DEVELOPMENT OF COMMERCIAL NEUTRON ACTIVATION ANALYSIS SERVICE WITH A SMALL REACTOR

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1. INTRODUCTION

École Polytechnique, the engineering faculty of the University of Montréal, has operated a SLOWPOKE reactor since 1976. In the early 1980s, in a context of constantly decreasing educational funds and government research grants, a commercial neutron activation analysis (NAA) service appeared to be the only solution for pursuing operation of the reactor facility. The new self-sustainability requirements motivated the reactor staff to develop and to implement a unique commercial service. Key to the success were the first customers, École Polytechnique engineering graduates and University of Montréal research users who went to work in industry and remembered the chemical analysis possibilities they had seen at the reactor facility. The commercial service evolved naturally as satisfied customers promoted the service to their colleagues in the same or related industries, and the increasing revenues matched fairly well the increasing needs.

As can be seen in Figure 1, commercial revenues increased rapidly from 1980 to 1992 as the analysis capabilities improved and then leveled off when revenues were sufficient and a solid customer base was in place. From 1991 to 2006, the commercial NAA service generated revenues to pay 80% of all the reactor laboratory's expenses, including salaries and reactor maintenance. After 2007, when government infrastructure grants were terminated, these commercial revenues paid 100% of all expenses. The dips in 2009 and 2010 are due to the economic recession combined with a transition stage due to staff renewal. As the recession continued, a substantial effort was required in 2010 and 2011 to bring revenues back up to the required level in 2011. This consisted mainly of improved communication with potential customers and a better laboratory management approach implemented by a young staff.

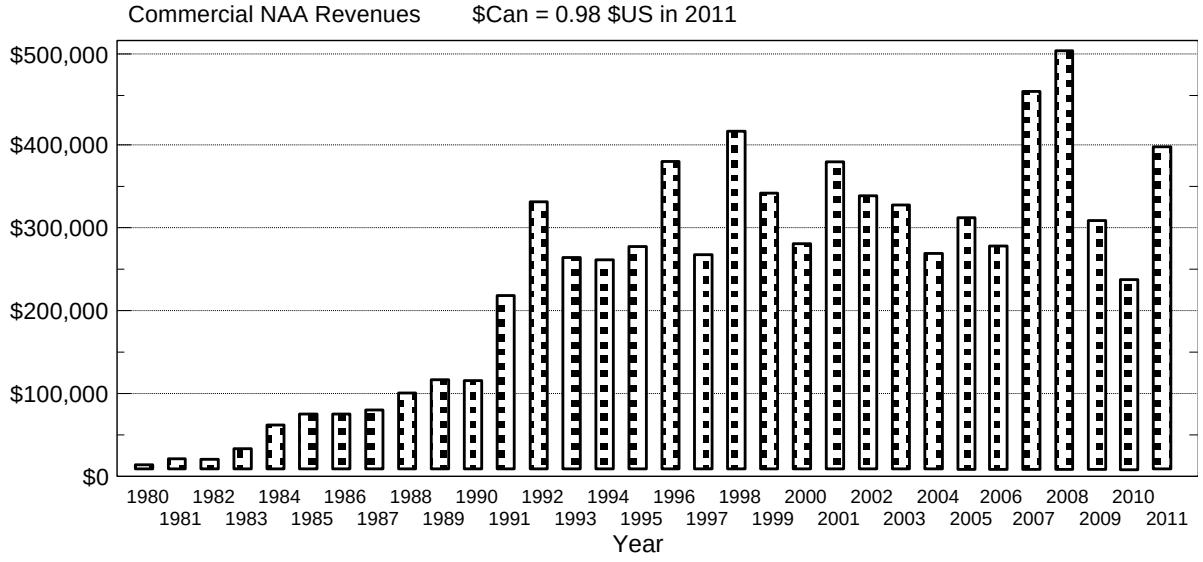

Fig. 1. Annual commercial revenues since 1980.

Since the SLOWPOKE reactor is simple to operate, in the last 30 years the staff has consisted of only two reactor operators who are also NAA analysts and a reactor technician. Reactor maintenance is done each Monday morning. Each day the reactor is started up in automatic mode at constant neutron flux, and the analysts spend the rest of the day analyzing samples.

Besides its low maintenance and ease of operation, the other features of the SLOWPOKE reactor that make it ideal for a commercial NAA service are its reproducible neutron flux, up to 10^{12} $cm^{-2}s^{-1}$, and its extreme reliability, which facilitates the fast turn-around time required by industrial users. About 6000 samples are analyzed annually, 90% for one element or a few elements and 10% for the complete suite of elements. In addition to the commercial NAA service, around 800 irradiations are performed annually for university researchers mostly for radioactive tracer studies. The reactor is also used for teaching in various fields such as nuclear engineering, engineering physics and applied chemistry.

The revenues shown in Figure 1 can be categorized as follows: 7% university researchers, 9% government research institutions, and 84% private industry, mainly quality control or product development samples. 41% of the samples analyzed came from Canada, 33% of these from the home province of Quebec; 58% from the USA; and 1% from Europe. In 2012, the price for industrial users starts as low as US $80 per sample and reaches US $400 for a 40 element full scan of the sample. Before 2007, when the reactor facility was partly funded from an infrastructure grant from the Natural Sciences and Engineering Research Council of Canada, university researchers benefited from greatly reduced prices; they must now adapt to the new economic reality and pay a more realistic service price.

Over the years other analysis techniques have evolved, making NAA obsolete for some applications such as for trace element content in water and in certain biological materials. However, NAA has no real competition for many applications requiring accurate average bulk chemical analysis in solid materials with no sample preparation. The total market for NAA in Canada and the USA is estimated at US $20M annually, including only routine analyses by current NAA techniques and for which NAA is better than any other method. About 20 reactor facilities in Canada and the USA currently offer a commercial service with total annual revenues of about US $5M. Thus it can be estimated that three-quarters of the potential users have not yet learned of the existence of NAA and are analyzing their samples by more laborious and less accurate techniques.

Past experience proved that a successful commercial NAA service must be developed to meet customer needs. Constant communication with all lab clients or potential customers helps to determine their exact needs and how these can best be met. The foundation of a sustainable commercial activity is the motivation to understand and meet the requirements of the customers. Industrial clients require the following, in decreasing order of importance:

— Fast turn-around time;
— Reliability;
— High accuracy;
— High sensitivity; and
— Range of concentrations from low to high.

Each new project requires some time for adjusting the NAA method. Once the method is ready, analysis can begin as soon as the samples are received. The time limitation is usually the half lives of the elements of interest and the interfering elements.

Reliability and accuracy depend mainly on the expertise and vigilance of the NAA analyst, but also on the reliability of the irradiation and counting equipment and the analysis software. The analyst must be aware of all possible interferences and the various matrix effects, including sample inhomogeneity, neutron self-shielding, gamma ray absorption, spectrometer dead time, etc. He must constantly strive to avoid mistakes such as in labeling samples, weighing and recording measurement parameters. He should be aware of the importance to do so. Mistakes have been reduced by the use of written procedures, and all analyses are fully documented and verified. A quality assurance programme based on a "culture of quality" and common sense proved its superiority to a classical quality assurance programme with unmotivated staff. We have found that providing a commercial service can be quite fulfilling for the analysts, sometimes even more than research work, because the customers often show their satisfaction for the excellent results received.

The relatively low neutron flux of the SLOWPOKE reactor, ten times lower than some larger research reactors, has not been found a limitation to the sensitivity that can be achieved in most cases. Optimized counting techniques combined with powerful spectrum analysis software have led to low detection limits, as they depend mainly on the ability to resolve the peak of the gamma ray of interest from the Compton background.

The challenge in NAA is to be able to analyze quickly and accurately any material for any element out of the 60 elements commonly measured by NAA. The classical relative method implies a very time consuming standard preparation step for every element requested in each batch of samples. Fortunately, the extreme stability of the SLOWPOKE reactor and our gamma ray spectrometers have led to a unique NAA approach, our improved relative method. Each element and counting geometry is standardized once, the resulting sensitivity constants are stored in libraries, and each is used for years without modification. Besides quality control standards, no standards and no flux monitors are irradiated with a sample or a batch of samples analyzed.

Differences in sample size and composition between the standards and the unknowns are corrected for using accurate models of the activation and detection processes. With the k_0 standardization method, it is not necessary to irradiate a standard of every element. The parameters of the models and of the k_0 method are now sufficiently accurate to determine the concentrations of all elements in any material using any irradiation channel and any detector configuration.

To expedite the analysis of large batches of samples for elements with short lived nuclides, an automated pneumatic irradiation system is used. It can handle up to 50 samples at a time, sending them to the reactor and then to the detector. For counting batches of samples overnight, four of the five germanium detectors are equipped with mechanical sample changers.

École Polytechnique's NAA software, EPAA, was developed to quickly and reliably calculate the elemental concentrations. The software reads the spectrum and calculates the areas of only the peaks needed for the elements requested. The least squares peak fits can be verified and easily improved interactively, and the output, concentrations and uncertainties are imported into a spreadsheet for preparation of the analysis report.

A major limitation to NAA was the inability to predict the amount of neutron self-shielding, especially for epithermal neutrons, in materials containing high concentrations of neutron absorbing elements. This severely limited the materials that could be analyzed. A simple and accurate method for correcting neutron self-shielding was recently developed, extending our

commercial NAA service to many new materials with high concentrations of neutron absorbing elements.

2. TYPES OF MATERIALS ANALYZED

The types of materials that have generated the greatest revenues are listed first.

2.1. Plastics

Petrochemical industries use our service for quality control of products and processes, including the detection of catalyst residues, fire retardants and impurities, and for product development. The in-house laboratories of these industries have access to ICP-MS and XRF, but they prefer NAA for its reliability and sensitivity. Since quality control requires fast turn-around, in most cases the elements requested are determined using short lived nuclides, and the analysis report is sent within one day of receipt of the samples.

For example, in two cases of plastic pipes and polyethylene insulation on high voltage cables, the materials are analyzed for impurities before starting the main production process or during the production adjustment stage by studying failed products.

2.2. Treated wood

Construction lumber for indoor use is often treated with the chemical 3-Iodo-2-propynyl butylcarbamate (IPBC), which contains iodine to prevent the growth of mold. NAA is used for quality control of these wood products or to develop new treatment procedures by measuring penetration profiles.

Wood for outdoor construction also needs to be treated to prevent decay. The old commonly used preservative, chromated-copper-arsenate, has been replaced in Canada by new chemicals based on Cu but not Cr and As. For wood preservative environmental leaching assessments or quality control in applications with new treatment procedures, NAA remains the most accurate technique.

2.3. Paper

Wrapping papers for products that will be stored in a humid environment, like soap, are treated with IPBC to prevent mold; the amount of preservative treatment must be verified for quality control purposes. NAA is also used to determine the thickness of metallic coatings on papers and the thickness of colored ink on printed papers if the ink contains a detectable element such as copper.

2.4. Textiles

Textiles or artificial leather are analyzed for elements present in fire retardants and in chemicals added to prevent mold or toxic elements such as arsenic and mercury. High quality cloth for surgical bandages may contain Ag to promote healing. The Ag content is verified by NAA for quality control.

2.5. Air pollution samples

All petrol used in automobiles in Canada used to contain the anti-knock additive methylcyclopentadienyl manganese tricarbonyl (MMT), an organic compound containing manganese. To prove that emissions did not lead to unacceptable atmospheric Mn levels,

many air particulate samples were collected on filters and analyzed for this element. Other particulate samples are now analyzed for various heavy metals in pollution studies.

2.6. Rocks and minerals

NAA has been replaced by other analysis methods in most cases but is still used for specific types of rocks and minerals, and for rare earth elements and platinum group elements NAA is still a method of choice. Mineral refineries use NAA to verify their products.

2.7. Archaeological samples

A large database has been built from the chemical signatures of Amerindian ceramic artifacts, 30 elements per sample. These are used in provenance studies to determine trade patterns. Similar studies have been carried out with lithic and metallic copper artifacts.

2.8. Metals

The relatively low neutron flux of the SLOWPOKE reactor is not sufficient for measuring ultra-trace impurities in semiconductor silicon. However, it has proven useful for the analysis of silicon in cases where impurity levels are higher and for measuring the thickness of metallic coatings. High purity tellurium has been analyzed for traces of Se using the very short lived nuclide ^{77m}Se.

2.9. New materials

In fuel cells, the life of the platinum catalyst can be prolonged if the rate of reactions producing impurities can be reduced. NAA is used to verify the composition of product materials in research on improving the catalysts and in developing new less expensive catalysts not based on Pt.

2.10. Biological tissues

NAA is not the best method available for the analysis of blood and most other biological tissues. It is, however, recognized as a good method for the determination of the selenium status in humans through the analysis of toenails. Over the years a large number of toenail samples were analyzed for Se content in case control cancer studies.

2.12. Pharmaceuticals, food supplements, food

For quality control, pharmaceutical products are assessed for undesired impurities. Food supplement tablets are analyzed to verify the amounts of essential elements like Mg, Ca, Fe and Zn. The properties of maple syrup can be altered by the illegal addition of a chemical substance containing sodium, which is easily detected by NAA.

3. CONCLUSIONS

It has been shown that with sufficient motivation the staff of a SLOWPOKE type reactor facility can develop a commercial NAA service generating enough revenues to pay the salaries of all those involved as well as reactor maintenance costs. The NAA service should be fast and continuously available; industry often requires a turn-around time of one day. At the École Polytechnique NAA Laboratory, years of work have led to the successful development of a hybrid NAA method combining the k_0 method and the improved relative method. It offers large savings in time as well as improved flexibility and accuracy.