SIGNIFICANCE OF X-RAY FLUORESCENCE SPECTROMETRY IN ARCHAEOLOGICAL SCIENCES: An overview

Original Research Article

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ABSTRACT

An overview of the applicability of X-ray fluorescence (XRF) as a tool for non-destructive investigations of objects of art and archaeology is discussed. X-ray fluorescence (XRF) is a standard technique widely used and accepted by art historians, archaeologists, curators and conservators. Synchrotron radiation was applied for the analysis of photo graphic prints, liquid samples, glass artifacts and coins. Sixty one studies have been described in this paper with the basics and uses of XRF. Recent requirement is also mentioned about the XRF techniques in archaeological sciences.

Keywords:

Archaeological Sciences,
ASI,
TRXRF,
WDXRF,
EDXRF

I. INTRODUCTION

X-ray techniques have been employed widely throughout the course of advancement of Archaeological Science [1]. Archaeological Chemists are champions at using technology invented and used by other disciplines. For the last several years, X-ray fluorescence spectrometry (XRF), adopted mainly from geological applications, has been used particularly for the analysis of volcanic rocks [2],[3]. In the last decade indeed, the last five years archaeologists, particularly in North America, have been experimenting and employing portable X-ray fluorescence spectrometry (pXRF) for a host of applications of volcanic rocks, all other stone, ceramics, and soils [3],[4]. Cultural Heritage scientists examine works of art and archaeology by means of technical and scientific methodologies to understand when and how these artifacts were made, and, as well important, how are they to be preserved, what conservation treatment represents the best option and why[5]. The present study describes the importance, with the basics of XRF spectroscopy and its advance applications in the field of Archaeological Sciences.

II. X-RAY FLUORESCENCE SPECTROPHOTOMETER

Basic Theory

An electron can be ejected from its atomic orbital by the absorption of a light wave (photon) of sufficient energy. The energy of the photon (hv) must be greater than the energy with which the electron is bound to the nucleus of the atom. When an inner orbital electron is ejected from an atom, an electron from a higher energy level orbital will be transferred to the lower energy level orbital. During this transition a photon maybe emitted from the atom. This fluorescent light is called the characteristic X-ray of the element. The energy of the emitted photon will be equal to the difference in energies between the two orbitals occupied by the electron making the transition. Because the energy difference between two specific orbital shells, in a given element, is always the same (i.e. characteristic of a particular element), the photon emitted when an electron moves between these two levels, will always have the same energy. Therefore, by determining the energy (wavelength) of the X-ray light (photon) emitted by a particular element, it is possible to determine the identity of that element. For a particular energy (wavelength) of fluorescent light emitted by an element, the number of photons per unit time (generally referred to as peak intensity or count rate) is related to the amount of that analyse in the sample. The counting rates for all detectable elements within a sample are usually calculated by counting, for a set amount of time, the number of photons that are detected for the various analyse characteristic X-ray energy lines. It is important to note that these fluorescent lines are actually observed as peaks with a semi-gaussian distribution because of the imperfect resolution of modern detector technology. Therefore, by determining the energy of the X-ray peaks in a sample's spectrum, and by calculating the count rate of the various elemental peaks, it is possible to qualitatively establish the elemental composition of the samples and to quantitatively measure the concentration of these elements [6],[7], [75].

Detector systems:

There are two main types of XRF spectrometers [Wavelength dispersive (WDXRF) and Energy dispersive (EDXRF)] differ entirely in their detection systems. EDXRF systems depend on semiconductor-type detectors which receive the entire emitted spectrum from the sample and decode it into a histogram of number of counts versus photon energy. WDXRF spectrometers, however, use an analyzing crystal to disperse the emitted photons based on their wavelength and place the detector in the correct physical location to receive X-rays of a given energy. CCD were used in the breadboard instrument to compare split events. The x-ray source is run at 30 kV and 30 mA to generate X rays. Total Reflection X-Ray Fluorescence (TXRF) has become increasingly popular in micro and trace elemental analysis in the several research fields such as geology, biology, materials science, medicine, forensics, archaeology, art history, and more. TXRF is basically an energy dispersive analytical technique in special excitation geometry [75].

Comparison of EDXRF and WDXRF spectrophotometer [74]

Table 1. describes the valuable comparison between the EDXRF and WDXRF spectrometers. WDXRF detects the elements from Beryllium to Uranium whereas EDXRF investigates the elements from sodium to Uranium. WDXRF more better detection limits for the heavier elements and more sensitive for low Z elements. WDXRF is more expensive than EDXRF. Sequential and simultaneous measurements are done by WDXRF.

Table no 1. Comparison between EDXRF and WDXRF spectrophotometer.

Entry	Essentials Nuts	EDXRF	WDXRF
1	Elemental range	Sodium to Uranium	Beryllium to Uranium
2.	Detection limit	Less optimal for light elements. Good for heavy elements	Good for Be and all heavier elements
3.	Sensitivity	Less optimal for light elements. Good for heavy elements	Realistic for light elements. Good for heavy elements.
4.	Resolution	Less optimal for light elements. Good for heavy elements	Good for light elements. Less optimal for heavy elements.
5.	Costs	Relative inexpensive	Relative expensive
6.	Power consumption	5 to 1000W	200 to 1000W
7.	Measurements	Simultaneous	Sequential/simultaneous
8.	Critical moving parts	No	Crystal, goniometer

III.XRF IN ARCHAEOLOGICAL SCIENCE RESEARCH

Archaeological scientist focused their interests for the investigation of traditional trade routes, ancient material characterization, and identification of archaeological evidences using advance instruments technology. In the advance technology, XRF is most valuable techniques for identification and characterization of archaeological materials (sixty one different studies) which were described in table no.2. According to archaeological materials studies are described.

Table no 2. Details of different studies which have been done by researcher using advance XRF technology.

Entry	Name /Type of Samples	Elements / Composition analyzed	Type of Instruments	Ref
1	Cleaned surfaces of Pi-Ramesse crucible fragments(on site)	Fe, Ti and other major elements	Handheld X-ray fluorescence (HHXRF)	[13]
2	Building stone	Major and trace elements	Portable X-ray fluorescence (p-XRF)	[14]
3	Traditional building material of copper hall (Timber & copper alloy)	Leaded bronze (Cu–Pb–Sn), leaded copper (Cu–Pb), leaded gunmetal (Cu–Zn–Pb–Sn), leaded brass (Cu–Zn–Pb), brass (Cu–Zn), and red copper (Cu),	p-XRF (Niton XLt 898; Thermo Fisher Scientific Inc.)	[15]
4.	Colouring materials and ink in manuscript	Fe, S, Cl, Ar, K,Ca, Si,Cu, Zn, Iron sulphate, and Hg	Handheld X-ray fluorescence (XRF) (Tracer IV-SD, Bruker)	[16]
5	Copper-Based Alloy	Zn, Sn, Pb, Zn, Ag, Sb, As and Au, Fe, Mn, Ca, Ba, etc.	Energy Dispersive X-Ray Fluorescence (ED-XRF), Amptek Inc. (Bedford, MA, USA).	[17]
6.	Ancient Pottery	Major oxides with Zn	XRF(Make : Not Mention)	[18]
7.	Rocks (Dolerite samples)	Major oxides with trace elements	Wave dispersive X-Ray Fluorescence (WDXRF) (PANalytical PW2404)	[19]
8.	Ribbed daggers	Major alloying modes, tin bronze and arsenical copper	XRF(Make : Not Mention)	[20]
9	Roman brooches	Zn, Sn and other major elements	XRF(Make : Not Mention)	[21]
10	Soil pollutant	Heavy metals (As, Cr, Cu, Ni, Pb, V and Zn)	Handheld ED-XRF (Thermo Scientific XLTj-793 NITON)	[22]
11	Gold and gold work	Major elements with base alloy	XRF(Make : Not Mention)	[23]
12	Archaeological potsherds	Major oxides and trace elements	XRF-microscope (Make : Not Mention)	[24]
13.	Excavated obsidian - Artifacts	Major and trace elements	XRF(Make : Not Mention)	[25]
14.	Archaeological bone	Trace elements with elemental maps of calcium, strontium, and lead	Synchrotron radiation X-ray fluorescence (SR-XRF) (Make : Not Mention)	[26]
15.	Metal slag	High Ti – Zr group and low Ti – Zr group, Ca and Mn contents	Handheld X-ray fluorescence spectrometry (HH-XRF) (Make : Not Mention)	[27]
16.	Excavated obsidian projectile points	Mn, Ca, K, Ti, Fe, Rb, Sr, Y and Zn	EDXRF(SAE-2010, Seiko Instrumnts Inc.)	[28]
17.	Archaeological ceramics	Major elements	(HH-XRF) (Make : Not Mention)	[29]
18	Rock phyllite samples	10 macro-elements with 39 micro-elements.	XRF(Sequential, Siemens SRS-3000)	[30]
19.	Pottery fragments and Soil samples	Major oxides with trace element concentrations,	XRF(Make : Not Mention)	[31]
20.	Archaeological ceramic	Major components	SR-XRF (Make : Not Mention)	[32]
21.	Gold, silver and billon coins	Base metal and Authentication	Portable ED-XRF with a 238Pu source ($_p$XRF-LFNA01)	[33]
22.	Yellow blocks	Major and trace elements	$_p$XRF (Bruker Tracer III-SD)	[34]
23.	Gold leaf	Au-Cu-Ag commercial , Au-Cu-Ag-In preliminary test alloy Au-Cu-In test alloy, chemically pure titanium dioxide (TiO2, titanium white)	pXRF (Make : Not Mention)	[35]
24.	Ceramic artifacts	Na, Mg, Al, Si, P, S, K, Ca, Ti, V,Mn, Fe, Ni, Cu, Zn, Br, Rb, Sr, Ba, and Pb.	WD-XRF (Bruker S8-Tiger)	[36]
25.	Ceramic sherds (on-site)	Sb, Sd, Ag, Sr, Rb, Pb, Se, As, Hg, Zn, Cu, Ni, Co, Fe, Mn, and Cr.	Portable EDXRF (NITON XLt-793W)	[37]

Entry	Name /Type of Samples	Elements / Composition analyzed	Type of Instruments	Ref
26.	Pottery shards and soil	Major oxides and trace elements	XRF(Make : Not Mention)	[38]
27.	Split (sediment) cores and solid samples	Identify Holocene facies changes, major Oxide and trace elements	Portable EDXRF (Thermo Scientific Niton XL3t)	[39]
28	Silver Coins	Base metal elements with Fe, Cu, Zn, Ag, Au and Pb	WDXRF (Philips PW 2404)	[40]
29	Metal musical instruments, metal alloy and of the various soldering materials	Ca, V, Mn, Fe, Cu, Zn, Pb, Sn, Cu, Zn, Pb, Sn	Non-invasive portable XRF(Make : Not Mention)	[41]
30	Archaeological pottery	K,Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr	ED XRF (Make : Not Mention)	[42]
31	Obsidian artifacts	Major and trace elements	EDXRF (Make : Not Mention)	[43]
32	Obsidian artifacts (Army)	Ti, Mn, Fe, Zn, Ga, Rb, Sr, Y, Zr, and Nb; Rb, Sr, Y, Zr, Nb,and Ba.	EDXRF(Spectrace Quanx, Thermo-Electron Quanx-EC)	[44]
33	Obsidian artifacts (Army)	Sub source /finger prints identification	XRF (Make : Not Mention)	[45]
34	Moss *Polytrichum commune* (Bryophytes)	S, Pb, K, Ca, Cr, Mn, Fe, Cu, Rb, Sr, Mo, Ba and Zn	HH XRF (Delta Classic, USA).	[46]
35	Andesite and Dacite source rocks	Major, minor and trace elements	EDXRF (Thermo Scientific *Quant'X*)	[47]
36	Rocks, ancient ceramic and soil	Major Oxides and trace elements	Micro X-ray fluorescence (μ-XRF) (Series 5011 XTF, Oxford Instruments)	[48]
37	Ochre	Major and trace elements	p-XRF(Innov-X Delta Premium model)	[49]
38	Copper and bronze artifacts	Major and trace elements	EDXRF (Make : Not Mention)	[50]
39	Obsidian artifacts	TiO2, MnO,Fe2O3 and Zn, Ga, Rb, Sr, Y, Zr, and Nb.	EDXRF(Spectrace/Thermo-Noran_ QuanX)	[51]
40	Byzantine Mosaics and Glass	Major Oxide with trace elements and pigments	EDXRF (Cameca SX-50.10, Bench top)	[52]
41	Miniature tuareg tamzak	Rb, Sr, Zr, and Y are, Cu (traditional green colorant), Zn, Pb and Cl with Cu (chloride corrosion)	p-XRF (Bruker Tracer III-SD)	[53]
42	Pigments in paint layers and illuminated manuscripts, of iridescent glasses and of medieval coins	Major oxides, trace elements, composition of used oils and binding media	Specially designed XRF (1 _ 1 mm pixel resolution) (Not mention)	[54]
43	Surface Soil	Cr, Ni, Cu, Zn, Zr, Rb, Y, Ba, Pb, Sr, Ga, V and Nb	XRF (Philips PW X-Unique II)	[55]
44	Archaeological obsidian artifacts	K, Mn, Fe, Ga, Th, Rb, Sr, Y, Zr, Nb.	HHXRF (Bruker AXS Tracer III-V)	[56]
45	Quartzite	Fe, Na, Sc, Cr, Co, Ni, Zn, Rb, Sr, Cs, Ba, La, Ce, Nd, Sm, Eu, Tb, Yb, Lu, Zr, Hf, Ta, Th, and U.	WD-XRF((Make : Not Mention)	[57]
46	Italian manuscript cuttings	Elements composition of Pigments	μ-XRF (ArtTAX)	[58]
47	Pottery	Major oxides and element composition	p-XRF (Bruker AXS Tracer III-V)	[59]
48	Pots, plates and provenance	Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Rb, Sr, Zr, T, Sn, With major Oxide	X-ray Analytical Microscope (XGT 7200, Horiba, Japan)	[60]
49	Oil-painted (mural and on wood-icons)	Inorganic pigments (Fe, Co, Cu, Zn, As,Pb, Hg, Ag, Au, Sn, Sb, Ba).	p-XRF (Oxford Instruments X-MET 3000TX).	[61]
50	Archaeological mural samples	Pigments with respect to Maya blue	Spot- and scanning XRF (Make : Not Mention)	[62]

Entry	Name /Type of Samples	Elements / Composition analyzed	Type of Instruments	Ref
51	Porphyritic volcanic materials	Geo-chemicals	HHXRF (Bruker Tracer III-V)	[63]
52	Silver objects	Base elements and its alloys	XRF (Bruker Mistral M1)	[64]
53	Early Glass Objects	Trace elements	XRF (Make : Not Mention)	[65]
54	Mimbres and Jornada pottery sherds	Major and trace elements	HH XRF (Bruker Tracer III-V)	[66]
55	Obsidian artifacts	Major and trace element	EDXRF (Spectrace/Thermo Noran QuanX)	[67]
56	Cortical bone	Lead poisoning	Synchrotron microprobe X-ray fluorescence (SMXRF) (Make : Not Mention)	[68]
57	Feather headdress	Organic and inorganic pesticide , base decorative mtal	HHXRF (Make : Not Mention)	[69]
58	Archaeological sediments and ceramics	Method validation, major and trace elements	EDXRF (Make : Not Mention), WD XRF (Make : Not Mention)	[70]
59	Silo Science	Validation of published International Standard	Portable X-ray fluorescence (P-XRF), (Make : Bruker PXRF)	[71]
60	Liquid samples	Trace and ultra-trace analysis	X-ray fluorescence spectrometry (XRF), (Make : Not Mention)	[72]
61	platinum photographic papers	Sensitized surface, Major elements	X-ray fluorescence spectrometry (XRF), (Make : Not Mention)	[73]

Metal and its alloys:

Zhang et al, (2012) were analyzed the building materials used in traditional Chinese copper halls (Kunming copper hall) using X-ray fluorescence (XRF) spectrometry data into the geographic information system (GIS) to examine the relations between the building components and their materials [15].

Shalev et al, (2008) were studied the metallurgy of 11 ribbed daggers from different M.B.II tombs in Israel (Ein Kinya, Aphek, Ajjul, Megiddo, Lachish, Rehov) and Egypt (Tell El-Dab'a). The two major alloying modes, one of Cu+Sn (13 objects), another of Cu+As (5 objects) and a third group of mixed composition (14 objects) was identified. Lead was used as additional alloy in some of the tin bronzes and some of the arsenical coppers and in most of the mixed ones [20].

Robcis et al,(2016) were investigated for the development of such alloys, including choice of chemical markers, elaboration process and thermo-mechanical treatments to be applied during the fabrication of foil and leaf. The metal leaf was tested on various substrates and analysed with ion beam analyses using the C2RMF particle accelerator by particle induced X-ray emission (PIXE) and Rutherford backscattering spectrometry (RBS) to validate the pXRF analysis [35].

Nicholas et al,(2014) were reported the assessment of the applicability of the Bruker AXS Tracer III-SD HHpXRF to non-destructive analyses of archaeological copper alloys with focus on the characterization of bulk alloy compositions, the effects of corrosion, tinning and sample geometry [12].

The percentage composition of metallic silver coins can be used to analyse and explain the locations and identification of coin mines reported by Sodaeia et al, [2013]. Furthermore, it provides certain information about the economic and political conditions of the era under study [40].

Pelosi et al, (2006) were investigated metal musical instruments, from the Roman period, by combining non-invasive portable X-ray fluorescence spectroscopy. The study was part of the European project EMAP (European Music Archaeology Project, 2013-2018) which aims to highlight Europe's ancient cultural roots from variety of perspectives, including: musical, scientific and "sensorial". The alloys utilised in the cornua from Pompeii are made up of copper and tin, with a tin content of around 1%. Solders are made from copper, lead and zinc (about 4-5%). Mouthpiece, receivers when present, exhibited high counts of zinc. The use of a brass alloy for solders identifies a sophisticated technological ability which was employed when creating the musical instruments [41].

Gueraa et al, (2008) were analysed the coins and casted simple objects to intricate jewellery comprising many diverse parts joined together, and also identify with the authenticity and the localization of the exploited sources of gold[23].

Scott et al, (2017) were investigated the 45 metal slag in the field order indicated two principle groups (a high Ti – Zr group and a low Ti – Zr group). The Ca and Mn contents also split the data into two groups but these were not consistent with the previous Ti – Zr groups. These differences could be related to the choice of ores and fluxes used for iron production [27].

Parreira et al, (2009) were used (pXRF) with a 238Pu source to analyse a set of gold, silver and billon coins from the collection of the Museu Histórico Nacional do Rio de Janeiro (MHN), struck during the Brasil Colônia period, Which show about 80.5% gold and 96.8% silver [33] while Sorrentino et al, (2015) described the composition of some Etruscan copper alloy findings and archaeological materials were classified according to their composition [17].

Blakelock et al, (2015) were evolved using XRF analysis of the fronts of hilt-plates revealed that half had been mercury gilded. The composition of most of the hilt-plate fragments fell in the range of c.75-88 wt% silver, 5-12 wt% copper, 2-3% tin and 1-5 wt% gold. In this study a thorough study of an additional 43 silver objects was undertaken [64].

Ceremics and Pottery

Gajić-Kvaščev et al,(2012) reported that Portable energy dispersive X-ray fluorescence (pEDXRF) spectrometry analysis was applied for the characterisation of archaeological ceramic findings from three Neolithic sites in Serbia. Two dimension reduction techniques, principal component analysis (PCA) and scattering matrices-based dimension reduction were used to examine the possible classification of those findings, and to extract the most discriminant features [76].

Aimers and their team were discussed in their investigations of Maya ceramics from Belize. The focus of this study is not to determine the source/provenance of the clay bodies, but to investigate the potential for establishing handheld XRF as an on-site analytical tool for the characterization and potential classification of ceramics based on their chemical signatures [29].

Kasztovszky et al, (2007) were demonstrated in their study that the applicability of PGAA on pottery archaeometry has been proved in investigations of pre-Columbian figurines from Venezuela. They were also reported the major components of the bulk material with some accessory and trace element concentrations [31].

A wavelength-dispersive X-ray fluorescence (WD-XRF) calibration is developed for small powdered samples (300 mg) with the purpose of analyzing ceramic artifacts that might be available only in limited quantity. The advantage with the analytical method presented that it was rapid and requires only a small amount of sample that can easily be re-used for further analyses. This method has great potential in ceramic provenance studies reported by De Vleeschouwer et al, (2011)[36].

Morgenstein et al, (2005) were described that the utility of a portable EDXRF unit for obtaining geochemical analyses of pottery suitable for provenance and other ceramic classification studies. The geochemical behavior of iron, strontium and rubidium is discussed in relation to geological source materials utilized for pottery manufacture [37] While Freeland 2010 was reported in his thesis that the utility of pXRF for the analysis of archaeological ceramics. The thesis highlights the need for independent theory and protocol governing non-destructive analysis of ceramics. That pXRF analysis “averages” the geochemistry of the ceramic paste constituents is, in light of this broader understanding of ceramic composition, actually advantageous [77].

Speakman et al, (2011) were analyzed the seventy-five intact Mimbres and Jornada pottery sherds from the American Southwest using portable XRF and instrumental neutron activation analysis (INAA). They were concluded that sourcing intact ceramics by portable XRF is challenging and that bulk analytical measurements, such as INAA, remain a better approach for sourcing archaeological pottery [66].

Hunt et al, (2014) were reported the significant interest in the use of portable X-ray fluorescence spectrometers (pXRF) for cultural materials applications, especially ceramics and sediments. They evaluated the strengths and limitations of p-XRF analysis for the quantitative compositional analysis of archaeological ceramics and sediments and propose an analytical protocol and calibration designed to optimize p-XRF performance for cultural materials [70].

Pantos and his team were established the feasibility studies with the aim of demonstrating the advantages, and evaluated the effectiveness, of synchrotron radiation over conventional methods in the context of Archaeological Science. The combination of X-ray diffraction, X-ray fluorescence and small/wide-angle scattering measurements using SR, coupled with uniquely SR techniques such as X-ray absorption spectroscopy, offers new opportunities for novel applications and prospects for new directions in archaeological science [32].

Attaelmanan et al, (2014) were analysed the 26 potsherds collected at Mleiha, using an X-ray fluorescence microscope. Analysis confirms the homogeneity of the group called Late Mleiha ware, and the variability of other groups as Grey and Black wares. It was convey new insights, as the relation of some samples with Indian productions [24].

Rademakers et al, (2016) were concluded their study with the aims of understanding technological choices of ancient craftspeople, their use of different raw materials and, by extension, the organisation of production and trade. Complete crucible examples were rarely found and it was often difficult to reconstruct full crucible profiles based on the fragmented remains [13].

Sarhaddi-Dadiana et al, (2015) were determined whether pottery sherds from new archaeological survey in south region of Sistan are locally made or imported. The analytical techniques involved X-Ray Fluorescence (XRF) and X-Ray Diffraction (XRD), that were applied to determine the major and trace elements and also the mineral content of the pottery sherds. The results also showed that local community at Sistan since prehistoric period are very skilful and keep a tradition in pottery making until Islamic Period and the material was locally found [38].

Ludvig Papmehl-Dufay et al, (2016) were reported the results of technical, functional and stylistic analyses on pottery from two Early Neolithic sites on Öland – Resmo and Runsbäck. Analyses include thin sections and XRF of clays and wares, lipid residue analysis and recording of stylistic attributes. C14 dates place the activities at the sites at c. 3900–3600 BC and 3600–3100 BC respectively. They were suggested that the observed differences reflect differences in function and duration between the analysed sites [78].

Kumar et al, (2006) were analysed the archaeological pottery samples four different civilization from Sanghol, India using EDXRF. They indicates that the pottery of different periods was made from the samples types of the soil of the Sanghol region and pottery making was probably well developed and technology at Sanhgol, India [42].

Nostrom et al, (2014) was reported that the statistical analysis indicate that the same clay sources were exploited for both occupation periods, though evidence suggested that the dominant clay source in use did change over time. Thesis results also imply that the same clay sources were utilized in the production of plain and decorated pottery, which suggests that at least some portion of the decorated pottery excavated from the Bayshore site was produced locally, and not obtained through trade. Finally, the results of this research demonstrate that pXRF is a useful tool for preliminary differentiation of clay sources in Florida [59].

Kelloway et al,(2008) were explored the advantages of using chemical characterisation to investigate provenance and manufacturing processes at two colonial potteries: the Thomas Ball Pottery in the Sydney Brickfields, and Irrawang in the lower Hunter Valley, New South Wales. A total of 64 earthenware sherds were analysed using X-ray fluorescence spectroscopy (XRF) and 11 lead-based glazes using Raman microspectroscopy to determine the composition of the ceramic bodies (fabrics) and glazes respectively [18].

Reddy et al, (2012) were identified more than 25% of the pottery sherds from the late PIR.D period (ca. 2nd - mid. 3rd c. AD) assemblage from the excavated building H at Mleiha as Indian is based on form and fabric, but using only visual assessment. Initial review of the XRF results indicates that the Maharashtra and Gujarat regions of India are probable source areas for at least two of the types of wares [60].

Glass and Obsidian

Smirniou et al, (2012) was reported in their study on twenty-eight glass samples which were examined using X-Ray Fluorescence Spectrometry (XRF) and sixteen samples were analysed by Laser Ablation with Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) to determine the samples' chemical composition, to characterize the trace elemental content in glass and to identify their raw materials and place of origin [65].

Two obsidian sources have been identified by Neri, (2007) in the Philippines. X-ray fluorescence spectroscopy (XRF) was used to obtain a chemical signature of these sources and to link obsidian artefacts recovered at three archaeological sites to their geological source [8].

Source identification of obsidian projectile points/ blades from Kaman-Kalehoyuk was reported by Kabayashi et al, (2007) using XRF methodology [28] while Julia et al,(2004) was evaluated in the results of source analysis by EDXRF of obsidian artifacts from the Mesoamerican site of Cerro Palenque in Honduras and changes over time discussed. Sources of obsidian include Ixtepeque, El Chayal, Jalapa, San Martin Jilotepeque, and San Barolome in Guatemala [43].

Ogburn et al, (2009) were evaluated ninety-nine obsidian artifacts from fortified and non-fortified sites in the Pambamarca region of Northern Ecuador using XRF to examine patterns of procurement of obsidian by soldiers in the Inka army and by the local Cayambes who were resisting Inka conquest and also reported the Inkas were acquiring some obsidian from the Yanaurco-Quiscatola source, which had been previously abandoned around AD 1000 [44].

Eerkensa et al,(2004) were discussed that the archaeologists frequently assign artifacts to chemically discrete subsignatures of major obsidian sources [45]. While the technical ability to do so has been demonstrated, it remains to be shown that such information is behaviorally meaningful. Using a case study from the Coso Volcanic Field, which has at least four distinct subsignatures, they were examined this problem and conclude that subsource identification can be useful and quite interesting. This was particularly so when large datasets encompassing spatially expansive areas can be assembled and statistically analyzed [45].

Negash et al, (2006) were reported the source provenance of 10 Early Stone Age obsidian artifacts from the localities in Melka Konture has been determined by EDXRF. Results showed that the early to mid-Pleistocene makers of the artifacts derived the raw material from a source located in their proximity, supporting the previously proposed short distance transport of raw material for the time period [51].

Phillips et al, (2009) were reported about the 131 Obsidian artifacts had been recovered from 18 archaeological sites on eight islands across the Kuril Island archipelago in the North Pacific Ocean, suggested a wide-ranging distribution of obsidian throughout the island chain over the last 2,500 years with the help of portable XRF technology [56].

Colour, Manuscripts, Miniature, Feather, Textiles and Photo graphic material

Fourteen manuscripts (18th - 19th c., Monastery of Dochiariou, Mount Athos) were investigated by Karapanagiotis (2014) using a portable X-ray fluorescence spectrometer. The relative compositions of black ink, red and green pigments were measured [16].

Burgio et al, (2010) were reported about the Italian medieval and Renaissance manuscript cuttings and miniatures from the Victoria and Albert Museum were analyzed by Raman microscopy to compile a database of pigments used in different periods and different Italian regions. The use of a needle-shaped form of iron gall ink as a pigment rather than a writing material was established by both Raman microscopy and X-ray fluorescence spectroscopy for the Madonna and Child by Franco de' Russi [58].

Elizabeth Burr was reported the non-destructive analysis of miniature Tuareg tamzak using X-radiography and X-ray fluorescent spectroscopy to understand the craftmanship of tuareg [53] while Barret et al, (2012) were reported the analysis of historical paper in Open book using XRF as no destructive technique [9] .

The 16th century feather headdress in the Welt Museum Wien (WMW), an affiliated institution of the Kunsthistorisches Museum (KHM) in Vienna, is the most renowned of the few remaining pre-Columbian "Arte Plumaria" artefacts, which were made by feather artisans (Amantecas) using traditional techniques in the territory of present day Mexico reported by Karydas et al 2104 [69].

Ghia et al, (2008) were reported the µXRF method in order to determine the concentration of the main compounds in the raw materials and on the other hand to make a classification of the different types of brooches discovered at Tomis, an archaeological site in Romania[21] .

Rock and Soil

A review of rock studies for archaeologists, and an analysis of dolerite and hornfels from the Sibudu area, KwaZulu-Natal described by Wadley et al, (2011) [19].

Using ceramic petrography, Ixer et al 2014, were reported that the dominant fabric of Cuzco Inca pottery was compared with those of two pre-Inca wares, Killke and Lucre. Andesite temper, identified in the Lucre and Cuzco Inca fabrics, was compared with samples of andesite from local geological outcrops [10].

Hoelzmann et al, (2017) reported the strength of combining p-ED-XRF analyses with this new sample chamber to identify Holocene facies changes (e.g. marine vs. terrestrial sedimentary facies) using a sediment core from an estuarine environment in the context of a geoarchaeological , investigation at the Atlantic coast of Southern Spain [39].

Garzón et al, (2012) were presented the results obtained of a multivariate statistical analysis concerning the chemical and phase composition, as a characterization purpose, carried out with 52 rock phyllite samples selected from the provinces of Almería and Granada (SE Spain) using X-ray fluorescence (XRF)[30].

Shackley et al, (2012) were reported the study on X-Ray Fluorescence analysis of major, minor, and trace element composition of andesite and dacite source rocks from Northern New Mexico [47] while Sepúlveda et al, (2013) were analyzed the yellow blocks from the archaeological site Playa Miller 7 (PLM7), on the coast of Atacama Desert in northern Chile, using Raman spectroscopy and X-ray fluorescence (XRF) portable [34].

Ogburn et al, (2013) were examined the effects of surface contamination and chemical weathering on the ability to assess provenance of igneous building stones used in the Cuzco region of Peru using portable X-Ray Fluorescence (PXRF). Surface contamination was assessed through comparing low-impact cleaning methods on diorite and andesite blocks, and weathering was examined by comparing weathered vs. fresh surfaces of samples from two andesite quarries [14].

Bernaa et al,(2006) were characterized natural sediments sampled on and in the proximity of the tell and monitor their transformations due to exposure to high temperatures in an oven and in open fires, focusing in particular on the transformations of the clay mineral components of mudbrick materials. The analytical techniques used include micromorphology, Fourier transform infrared spectrometry (FT-IR), X-ray powder diffractometry (XRD) and Xray fluorescence (XRF) spectrometry[11].

MacDonald, (2015) were reported in his thesis that the methodological developments for the geochemical Analysis of ochre from archaeological contexts: case studies from British Columbia and Ontario, Canada [49].

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Pitblado et al, (2008) were reported the results of pilot-study efforts to develop methods to profile quartzite, a rock type and also reported the petrography, ultraviolet fluorescence (UVF), wavelength dispersive X-ray fluorescence (WD-XRF), instrumental neutron activation analysis (INAA), and inductively coupled plasma mass spectrometry—both acid-digestion (AD-ICP-MS) and laser ablation (LA-ICP-MS)—as means to differentiate among the specimens and the sources they represent [57].

Scharlotta et al, (2015) were described the geochemical research using aphanitic volcanic rocks such as basalt and obsidian has long contributed to archeological understanding. This study also investigated the potential for using pXRF for provenance research on fine-grained volcanic materials in southern California. Results indicate that volcanic materials can be suitably discriminated using pXRF that sourcing porphyritic volcanic materials is possible and can be applied to archeological assemblages [63].

Ene et al, (2009) were reported in his work X-ray fluorescence (XRF) technique was used to evaluate the soil pollution with heavy metals (As, Cr, Cu, Ni, Pb, V and Zn) in the vicinity of Iron and Steel Works at Galati, Romania, which is one of the most important metallurgical complexes in the South-East of Europe [22].

El-Bahi et al, (2013) were reported the analysis of environmental pollution with some heavy metals for twenty four surface soil samples collected from Qarun Lake and Wadi El Rayan region in Faiyum, Egypt utilizing X-ray fluorescence (XRF) spectroscopy. The results establish a database reference of radioactivity background levels around these regions [55].

Silo Science

A study described by Frahm (2013) on the application of portable XRF (PXRF) for chemical characterization of obsidian ignores fundamental issues of reliability and validity in the measurements, and justifies "internally consistent" measurements as acceptable. Speakman et al,(2012) were argued this form of science is unacceptable, point out several flaws in Frahm's paper, and provide some examples of PXRF measurements that are valid and reliable and conform to international standards as published [71].

Bone

Swanston et al, (1984) were reported Lead poisoning has been suggested as being partially responsible for the 'demise' of the British military in the West Indies during the colonial era. A bone sample taken from an individual excavated from a cemetery associated with a Royal Naval Hospital cemetery (c. 1793-1822 C.E.) in Antigua was used for initial testing [26].

IV. RECENT REQUIREMENTS

Archaeological Chemists / Scientists face the versatile type of investigative and conservation challenges. They require advanced, integrated, nondestructive, handheld, X-ray spectrometer which can be investigate the chemical composition of archaeological materials in situ/on site as well as authenticate the antique objects.

V. CONCLUSIONS

XRF is a most fruitful nondestructive technique which analyze the chemical weathering in small quantity of the samples. Liquid samples can also analyze by the XRF which offers new approaches for novel application and prospective for new research in art and archaeology.

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