2022 IMEKO TC-4 International Conference on
Metrology for Archaeology and Cultural Heritage
University of Calabria, Italy, October 19-21, 2022

Fuel contamination problems in Roman wood-fired glass furnaces: Carbon determination in Roman glass by deuteron activation technique

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Abstract **– Carbon analysis in glass is a very difficult task. In the production of glass with Roman wood-fired glass furnaces, one can expect carbon contamination from absorption of fuel gases and/or powdery residues from furnace walls in the glass melt, and also residues from plant-ash used as flux. Sometimes carbon was intentionally added to get a distinct colour to glass. We have developed a highly sensitive non-destructive nuclear technique for carbon analysis by deuteron activation based on C-12(d,n)N-13 reaction. The method is simple, rapid and can help archaeologists understand more about the purity of ancient glass production and contamination problems associated with it. The theoretical detection limit for carbon is 5 ppm. The method is also suitable for carbon analysis of pottery.**

Keywords: **Carbon analysis in glass, deuteron activation analysis, nuclear reactions, radioactive measurements, gamma-ray spectroscopy**

I. INTRODUCTION

Silica, the main component in making glass requires high temperatures to melt which the wood-fired Roman furnaces could not provide. To lower the melting point, Romans used either natron, a carbonate mineral of sodium found at Wadi El Natrun in Egypt or plant ash (eg: Salsola, Salicornia). Plant ash contains, along with higher amounts of magnesium, lime and potassium, also small amounts of charcoal [1]. If there is incomplete burning of natron or plant-ash during glass-making, it can leave some carbon residue in the glass made at these "primary" glass production centres. From here, the raw glass got transported to different places across Europe for making glass objects. Further, if the glass is retained for a longer time in the molten state in the furnace, it can get contaminated with the powdery residues from the furnace walls [2-3]. Taylor and Hill [4] have described the construction and operation of a Roman glass furnace and observed in their experiments how the ash layers from the fuel got settled in the molten glass and finally absorbed by it. Sometimes, charcoal was intentionally added to get a required glass colour. Paynter and Jackson [5] have shown how amber coloured glass can be produced in the laboratory by adding wood chips or charcoal during production process. Thus, there are many ways how carbon can enter glass. Carbon is a very difficult element to analyse and popular techniques like XRF, EPMA, ICP-OES, ICP-MS, NAA, PIXE and PIGE are not suitable.

Our CNRS-CEMHTI laboratory specialises in the analysis of light elements (B, C, N, O, F etc.) in high-tech semiconductors, metals, ceramics etc. by various nuclear techniques (PIXE, PIGE, RBS, NRA) including Neutron Activation Analysis (NAA) and Charged Particle Activation Analysis (CPAA). CPAA of light elements has very high accuracy and precision and one of the key techniques used in developing Standard Reference Materials (SRMs) required by industry and research laboratories.

Among various CPAA techniques, carbon analysis by Deuteron Activation Analysis (DAA) is extremely sensitive because, already with 2 MeV deuterons, the nuclear reaction C-12(d,n)N-13 (threshold: 0.3 MeV) has a high activation cross-section of nearly 170 mb, permitting its determination in high purity materials [6-7] at parts-per-billion (ppb) level.

In the recent years, we have extended CPAA to archaeology. Besides developing Proton Activation Analysis (PAA) for 14 elements [8,9] in archaeological glass and pottery, we have also developed DAA for the analysis of C, Na, Mg and Al in these materials [10-13].

It must be mentioned that carbon analysis by DAA is nearly 70 years old [14], but, its application to archaeology is very new. Also, the nuclear reaction used here for carbon analysis is extensively used in nuclear medicine in PET scanning where nitrogen-13, in a suitable form, is injected into patients with cancer and heart diseases.

II. EXPERIMENTAL

A. Samples and standards

All the analysed glass samples were collected from Moguntiacum (Mainz) which was a military town under Roman rule. The Roman pottery samples came from Gross-Gerau, Germany. As standards, glassy carbon, thin metallic disc for Mg (supplier: Goodfellow) and thin metallic foil for Al were used. For Na, pressed thick pellets were prepared from powders of high purity NaCl and NaF.

B. Irradiations and counting

The irradiations were performed with 2.0 MeV deuterons (beam size: 2 mm x 1 mm) from the pelletron accelerator at CNRS-CEMHTI, Orleans. The nuclear reaction suitable for carbon analysis is shown in Table 1. With 2 MeV deuterons, nuclear reactions on Na, Mg and Al are also possible enabling sensitive determination of all these 3 elements simultaneously. Hence, they are also included in this table.

Table 1. Useful nuclear reactions with deuterons for the analysis of 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)

The irradiations were performed at 20-30 nA current and lasted 10 min. each. After irradiation, the counting was done with HPGe detector in a separate low-background room and the time required for transferring the irradiated sample / standard from accelerator to the counting room was 5-8 min. The counting of each sample/standard was done from 10 to 15 min.

As the counting involves measurement of short-lived nuclides like Al-28, very precise radioactive decay corrections, in seconds, from the end of irradiation to the beginning of counting, of the irradiated samples are necessary.

It is important to note that in CPAA, similar to PIXE and PIGE, depending on the irradiation energy, only a thin layer on the glass surface gets activated. With 2 MeV deuterons, this layer is approximately 30 µm. As the irradiated glass object is much thicker than this, it is necessary to see that the irradiated side faces the detector for counting to minimise self-absorption of gamma-rays within sample thickness.

C. Quantification

The quantification is simple and done according to the method of Ricci and Hahn [15] and given by the following equation. The details were given in our previous publications [8-9].

$$C_{sample} = \frac{A_{sample}}{A_{standard}} \; x \; \left(\frac{S_{sample}}{S_{standard}}\right)_E x \; C_{standard} \quad (1)$$

Here, C_{sample} and $C_{standard}$ = concentrations of the sought element in the sample and standard (ppm or (µg/g)), and A_{sample} and $A_{standard}$ are activities of sample and standard (counts/s/µC/at end of irradiation) and S_{sample} and $S_{standard}$ are stopping powers (MeV/(mg/cm^2)) of sample and standard for 2 MeV deuterons. Here, the only unknown parameters are the activities of standard and sample for which we do the counting. All others are known, or can be calculated. The concentration of sought element in standard is known from its stoichiometry. The stopping power ratio can be calculated from published tables [16] using the composition of any "low-lead" glass as a reference. The stopping powers in compounds can be calculated using Bragg's law. As an example, we took Roman glass from Bubastis, Egypt [17] for the calculations. Small variations in composition from glass to glass do not influence the stopping power calculations.

III. RESULTS AND DISCUSSION

The gamma-ray spectrum of a Roman glass (glass F), irradiated with 2 MeV deuterons is shown in Fig 1. In this glass, carbon is present at 1320 ppm level and Na, Mg and Al at percentage level. As carbon has the highest sensitivity among all analysed elements, the strongest peak seen in this spectrum is also from carbon.

It must be emphasized that in any experiment involving nuclear activation analysis, especially in 2 MeV DAA of carbon, precise "timing" of the measurements from the end of irradiation is very important. After irradiation, as mentioned above, it requires 5-8 min., in our laboratory, to transfer the irradiated specimen from accelerator to the counting room. The counting was started immediately after this transfer because, with the exception of Na-24 (Na), all other nuclides produced are short lived.

If the delay is too long in starting the first counting, we lose counts from Al-28. To have a deeper understanding of the 511 keV peak of carbon, a systematic study of

Roman glass-F was made with several

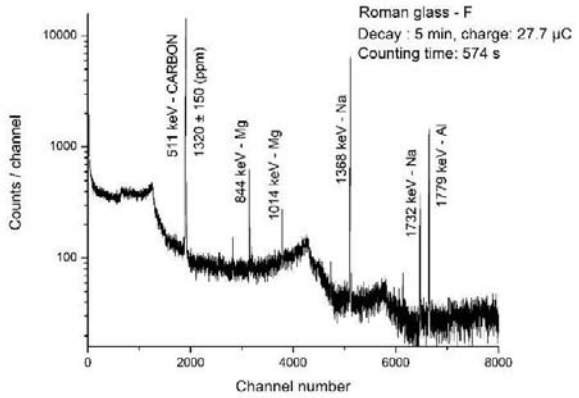

Fig. 1. Gamma-ray spectrum of Roman glass - F after a decay of 5 min. (The strongest peak seen is from carbon).

measurements of 10 min. each of glass - F, and a "decay curve" analysis is made [13]. One such measurement made after 75 min. decay is shown in Fig. 2. Here, the peaks of Mg and Al are totally missing. There is very little contribution of carbon (N-13) under 511 keV peak and what one sees is essentially F-18 (blank) from oxygen (see below). So, if we use this measurement for analysis, it will give totally wrong result for carbon.

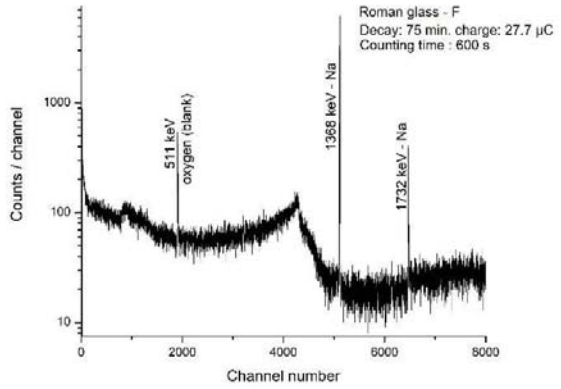

Fig. 2. Gamma-ray spectrum of Roman glass – F after a decay of 75 min. (carbon: negligible, magnesium and aluminum peaks: absent).

The results for carbon in different Roman glasses (A, B, E, F) are shown in Table 2. Results for Na, Mg and Al are also included in this table [12]. The experimental procedure for pottery analysis is identical to glass and some pottery results are also included here. All analyzed glasses contain a minimum of 0.1 % carbon. Roman glass E has a maximum (4380 ±350) ppm.

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Pottery D has a maximum of (7.0 ±0.5) % of carbon. The very high content of carbon in pottery is caused by "surface coating" of carbon, which is also responsible for its " dark grey" colour and does not represent the "bulk" carbon content of its inner layers. This carbon coating must be removed to get the "true" carbon concentration of deeper layers of pottery.

Table 2. Carbon concentration in Roman glasses and pottery. Errors (Na, Mg, Al): 5-12 %.

Sample	Colour	Concentration (by weight)			
		C (ppm)	Na	Mg	Al
Glass A	pale blue	3200 ± 300	10.40%	0.39%	1.09%
Glass B	pale blue	3800 ± 300	6.86%	0.41%	1.04%
Glass E	dark green	4380 ±350	10.07%	0.64%	1.08%
Glass F	silver grey	1320 ± 150	12.50%	0.55%	1.02%
Quartz disc	xx	50 ± 15	xx	xx	xx
Pottery C	red	2050 ±150	0.06%	0.85%	10.21%
Pottery D	dark grey	(7.0 ± 0.5)%	0.41%	2.83%	6.38%

A. Requirement of 2 countings to determine all 4 elements (C, Na, Mg and Al) with 2 MeV deuterons:

Our main aim with 2 MeV DAA is to determine carbon in glass but we also get the results for Na, Mg and Al in the same irradiation. But, as Al-28 (Al-27(d,p)Al-28) is a short-lived nuclide (half-life: 2.24 min) the entire counting procedure is drafted giving priority to Al-28 and starts with a time delay of 5 to 8 min from the end of irradiation. This short decay can influence carbon result as O-16, the main component among oxygen isotopes contributes a blank (F-17) via O-16(d,n)F-17 (half-life: 64.5 s) reaction.

So, ignoring the result obtained for carbon in the first counting, more accurate result for carbon will be obtained in a separate counting (second counting) meant exclusively for carbon, after total decay of F-17. If the first counting is done for 10 min., the second counting will start after 15 to 18 min, from the end of irradiation.

If the analyst is only interested in simple carbon analysis, then the counting can be started with a time delay of 15 min, from the end of irradiation, by which time F-17 would have totally decayed.

B. Differences between PIGE (Particle Induced Gamma-ray Emission) and DAA:

As many archaeologists are familiar with PIGE, it is appropriate to compare DAA with PIGE. DAA can be introduced in any PIXE/PIGE laboratory and the time required for a complete analysis, which includes irradiation and counting, is about 45 min. Actually, in Orleans, we use a PIGE set-up to do DAA. The important difference between the two techniques lies in the application of different nuclear reactions. Further, PIGE is mostly done with protons and the counting of prompt radiation is done "during" irradiation at the accelerator site itself. In DAA, radioactivity is counted "after" irradiation in a separate low-background counting room, resulting in higher sensitivity and improved detection limits for C, Na, Mg and Al, than in PIGE. As the counting is done in a separate room, the signal/background ratios are much higher than in PIGE resulting in improved precision of the analytical results. Additional requirement in DAA is that by applying decay corrections, all radioactive measurements have to be normalized to the end of irradiation.

C. Carbon contamination from environment

Carbon is present everywhere in the environment. CO_2 and CO molecules are always present in the atmosphere contributed by automobiles, furnaces, wood and gas burning for heating houses etc. Household dust can contain several types of hydrocarbons. Some of these carbon molecules can get deposited on the surface of archaeological glass specimens contributing to some "blank". A preliminary study [13] on quartz, analysed under same conditions as Roman glasses, has shown the "blank" contribution to carbon from this type of contamination is < 50 ppm. Additional work is required for better understanding of this problem.

D. Interference from oxygen:

N-13, the nuclide used for carbon analysis is a positron emitter. An archaeological glass consists of a mixture of several oxides with SiO_2 as the major component. The total oxygen in glass can be at 40-45 %. Deuterons can induce reaction on oxygen via O-17(d,n)F-18. As F-18 is also a positron emitter, it can interfere with carbon analysis which is demonstrated in Fig.2 where the counting of the glass was done after 75 min. decay. In this spectrum, the major contribution to 511 keV peak came from oxygen (F-18) and negligible counts from carbon (N-13).

F-18 has a half-life of 109.7 min and since N-13 has a shorter half-life of 9.96 min, F-18 interference cannot be avoided. Luckily, the natural abundance of O-17 responsible for this interference is only 0.038% and its contribution to carbon result is at 150 ppm level, which is small. A detailed discussion of this interference was given in our earlier publication [13].

E. Detection limit for carbon:

The theoretical detection limit for carbon in glass is 5 ppm. However, this limit cannot be achieved as the carbon result is influenced by environmental contamination and oxygen interference contributing a total blank of 150 to 200 ppm. So, with 2 MeV deuterons, carbon determination < 200 ppm is not possible.

F.Reduction of blank value and counting time:

Glass is a mixture of several oxides with SiO_2 and Na_2O as major components and MgO, CaO, Al_2O_3 etc. as other components. If we apply higher deuteron energy (> 2 MeV) for analysis, there can be formation of additional positron emitters from other elements present in glass making the decay curve analysis for carbon more complicated. So, higher energy DAA is not recommended.

On the other hand, work is being done in our laboratory to see if the "blank" contribution from oxygen can be reduced at lower irradiation energies (< 2 MeV). Also, it is being tested if, at lower energies, the total analysis of all 4 elements can be done in a single counting which means a reduction in total analysis time from 45 to about 30 min.

IV. CONCLUSIONS

DAA is unique and an extremely sensitive analytical method for carbon and has the potential to serve as a new marker in provenance studies. As very low irradiation energy and current are applied, there is no damage to the archaeological specimen and will be safe for returning after total decay of radioactivity (Na-24), which will be about 10 days after analysis.

The experiment designed for carbon analysis also gives results for Na, Mg and Al simultaneously.

As analysts, we expect all plant-ash based glasses to contain some traces of carbon which can be analysed by DAA. Further, carbon analysis gives an estimate of the contamination problems associated, in general, with glass production in ancient wood-fired furnaces.

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