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Combined prompt gamma activation and neutron diffraction analyses of historic metal objects and limestone samples(*)

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Summary. — Two non-destructive neutron techniques have been used for the analysis of archaeological objects, among them English monumental brass plates, Dutch tin-lead spoons, a Roman leaded bronze fibula and several limestone samples. Prompt Gamma Activation Analysis (PGAA) is a non-destructive method for determination of the major and trace element compositions of various archaeological materials. Time-Of-Flight Neutron Diffraction (TOF-ND), on the other hand, is a non-invasive diagnostic tool for obtaining structural information from ceramic and metal objects. The element information (PGAA) holds the key information for addressing questions of provenance and authentication, whereas the structure information (TOF-ND) addresses questions of ancient materials and making techniques. Here we present data from those two complementary neutron methods, applied to different types of materials and artefacts, in order to highlight commonalities and differences.

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1. – Introduction

A guided beam of neutrons is a versatile probe for collecting information from the interior of undisturbed museum objects and archaeological findings. Neutrons penetrate through coatings and corrosion layers deep into centimetre-thick artefacts, a property that makes them ideal for non-destructive analyses. A particular attraction of neutron techniques for archaeologists and conservation scientists is the prospect of locating hidden materials and structures inside objects. Neutron analysis techniques are based on the following simple principle. A material is placed in a beam of neutrons which may interact with the atomic nuclei in two ways: the neutrons are either absorbed or scattered. A captured neutron may lead to an excited compound nucleus (nucleus+neutron) that may emit gamma radiation in a delayed or prompt decay process. The characteristic energies of the emitted gamma-rays identify the isotope. This is the basis of the various neutron activation techniques and elemental analysis of a sample [1-5]. Scattered neutrons, on the other hand, may be utilized to extract information on the structure of a material, for instance in terms of the mineral phase abundance, the microstructure, the texture or the porosity. This is the task of the neutron diffraction techniques [6-8]. A further important field of neutron archaeometry is neutron radiography and tomography which are based on the selective attenuation properties of neutrons for isotopes [9, 10].

During the past year, and in the frame of different research projects, we have utilized two complementary neutron diagnostic techniques, Prompt Gamma Activation Analysis (PGAA) and Time-Of-Flight Neutron Diffraction (TOF-ND) for characterising various archaeological materials, among them four 12th-17th century English monumental brass plates, a series of antique Dutch spoons from 14th-18th century, several Roman leaded bronze objects, and several Egyptian limestone samples. The gamma spectroscopy data were collected on the PGAA beamline at the Budapest Research Reactor in Hungary [1], and the diffraction data were obtained on the ROTAX beamline of the spallation source ISIS at the Rutherford Appleton Laboratory, UK [6].

The objective of this paper is to compare the results of two complementary neutron techniques applied on the same objects. The elemental information (PGAA) holds the key information for addressing questions of provenance and authentication of objects, whereas the structure information (TOF-ND) addresses questions of ancient fabrication techniques. Both neutron techniques use thermal or cold neutrons, both are completely non-invasive methods, providing information on the bulk. No preparation of an object is required prior to the experiments. The paper compares the results on prevalent materials in archaeology, limestones and metals, in order to highlight the similarities and the differences of the two methods. Representative objects were selected from the objects series in order to emphasise advantages and limitations:

a) Monumental brass plate, "The Civilian" 1400 AD [11]. Medieval monumental brasses [12] start to appear in English churches around 1300 AD, with time replacing the full relief monumental effigies. The flat incised brass is often laid on the church floor. Over the last decade much research has been directed towards the identification of specific workshops. However, little is known about the material properties of the monumental brasses, only but a few have been investigated with XRF and microprobe, indicating that the alloys typically contain Cu, Zn, Pb, Sn, as well as Fe, sometimes changing over time. The brass object chosen for this study, "The Civilian" (fig. 1), is an impressive one with a height of about 25 cm.

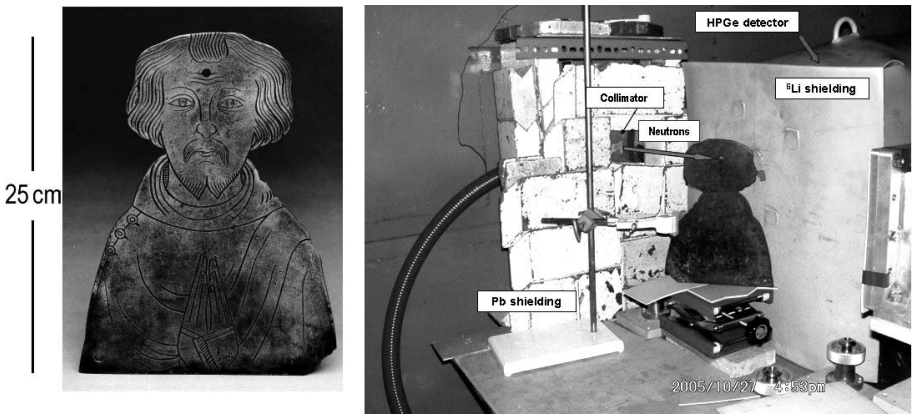

Fig. 1. – Monumental brass plate, "The Civilian" (left), on the PGAA station at the Budapest research facility (right).

b) Medieval Amsterdam tin-lead spoon (Vara-47-1). Within the town boundaries, the department of Archaeology of Amsterdam excavated over time more than 800 complete tin spoons and numerous incomplete parts. Many of these objects have been well preserved due to the peaty soil found in the Amsterdam area. The spoons are roughly dated by hammer and rose-marks, form and decoration. Iron core reinforced spoons were produced during 1350-1500 AD. A large variation in Pb content has been found by XRF, the early spoons (1350-1450) may contain up to 40–50% Pb. Due to the recognised health hazards of Pb, the production of tin spoons was regulated and overseen by the Guild after 1530. From then on, only a low Pb content ($\sim$ 5–10%) was allowed. However, the X-ray data seem to suggest that this control was more or less lost after 1600 [13].

c) A Roman bronze fibula from the excavation site of the Poulton project [14] in Cheshire, UK, has been investigated. Some years ago the Poulton site revealed unexpected evidence for Roman and prehistoric occupation in addition to the medieval archaeology. The investigated bronze fibula (about 5 cm long) is one among the numerous finds such as red-slipped pottery, brooches and coins from the Roman period.

d) Egyptian limestone samples (M1, M2, GMO-1, Sample3, MB). Recently there have been ideas brought forward on the construction of the Egyptian pyramids using geopolymers as a building material [15]. Here, a sample of the Queens chamber of the Cheops pyramid (MB), a casing stone from the Cheops pyramid (sample 3) are compared with limestone samples from Egyptian quarries (M1, M2, GMO-1, obtained from Prof. J. Harrell, Toledo University).

The full results of the different projects and the archaeological interpretations of the data will be given elsewhere.

2. – Experimental details

2˙1. *Prompt gamma activation analysis (PGAA).* – The Budapest PGAA station is installed on a horizontal guided neutron beam of the Budapest Research Reactor in

1995. Since 2000, it uses a beam from a so-called Cold Neutron Source, a liquid-hydrogen moderator cell at 16 K. In order to perform elemental analysis, the prompt- and delayed gamma photons are detected, which are emitted following the (n, γ) nuclear reaction. The applied detector system consists of a High Purity Germanium (HPGe) detector, surrounded by scintillator detectors in Compton-suppression set-up. The detailed description of the cold neutron PGAA-system has been given before [1].

The obtained spectra are evaluated using the HYPERMET-PC gamma-spectrum analysis software. The qualitative and quantitative elemental analysis is achieved by the precise energy and intensity identification of the characteristic gamma peaks. The concentration calculation is based on the prompt k0-method [3], the standardisation measurements had been previously done at the Institute of Isotopes, Budapest.

For measuring the brass plate (The Civilian), it was necessary to remove the sample holder chamber and to mount the object into the path of the neutron beam (fig. 1). Collimated beams of different cross-sections have been used to selected different points of the objects. The beam size was varying from 1 mm^2 to 400 mm^2 and has been adjusted to obtain optimal count rates of γ-photons. The Civilian has been examined on 5 different spots. The scoop and handle of the tin-lead spoon, the "foot" part of the fibula, and the limestone samples have been measured in the standard sample holder chamber. The powdered limestone material was packed into a special Teflon (FEP) film. In most cases the measurements were performed in air atmosphere, although whenever possible, the sample chamber was evacuated. Background corrections have been applied for each case. The acquisition time was set so as to reach sufficient counting statistics for the elements of interest. For the brass and lead-tin alloys, the lead concentration turned out to be the limitation factor. The typical acquisition time was between 6600 and 82500 seconds.

2˙2. *Time-of-flight neutron diffraction (TOF-ND).* – The neutron diffraction experiments were performed on the ROTAX diffractometer at ISIS, UK. ROTAX is on a liquid 100 K methane moderator. The flight path on ROTAX is about 15 m from moderator via the sample to the detectors; the flight times are in the order of 1 to 20 milliseconds. The scattered neutrons are registered by three linear position-sensitive scintillation detectors at low and high scattering angles. The time-of-flight (TOF) method makes use of the polychromatic beam of neutrons possessing wavelengths ranging from 0.5 to 5 Å which correspond to neutron velocities from approximately 8000 to 800 m/s. The detectors at backscattering angles (diffraction angle > 90 degree) have a special relevance in TOF neutron diffraction because diffraction patterns of bulky samples and of objects with irregular shape can be easily collected. Actually, sharp diffraction peaks are mostly measured at backscattering angles, to a large extent independent of the sample thickness. This special feature of TOF diffraction is of advantage for multiphase analyses and for studying fabrication related peak broadening effects [16].

For the data collection on the metal objects a neutron beam size of 10×10 mm was used. The Civilian was measured in air atmosphere at 5 points, distributed on a 15 cm long central, vertical line. Data were collected from the scoop and handle of the spoon, and from the centre part of fibula, with the objects in the evacuated ROTAX sample chamber. The limestone samples were measured as they were, as course grain powder (MB) and as solid lumps inside a pocket made of thin vanadium foil, with a neutron beam size of 20×20 mm. Data collection times were in the order of 1-2 hours for each analysis point. Each measurement on ROTAX yields 3 diffraction patterns from the 3 detector units which are analysed simultaneously with the Rietveld method to extract phase and structure parameters. Here we used the program suite GSAS [17]

for the Rietveld analysis, for phase identification, lattice constant determination and quantitative assessment of the phase compositions.

3. – Results

The PGAA results of bulk elemental concentrations are given in weight % or in atomic %. The concentration data are always summed up to 100%. In case of samples of geological origin, like limestone, the oxygen contents are calculated according to stoichiometry. The error bars can be specified in absolute or relative uncertainties. TOF-ND yields structure and microstructure parameters related to the crystallographic phases. The basis of the phase analysis is quantitative Rietveld analysis assuming that Bragg intensities are proportional to the phase content in the mixture [6]. A "chemical analysis" for binary solid solutions via Vegards law can be achieved with good accuracy [16], for instance the Sn content can be determined in a Cu/Sn bronze. Lead always appears as separate inclusion phase in the data and can be quantified by TOF-ND through multiphase Rietveld analysis as long as the texture of the alloy is negligible.

The results of the quantitative PGAA analyses and the structure parameters from TOF-ND are compiled in tables I-IV.

3˙1. *The Civilian.* – PGAA identifies the major components of Cu, Zn, Sn and Pb as well as trace elements of Ag and Cl. The concentrations of Sn and Pb exhibit larger uncertainties than others because of the low neutron capture cross-sections. The Sn and Zn contents from PGAA are in good agreement with 6 wt% Sn and 7 wt% Zn as determined by electron microprobe on a broken-off piece of the object [12]. According to major and trace components, the brass plate shows homogeneous composition over the analysed points within the measurements uncertainties. TOF-ND recognizes the Cu-type alloy phase and the Pb inclusion phase. Cl and Ag are not visible in the TOF-ND data. The diffraction data indicate considerable peak broadening and strong, varying texture across the five analysis points. The lattice parameter of the alloy, however, shows no significant variation for different sampling points, in agreement with a homogeneous elemental composition as evidenced by PGAA. The strong variation of Pb from TOF-ND is artificial and false, demonstrating that the quantitative phase analysis breaks down in the presence of strong crystallographic texture. In general, however, the phase fraction ratios of the texture-free phase components remain reliable quantities. In order to obtain reliable Cu/Sn/Zn phase contents, the preferred orientation can be determined by texture analysis [18]. The lattice parameter as determined from TOF-ND is a reliable, reproducible and characterising materials parameter, even in the presence of texture. The lattice parameter (3.664 Å) calculated from the PGAA results using Vegards law is in reasonable agreement with the measured average lattice constant (3.659 Å) by TOF-ND. Nevertheless, it can be concluded that for the case of ternary or quaternary alloys such as the Civilian, the characterisation by an elemental analysis method like PGAA is absolutely essential.

3˙2. *Tin-lead spoon.* – Besides the alloying components of Pb and Sn, it was possible to determine trace elements on the scoop and on the handle of the spoon (table II). Some of the latter presumably can be attributed to metallurgy (Cu, Co, Ag, Hg), others (S, Cl, Ca, H) are probably contaminants from the environment or corrosion components. Significant amounts of Fe can be measured in the handle, compared to the scoop. Sn-Pb

TABLE I. – *Brass object "The Civilian": elemental analysis from PGAA (top) and structure analysis from TOF-ND (bottom). The element fractions from PGAA are given with the relative uncertainties (R.U.). Five analysis points for PGAA (P1-5) and for TOF-ND (D1-5) were chosen to check for variations of the elements and phases, respectively. The TOF-ND table lists the lattice parameters of the* Cu/Sn/Zn *alloy from which the upper limits for* Sn *and* Zn *contents are derived. The broadening parameter* ε_γ *signifies the deviation from* $\varepsilon_\gamma = 0$ *for a homogenised alloy, due to microstrains and/or* Sn/Zn *compositional variations within the illuminated volume.*

PGAA	P1		P2		P3		P4		P5	
	wt%	R.U. (%)	wt%	R.U. (%)	wt%	R.U. (%)	wt%	R.U. (%)	wt%	R.U. (%)
Cl	0.063	0.003	-	-	-	-	0.019	0.001	-	-
Cu	72.3	1	73.3	2.3	74.9	1.3	74.3	1.1	72.1	2.8
Zn	5.7	0.2	5.3	0.3	4.5	0.3	3.8	0.3	5.7	0.7
Ag	0.46	0.01	0.17	0.01	0.35	0.01	0.30	0.01	0.17	0.01
Sn	7.5	0.3	6.2	0.4	6.9	0.3	7.1	0.3	7.3	0.8
Pb	14	1	15	2.6	13	1.4	14	1.2	15	3.2

TOF-ND	D1	D2	D3	D4	D5
a (Å)	3.6604	3.6590	3.6570	3.6561	3.6596
max. Sn	8.0	7.8	7.5	7.3	7.8
max. Zn	27.7	26.9	25.2	25.2	27.0
wt% alloy	87.3	88.7	84.5	95.7	75.5
wt% Pb	12.7	12.3	15.5	4.3	24.5
ε_γ (%)	0.36	0.44	0.41	0.32	0.46

is an eutectic system, hence TOF-ND exhibits separate phases for Sn and Pb. The lead contents in scoop and handle are in good agreement. The handle diffraction patterns clearly show ferrite, alpha-iron, although in smaller weight fraction as from PGAA. The diffraction analysis shows a large amount of a SnO corrosion phase on the scoop only whereas $SnSO_4$ is found on both spoons parts. Surprisingly an eta-bronze phase, Cu_6Sn_5, is observed in amounts consistent with the PGAA results. The PGAA results helped with identification but the structure of this special intermetallic phase is only visible by diffraction. This result may point to particular making processes involving copper/bronze containers or moulds as the bronze phase is present on most of the spoons studied in the project.

3˙3. *Roman bronze fibula.* – Figure 2 shows a section of the PGAA pattern on the fibula. Figure 3 shows the diffraction pattern collected on ROTAX bank 2. The elemental and phase compositions obtained by PGAA and TOF-ND are summarized in tables III. The PGAA analysis enables to determine all the major components and some trace

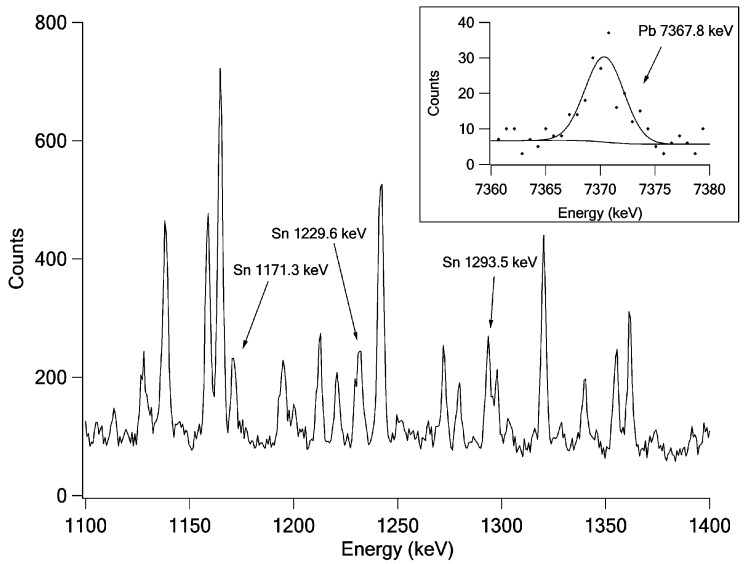

Fig. 2. – Section of the PGAA spectrum collected from the Roman bronze fibula. Some of the Sn lines are indicated in between the Cu lines. The insert shows a Pb gamma peak at higher energies.

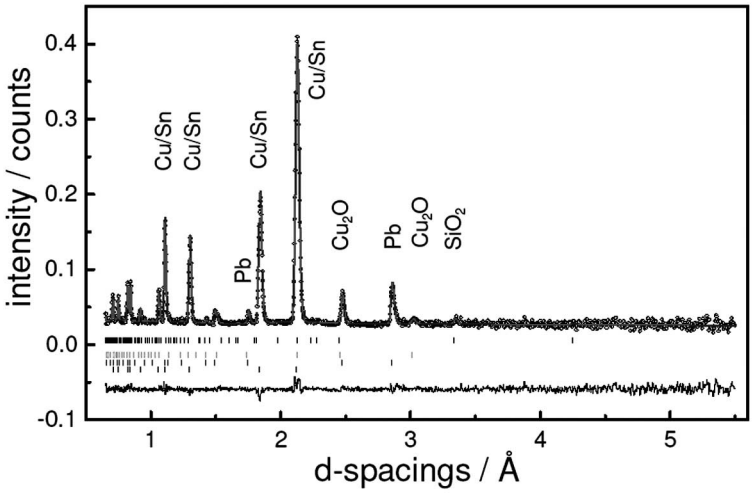

Fig. 3. – Neutron diffraction pattern obtained from the bronze fibula. The observed data (circles) are compared to the theoretical (line) and difference (lower curve) patterns. The four sets of bars under the profile mark the positions of the diffraction effects from bronze (bottom), lead, cuprite, and quartz (top).

TABLE II. – *Medieval Amsterdam tin-lead spoon (Vara-47-1): Elemental analysis from PGAA (top) and structure analysis from TOF-ND (bottom). The element fractions from PGAA are given with the relative uncertainties (R.U.). The phase fractions from TOF-ND have estimated errors of* ± 0.2 *wt%, except* Pb *for which the error bar and detection limit is about* 1 *wt%. The TOF-ND table lists the crystallographic symmetries (space group and crystal system) of the phases.*

PGAA	Scoop		Handle	
	wt%	R.U. (%)	wt%	R.U. (%)
H	0.1269	*2.6*	0.0315	3.2
S	0.141	*6.8*	0.261	3.4
Cl	0.038	0.038	0.022	5.9
Fe	0.0542	*11.0*	21.4	2.1
Ca			0.14	8.7
Cu	1.34	*2.7*	0.887	2.8
Co			0.0139	3.5
Ag			0.00632	6.4
Hg			0.0016	1.6
Sn	96.1	*0.2*	74.2	0.7
Pb	2.2	*9.8*	3.0	9.1

TOF-ND	Space group	System	Scoop	Handle
			wt%	wt%
Tin	$I4_1/amd$	tetragonal	86.1	85.6
Lead	Fm3m	cubic	1.6	2.1
Iron	Im3m	cubic	0.0	7.0
Cu/Sn	C 2/c	monoclinic	4.4	4.5
SnO	P4/nmm	tetragonal	7.4	0.4
$SnSO_4$	Pnma	orthorhombic	0.5	0.4

elements like H and Cl. The PGAA analysis identifies the fibula as made of leaded tin bronze with low or negligible zinc content. The diffraction data confirm these findings, and additionally reveal a Cu_2O corrosion phase and small amount of quartz, probably on the surface. The diffraction data also reveal that the alloy is mostly free of preferred orientation but the peak broadening is significant, indicating that the fibula was not completely homogenised.

TABLE III. – *Roman fibula: Elemental analysis from PGAA (top) and structure analysis from TOF-ND (bottom). The element fractions from PGAA are given with the absolute uncertainties (Abs. unc.). The TOF-ND table includes the refined lattice parameter and the* Sn *content derived from it. The broadening parameter* ε_γ *signifies the deviation from a homogenised bronze* $\varepsilon_\gamma = 0$*. Alloy compositions (*Sn *and* Cu*) and phase fractions are given in wt% with probable error bars.*

PGAA	wt%	Abs. unc. (%)
H	0.095	±0.004
Cl	0.137	±0.008
Cu	71.2	±1.9
Zn	< 3	
Sn	10.7	±0.6
Pb	17	±3
Cu/Sn	6.7	±0.4

TOF-ND		Abs. unc. (%)
Rietveld structure parameters		
a (Å)	3.6748	±0.0002
wt% Cu	89.6	±0.5
wt% Sn	10.4	±0.5
ε_γ	0.71	±0.01
texture	weak	
Phase fractions	wt%	
bronze	77.3	±0.2
Pb	19.1	±1.0
Cu_2O	2.9	±0.2
SiO_2	0.7	±0.2
Cu/Sn	8.6	±0.4

TABLE IV. – *Elemental analysis from PGAA (top) and structure analysis from TOF-ND (bottom) of limestone samples (wt in %, unc. in %). M-1, M-2: Ancient Maasara Quarry; GMo-1: Gebel Mokattam Quarry; MB: Cheops Queens Chamber; Sample 3: Cheops casing stone (G. Demortier). The TOF-ND table includes the refined lattice parameter and phase analysis (wt%). The estimated error is ±0.2 wt% for the phase fractions. The oxygen contents, not visible in PGAA, are calculated according to stoichiometry.*

PGAA	M-1		GMo-1		MB		Sample 3	
	wt%	R.U. (%)	wt%	R.U. (%)	wt%	R.U. (%)	wt%	R.U. (%)
H	0.092	1.4	0.116	2.2	0.090	1.7	0.084	1.3
B	0.000499	1.3	0.00108	2.0	0.00119	1.7	0.000621	1.3
C	13.8	4.9	12.8	9.2	12.1	5.6	13.3	5.0
Na	0.138	5.8	0.513	3.5	0.377	2.2	0.100	6.6
Mg	6.33	5.2	0.97	7.7	0.78	6.5	0.49	7.0
Al	0.10	9.4	0.547	4.5	0.495	4.6	0.356	3.0
Si	0.41	4.6	1.40	4.1	1.96	2.6	0.92	3.2
S	0.043	7.0	0.16	4.7	0.037	8.8	0.069	4.7
Cl	0.097	5.1	0.56	3.9	0.52	4.1	0.076	4.6
K			0.099	5.0	0.124	2.6	0.066	3.7
Ca	26.1	3.0	31.5	2.3	33.0	1.9	33.0	3.1
Ti	0.0037	8.2	0.0498	3.4	0.0562	2.3	0.0251	3.1
Mn			0.0037	15.4	0.0092	5.3	0.00733	3.3
Fe	0.033	9.2	0.397	2.9	0.531	2.3	0.364	2.5
Sm	5.0×10^{-6}	15.0	4.4×10^{-5}	3.8	5.7×10^{-5}	2.4	3.9×10^{-5}	3.2
Gd			5.8×10^{-5}	4.6	7.8×10^{-5}	3.7	5.2×10^{-5}	3.4
O (calc)	52.8		50.9		49.9		51.2	

TOF-ND		M-1	M-2	MB	Sample 3
		wt(%)	wt(%)	wt(%)	wt(%)
Calcite	$CaCO_3$	41.2	99.8	96.7	34.2
Dolomite	$CaMg(CO_3)_2$	58.0	0.0	1.9	46.6.0
Quartz	SiO_2	0.8	0.2	1.3	14.5
Sepiolite	$Mg_8(OH)_4(Si_{12}O_{30})(H_2O)_{12}$	0	0	0	~ 4.1
Palygorskite	$Mg_5(Si_4O_{10})_2(OH)_2(H_2O)_8$	0	0	0	< 1
Illite-Muscovite	$K_yAl_4(Al_ySi_{8-y}O_{20})(OH)_4$	0	0	+ + +	+ + +

+ + + Present, not quantified due to uncertain structure model.

Comparison of PGAA and TOF-ND shows some similarities but also some differences. Both analysis methods agree with a high Pb content close to 20 wt%. There is a slight discrepancy in the Sn content, expressed by the Cu/Sn concentration ratio. The bronze lattice parameter points to a 10 wt% tin bronze whereas the total Sn content from PGAA is higher. The presence of Cu_2O further enhances this Cu/Sn discrepancy.

3˙4. *Limestone samples.* – A sample of the Queens chamber of the Cheops pyramid (MB), a casing stone from the Cheops pyramid (sample 3) are compared with limestone samples from Egyptian quarries. With PGAA we quantified the major components of H, C, Na, Mg, Al, Si, K, Ca, Ti, Mn and Fe as well as traces of B, S, Cl, Sm and Gd. Out of the detectable components, the concentration of H, *i.e.* the presence of water in the sample, is thought to be crucial. The elemental analysis reveals similar small hydrogen concentrations for the building and quarry samples M-1, GMO-1 and MB, and Sample 3, respectively. The phase analysis shows up hydrogen in MB and Sample-3 through the presence of small amounts of clay minerals (illite-muscovite, sepiolite, palygorskite, table IV). Mostly, the diffraction analysis reveals typical limestone contents, where sample MB and M-1, on the one hand, and Sample-3 and M-2, on the other hand, have similar mineral contents of calcite and dolomite.

In principle, the elemental and phase concentrations can be related by listing the crystal structure constituents of the latter. For M-1, for instance, which contains calcite, dolomite and quartz as main phase components, this leads to (wt%): 0.268 Ca, 0.127 C, 0.095 Mg, 0.002 Si, 0.508 O. These concentrations compare reasonable well with the elemental analysis (wt%, table IV): 0.261 Ca, 0.138 C, 0.063 Mg, 0.043 Si, 0.528 O. In practice, estimating the elemental contents from the phase analysis results can be bedevilled by varying stoichiometry of complex components such as clay minerals.

4. – Concluding remarks

We have performed PGAA and TOF-ND analyses on several archaeological metal objects as well as on limestone samples. Both neutron techniques are non-invasive bulk techniques and both can be applied to intact, rather big objects. The two methods yield different aspects of the materials in terms of element and phase concentrations, respectively. PGAA provides information from the whole illuminated sample volume whereas TOF-ND "sees" the crystalline portion of the material only. This is why the element weight fractions from both methods do not always match up.

Elemental analysis provides main and trace element concentration. Diffraction is very strong in separating out corrosion phases and secondary phases, allowing an unobstructed view onto the original ceramic or alloy components of the object. Diffraction analysis, however, only provides indirect information on the chemical compositions, for example via lattice parameter measurements and application of Vegards law. This kind of "chemical analysis" assumes that the lattice parameter of a solid solution varies linearly as a function of the concentration of the extra element like Sn or Zn. For a ternary alloy, for instance Cu with Sn and Zn, this method does not provide unambiguous elemental contents. For example, the diffraction pattern of a bronze Cu/Sn with 4 wt% Sn is indistinguishable from a diffraction pattern of a brass Cu/Zn with 12 wt% Zn. With PGAA it is possible to distinguish between tin-bronze (with Sn content higher than 1 wt%), leaded bronze (with Pb content higher than 5 wt%) and brass (with Zn content higher than 2 wt%).

It can be concluded that non-destructive elemental and phase analysis by PGAA and TOF-ND constitutes a powerful combination in archaeological sciences, as it was for instance shown in the case of the Cu content and the unusual Cu/Sn phase in the Amsterdam tin-lead spoons. PGAA is a valuable tool for characterising the bulk alloy properties in terms of the elemental content for provenance and attribution questions. The interpretation of the PGAA results comes "natural" to archaeologists and can be directly related to result tables from conventional archaeometric analysis methods. Structural parameters and their interpretation are more abstract but are indispensable for describing and reconstructing historic material treatments and fabrication techniques. The presence of texture that prevents a quantitative phase analysis in the case of the Civilian can be turned into an advantage if the TOF-ND diffraction techniques are used to their full power on dedicated engineering stations.

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