GGR 2017 Review: Instrumental neutron activation analysis (INAA) and X-ray fluorescence (XRF)

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**INAA**

Instrumental neutron activation analysis (INAA) is an established technique that, although used in many laboratories, has become less popular in recent years. A major issue facing this technique is access to a suitable neutron source; for geochemical purposes, this source is a nuclear reactor. Among the global 241 research reactors, most are aging (Meier et al., 2017) with more than 70 % being at least 30 years old and more than 50 % being at least 40 years old. Worldwide capacity to undertake INAA will therefore soon be challenged. Citation numbers for the most cited INAA papers published in 2015 and 2016 are relatively low (generally five or six citations, with a maximum of ten citations for the most cited INAA paper). In comparison, the most cited XRF papers for the same years have 30 to 40 citations while the most cited paper has 81 citations. Such low citation numbers for papers using INAA suggests that interest for neutron activation analysis is truly on the decline (Bédard and Linge, 2010). Nonetheless, INAA offers a unique perspective when determining elemental concentrations because it uses an atom's nuclear properties rather than ionic radius and valency. As such, INAA should be maintained within the geoanalytical toolbox.

In geochemistry, INAA is used as a routine analytical technique for trace elements (see Akinlua et al., 2016; Mizera et al., 2017, Santos et al., 2015, among others for examples of its use) and for some niche analyses including selenium (Duran et al., 2016), iodine and bromine (Sekimoto and Ebihara, 2016) (radiochemical NAA in this cited case), graphite (Janczyszyn and Kwiecińska, 2016) and the investigation of difficult or complex matrices such as chromitite (Akhter et al., 2016). An interesting development of INAA is the capacity for non-destructive analysis of very small samples, offering an advantage over the ubiquitous yet destructive method of laser ablation. Sekimoto et al. (2016) developed a protocol for microgram-scale samples (having less than a few milligrams) and tested this approach a meteoritic grain and a magnetic spherule), with calibration using either Allende meteorite powder (USMN 3529, Smithsonian Institution) and JB-1 reference material (GSJ). They developed a novel sample holder; a quartz disk 9 mm in diameter × 1 mm in thickness having a small pit to receive the sample. Another quartz disk then covered the sample and the assemblage was wrapped in aluminium foil. Samples were then irradiated for 45 h using a thermal neutron flux of 1.6 x $10^{13}$ n $cm^{-2}$ $s^{-1}$ and a fast neutron flux of 7.8 x $10^{12}$ n $cm^{-2}$ $s^{-1}$. Claimed detection limits (all in picograms for a 0.05 μg meteorite) were, for example, 20 for Na, 0.4 for Sc, 2800 for Fe, 0.3 for Ir and 0.02 for Au. Shirai et al. (2015) modified an INAA protocol to analyze and classify iron meteorites based on chemical composition. Canyon Diablo and Cape York iron meteorite samples, having respective masses of 0.116 and 0.189 g, were sawn into 1 × 1 × 4 mm plates. They were irradiated twice: once for 10 s (neutron flux: thermal 4.6 x $10^{12}$ n $cm^{-2}$ $s^{-1}$ and fast 9.6 x $10^{11}$ n $cm^{-2}$ $s^{-1}$) and a second time for 4 h (neutron flux: thermal 5.6 x $10^{12}$ n $cm^{-2}$ $s^{-1}$ and fast 1.2 x $10^{12}$ n $cm^{-2}$ $s^{-1}$). Gamma rays were measured a few times after irradiation to ensure an optimal decay for each

element. A correction for the self-absorption of gamma rays was also applied. Analytical results agreed with those of the published literature, with this protocol providing a rapid means for classifying iron meteorites.

**XRF**

X-ray fluorescence (XRF) has been used in geochemistry for many decades and remains a very popular technique. The development of portable XRF (hand-held or larger) and micro-XRF has fostered a profusion of new applications for XRF, as reflected by the higher number of published papers and citations relative to established techniques such as INAA. In geochemistry, the most active areas of XRF publication are micro-XRF followed by portable XRF. The use and applications for XRF have been reviewed in numerous books and journal papers, including the extensive annual reviews in the Journal of Analytical Atomic Spectrometry (West et al. 2015, 2016, 2017). A recent book (Croudace and Rothwell, 2015) discussed the use of micro-XRF for analyzing sediment cores, covering the history, its applications and the technical issues related to its use. Flude et al. (2017) reviewed benchtop micro-XRF applications for assessing geological samples while Sun and Ding (2015) reviewed confocal X-ray technology with capillary X-ray optics, a technology gaining interest among geochemists.

The use and application of portable XRF has increased markedly in the recent years. Carbonates have recently been the focus of portable XRF studies (e.g. Cohen et al. 2017, Quye-Sawyer et al., 2015 and de Winter et al. 2017). These three cited articles each argue that calibration (or a correction) is a critical step to ensure the quality of results obtained from portable XRF. Although fossils are important markers for many studies, identifying the fossil-bearing units can

often be difficult. Cohen et al. (2017) therefore used portable XRF to characterize carbonate units and identify those units hosting vertebrate fossils. They also used portable XRF to differentiate Cambrian and Cenozoic limestones. Their instruments were calibrated using a suite of carbonate reference materials. In their study, some initial tests were performed on cleaned outcrop surfaces of interest using dilute HCl cleaning followed by a water rinse. However, Cohen et al. (2017) found that, except for a small increase in Ti and Zr, cleaning did not alter estimates of trace element concentrations and subsequently the surfaces analyzed were not cleaned beforehand. Using factor analysis, Ca, P, Sr, U and Zn were determined to be the discriminant analytes for detection of fossiliferous materials. Quye-Sawyer et al. (2015) undertook an exhaustive study to develop a portable XRF-based methodology for determining concentrations of *in-situ* carbonates as applied to both field geochemistry and limestone building conservation. Different parameters were tested including measurement time and sample surface preparation (thin film covered, sieved powder, polished surfaces, rough hammered and weathered surfaces). Multiple carbonate reference materials (38) were used in their study. As expected, longer measurement times and flatter surfaces improved results. However, with an exception for Mg, the quality of the measured surface did not significantly influence the results. However, in contrast to the findings of Cohen et al. (2017), surface carbonate weathering did affect results. The effect of weathering was alleviated by measuring on freshly hammered surfaces. Finally, de Winter et al. (2017) proposed measurement strategies for defining the minimum requirements for reliable (micro- and portable-) XRF measurements of carbonates based on the agreement of measured value with certified value ~~total accuracy~~ using a manually pressed powder. For Ca, Fe, Sr and Mn, different integration times and measurement strategies (single spot, multiple spot and map) were tested. de Winter et al. (2017) proposed using an

asymptotic curve where integration time (or another parameter) is plotted against the relative standard deviation. Along this curve, a suitable threshold can be selected. Such a strategy accounts for the matrix effects and is more likely to represent the field conditions.

Macro-XRF is a technique that could be of interest for geoanalysts. It was recently used to chemically image a large (57 × 58 cm) stained glass window (Van der Snickt et al., 2016). In this process, X-rays from a Rh tube illuminated the surface and were coupled to two 50 mm$^2$ silicon drifted detectors (SDD) placed at 65° to the surface being imaged. A scanning speed of 4 mm·s$^{-1}$ resulted in a total acquisition time for the above-mentioned stained glass of about 25 h. The macro-XRF images of the stained glass successfully represented spatial distribution of some elements (Ag, Co, Cu, Rb, Sr). Although not quantitative, this approach could be useful for chemically imaging large petrographic slabs. Romano et al. (2016) took a different approach for imaging elements in biological and geological samples without scanning, using micro-XRF technology. The technique can be used with nonflat samples which could be an important advantage. A straight polycapillary served as an X-ray imaging optic placed in front of a full field-X-ray camera (CCD detector of 1024 × 1024 pixels). The detector relied on single photon counting for which the authors wrote a signal processing algorithm. Prior to analysis of a mineral sample, the apparatus was calibrated using pure target materials. In their tabletop version, Romano et al. (2016) used a 3 kW X-ray Mo anode tube that could be operated at 50 kV and 60 mA to illuminate an area of 5 × 5 cm$^2$. The distance between sample and source was 100 mm having an incident angle between 20° and 45° for different setups. The full field-X-ray camera was used to study lapis lazuli (a mixture of lazurite (($Na$, $Ca$)$_8$($AlSiO_4$)$_6$($SO_4$, $S$, $Cl$)$_2$) with minor

calcite, pyroxene ± pyrite). Based on the obtained chemical image, they proposed a Siberian origin for the gem.

Assessing the test mass portion for samples expected to contain nuggets of precious metals can be difficult. A common procedure is to assume that all precious metals are held in nuggets and that none are found in sulphides and oxides (or less likely in silicates). This assumption likely overestimates the abundance of nuggets as some precious metals are often held in sulphides. Bédard et al. (2016) used micro-XRF to quantify nuggets in precious metal bearing reference materials to better estimate the minimal test mass portion for pulverized materials. Their proposed method provided a realistic measure of nuggets' post-sample preparation (where some nuggets may have been pulverized). Such a method could be useful for determining the minimum test mass portion for samples where nuggets are present or expected and the use of a large test mass portion is not possible.

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