2 countings (one short and one long), for each sample, were necessary. The first counting (4 to 5 hours) was meant for short-lived nuclides produced by Ga, Zn, Sr, Zr etc., starting some hours after the end of irradiation. The second long counting of 60,000 to 80,000 s was started, after a decay of 6 to 8 days, to analyse long-lived nuclides produced by Fe, Cu, Sb etc. The standards were counted for shorter times [7].

In DAA, because of Si and O interference on C, two short countings of 10 min. each became necessary and the second with minimal interferences, was exclusively used for C analysis, with details given elsewhere [15-17].

C. Quantification

The method of Ricci and Hahn [19] was used for quantification, both in PAA and DAA, and the details were given in our previous publications [7,8].

Table 1:Nuclear reaction useful in PAA

Element	Nuclear reaction	Half-life	Major γ-rays (keV) with intensities
Ca	Ca-44(p,n)Sc-44m	2,44d	271(86%)
	Ca-48(p,n)Sc-48	1,82d	983(100%),1037(98%),1312(100%)
Ti	Ti-48(p,n)V-48	16,1d	944(8,0),983(100%),1312(98%)
V	V-51(p,n)Cr-51	27,8d	320(9,8%)
Cr	Cr-52(p,n)Mn-52	5,60d	744(85%),935(93%),1434(100%)
Fe	Fe-56(p,n)Co-56	77,3d	846(100%),1038(14%),1238(67,6%)
Cu	Cu-65(p,n)Zn-65	243,8d	1115(49,8%)
Zn	Zn-67(p,n)Ga-67	78,1h	185(20,4%),300(15%)
Ga	Ga-69(p,n)Ge-69	39.05 h	1107 (26%)
As	As-75(p,n)Se-75	120. d	121 (16.5%), 135(58%),264(58.5%)
Sr	Sr-86(p,n)Y-86	14,6 h	443(16,9%),627(32,6%),703(15,4%)
	Sr-87(p,n)Y-87	80,0h	485(96%)
	Sr-87(p,n)Y-87m	14,0 h	381(74%)
	Sr-88(p,n)Y-88	107,0 d	898(93%),1836(99,3%)
Y	Y-89(p,n)Zr-89	78,4 h	909(99%)
Zr	Zr-90(p,n)Nb-90	14,6 h	141(67%),1129(92)
	Zr-92(p,n)Nb-92m	10,16 d	934(95,5%)
	Zr-96(p,n)Nb-96	23,35 h	460(28%),569(59%),778(97%)
			850(22%),1092(49%),1200(21%)
Nb	**Nb-93(p,n)Mo-93m**	**6.95 h**	**263(61.2%),684(91.9%),1477(99.4%)**
Sb	Sb-121(p,n)Te-121m	154,0d	212(81,0%)
	Sb-121(p,n) Te-121	17,0d	573(79,1%)
	Sb-123(p,n)Te-123m	120,0d	159(83,5%)
Pb	Pb-206(p,n)Bi-206	6.243 d	537 (29%),803(100%),881(67%)

Table 2: Nuclear reactions with DAA on C, Na, Mg and Al

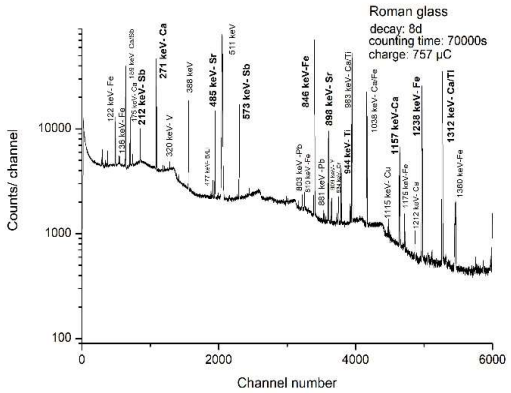
Element	Nuclear reaction	Half-life	Major γ-rays (keV) with intensities (%)
C	**C-12(d,n)N-13**	**9.965 min**	**511 (100)**
Na	Na-23(d,p)Na-24	14,959 h	1368 (100), 2754 (100)
Mg	Mg-26(d,p)Mg-27	9,458 min	844 (72), 1014 (28)
Al	Al-27(d,p)Al-28	2,2414 min	1779 (100)

III. RESULTS AND DISCUSSION

A) PAA of medium Z elements:

The gamma-ray spectrum of a Roman glass, irradiated with 12 MeV protons is shown in Fig 2. In this spectrum, the strongest gamma-ray peaks seen are from Ti, Fe, Sr and Sb, also indicating that PAA has very high sensitivity for these elements. The gamma-ray spectrum of a Roman pottery, shown in Fig. 3 looks similar to glass spectrum, indicating PAA is equally suitable for pottery. Further, PAA is also suitable for mortar, impact glasses (eg. Moldavite, Libyan glass) etc.

Fig. 2. PAA: Gamma-ray spectrum of Roman glass (from Mainz)



The analytical reults obtained for Roman glass, pottery and Moldavite are shown in Table 3. The "power" of CPAA will be evident when one looks at the detection limits for various elements in Roman glass, which for many are at 1-10 ppm (mass) level.

Provenance studies:

In Table 4, 5 cut pieces of a large Roman glass object (Fig. 4) were analysed for checking the reproducibility of results and verify the homogeneity of mixing of primary ingredients(eg. Sb), in ancient times. One can see that PAA offers excellent reproducibility of results for certain elements. The results obtained for Ti are within ± 0.9 % and for Fe, within ± 2.3%, respectively. Such a good reproducibility is mainly due to high nuclear reaction cross-sections and long counting times applied (60,000 to 80,000 s) resulting in large number of counts (see Table 4) accumulated, followed by utilisation of Nb foil for proton flux measurements. (see ratios of element counts/Nb monitor foil counts, in Table 4). As Ti and Fe are impurities in sand, they can serve as excellent markers in knowing the sand origin [20]. Such *"precise"* results cannot be obtained by ICP-MS, XRF, EPMA etc. This is the unique feature of PAA. Similar results with good precision are obtained for Sb (used in decolurisation of recycled glass) and Sr.

In provenance studies of Ti, to get ± 0.9 % precision, one must use 1312 keV gamma ray and a third counting is done, after a decay of 30d to avoid, totally, the Ca interference via Sc-48 on Ti [7].

Fig. 3. PAA: Gamma-ray spectrum of Roman pottery (from Gross Gerau)

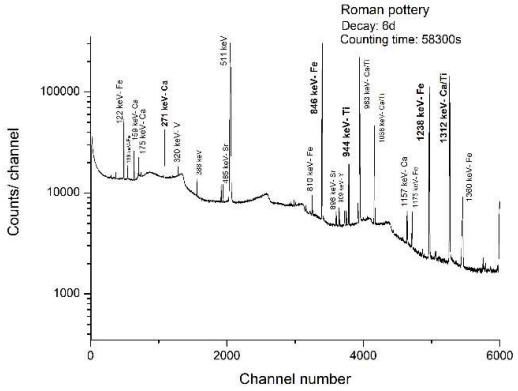


Table 3: Analytical results for 14 elements by PAA in Roman glass, pottery and Moldavite glass, including detection limits for Roman glass. (Errors: ±5-15%, depending on the element) [8,21].

element	γ-ray (keV)	Concentration (ppm)			Detection limit in glass (ppm)
		Roman glass	Roman pottery	Moldavite	
Ca	**271**	6,32%	6.30%	1.60%	**150**
Ti	**944**	395	6190	1620	**2**
V	**320**	9,8	130	21	**10**
Cr	**744**	15	126	24	**10**
Fe	**1238**	3525	4.17%	1.51%	**7**
Cu	**1115**	162	<80	<35	**35**
Zn	**185**	68	172	<20	**20**
Ga	**1107**	<1	<1	<1	**1**
As	**264**	<2	<12	<2	**2**
Sr	**898**	340	305	95	**5**
Y	**910**	8	45	15	**2**
Zr	**141**	43	240	260	**3**
Sb	**212**	436	<60	<20	**20**
Pb	**803**	322	<40	<20	**20**

B): DAA of light elements (C, Na, Mg and Al)

The emphasis in DAA is on "sensitive" carbon analysis of arhaeoligical glass which is not possible by any other

standard anaytical method. Actually in DAA, the entire experimental conditions are tuned for carbon analysis and the results for Na, Mg and Al are obtained as a by-product. The method was discussed in detail elsewhere [15-17]. As an example, the gamma-ray spectrum of a Roman glass bead irradiated with 2 MeV deuterons is shown in Fig. 5 and the obtained analytical results in Table 5.

Fig. 4. Roman glass from Mainz, partly cut into small pieces for analysis.

Table 4: Reproducibility of results for Ti, Fe and Sb in five cut pieces of a Roman glass sample, with Nb flux monitor [8].

element	charge	fragment	counts at end of irradiation		ratio	concn.
	(μC)		photopeak (a)	Nb monitor	photopeak/	(ppm.wt)
			(total counts)	(counts/s)	Nb monitor	
Ti	410.7	1	110160	1350	81.6	**395**
(1312 keV)	506.1	2	110062	1334	82.5	**400**
	660.0	3	201200	2466	81.6	**396**
	756.9	4	241971	2955	81.9	**397**
	783.5	5	243673	3038	80.2	**390**
					average	**395 ± 0.9%**
Fe	410.7	1	203885	1350	151.0	**3427**
(846 keV)	506.1	2	204000	1334	152.9	**3471**
	660.0	3	386684	2466	156.8	**3556**
	756.9	4	466305	2955	157.8	**3580**
	783.5	5	453351	3038	149.2	**3386**
					average	**3484 ± 2.3%**
Sb	410.7	1	9610	1350	7.12	**426**
(212 keV)	506.1	2	9578	1334	7.18	**432**
	660.0	3	18709	2466	7.58	**454**
	756.9	4	21922	2955	7.42	**445**
	783.5	5	21563	3038	7.10	**425**
					average	**436 ± 2.8%**

a) Counting time for each fragment : 70,000 s

Fig. 5. DAA: Gamma-ray spectrum of a Roman glass bead irradiated with 2 MeV deuterons.

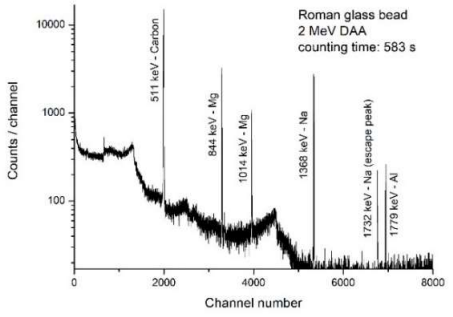


Table 5. C, Na, Mg and Al analysis of a Roman bead. Errors: C: ± 5%, (Na, Mg, Al): ± 5-12 % [17].

Concentration (wt.)			
C	Na	Mg	Al
2200 ppm	9.50%	5.86%	0.51%

IV. CONCLUSIONS

Both PAA and DAA are non-destructive nuclear techniques, offering high sensitivity and accuracy for several elements and can be introduced in any laboratory where the analysts are familiar with PIXE, PIGE and/or NAA methods. Especially for ancient glass, PAA method offers unique possibilities to answer certain special questions on provenance studies. For elements like Ti and Fe, small differences of 10-15 % from glass to glass can be "confidently" attributed to differences in the sand origin, used for making glass.

Because of its high accuracy and precision, CPAA is an extremely important technique in material science, applied in the development of trace element "reference standards" (eg. NIST standards) and it can be equally useful in developing such standards in archaeology. If single element standards have to be prepared (eg. reference standards for Fe in glass, Sr in glass etc.), then it is recommended to use the *highly accurate* "average stopping power" method [22,23] than the Ricci and Hahn method [19] as the latter can have some "formula error" due to the assumptions made in developing it. But, achieving results with such high accuracy involves some additional experimental work [23]. (It must be stated that in any provenance studies which involves a "comparison" of the results of several samples (glasses/ pottery etc.), it is sufficient to use the simple "Ricci and Hahn method". Any minor formula error, even if present in it cancels out because the same formula is used to calculate the analytical results of all samples).

Also, if there is a serious disagreement in the analytical results obtained for some elements by other methods like ICP-MS and EPMA, CPAA being a physical method based on nuclear reactions, is an excellent alternative to cross-check the "contradicting" results.

For PAA, regular cyclotrons meant for research in material science, or even medical cyclotrons delivering proton beams in the energy range 10-12 MeV, built for the production of radioisotopes required by the hospitals, can be used.

DAA is a unique technique, with high sensitivity and accuracy, for carbon analysis. The method is useful also in understanding various technical problems like delivery of quality fuels, proper maintenance, furnace accidents etc. faced by the ancient glass industry [16,17]. DAA is also useful in understanding the role played by carbon in

making Roman amber glass.

For DAA, electrostatic accelerators meant for PIXE, PIGE studies are useful.

DRAWBACKS: The main problem with CPAA is it requires very special experimental facilities (cyclotron/Van de Graaff/Pelletron/Tandetron) with relatively high operational costs, and specially trained people to work with radioactivity. Further, PAA is a time consuming analytical method, requiring long counting periods (about 2 weeks for the irradiation and analysis of 10 samples) and at least 2 countings. (For provenance studies of Ti with 1312 keV as marker, even a third counting becomes necessary).

CPAA is "*not*" recommended as a routine analytical method in archaeology. Other methods like EPMA, XRF, ICP-MS are much more simpler, faster and cheaper to use. Further, in PAA, because of long-half lives of some nuclides, a minimum waiting time of about one year is necessary for the return of the samples to the owner. In DAA, because of short half-lives of the nuclides produced, samples can be returned in 2 weeks after analysis. Both PAA and DAA are not suitable for the analysis of bone and ivory as they can get burnt due to heat generated during irradiation.

But, due to the non-destructive nature of CPAA requiring no dissolution of the samples, its higher "precision and accuracy" in comparison to several other analytical methods, very high sensitivity for certain elements like Ti, Fe, Sr and Sb, PAA becomes "indispensable" (when used with Nb flux monitor) for special applications like provenance studies of glass and development of trace element reference standards. Through carbon analysis by DAA, the "ups and downs" faced by the Roman glass industry can be better understood.

Thus, CPAA can play an important role to solve "special problems" in archaeology.

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