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# The Joy of Using Nuclear Analytical Tools in Environmental Studies

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## Nuclear Analytical Tools

Analytical scientists commonly face a wide range of questions when using instrumental analytical tools, such as their applicability, analytical figures of merit, measurement uncertainty issues, availability of reference materials, understanding of samples, and last but not least – whether an analysis is cost-effective. In so far as all these factors are not either at conflict or troublesome in any way, then a (geo) chemist is lucky: they are free to choose what should be measured without worrying how to measure it. If complex natural materials are to be investigated, a new set of tools and techniques is becoming available. Hereby, geoanalysis has evolved rapidly in the past decades while shifting towards other disciplines and changing research foci. As comparability of analytical measurements made on geological materials has been widely recognised, current trends are multi-analytical approaches estimating the uncertainties of these measurements.

This review refers to the application of proton-induced X-ray emission (PIXE) as a complementary method to (geo) chemical environmental problems, particularly trace element sorption to soils and sediments which is the most important factor as regards their transport and fate. Since these materials are complex and diverse, their characterisation is usually quite challenging. They are inherently heterogenous, mainly composed of silicate phases whose major constituents are light elements, while their trace element pool (i.e. heavier elements) is low. However, the role of trace elements in the environment is disproportionately high, being a target of countless eco-friendly studies. In addition to numerous questions related to a sampling plan, there has to be chosen the proper technique to determine the analytes of primary interest. Essentially, there is no technique which could solve all multi-element analytical problems commonly encountered when working with geological/environmental samples. Traditionally, total elemental analyses of soils and sediments have been routinely performed either by AAS/ICP techniques following the destructive acid digestion of samples, or by the non-destructive XRF/PIXE techniques which require only pressed powder pellets. Although the wet ICP methodology ensures the very low detection limits for most metals and high precision, the incomplete digestion of silicates (unless HF is used) as well as instability of certain elements (e.g. Se) in acid medium and their concomitant loss are noteworthy problems which can render data unsuitable for comparisons. In fact, in environmental pollution studies, a choice of the digestion procedure should depend principally on a given type of soil, and then on a range of elements in terms of data quality. Furthermore, the wet approach is necessary in the case of increasingly popular sequential extraction which is a tool for obtaining information on potential mobility of trace elements in the environment. As regards the dry XRF/PIXE methods, they had been related to compromise of detection limits or precision, but that has been substantially enhanced recently, and they yield absolute concentrations the interpretation of which is straightforward.

During the last few decades, analytical scientists from various branches (archaeology, art, atmosphere, biology, Earth and environmental sciences, etc.) have come to view PIXE as a viable analogue of XRF as well as an alternative to the established ICP method. In the PIXE experiment, energetic positive ion beam impinges on the sample surface and excites its atoms which then emit characteristic X-rays. By and large, XRF is more sensitive for heavier elements while PIXE is more sensitive for light elements. From geological point of view, portable XRF systems are surpassingly convenient for field survey investigations. On the other hand, the ion beam facilities (i.e. PIXE) are very complex and expensive, and therefore not in widespread use. The strengths of both techniques mainly derive from a/their nondestructive mode, and b/the simultaneous and multi-element nature of the analyses. Although the former means that there is a minimal sample manipulation, a special attention must be paid to the homogenisation step as a grain size distribution can influence the results, while the latter factor contributes to rapidity of analyses. In view of the PIXE experimental parameters, shortfalls are associated with a/spectral intreferences, and b/the depth of penetration of the proton beam. Spectral overlap usually occurs for the K series lines of the elements with Z around 12 (i.e. common major elements in most petrogenic minerals) with the L and M series lines of heavier elements (i.e. those present in trace levels in rocks and minerals), depending on the atomic number; e.g. K lines of Mg overlap with L lines of As, K lines of S overlap with M lines of Pb, and K lines of Ti overlap with L lines of Ba. By means of two detectors, one optimised for the low Z elements and the other one for elements heavier than Ca, it is possible to set off the contribution of heavier trace elements; notwithstanding, spectral interferences will be still present. As for the probed depth, sample matrix corrections are necessary due to proton stopping and X-ray attenuation in the sample; an alternative could be PIXE analysis on post-digestion residues so as to envisage the elemental elution factors of a particular soil/sediment matrix.

This review closes with an optimistic tone since the recent advances in nuclear analytics certainly entail an encouragement for their use in environmental (geo) chemical researches. They have been allowing us to solve problems by considering about what to explore, freeing us from the operational how.