

METHODOLOGY AND PROCEDURES by Sabrina SAVE

Geochemical analysis applied to archaeology and deployed as a survey method has been practiced in Europe since the 1970s (Sjöberg 1976). A variety of methods have been used, supported by the development of new technologies: phosphate concentration (Crowther 1997; Holliday et Gartner 2007; Parnell *et al.* 2001; Roos et Nolan 2012; Rypkema *et al.* 2007; Sjöberg 1976), ICP-OES (Dirix *et al.* 2013; Middleton et Price 1996; Oonk *et al.* 2009a; Vyncke *et al.* 2011; Wilson *et al.* 2008, 2009), ICP-MS (Cuenca-Garcia 2015; Huisman 1998; Misarti *et al.* 2011), and XRF and pXRF (Booth *et al.* 2017; Ciminale *et al.* 2009; Cook *et al.* 2014; Cuenca-Garcia 2015, 2019; De Langhe K. 2015; Frahm *et al.* 2016; Huisman 1998; Hunt et Speakman 2015; Janovský et Horák 2018; Oonk *et al.* 2009a, 2009b; Tereygeol *et al.* 2010; Vos *et al.* 2018). Of these methods, pXRF (portable X-Ray Fluorescence spectrometry) presents many advantages: portability, rapidity and cost-efficiency. The calibration of the equipment with certified sediment standards allows us to measure semi-quantitatively to quantitatively around 20 chemical elements, and ensure the validity and reproducibility of the results.

1. Note on X-Ray Fluorescence Principles

XRF spectrometry measures the energy level of x-rays emitted by chemical elements when these elements are irradiated by a radiation source, resulting in the excitation of the electrons gravitating around the nucleus of the atoms (Kilbride *et al.* 2006; Piorek 1997). The emitted energy, in the form of x-rays, is characteristic and unique for each chemical element (Kalnicky et Singhvi 2001; Piorek 1997).

Our pXRF spectrometer is equipped with an x-ray generator. The generated x-rays are emitted from the source as photons organised, or focused, into a beam. When these photons meet the atoms of the element, or elements – in the case here sediment samples taken from the site and compressed into uniform pellets which are then placed against the measurement window of instrument - they collide with the electrons gravitating around the nucleus of the atoms. When a photon collides with one of the electrons, the photons transfer part of their energy and eject the electron from its natural orbit, much like when snooker balls collide (cf. illustration 1, step 1). The displacement of the electrons disrupts the electron cloud of the atom, forcing the atom to capture new free electrons to remain stable. This process of reassembling the atom's electron cloud produces energy in the form of fluorescent x-rays. These new x-rays are detected by the pXRF's sensor. Their energy is a type of “digital print” corresponding to the element from which they were emitted. Each element (whether it be magnesium, chromium, lead or any other element) emits fluorescent x-rays with specific energy which allows us to determine the elementary composition of the matter under study. The quantity of fluorescent x-rays detected is proportional to the concentration of the chemical element in the matter, which allows us to determine the proportion of each element, and allows the qualitative and quantitative analysis of the matter (cf. illustration 1, step 2).

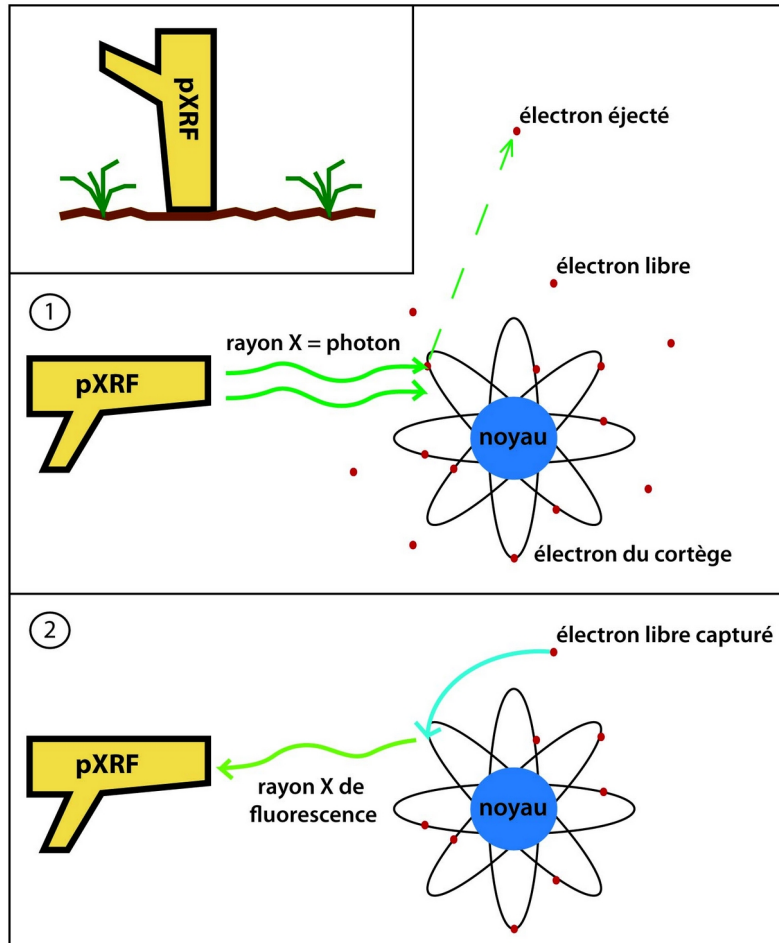


Illustration 1: Simplified scheme of the interaction of the x-rays emitted by the pXRF with matter

2. Equipment

We are equipped with an Innov-X Delta Premium spectrometer, using a silicon drift detector, a 4W x-ray generator with a rhodium target operating between 10 and 40kV with a maximal amperage of 200 μ A. It measures all elements between magnesium (Mg) and uranium (U) (illustration 2) in ppm (parts per million). The spectrometer is equipped with seven different filters designed to improve the detection of specific chemical elements. The instrument adapts its calibration to the atmospheric pressure. The raw data (the ppm of each measured element within a given sample) was processed using third-party software specifically developed for geochemical analysis (IoGAS), with the raw data transformed into contour isobar maps and interrogated statistically (correlation matrix, K-mean cluster analysis).

The spectrometer can be used in the field or in laboratory conditions. The Innov-X spectrometer has different measuring “modes” available, depending on the type of material being analysed and the research questions. For sediments, the “Soil mode” is selected: sample excitation and measurement times for each of the filters (table 1) are “long”, ensuring better precision and accuracy of the results (Johnson *et al.* 1995; Kalnicky et Singhvi 2001; Kilbride *et al.* 2006; USEPA 2007).

For this project, the spectrometer was used in laboratory conditions, with the spectrometer mounted within a dedicated workbench station and the measurements controlled from a laptop computer using Innov-X software. Sediments were sampled in the field, with a small volume of sediment collected into plastic bags; the sediment was then conditioned into specific xrf-compatible cups in the lab (see the next section on sample preparation). The prepared sediment cup is then placed against the measurement window, the workbench station closed and the measurement procedure

started. The Innov-X spectrometer has different measuring “modes” available, depending on the type of material being analysed and the research questions. For this project, the “Soil mode” was used: sample excitation and measurement times for each of the filters (table 1) are “long”, ensuring better precision and accuracy of the results (Johnson *et al.* 1995; Kalnicky et Singhvi 2001; Kilbride *et al.* 2006; USEPA 2007).

Appareil	Cible	Mode	Faisceau	Filtre	Voltage kV	Ampérage μA	Temps de mesure (s)
InnovX Olympus Delta Premium	Rh	Soil	1	3	40	100	60
			2	2	40	100	60
			3	5	15	200	80

Table 1: Technical characteristics and set up of the equipment

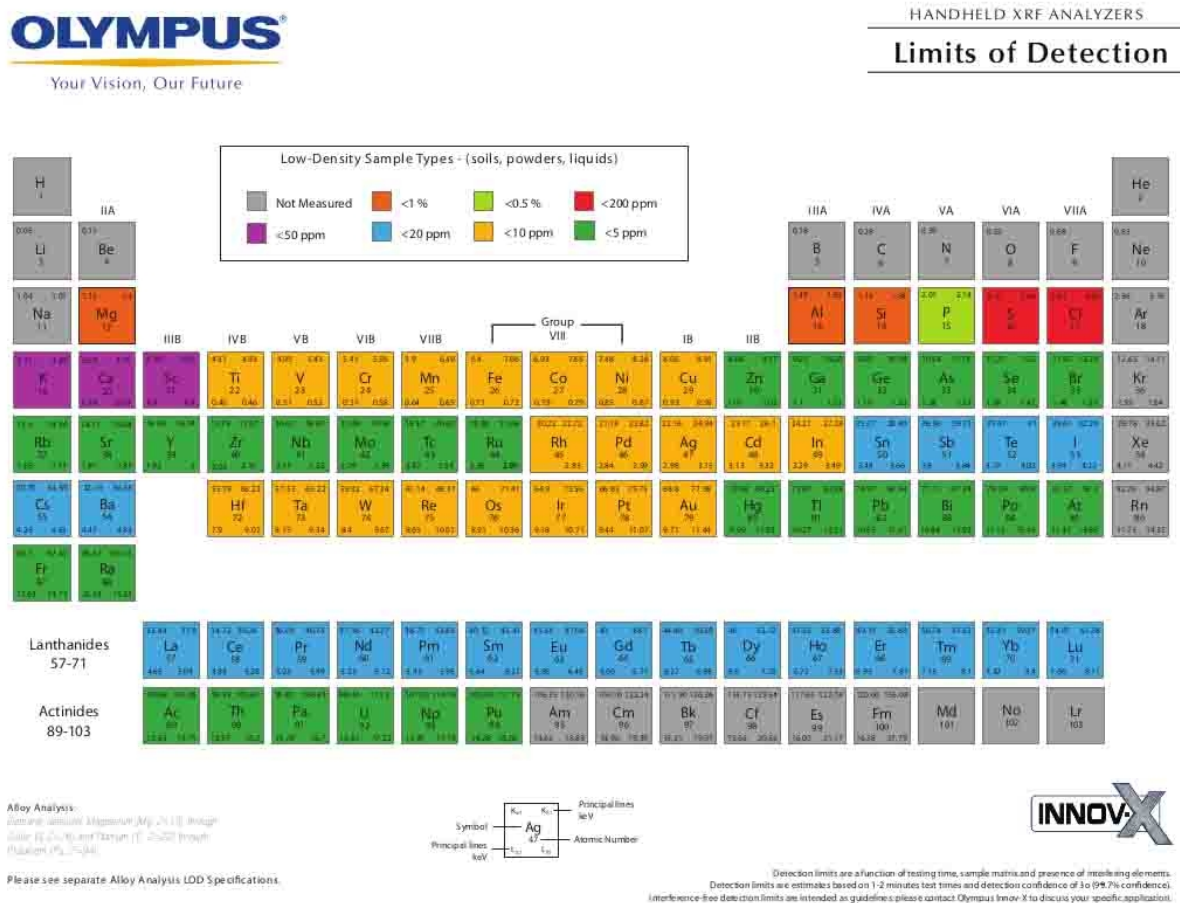


Illustration 2: Mendeliev periodic table figuring the detected chemical elements and their detection limit

3. Sediment preparation and analysis methodology

All the measurements are taken in Soil mode with a total measurement time of 200s. The raw data are exported in a .csv format. All the measurements are expressed in ppm, with the standard deviation for each also recorded (for example: 23500ppm±100 means between 23400ppm and 23600ppm). The raw data is then treated statistically and graphically in IoGAS. While the data produced is quantitative in nature, for this study we are interested in the qualitative analysis of the data as our interest lies in the variation and concentration of chemical elements across a given

archaeological surface rather than the absolute value of each element (absolute values of a single element and combinations of select groups of elements is commonly used during materials sourcing studies). In addition, the local geological composition of the sediments being analysed plays an important role in "colouring" the overall background geochemistry of each site analysed and therefore makes direct quantitative comparisons between the sediments of different sites difficult.

For some chemical elements, the measured concentration can be below the detection limit of the equipment. However, if these elements are also present in the sediment standards used to calibrate the spectrometer, the standard deviation can be used as a proxy for the concentration of the element. While our understanding of why this proxy appears to work is limited, our experience when comparing elements with similar origins (such as calcium and phosphorus), indicates the isobar maps produced by the standard deviation data is reliable.

4. Certified sediment standards

All recent pXRF spectrometers are able to perform a reliable analysis of different archaeological materials.; there remains, however, some variation in precision and accuracy between spectrometers (even between different instruments from the same brand) (Shackley 2011). It is therefore very important to calibrate the equipment regularly by measuring certified standards, with the results of these measurements published along side the data in order to maximise the possibility that the measured data and results are both valid and reproducible.

REFERENCES

Booth A.D., Vandeginste V., Pike D., Abbey R., Clark R.A., Green C.M., Howland N. 2017, "Geochemical insight during archaeological geophysical exploration through in situ X-ray fluorescence spectrometry", *Archaeological Prospection* 24, p. 361-372.

Ciminale M., Gallo D., Pallara M., Laviano R. 2009, "Understanding the origin of magnetic anomalies in Monte San Vincenzo (Southern Italy) archaeological Site: susceptibility measurements, PXRD, XRF and optical analysis", *ArchéoSciences, revue d'archéométrie*, suppl. 33, p. 43-45.

Cook S.R., Clarke A.S., Fulford M.G., Voss J. 2014, "Characterising the use of urban space: a geochemical case study from *Calleva Atrebatum* (Silchester, Hampshire, UK) *Insula IX* during the late first/early second century AD", *Journal of Archaeological Science* 50, p. 108-116.

Crowther J. 1997, "Soil Phosphate Surveys: Critical Approaches to Sampling, Analysis and Interpretation", *Archaeological Prospection* 4, p. 93-102.

Cuenca-García C. 2019, "Soil geochemical methods in archaeo-geophysics: Exploring a combined approach at sites in Scotland", *Archaeological Prospection* 26, p. 57-72.

Cuenca-García C. 2015, "Inorganic Geochemical Methods in Archaeological Prospection", in Sarris A. (dir.), *Best Practices of GeoInformatic Technologies for the Mapping of Archaeolandscapes*, Archaeopress Archaeology, p. 219-229.

De Langhe K. 2015, *Beyond the Beam. Evaluation and Application of Handheld X-ray Fluorescence in Archaeology*, Thèse de doctorat, Universiteit Gent.

Dirix K., Muchez P., Degryse P., Kaptyn E., Music B., Vassileva E., Poblome J. 2013, "Multi-element soil prospection aiding geophysical and archaeological survey on an archaeological site in suburban Salagassos (SW-Turkey)", *Journal of Archaeological Science* 40 (7), p. 2961-2970.

- Frahm E., Monnier G.F., Jelinski N.A., Fleming E.P., Barber B.L., Lambon J.B. 2016, "Chemical soil surveys at the Brenner Site (Dakota county, Minnesota, USA): Measuring phosphorous content of sediment by portable XRF and ICP-OES", *Journal of Archaeological Science* 75, p. 115-138.
- Hayes K. 2013, "Parameters in the use of pXRF for archaeological site prospection: a case study at the Reaume Fort Site, Central Minnesota", *Journal of Archaeological Science* 40 (8), p. 3193-3211.
- Huisman D.J. 1998, *Geochemical Characterization of Subsurface Sediments in the Netherlands*, Thèse de doctorat, Agricultural University, Laboratory of Soil Science and Geology.
- Janovský M. et Horák J. 2018, "Large Scale Geochemical Signatures Enable to Determine Landscape Use in the Deserted Medieval Villages", *Interdisciplinaria Archaeologica Natural Sciences in Archaeology* IX (1), p. 71-80.
- Johnson B., Leethem J. et Linton K. 1995, "Effective XRF field screening of lead in soil. DuPont Environmental Remediation Services, Houston, TX".
<http://info.ngwa.org/gwol/pdf/950161762.PDF>. p. 629-642.
- Kalnicky D.J. et Singhvi R. 2001, "Field portable XRF analysis of environmental samples", *Journal of Hazardous Materials* 83, p. 93-122.
- Kilbride C., Poole J. et Hutchings T.R. 2006, "A comparison of Cu, Pb, As, Cd, Zn, Fe, Ni, and Mn determined by acid extraction/ICP-OES and ex situ field portable X-ray fluorescence analyses", *Environmental Pollution* 143, p. 16-23.
- Knudson K.J. et Frink L. 2010a, "Ethnoarchaeological analysis of Arctic fish processing: chemical characterisation of soils on Nelson Island, Alaska", *Journal of Archaeological Science* 37, p. 769-783.
- Knudson K.J. et Frink L. 2010b, "Soil chemical signatures of a historic sod house: activity area analysis of an arctic semisubterranean structure on Nelson Island, Alaska", *Archaeological and Anthropological Science* 2, p. 265-282.
- Knudson K.J., Frink L., Hoffman B.W., Prize T.D. 2004, "Chemical characterization of Arctic soils: activity areas analysis in contemporary Yup'ik fish camps using ICP-AES", *Journal of Archaeological Science* 31, p. 443-456.
- Lambert J.B., Simpson S.V., Buikstra J.E., Charles D.K. 1984, "Analysis of soil associated with Woodland burials", in Lambert J.B. (ed.), *Archaeological Chemistry III*, American Chemical Society, Washington DC, p. 97-113.
- Linderholm J. et Lundberg E. 1994, "Chemical characterization of various archaeological soil samples using main and traces elements determined by inductively coupled plasma atomic emission spectrometry", *Journal of Archaeological Science* 21, p. 303-314.
- Maschner H., Benson B., Knudson G., Misarti N. 2010, *The Archaeology of Sapsuk River: Occasional papers in Alaskan Field Archaeology n°3*, Bureau of Indian Affairs, Alaska Region, Branch of Regional Archaeology, Anchorage, Alaska.
- Middleton W.D. et Prize T.D. 1996, "Identification of activity areas by multi-element characterization of sediments from modern and archaeological house floors using inductively coupled plasma atomic emission spectroscopy", *Journal of Archaeological Science* 23, p. 673-687.

Misarti N., Finney B.P., Machner H. 2011, "Reconstructing site organization in the eastern Aleutian Islands, Alaska using multi-element chemical analysis of soils", *Journal of Archaeological Science* 38, p. 1441-1455.

Oonk S., Slomp C.P., Huisman D.J., Vriend S.P. 2009a, "Effects of site lithology on geochemical signatures of human occupation in archaeological house plans in the Netherlands", *Journal of Archaeological Science* 36, p. 1215-1228.

Oonk S., Slomp C.P., Huisman D.J., Vriend S.P. 2009b, "Geochemical and mineralogical investigation of domestic archaeological soil features at the Tiel-Passewaaij site, The Netherlands", *Journal of Geochemical Exploration* 101, p. 155-165.

Parnell J.J., Terry R.E., Golden C. 2001, "Using In-Field Phosphate Testing to Rapidly Identify Middens at Piedras Negras, Guatemala", *Geoarchaeology: An International Journal* 16(8), p. 855-873.

Piorek S. 1997, "On-site, in-situ characterization of contaminated soil and liquid hazardous waste with field portable X-ray analyzer - A cost effective approach", in Gottlieb J. (eds), *Field Screening Europe*, p. 329-333, Kluwer Academic Publishers.

Roos C.I., Nolan K.C. 2012, "Phosphates, plowzones, and plazas: a minimally invasive approach to settlement structure of plowed village sites", *Journal of Archaeological Science* 39, p. 23-32.

Rypkema H.A., Lee W.E., Galaty M.L., Haws J. 2007, "Rapid, in-stride soil phosphate measurement in archaeological survey: a new method tested in Loudoun County, Virginia", *Journal of Archaeological Science* 34, p. 1869-1867.

Shackley S. (dir.) 2011, *X-Ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, Springer.

Sjöberg A. 1976. "Phosphate Analysis of Anthropogenic Soils", *Journal of Field Archaeology* 3(4), p. 447-454.

Téreygeol F., Arles A., Foy E., Florsch N., Llubes M. 2010, "Dosages par fluorescence X portable d'ateliers médiévaux de production des métaux non-ferreux: les exemples de Castel-Minier et d'Agneserre (Aulus-les-Bains, 09)", *Archéosciences, revue d'Archéométrie* 34, p. 253-267.

USEPA 2007, *Field portable X-ray fluorescence spectrometry for the determination of elemental concentrations in soil and sediment*, USEPA, Washington, DC.

Vyncke K., Degryse P., Vassilieva E., Waelkens M. 2011, "Identifying domestic functional areas. Chemical analysis of floor sediments at the Classical-Hellenistic settlement at Düzen Tepe (SW Turkey)", *Journal of Archaeological Science* 38, p. 2274-2292.

Wilson C.A., Davidson D.A., Cresser M.S. 2008, "Multi-element soil analysis: an assessment of its potential as an aid to archaeological interpretation", *Journal of Archaeological Science* 35, p. 412-424.

Wilson C.A., Davidson D.A., Cresser M.S. 2009, "An evaluation of the site specificity of soil elemental signatures for identifying and interpreting former functional area", *Journal of Archaeological Science* 36, p. 2327-2334.

Woods W.I. 1984, "Soil chemical investigation in Illinois archaeology: two example studies in archaeological chemistry", in Lambert J.B. (dir.), *Archaeological Chemistry III*, American Chemistry Society, Washington DC, p. 67-78.