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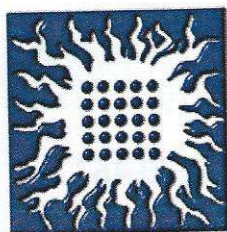
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2nd National Workshop

**NUCLEAR TECHNIQUES
AND
OTHER INSTRUMENTAL METHODS
IN
INVESTIGATION OF CULTURAL HERITAGE ARTIFACTS**

Београд, 16 – 17. април 2007.

Nuclear and Other Instrumental Analytical Techniques in Investigation of Cultural Heritage: Complementarity and Competitivity

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Abstract

Nuclear analytical techniques (NATs), including INAA, XRF, PIXE, stable and radioisotopes, α , β , γ -spectrometry, AMS, etc. have been applied to a wide range of cultural heritage materials with varying success. NATs featuring some intrinsic quality control aspects, such as multi-nuclide and isotope analysis, frequently serve as reference methods to cross-check critical results of other instrumental analytical techniques (ATs). As nuclear properties of elements are targeted, matrix problems seem to be negligible to a great extent. Other instrumental ATs either complement or compete NATs. Trace elements determination is the issue where these two groups of techniques most often interfere. While some NATs in trace element studies nowadays can be successfully replaced by AAS, ICP-OES or ICP-MS, a number of isotopic and elemental analyses are being done by NATs with no alternative.

1. Introduction

Modern studies on objects and materials of historical and/or cultural value usually involve the use of various analytical methods and techniques to extract objective information from these materials [¹ - ⁹]. In many cases, the chemical composition and isotope ratios are the primary type of information that is needed. The objects involved are often unique in nature (e.g. paintings, statues, utilitarian objects of different shapes and sizes in metal, glass, wood, stone, ceramics, etc.).

What results can nuclear and other instrumental analytical techniques offer to cultural heritage?

First, identification of chemical substances in materials of artistic and archaeological interest in order to get useful information about:

- the techniques and materials used by the artists as well as materials used in the restoration of objects,
- the processes that alter the archaeological material,
- methodology for the evaluation of the state of conservation and recommendations for conservative interventions on objects exposed to pollution.

Second, the isotope ratio analysis in order to:

- date the artifacts,
- get information about their provenance.

NATs add value to current efforts in cultural heritage studies on the regional and global scale and effectively complement the existing non-nuclear ATs. Four well-established NATs have been frequently used to support these studies. These are x-ray fluorescence spectrometry (XRF), neutron activation analysis (NAA), accelerator mass spectrometry (AMS) and proton induced x-ray emission spectrometry (PIXE) with related ion beam analysis (IBA) supplemented by a range of non-nuclear techniques, such as atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectroscopy (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS).

A literature survey for the published articles in ISI database "web of science", for the period 2000 - 2007, revealed a total of 330 articles for the search term: (analysis OR examination OR characterisation) AND ("cultural heritage" OR "art object" OR "archaeological object" OR archaeometry). When this search results was refined using the term ("x-ray fluorescence" OR XRF OR EDXRF), the resulting number of retrieved articles was 53. This review points out the popularity trend of the investigation of cultural heritage and the use of XRF in this field.

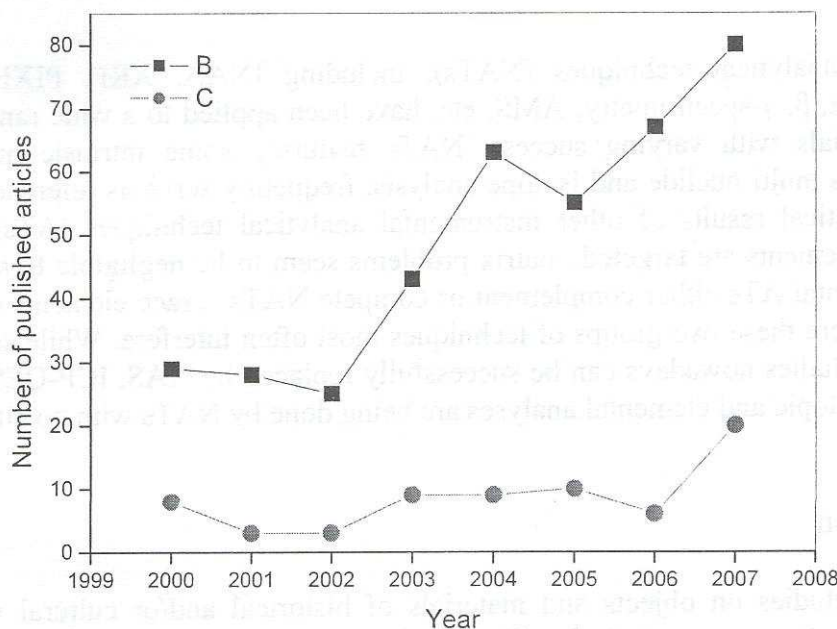


Figure 1.

2. Description of analytical techniques

2.1. X-ray fluorescence spectrometry (XRF)

In XRF analysis, the sample is irradiated with a beam of x-rays. In a recombination process the elements in the sample emit characteristic x-rays. The x-ray energy determines the elements present in the sample. Many elements can be measured simultaneously with the quantity of each element determined from the intensity of the x-rays. This analytical technique is non-destructive and requires minimal sample preparation - the sample is inserted directly into the instrument for analysis. This technology is relatively inexpensive and the detection limit is similar to other analytical techniques. XRF depends on the availability of excellent standards.

Two laboratories are currently main suppliers for various standards – the National Institute for Science and Technology (NIST) in USA and the Institute for Reference

Materials and Measurements (IRRM) in Belgium. Development and availability of standards suitable for XRF techniques is key to ensuring the competitiveness of XRF techniques.

2.2. Neutron activation analysis (NAA)

In NAA, the sample and an appropriate standard are exposed to a large neutron thermal flux in a nuclear reactor or accelerator. The sample elements are transformed into radioactive isotopes that emit gamma rays. The distribution or spectrum of energy of the gamma rays can be measured to determine the specific isotopes present. The intensity of the gamma rays can also be measured and is proportional to the amounts of elements present. NAA is a simultaneous, multielement method that can be used to measure more than 40 elements and does not generally require significant sample preparation. It is highly sensitive, though it does not quantify elements such as sulphur and lead. NAA is a non-destructive technique and does not require the addition of any foreign materials for irradiation. Thus, the problem of reagent introduced contaminants does not occur.

2.3. Proton induced x-ray emission spectroscopy (PIXE)

PIXE analysis is very similar to XRF analysis in that the sample is irradiated by a high-energy source, in this case high-energy protons, to remove inner shell electrons. Characteristic x-rays are detected using the same detection methods as in XRF. The protons after having been accelerated to high energy are fired onto the target that sits under high vacuum conditions. High-resolution x-ray detectors are used to measure the x-rays generated by the proton-atom interaction. Specific experimental set-ups are used to measure samples semi-automatically. This multielement analytical technique can measure more than 25 elements in short times due to higher cross-sections compared to XRF.

2.4. Accelerator mass spectrometry (AMS)

Accelerator mass spectrometry (AMS) is a technique for measuring long-lived radionuclides that occur naturally in our environment. AMS uses a particle accelerator in conjunction with ion sources, large magnets, and detectors to separate out interferences and count different radionuclides. They are used for a wide variety of dating and tracing applications in archaeology.

2.5. Atomic absorption spectrometry (AAS)

The two AAS options flame AAS (F-AAS) and graphite furnace AAS (GF-AAS), are similar in that the measurement principle for these two options is the same. However, they differ in how the sample is introduced into the instrument. Both types of atomic absorption spectroscopy involve irradiating the sample with light of a single wavelength and measuring how much of the input light is absorbed. Each element absorbs light at a characteristic wavelength; therefore, analysis for each element requires a different light source, and only one element can be determined at a time. In F-AAS, the sample is atomized and introduced into the optical beam using a flame, typically air/acetylene or nitrous oxide/acetylene. In GF-AAS, a graphite furnace electrothermal atomizer is used. These analytical techniques are destructive and require that the sample be extracted or digested for introduction into the system in solution. The detection limit of GF-AAS is typically about two orders of magnitude better than F-AAS.

2.6. Inductively Coupled Plasma optical emission spectroscopy (ICP-OES)

In ICP-OES analysis, the sample is excited using an argon plasma "torch." When the excited atoms return to their normal state, each element emits a characteristic wavelength of light. The wavelengths detected and their intensities indicate the presence and amounts of particular elements. Up to 50 elements can be determined simultaneously. As with FAA and GFAA, the sample must be extracted and digested for ICP-OES analysis, and the material introduced into the instrument is destroyed during analysis. The ICP-OES detection limit for many elements is equal to or somewhat better than that for F-AAS. With particular elements,

however, one or the other analysis technique is very superior to the other. The GF-AAS detection limit is better than that for ICP-OES for most elements.

2.7. Inductively coupled plasma/mass spectrometry (ICP-MS)

Analysis by ICP-MS also uses argon plasma torch to generate elemental ions for separation and identification by mass spectrometry (MS). This analysis technique allows many more than 70 elements to be determined simultaneously, and even the isotopes of an element can be determined. For ICP-MS analysis, the sample must be extracted or digested, and the analysis is destructive. An ICP-MS instrument is the most costly of those non-nuclear included in this article, and its detection limit is the lowest.

3. Comparison of analytical techniques

Major advantages and disadvantages of the above discussed analytical techniques are summarized in Table 1. Each technique has its own merits, specificities, advantages, and disadvantages. The choice of method is guided by the problem to be investigated. While factors such as element specificity and sensitivity (Figure 2) are critically important, considerations such as cost and throughput (the number of samples and number of elements to be determined per sample) are also important (Figure 3).

NATs, except XRF, usually require large non-portable facilities, therefore, sample have to be analyzed at the NAT facilities. Quality assurance (QA) and quality control (QC) are also important issues. An important risk is that in some NATs in particular NAA, samples with unknown elemental concentrations are irradiated with thermal neutrons in a nuclear reactor requiring the need for radiation protection measures.

Table 1. Advantages and disadvantages of analytical techniques

Technique	advantages	disadvantages
XRF	<ul style="list-style-type: none"> • multi-elemental (Na - U) • non-destructive • minimal sample preparation • short analysis time • good sensitivity for many elements 	<ul style="list-style-type: none"> • standard/sample must match closely (matrix) • particle size effects for low Z elements • inter-element interferences • blind spots due to limitations of excitation mode or overlapping x-ray lines
PIXE	<ul style="list-style-type: none"> • multi-elemental (Na - U) • non-destructive • minimal sample preparation • high sensitivity for some elements • can handle small samples 	<ul style="list-style-type: none"> • standard/sample must match closely (matrix) • not cost effective • requires access to particle accelerator
NAA	<ul style="list-style-type: none"> • multi-elemental • non-destructive • minimal sample preparation • high sensitivity (ppb range) • can handle small sample sizes (<1mg) • well documented applications 	<ul style="list-style-type: none"> • some elemental interferences • standard sample matrix corrections • requires multiple counting regimes to detect many elements • not cost effective • does not include key elements for some studies, such as sulphur and lead • requires access to research nuclear reactor
F-AAS	<ul style="list-style-type: none"> • easy to use • extensive applications 	<ul style="list-style-type: none"> • higher concentration • sample dissolution is required • one element at a time
GF-AAS	<ul style="list-style-type: none"> • well documented applications • very low (ppb) detection limits than 	<ul style="list-style-type: none"> • limited working range for sample • low sample throughput • one element at a time • more operator skill • sample dissolution is required
ICP-OES	<ul style="list-style-type: none"> • multi-element • high sample throughput • well documented applications • intermediate operator skill • very large linear range 	<ul style="list-style-type: none"> • higher concentration • sample dissolution is required • other elements can interfere
ICP-MS	<ul style="list-style-type: none"> • multi-elements • very sensitive for many elements • isotopic analysis • high sample throughput 	<ul style="list-style-type: none"> • limited documented applications • sample dissolution is required

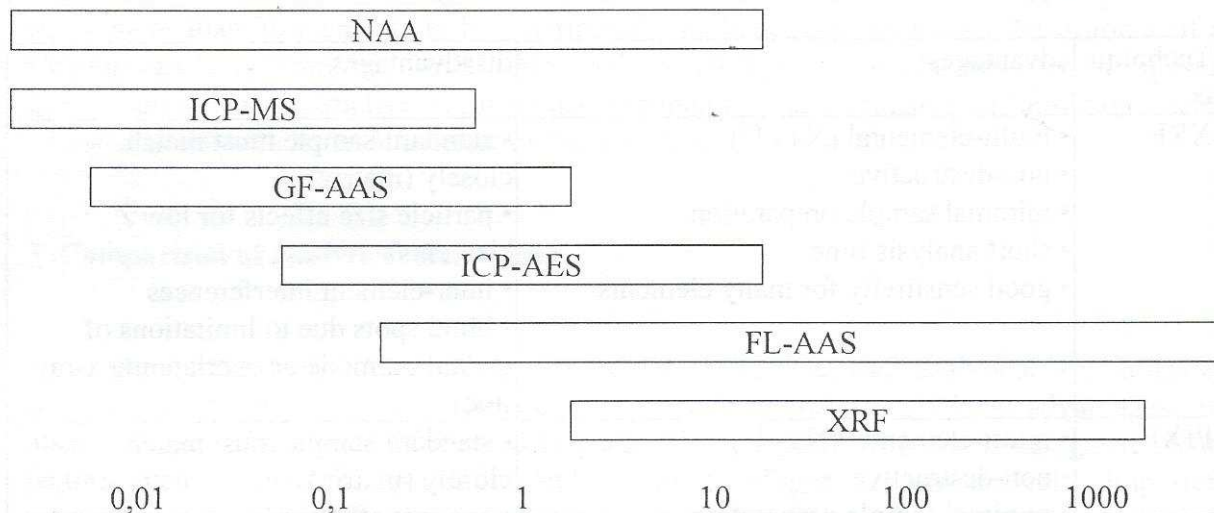


Figure 2. Typical concentration range for different techniques (ppm).

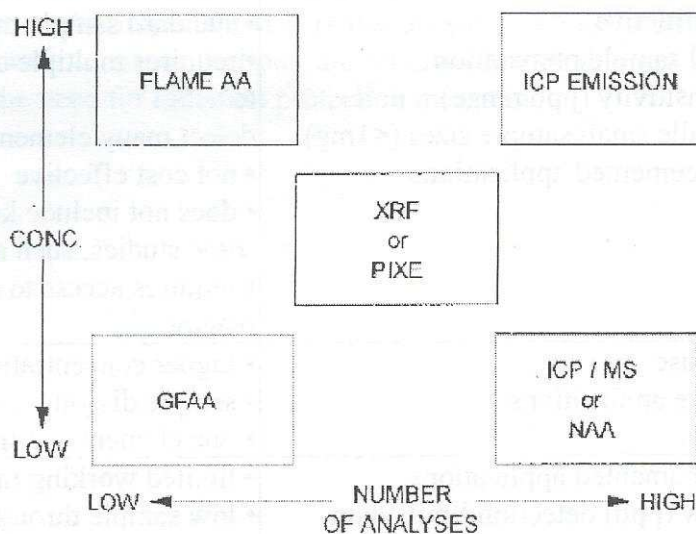


Figure 3. Analytical technique options

4. Applications of instrumental analytical techniques in art and archeology

A good example of applications of NATs and non-nuclear ATs cultural heritage is EU-ARTECH project¹⁰. Table 2 shows frequency of use of different analytical techniques within this project.

Table 2. Frequency of use of different analytical techniques within EU-ARTECH project¹⁰.

1	Reflection Light Microscopy	87
2	Scanning Electron Microscopy (SEM)	76
3	Transmission Light Microscopy	75
4	Classical Visible Light Digital Photography	70
5	Classical Visible Light Silver Emulsion Photography	67
6	Infrared Spectrometry	60
7	Powder Diffractometry	49
8	Diffractometry	48
9	Ultraviolet Fluorescence Photography	47
10	Visible & Ultraviolet Spectrometry	47
11	Standard Colorimetry	47
12	Digitisation & Image Archiving	44
13	Infrared Spectrometry Microscopy	43
14	Low HV (<150 kV) X-ray Radiography	42
15	Environmental Weathering Tests (Chambers)	42
16	Gas Chromatography (GC)	38
17	High Performance Liquid Chromatography (HPLC)	38
18	Gas Chromatography - Mass Spectrometry (GC-MS)	36
19	Low Angled Photography	33
20	Differential Thermal Analysis (DTA / TG / DTG)	33
21	Infrared Reflectography Electronic Camera	32
22	Infrared Silver Emulsion Photography	31
23	Universal Mechanical Testing	31
24	X-ray Fluorescence Analysis - X-ray Tube - Laboratory Fixed Instrument	30
25	Spectro-Photo-Colorimetry	29
26	High voltage (150 < HV < 450 kV) X-ray Radiography	28
27	Accurate Colour High Resolution Digital Photography	28
28	Ion Chromatography	28
29	Raman Spectrometry	25
30	Thin layer Chromatography (TLC)	24
31	Electron Microprobe	24
32	Atomic Absorption Analysis (AAA)	23
33	X-ray Fluorescence Analysis - X-ray Tube - Portable	23
34	Atomic Emission spectrometry (ICP-AES)	23
35	Pyrolysis Gas Chromatography (Py-GC)	19
36	Environmental Natural Weathering Tests (Outdoor)	19
37	Mercury Porosimetry	18
38	Particle Induced X-ray Emission (PIXE)	17
39	Pyrolysis Gas Chromatography - Mass Spectroscopy (Py-GC-MS)	16
40	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	16
41	Electron Impact Mass Spectrometry (EI-MS)	15
42	Ultra-Sound Testing	13
43	Contact Angle measurement	13
44	Specific Surface Area Measurement (BET)	13
45	Fluorescence Spectrophotometry	13
46	Rutherford Backscattering Spectrometry (RBS)	13
47	Environmental Scanning Electron Microscopy (ESEM)	13
48	Synchrotron radiation examination	13
49	Scanning Infrared Reflectometry	12
50	Thermoluminescence Dating (TL)	12
51	Transmission Electron Microscopy (TEM)	12
52	Laser Ablation Mass Spectrometry	11
53	X-Ray Induced Photoelectron Spectrometry (XPS)	10
54	Ultraviolet Fluorescence Microscopy	10
55	Nuclear Reactions (PIGE - PIGME)	10
56	Environmental monitoring	10

Literature

Figure 1. Number of published articles in "web of science" ISI database over the period 2000-2007. The number of articles for 2007. was multiplied with 4 to extrapolate the number of articles for whole year (the database was searched on March 30, 2007). The search terms: A - ("cultural heritage" OR "art object" OR "archaeological object" OR archaeometry); B - ("cultural heritage" OR "art object" OR "archaeological object" OR archaeometry) AND ("x-ray fluorescence" OR XRF OR EDXRF).

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