

## TWENTY FIVE YEARS OF NEUTRON ACTIVATION ANALYSIS: A PERSONAL PERSPECTIVE ON UTILIZATION OF THE TECHNIQUES

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### Abstract

Since the late 1970's there have been enormous changes in the methods, techniques and applications of neutron activation analysis. Having been a research scientist at the National Research Council of Canada and the McMaster Nuclear Reactor, as well as a professor for ten years at the University of Illinois and 15 years at the University of Texas, I have a unique perspective on the research performed by my many MS, PhD and even undergraduate students. Below is a personal perspective on the utilization of the neutron activation analysis.

### 1. INTRODUCTION

As of 2010, [1] there are 236 research reactors worldwide and another 6 under construction. Neutron activation analysis (NAA) still remains the most used technique in these facilities. However, the analytical demands for low detection limits for environmental, geological and biological specimens have made other methods such as Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and ICP-Mass Spectrometry (ICP-MS), X-Ray Fluorescence (XRF) and Particle Induced X-Ray Emission (PIXE) very attractive. Furthermore, many of the analytical systems are totally automated to produce results almost instantaneous. However, this paper will focus on the development of facilities and instrumentation in NAA that my group has been able to vastly improve the detection limits and ultimately the precision of many typically difficult elements to determine by routine NAA.

### 2. THERMAL NEUTRON ACTIVATION ANALYSIS

The use of thermal neutrons is the mainstay of NAA for all the facilities. Although thermal NAA can be used to determine many elements, the presence of aluminum, chlorine, sodium and manganese can inhibit the determination of several short-lived radionuclides due to increased backgrounds from the various reactions:  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ ,  $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$ ,  $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$  and  $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ . For medium-lived NAA the presence of  $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$  and  $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$  can also greatly add to the Compton continuum to the point that elements such as arsenic need to be determined by radiochemistry. Lastly, the reactions of  $^{45}\text{Sc}(n,\gamma)^{46}\text{Sc}$  and  $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$  can also add greatly to the Compton continuum limiting the detection of other elements such as silicon, nickel, iodine, several rare earths and even zinc. Of course not in all different types of samples do these reactions decrease the sensitivity but these usually appear in most samples particularly in geological, soil and biological specimens. While NAA may suffice for determining a series of 25-30 elements, laboratories that have not advanced the below mentioned methodologies, are hampered to expand the research and customer base. In many cases not able to achieve the required sensitivities and accuracies in a very competitive analytical service market. Below is a series of methodologies my group has employed over

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the past quarter century to expand the array of trace elements that can be determined using non-conventional thermal NAA.

### 3. EPITHERMAL NEUTRON ACTIVATION ANALYSIS

Since the late 1960's epithermal NAA (ENAA) has been shown to greatly enhance the detection of many elements. NAA This is due that certain elements have strong resonance integrals and that coupled with the poor resonance integrals for all these reactions:  $^{27}\text{Al}(n,\gamma)^{28}\text{Al}$ ,  $^{37}\text{Cl}(n,\gamma)^{38}\text{Cl}$ ,  $^{23}\text{Na}(n,\gamma)^{24}\text{Na}$  and  $^{55}\text{Mn}(n,\gamma)^{56}\text{Mn}$ ,  $^{45}\text{Sc}(n,\gamma)^{46}\text{Sc}$  and  $^{59}\text{Co}(n,\gamma)^{60}\text{Co}$  can significantly enhance the determination of these radionuclides as seen in Table 1. The reaction  $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$  does have a good resonance integral so using epithermal neutrons is not advantageous. Steinnes [2-4] was one of the original pioneers for epithermal NAA. My own work began with the determination of nickel in lung tissue [5], indium and arsenic in Arctic air filters [6] aluminum in biological samples [7]. A perusal of the literature reveals a large amount of work that employed ENAA in the 1970's, 1980's and 1990's, but there appears to be a many fewer published papers employing this technique is used.

Table 1. Resonance Integrals of Reactions Favorable to Epithermal NAA

| Nuclear Reaction                                   | $I_{\gamma}/\sigma_{\gamma}^0$ |
|--|--------------------------------|
| $^{59}\text{Co}(n,\gamma)^{60\text{m}}\text{Co}$   | 1.91                           |
| $^{186}\text{W}(n,\gamma)^{187}\text{W}$           | 12.80                          |
| $^{75}\text{As}(n,\gamma)^{76}\text{As}$           | 13.56                          |
| $^{109}\text{Ag}(n,\gamma)^{110}\text{Ag}$         | 15.38                          |
| $^{115}\text{In}(n,\gamma)^{116\text{m}}\text{In}$ | 16.33                          |
| $^{81}\text{Br}(n,\gamma)^{82}\text{Br}$           | 18.52                          |
| $^{127}\text{I}(n,\gamma)^{128}\text{I}$           | 23.71                          |
| $^{121}\text{Sb}(n,\gamma)^{122}\text{Sb}$         | 33.90                          |
| $^{68}\text{Zn}(n,\gamma)^{69\text{m}}\text{Zn}$   | 43.06                          |
| $^{124}\text{Sn}(n,\gamma)^{125\text{m}}\text{Sn}$ | 61.54                          |
| $^{29}\text{Si}(n,p)^{29}\text{Al}$                | -----                          |

### 4. COMPTON SUPPRESSION NEUTRON ACTIVATION ANALYSIS

Although Compton suppression (CS) was used in many nuclear physics experiments it began to be used in NAA in the late 1980's, and then in only relatively very few laboratories. In the last 10 years many more laboratories have used CSNAA techniques which have greatly benefited the determination of radionuclides in thermal and epithermal neutron activation analysis. Compton suppression method is a technique ideally suited for determination of key elements which cannot be accomplished by the use of thermal neutrons alone due to interference problems emanating from Compton plateau and background elevation. My laboratory was the first to pioneer the full potential usage of CSNAA while at the University of Illinois [8-10]. A comparison of four spectra for short-lived NAA for a geological sample is seen below: A: thermal and normal counting; B: thermal and Compton suppressed counting; C: epithermal and normal counting and D; epithermal and Compton suppressed counting. The advantages of such a system are seen in the spectra below on Figure 1.

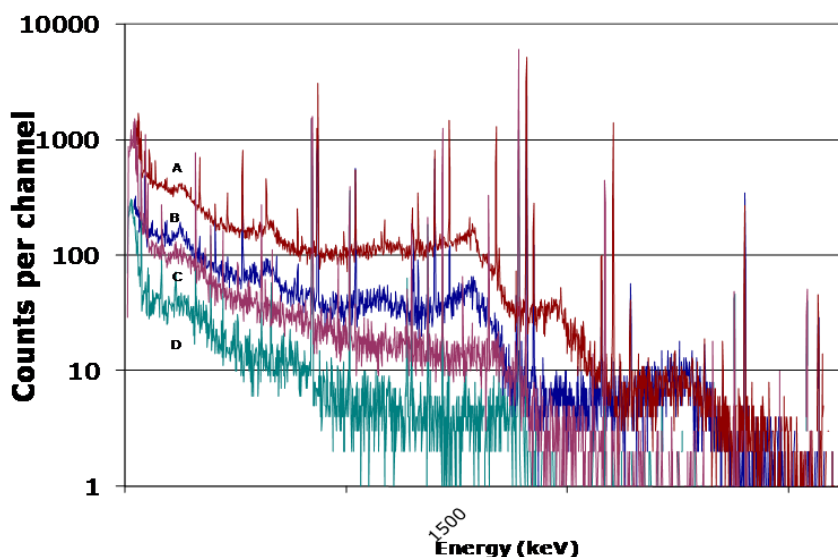


Figure 1. Comparison of Thermal and Epithermal NAA with and without Compton Suppression for Short-Lived NAA of a Coal Sample. A: Thermal Normal; B; Epithermal Normal, C; Thermal Compton Suppression and D: Epithermal Compton Suppression

For the past 20 years my group has judiciously used the combination of ENAA and CSNAA for a large variety of environmental projects [11-15]

#### 5. CYCLIC ACTIVATION ANALYSIS (CNA)

CNA has also been used since the 1970's. Three of the earlier papers [16-18] established the technique. It can be effectively used for several key elements such as selenium, silver and fluorine in environmental samples. My own work first appeared in 1984 [19] on the determination of selenium in marine samples. More recently we have published a paper on the determination of silver in geological ores [20]. A perusal of the literature reveals that most cyclic activation analysis is not suitable for most geological samples, unless there are very high concentrations of a particular element in samples like ores.

#### 6. PHOTON ATTENUATION

Photon attenuation remains a problem that is constantly overlooked particularly when trying to correctly determine low energy gamma rays ordinary matrices. The problem is severely compounded when there samples have high-Z materials. My group has published two papers on the potential pitfalls that needed to be addressed [21-22].

#### 7. NEUTRON FLUENCE MONITORING FOR SHORT-LIVED NAA

Another area which needs attention is the monitoring of neutron fluence that a sample receives for short-lived NAA. While some reactors such as the 20 KW Canadian SLOWPOKE and the 30 KW Chinese Miniature Neutron Source reactor (MNSR) have very stable neutron fluxes that vary only 1-2 %, other reactors such as TRIGA have neutron fluences that vary  $\pm 5-7\%$ .

#### 8. NAA OF RARE-EARTH ELEMENTS

Rare-earth analysis by NAA still remains a very popular technique. However, even after decades of its use, there are still areas for improvement. These include the use epithermal

neutrons and a careful evaluation of fission and spectral interferences. It still remains surprising how many paper using NAA fro rare-earth analysis do not take into account any of these interferences.

My group has published several papers on these matters [23-25]. As well Compton suppression NAA can significantly enhance rare-earth analysis. Below in Figure 2 is depicted a long-lived NAA spectrum of soil sample irradiated and counted in two separate modes. As can be seen Tb-160 can be much determined better using epithermal NAA and Compton suppression in the presence of the strong 889 keV gamma-ray belonging to Sc-46.

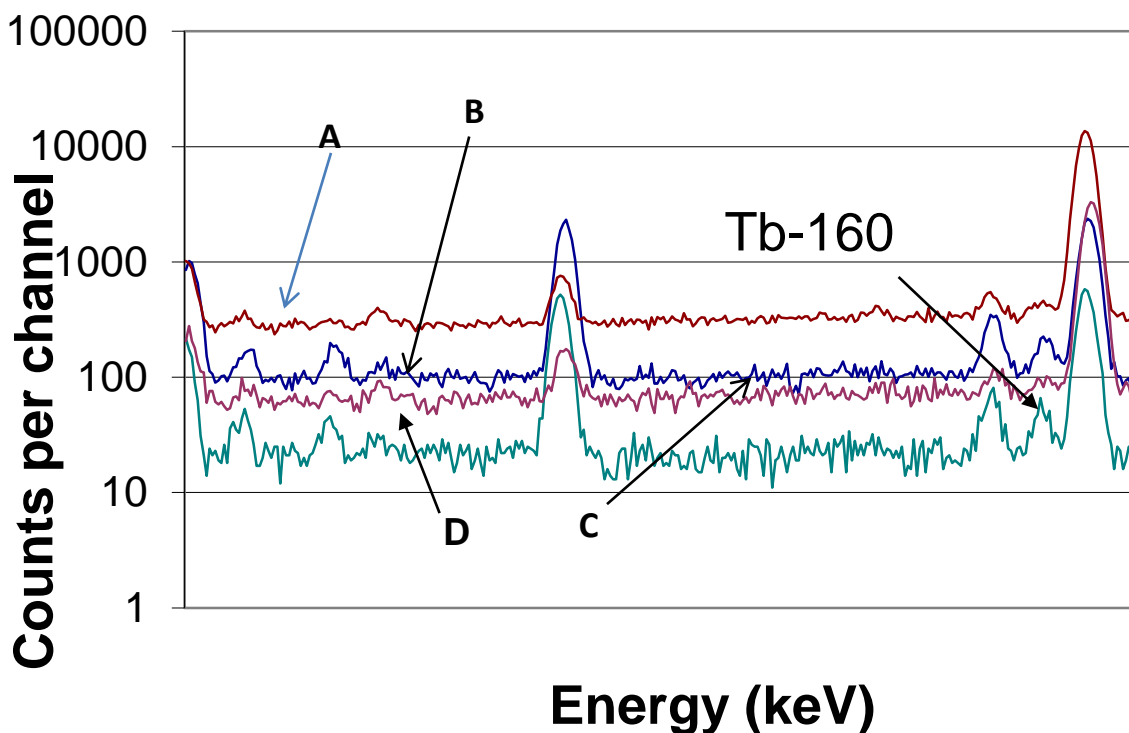


Figure 2. Comparison of Thermal and Epithermal NAA with and without Compton Suppression for Long-Lived NAA of a Soil Sample. A: Thermal Normal; B: Epithermal Normal, C: Thermal Compton Suppression and D: Epithermal Compton Suppression.

## 9. NEW DIRECTIONS

In the recent past my group has been involved in the nuclear forensics and nuclear fuel cycle experiments. We have judiciously used NAA to produce fission products to test our low level Compton suppression system [26] and to produce surrogates for nuclear fuel cycle separation experiments conducted at national laboratories.

## 10. EDUCATION

Perhaps the one are that is neglected is the pedagogical aspects of NAA. It has been 40 years that the last comprehensive NAA book has been written by Soete, Gijbels and Hoste [27]. While different aspects of NAA are covered in other nuclear and radiochemistry courses, there appears to be no course completely dedicated to NAA. Given the enormous advances that NAA has undergone, it behooves the community to write another book.

## 11. CONCLUSIONS

Considering the costs of reactor resources, it is very advantageous to install both epithermal and Compton suppression systems to augment the array of elements that can be

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better determined in a variety of samples. While a cyclic system may only be beneficial for a few elements, the automation and control of irradiation, decay and counting times for short-lived NAA would greatly enhance quality assurance procedures.

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