INTERNATIONAL ATOMIC ENERGY AGENCY

Technical Meeting
on
Commercial Applications of Nuclear Analytical Techniques

MEETING REPORT

Vienna, Austria
23–26 November 2004

FOREWORD

Over the last 20 years, the International Atomic Energy Agency (IAEA), through its science and technology promotion and technical cooperation mechanisms, has helped to establish nuclear analytical laboratories in several institutions and universities of its Member States. The IAEA has continued supporting these laboratories by providing equipment and training in the use of various nuclear analytical techniques that include alpha, beta and gamma ray spectrometry, radiotracer methodology, neutron activation analysis and X ray fluorescence analysis.

At the IAEA General Conference in September 2003, the Scientific Forum, triggered by declining resources in research and development, addressed, *inter alia*, an appraisal towards the capabilities of nuclear techniques in products and services to the society; their impact was also assessed. More recently, the Standing Advisory Group on Nuclear Applications (SAGNA), in its analysis of the concept of self-reliance and sustainability, recognized that initiatives towards greater self-reliance may need to address and consider such aspects as market surveys, marketing plans, business plans, and cost of delivery services. The analytical applications of nuclear techniques form a discrete segment of the general services of nuclear institutions. This sector has a great potential but is challenged by a strong competition from non-nuclear techniques.

This report summarizes the findings of the Technical Meeting on the Commercial Applications of Nuclear Analytical Techniques held in Vienna on 23–26 November 2004, where an assessment was initiated of the world capacity and market potentials for neutron activation analysis and nuclear spectroscopy, including an estimation of economic revenues. Industry and governmental agencies were identified as stakeholders for these laboratories. Examples are given of potential benefits of these techniques to the stakeholders.

The IAEA wishes to thank all the meeting participants for their valuable contributions. Mr. P. Bode drafted the executive summary of this report. The responsible IAEA officer was Mr. Matthias Rossbach of the Division of Physical and Chemical Sciences.

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EXECUTIVE SUMMARY

1. INTRODUCTION

Georg von Hevesy (1885–1966) received the Nobel price in Chemistry in 1943 for his pioneering work on the radiotracer methodology. His work, to which also belong the first experiments in neutron activation analysis, marks the birth of nuclear analytical techniques. The availability of nuclear research reactors as powerful sources of neutrons have further stimulated the growth and versatile application of these techniques, that now include alpha, beta and gamma spectrometry; radiotracer technique; neutron activation analysis and (total reflection) energy-dispersive X ray fluorescence analysis. In principle, nuclear analytical techniques are based on the properties of the nucleus itself. However, no sharp line can be drawn between nuclear and non-nuclear techniques. In mass spectrometry the signal is determined from mass differences of the nucleus. Other techniques are based upon a combination of nuclear and electronic properties, like Mössbauer spectroscopy. Particle induced X ray emission spectrometry (PIXE) is often incorporated, as an ion beam technique, in the domain of the nuclear physicist, and other hyphenation is found in radionuclide induced X ray fluorescence spectrometry. Therefore both nuclear and isotope techniques are here included in the term "nuclear analytical techniques". The techniques have found applications, selected on basis of their analytical characteristics, in research and assessments in many areas dealing with industrial development, trade, health, safety and consumer protection, food and nutrition, and environmental protection. Economical, ecological, medical and legal decisions are often based on the results of nuclear analytical laboratories.

However, nuclear analytical laboratories are typically affiliated with scientific research centers such as universities or national institutions. The worldwide trend of declining resources in research and development and the oscillating (public) debates on the benefits of nuclear research reactor facilities are a continuous threat to many nuclear institutions. University affiliated nuclear institutions face additional problems like the relatively high overhead costs of the nuclear research reactor, and the tendency of universities allocating budget to more contemporary sciences like molecular biology and nanotechnology so as to be more attractive to students.

Many research reactors and their associated facilities can only remain operational and kept properly maintained if an additional budget is realized, e.g. by providing analytical services or making the facilities available to provide measurements on request by outsiders. Ideally, such activities should be sustainable, but even the existence of customers may already lead to consider the center of national or even regional relevance. It all contributes to demonstrate the relevance and viability of an expensive facility like a nuclear reactor center to many branches of natural sciences [2].

Developing 'commercial' service activities in a research center confronts the scientists with several challenges of organizational, administrative and technical nature. Business plans, market surveys and marketing strategies have to be developed as well as cost analysis. Many nuclear institutions are already using their nuclear analytical techniques for commercial applications by providing services like routine measurements and analysis to industry, governmental bodies and third parties. The revenues generated from these services are directly measurable and may therefore be a decisive factor for decision makers on the continuity of the facility. However, these revenues represent only a fraction of the total benefits for beneficiaries and end-users of the measurements.

This Technical Document addresses the potentials for commercial applications of two such nuclear analytical techniques, *viz.* neutron activation analysis and nuclear spectroscopy (measurement of alpha, beta and gamma ray emitting radionuclides). First estimates are given of the worldwide capacity of these laboratories, suggestions and examples are given for potential markets and the typical organizational and technical constraints are discussed.

Two case studies of commercial neutron activation analysis laboratories at a small and a medium-size reactor are given in the 'individual contributions' section of this document. Other nuclear analytical techniques such as X ray Fluorescence Spectrometry, Particle Induced X ray Emission Spectrometry or Ion Beam Analysis Spectrometry can only be assessed after a comprehensive collection of background information has been completed along a similar mechanism as for the techniques mentioned in the preceeding paragraph.

2. CAPACITY AND IMPACT OF NUCLEAR ANALYTICAL TECHNIQUES

2.1. Estimate of the world capacity and revenues

Neutron activation analysis (NAA) is one of the techniques that can be operated with nuclear research reactors and other neutron sources. The mission of NAA laboratories at university based research reactors is usually to perform innovative research, education of undergraduate and graduate students, and training of highly qualified personnel. At national institute based research reactors the NAA laboratory typically carries-out innovative and basic research in view of national programs

In addition, there are NAA laboratories at universities, research establishments or industry without having the research reactor on-site. Being less affected by the high overhead costs of the reactor infrastructure, these laboratories may experience a smaller driving force for providing analytical services. However, they still may consider taking advantage of the characteristics of NAA for providing services.

Neutron activation analysis is further applied directly in industry, e.g. for on-line monitoring and process control of manufactured products (e.g. coal, cement) and for e.g. well-logging in mineral exploration. An emerging application of NAA is found in airport security via baggage screening devices for explosives. The neutrons for these applications are provided by isotopic neutron sources or neutron generators. However, there is insufficient information on the worldwide scope of such applications to take them fully into account in this overview. Some indication of the market share can be derived from the number of instruments sold annually.

2.1.1. Neutron activation analysis

A rough estimate of the number of NAA facilities worldwide is given in Table I. An estimate of the potential world revenues of commercial NAA services is based on the following facts (via the IAEA research reactor database) and assumptions:

- 274 Research reactors are operational world wide (2004)
- 71 Research reactor have claimed using NAA

A total of 130–160 NAA laboratories have been estimated taking into account also the laboratories not directly affiliated to a nuclear reactor:

- On average 3 counting facilities per laboratory are assumed
- On average 10–20 samples per day may be processed; on basis of 200 working days per year results in 2,000 – 4,000 samples per detector per year.
- Consequently, the maximum capacity per NAA lab: 6,000–12,000 samples/year.

Assuming an average price per analysis of US $ 100, the potential maximum worldwide revenues for NAA laboratories could amount to 80–200 Million US $/year.

In practice, laboratories may run at only ~10 % of their maximum analytical capacity. Assuming that marketing and acquisition would be effective with little effort, a quick growth towards 20% capacity seems to be realistic for many laboratories. Hence, this would result in practical world revenues of 16–40 Million US$/year by nuclear analytical services.

TABLE I. ESTIMATE OF NUMBER OF NAA LABORATORIES WORLDWIDE

Region	No. of NAA laboratories
Africa Egypt, Ghana, Libya, Tunisia, Morocco, Nigeria, Zaire, South Africa, Algeria	10
Americas Argentina (2), Brazil (3), Chile, Peru, Jamaica, Mexico, Canada (6), USA (20)	30–40
Asia Syria, Israel, Iran (2), Kazakhstan, Uzbekistan, Pakistan, India (10), Bangladesh, Thailand (2), Vietnam, Indonesia (4), South Korea (2), China (15), Japan (10), Australia	50–60
Europe UK, Netherlands (3), Belgium (2), France (2), Portugal, Italy (3), Greece, Sweden, Norway, Germany (5), Austria, Poland (2), Czech Republic, Hungary (2), Slovenia, Serbia and Montenegro, Romania, Turkey (2), Russia (10)	40–50
World	130–160

2.1.2. Nuclear spectroscopy

Measurement of natural and man-made alpha, beta and gamma radiation emitting radionuclides is an activity present in most of the countries in the world. Since the work with often low or natural level radioactivity does not set radiological demands to the laboratory, which clarifies why many of these nuclear spectroscopy laboratories are found outside reactor based institutions; sometimes at universities. As an example, many countries in Europe established radioactivity monitoring stations for air, surface water and vegetation at several locations after the 1986 Chernobyl incidence. The prime mission of many of these laboratories lies with measurements for enforcement of legislation and for routine monitoring.

In addition, the measurement of natural and man-made radionuclides, especially gamma ray emitters, may be an additional niche for neutron activation analysis laboratories; equally so, the measurement of natural and man-made alpha and beta emitting radionuclides may be an interesting niche for (university) laboratories operating these instruments for radiotracer studies. Many hospitals are using radiotracers in nuclear medicine studies and assays have to be made using, e.g., liquid scintillation counting or gamma ray spectrometry. Although the measurements may include measurement of total alpha and total beta radioactivity, all of these laboratories will further be denoted as ‘nuclear spectroscopy laboratories”.

The world analytical capacity of nuclear spectroscopy laboratories and potential revenues of their services has been estimated on the basis of the assumptions below and given in Table II:

- On the average, two laboratories for governmental measurements per country, ten hospital facilities per country and 200 countries worldwide.

- Routine monitoring for government, industry (e.g. chemical industry, fertilizer industry, food processing), Uranium mining, nuclear power plants, fuel processing, waste management facilities, research reactors.
- Three detection systems per laboratory.
- Monitoring of air, (ground, surface) water, food and soil.
- Monitoring of imported and exported products, including foodstuff.

The estimated number of laboratories (4,000 worldwide) is of similar size as the total number of customers of IAEA reference materials that include materials characterized for the radionuclide content.

TABLE II. CURRENT ECONOMICAL REVENUES OF NUCLEAR SPECTROSCOPY LABORATORIES

	No. of worldwide laboratories c.q. facilities	No. of measurements/year and facility	Total existing no. of measurements/year
Government, legislation hospitals,	400 2000	200 200	80,000 400,000
Import/export monitoring	50	1000	50,000
Industry	500	200	100,000
Uranium mining	50	50	2,500
Fuel production	10	100	1,000
Nuclear power plants	500	400	200,000
Waste management facilities	50	100	50,000
Research reactors	250	100	20,000
Fuel reprocessing	20	100	2,000
Total estimation	~ 4,000		~1,000,000

At an average cost of 50 US$/measurements, this represents potential worldwide revenues for nuclear spectroscopy laboratories of approximately 50 Million US$

2.2. Potentials and markets

Industry and governmental agencies are the stakeholders for nuclear analytical laboratories. Interaction can be mutually and highly beneficial in many ways including human capacity building, further research collaboration, possible employment opportunities, instrument sharing and consulting. Interaction can be by:

- Development of new methods with potential commercial applications
- Projects funded by granting agencies with no expectation of commercial applications at the time of development
- Projects funded by industry for direct commercial applications
- Projects funded by government agencies which led to research grants and/or commercial contracts
- Direct commercial application of the nuclear analytical technique without further development
- Projects funded by industry
- Projects funded by government for regulatory purposes and health care

The markets for neutron activation analysis and nuclear spectroscopy are elaborated on in the following paragraphs, together with some examples of successful commercial applications.

2.2.1. Neutron activation analysis

NAA is marketed on basis of those analytical characteristics that favorably differentiates the technique from others and that are extensively described in e.g. [4]. Niches exist for

- Determination of the total bulk elemental composition of materials difficult to dissolve completely or in which elements may be lost during dissolution.
- Precious samples that must be analysed non-destructively
- Studies involving samples for which other methods of analysis have difficulties in the calibration step due to chemical matrix effects. This applies particularly to studies in which the matrix composition varies considerably in an unpredictable way, or for which no matrix-matching calibrants exist.
- Samples in which the trace element levels are so low that contamination or losses may occur easily during the sample dissolution or digestion step.
- Analyses requiring a high degree of accuracy, but even more reliability, to ensure full comparability of data obtained over a long period of time.
- Samples with a high degree of inhomogeneity, requiring the processing of a relatively large analytical portion to ensure representativeness.
- Samples in which the element concentration between samples may vary over several orders of magnitude; here the linearity of NAA is of importance.

There is a clear demand for nuclear analytical services in various industries. Industrial customers have requirements which must be met not only for technical contents but also for all other logistics such as delivery on time, and proper non-disclosure agreements. For a successful commercial opportunity the infrastructures must be built to have business like interaction between the service provider and the industry. Industrial customers require priority, confidentiality, and on-time delivery. Service providers must show long term commitment so that industrial customer can rely and plan future manufacturing.

In this regard an operational quality system (and formal accreditation) is of particular advantage. Service laboratories, in many cases, have to demonstrate to their customers that they are working according to internationally accepted standards, such as ISO/IEC 17025 (1999). In recent years a lot of progress was made to assist nuclear analytical laboratories in their attempt to comply with these requirements [5, 6].

Examples of industrial opportunities are:

- Analysis of trace oxygen in Steel, and petroleum processing, which direct measurement of oxygen is only provided by (14MeV) NAA.
- Determination of chlorine in steel and in nuclear materials
- Hydrogen analysis in the Ti metal aerospace industry by Prompt Gamma NAA
- Hydrogen determination in energy storage devices
- Halogens and metals in the polymer and rubber industry can be uniquely addressed by NAA. Dow Chemicals has installed a research reactor for their own use at their Midland manufacturing facility in Michigan; Dutch State Mines (DSM) has its own on site NAA laboratory for similar types of assays.
- Industries producing ceramics, graphite, industrial diamond and other highly refractory or insoluble materials like AlN, Si_3N_4, W.
- Impurities in emerging nano materials, e.g. carbon nano tubes
- Bulk analysis of Si-wafers and SiC, quartz, graphite liner or silicon nitride. The need for such analysis in the semiconductor industry is a daily phenomenon and currently not being met adequately.

- Determination of ^{129}I in environmental samples
- Dual energy gamma ray metering for multiphase flow in petroleum industry
- Precious metals in minerals, catalysts and its wastes

Similarly, NAA can be interesting for governmental agencies for regulatory purposes and health care:

- As in wine
- As in hair for forensics
- Br in neonatal blood
- Trace elements in air filters
- U in ashed tissues
- Organochlorines in fisheries samples
- Iodine in biological materials (food)

The IAEA published in 2004 a Technical Report [7] demonstrating how analytical problems could only be solved with nuclear analytical techniques. Laboratories may further choose from the vast variety of matrixes to which it has been demonstrated that NAA can be the method of choice:

1. Archaeology — amber, bone, ceramics, coins, glasses, jewelry, metal artifacts and sculptures, mortars, paintings, pigments, pottery, raw materials, soils and clays, stone artifacts and sculptures.
2. Biomedicine, animal and human tissues activatible tracers, bile, blood and blood components, bone, brain cell components and other tissues, breast tissue, cancerous tissues, colon, dialysis fluids, drugs and medicines, eye, faeces, fetus, gallstones, hair, implant corrosion, kidney and kidney stones, liver, lung, medical plants and herbs, milk, mineral availability, muscle, nails, placenta, snake venom, rat tissues (normal and diseased), teeth, dental enamel and dental fillings, thyroid, urine and urinary stones.
3. Environmental science and related fields — aerosols, atmospheric particulates (size fractionated), dust, fossil fuels and their ashes, flue gas, animals, birds, insects, fish, aquatic and marine biota, seaweed, algae, lichens, mosses, plants, trees (leaves, needles, tree bark), household and municipal waste, rain and horizontal precipitations (fog, icing, hoarfrost), soils, sediments and their leachates, sewage sludges, tobacco and tobacco smoke, surface and ground waters, volcanic gases.
4. Forensics — bomb debris, bullet lead, explosives detection, glass fragments, paint, hair, gunshot residue swabs, shotgun pellets, drugs, narcotics
5. Airport security – neutron imaging of luggage and transport containers.
6. Geology and geochemistry — asbestos, bore hole samples, bulk coals and coal products, coal and oil shale components, crude oils, kerosene, petroleum, cosmo-chemical samples, cosmic dust, coral, diamonds, exploration and biogeochemistry, meteorites, ocean nodules, rocks, sediments, soils, glacial till, ores and separated minerals.
7. Industrial products — alloys, catalysts, ceramics and refractory materials, coatings, electronic materials, fertilizers, fissile material detection and other safeguard materials, graphite, high purity and high tech materials, integrated circuit packing materials, on line, flow analysis, oil products and solvents, pharmaceutical products, plastics, process control applications, semiconductors, pure silicon and silicon processing, steel, textile dyes, thin metal layers on various substrates, wood.
8. Nutrition — composite diets, foods, food colors, grains, honey, seeds, spices, vegetables, milk and milk formulae, yeast.
9. Quality assurance of analysis and reference materials — certification of element contents and homogeneity testing of mainly biological and environmental reference materials of chemical composition, method intercomparisons.

2.2.2. Nuclear spectroscopy

A market for commercial nuclear spectroscopy laboratories exists in the determination of natural and man-made radioactivity (like ^{137}Cs and ^{90}Sr) in e.g.,

- Food industry: control of water and food, especially in areas with high natural abundance of Th and U
- Building industry: control of building materials (Ra, K)
- Chemical industry: control of manufacturing and recycling
- Mineral and oil exploration: control of natural radioactivity such as ^{210}Po, ^{210}Pb
- Customs: measurement of imported products
- Trade: control of import and certification of export
- Health: Rn monitoring in houses and offices
- Environmental monitoring: radioecology

Except for the assessments as such, the laboratory may also provide, as added value to the measurement results, services in the interpretation of the results and the verification towards legal and health regulations.

In addition to that a unique field of nuclear spectroscopy application is the measurement of radionuclides for nuclear forensics, e.g. illicit trafficking of nuclear materials. Here α, β, γ spectrometry is indispensable and adds particularly to the security of the society rather than to individual welfare.

2.3. Potential benefits to stakeholders of NAA and nuclear spectroscopy

The benefits to the stakeholders (industry and governmental agencies) of the nuclear analytical laboratories (NAA + nuclear spectroscopy) are both end-user oriented and supplier oriented.

2.3.1. Direct spin offs

Examples of end-user oriented benefits on basis of the interpretation and further processing of the analytical measurement results are, for some selected sectors:

- Industry: Optimization of manufacturing and recycling processes; insight in waste streams.
- Nuclear industry: Assays in all aspects of the nuclear fuel cycle, from Uranium exploration toward waste depositories. Contribution to control of illegal trafficking.
- Transportation: Assurance of airline business by passenger confidence, related to airport security checks
- Mining: Determination of new resources, environmental and radiological impact of e.g. waste tailings.
- Trade: International acceptance of products.
- Agriculture: Quality of soil; insight in essential elements for crop growth; quality of fertilizers.
- Health care: Insight in nutritional quality of food, reduction of under-nourishment, toxic effects of inorganic substances, trace element metabolism in man and animal.
- Forensics: Investigation of fraud, insurance cases, crime investigation.
- Environmental: Insight in sources of inorganic air pollution, quality of soil and water resources, quality of domestic, hospital and industrial waste streams, background/reference values of unpolluted areas.
- Metrology and standards: Development of reference materials for quality control and traceability.
- Archaeology and art history: Origin and authenticity of historical objects, including art; identification of fraud and illegal trafficking

2.3.2. Indirect spin-offs

- Consumer protection by assurance on the quality of products and by baggage screening devices in airports.
- Employment, within the nuclear laboratories, for at least 15,000 scientists worldwide. Related to this are jobs created by the primary sector, amongst which suppliers, see below. An estimate for the situation is the USA may be indicative for this impact; a number of approximately 4–5 million jobs related to the entire radiation technology sector has been reported [8].
- Human capacity preservation and building for current and future nuclear measurements and use of radioactivity.

Governmental agencies may further consider some of the applications of nuclear analytical techniques to inform scientific journalists so as to improve the public perception of:

- The beneficial use of radioactivity and of nuclear sciences at large.
- The governments' abilities to control the monitoring of natural and man-made radioactivity.

2.3.3. Supplier oriented benefits

The supplier oriented benefits deal with the world turnover of instrumentation for the nuclear analytical laboratories and facilities. This industry also implies employment for at least positions. An indication of instrument turnover in a company providing equipment for nuclear analytical laboratories can be obtained from Table III.

TABLE III. ESTIMATION OF WORLDWIDE ANNUAL SALES OF SELECTED NUCLEAR ANALYTICAL INSTRUMENTS FOR ONE SELECTED COMPANY

Applications	No. of instruments/year	Typical price (1000 US$)	Annual turnover (Million US $)
NAA	20	50	1
Gauges:			
Moisture	1000	10	
Thickness	500		
Density	500		
Level	500		
Total			25
PGNAA – process monitoring:			
Security	500	100–2,000	
Mining	100	40	
Well logging	100	75	
Total			61.5
XRF			
Handheld	1000	15	15
Other Dating			
Mineral tracing	40	80	
Total	50	100	8.2
Overall total			~120

3. GUIDANCE TOWARDS COMMERCIAL ACTIVITIES

3.1. NAA services

The NAA laboratories can be also classified as:

- NAA laboratories, fully dedicated to their prime mission
- NAA laboratories that, besides working within their prime mission, also use their excess irradiation and counting capacity for providing analytical services
- NAA laboratories that operate mainly for providing analytical services

The first category has to merge the new service activities with the scientific work which implies both changes in the conduct and attitude to work. Both technique and laboratory must satisfy several criteria before it is fit for contacting outsiders for potential use, such as:

- Demonstrated method validation
- Some degree of automation
- Customer directed attitude
- Management with a focus on quality (quality system implementation)
- Priority setting by management
- A business plan, including market survey, marketing strategy and cost analysis

In general, the laboratory will start with providing a package of determinations for which they have ample proficiency and satisfying degree of accuracy.

The second category may, being already successful, face priority setting problems. “Making money” may become so tempting and demanding on the availability of the facilities and human resources that time and flexibility for new scientific research becomes scarce. The commercial success may have a negative effect to the scientific quality and output of the laboratory. An advantage of using the facilities for both research and services is that the laboratory has some opportunity for providing custom tailored solutions to specific requests.

The third category laboratories may be found in nuclear institutions as well as in analytical services providing companies. These laboratories offer standard analysis packages and often have less time and opportunities for custom tailored analysis protocols.

3.2. Nuclear spectroscopy services

Nuclear spectroscopy laboratories can be classified in the same way as neutron activation analysis laboratories, viz. (i) laboratories working in line with their prime mission (e.g. academic research or legal monitoring), (ii) laboratories with both prime mission activities and openings for commercial services to third parties and (iii) laboratories solely operating on a commercial basis. Hence, the same challenges and problems apply as for neutron activation analysis laboratories

3.2.1. Constraints and obstacles for nuclear analytical services

Laboratories providing nuclear analytical services will see themselves faced with a set of constraints and obstacles that may be new to them.

- Priority setting. Management has to decide the priorities if facilities and other resources (including manpower) are shared for both scientific research and analytical services.

- Market position and competition.

As an example, four situations can be identified:

a) There is only one nuclear analytical laboratory (for NAA or nuclear spectroscopy) and NAA is the only available technique within the organization of country. There is essentially no competition. The nuclear laboratory has a monopoly position, and care should even be taken that this will not render in arrogance.

b) There are other similar nuclear analytical laboratories within the country. Opportunities should be sought on basis of uniqueness of facilities, expertise, customer relations, turnaround time and costs. Alternatively, strategic alliances with the other laboratories could be an opportunity to strengthen the market position versus institutions with competing techniques.

c) Other techniques and laboratories available for element determinations, within the organization and/or in the country. These techniques may have competing characteristics to solve the analytical problem. Strengths and weaknesses of both the nuclear analytical technique and the laboratory, and the competitors have to be evaluated (see below).

d) The analytical request fit best within the scope of the alternative techniques; NAA laboratories should then not even consider applying for related tenders. Examples are, e.g. the determination of trace elements in water, which best could be done by AAS, ICP or even TR-XRF. However, if such a request is part of a larger analytical evaluation in which also materials are analysed more appropriate to NAA, the laboratory could still consider to apply for the tender and subsequently sub-contract the water analysis.

Nuclear spectroscopy (as here defined: the measurement of alpha, beta and gamma radiation emitting radionuclides) has no real competition by other analytical techniques. The situation is different, of course for neutron activation analysis. Although there are many situations in which NAA has – on paper – better analytical characteristics than other methods of elemental analysis, it is important to remain realistic in evaluating the role and possibilities of NAA. Therefore, the traditionally mentioned advantages of NAA are revisited in view of the alternatives available.

(1) Sensitivity and applicability for minor and trace elements in a wide range of matrices

(2) Virtual absence of an analytical blank.

(3) Relative freedom from matrix and interference effects; not always a need for renewed method validation.

(4) The possibility to perform bulk analysis without dissolution; NAA is the only existing technique for non-destructive bulk element analysis

(5) High specificity based on the individual characteristics of the induced radionuclides

(6) The capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices

(7) An inherent potential for accuracy compared to other analytical techniques. Since the theoretical basis of NAA is well understood, a complete uncertainty budget can be made

(8) The totally independent nature of the method as a nuclear based property in contrast to the electronic nature of most other analytical techniques

(9) The isotopic basis of the method offers a choice of analytically independent routes for element determination. Since different nuclides of one element can be determined either simultaneously or via different protocols, NAA has a self verifying character.

(10) In cases where the induced radionuclides of trace elements are masked by matrix activity, radiochemical separation provides interference-free detection limits close to the theoretical ones. In the radiochemical mode of NAA (RNAA), the technique has other advantageous features. However, the laborious activities related to RNAA have to be compared to the simplicity of e.g. ICP, offering often comparable or even better detection limits.

(11) Trace and ultra-trace (radio) chemistry can be performed under controlled conditions by using inactive carrier additions. Alternatively, stable isotope tracer techniques can be followed if ICP(MS) is available.

(12) The chemical yield of the separation can be obtained by simply using carrier budgeting or the radiotracer method.

At least seven favourable areas for neutron activation analysis can be derived from such a comparison:

- Determination of the total bulk elemental composition of materials difficult to dissolve completely or in which elements may get lost during dissolution.
- Precious samples that may not be consumed by dissolution or damaged otherwise.
- Studies involving samples for which other methods of analysis have difficulties in the calibration step due to chemical matrix effects or absence of suitable calibrants.
- Samples in which the trace element levels are so low that contamination or losses may occur easily during the sample dissolution or digestion step.
- Analyses requiring a very high degree of accuracy (known trueness and uncertainty).
- Samples with a high degree of inhomogeneity, requiring the processing of a relatively large analytical portion to ensure representativeness.
- Samples in which the element concentration between samples may vary over several orders of magnitude.

3.2.2. Organization and infrastructure. Offering analytical services imply that the customer's request has to be fulfilled as agreed upon, and planning is one of the crucial factors. Scientists are, generally, not used to comply with strict planning schedules. Reactor schedules must be reliable and available well in advance. Equipment should be fit for the purpose when necessary. Procurement obstacles for e.g. spare parts and consumables (vials, reference materials, liquid scintillation cocktails) should be solved.

3.2.3. Automatization. There are no stand alone, automatic operating neutron activation spectrometry apparatus, which is a big difference with the status of other analytical techniques. Automation of gamma ray spectrometers is a necessity to realize counting capacity during 24 hours per day, 7 days per week and to reduce part of the labor costs. In addition, software needs to be adapted for automatic acquisition.

3.2.4. Quality system. A management system with the emphasis on quality at all levels of the organization and conduct of the analysis is indispensable to reduce the running costs of the laboratory, to assure the (analytical) quality and to be (and to remain) competitive. Formal accreditation for compliance with the ISO/IEC 17025:1999 international standard may be demanded by the customers so as to ensure international acceptance of the results. A quality system can be implemented in any nuclear analytical laboratory, irrespective of its size and number of staff, and accreditation can be obtained within 2–3 years as has been demonstrated via several IAEA technical cooperation projects [6]. The running costs of an accredited quality system can be incorporated in the costs of the analysis.

3.3. Costs and tariffs.

Cost analysis procedures may exist in governmental organizations and once the costs have been identified, tariffs have to be derived. This requires also evaluation of potential (inter)national competitors and an estimate of the economical benefits of the services. An organization may decide to offer tariffs lower than the actual costs, e.g., at market penetration or if it is more important to have end-users than to be fully sustainable since the number of end-users may contribute to the visibility of the organization. As such, for instance, the reactor costs may be dropped (which is often done, and justified as 'the reactor and the neutrons are available anyhow').

It should also be noted that some customers may interpret ‘cheap’ (= low priced) tariffs also as non-professional. Alternatively, a laboratory may charge a higher price than the costs if competition allows.

Cost analysis clarifies which components need to be improved to reduce the cost. If the reactor costs are important, short irradiations and measurements at a higher counting efficiency (like with large volume and well type Ge detectors) may be considered. Also the use of short half-life radionuclides (and short irradiations) may contribute to reduce the reactor costs. If the depreciation of equipment is the dominant factor, shorter counting times – and thus higher throughput, and automation – via sample changers, are remedies to reduce the costs. Even larger sample masses and higher induced activities may be considered. Shorter counting times may result in a poorer precision but often there is no need to count until peak statistics are better than, e.g., 1 %; 10 % or perhaps even 25 % counting statistics may already satisfy the customer. It implies a dramatic reduction of counting time and increase of throughput.

Labor costs may be a determining component, especially in countries with a developed economy. Labor costs related to preparation of standards and spectrum analysis/interpretation may be reduced if the number of elements to be reported is reduced. Many customers are interested in a few elements rather than in full multi-element scans. The simple relative method for calibration has to be preferred above more sophisticated comparator or k0 methods that require more calibrations and dedicated software.

Labor costs can further be reduced by automation. Sometimes laboratories choose to reduce the labor costs by having the analysis done by lower paid and thus lower educated personnel, sometimes by hiring students. This is acceptable as long as the laboratory can demonstrate the technical competence of its workers.

Marketing, networking and commercial communications are ingredients of a service laboratory to which most nuclear physicists and/or radiochemists have never been introduced and trained. Finding customers (see the paragraph on “Potentials and Markets”) is one step; getting the customer’s interest and orders depends strongly on communication; the laboratory’s ability to listen to the customer; to translate his needs into an analytical problem; to explain the laboratory’s solution in an understandable way and to present, eventually, the results.

4. CONCLUSIONS

The benefits to the stakeholders (industry and governmental agencies) of nuclear analytical techniques like neutron activation analysis and nuclear spectroscopy can easily be spelled out but are hard to be quantified in financial terms. Neutron activation analysis, in spite of the existence of many other techniques for element determination, still has unique features making it indispensable for certain applications. The inspection for explosives in baggage is currently perhaps one of the most imaginative examples. Nuclear spectroscopy is obviously indispensable for assessments of natural and man-made radioactivity. There are ample opportunities in each country for institutions employing these nuclear analytical techniques to serve their society so as to demonstrate the relevance of the institution and the nuclear sciences.

The reduction of budgets for research and development set demands to the creativity of the scientists implementing an infrastructure for ‘routine’ service activities and merging this thus with the normal activities for exploring scientific research that these can continue smoothly. Quite a few gaps in information have been noticed.

There is an urgent need for quantitative information on the economical impact of analytical measurements at the end-user like about the consequences for the end user of eventual non-availability of nuclear techniques and the economical consequences of poor results. Such information may not always be easily retrievable whereas also a cascade of consequences may be identified. Still, scientists should try to retrieve such information since it will contribute positively to the acceptance, preservation and possibly expansion of the nuclear analytical capacity.

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REPORTS BY PARTICIPANTS

POSSIBILITIES OF A COMMERCIAL NEUTRON ACTIVATION ANALYSIS SERVICE WITH A SMALL REACTOR

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Abstract

The commercial experience has shown that NAA service should be fast and continuously available in order to attract industrial end users. Industry often requires a turn-around time of one day. Also, methods must be developed which ensure accurate and reliable results; too many mistakes will result in the loss of customers. The staff should think like businessmen and provide customers with exactly what they ask for; at the same time they should think like researchers and strive to continually improve the methods.

1. INTRODUCTION

Ecole Polytechnique, the engineering faculty of the University of Montreal, has operated a SLOWPOKE reactor since 1976. By 1980, with funds from the educational budget and government research grants decreasing, administration decided that a commercial neutron activation analysis service was necessary for continued operation of the reactor facility. The staff have developed and operated the service since then. The first customers were our engineering graduates who went to work in industry and remembered the chemical analysis possibilities they had seen at the reactor facility. Since then, the commercial service evolved naturally as satisfied customers told their colleagues in the same and related industries. The publicity brochures that were sent out brought no new customers, but it was never necessary for facility staff to go out to solicit business, since the increasing revenues matched fairly well the increasing needs.

As can be seen in Fig. 1, the commercial revenues doubled about every three years from 1980 to 1992 and then leveled off. The bumps are due to a few large short-term contracts. Since 1991, the commercial NAA service has generated revenues to pay 70% of the all the reactor laboratory's expenses, including salaries. On a few occasions during the 1990's, when revenues were sufficient and the workload exceeded capacity, new customers were re-directed to two other Canadian facilities. The staff consisted of a supervisor-analyst, one reactor operator-analyst, and a reactor technician. As the work increased, a second analyst was hired. The SLOWPOKE reactor being rather trivial to operate, the analysts are also the reactor operators. Reactor maintenance is done Monday morning and 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$10^{12}/cm^2/s$, and its extreme reliability, which facilitates the fast turn-around time often required. About 6,000 samples are analysed annually, 95% for one element or a few elements and 5% for the complete suite of elements. Besides the commercial service, about 4,000 irradiations are also performed annually for university researchers, some for radioactive tracer studies, but most for research requiring NAA, with the samples either counted at the reactor facility or shipped to the users' laboratories if they have their own gamma ray spectrometers.

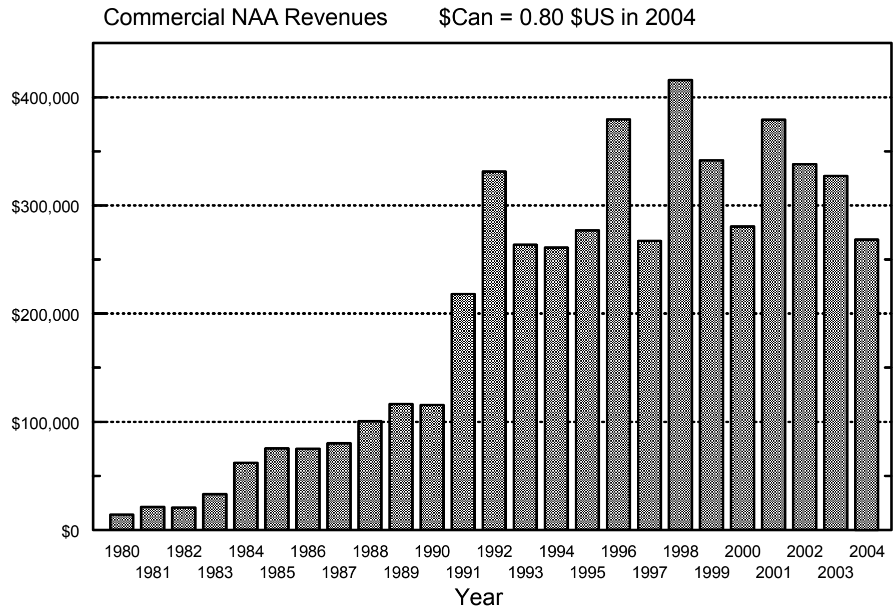

FIG. 1. Annual commercial revenues since 1980.

The revenues shown in figure 1 can be broken down as follows: 7% from university researchers, 9% from government, mainly government research institutions, and 84% from private industry, mainly for quality control of their products. 58% of the samples analysed come from Canada, one-third of these from the home province of Quebec, 41% from the USA, and 1% from Europe. In 2004, the price for industrial users is US$70 per sample for the first element and US$10 for each additional element. Discounts are given for large batches of samples. The complete analysis of a sample is US$350; usually the concentrations of about 40 elements are reported. Since the reactor facility is partly funded from an infrastructure grant from the Natural Sciences and Engineering Research Council of Canada, university researchers benefit from greatly reduced prices.

As other analysis techniques have evolved over the years, often offering great sensitivity and rapidity, NAA has become obsolete for some applications, such as for trace elements in water and in certain biological materials. But there is no danger that NAA will become obsolete for many applications where it has no real competition. It is the only method that can determine accurate average bulk concentrations of many elements in solid materials with no sample preparation. We estimate the total market for NAA in Canada and the USA to be US$20M annually; this includes only routine analyses that can be done using 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. We thus estimate 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, or are not analyzing materials they should be analyzing. We feel there is a substantial market waiting for an NAA laboratory with a knowledgeable salesman who can contact the potential customers.

2. TYPES OF MATERIALS ANALYSED

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

Plastics

The petrochemical industry uses our service for quality control of products, including the detection of catalyst residues, fire retardants and impurities, and for product development.

The technical centres of this industry have access to ICP-MS and XRF, but they prefer NAA for its reliability and sensitivity. For quality control, fast turn-around time is important because the products are waiting to be shipped. In most cases the elements requested can be determined using short-lived nuclides and the analysis report is sent within one day of receipt of the samples.

High-voltage cables, used for the transport and distribution of electricity, are often insulated with polyethylene covered by a black semi-conductor. Impurities in the components of the insulation may lead to electrical breakdown if they migrate to form conduction pathways. The materials are therefore analysed by NAA before production of the cables.

Treated wood

Construction lumber is often treated with the chemical IPBC, which contains iodine, or TBTO, which contains tin, to prevent the growth of mold. For quality control, a thin wafer is punched out from the four surfaces of the board to be verified. Wood used for windows and doors is treated with the same chemicals. Good penetration is needed to prevent decay over prolonged use; thicker samples are analysed. To develop new treatment procedures, samples are cut into thin slices to measure penetration profiles.

Wood used for outdoor construction needs to be treated to prevent decay. The commonly used chemical, containing Cu, Cr and As, is being replaced in Canada by new chemicals with Cu but not Cr and As. Many analyses are needed for the quality control of the new treatment procedures.

Paper

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

Air pollution samples

All gasoline used in automobiles in Canada contains the anti-knock additive MMT, an organic compound containing manganese. To prove that emissions have not led to unacceptable atmospheric Mn levels, many particulate samples were collected on filters and analysed for Mn.

Rocks

NAA has been replaced by other analysis methods in most cases, but is used for specific types of rocks and minerals and for rare-earth elements and platinum group elements, the latter with pre-irradiation chemical separation done by the customer-researcher.

Archaeological samples

A large database has been built up of 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 (chert) and metallic (copper) artifacts.

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 used for applications where the impurity levels are higher, and for measuring the thickness of metallic coatings.

High-purity tellurium has been analysed for traces of Se using the very short-lived nuclide Se-77m. For another application, high-purity Se was required to contain less than 2 ppm Cl. The measurement is hindered by the intense low-energy gamma rays emitted by short-lived Se nuclides. The detection of the high-energy Cl gamma rays was made possible by the use of a large volume Ge detector and by placing a 10 mm thick lead plate between sample and detector to preferentially filter out the low-energy gamma rays.

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.

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 for Se. We have analysed a large number of toenail samples for Se in a case-control cancer study.

Oil

Used motor oil has been analysed for metals to study engine wear. For an oil refinery, expensive catalysts are analysed regularly to determine when they need to be regenerated.

Pharmaceuticals, food supplements, food

For quality control, pharmaceutical products are analysed for undesired impurities. Food supplement tablets are analysed 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 containing sodium, which is easily detected by NAA.

3. SPECIAL METHODS

Industries require fast turn-around times and accurate and reliable results. Accuracies of 5% are usually sufficient, but it is important to eliminate all mistakes and systematic errors greater than 5%; otherwise customers will be lost. To simplify the standardization, we always try to use only two sample sizes, 1.4 mL and 7 mL, and three sample-detector distances, 1 mm, 35 mm and 100 mm. Element sensitivities measured for these geometries are stored in libraries and can be used for years without modification because of the excellent reproducibility of the neutron flux of the SLOWPOKE reactor. Repeated preparation of standards and the use of flux monitors are not necessary. A quality assurance standard is run about three times a week.

Our own software was developed to quickly and reliably calculate the concentrations. The software reads the spectrum and calculates the areas of only the peaks needed for the elements requested. The least-squares fits can be verified and easily improved interactively. The output, concentrations and uncertainties, is imported into a spreadsheet for preparation of the analysis report.

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.

4. CONCLUSIONS

We have shown that, with sufficient motivation, the staff of a reactor facility can develop a commercial NAA service generating enough revenues to pay the salaries of those involved. A salesman with a good knowledge of the NAA technique will accelerate things; otherwise, it may take several years for the business to grow to the desired level. To maximize revenues, the salesman should look for materials that are easy to analyse and for which NAA is obviously the best technique. The analysts will be wasting their time if they need to do difficult measurements, such as radiochemical separations, just to compete with other techniques. The NAA service should be fast and continuously available; industry often requires a turn-around time of one day. Also, methods must be developed which ensure accurate and reliable results; too many mistakes will result in the loss of customers.

The staff should think like businessmen and provide customers with exactly what they ask for; at the same time they should think like researchers and strive to continually improve the methods. 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.

NUCLEAR ANALYTICAL TECHNIQUES FOR COMMERCIAL APPLICATIONS IN CHINA

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Abstract

Since the establishment of the first Chinese nuclear reactor and accelerator in 1958, the nuclear analytical techniques (NATs) in China have dramatically developed in past half century. Nowadays 10 research nuclear reactors and over 100 small accelerators are available in China. Roughly, about 50 % of the machine time are applied for commercial purpose at the moment. The versatile nuclear analytical methods, mainly NAA, PIXE, XRF, etc., in China have been and are being applied widely and extensively in the following three fields: scientific, training, and commercial. This paper will briefly describe the past experience and present status about NATs for commercial applications. Some practical examples to demonstrate the role of NATs in this aspect will be given as well.

1. INTRODUCTION

Nuclear analytical methods for commercial applications in China. Basically, the NATs used for the commercial applications in China can be divided into two types, i.e. off-line and on-line. The former mainly includes instrumental neutron activation analysis (INAA) for compositional determination, particle induced X-ray emission (PIXE) also for compositional analysis, accelerator-based mass-spectrometry (AMS) for analysis of C-14, Be-7, Cl-36 and other long-lived radioactive nuclides, solid state nuclear track detector (SSNTD) for analysis of fissile elements, e.g. uranium, and other techniques.

The on-line method refers to prompt gamma neutron activation analysis (PGNAA), X-ray fluorescence (XRF) and neutron inelastic scattering (NIS), all for compositional analysis, gamma ray-based Compton scattering for determination of sample density, X ray computerized tomography (XCT) for industrial image diagnostic, and positron emission tomography (PET) also for clinical image diagnostic. Of course, more NTAs are available in China for commercial applications, e.g. Moessbauer spectrometry, isotopic tracing, etc. The advantages of on-line analysis lie in:

1. rapid, accurate and continuous measurement;
2. reduction of sampling errors compared to conventional sampling and off-line analysis;
3. improvement of process control (higher efficiency, more consistent product quality);
4. suitability for extreme conditions, e.g. high temperature, high pressure, intensive radiation

What is commercial application? In fact, NATs will be continuously used in many industrial and economical fields to enhance the labor efficiency or to improve the product quality. The commercial applications of NATs discussed here, as far as we understand, cover two types:

1. The so-called pure commercial application, i.e. analytical service with income, which could be used to increase pay of analytical workers or to improve laboratory infrastructure;

2. The hybrid commercial application means a combination of commercial service and scientific interest, i.e. this service is in accordance with the research direction of nuclear institutions. In China both application types are widely and extensively implemented.

Fields of commercial applications of NATs in China. Fields relying on commercial applications of NATs are varied, including geological, environmental, biological, agricultural, industrial, archeological and forensic. Because of the limited volume, some representative examples are briefly highlighted to demonstrate the role of NAT in commercial applications.

2. CASE STUDIES

2.1. Example 1: Off-line Drug analysis

The drug trafficking is one of the most serious issues in the today's world. The epidemic of drug abuse and its associated problems have constituted a true threat to the social and economic structure and the stability of nations. In order to crack down on drug crimes, it is imperative to identify whether confiscated drug samples came from the same batch or region. In this way, it may be possible to find its trading routines. For this purpose, the data for elemental concentrations together with the data obtained by other techniques, such as gas chromatography and high-performance liquid chromatography, are expected to be useful for identifying drug samples.

The State Ministry of Public Security of China is the main stakeholder. Because of the small sample amount and low contents of chemical elements, INAA is an excellent technique characterized by its high sensitivity, good accuracy, capability for multi-elemental analyses, and no reagent blank compared with other analytical techniques, to provide multi-elemental abundances, by which a data bank of drugs for element fingerprint spectrum to identify the sources and transportation route of drugs is being established. The contents of trace elements in about 1000 illicit heroin samples were analysed by INAA. The aim was to characterize the contents of trace elements in these heroin samples, which may then finally be used to identify their sources and trade routes.

The concentration ranges of the elements are shown in Figure 1. The element of the highest concentration in the illicit heroin samples was calcium. The lowest and highest values of calcium were 89 and 694 μg/g, respectively. The second highest element found in the region A heroin samples was zinc, while in the region B samples it was sodium. Gold and samarium concentrations were very low in all samples. The median concentrations of barium, bromine, sodium, thorium, and zinc were similar in the samples from the two regions. The median concentrations of cobalt, chromium, and antimony in the region A samples were higher than those in the region B samples. The median concentrations of the other elements, gold, calcium, cerium, iron, lanthanum, scandium, and samarium, were higher in the region B samples [1].

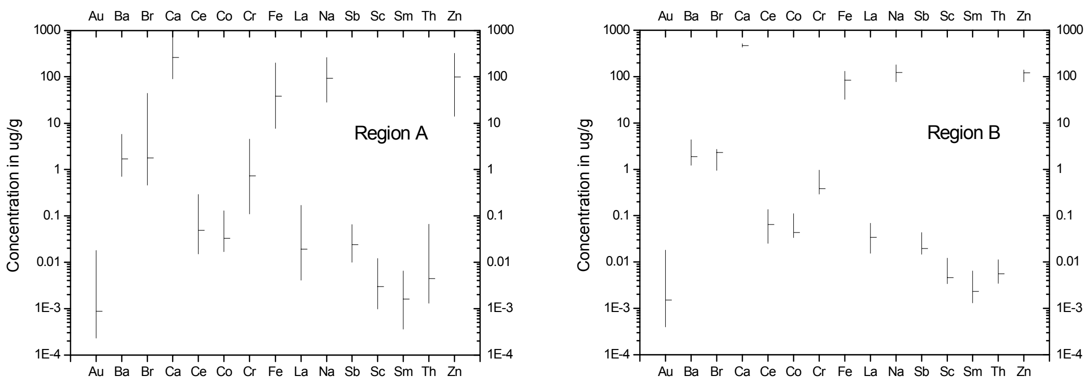

FIG. 2. Concentration ranges and median values of 15 trace elements in μg per gram of original heroin powder (850 samples from Region A and 150 from Region B)

To improve the group classification of a large amount of concentration data, the hierarchical cluster analysis was a good approach. For this statistical analysis, all 15 elements presented in Figure 1 were used as variables. Figure 2 shows the dendrogram deduced by this method. As it can be seen, the samples from Region A and Region B are clearly separated into two main groups. The region A samples are located at the upper part of the dendrogram, and the Region B samples at the lower part. The samples from the two main groups can be further separated into subgroups according to the similarities and differences among the samples. This application of NATs has important social impact to maintain national security, along with the substantial payment for nuclear laboratory. The future work will be focused on the isotopic identification and on-line analysis of drugs, which will produce more socio-economic values.

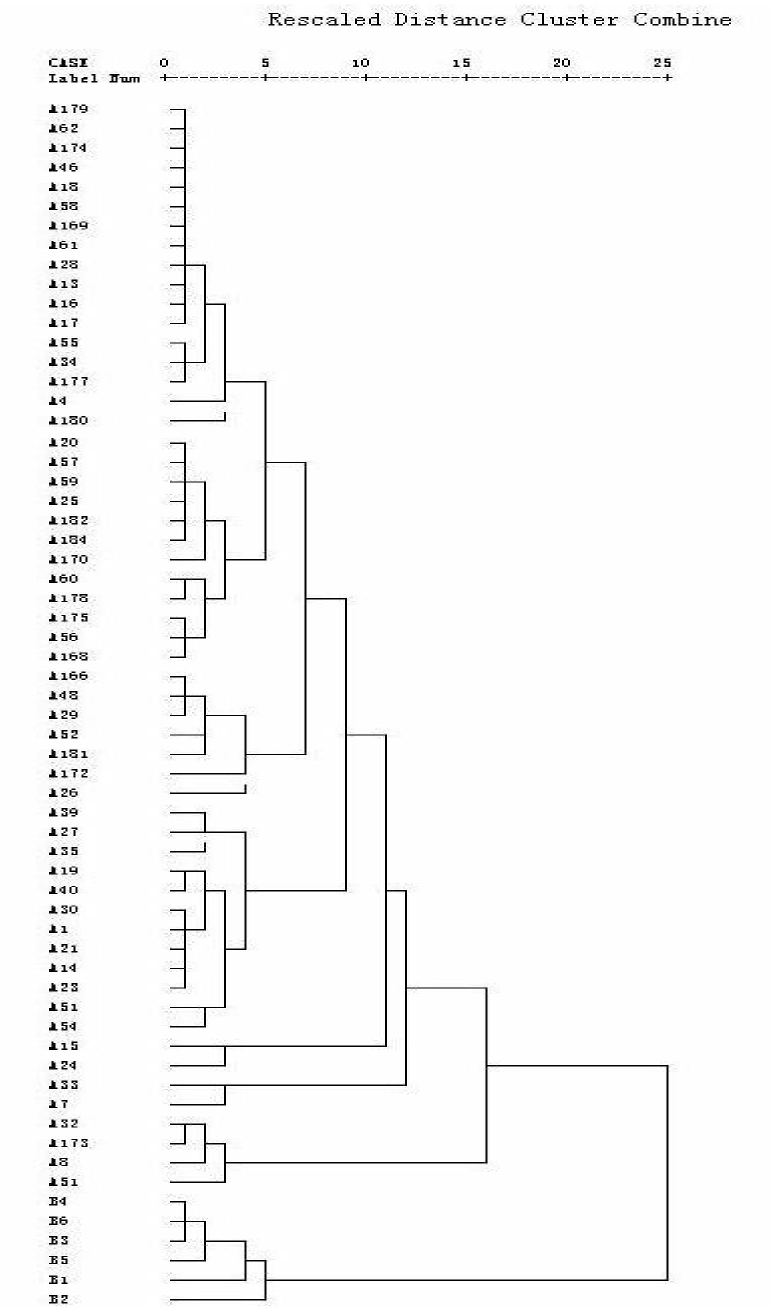

FIG. 3. Cluster diagram for 62 heroin samples using 15 elements

2.2. Example 2: Off-line archeological identification: a case application

INAA and SRXRF were used to provide the multi-elemental abundances in Chinese ancient pottery, porcelain and Tang-San-Cai specimens. Some big figures were identified by NATs for their true and false with very high pay.

Tang Sancai is a general name for the colour-glazed pottery produced in the Tang Dynasty, especially in the Prospering and Middle Tang periods. "Sancai" in Chinese means "three colors". Yellow, green and white are the three dominant colours in Tang Sancai's glaze. This technique somehow symbolizes the cosmopolitan and colourful life of Tang Chinese. Tang Sancai was famous for its distinctive and multiple colors along the "Silk Road". Some favorite Tang Sancai of camels, guardian figures and a woman on horseback are the "Silk Road" highlight. Many Tang Sancai specimens have been unearthed mainly near the two capitals of the Tang Dynasty, Chang'an in Shaanxi Province and Luoyang in Henan Province. Even with its paramount importance to archaeological, historical and ceramic research, the provenance of many kinds of Tang Sancai, especially the large figures, has not been well identified until now.

Our laboratory was requested in a payment basis to involve in identification of Tang-Sancai specimens recently unearthed by NATs. In order to clearly distinguish the chemical differences among specimens from different kilns, the contents of Ce, Nd, Eu, Yb, Lu, Ta, Th, Sc, Cs, La, Sm, U and Tb of body samples from the four kilns (Huangye, Huangbu, Xi'an and Xing Kiln) were all processed by factor analysis using the SPSS program. In Fig. 3, factors 1 and 2 account for 77% of the total variation, indicating that the two factors contain the majority of total variation. In rotated component matrix, factor 1 is mainly related to the variations of Hf, Ta, Th, Sc, Cs, U, Yb and Lu, while factor 2 denotes strong and high contribution of the variations of Eu, Tb, Yb, Cs, Nd, Eu, Tb, Yb, Lu and Sm. Most of the data points for the Tang Sancai samples from the Huangye, Huangbu, Xing and Xi'an Kilns are located inside circle A, B, C and D, respectively. [2] Further analytical service for identification of big figures will be continued with good income.

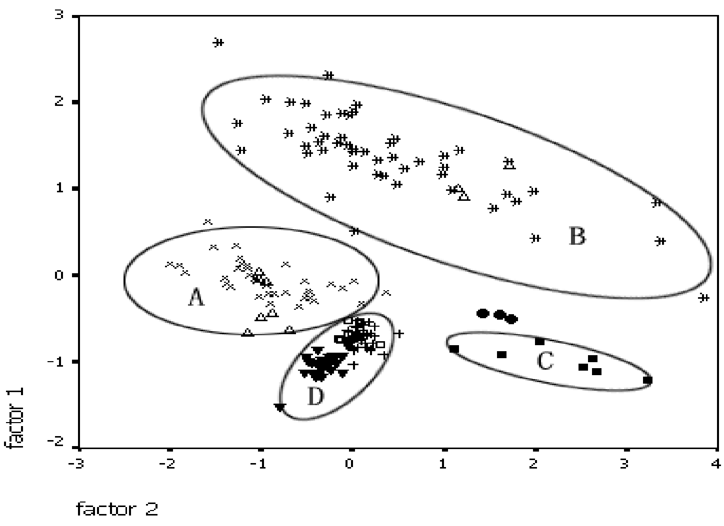

FIG. 4. Factor Analysis for Tang Sancai from Xi'an, Huangbu, Huangye and Xing Kiln A: Huangye Kiln B: Huangbu Kiln C: Xing Kiln D: Xi'an Kiln: Body color : + Red ▼Offwhite ●Pink □Gray White

2.3. Example 3: On-line coal analysis

In 80s of last century, over ten thousands of coal samples from the main 19 Chinese coalfields were analysed by INAA. The former Ministry of Coal and Charcoal Industry was the No. 1 customer. But nowadays on-line coal analysis is preferred for process control, whose purpose is aimed at (1) raw coal quality monitoring; (2) coal sorting; (3) stockpile management; (4) monitoring at shipping ports; (5) power station – feed monitoring; (6) meeting ISO requirement; (7) alleviating environmental pollution; (8) economic analysis; and (9) enhancing coal burning efficiency at boiler.

Commercial on-line Element Analysis of Coal based on PGNAA using D-T neutron generator，combined with fast neutron inelastic scattering technique for analysis of C, H, O, N, S, Al, Si, Fe, Ca, and Ti in coal used for power plant (Fig. 4) [3].

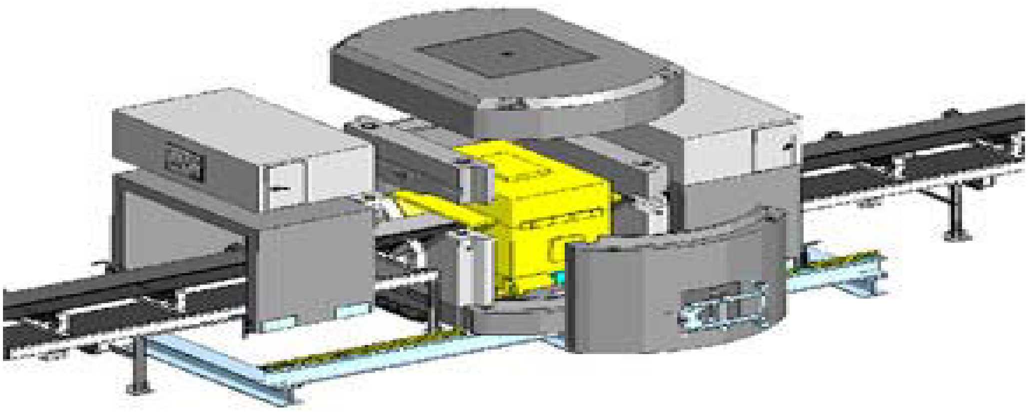

FIG. 5. Layout of PGNAA on-line analytical facility for coal analysis

2.4. Example 4: Container inspection system

The density detection based on gamma ray attenuation produced by linear accelerator has been used for container inspection system. Over 30 sets of the Chinese product for the container inspection have been well equipped at the Chinese customs and also exported to over 20 countries, which are playing important role to inspect the smuggling cases. The detailed description of this nuclear analytical device can refer to [4]

3. MARKET-ORIENTED PHILOSOPHY

A very important issue in the commercial applications of NATs is to develop a market-oriented strategy system. The Chinese experience lies in the following five points.

1. Customer is God: This motto is also suitable for nuclear analytical workers in the commercial service.
2. Price is key: The price for each sample should be competitive against the challenge from non-nuclear methods, e.g. ICP-MS, AAS and others.
3. Time is money: Fast response to customer’s needs is imperative. Otherwise, customers will leave for other laboratories.

4. Quality is life: Wrong data is worse than no data. The life of NATs lies in its good accuracy. Thus, the accreditation system is highly needed.
5. Knowledge is capital: The know-how of nuclear analysts is a precious asset to win a certain quotient in severe market competition. It is impossible to attract customers without any basic interdisciplinary knowledge.

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ANALYTICAL METHODS USING RADIOACTIVE COMMERCIALLY AVAILABLE SEALED SOURCES — MOISTURE AND DENSITY GAUGE

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Abstract

Radioisotope and radiation techniques are largely applied in industry since many years. Not only real analytical methods but also indirect analytical methods such as nuclear gauges make use of beta, gamma and neutron radiation for measuring densities, thickness and moisture content of different material. An application which analyses moisture content and density of construction materials, soil, asphalt and more will be illustrated hereafter.

1. INTRODUCTION

Many radioactive isotopes find directly or indirectly use in industrial analytical systems such as chromatographs (Detection of halogen containing compounds like pesticides in e.g. drinking water, explosives), X ray fluorescence spectroscopy (a method, which is widely used to measure the elemental composition of material by measuring the wavelength of stimulated X rays), activation analysis and others.

Other complementary techniques include:

Nucleonic gauges: All nucleonic gauging methods have in common that ionising radiation is attenuated or scattered when passing through matter. By detection of radiation which passed through matter different data provides information about that material's density, thickness or water content is obtained. Radioisotope sealed sources used for designing such kind of nucleonic gauge encapsulate radioactive material which under normal conditions will not leak out of its containment. It is very unlikely that contamination of the environment occurs.

The chapters hereafter give attention to so-called nuclear density and moisture gauges, which are making use of not only neutron sources but also gamma sources.

2. NUCLEAR DENSITY AND MOISTURE GAUGE

Problem and challenge

Densities and moisture content of e.g. asphalt, concrete, rocks, soil, soil bases, aggregates and other shall be determined fast, accurately and economically and, if possible, on-site while e.g. road and rail road construction (see picture below).

Why a nuclear technique?

NDA technique: A density gauge measures density of material such as mentioned above without the use of core samples or other destructive methods. Since this type of instrument can be constructed very compact and it can even host together another nuclear gauge i.e. a moisture gauge, practical advantages are obvious. Drilling holes, excavating and analysing samples in laboratories is time consuming, work intensive and needs laboratory space. Evaluation and analysis of data and material by use of a nuclear gauge, however, is performed almost instantly i.e. such gauge provides continuous on-line measurements. This method, in comparison to other chemical or physical techniques, measures detected in situ and is independent from temperature, pressure, pH-value and colour of the material itself.

How is the problem solved?

Moisture measurements: fast neutrons from a neutron source are moderated by elastic scattering with hydrogen atoms and reflected into the detector volume. (The detector in the gauge detects only slow neutrons. See figure below.) Hydrogen which is a part of the water molecule is a very effective neutron moderator and the number of moderated neutrons is proportional to the presence of hydrogen atoms. However, there are other sources of hydrogen in soil such as roots and organic matters. The purpose of the moisture gauge is to measure free water; therefore knowing the soil characteristics is important.

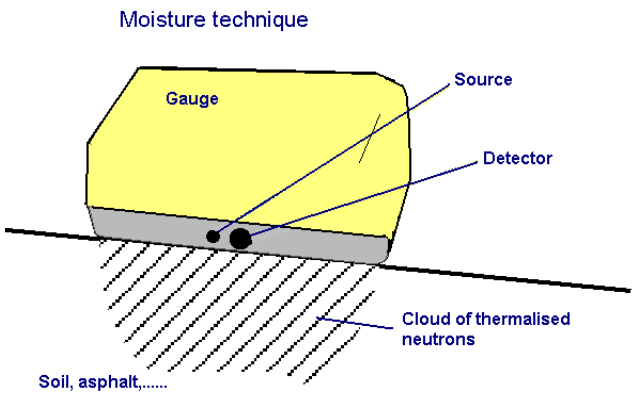

FIG. 1. Principle of density-moisture gauge

The density gauge uses a gamma source, Cs-137 (661keV). - Density measurements involve the same principles as thickness measurements: the measured material absorbs or scatters in proportion to its density.

Neutron Sources

Portable neutrons sources consist either of (α,n) sources or of sources with isotopes undergoing spontaneous fission.

The most common and known one of the first group is Am-241 as α-source and Be as target while Cf-252 is the most prominent isotope of the second group. Cf-252 provides higher neutron flux than an (α, n)-source of similar α-activity. Nevertheless, due to its shorter half-life (2.6 years vs. 430 years), handling and price of raw material the Am-Be-source is the preferred one for most moisture gauge applications. The homogeneous mixture of Am-241 oxide and Beryllium metal is encapsulated in welded double stainless steel capsules, forming a so-called sealed source. Neutrons from an Am/Be source are "fast", they have an average kinetic energy of about 4.5 MeV. The Q-value (neutrons per million alpha particles) is about 76.

Detection of neutrons

Different neutron detectors exist. Since neutrons carry no charge, they cannot interact with matter by means of the Coulomb force, which dominates the energy loss mechanisms for charged particles. Most neutron detectors, therefore, utilise conversion of the incident neutron energy into secondary charged particles, which can then be detected directly. Typical types of neutron detectors combine a target material, which carries the conversion out, together with a conventional charged particle detector. The moisture gauge under discussion uses a gas cylindrical proportional detector, a so-called He-proportional counter. The conversion reactions of interest here are a) elastic scattering $^3He(n,n)^3He$ and the b) absorption reaction $^3He(n,p)t$.

Neutron Moderation

Through collisions with sample atoms neutrons are slowed down loosing their energy which then can be detected by proportional counters. From fundamental physics it is known that elastic scattering is most effective when particles are colliding with particles of equal mass. Hydrogen atoms (one single proton as nucleus) have low mass, equal to the neutron mass, and can therefore be considered as perfect moderator for (fast) neutrons.

Density Measurement

Can either be performed by transmission or backscatter technique, the choice being usually one of convenience e.g. when drilling of a hole is difficult (accessible from only one side) density gauges may use the backscatter mode (see figures below).

Both modes are proportional to the density of the measures sample. Gamma-radiation has sufficient penetration for measuring the thickness of dense materials. In transmission mode the attenuated radiation is detected. The less radiation detected the less dense the material.

On the other hand the denser the material the more photons are Compton back-scattered. In backscatter mode Compton scattered radiation from the material is detected.

Typical detectors are appropriate Geiger-Müller or scintillation counters.

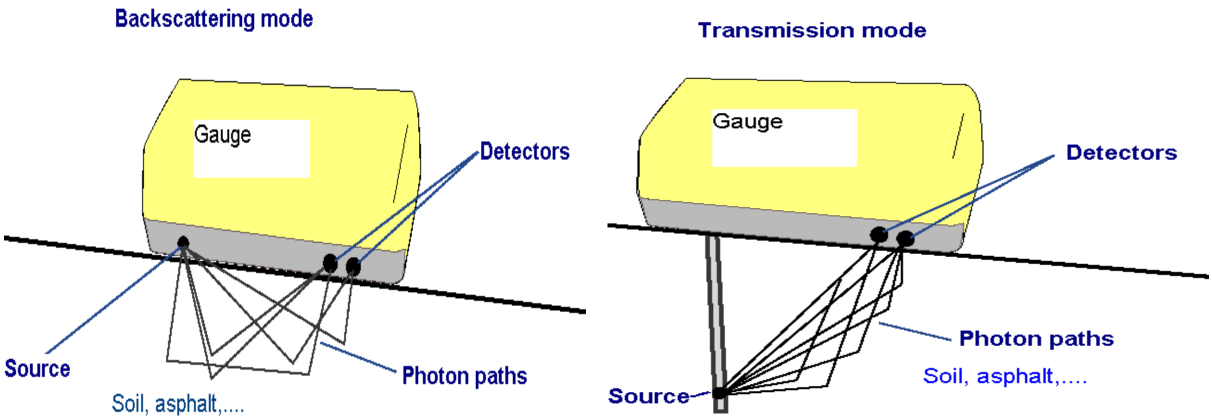

FIG. 2. Principle of backscattering and transmission modes

Functioning of the nuclear density and moisture gauge

Neutron source and detector both are located inside the gauge, just above the surface of the test material. Close to the neutron source location a cloud of slow neutrons is created which concentration depends in principle only on the amount of hydrogen respectively on the moisture in that volume. A number of moderated neutrons is scattered into the He-detector volume which is directly proportional to the amount of moisture in the sample. Besides the hydrogen content of the free water (or moisture) also the bound hydrogen atoms in the sample or cristal water is measured. By knowing the sample characteristics and appropriate calculation models results are achieved which are proportional to the amount of free water.

Detection of the gamma rays emitted by the Cs-137 allows determining the density of material by calculating the attenuation of the intensity or the backscattering of the gamma radiation through the absorbing environment.

Both sources (Am-Be and Cs-137) are usually grouped together in the same housing. While the Cs-137 source is located in a metallic shielding of high density the neutron source is shielded by hydrogenic material of several centimetres thickness, which plays an important role when considering the weight of the device.

Commercial effect

Worldwide many systems for road construction exist and are (still) sold. Depending on the conditions and features the representative price of a nuclear density and moisture gauge is about 10,000 USD. For the time being in the order of 1,000 pieces are acquired per year and some 100 disposed.

Summary:

Nuclear gauges provide an inexpensive, yet highly reliable and accurate method of measuring the moisture, density, or composition of materials. Stationary alternative techniques are available but not as easy to use.

However radiation protection measures, such as training and shielding, and special transport procedures have to be respected

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CONTRIBUTIONS OF RADIOCHEMISTRY AND NUCLEAR ANALYTICAL TECHNIQUES TO SOCIETY AND TECHNOLOGY: SOME EXAMPLES OF 35 YEARS EXPERIENCE IN DELFT

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Abstract

The Radiochemistry department of the Interfaculty reactor Institute of the Delft University of Technology has a tradition in making its facilities available to both scientists from faculties of other universities as well as for (commercial) services to society. Neutron activation analysis is the major service activity, resulting in sustainability, on basis of the additional budget generated, of the NAA facilities for more than 25 years. Organizational structures, customer relations, analytical aspects and problems associated with frequently changing university policies are discussed. The radiotracer technique and (non-medical) radiotracer production is another opportunity for servicing society. Licensing-related problems have resulted in industrial applications in pilot-plant and small-scale technological devices at the institute itself rather than 'on-site. Finally, an overview will be given of the marketing and quality requirements to university institutes, wanting to go commercial.

1. INTRODUCTION

Budget cuts and the oscillating (public) debates on the benefits of nuclear research reactor facilities are a continuous threat to many nuclear institutions. University affiliated institutions often face additional problems if their facilities offer sufficient scientific challenge and if an education in nuclear sciences provide students a sound outlook for a professional career. Such discussions may be an excuse for non-fulfillment of vacancies and reduced priority in the academic curriculum. Universities tend to reallocate their funds to more contemporary sciences such as molecular biology and nanotechnology. Their choices are based on relevance, quality viability and productivity. Relevance is often measured on the basis of external funding of research programs as well as on career opportunities for students. However, the areas with opportunities for external funding are largely determined by socio-economical developments, sometimes even at the (inter)national political level. The thematic areas in the scientific Framework Programs of the European Union [1] illustrate this.

The relevance and viability of an expensive facility like a nuclear reactor center can also be demonstrated by making the facilities available to provide measurements on request by outsiders. Ideally, such services should be sustainable, but even the existence may lead to consider the center being of regional or national importance. Nuclear reactor centers have various options for such services, like production of radionuclides; neutron transmutation doping; neutron activation analysis; neutron radiography and others.

This contribution gives examples of the typical analytical services provided by the Interuniversity Reactor Institute of the Delft University of Technology. This institute houses the only university research reactor in The Netherlands, a 2 MW swimming pool reactor, with associated facilities for neutron research, neutron activation and radiochemistry. Within the services provided by the Radiochemistry department, emphasis is given to neutron activation analysis and the radiotracer method.

2. HISTORICAL BACKGROUND

The Radiochemistry department has a long history and culture in making their facilities available to outsiders. As from the start of its operations, in the early 1960s, the policy of the institute was to demonstrate the opportunities of radioactivity and nuclear measurements to scientists in the applied fields.

This approach showed to be more successful for radiochemistry than for reactor-physics and neutron-physics. Initially, academic collaborations were pursued, but rapidly also governmental organizations showed interest in the use of e.g. radioactive tracers, measurement of natural radioactivity and neutron activation analysis. The use of radiotracers was advocated in the academic curriculum, resulting in much collaboration within the faculties of chemical engineering and applied physics with the university.

3. NEUTRON ACTIVATION ANALYSIS

Neutron activation analysis, in the end of the 1960s and early 1970s the only multi-trace-element technique, rapidly found interest at many other universities. The growing number of requests for analyses in Delft evoked the development of a 'laymen's system' for INAA [2] in which the students from the other university faculties in applied fields such as geology, geochemistry, environmental sciences and biology, were trained to perform their own analysis using the institute's facilities without having a specific education in radiochemistry and/or nuclear physics. Initially this was done cost-free, but the growing demand also implied an extension of the gamma ray spectrometers. This marked the onset of paid analysis, even by the universities, although initially this was often realized by payment '*in natura'* via the procurement of detectors or spectrometer components.

Via the contacts with various governmental organizations also a network developed with links to the private sector. The "Cd decree", a national regulation in the midst 1980s following EU directives, caused such a growth in demand for determinations of Cd in plastics using INAA that a business-type unit was created with permanent additional personnel performing the analyses and managing the requests and accounting. The staff involved was trained in commercial communications and several advertising campaigns were initiated to improve the visibility. The income from these analyses was earmarked for the INAA group, providing the opportunity for improvement and further extension of the NAA facilities. One important spin-off of the contacts with customers was that many of the –at least by radiochemists mentioned- 'advantages' of INAA seldom appear to excite customers. As such, new strategies for marketing had to be developed. Moreover, it became necessary to improve the efficiency, effectiveness and quality of these services. This culminated in the EN 45001 accreditation of the quality system by early 1993 (later followed by ISO/IEC 17025 accreditation). The services require a high degree of automation (sample changers and dedicated software) and parallel measurement systems. The automation stretches further than just sample changers. Already by the end of the 1970s the INAA software had been developed in such a way that a full gamma ray spectrum analysis and interpretation towards element concentrations could be realized in about 1 minute per spectrum [3]. In addition, software was developed to schedule the measurements on the sample changers so as to measure 24 h/day, 7 d/week. Moreover, the software allows for different counting times of samples and flux monitors, and generates and interprets automatically quality control charts.

However, operating the software as a 'black box', which basically is possible, will inevitable lead to wrong results. Building technically competence of personnel with the ability to optimize analytical protocols and with insight in possible sources of spectral interference and other sources of error may require typically at least 5 years of full commitment to INAA and gamma ray spectroscopy. The facilities for INAA and the quality system of the laboratory have been described elsewhere [4-8].

The organization of the INAA services has changed several times in the past decade as a result of changes in the Institute's policy. At the start of the 1990s, a commercial business unit was established, consisting of a marketing and public relations manager, administrative support, and 3 technicians. All salaries were covered by the income from the analyses. This business unit worked in liaison with the nuclear analytical methods research group, which was responsible for the operationality of the facilities and the analytical quality of the results.

The laboratory for INAA identified 'external' and 'internal' customers. Scientists from other universities or research establishments, governmental bodies and industry form the first category. The internal customers were scientists within the mother Institute, mainly from the department of Radiochemistry. Some of these internal customers were trained by the laboratory to carry out the analyses on their own. The external customers were fully charged for the analyses whereas the internal customers only paid for the consumables (capsules, internal quality control samples etc). The remaining revenues of the analyses remained earmarked so as to facilitate maintenance, replacement and extension of the facilities.

The advantage of this structure was that the research group was not hindered by the paradox of priorities for research or for satisfying commercial customers. A disadvantage was the absence of technical knowledge with the business unit manager, requiring regular back-up by the research group for advises on the feasibility of analysis. The university's public relations department assisted in the development of brochures and material for boots at exhibition. One important spin-off of the contacts with customers was that many of the –at least by radiochemists mentioned- 'advantages' of INAA seldom appear to excite customers. As such, new strategies for marketing had to be developed.

By the end of the 1990s, the management of the institute did not allow fulfilling vacancies in the administrative support and the management of the business unit, and the unit was merged with the nuclear analytical methods group. Moreover, the university decided that providing commercial services was not acceptable for a academic institution, with exception for those services that could be considered as 'unique' for the reactor center. A financial evaluation by the university accountants resulted in an estimate of an analysis cost that was a multifold of the cost, estimated by the institute itself. The university considered that there was no viability for commercial services, and the institute's management decided that NAA services could only be provided primarily for scientific collaborations rather than to serve industry and governmental institutions. Consequently, a network of industrial customers was replaced by a network of academic institutions. However, academic institutions seldom are able to pay the full cost price of services but the deficit was allowed to be accounted for by co-authorship in resulting scientific publications.

The advantage of this structure was that a network of scientific collaborations could be developed –resulting in several jointly acquired research grants and various scientific publications- by which also additional budget was obtained. It should also be noted that in research grants lead to a higher academic respect that third-party income. A disadvantage was the increased paperwork since also all accounting and client relations had to be maintained by the research group.

By 2005, the policy of the institute has changed again because of budgetary problems. The value of scientific publications is no longer considered anymore in the turnover of the NAA services. A new cost analysis has been carried out based on a different view to the contribution of the depreciation of equipment, resulting in a cost price much lower than prescribed 5 years earlier by the university. Also a new structure has been designed, in which the NAA services will be completely separated from the nuclear analytical methods research group. Marketing and accounting will again be done by a separate manager with background in physics rather than in chemical analysis. The focus will be again on the industrial market rather than on collaboration with academic organizations.

Characteristics of the various organization structures have been summarized in Table I. It should be noted that short-term policies as described in the above –often characteristic for university environments- are detrimental for the motivation of personnel, for maintenance of a network of customers (both industrial as academic) as well as for the credibility of the marketing.

TABLE I. SUMMARY OF ADVANTAGES AND DISADVANTAGES OF VARIOUS ORGANIZATION STRUCTURES FOR COMMERCIAL APPLICATIONS OF INAA AT IRI, DELFT

Organization structure	Advantages	Disadvantages
1975-1990 Laymen's system	Easy access, no paperwork, no additional personnel needed, no marketing needed, payment *in natura'*	Training, control of analytical quality, sustainability, some conflicts of interest between research group and external users, very low cash flow
1990-2000 Service unit	No paperwork for research group, well-organized structure, no conflicts of interest, high cash flow	Technical know-how of manager, problems with marketing
2000-2005 Scientific collaborations	No conflicts of interest, know-how in marketing and communications, high publication output, use of scientific network	Paperwork, need for discounts to universities, reduction of cash flow

3.1. NAA Sample types

An overview of the sample types analysed currently and 5 years ago is given in Table II. Plastics have been a major market segment for long, being a perfect niche for INAA since it can be done non-destructive.

TABLE II. PERCENTAGE INDICATIONS OF SAMPLE TYPES FOR INAA

Sample types	1995	2000	2005
Plastics	60	80	5
High-tech materials	5	5	5
Bio-indicators	20	10	10
Nail clippings	-	-	70
Sediments, soils, rocks	5	-	-
Others (e.g. catalysts)	5	5	10

The analyses dealt with the enforcement of he Cd decree for reduction of the use of Cd in plastics [9, 10]. However, in 2001 also XRF was accepted as a screening technique upon extensive validation using INAA. This reduced the incoming stream of sample considerably. In addition, the forced change from industry oriented to academic oriented by about the year 2000 caused also a major change in the type of samples analysed. By 2004, the majority of analyses were done for collaborative projects with epidemiologists in which nail clippings are involved. In addition, there is a small persisting market for analysis of new materials, composites, siliconcarbide, carbonfiber, alumina etc. It should be noted that there is hardly an industrial market for geological and related analyses in The Netherlands. Moreover, the emphasis in environmental assessments is with water analysis and organic residues., whereas there is a remaining quest for determination of elements like Pb and Cd, for which NAA has none or very limited capabilities.

The samples from internal users mostly result from various biomonitoring projects (lichens, mosses, tree bark, soil, air particulate matter).

3.2. NAA Analysis protocols

The traditional protocol for multi-element analysis was (and still is): 2 irradiations, 3 measurements (the shorts, one after 1 week and one measurement after about 1 month); 50-60 elements reporting. The various requests and particularly the needs of the external customers made necessary to develop different analysis protocols.

Most external customers appear not to be interested in full multi-element analysis, even not when the data is given for 'free' together with the data requested in the first place. Customers are usually oriented to one or a few given element(s) (see Figure 1) whereas their main demand lies with turnaround time. Here lies a fundamental change to be made for an INAA laboratory when operating at the commercial market. "Good is good enough" implies that the analyst should refrain from traditional scientific protocols aiming at the best precision and detection limits. Many customers are interested in order of magnitude indications rather than indications with a precision e.g. better than 10 %.

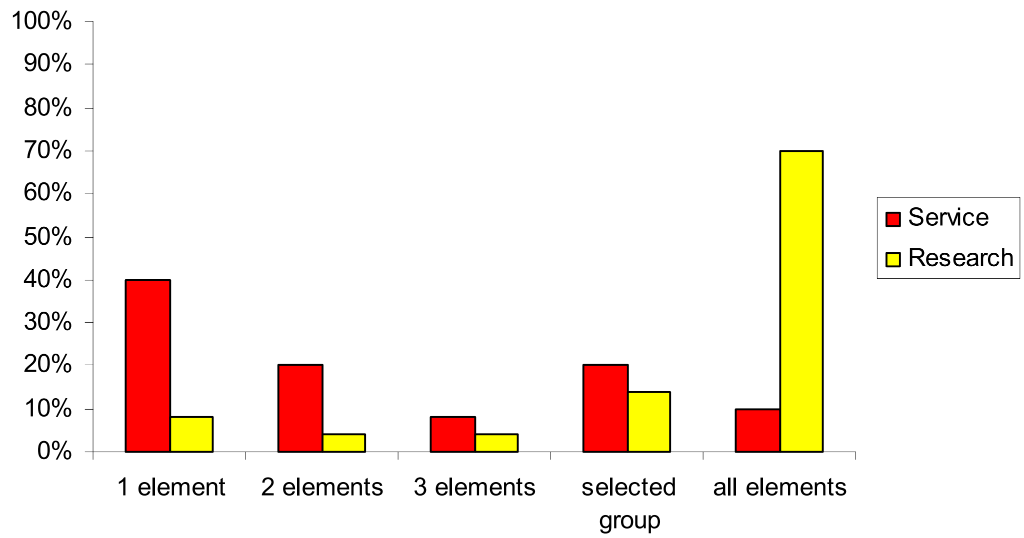

FIG. 1. Indication of interest in number of elements to be reported via INAA from industrial customers (service) and customers in scientific collaborations (research).

The majority of the work for external customers deals with one measurement 2-4 days after irradiation and determination of 1-10 elements. The turnaround time of these measurements is about 1 week - 10 days (see Figure 2). This is usually acceptable for customers who compromise between number of elements and turnaround time. In addition, dedicated protocols have been developed too, in which routinely results could be reported within 3 working days turnaround time for a group of 12 elements.

The academic market segment, on the contrary, is mainly interested in full multi-element analyses at the best measurement capabilities. Experience with services to groups at other universities learned that requests for multi-element data changed rapidly in request for a limited number of elements when the groups were fully charged for the analyses.

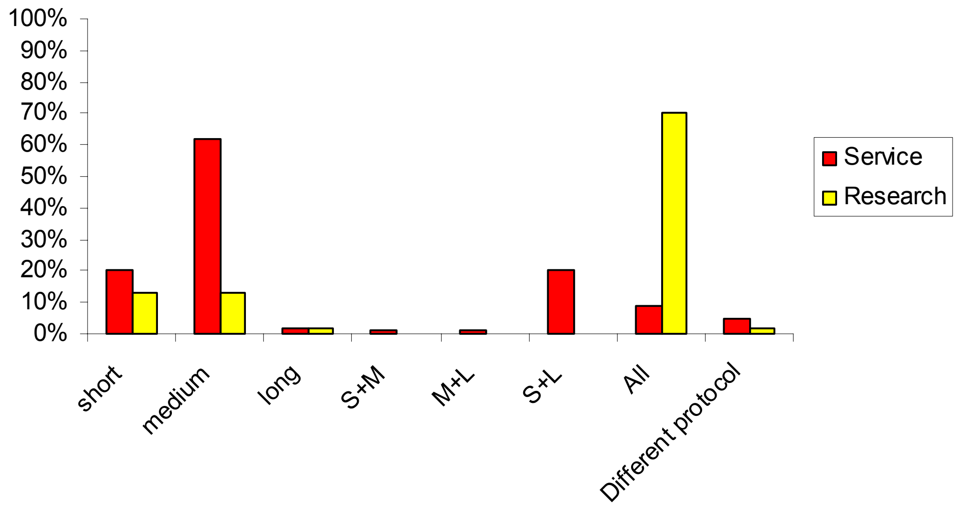

FIG. 2. Indication of analytical protocols, needed for samples from industrial customers (service) and customers in scientific collaborations (research). Typical conditions:"Short" : t_{irr} 5-30 s, t_d 0.5 – 10 m, t_c 0.5-5 m; "Medium": t_{irr} 1-4 h, t_d 5 d, t_c 1 h ; "Long": t_{irr} 1-4 h, t_d 3 w, t_c 1-4 h

3.3. Costs and tariffs

Cost analysis of INAA services in a university environment, and particularly in an institution operation a nuclear research reactor, is a complicated issue. Basically, the cost analysis is simple. Estimates are needed of the salaries of the people involved, the running costs (consumables) of the laboratory, the depreciation of equipment and the costs of using the infrastructure. Problems started with e.g. estimation the costs of depreciation of equipment; the university prescribes 3 years whereas it is well-known that e.g. semiconductor detectors easily can last for 10 years or many more. Additionally, discussions came about the costs of equipment shared for research and services; equally so for consumables (like LN2). The costs of infrastructure, especially the costs of 'neutrons', was never formally decided upon at IRI, and actually never accounted for. In addition, it had to be decided if the number of samples, the number of spectra measured, the number of elements reported or another denominator should be taken to estimate the costs of the service.

The tariffs, however, should be also based on the market tariffs for analytical services as set by other analytical service laboratories. It should be noted that these organizations may not be striving to have each component of their services fully sustainable, as long as the overall organization remains sustainable. Tuning the tariffs for INAA services to the market tariffs is needed to create a competitive position, especially in the staring phase. It is sometimes better to aim at building a network and trust as a reliable partner, even at prices under the cost level, than aiming at fully coverage by prices equal to the analysis costs.

4. NON-MEDICAL RADIOTRACER APPLICATIONS

Both INAA and the applications of the radiotracer method require custom-tailored protocols. However, in INAA use is made of many standardized components (irradiation, counting equipment, spectrum analysis software) whereas the radiotracer method is typically characterized by custom-tailored experimental design, including source preparation and/or development, choice of equipment, (collimator) and data acquisition systems, up to modeling and tracer kinetic analysis. Radiotracer applications can therefore hardly be classified as 'routine', feasible for wide-scale marketing.

There is a large potential of (industrial) applications in all applied sciences. In many cases the systems studied are remote, e.g. industrial installations or laboratories, environmental systems (like estuaries) or medical institutions. Radiotracer methods are characterized by non-invasive measurements which offer for industry the possibility of non-interrupted processes, a direct economic benefit. Unfortunately, these applications with outlook for commercial services- are strongly hampered by requirements to licensing the use of radioactivity. Licensing procedures may be very time consuming irrespective of the risks involved, and authorities may sometimes formulate impractical or costly precautions. These licensing problems are one of the main reasons that most of the radiotracer applications by the Reactor Institute for third parties dealt with their use in scientific research on processes and systems of industrial relevance rather than in industrial problem-solving tasks [11].

4.1. Examples of radiotracer research of industrial relevancy are

Classification of particles in a solid-liquid fluidized bed.

Fluidized beds are one of the most important chemical engineering technologies. This project aimed to estimate the velocity of a single particle falling down through a fluidized bed. To this end, ^{113m}In (half life 99.5 m) labeled ion-exchange particles were let to fall down a tube through a bed of (smaller) ion-exchanger particles fluidized by de-ionized water.

Gas-liquid contacting in a stirred vessel

Stirred vessels are also applied in chemical engineering to carry out reactions between gases and liquids. There is a continuous need to describe them in terms of basic engineering, physics and chemistry that underlie the fluid flow, interphase transfer and chemical reaction. Since argon matches oxygen in diffusivity and solubility in water, ^{41}Ar is an ideal tracer to study the oxygen residence time distribution in stirred vessels.

Gas flow and mixing in a pressurized fluidized bed combustor

A pressurized fluidized-bed combustor is one of the new technologies for environmental friendly burning of solid fossil fuel. The flow and mixing of gas have a significant influence on the heat transfer and the kinetics of the burning process. ^{41}Ar is a suitable tracer to determine the pattern of gas passage through the bed. New information was obtained that could be utilized for the development and design of industrial scale fluidized-bed coal combustors.

Mixing of particulate solid in a batch-type solids mixer

A Nauta mixer is a well-known and widely used industrial mixer for solids. The device consists of a conical hopper and a rotating and orbiting screw. Mixing times (time needed to obtain an equilibrium mixture) were determined using ^{128}I labeled sand particles.

Movement of a textile piece in a laundry machine drum

The influence of the mechanical agitation on the washing efficiency of a domestic drum-type fabric laundry machine is still subject of research. It is of course not easy to observe the individual movements of the textile and wash liquids. A solution was found by attaching a suitable radioactive source (^{99m}Tc) to a piece of textile and to visualize the position of that particular piece, as a function of time, using a gamma-camera. The project has led to improvements of both the laundry machine and the economics of the washing procedure.

The examples given above demonstrate that the radiotracer method offers a good outlook for services and creative solutions to industry. Some of the examples given were indirectly financed by the chemical industry, by making equipment available and/or via payment of the radiotracer production. The real cost effectiveness of such scientific services is low, since quite some effort is involved in the experimental design and data evaluation. The benefits for the mother organization are its embedding in the country's industrial infrastructure, with additional scientific spin-offs.

Once licensing has been realized, the production of radionuclides for industrial application of the radiotracer method can be economically attractive, especially for "specials" such as radionuclides with short half-lives, gaseous tracers or for custom-tailored labeled compounds or particles. However, it is doubtful if the total turnover of such a service can grow to a same level as attainable by INAA.

5. MEASUREMENT OF NATURALLY OCCURRING RADIONUCLIDES.

Measurement of naturally occurring radionuclides is a trivial (commercial) activity in many nuclear centers. The measurements mostly deal with determination of e.g. ^{3}H, ^{137}Cs, and/or ^{90}Sr in food products or environmental systems. Laboratories performing gamma ray spectroscopy or LSC counting of these radionuclides can relatively easy be licensed which implies competition by outsiders.

Better opportunities for unique commercial services are with determination of alpha-radiation emitting radionuclides requiring radiochemical separations. Many sediments and ores are rich in uranium and thorium, and thus in the decay products of ^{238}U, ^{235}U and ^{232}Th. Phosphate ore –used for phosphoric acid, phosphate fertilizer and gypsum production may serve as an example. The daughter isotopes of the uranium-radium series (particularly ^{226}Ra, ^{210}Po, ^{210}Pb) end-up in the gypsum fraction, and finally in the surface waters. The Reactor Institute in Delft was invited by such a phosphate fertilizer producing company to make an assessment of its discharges in view of renewal of its license. An estimate of the dose to the population was required which made necessary to determined the amounts of these radionuclides in the various steps in a production process. ^{226}Ra, ^{238}U, ^{235}U and ^{232}Th have been be determined by direct gamma ray spectroscopy, ^{210}Po and ^{210}Pb by radiochemical separations and alpha spectrometry and gamma ray spectroscopy, respectively.

A similar project on the determination of alpha-emitting radionuclides and beta-emitting radionuclides in Dutch freshwater systems was carried out for the Dutch ministry of Environmental Affairs. Three kinds of alpha-emitting and beta-emitting radionuclides were distinguished: (1) Natural sources of natural alpha and/or beta -emitters, (2) Human activities by which the levels of natural alpha and/or emitters is increased ('technological enhancement" and (3) Nuclear facilities that enrich uranium, produce transuranic alpha-emitters (power stations and other nuclear reactors), or produce anthropogenic beta-emitters.

Characteristic for such projects is that the project-teams are usually large; that extensive reporting is required but also that the assessments are not regularly returning, perhaps only once every 10 or more years. The positioning of the nuclear institute as a national expert center for such assessments is, however, established. The oil and natural gas exploration is another market for such assessments since it has been observed that radionuclides also accumulate in e.g. ducts and at (oil, gas) exploration rigs.

6. PITFALLS IN COMMERCIAL ACTIVITIES.

The Reactor Institute has also been active in the color enhancement of topaz gem stones by reactor irradiation. In the 1980s the technology of changing the color of topaz stones from worthless colorless to more valuable blue was implemented at IRI and approaches were found to limit the induced radioactivity of impurities. Customers providing the colorless stones were attracted resulting in a large-scale activity.

A dedicated irradiation facility was constructed as well as an automatic device in which, upon pre-defined cooling, the radioactivity of each individual stone could be assessed and the stones could be sorted as well. It all involved a considerable investment by the institute, which was accounted for via the contract with the supplier. However, but the early 1990s the market for topaz gem stones collapsed; the supplier got bankrupt and the institute had to shut down its operations. In addition, the supplier had no funds anymore to pay for the several kilograms of irradiated gem stones which remained, hitherto, stored in the institute's vaults.

Organizations seeing commercial marketing of their regular activities –as with nuclear techniques- should realize that it introduces also some vulnerability. Another example was already outlined in the above, for INAA of plastics. National regulations prescribed explicitly INAA as method of preference and for many years thousands of samples were analysed annually by INAA for the Cd content. However, desktop XRF machines became available with satisfying performance for screening purposes, and this approach took largely away the market for INAA.

Another example deals with use of INAA for the determination of trace elements in soil using large sample INAA [12]. Here, though convinced of the benefits of large sample INAA, decision makers decided not to prescribe this method so as to avoid that the Reactor Institute would have a national monopoly position for such assays.

7. MARKETING, PUBLIC RELATIONS AND QUALITY ASPECTS.

Scientists and especially university academics generally do not stand out by strictly keeping to deadlines. This is one of the main cultural changes, required for success in commercial activities. Time for reporting belong, together with price, to the first points of discussion in contacts with third parties.

Marketing of the business activities for INAA were already in an early stage (1980s) supported by the 'contract bureau' of the Delft University. The first support dealt with advice on the preparation of hand-outs for use when operating a booth at fairs and exhibitions. Training in commercial application and approaching visitors at fairs also were taking into account.

In the 1990s more professional help was provided in the preparation of brochures. This was eye-opening regarding the type and style of information (text and pictures) to be displayed. This all was another cultural change: public information on INAA should contain not the scientific description and typical advantages of the techniques, but requires anticipation on the perception by potential clients. The photographs in the brochures were made by a professional in advertisement, who selected himself the photogenic parts of the laboratory, even if they were scientifically irrelevant.

Cost analysis has been a continuous point of discussion. The university developed general guidelines (like hourly rates, depreciation rules etc) for calculating the costs of its services. Several unresolved specific cases remained, such as the costs of equipment shared for research and for services; accounting for equipment that already passed the formal depreciation term; accounting for compensation 'in natura' by universities, e.g. via co-authorship of publications. The cost of the neutrons was never decided on by the institute's management and left-out from the calculations. In general, a certain degree of opportunism was often included in the price negotiations; also taking into account the tariffs set by other laboratories offering analytical services (like AAS, ICP, XRF). The situation changed a little, as outlined in the above, when by the turn of the century the university accountants advised the institute's management to develop a tariff structure for INAA strictly applying the university rules. It would have raised the analysis price for third parties by 300 %, which would completely put out of action. Therefore, it was decided to turn from pure commercial industry oriented services towards services in the frame of scientific collaborations.

The absence of a tariff structure for the use of the reactor neutrons also affects the cost estimation in radionuclide production. Projects, like the ones outlined above, were typically financed at mutual consent, largely covering either labor costs (for production of radionuclides to be used by the customer himself) or instrumentation costs (when the application took place at the institute).

Finally, a management infrastructure focused on quality appeared to be essential to reduce running costs by improving the efficiency and effectiveness of the operations. Implementation of a quality system, following the ISO/IEC 17025:1999, with associated accreditation, is nowadays often inevitable [5] for testing laboratories to be competitive with other analytical laboratories offering routine services, whereas many ISO 9001 certified companies often only sub-contract analyses to a laboratory that is accredited. It can be shown that the additional costs of quality system implementation and accreditation are rapidly 'paid back' from the reduction of costs of non-quality.

8. FINAL REMARKS

There are several opportunities to make nuclear analytical techniques available to society, and to demonstrate the socio-economical benefits. In fact, the various activities by the Radiochemistry department of the Reactor Institute in Delft were often embraced by the Institute's management for public relation purposes and to improve the public view, e.g. of the citizens of Delft, on the viability of the nuclear institution and its research reactor.

There seems to be a worldwide tendency in universities to have regularly drastic changes of the organizational structure, of mission statements, policies and priority areas. Building confidence and credibility as a trustworthy partner in commercial communications may be strongly affected by this.

Radiotracers, especially those with half-lives in the order of hours to a few days, offer unique opportunities for field application and use on-site in e.g. chemical industry. The success of such applications depend entirely on the national regulations for licensing the use of radioactivity.

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EVALUATION OF TRACE METALLIC IMPURITIES IN ELECTRONICS-GRADE SILICON

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Abstract

Electronics-grade silicon is the fundamental building material for semiconductors, which in turn, are vital components of virtually all electronics goods, including computers, telecommunications products, and consumer electronics. Rapidly increasing complexity of the modern semiconductor devices is driving today's silicon materials to ever more stringent specifications. Ultra-high purity of electronics-grade silicon is one of the key requirements. Reliable operation of semiconductor devices limits the contents of the critical metallic impurities to the levels of 1E+10 at/cm^3 in the bulk and 1E+10 at/cm^2 on the surface of silicon wafers on which the devices are fabricated. This imposes very strong demand for highly sensitive analytical methods that can be used by silicon and device manufacturers at the process development stage as well as for on-line process control. After a brief overview of the current trends of the silicon market our presentation will focus on the properties of metallic impurities in silicon and the potential sources of contamination during the manufacturing process. Currently available analytical methods, capable of measuring trace metallic impurities both in the bulk and on the wafer surface, will be discussed in details. Special emphasis will be put on the strengths and limitations of the neutron activation analysis, the method that has been widely used for the evaluation of bulk impurities in silicon.

1. WORLD MARKET OF ELECTRONICS-GRADE SILICON MATERIALS

Since the invention of the first semiconductor integrated circuit (IC) in 1958, silicon has been the dominant material in the rapidly developing semiconductor industry. Today, polished and epitaxial silicon wafers, manufactured from Czochralski-grown silicon (CZ-Si) single crystals, are used as starting materials (substrates) for majority of semiconductor devices, including discrete devices, Logic ICs, ASICs, DRAMs, MPUs, etc. A number of discrete devices or IC chips are simultaneously fabricated on a silicon wafer. In order to attain more chips per wafer, silicon wafers of an ever larger diameter have been demanded by semiconductor manufacturers. In early 1960-ies ~25-mm (1-inch) silicon wafers were commercially available, while today's most advanced ICs are produced on 300-mm wafers. It is expected that in the next decade silicon wafer diameter will reach 450 mm. Tables I-III overview the current status of the world silicon market. There is no doubt that in the coming years silicon will retain its position as the most important material in the semiconductor industry.

TABLE I. YEAR 2003 WORLD REVENUES OF SILICON-BASED INDUSTRIES [1].

Industry	Products	Year 2003 Revenue
Polysilicon Industry	Chunks and rods of polycrystalline silicon – the raw materials for the manufacturing of silicon single crystals.	US$0.6 Billion
Silicon Wafer Industry	Silicon single crystals grown by Czochralski or Float-Zone methods. Nonpolished, polished and epitaxial thin round discs (wafers) sliced from single crystals.	US$5.8 Billion
Semiconductor Industry	Semiconductor components: microprocessors, memory chips, logic chips, discrete devices.	US$160 Billion
Electronics Industry	Electronics goods: computers, telecommunications products, consumer electronics.	US$900 Billion

TABLE II. YEAR 2003 WORLD PRODUCTION OF SILICON WAFERS [1].

Wafer diameter	Number of wafers per month
100 mm	818,000
125 mm	1,740,000
150 mm	4,440,000
200 mm	5,270,000
300 mm	433,000

TABLE III. HISTORICAL SILICON DATA [2].

Yearly Shipments of Silicon Wafers [Millions of Square Inches]				
Year	Nonpolished	Polished	Epitaxial	Total
2000	278	4,133	1,141	5,552
2001	188	2,972	780	3,940
2002	217	3,521	943	4,681
2003	224	3,812	1,111	5,147

2. KEY QUALITY REQUIREMENT – HIGH PURITY OF SILICON WAFERS

Over the years, due to rapidly increasing component density and device complexity, both ICs and their fabrication processes have been proving more and more sensitive to starting-material characteristics. These, as well as the increased wafer diameter, are driving today's silicon wafers to ever more stringent specifications (Table 4). One of the most important quality requirements is ultra-high purity of silicon wafers. The International Technology Roadmap for Semiconductors (ITRS) enforces very severe limits on metallic impurities in the bulk and on the surface of silicon wafers [4].

The primary detrimental effect surface metals have on the device performance is the reduction of the breakdown voltage of gate oxides. Critical surface metals are grouped into three classes: (a) Mobile metals which may be easily cleaned such as Na and K; (b) metals which dissolve in silicon or form silicides such as Fe, Ni, Cu, Cr, Co; and (c) major gate-oxide-integrity (GOI) killers such as Ca. The target value listed in Table 4 is the limit for each of the above metals. In the past roadmaps, metal contamination targets have been based on an empirically derived model predicting failure due to metal contamination as a function of gate oxide thickness.

Each new device generation set more stringent impurity targets. The value of 1.2E+10 at/cm^2 was the limit for the Technology Node (TN) of 130 nm, whereas TN = 30 nm set the target of 3.4E+09 at/cm^2 [2000 ITRS]. However, the oxides used in the experiments from which this model was derived were far thicker than gate oxide thicknesses used today. Thus, current target value of 1E+10 at/cm^2 is based on new empirical data. The targets are left constant for future years due to the absence of an appropriate model.

The potential sources of surface metallic impurities during silicon manufacturing process include tools used for the wafer shaping, wafer handlers, polishing slurry, chemicals used for wafer etching and cleaning as well as clean-room environment. The contamination with metallic impurities is especially pervasive during high-temperature treatments of silicon wafers, which include thermal oxidation, polysilicon deposition, hydrogen annealing, and epitaxial layer growth. Total bulk content of Fe impurity allowed in both currently produced and future Si wafers can not exceed the level of 1E+10 at/cm^3 (0.2 ppta) (Table IV).

Although ITRS does not address other bulk metallic contaminants, it is widely accepted in the silicon community that the requirement of ≤ 1E+10 at/cm^3 stands for all bulk metallic impurities recognized as having highly detrimental effect on the device performance. They include mainly Zn and 3d transition metals such as Cr, Fe, Ni, and Cu. The primary electrical effect of bulk metallic impurities is the introduction of energy levels close to the center of the bandgap of silicon. Since these levels act as effective recombination centers, metallic impurities cause a decrease in minority carrier lifetime and an increase in the leakage currents of p-n junctions. They also enhance the formation of extended lattice defects such as oxidation stacking faults (Table IV). 3d transition metals in silicon exhibit very high interstitial diffusivities with small migration barriers (Table V). Copper is mobile even at room temperature; it can move across silicon wafer (~600 μm) within a few days. High electrical activity and unusual physical properties of 3d elements make them critical metallic impurities both in the bulk and on the wafer surface [5, 6]. Metallic impurities can be incorporated into silicon bulk during the crystal growth. Polycrystalline silicon raw material, quartz crucible and graphite parts of the puller are the potential contamination sources during the Czochralski growth process. Impurities may also diffuse from the wafer surface into the bulk at elevated temperatures.

TABLE IV. STARTING MATERIALS TECHNOLOGY REQUIREMENTS (SELECTED ITEMS) [3].

Year of Production		2001	2004	2007	2010	2013	2016
Generation of Semiconductor Devices							
Technology Node (nm)		130	90	65	45	32	22
MPU Physical Gate Length (nm)		65	37	25	18	13	9
Silicon Wafer Characteristics (99% Chip Yield)							
Wafer diameter (mm)		300	300	300	300	300	450
Edge exclusion (mm)		3	2	2	2	2	2
Site flatness (nm)		≤ 130	≤ 90	≤ 65	≤ 45	≤ 32	≤ 22
Front surface particles	Size (nm)	≥ 90	≥ 45	≥ 33	≥ 23	≥ 16	≥ 11
	Number per wafer	≤ 123	≤ 164	≤ 77	≤ 77	≤ 47	≤ 95
Critical surface metals (at/cm^2)		≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10
Oxidation stacking faults (cm^{-2})		≤ 1.0	≤ 0.5	≤ 0.3	≤ 0.2	≤ 0.1	≤ 0.1
Total bulk Fe (at/cm^3)		≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10	≤ 1E+10

TABLE V. BASIC PROPERTIES OF CRITICAL BULK METALLIC IMPURITIES IN SILICON [4].

Element	K_0	C_0 (at/cm^3)	D_0 (cm^2/sec)	Q (eV)	L (μm)
Zn	~ 1E-05	6E+16	1E-01	1.40	325
Cr	1.1E-05	–	1E-02	1.00	622
Fe	8E-06	3E+16	1.3E-03	0.68	972
Ni	3E-05	8E+17	2E-05	0.47	3100
Cu	4E-04	1.5E+18	4.7E-03	0.43	5800

Where:
K_0 – equilibrium segregation coefficient;
C_0 (at/cm^3) – maximum solid solubility;
D_0 (cm^2/sec), Q (eV) – diffusion constants;
L (μm) – one-hour diffusion length at 1000°C.

3. METALIC IMPURITY ANALYSIS

In order to comply with the quality targets, intensive evaluation of metallic impurities in silicon materials is required throughout development and optimization of process steps as well as for process control. Each evaluation method must provide multi-element analysis with very high sensitivity and accuracy. Other highly desired features of the method are simplicity of operation and on-line analysis capability.

Table VI briefly describes the analytical methods currently used for the evaluation of surface metallic impurities on the silicon wafers. They include:

- TXRF (Total Reflection X-Ray Fluorescence);
- VPD – TXRF (Vapor Phase Decomposition – Total Reflection X-Ray Fluorescence);
- VPD – AAS (Vapor Phase Decomposition – Atomic Absorption Spectroscopy);
- VPD – ICP-MS (Vapor Phase Decomposition – Inductively Coupled Plasma Mass Spectroscopy).

In the past several years TXRF has become widely accepted as a powerful method available for detection of elemental surface contaminants on silicon surfaces. Total reflection X-ray spectrometers, commercially available from the companies such as Atomica Instruments, Rigaku, and Technos, are typical on-line operating tools. Atomica's spectrometers operate under ambient conditions with sealed X-ray tubes and with the high throughput (the measurement of one wafer takes a few minutes). The tools provided by Rigaku and Technos operate under vacuum conditions. Due to that they have lower throughput (only a few wafers per hour can be measured) but offer higher sensitivities. All commercially available spectrometers are fully automated. Production personnel can easily learn how to operate them. The major disadvantage of TXRF is its inability to detect metallic impurities with required sensitivities.

Nowadays, Vapor Phase Decomposition (VPD) method in combination with TXRF (VPD – TXRF) is quickly becoming the industry standard for surface analysis of silicon wafers with contamination levels below 1E+10 at/cm^2. Compared to straight TXRF it is more sensitive by a factor of over 100 and provides information about the total wafer surface. Fig. 1 explains the principle of VPD. Gaseous HF decomposes native or chemical oxide that covers the surface of analysed silicon wafer. Then the ultra-pure 100 to 200µl droplet composed of HF and H_2O_2 scans the entire wafer surface collecting metallic impurities. Finally, TXRF evaluates the residue formed locally on the wafer surface after the contaminated droplet is dried. Automatic VPD tools are now commercially available.

Metallic impurities inside VPD droplets can be also analysed by means of typical chemical methods such as AAS and ICP-MS. VPD – ICP-MS is the unique method providing reliable evaluation of all critical surface metals with record sensitivities of below 1E+8 at/cm^2. However, the measurements are very difficult and require the personnel to be highly trained. The method also needs very advanced clean-room facilities and is thus inappropriate for on-line analysis. VPD – ICP-MS is most suitable at the process development stage as well as a reference method for TXRF and VPD – TXRF tools. Evaluation of critical bulk metallic impurities with required sensitivities is far more complicated. Available techniques are described in Table VII. They include:

- DLTS (Deep-Level Transient Spectroscopy);
- µ-PCD (Lifetime measurement method – detection of the photo-conductive decay by microwave reflection);
- ELYMAT (Lifetime measurement method – measurement of the photo-current collected by a silicon-electrolyte contact).

- SPV (Surface photo-voltage method. This is lifetime measurement method, in which the variation of surface potential upon illumination is measured versus different light wavelengths;

4. INAA (INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS).

DLTS is a very powerful method for study of deep levels in the silicon bandgap. Assuming that all impurities stay in their basic active state DLTS is capable of measuring their concentrations with the sensitivities close to 1E+10 at/cm^3. In practice, however, DLTS proved itself to be useful for Fe evaluation only. Difficulties with sample preparation and data analysis make DLTS useless for on-line impurity evaluation.

μ-PCD, ELYMAT and SPV are all measuring lifetime of minority carriers in silicon. These methods are highly sensitive to metallic impurity content. They have short measurement time and provide the full wafer mapping capabilities. Nevertheless, they are just the qualitative methods used to detect the possibility for increased impurity content, with the exception of SPV measurements of boron-doped silicon wafers, where it is possible to identify and quantify Fe impurities by optical splitting of FeB pairs. Fe concentration in the silicon wafer bulk can be determined with the sensitivity of 4E+09 at/cm^3. Among lifetime techniques, SPV method is also the simplest one; it does not require special surface passivation (like μ-PCD) or use of chemicals (like ELYMAT). As a result, commercially available SPV tools are widely used for on-line process control.

INAA is currently the only method, which provides element specific, quantitative information about bulk contamination of silicon materials, both in the raw polycrystalline and single crystal silicon. It has been used for years for that purpose. However, recent improvements of the silicon purity have put in question further intensive usage of INAA. Comparison of INAA sensitivities between various labs (Table 8) suggests that even highly optimized measurement procedures do not offer the required sensitivities for all critical metallic impurities. This is especially the case with as-grown silicon single crystals, where metallic impurity content rarely exceeds the level of 1E+10 at/cm^3. This is also the case with majority of today's polysilicon materials, where trace metallic impurities can hardly be detected by means of INAA. Nevertheless, polysilicon manufacturers continue using INNA for periodic quality check of their products. Insufficient sensitivity, limited capacity, too long turnaround time and high price of INAA measurements force silicon manufacturers to look for alternative methods.

TABLE VI. ANALYTICAL METHODS USED FOR THE EVALUATION OF SURFACE METALS ON SILICON WAFERS.

Method	Detection Limits (at/cm^2)	Advantages	Disadvantages
TXRF	~1E+13 (Na) ~2E+11 (K, Ca) 1÷5E+10 (Cr, Fe, Co, Ni, Cu)	- Simple operation - Fast on-line analysis	- Low sensitivity
VPD – TXRF	~1E+11 (Na) 1÷8E+08 (Other critical metals)	- High sensitivity to most impurities - On-line analysis	- Low sensitivity to Na
VPD – AAS	1÷5E+09 (All critical metals)	- High stability	- In-lab analysis
VPD – ICP-MS	≤1E+08 (All critical metals)	- High sensitivity to all impurities	- In-lab analysis - Difficult, needshighly trained personnel

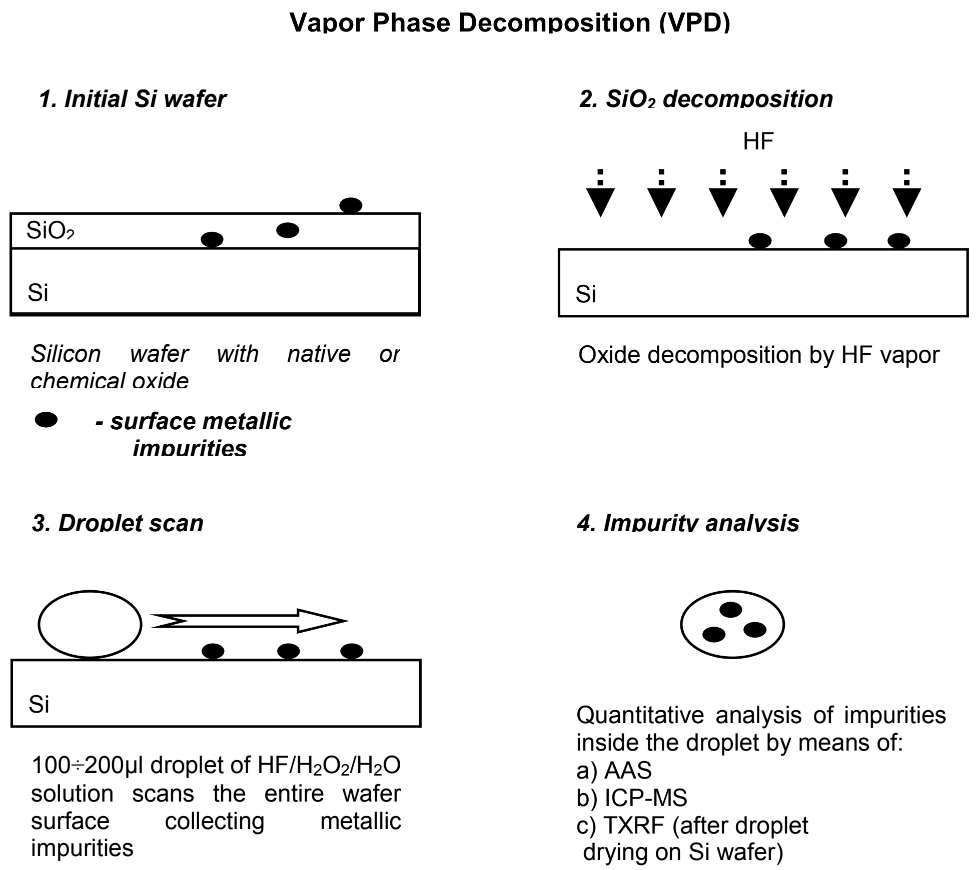

FIG. 1. Principle of Vapor Phase Decomposition (VPD) method.

TABLE VII. ANALYTICAL METHODS USED FOR THE EVALUATION OF BULK METALS IN SILICON.

Method	Detection Limits (at/cm^2)	Advantages	Disadvantages
DLTS	>3E+10 (Fe) (Potentially for all critical metals assuming they are electrically active – rare case for Cu and Ni)	- None	- In-lab analysis - Measures exclusively electrically activemetals - Difficult preparation of samples - Difficult data analysis
µ-PCD ELYMAT	NA	- High sensitivity to overall contamination - Wafer mapping	- Qualitative methods
SPV	4E+09 (Fe) NA (Other critical metals)	- High sensitivity to Fe - On-line analysis	- Fe can be measured in B-doped wafers - Qualitative method for other impurities
INAA	2E+10 (Zn) 8E+09 (Cr) 3E+11 (Fe) 1E+11 (Ni) 4E+11 (Cu)	- Multi-element analysis - Measures total content of each element - Simple preparation of samples	- Low sensitivity to Fe, Ni,Cu - Out-fab analysis - Limited number ofsamples - Long turnaround times - Expensive

TABLE VIII. INNA SENSITIVITIES FOR BULK CRITICAL METALS AT VARIOUS LABORATORIES.

Element	INCT		MURR		GeMeTec	
	pptw	at/cm^3	pptw	at/cm^3	pptw	at/cm^3
Zn	45	1E+12	45	1E+12	0.7	2E+10
Cr	20	5E+11	20	5E+11	0.3	8E+09
Fe	300	8E+12	800	2E+13	10	3E+11
Ni	200	5E+12	400	1E+13	4	1E+11
Cu	30	6E+11	30	6E+11	20	4E+11

Where:

INCT – Institute of Nuclear Chemistry and Technology (0.2÷5g specimen, 240 hrs irradiation, 1E+14 $n \cdot cm^{-2} \cdot sec^{-1}$ thermal neutron flux);

MURR – University of Missouri Research Reactor (15g specimen, 40 hrs irradiation, 2.5E+13 $n \cdot cm^{-2} \cdot sec^{-1}$ thermal neutron flux);

GeMeTec – Gesellschaft für Meßtechnik und Technologie mbH, Munchen (1500g specimen, 48 hrs irradiation, 1E+13 $n \cdot cm^{-2} \cdot sec^{-1}$ thermal neutron flux);

5. SUMMARY

Currently available analytical methods, capable of measuring trace metallic impurities both on the surface and in the bulk of silicon wafers have been presented. It has been pointed out that VPD – TXRF is becoming the industry standard method for surface metal evaluation, mostly due to its high sensitivity, operation simplicity, and on-line process control capability. Although neutron activation analysis still maintains its position of being the only quantitative element-specific method for bulk impurity analysis, INAA's insufficient sensitivity makes its further applicability uncertain.

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SELF-RELIANCE AND SUSTAINABILITY OF NUCLEAR ANALYTICAL LABORATORIES IN SMALL STATES OF CENTRAL EUROPE: THE SLOVENIAN CASE

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Abstract

The Laboratory for Radiation Measuring Systems and Radioactivity Measurements belongs to the "Jožef Stefan" Institute, which is the largest national research institution in Slovenia, housing also several other nuclear analytical laboratories. The service the Laboratory provides and its customers are briefly described, as well as the role of the regulatory bodies in providing the service. The compatibility of the interests of the regulatory bodies and the national nuclear institutes is described, as well as the actions that have to be performed by both of them to secure their interests. As a result the nuclear analytical laboratories, which form part of the Institute attain an opportunity to achieve self-reliance and sustainability.

1. INTRODUCTION

The "Jožef Stefan" Institute is the largest research institution in Slovenia devoted to research in many fields of science and technology. Within the Institute several nuclear analytical laboratories operate, making it the largest nuclear research institution in Slovenia. The Laboratory for Radiation Measuring Systems and Radioactivity Measurements belongs to the Department for Medium and Low Energy Physics, which is engaged mainly in nuclear physics, interactions of radiation with matter and its applications, and in providing a service in radiation measurements and dosimetry. The laboratory was founded almost thirty years ago, when the three accelerators, which formed the basis of the research infrastructure of the department, came to the end of their working lives. The personnel took the opportunity to participate in the programme of radioactivity monitoring of the Krško Nuclear Power Plant, which at that time went into operation. The equipment, i.e. the detectors, electronics and computers, was available, but the expertise was limited to the techniques of measurement and analysis in gamma ray spectrometry. The absence of the expertise in radiochemistry was a serious drawback, therefore new methods in detector calibration had to be developed. In the following years the laboratory participated not only in the monitoring programme of the nuclear power plant but also in other radioactivity monitoring programmes in Slovenia. Since its foundation the laboratory did not receive any financial support either from the state or from the department. Support in equipment and expertise was received from the International Atomic Energy Agency, the Government of the United States and the United Nations Development Programme.

The laboratory is engaged mainly in gamma ray spectrometric measurements of samples from the natural, living and working environments. The main customers are the Krško Nuclear Power Plant and governmental organizations and agencies. The work for these customers is performed under contracts lasting at least one year. The main customer is the nuclear power plant, which accounts for about 80% of the income.

The Laboratory is not the only provider of services in gamma ray spectrometry either within the Institute, or in Slovenia. Therefore it is exposed to the pressures of the competitive market, but also to pressures originating from informal ties between the users and other providers of the monitoring service. It should be observed that in a small country the influence of such ties is more important relative to the influence of the market than in larger countries, where the size of the market provides more opportunity for substitution or acquisition of new customers. The large share of one customer in its income makes the Laboratory extremely vulnerable. It should be observed as well that Slovenia has become a member of the European Union and therefore its market is open to competitors from abroad.

2. THE MARKET IN SLOVENIA

The monitoring of radioactive contamination in the environment is carried out mainly according to prescribed monitoring programmes. The financing of general monitoring is provided by the Ministry of Health and the Ministry of Environment, Spatial Planning and Energy. Site-specific monitoring programmes refer to facilities, that are permitted to emit radioactive substances to the environment. The size of the programme is related to the expected activities released and the influences of the emissions on the population and environment. Besides the nuclear power plant, the Uranium Mine in Closure, the Reactor Centre, managed by the "Jožef Stefan" Institute, and the Central Interim Storage for Low and Intermediate Level Waste, managed by the Radwaste Management Agency, operate site-specific monitoring programmes. The costs of all programmes together amount to approximately 900,000 € annually but the sum is likely to drop below 700,000 € in the near future.

All programmes have to be approved by the regulatory bodies. The statutory regulatory bodies, for radioactivity are the Slovenian Nuclear Safety Administration and the Slovenian Radiation Safety Administration. Besides approving, the regulatory bodies report yearly on the monitoring results to the National Assembly. As a consequence, the end users of the results of the monitoring programs, beside the operators of the facilities, are also the regulatory bodies. It is therefore in their interest to maintain a high quality of the programmes. On the other hand, the operators are free to choose the provider of the monitoring service, as long as the provider complies with the specifications of the programme.

Besides monitoring programmes the possibilities to use gamma ray spectrometric measurements for other purposes are small. These are mainly related to food control and small contracts with the regulatory bodies, aimed at specific radiological or radioecological projects. At the time being there are two providers of gamma ray spectrometric measurements in Slovenia which are accredited, one a public research institute and the second a private company. It was the policy of the large customers to maintain two providers of the monitoring service in order to prevent monopolistic behaviour. After joining the European Union, this policy is likely to change, exposing the providers from Slovenia to competition from providers from other member sates.

However, the possibility of loosing both Slovenian providers would leave the regulatory bodies and also operators of nuclear installations without expertise at hand in many fields of radiation measurement, especially the expertise needed in event of an emergency. It is therefore not in their interest to loose both providers, but they may sacrifice one in order to keep the prices as low as possible.

3. THE PROTECTIVE MECHANISMS

As was shown, the Slovenian market for gamma ray spectrometric measurements is small and divided between two providers of the service. The capacities of the personnel and the equipment are therefore not fully engaged which incurs additional costs to the service. Both providers are therefore vulnerable to competition, especially to low-price offers from other member states of the EU.

To protect local expertise connected with the provision of environmental monitoring services, the regulatory bodies are inclined to set up protective barriers in order to prevent low-price competitors from abroad successfully tendering for their offers. The kind of barriers they are prepared to set up promote the quality of the expertise they expect from the providers of the monitoring service. They are therefore inclined to set high standards for the quality of the service. On the other hand, the providers accept the quality imposed in order to decrease their vulnerability.

It should be observed that this process mimics the situation which occurs in service to industry. In contrast to the measurements performed for industry, where the demand for quality is high, the quality in control measurements, such as measurements performed within prescribed monitoring programmes, is defined in the legislation. The motivation for requesting a high quality of service in the legislation on one hand and preparedness to offer or even surpass the requested quality on the other hand introduces a working regime similar to that in industry. Here a kind of synergy can be identified resulting in a high quality of the service and better sustainability of the providers of the service.

National nuclear research institutions are capable of meeting the high standards because of their expertise in research in the nuclear field and their traditions. Because of their broad capabilities, as compared to private companies, the regulatory bodies regard them as natural partners in managing the technical aspects of radiation monitoring such as checks of equipment of the providers of the service, assessment of the quality of their systems, design of the system of control measurements, assessment of the quality of results, advising in case of changes of legislation, etc. Their main drawback with respect to private companies is their smaller possibility to influence the costs, but here their corresponding advantage is their smaller motivation to make a profit, because they are not free in allocating it.

The protective mechanisms are a set of criteria, which the providers can fulfill but on the low-price competitors they are posing additional costs, therefore they must increase their prices. The barriers, set up to reduce the pressure of competitors from abroad, can be structured in analogy to the main virtues which the customers prize when evaluating suppliers of goods: price, quality, delivery time, service. All requirements for these properties, except the price, can be incorporated in some kind of regulation. The quality can be described by the minimum detectable activities for radionuclids, which are rarely detected, relative uncertainties for radionuclides which are often detected, by prescribing minimal technical requirements for the equipment, requiring participation in proficiency tests, prescribing minimal success in these tests, etc. The requirements characterizing the conditions of reporting, which represents the delivery, may comprise the form and content of the reports (reporting uncertainties, dose estimates), requirement to report the activities of all radionuclei recorded in the spectra, conditions when special reports must be submitted (e.g. in the case of increased concentrations or detection of new radionuclides) etc. In the case of monitoring the service represents the ability of the provider to assist the customer in the case of unforeseen events or to support him in performing other tasks related to monitoring of radioactivity. Requests the regarding service can be expressed in terms of the number of measurements which the provider must be able to perform in addition to the contracted measurements, the competence of the personnel, etc.

The criteria, used by regulatory bodies for evaluation of the providers, increase the efficiency of the protection. By requesting fulfilment of high criteria for the quality of monitoring, reporting and the ability to service other needs of the costumer, the protection of one provider is not absolute, since other providers may be able to fulfill the criteria. Therefore the providers, or the institutions where they reside, must undertake actions on its own to decrease their vulnerability.

4. THE NATIONAL NUCLEAR INSTITUTES

Traditionally, national nuclear institutions are research oriented. They may maintain close contacts with universities to participate in the education process. The environment is academic and therefore important criteria for promotion of personnel are related to the number of publications, mentorship of graduate and postgraduate students and other measures of excellence in research. Personnel may be not motivated to engage in activities where the main burden of work lies in performing routine tasks such as sampling, sample preparation and measurements. Also the management of national nuclear research institutions may be in doubt whether these activities belong to an organization which is primarily devoted to research.

Since it is not expected that the national nuclear institutes will adapt the criteria for evaluation of the nuclear analytical laboratories the described situation poses an additional pressure on the laboratories providing services related to monitoring of radioactivity. To demonstrate their compatibility with the environment in which reside, their activities must result in achievements, which the academic sphere prizes. One possibility is to keep the quality of their work at a level which enables its publication. As the result, not only the recognition of their peers is attained, but also the vulnerability is smaller since the quality of the service and the reputation of the laboratory are improved.

In order to demonstrate the compatibility of the engagement of the Laboratory for Radiological Measuring Systems and Radioactivity Measurements with that of the Institute, it was decided not to rely on standard methods in gamma ray spectrometry during the process of acquiring accreditation according to the ISO 17025 standard, but to develop original methods. As the result, the scientific output of the laboratory was extremely high when compared with other laboratories of similar size within the Institute on the basis of bibliographic criteria. In addition to that, a broad scope of accreditation was achieved, namely measurements the activity of any gamma- or X-ray emitters in homogeneous cylindrical samples of any homogeneous material.

Similar to the scientific and technical performance, the business performance can be improved as well. But here it has to be taken into account that the education of the personnel in national nuclear institutes is mainly technical therefore it may not possess the necessary knowledge and skills. It can be observed that the ISO 17025 standard requests some elements of good business practice to be implemented. To expand the knowledge the laboratory management already acquired during the accreditation process in a broader framework and to increase their competence, education and training of the laboratory management may often be necessary. The corresponding courses should build on the requirements of the ISO 17025 and ISO 9001 standards, since these represent the basis of the existing knowledge of laboratory management. Here the International Atomic Energy Agency could provide the necessary opportunities for acquisition of relevant knowledge.

Other actions aimed at reducing the vulnerability of nuclear analytical laboratories require deeper adaptation of the organization of the national nuclear institutes. Reducing the price, for instance, is difficult for public organizations since they lack many possibilities to reduce the costs of the service.

5. CONCLUSION

National nuclear institutes are often research oriented public organizations with extensive expertise in radiation measurements, dosimetry and metrology of ionizing radiation. In small countries a large part of the national capabilities, which can provide the service and expertise in the fields of use of radioactivity and ionizing radiation, resides in such national nuclear institutes. Therefore they represent a valuable asset for the regulatory bodies which are authorized for radioactivity and ionizing radiation. These bodies are in charge to assure the compliance of the practice with the requirements in the legislation. As a consequence, the regulatory bodies are prepared to support the aims of national nuclear institutes to maintain their capabilities and to increase the quality of the service and the expertise related to the use of radioactivity and ionizing radiation. The national nuclear institutes, on the other hand, must be able to promote the quality of service and to offer their capabilities to the regulatory bodies and other external users under conditions which are compatible with that of the free market. In this way the nuclear analytical laboratories, which are part of the national nuclear institutes and are engaged in providing the service and expertise, can achieve and maintain self-reliance and sustainability.

COMMERCIAL APPLICATIONS OF NUCLEAR ANALYTICAL TECHNIQUES AT THE OFFICE OF ATOMS FOR PEACE, THAILAND

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Abstract

The Office of Atoms for Peace (OAP) is the government research institute under the Ministry of Science, Thailand. It is a nonprofit organization aiming to promote nuclear technology in Thailand. From the fiscal year 2001-2004, 90% of the revenue was from the government support; only 10 % is from providing services. Out of this 10 percent service charge, only 25% is from the nuclear analytical services. The services include: NAA, XRF certification of radioisotopes for export goods, radiation certification of packaging for export, and radio-tracer applications in industry. At present, the fee for analytical services are calculated based on variable cost. Our future trend shown that there are not much local competitors and the services fee should be readjusted. The future projection for commercial applications of NAT at OAP will also be presented.

1. INTRODUCTION

The Office of Atoms for Peace (OAP) found on April 26, 1961 is a research institute under the Ministry of Science and Technology, the Royal Government of Thailand. It is a non-profit government organization responsible for research development, service of nuclear technology and regulation of nuclear technology utilization. major responsibilities are to provide recommendation and strategic planning to the government on the peaceful use of nuclear technology, to regulate the use of technology for safety of the Thai people, to perform research and development on nuclear technology through proper management of nuclear energy, to regulation for safety use of radiation and nuclear energy to fulfill the mutual agreement with other countries and to meet the international standards.

The OAP will be separated into 2 organizations, Office of Atoms for Peace (OAP) and Thailand Institute of Nuclear Technology (TINT). The new OAP will still be a government organization which responsible for regulatory issue, meanwhile, the TINT will be a public organization which responsible for research development and service of nuclear technology. However, TINT is still under the Ministry of Science and Technology. The establishment of TINT is under processing and will be finished in the near future.

The OAP has developed such important and profitable strategic alliances with other research centers, nuclear medicine centers, universities that will enable us to cooperate, work along side with them for our research development and utilization of nuclear technology.

The institute has strong links with the IAEA, the UN agency, which is responsible for the peaceful applications of nuclear energy, isotopes and radiation. We has also bilateral agreements, with others nuclear related agencies such as JAERI in Japan, KAERI in Korea, and those in the US. These institutes can give us support not only in research development work cooperation but also technical information exchange.

2. MISSION OF THE INSTITUTE

The OAP's goal is to be the leading organization in research development, provide service in nuclear technology, and also responsible for regulation of nuclear technology utilization in Thailand.

2.1. Organization of OAP

At present, OAP is composing of 5 units which are:

- The Office of Secretary responsible for all administration and procurement.
- Bureau of Radiation safety Regulation
- Bureau of Atomic Energy Administration and Management
- Bureau of Nuclear Safety Regulation
- Bureau of Technical Support for Safety Control

Additionally, there are 7 research programs to carry out the research and development on nuclear technology, providing services and promote the use of nuclear technology to the Thai society. They are:

1. The Radioactive Waste Management Program.
2. The Radioisotope Production Program
3. The Reactor and Nuclear Technology Operation Program.
4. The Radiation and Nuclear Protection Program.
5. The Radiation Research for Agriculture Program
6. The Chemistry and Material Science Research Program
7. The Physics and Advanced Technology Research Program

2.2. Manpower

At present, the OAP have approximately 660 staffs most of which are scientists and engineers. During the past 10 years, we have almost zero growth rates due to the national policy to down sizing in the governmental organizations.

2.3. Facilities and Services

The major facilities as follows:

- 1 MW Research Reactor
- Radioisotope Production facility
- Co-60 Irradiation facility
- Radioactive Waste Management facility
- Secondary Standard Dosimetry Laboratory
- Nuclear Technology Analytical Laboratory
- Non Destructive Testing unit
- Radiation Protection unit

The facilities that enable us to carry on research and development works and also provide R&D products and services such as,

- Radioisotopes and radiopharmaceuticals products
- Food irradiation (gamma)
- Sterilization of medical products
- Gem stones color enhancement by irradiation
- Radioactive waste management
- Radiation protection services
- Radiographic testing for industrial sectors
- Plant mutation
- Sterile insect technique
- Nuclear analytical method

3. NUCLEAR ANALYTICAL METHODS

Several nuclear analytical techniques have been carried out at OAP since the establishment of the institute 40 years ago. OAP provides services as well as R&D by these developed NATs in various fields. The techniques used are gamma, beta and alpha measurement. Natural radioisotopes measurement also received constant request from customers for Cs-137, K-40, Sr-90, Th-232, H-3, C-14 etc. as well as gross gamma and gross beta measurement. Others are for example: neutron activation analysis, EDXRF, WDXRF, LSC measurements. These services can be listed as the decreasing order in the income generated as follow:

- Analysis of radioactivity in export (food) products.
- Nondestructive testing in industries e.g. refinery column scan and radiographic testing.
- Compositional analysis of rocks, soil, fertilizers ores by NAA and XRF. For NAA we are capable for providing services by comparative INAA, RNAA and PGNAA.
- Analysis of natural radioisotopes like radon, tritium, thorium-232, uranium-238, uranium-235 and C-14, and anthropogenic radioisotopes like Cs-137, Sr-90 etc.

3.1. Revenue

Since OAP is a nonprofit organization under the Ministry of Science and Technology, the budget are totally supported by the government. The funding will be provided as fiscal year budget. However, OAP generates some small income from various services. From Table I, the total revenue of OAP from 2001-2003 is about 180 million baht (approximately 4.5 million US$) in which 90% is from the government support. Only about 10% is from providing services in various field of nuclear technology. In the year 2004 higher revenue from the government results from the investment in the investment for the new research reactor at Ongkharak Distric, Nakhon Nayok Province, some 80 km northeast of the present location.

TABLE I. REVENUE OF OAP DURING THE FISCAL YEAR 2001-2004

Fiscal Year	2001	%	2002	%	2003	%	2004	%
Revenue from the government (M-baht)	149.73	88	170.66	90	164.98	90	247.47	92.25
Services and fees (M-baht)	20.77	12	18.36	10	19.04	10	20.80	7.75
Total revenue (M-baht)	170.50	100	189.00	100	184.02	100	268.27	100

Table II demonstrates the revenue from all services compare with those gained from NAT. The results clearly shown that after 40 years of services, OAP gained very small percentages of income from providing services in NAT.

TABLE II. COMPARISON OF TOTAL INCOME FROM SERVICES TO THOSE FROM NUCLEAR ANALYTICAL TECHNIQUES

Fiscal Year	2001	%	2002	%	2003	%	2004	%
Other services and fees (million baht)	17.67	85	15.11	84	15.51	81	17.64	85
NAT (million baht)	3.10	15	2.95	16	3.53	19	3.16	15
Total services and fees (million baht)	20.77	100	18.36	100	19.04	100	20.80	100

3.2. Service fee and customers

Since OAP is a 100% government supported institute, by the regulation, all income generated from various services is considered government income. OAP has to declare these revenues and must return to the Ministry of Finance without any exemption. The service fee has been set up by an OAP committee over ten years ago based on estimated time of analysis multiply by the average salary of the researcher plus some chemicals if needed. The service fees for several NAT are listed in Table III.

TABLE III. SERVICE FEES FOR SERVICES ON NAT

Type of service	Service fee in Thai baht (US$)	Customers
NAA	500 (12 US$) minimum, 300 (7.5 US$) /additional elements	Mining Co., fertilizer Co., SME, traders, etc
XRF	500 (12 US$) minimum, 300 (7.5 US$) /additional elements	Mining Co., fertilizer Co., SME, traders, etc
Gross activity + certificate	700 (18 US$)	Food exporters
Natural radioisotope	700 (18 US$)	Exporters and industrial sectors
C-14 analysis	1300 (35 US$)	Archeologist
H-3 analysis	3000 (75 US$)	Archeologist, dam operator, groundwater studies
Radiographic testing	250-500 (5.5-11 US$) depend on size of sample	Manufacturers
Column scan		Petrochemicals and Refineries

3.3. Competitiveness of NAT

- For elemental analysis, there are other competitive techniques available.
- Some of our products and services are unique because we are the only certified bodies in nuclear field and radioactivity measurement.
- We have a competitive advantage because of our low service fee and good customers relationship.

3.4. Manpower development

At present, OAP personnel received training not only in scientific area, but also in the other areas. To strengthen commercial background, selected OAP workers are being educated in short business course. For example, they are trained to do the swat analysis to see the potential of improving their business skill in order to providing more meaningful outcome from their work and to enhance the job of OAP. From this exercises, several important issues are pointed out for future improvements.

3.5. Conclusion

Even though the main objective of OAP is not providing services, but, if we want to sustain the services in this area, several aspects have to be taken care of. This should include:

- Increase market share and revenue.
- .Build up customer's satisfaction by focusing on quality of the products and services. This can be done by establishing the Good Manufacturing Practice (GMP) and Quality Assurance and Quality Control (QA/QC) in our laboratory. The quality management is established in order to ensure the quality of our products and services.
- Analyse the potential market for our products and services as well as to introduce new R&D products to the market.
- Recalculate of the service fees to reflect the real and up-to-date cost of analysis and gradually adjusted the price accordingly.
- .Develop human resource on business administration and marketing.
- Need strong support from the management level.
- To established a regulations through various strategies: metrology, regulations, standard testing methods etc.
- To strength strategic partners local and aboard. For example, services
- Advertising through web pages

COMMERCIAL NAA – IS IT A SUCCESS? EVALUATION OF A TWENTY YEAR EXPERIMENT

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Abstract

This paper describes experiences gathered over twenty years of running a commercial neutron activation analysis and radiochemistry service in the UK. The service was set up in 1984 following a reduction in government funding to what was then the University of London Reactor Centre. The analytical service was introduced to make up the shortfall in funding required to support the small (100 kW) nuclear research reactor operated by Imperial College London. Initially the work built up slowly, mainly based on mineral exploration, working for a few key customers. As the customer base developed the work became diverse and included everything from small specialist jobs on a few samples to routine analysis of thousands of samples per year, providing an income of several hundred thousand dollars per year. Irradiation facilities were developed for specialist analyses, such as delayed neutron counting, providing further sources of income. Typical jobs, including work for chemical, oil, minerals and nuclear industry, are discussed with a description of how demands have changed over the years. The particular problem of advertising and where to seek customers is a key area for the development of a successful service and this paper includes reference to ways of sourcing business. It also describes how a quality system can be operated with a small team of staff and how staffing levels are maintained with fluctuating levels of work. Finally the paper evaluates the reasons why the income from the nuclear analytical service is no longer adequate to support the operation of the nuclear reactor and discusses the problems that can arise from taking too commercial a view of running a research reactor.

1. INTRODUCTION

Imperial College chose to introduce a commercial NAA service in order to increase income to the Reactor Centre following a reduction in government funds in the early 1980s. At the time there were three university research reactors in the UK plus a number of other reactors capable of carrying out analyses using neutron activation techniques and several offered commercial analyses. Although competition existed it also meant that there were potential customers who were aware of the technique and its capabilities. The work developed slowly, allowing time to increase staff in a step-wise manner to keep pace.

Initially the work was centred on mineral exploration and geochemistry but soon the work became diverse, including chemicals, plastics, catalysts, pharmaceuticals, forensic material, biological samples, food and environmental material. Much of the work was straightforward instrumental neutron activation analysis but some of the most rewarding depended on specialist techniques, such as delayed neutron counting, cyclic activation analysis and radiochemical separation procedures. During the service's busiest period we were processing thousands of samples per year, representing an annual income of several hundred thousand dollars.

2. REASONS FOR 'GOING COMMERCIAL'

There are several reasons why an institution may wish to start analysing samples for industry. The obvious one is to provide an income in direct support of operations, *if that is possible*. Some public organisations do not have the mechanism to benefit directly in this way and it may require a change in mind-set to establish the environment where income can be retained by an organisation for its own benefit. For example, if a university department does not receive overheads brought in by its staff there will be little incentive to gain external income. On the other hand those universities with consultancy businesses, and senior management involved with attracting external funding, will be more accommodating with the way that profit is dispersed and will be happy to see staff involved in consultancy work that is benefiting the institution.

Even if it is not possible for income to be retained, it is important for any institution to support the economy of the country and this can be a real benefit for those establishments with government funding. It can provide an institution with a valuable purpose and raise its profile in a way that may result in further funding in the future, or at least guarantee its survival.

Interactions with industry can generate consultancy work and provide collaborations in support of research. Such contacts have benefited Imperial College in many ways over the years. For example, contacts with the nuclear industry at Imperial College, which began with a request to develop a method for the determination of radioactivity in milk, resulted in a series of research collaborations which included three PhD students, several publications in scientific journals and ten years of commercial work. Similarly development work on chlorine in reactor steels funded research work that resulted in a publication in Analytical Chemistry as well as providing a large source of income for several years. Companies are often happy to see the results of their work published, provided that there are no confidentiality restrictions. On the other hand if there are issues of intellectual property rights, it may not even be possible to discuss the work with others.

Teaching activities can be enhanced by the collaborations with commercial organisations, providing contacts for student visits, external lecturers and potential supervisors for research projects. The MSc in Environmental Diagnosis at Imperial College has over thirty sponsors who offer five month research projects for the students each year. Many of those sponsors are the result of contacts through commercial work and a number of our graduates are now employed by them.

3. IMPLEMENTATION OF THE SERVICE

3.1. Management support

The decision to form a commercial facility is an important step that requires full commitment from the management of the organisation. Support at the very top is essential if the service is to be successful in the long term because it will probably require significant investment. It will take some time to develop sufficiently to be offered as a professional facility and during that time there will be little return for necessary staff investment. Infrastructure will have to be committed by management, including space, equipment and administrative support. In summary, with support from the top the business could flourish, without it, it will definitely not succeed. It is essential to view the venture as a professional business and plan it accordingly.

3.2. Business plan

A proper business plan should include staff, equipment, consumables, irradiations, maintenance and also cover overheads including space. Overheads applied will depend on the organisation, for example 100% on staff costs is used in some UK academic institutions. If a full business plan is developed, costing everything realistically, the price per analysis becomes so high that there can be no possibility of gaining business.

Figure 1 is a breakdown of costs for commercial services at Imperial College in 2002/3. The income that was year was several hundred thousand US dollars and the main costs were staff and associated overheads plus irradiation charges. Reactor charges are based on full economic cost of running the reactor shared amongst users. Typically the irradiation cost per sample is around US$ 50. The overheads are effectively the profit element for the department, to support activities associated with the staff working with the service, including space, radiological protection provision, health and safety and administration. The cost under administration in the pie chart is the fee charged by the College for managing the finances, including invoicing and insurance. This model represents full costs associated with the business.

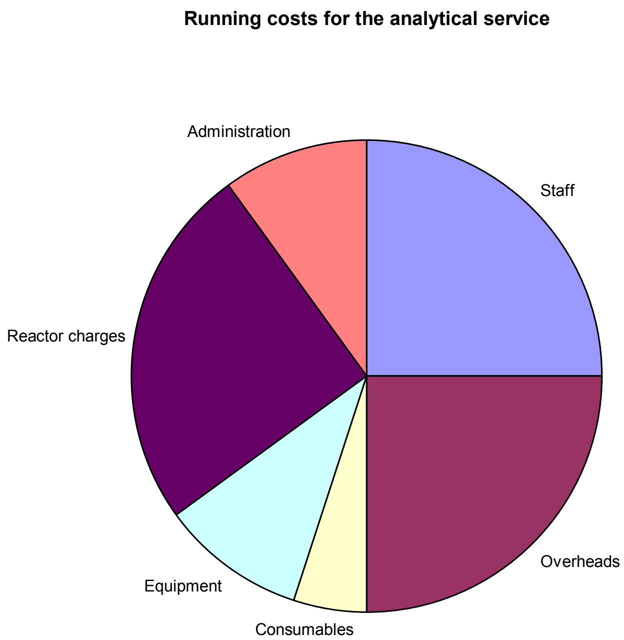

FIG. 1. Typical breakdown of the proportion of running costs for the analytical service.

There are a number of factors such as full economic cost of irradiations that may be shared or avoided all together. Space may be provided by the institution, equipment and staff may be shared. In my experience this is probably the only way that an NAA service can be a commercial proposition.

4. NATURE OF THE WORK

The nature of the work that can be offered as a service will depend on what facilities and skills are available in the organisation. Having a niche is very useful, particularly if it is unique in the country. It is worth spending some time discussing the characteristics of the facility, using workshops and brainstorming methods, to ensure that the ground work is done thoroughly. This should include an understanding of what the organisation wants to achieve and what customers it wishes to target. At Imperial College the NAA service started up just as ICPMS was being commercialised so it was still at the stage where one could offer rare earth element determinations as a straightforward alternative to ICPAES. One would not try to follow that market now, unless there were no commercial organisations offering ICPMS in the country.

4.1. Facilities

It is important to evaluate what facilities are available that can be offered as part of the service. In NAA it is useful to have both instrumental and radiochemical methods available. Specialised techniques such as epithermal NAA, cyclic NAA and delayed neutron counting can be applied to special measurements, plus the use of large sample irradiation devices and prompt gamma ray systems. Figure 2 shows a typical distribution of work broken down by type of analysis.

We are fortunate at Imperial College that we can irradiate liquids, which has been a great advantage over other higher flux reactors. We are also able to irradiate samples in polyethylene for two weeks which makes sample preparation easier in some cases.

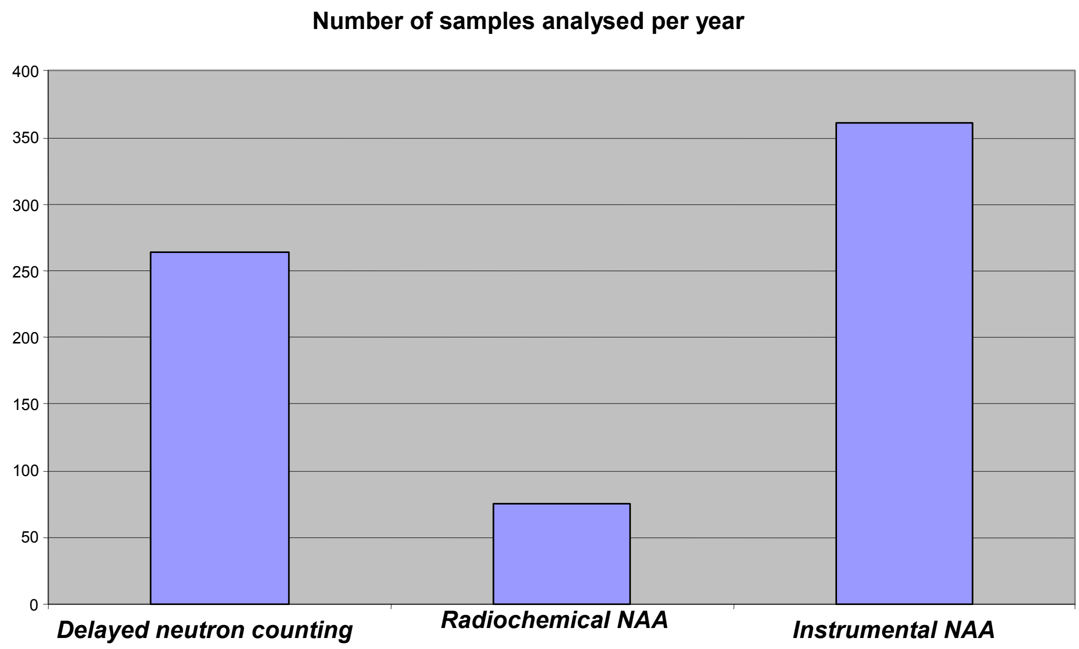

FIG. 2. Typical number of samples analysed per year by type of analysis.

Consideration should be given to what supplementary techniques are available. For example, the ability to handle medical samples safely or having clean room facilities can be an advantage. Crushing and grinding facilities are important for rock analysis and Imperial College implemented fire assay preconcentration at the request of a customer (and at his expense) in order to determine the platinum group elements in exploration samples. Experience in digesting large crop and food samples for analysis is valuable and microwave digestion techniques can be useful. In other words, experience in sample preparation is just as important as the analytical stage.

Having other analytical techniques available in the same establishment is often attractive to customers who want more than one method of analysis. For example, NAA is fine for the determination of heavy metals in environmental samples but if the customer is also interested in lead, then it could be useful to have atomic absorption spectrometry, ICPAES or ICPMS. Companies are happy to visit a 'one stop shop'.

4.2. Skills

The service will only be as good as the people in it and most nuclear establishments already have staff with the skills to provide specialised analytical capabilities. These specialised techniques are a key asset and can be offered commercially with less danger of competition that for more general analytical services. For example, the author's expertise was in geochemistry when the Imperial College NAA service was started. This formed a base from which the work expanded over time but initially the customers were from the exploration and minerals industries. In time additional staff can be taken on specifically to work on the service but to start with there are obvious advantages in specialising in areas of expertise.

Certain skills will be particularly helpful when operating an analytical service, and radiochemistry is one that offers a unique capability compared to other more common analytical techniques.

4.3. Capabilities

As well as addressing what staff and equipment is available it is important to consider what type of service can be offered. At Imperial College the reactor operates from 9 am until 5 pm on Monday to Friday, so weekend working is generally not possible. However, the reactor staff are sufficiently flexible to operate at the weekend when a company needs immediate turn round and is willing to pay a premium for that. It is possible to offer same day turn round for quality control samples and this is essential for an operating plant. Staff have to be flexible and willing to work on in the evening but that is acceptable if it means that the business is a success. Automation allows hundreds of samples to be analysed per day if necessary and that can be important for screening work or contaminated land studies. It may be that some investment may be required to implement the necessary devices but this can be done as the work builds up.

Reactor shut-down for maintenance is a real problem and can interrupt essential work that has been built up for a particular customer. It is possible to find alternative services for a customer to keep them supplied with data over a one month shut-down and still retain their custom once the reactor is at power again. This can be done if the customer sees that the quality of work could not be matched by the alternative. An important question is what priority is given to the customer. At Imperial College the income was initially essential for the continued operation of the reactor, so the reactor gave the work priority. Samples arriving at short notice were accommodated and extra time given if necessary. That ethos continues today and so there have been no serious issues relating to customer priority.

4.4. Investment

Clearly setting up a service requires considerable investment in staff, equipment and reactor time. Sharing staff, space and equipment is a helpful cost saving strategy but care must be taken when applying it. Using the expertise of staff will enhance the service, particularly in the area of radiochemistry, but as the work builds up it may be necessary to consider dedicated technicians to ensure that deadlines are met. The staff at Imperial College have generally been dedicated to the analytical service although occasionally additional people have been employed for particular contracts. There is a particular danger associated with the use of students in such a venture because the customer may have the perception that you are using untrained staff. Also care must be taken over whether students and other staff are allowed to use the equipment that is part of the service. The best approach is to introduce a quality system and train users to work within the system. Then there is control over what they are doing and they have the advantage of working with equipment that is regularly calibrated and maintained. Consequently there are properly trained staff (who may also be students) available should extra work appear and the students can benefit both financially and by gaining QA experience.

5. SOURCES OF BUSINESS

5.1. Type of analyses

Once the decision has been made on what skills and equipment are available and what capabilities are achievable, a strategy can be developed for the analytical service. Imperial College began with experience in instrumental NAA and radiochemistry and a special expertise in geochemistry and the platinum group elements in particular. A radiochemist was employed specifically for commercial work and the author managed the service among a number of other academic duties.

For a number of years the main work of the service was mineral exploration and geochemistry plus some quality control for industry. A chemistry technician was employed as work increased and the income allowed. As a number of other reactors shut their NAA work was taken over by the service, which expanded the range of analyses, introducing delayed neutron counting at the request of a customer, who paid for installation of the necessary irradiation and counting equipment.

This allowed the addition of two more members of staff: a physics technician to support delayed neutron counting and a physicist to mange the service under the author's direction. To concentrate on one's areas of expertise is practical since it will be what you are well known for and initially with provide your best quality analyses. As the business expands it is possible to broaden the expertise of the staff and attract work from other areas. Radiochemistry is a specialist area which can generate income and Figure 3 highlights that although the number of samples analysed using radiochemistry is lower than those analysed by instrumental methods, the income is greatly in excess.

5.2. Industry

Customers in industry expect a professional service with good communication and rapid turn-round for their samples. They are often not familiar with nuclear analytical techniques and therefore will require some information regarding what is happening to their samples. They will appreciate the expertise that is offered and initial success in one area may lead to further work from other sources in the company. The range of work from industry is almost endless. Examples of work Imperial College has had in the past include solids and liquids, inorganic and organic materials. The analyses range from the determination of sulphur for the chemical industry, fluorine in rubber, trace elements in silica, platinum in minerals, iodine in milk and pet food, assorted elements in pharmaceuticals, precious metals in catalysts, cadmium in plastics, analysis of industrial diamonds and uranium in graphite. Batches of samples are generally not large, except for uranium determinations using delayed neutron counting, where hundreds of samples can be processed rapidly. Fast turn-round may be required and we have had customers who send samples in the morning and expect the report by evening. This is perfectly achievable if a short irradiation is used. Work for industry may be commercially sensitive and staff must be made aware that the work is confidential. Figure 4 is a typical breakdown of sources of income that demonstrates the importance of work for industry.

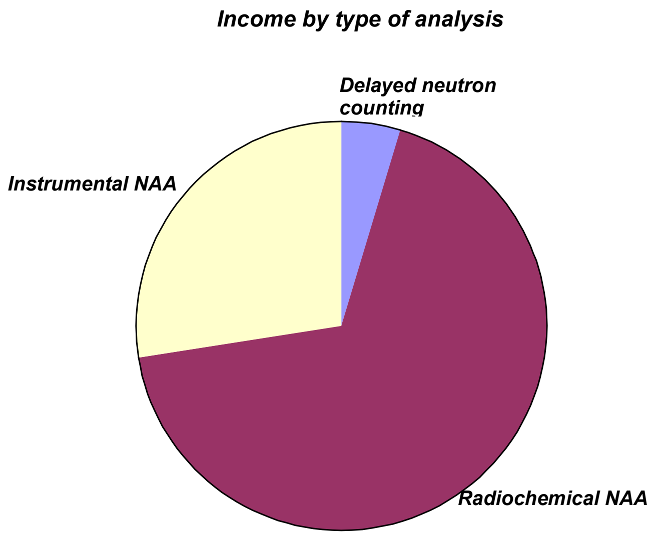

FIG. 3. Typical sources of income by type of analysis.

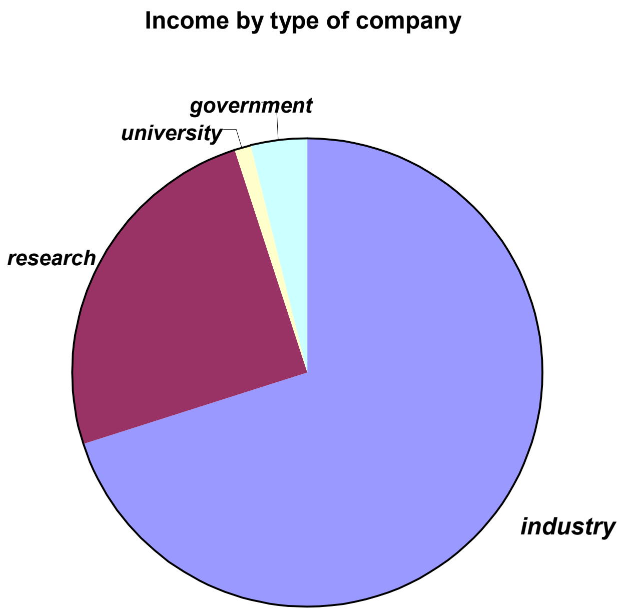

FIG. 4. Typical sources of income by type of company

5.3. Research & Government Organisations

Researchers in other organisations will appreciate high quality work and are unlikely to want to process large batches of routine samples. Their request may require some development work and therefore the collaboration could result in joint publications. Examples of work I have been involved with research organisations include analysis of organic dyes, bromine in neonatal blood, analysis of carbon, uranium in ashed tissue, aluminium in proteins, rare earth elements in soils, bromine in organic liquids, arsenic in hair for the forensic services, platinum in bitumen, calcium on air filters, arsenic in plastics, uranium and thorium in porcelain, uranium in waters, iodine in rice, precious metals in glass and steel, and zinc in insects. Uranium analyses are also carried out for the Food Standards Agency as part of their annual monitoring programme around nuclear installations.

5.4. National Standards Programmes

Work for National Standards Organisations can be particularly rewarding since it identifies the analytical service as a high quality facility. Such work will raise the profile of the service with the government and the community, ensuring that the facility survives. In the UK the service has worked with both national and overseas standards organisations such as IRMM, JRC and NIST. The UK organisations are the National Physical Laboratory and the Laboratory of the Government Chemist. Collaborations have included the development of a reference material for paints used in children's toys, homogeneity testing for a catalyst reference material and development of standard Al/Au and Al/Ag alloys.

6. GAINING BUSINESS

During twenty years operation of the NAA service the majority of work came ‘by word of mouth’. In the 1980s there were several facilities offering NAA so there was some understanding of its capability. Now Imperial College is the only institution in the UK that offers NAA and the technique has a lower profile. In 2004 if a customer is actively looking for NAA there is not a problem because the internet search will locate suitable sites, including Imperial College, very rapidly. However, a potential customer often is not aware that he or she needs NAA and it requires skill to attract work.

6.1. Leaflets and brochures

In the past Imperial College has produced leaflets and advertised the NAA service in journals, indicating the nature of work that can be undertaken. Distribution of leaflets is an expensive business and targeting is important but very difficult and it is rarely cost effective. However, it is important to have a leaflet or brochures available when speaking to customers so it is certainly necessary to produce a limited number. It is worth investigating whether a journal or manufacturer would be willing to distribute leaflets with their mailings, if the cost is small.

6.2. Professional activities

It is possibly more effective to inform the potential customer by speaking at conferences and visiting companies, offering seminars and invitations to visit the reactor. In the 1990s I made a special effort to attend conferences that were outside the nuclear field to talk about NAA. The talks generated a lot of interest on the day but resulted in few contacts. Visiting companies and offering seminars was useful but only in those cases where there was already some initial work going on. There was certainly an advantage in helping the existing customer understand the full capabilities of the analytical method and often more work resulted. Experiments in taking a stand at one or two exhibitions resulted in visitors who were more interested academic matters and courses than commercial contacts. Invitations were issued to reactor open days and contacts were made but little work resulted. In summary, efforts to initiate new contacts were not very successful.

6.3. Personal contacts

In the author’s experience the majority of work that comes to the analytical service is the result of personal contact. In the UK the nuclear industry is a ‘small world’ and the author’s work is well known. Consequently people make direct contact or are passed on by a third party. Most of the approaches received start with ‘Someone told me that you could help me’. The research and teaching activities of the institution plays an important role in setting the analytical service up as a centre of expertise. If the institution is the nuclear centre in a country, that is better than any amount of advertising in trade journals.

6.4. Working with others

If the organisation is small it may be easier to work as a subcontractor for another bigger company offering analytical services. If the nuclear analytical techniques that offered are unique then the niche capability may be attractive to the larger organisation. If the service is part of a large organisation there may be other capabilities in house that could combine to offer a more comprehensive service. Economies of scale in either case are very useful, reducing the cost of administration, advertising and other activities such as invoicing.

7. KEEPING THE BUSINESS

7.1. Quality assurance

If the aim is to bring money into the institution it should be appreciated that a professional level of service will be expected by the customer. This will include operation of a quality system that is recognised by business, such as ISO 9001:2000 and ISO 17025: 2000. This raises a number of factors that must be addressed for compliance, including staff training, equipment calibration and maintenance, the use of traceable standards, reference materials, standard procedures for reporting, and written protocols for work carried out. Most importantly, someone must be identified as having responsibility for quality management. The cost of implementing a quality system and subsequent accreditation is not cheap. It is estimated that perhaps an additional 25% staff time is required to set up such a system. The additional paperwork is onerous but once checking systems are in place it is unlikely that erroneous data will be reported to the customer. The cost is not just in terms of staff time. The additional cost of regular maintenance and calibration must also be included and the cost of purchasing standards regularly. For example at Imperial College standard solutions for calibration are purchased every 18 months, the date when their certification expires.

Operating under a quality system has many advantages, not least the obvious one of bringing in work. Any business requires a system to ensure that it remains under control as work builds up and the facility becomes busier. Businesses working under a quality system are expected to place work with a subcontractor working to similar standards. Therefore customers will expect some minimum standard of quality assurance and will wish to audit in order to fulfil their own quality assurance requirements. Generally these days it is expected that analytical laboratories have some form of accreditation under ISO 17025: 2000. Each country has its own national system, and in the UK it is UKAS. Accreditation guarantees to the customer that work is to an acceptable standard and usually means that audits from customers will not be required in addition to the accreditation body. The UK Environment Agency and Food Standards Agency both only place work with analytical laboratories with UKAS accreditation. The exception is where there is no other similar facility available that has accreditation. Customers may not demand a quality system if they have no systems in place themselves [beware – their invoice payment system may be ineffective!] or when the method has no competitors. This, of course, is not uncommon with nuclear techniques and may allow work to start before a system is introduced.

7.2. Balancing commercial work with other activities

With the backing of management and the support of staff it is possible to build up a significant customer base providing analytical services across the country and abroad. This work should probably be balanced with other activities of the organisation, such as teaching and training and research. Imperial College is a university and the commercial service is rather an unusual aspect of the college's activities. It is therefore important that service work does not take over other activities on the reactor. Financial pressures have meant that it tends to take priority and over the years the research and teaching requirements on the reactor have sometimes had to take second place. The result is that both aspects of academic life have reduced significantly, particularly with respect to external users, mainly because of increased costs. However, justification for the facility will always depend on the perceived purpose and care must be taken to maintain a balance. The future of the reactor is currently being discussed by the community of users, mainly external organisations, and the future support for the reactor is in the hands of the industrial organisations, research institutions and National Standards laboratories that are now the main users of the reactor.

FIG. 5. Income over the last 20 years, normalised to the maximum income in late 1990s and early 2000s.

8. CONCLUSIONS

The commercial service at Imperial College was maintained for twenty years by juggling staff, equipment and irradiation facilities, building up when required and 'downsizing' when necessary. At no point was the service entirely self-sufficient since staff had more than one role and participated in teaching and research as well as the analytical service. The balance was of benefit to everyone concerned including students who have studied with us and gained experience of working within a well maintained and quality assured laboratory. The benefits of collaborating with industry cannot be overestimated, with the knock-on effects for research and teaching identified previously.

A key change took place a few years ago, which can be seen in Figure 5 by the fall in income from 2002. The author's academic department has become a separate cost centre to the Reactor Centre and irradiations are now being charged at a more realistic price. Once the true costs were built in, including space, overheads and irradiation charges, it was not possible to maintain a viable business plan without reducing staff to a non-viable number. As a result, this year the analytical service has been handed to the Reactor Centre, where the business can remain be viable because the irradiation charge have become income not expenditure.

In summary the introduction and operation of a commercial service is to be recommended, particularly in those situations where it can complement other parts of the organisation, such other analytical or academic activities. It is not practical to fund reactor operations entirely on commercial activities but it can result in a number of spin-offs that can increase other income streams, such as teaching and research projects. Over the past twenty years the analytical service at Imperial College has brought several million US dollars into Imperial College, which certainly helped the Reactor Centre survive. After all, it is now the only nuclear research reactor operating in the UK.

APPLICATIONS OF NUCLEAR ANALYTICAL METHODS FOR HIGH TECH INDUSTRY

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Abstract

High technology industry such as the semiconductor industry with Si substrate provides a unique opportunity for the application of nuclear analytical methods. Single crystal Si has been doped with P using neutron transmutation doping. Typical dopant such as boron has been depth profiled using reactor thermal neutrons. Trace contaminations of transition metals e.g. Fe, Cu, Zn, Cr etc have been measured with high flux neutron activation analysis. At AMD diffusion barrier such as Ta have been evaluated for the effectiveness of Cu movement across the barrier from metal line to the interlayer dielectric. Many manufacturing related problem solving efforts have used neutron activation analysis in order to resolve the issues. One such example is the dose calibration of As for a n-type ion implanted wafer. Neutron activation of the As provides high quality measurement that can be used to match As dose in a manufacturing facility with multiple implanters.

1. INTRODUCTION

Silicon based semiconductor chip manufacturing is a world wide high technology industry with numerous measurement issues. One of the major concerns in the semiconductor manufacturing is contamination such as the trace metal impurities. This concern is vividly illustrated by the fact that the manufacturing in this industry is done in ultra clean environment where the entire manufacturing facility or "Fab" is a clean room facility or each and every manufacturing tool is enclosed in a mini-environment Although semiconductor devices are fabricated on the surface of the Si wafers contamination in the bulk material is a major concern. Nuclear methods of analysis is uniquely suited for the contamination analysis in such a matrix.

2. OPPORTUNITIES FOR NUCLEAR ANALYTICAL METHODS:

Nuclear analytical methods can be used to provide many essential data needed for the chip manufacturing process technology both for R & D and manufacturing operations.

Neutron activation can provide trace impurities analysis at ultra low levels. The favorable neutron activation parameters for Si as a matrix makes such low level measurements possible. First Si leads to ^{31}Si which has a 2.6 hour half life so that matrix radioactivity decays quickly to virtually nothing creating an excellent low background condition. The impurities of interest are the first row transition metals, which typically have much longer half lives. NAA has high sensitivity for these elements. Detection limits for some elements are listed below in Table 1. These limits can be achieved by using reactor core irradiation at high flux positions. Turnaround time for such analysis for a set of samples can be upto 2 weeks since multiple counts may be necessary to include all the elements listed. High resolution gamma spectroscopy with good shielding is necessary to obtain these limits. Typical detection limits in silicon wafer are:

- Fe, Ni — 8 E 10 atoms/cm^2
- Cr, Mn, Co, Sc — 1 E 9 atoms/cm^2
- Cu, Ag, Zn — 1 – 5 E 10 atoms/cm^2
- Au — 1 E 7 atoms/cm^2
- Ta, Th, La, Eu — 1 E 9 atoms/cm^2
- As, Sb, U — 5 E 9 atoms/cm^2
- Na, K — 1 – 5 E 10 atoms/cm^2

However non-nuclear methods such as TXRF and VPD-ICP/MS can also make such low level measurements. The disadvantage of NAA is that typically it would take 2 weeks to obtain the results while both TXRF and VPD can provide data in less than a day. Furthermore TXRF is automated, and can be placed inside the Fab where in-line measurements can be done non-destructively. VPD is highly quantitative and NIST traceable standards are available. A major weakness of TXRF, and VPD is that data collected is from the surface of the wafer only. In case of TXRF the analysis depth is about few tens of nanometers, while VPD data is limited to the native oxide only. Any subsurface or bulk impurities would escape detection by these methods. This is where opportunities for NAA exist to complement the surface analysis by the TXRF, and VPD with bulk analysis results thus providing complete picture for trace metal contamination.

In fact for bulk analysis NAA is the preferred method and in some cases only method creating an opportunity to support the high tech manufacturing field. The high sensitivity of NAA for bulk measurements provides a unique solution to the semiconductor industry. Several types of samples can be analysed for bulk impurities. Most notably Si wafers, SiC, Graphite, Quartz, and Si_3N_4 are among the most widely used material needing such bulk analysis. Samples of the above type cannot be analysed with conventional methods such as ICP/MS since digestion of these materials leave high levels of Si in solution that must be diluted in order to run through the mass spectrometer. This necessary dilution makes the detection limits not attractive.

The analysis of Cu deserves special mention since it plays a pivotal role in chip manufacturing. The interconnect metal for semiconductor devices is shifting from Al to Cu for higher conductivity of the latter. However Cu has high diffusivity in Si and with modest temperature Cu can move from the backside of the wafer to the front or the polished side where the devices are fabricated. The Cu contamination control therefore is a big challenge, and monitoring Cu levels in the Fab is an on-going program. Since bulk levels of Cu must be monitored NAA becomes the method of choice for this very important measurement needs for the semiconductor industry.

Another opportunity is in the implant area of the process technology. For example As is used as the n-type dopant for Si. It is most often implanted into the Si with specific energy, and dose. After implantation, a temperature anneal is done typically ~ 1000 C to “Activate” the dopant atoms (in this case As atoms) where the As atoms goes in substitutionally in the Si crystal lattice. There are two issues that need to be monitored. For a manufacturing Fab there are multiple implanters that need to be matched with respect to the dose, hence total As analysis is needed. Secondly since As is volatile, it is important to determine after anneal at high temperature whether there a loss of Arsenic due to out diffusion. NAA can provide excellent answer to these very important questions and help set up process parameters needed for the successful fabrication of the devices.

There are unique environmental analysis needs in the semiconductor industry. One such need has been just created due to the ROHS (Restrictions on Hazardous Substances) ordinance agreed to in Europe. The EU countries after July 1, 2006 will require that all electronic products and components among other things be essentially free of metals such as Lead, Cadmium, and Mercury.

NAA has the advantage in measuring Hg quantitatively while the non-nuclear methods have serious problems. NAA method developed for this purpose is a great opportunity to meet the needs of regulatory compliance.

2.1. Neutron depth profile:

In addition to the above NAA opportunities there are other nuclear methods that can provide elegant solutions to the high tech industry. Neutron Depth Profiling (NDP) is a special technique that has unique applications in the Fab process technology. The most widely used p-type dopant for Si is boron, and the dose and the profile of boron is crucial for the functioning of the fabricated devices just like the case of As mentioned above.

Typically SIMS (secondary ion mass spectrometry) is used to provide the information about the boron. However a standard is needed for such measurement, and SIMS is very matrix sensitive. In fact SIMS is not reliable at all for measurements across an interface such as oxide/Si. This is because the SIMS "Yield" changes uncontrollably across any interface. NDP is neutron based and provides answers to these problems faced by SIMS. In this method implanted boron (^{10}B) is exposed to thermal neutron beam in an evacuated chamber. The fission reaction between ^{10}B and thermal neutron produces monoenergetic alpha particles of 1.47 MeV that are emitted isotropically. A surface barrier detector can measure the energy of the alpha particles, and can construct from the energy loss spectrum the boron implant profile. In addition it can also provide dose of the boron implant by integrating the area under the curve.

The advantage of NDP is that one can depth profile boron across an interface since neutron penetration is not sensitive to oxide/Si matrix. A true distribution of boron can be unambiguously measured. NDP can also generate standard samples that can be used in SIMS measurements to provide quantitative results. NDP is also advantageously used for borophosphosilcate glass (BPSG) analysis where boron concentration is critically monitored for process technology. Measurement of boron in BPSG by SIMS is at best difficult because of the charging issues associated with the thick oxide layer.

2.2. Prompt gamma for H analysis

A lot of the thin films that are deposited for device fabrication are oxides, and nitrides of Si. They are deposited using PECVD (Plasma Enhanced Chemical Vapor Deposition) or LPCVD (low pressure Chemical Vapor Deposition) techniques in which the precursor for Si is the Silane gas (SiH_4). This results in incorporation of Hydrogen in these films. Measurement of hydrogen in thin films (few hundred nanometers) is often needed to set up a deposition recipe for these films. Although hydrogen in these films can be measured using SIMS a standard is needed for quantitative results. For this purpose nuclear method of Prompt Gamma analysis can provide total hydrogen concentrations in these films. Prompt gamma is a robust measurement that can analyse films of different compositions such as SiO_2, SiON, Si_3N_4, etc.

2.3. Soft–error issues

Semiconductor devices containing BPSG layers has a unique problem with cosmic ray neutrons. These neutrons can undergo fission reaction with ^{10}B in the BPSG layer and generate energetic alpha particles (1.47 MeV). These charged particles will penetrate into the active area of the device, e.g. transistor or capacitor and cause single event upsets. For example in the memory array the charge stored can be discharged making the "Bit flip" from 0 to 1 or vice versa. Such undesirable bit flip known as soft error, and semiconductor manufacturers would like to limit such soft error-rate (SER) to a minimum. Opportunities exist for nuclear facilities to provide neutron flux for testing device configuration to evaluate a device design with respect to its resistance to SER. This is particularly important for the mobile computer that may operate at high altitude for example in an airplane in flight. Design alternatives can be worked out using nuclear methods of evaluation.

2.4. Pb bump technology

Many devices are being made with Pb bump technology where essentially a micro Pb solder replaces the traditional ball bonding with Au wire. Such a chip often contains a high density of Pb bumps. One issue with this technology is the possible contamination of Pb with radioactive ^{210}Pb which has a half life of 22 years. The radioisotope eventually emit alpha particles which can penetrate the thin metal layers and cause 'Bit Flip' in the sensitive area of the device.

Considerable design efforts have been devoted to offset the problem caused by this phenomenon. However ultra low radioactivity Pb is a better solution even though it is costly one often times at 10x the expense. Manufacturer of these C4 (that is what Pb bump technology is known as in the industry) devices need low level radioactivity measurements to evaluate the quality of the Pb being used for this purpose. A nuclear facility with low background counting set up can provide this service to the industry.

2.5. Conclusion:

Many opportunities in the semiconductor manufacturing field exist for the nuclear methods to provide support services. Contamination analysis by NAA, depth profiles by NDP, Prompt gamma analysis of H in thin films are a few examples. These needs are on-going and require commitment from the lab so that a manufacturing operation can rely on the delivery of these services when required.

3. INDUSTRIAL CUSTOMER NEEDS AND REQUIREMENTS

Manufacturing industries have demanding needs in the metrology, and analytical measurements. This is driven by the need for improvements of the products and efficient process technology. For example in semiconductor industry to support a manufacturing operation a well-equipped laboratory is essential. Such a laboratory may contain analytical tools such as XPS, Auger for surface analysis;SIMS for depth profiles of dopants, SEM, TEM for imaging and cross sections; TXRF, and VPD/ICPMS for surface contamination analysis; XRD for orientation and texture while Raman, FTIR, EDX for defect analysis. In addition there are metrology tool on line to gather data for CD (critical dimension) and thickness. However the bulk impurities analysis of the Si wafer substrate cannot be addressed by any of the above techniques. This is a “Gap” which can be ideally fulfilled by the NATs. High sensitivity NAA is an excellent choice to provide this critical data for the entire semiconductor manufacturing community. Bulk analysis of other materials such as SiC, Quartz, Graphite liner, Silicon nitride can also be accomplished by NAA. The need for such analysis in the semiconductor industry is a daily phenomenon and currently not being met adequately. Demand for such analysis worldwide is high, and NAA providers can develop a niche market for this service.

Another important example of the unique applications of NATs in the semiconductor industry is the analysis of dopants across an interfacial boundary which is a frequently needed analysis in the chip manufacturing. Typically SIMS is used for dopant analysis. Incidentally several commercial labs are set up just to provide SIMS data to the semiconductor manufacturing customers. However interfacial analysis by SIMS is not reliable because of the uncertainty inherent to the technique for the interfaces. NATs such as NDP is uniquely suited for the analysis of the boron across an interfacial boundary. Because of the insensitivity of the neutron to a matrix such as oxide/Si the profile of boron can be unambiguously obtained by NDP across such an interface. Chemical etching post neutron irradiation can provide such interfacial data for other dopants such as P, As, In etc. These high priority demands in the industry can be met by the NATs, and there exists a potential commercial market.

Outside of the semiconductor industry following is a short compilation of the unique applications of NATs in the industry. This is only an attempt to list a few relevant usage of the NATs and actual needs are much more widespread.

1. Analysis of trace oxygen in Steel, and petroleum processing. Such direct measurement of oxygen is only provided by NAT; in this case the 14 MeV fast neutron activation analysis.
2. Hydrogen analysis in the Ti metal industry for aerospace. PGNAA is a highly quantitative method that is unmatched by any other technique.

3. Halogens and metals in the polymer industry can be uniquely addressed by NATs. This is evidenced by the investment made by Dow Chemicals to install a research reactor for their own use at their Midland manufacturing facility in Michigan.
4. Industries that produce materials such as ceramics, graphite, and other highly refractory or insoluble materials have demands for NATs. The conventional methods of chemical dissolution not being available NATs can meet the trace analysis demands (e.g. AlN, glasses etc).
5. Impurities in emerging nano materials e.g. carbon nano tubes NAA is best suited for trace impurities analysis in this field.

There is a clear demand for NATs in the various industry, and a potential commercial market can be developed in order to satisfy such important industrial needs. However the industrial customers have requirements which must be met not only for technical contents but also for all other logistics such as delivery on time, and proper non-disclosure agreements. For a successful commercial opportunity the infrastructures must be built to have business like interaction between the service provider, and the industry. Industrial customers would require priority, confidentiality, and on-time delivery. Service providers must show long term commitment so that industrial customer can rely and plan future manufacturing (quality system required!).

Industry on the other hand must allocate annual budget items so that service providers can make investments for upgrading facilities, and tools. Such investment on the part of the provider is critical in order to meet the increasing demand of the manufacturing industry.

SERVICES AS PROVIDED TO CUSTOMER BY NUCLEAR ANALYTICAL TECHNIQUES AT DALAT NUCLEAR RESEARCH INSTITUTE

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Abstract

The Dalat Nuclear Research Institute (DNRI) of Vietnam has become an important R&D centre in the country for researches and applications of nuclear analytical techniques (NATs). The DNRI is in cooperation with various organizations, having growing needs for NATs, geological departments, mineral exploration companies, national environment agency, province's departments of science & technology, medical-nutritional-occupational health sectors and agricultural research institutes and centers, etc. Recently, the NATs at DNRI are challenged by a strong competition from non-nuclear analytical techniques (e.g. AAS, GC, IC, ICP-MS, etc). Therefore, in order to develop a strategy for sustainable operation, the improvements in aspects of method equipment and in particular of the implementation a quality system for NATs laboratories have been carried out. By these improvements, the annual analysis capability reaching to several thousands samples with tens thousands constituents analysed, the reliability of results ensured, thereof the customers are being expanded to also private and joint venture companies for mineral exploration in the country as well. The status of analytical services as provided to customer by the NATs at DNRI are presented and discussed.

1. INTRODUCTION

The nuclear analytical techniques (NATs) in DNRI are including neutron activation analysis (NAA) with both options of instrumental and radiochemical (INAA & RNAA), X-ray fluorescence analysis (XRFA), and low-level counting and spectrometry methods. The applications of NATs for determination of elemental composition, particularly important in providing data so-called trace elements, radionuclides and multi-element have been enlarged for objects of geology, mineral exploration, archaeology, agro-bio-medicine, health-nutrition and environment, etc. The accumulative results of more than 45,000 samples analysed with about 320,000 analytes determined have significantly contributed in many years for the requirements of socio-economic development in Vietnam.

However, the NATs at DNRI are recently challenged by a strong competition from non-nuclear analytical techniques (e.g. AAS, GC, IC, ICP-MS). Some NATs' analysts particularly in RNAA group have changed to non-nuclear analytical techniques. Therefore, in order to develop a strategy for sustainable operation, the re-identication of applications, the improvement in aspects of methodequipment and implementation a quality system for NATs laboratories have been carried out. Additional, the DNRI has opened a policy in which the analysts are encouraged to become more business like. The laboratories are to be received a part of benefits from services, also supported more equipment and upgraded a better working convenience. This paper will present briefly the above mentioned topics from which the services as provided to customer by NATs are shown and discussed.

2. MAJOR APPLICATIONS

At Vietnam, NATs have widely been applied in fields of geology, mineral exploration, archaeology, agro-bio-medicine, health-nutrition and environment. The nature of analysed samples were approximately as geology and mineral exploration (~55%), agro-bio-medicine (~15%), health-nutrition (~7%), environment (~20%), others (~3%). Figure 1 shows the distribution of analysed samples in the period of 1984-2003, in which the number of analysed samples was decreased in the period of 1993-1997 because of a general inspection for the reactor.

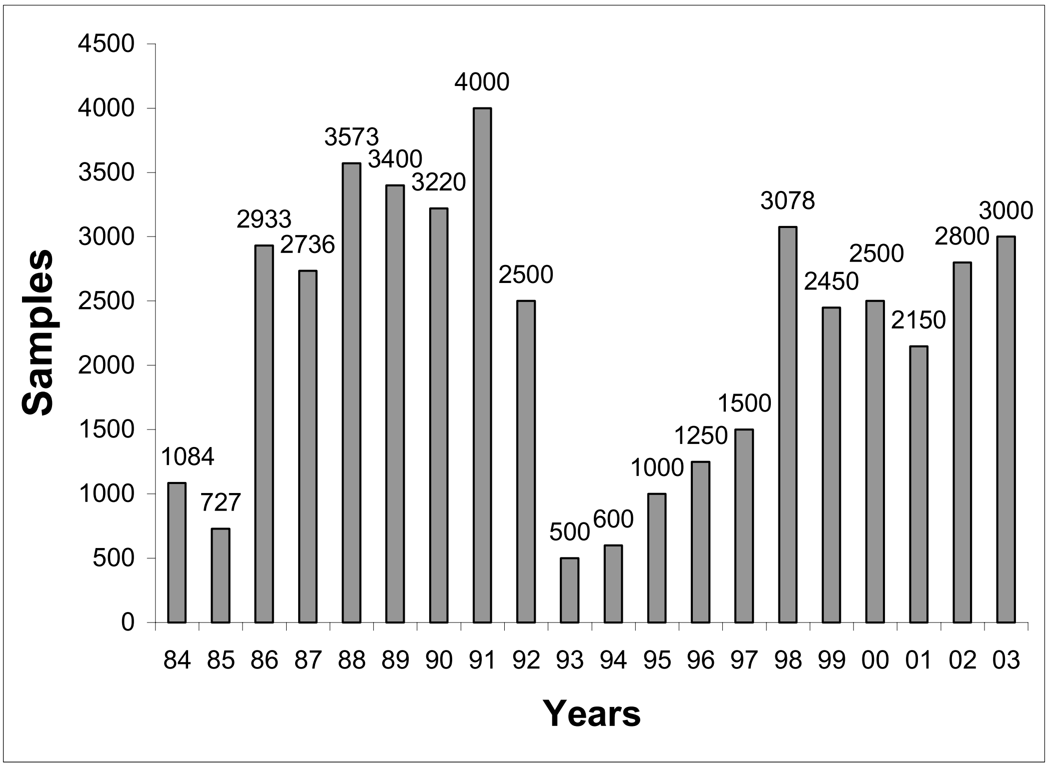

FIG. 1. Distribution of analysed samples in the period of 1984-2003

Through the implementation of national R&D programmes of Ministry of Science & Technology, Ministry of Environment & Resources; Coordinated research projects with other organizations in Vietnam; Coordinated research contracts with IAEA; and Analytical services, NATs at DNRI have been applied in the following areas:

- Acquisition of baseline data for elemental composition (mainly for toxic trace elements and radionuclides) in environmental objects and impact assessment of industrial wastes;
- Research and monitoring on air pollution;
- Supporting the sustainable development of agriculture and improving the quality of human life;
- The determination of specific distribution of microelements in plants used in traditional medicine;
- The nutritional role of microelements in agriculture plants growing in different soils;
- The concentration and distribution of mineral substances in food used for feeding domestic animals and live-stock;
- The control for heavy metal and toxic element concentration in foodstuffs;
- The determination of Hg, Me-Hg & Se in human head hair;
- The determination of multi-element in geological samples and mineral exploration for elements of precious metal, rare earth, etc.
- The determination of U, Th, K, H and trace elements in crude oil and base rock samples collected from bore holes;
- The investigation of marine environmental pollution;
- Providing the analytical services to customers of various fields.

3. IMPROVEMENT OF METHOD

The INAA has the advantages of non-destructive, high sensitivity, good selectivity and multi-element. Moreover, the k_0-standardization method of INAA (k_0-INAA) is capable to use without certified reference materials or standards, particularly suitability for computerization. Therefore, the development of the k_0-INAA method on Dalat research reactor has been carried out. Now, the k_0-INAA method with a simple experimental procedure and a complete computer software has sucessfully been applied in many sample objects, particularly in correlation studies.

The XRFA has the advantage of independent from reactor, the method has been focused to improve an option so-called the total reflection allowing to determine some toxic elements in liquid samples, particularly As in drinking water.

4. UGRADDING OF EQUIPMENT

Some new equipment for sample collection and sampling were upgradded including samplers for total airbone particulate mater, samplers for the collection of atmospheric aerosols in two size fractions (2-10 µm, < 2 µm), aquatic pollutant sampling system, pneumatic sediment corer. The short- and middle-term irradiation facility using pneumatic transfer system in cell 13-2 of Dalat research reactor was upgradded. The facility is operated and monitored using process control computer system allowing irradiations of several seconds.

The counting equipment for INAA was automated using an Ortec sample changer (ASC2 model), so the measurement capacity of counting equipment is higher and possibility to make use in night and week-end days. Moreover, the automation of counting system will make minimizing human errors. Some new germanium detectors were equipped (2 for low-level counting and spectrometry, 1 for RNAA, 1 for INAA, 1 for XRFA, 1 for PGNAA). The software packages for gamma ray spectrum accquisition and processing are accompanied with manufacturers of MCAs: GammaVision (Ortec) or Genie-2k (Canberra). The comparison and evaluation of these software packages have also been done at DNRI in order to assure for data processing quality and suitability for application purposes. The software package for computation of elemental concentration of k_0-INAA is home-made. For XRFA, the QXAS (IAEA) software is applied.

5. IMPLEMENTATION OF A QUALITY SYSTEM

A quality system for NATs laboratories has been established according to ISO/IEC 17025 international standard. The works concerning to the quality system for NATs have been implemmented step-by-step with the preparation of a quality policy, the documentation of standard operating procedures (SOPs) for sample collection, sampling, sample preparation and analysis, the participation in proficiency tests (international and national proficiency test), etc. Some NATs laboratories are expected to be accredited formally in the end of next year.

6. SERVICE TO CUSTOMER

In order to commercialize the NATs' services it may need consider aspects as marketing and cost of delivery analyses. Marketing is a process of identifying, anticipating, and satisfying customer requirements, i.e. making potential consumers aware of the NATs' existence and benefits. It is important to price an analysis. The two basic components that affect analysis pricing are costs of analysis and competition in selling. It is unprofitable to sell an analyse below the analysis' costs and unfeasible to sell it at a price higher than that at which other analytical techniques are being offered.

In attempting to provide the NATs' services to customers in the country, we have considered a variety of factors. The first is as a political reason, i.e. making public to aware about usefulness of nuclear techniques before we launch a nuclear power programme for the country in the near future. The second is as exploitation of research reactor for NATs besides the radioisotope production (anyhow the research reactor is there). Because NATs' services are intangible goods, so they must be calculated not only by income but also by quality of analytical results. Finally the benefits getting from the service will return to upgrade equipment and encourage the staff in order to keep them in operation (sometimes the benefits are not only money but also co-authorship of publications).

Moreover, now we have to look for budget to operate the NATs laboratories since the direct funding of research is insufficient to support all activities. A combination of ways to get fundings is done, i.e. research projects, research colaboration with different organizations, and client's paying, etc. The cost of NATs to customers was estimated and stated in a price list to make service, but it must be competitive. In order to encourage to find more applications and sell services we have opened a policy in which the laboratories are to be received a part of benefits from services, also supported more equipment and upgraded a better working convenience.

7. CONCLUSION

The NATs have recently been competed by non-NATs, so it is necessary to promote NATs in aspects of personnel, equipment & management in DNRI. In commercial sense, it may need consider aspects as marketing, cost of delivery analyses and turn-around time of NATs in DNRI. The quality of NATs' results is a prerequisite for mutual recognition between analysts and customers. It is necessary not only for an economic reason but also for the acceptance and credibility of research works.

Vietnam is a developping country, the science and social economy are in low level, and the NATs in the country are also not exception. So, this chance of the IAEA meeting on "commercial applications of NATs" would help to collect experiences from other laboratories in the world to enhance our activities and revenues.

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COMMERCIAL APPLICATIONS OF X RAY SPECTROMETRIC TECHNIQUES

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Abstract

The experience has proffed that the energy dispersive X ray fluorescence spectrometer (EDXRF) is more cost effective as compared to the wavelength dispersive X-ray fluorescence spectrometers (WDXRF). The energy dispersiceX ray fluorescence (XRF) technique is widely used in process control, industrial applications and for routine elemental analysis It also allows for designing compact instruments. Such instruments can be easily tailored to the needs of different customers, integrated with industrial installations, and also miniaturized for the purpose of *in-situ* applications.

1. INTRODUCTION

In XXI century, the X-ray fluorescence (XRF) technique is widely used in process control, industrial applications and for routine elemental analysis. The technique has multielement capability (capable of detecting elements with $Z \geq 10$, a few instruments are capable of detecting also elements with $Z \geq 5$), it is characterized by non-destructive analysis process, and relatively good detection limits (one part per million) for wide range of elements.

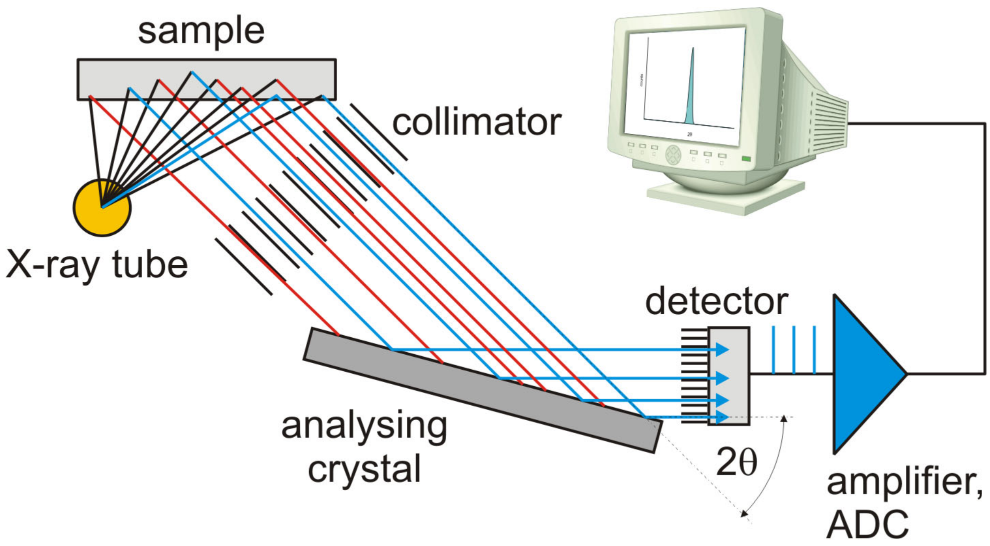

FIG. 1. Scheme of a wavelength dispersive X-ray fluorescence(WDXRF) spectrometer.

The first commercial XRF instruments have been introduced to the market about 50 years ago. They were the wavelength dispersive X ray fluorescence (WDXRF) spectrometers utilizing Bragg law and reflection on crystal lattices for sequential elemental analysis of sample composition. The advances made in radiation detector technology, especially the introduction of semiconductor detectors, improvements in signal processing electronics, availability and exponential growth of personal computer market led to invention of energy dispersive X-ray fluorescence (EDXRF) technique.

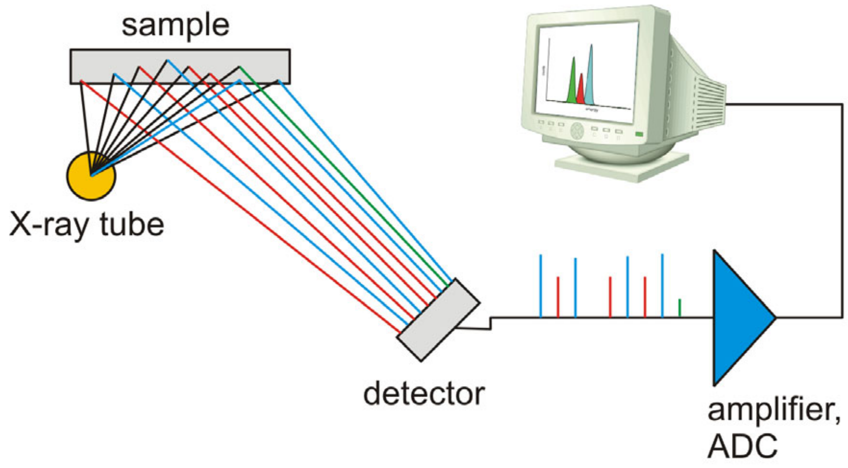

FIG. 2. Scheme of a energy dispersive X ray fluorescence (EDXRF) spectrometer.

The EDXRF is more cost effective as compared to WDXRF. It also allows for designing compact instruments. Such instruments can be easily tailored to the needs of different customers, integrated with industrial installations, and also miniaturized for the purpose of *in-situ* applications. The versatility of the technique has been confirmed in a spectacular way by using the XRF and X-ray spectrometric techniques, among few others, during the NASA and ESA missions in search for the evidence of life and presence of water on the surface of Mars. The XRF technique has achieved its strong position within the atomic spectroscopy group of analytical techniques not only due to its versatility but also due to relatively low running costs, as compared to the commonly used methods, e.g. atomic absorption spectrometry (AAS) or inductively coupled plasma atomic emission/mass spectrometry (ICP-AES/MS). Presently, the XRF technique together with X-ray diffraction (XRD) constitute about one third of the worldwide market for atomic spectroscopy or about $630 millions. In the next few years this market is expected to expand at a rate from 4.7% to 5.5% per year. This growth is generated by improving economic conditions, especially in Asia and also due to increased investments for instrumentation for environmental monitoring and testing worldwide, in industrialized nations as well as in developing countries.

Also other X ray related techniques, requiring more sophisticated instrumentation, are finding routine applications. In particular the ion beam analysis (IBA) methods such as proton induced X-ray emission (PIXE) are of importance in air pollution studies. The increasing number of synchrotron facilities enables for a routine use of X-ray micro-beam techniques in environmental studies, material research, structural research, and many other fields.

2. INDUSTRIAL AND ROUTINE APPLICATIONS OF XRF TECHNIQUES

The major applications of XRF techniques are described below based on: http://www.jordanvalley-apd.com/topapplications.htm).

2.1. Mining & Minerals

- Na, Mg, Al, Si, S, K, Ca, and Fe in cement, clinker, and raw meal
- Na, Mg, Al, Si, K, Ca, and Fe in lime, limestone, and dolomite
- Na, Mg, Al, Si, K, Ca, and Fe in sand and glass
- Mg, Al, Si, Ca, Ti, Fe in kaolin and other clays
- Al, Si, Ti, and Fe in bauxite

- P, S, Ca, Fe in phosphate rock and fertilizer
- Na, Mg, Al, Si, and Fe in cement wallboard
- Ca, S in Gypsum
- Determination of MDL's for trace constituents in coal fly ash
- Trace Ca and V in silica
- Qualitative and quantitative analysis of garnet
- Compositional analysis of:
- SiO_2/TiO_2, superconductors
- TiO_2, and zircon materials
- Feldspar, alumina, silica
- Portland cement
- Water-borne deposits and boiler scale
- Coal and coal products
- Building materials
- Silicate rocks
- Clays
- Limestone, lime, sludges
- Fluorspar and related by-products
- River sediments
- Ti ores
- Pb ores, sinter, slag
- Fly ash
- Phosphate rocks
- Diatomites
- Zeolites
- Gypsum

2.2. Metal and Ore Analysis

- Alloy analysis and scrap sorting
- Precious metals
- Ores, slags, feeds, concentrates, and tailings
- Silicon metal
- Metal foil thickness

2.3. Petrochemical

- Sulphur in oils and fuels
- Lead in gasoline
- Manganese in gasoline
- Chlorine in crude oil
- Nickel and vanadium in crude oil
- Sulphur, nickel, vanadium in residual oil
- Sulphur in coke or carbon
- Mg, P, S, Ca, Ba, Zn, Mo in lubricating oils
- S, Cl, As, Pb, Cd in waste Oil and waste fuel oil

2.4. Metallurgical Analysis

- Jewellery
- Compositional analysis of:

- Fe-based alloys
- Al-based alloys
- Co-based alloys
- U-based alloys
- Ferrous alloys and finished parts
- Ni-based alloys and finished parts
- Powder alloys
- Precious metal alloys
- Bronzes
- Phosphorus bronzes
- Brazes
- Steel and stainless steel analysis

2.5. Plastics and Polymers

- Zinc in polystyrene and other polymers
- Bromine and antimony fire retardants in Styrofoam and plastics
- P, Ca, Ba, Zn in polymers
- Silicones in polymers
- Sulphur in polyurethane
- Mg, Al, Si, Fe in fibreglass
- Plastics compounding
- Chlorine in rubber and plastic
- Sorting PVC from other plastics
- Trace P in plastic
- Si in Plexiglas
- Fe in extruded pellets
- Cl in polyethylene
- F in polycarbonate
- Ti in polyethylene powder
- Trace Ti, Al, Mg in polymer film

2.6. Chemical Process Control

- Process QC
- Plating solutions
- Active ingredients in fertilizers
- Trace ca and k in solutions
- Determination of Al, Mg, and Si in aqueous suspensions
- Potassium iodide solutions
- Analysis of Br in photographic fixers
- Trace Sn in silicon powders
- Trace Ta in niobium oxide
- Contaminants in boron carbide powder
- Analysis of Cu, K, and I in copper iodide/potassium iodide/aluminium distearate samples
- Analysis of S, Sn, F in organics
- Polyurethane, phenoxies, carbon black, tape coating and emulsions
- Analysis of ferrites and toner
- Analysis of tin process wastes, alumina, bisamide and lubricating stabilizers

2.7. Food

- Chlorine in snack foods
- Iron in flour, rice and other grain
- Calcium in orange juice, cheese, and other foods
- Titanium in cookies and snack cakes
- Iron in milk powder
- Na, Mg, P, Cl, K, Ca, Mn, Fe, and Zn in pet foods and animal feed
- Al, and P in dough
- Ash in flour
- Fe and ash content in flour
- Fe, Ca, Mn, Mg in nutritional additives
- Salt additives
- Al, P, Ca in food conditioners
- NaCl in meat snacks
- P and Al in dough
- Fe in milk powde
- Ca in cheese and cheese products

2.8. Environmental

- Lead in paint
- Air filter analysis
- Soil screening and analysis
- On-site and stack air monitoring
- Waste water
- Tissue samples
- PCB's in soil
- Particulate matter on air filter pads
- Pb, Cu, Hg in soils
- Trace elements in soil, water, ashes
- Matching and quantitative analysis of waste streams

2.9. Wood Treatment

- CCA (chromium, copper, and arsenic treatment) in wood and solution
- ACZA (an alternative treatment to CCA, contains ammonium, copper, zinc and arsenic) in wood and solution
- ACQ (preservative containing ammonium, copper and quantenary ammonium) in wood and solution pentachlorophenol in wood and solution
- Zinc borate treated wood and solutions
- IPBC (3-iodo-2-propynyl butyl carbamate) treated wood and solutions
- Bromine wood treatment

2.10. Pharmaceutical

- Bismuth in anti-diarrhoeal medication
- Calcium and magnesium in antacids
- Zirconium, and aluminium in deodorant
- Selenium in shampoo
- Lead in bone and blood
- Calcium in dietary supplements

- Chlorine in toothpaste
- Zinc in cold treatments
- Metals in vitamin tablets and supplements
- Iodine in sterilization products
- Silver nitrate on medical products
- Hazardous metal analysis in pharmaceuticals
- Silicone on condoms

2.11. Cosmetics

- Titanium and zinc in sunscreen
- Iron, titanium and zinc in base makeup
- Toxic metals in cosmetics
- Metal dyes in cosmetics

2.12. Forensic

- Crime Laboratory:
- Matching of glass fragments
- Matching of paint chips
- Bullet residue
- Metals
- Qualitative analysis of explosion by-products
- Soil
- Trace metals in human tissue
- Drug Analysis
- Analysis of starting materials of Methamphetamine synthesis

2.13. Art, Antiques, and Artefacts Analysis

- Identifying trace amounts of silver in bronze
- Determining the opacifier or alkali in glass
- Distinguishing percentages of silver in silver point drawings
- Identifying pigments such as cadmium and chrome on large paintings
- Determining if all of the gold in a piece of jewellery is the same karat

APPLICATIONS OF LABORATORY AND PORTABLE XRF ANALYSERS BASED ON RADIOISOTOPE EXCITATION

R.E. VAN GRIEKEN, A.A. MARKOWICZ, M. DEKKER
Handbook of X Ray Spectrometry, Second Edition Revised and Expanded,
New York, Basel (2002)

The first applications of portable XRF analysers were in mining and mineral prospecting. Since then, the range of the commercial applications has been expanded significantly.

TABLE I. TYPICAL COMMERCIAL APPLICATIONS OF RADIOISOTOPE BASED XRF ELEMENTAL ANALYSERS.

APPLICATION TYPE	TYPICAL EXAMPLES
Alloy sorting and identification	Low-alloy steels; stainless steels; nickel alloys; high-temperature alloys; titanium, aluminium alloys; speciality alloys; metal scrap
Mining and prospecting	Copper, lead, zinc, tin, arsenic, molybdenum, nickel, iron, chromium, bismuth, and uranium in commercial grade ores; concentrates and tailings; titanium and iron in silica sand; silicon, potassium, titanium, and iron in clays; phosphate rock
Pulp and paper	Thickness of silicone coatings on paper and polymer membranes; calcium, titanium, filler in paper
Environmental	Soil screening for metals (Cr, Cu, Ni, Pb, Zn, As, Cd, Hg, Sb); hazardous materials (e.g. lead, arsenic, chromium, or cadmium in waste sludge); trace elements in wastewater discharge; metals in air particulates on filters; chlorine (halogens) in waste oil; sulphur in diesel fuel
Fibers, films and coatings	Copper, zinc, tin, gold, silver and chromium plating thickness; metals in plating solutions; silver in photographic film, manganese coating thickness on magnetic tape; titanium on glass; ruthenium on electrodes
Chemicals and process control	Lead, titanium, and zinc in paint; sulphur, iron, alumina, silica, and calcium in cement, vanadium in catalysts; zinc, chromium, nickel in plating baths
Plastics	Calcium, lead, tin, and chlorine in PVC; zinc and bromine in polystyrene; chlorine in urethane rubbers; bromine and chlorine in butyl rubbers; silicon in polythene; TiO_2 in nylon; bromine in Styrofoam
Agricultural	Fertilizers (calcium, phosphates, potassium); copper, chromium, and arsenic in wood preservatives and treated wood; bromine in almonds; iron-zinc ratio in meat for grading; minerals in cattle feed; titanium in fillers
Cosmetics	Titanium, iron, lead in powders
Pharmaceutical	Metals in vitamin pills; zinc in insulin
Petroleum products	Lead, calcium, sulphur, vanadium, and chlorine in gasoline or oil; sulphur in petroleum coke, sulphur and ash in coal; lubricating oils additives

TABLE II. ON-LINE APPLICATIONS OF XRF/A ANALYSIS SYSTEMS.

APPLICATION	TECHNIQUE/DETECTOR/METHOD	MANUFACTURER
Metal content of mineral slurries	XRF, XRA/scintillation counter, solid state/in-stream	AMDEL
	XRF/gas proportional counter/sample line	ASOMA
	XRF/solid state/sample line	OUTOKUMPU MINTEC, OY
	XRF/solid state/in-stream	TEXAS NUCLEAR
	XRF/solid state/sample line	RAMSEY
Metal content of clay and mineral powders	XRF/gas proportional/sample line	ASOMA
	XRF/solid state/sample line	OUTOKUMPU MINTEC, OY
Iron and chromium in ore on conveyors	Dual-energy XRS/scintillation counter/on-line	OUTOKUMPU MINTEC, OY
Ore sorting	Dual-energy XRS/scintillation counter/on-line	OUTOKUMPU MINTEC, OY
Ash in coal on conveyor	Dual-energy XRS/scintillation counter/on-line	MCI; HARRISON COOPER; SAI
	XRS/scintillation counter/on-line	EMAG
	XRS/scintillation counter/sample line	HUMBOLDT-WEDAG
	XRS/gas proportional/sample line	SORTEX
Solid weight fraction and ash in coal slurries	XRF, neutron, and γ transmission/scintillation counter/on-line	AMDEL
Tin content of galvanizing solutions	XRS/gas proportional	RIGAKU
Calcium in cement raw mix	XRF/gas proportional	RIGAKU; OUTOKUMPU MINTEC, OY
Sulphur in oil, diesel fuel, gasoline	XRF/ion chamber/sample line	YOKOGAWA
	XRF/gas proportional/sample line	MITSUBISHI; METOREX INC.
Lead in gasoline	XRF/gas proportional/sample line	METOREX INC.
Metals in plating bath solutions (Ni, Cu, Cr, Ta)	XRF/gas proportional/sample line	ASOMA; METOREX INC.
Cement analysis for Ca, Si, Mg, Al, S, Fe	XRF/gas proportional/sample line	METOREX INC.
Corrosion products (Cr, Fe) in steam generator feedwater of nuclear power plants	XRF/gas proportional/sample line	DETORA ANALYTICAL
Ash content and/or mineral filler material in paper	XRA/gas proportional/on-line	SENTROL; YOKOGAWA; PAUL LIPPKE
	XRF/gas proportional/on-line	SENTROL
Coatings mass of Zn, Sn/Cr, Sn/Ni, Zn/Fe, Sn/Pb on steel and other substrates	XRF/gas proportional/on-line	DATA MEASUREMENT; FAG; GAMMAMETRICS

AIR QUALITY MONITORING WITH ROUTINE UTILIZATION OF ION BEAM ANALYSIS

UNDP/IAEA/RCA (RAS/8/082 PROJECT REPORT

Information on source contributions to ambient air particulate concentrations is a vital tool for air quality management. Traditional gravimetric analysis of airborne particulate matter is unable to provide information on the sources contributing to air particulate concentrations. Ion Beam Analysis is used to identify the elemental composition of air particulates for source apportionment and determining the relative contribution of biogenic and anthropogenic sources to air particulate pollution. The elemental composition is obtained by proton induced X-ray emission technique (PIXE), which is an ion beam analysis (IBA) technique. The element concentrations are deduced from the X ray spectra produced when the particulate collected on a filter is bombarded with a high-energy proton beam.

As part of the UNDP/IAEA/RCA Project RAS/8/082 'Better Management of the Environment, Natural Resources and Industrial Growth through Isotope and Radiation Technology' a collaborative alliance was formed between the Institute of Geological and Nuclear Sciences Limited and the Wellington Regional Council, New Zeland. The purpose of the project was to examine the elemental composition of air particulate matter and determine the origins through source apportionment techniques. In New Zealand PM10 and PM2.5 fractions have been collected at the industrial area of Seaview, Wellington over two years using a GENT stacked filter unit sampler. Concentrations of elements with atomic mass above neon were determined using Ion Beam Analysis and elemental carbon concentrations were determined using a reflectometer. Specific ambient source elemental 'fingerprints' were then determined by factor analysis and the relative contributions of various local and regional sources were assessed. The significant factors (sources) were determined to be: seasalt, soil, industry, and combustion sources. Local industry was found to contribute to ambient lead concentrations.

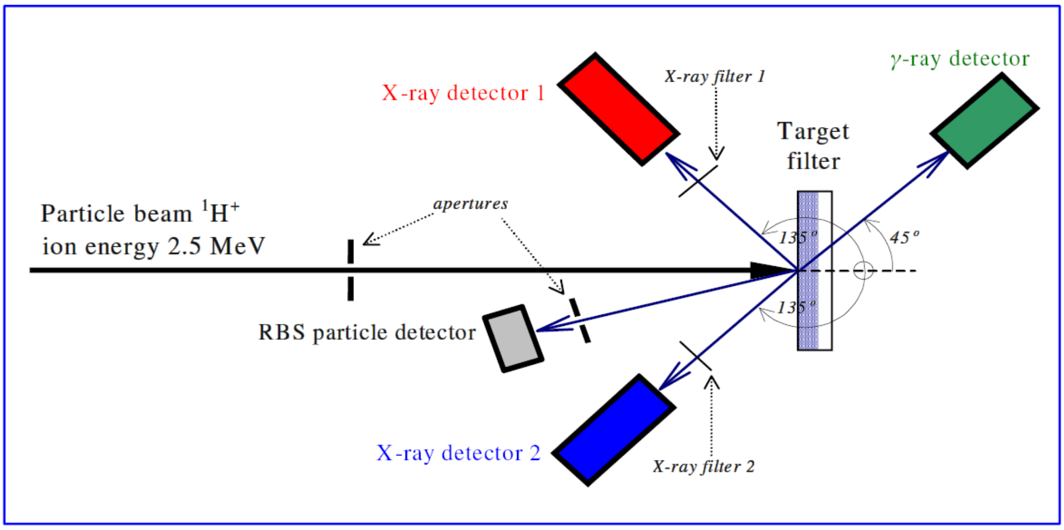

FIG. 1. Typical PIXE set-up.

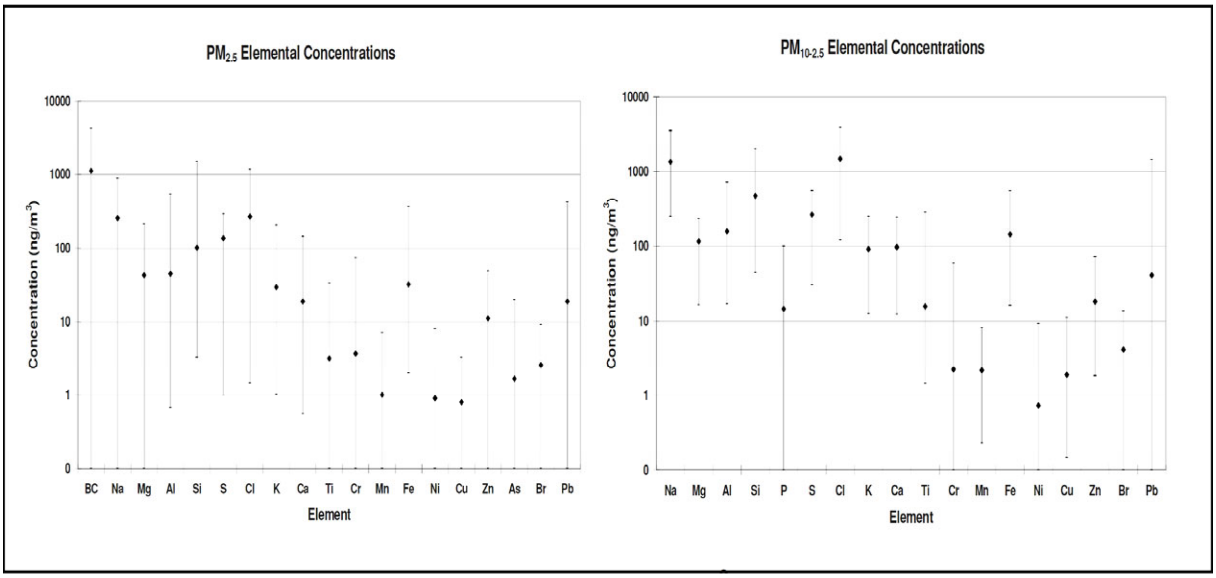

FIG. 2. Range of elemental concentrations (ng/m^3) for PM2.5 and PM10-2.5 respectively.

TABLE I. THE FINGERPRINTS OR FACTORS IDENTIFIED FOR THE PM10-2.5 FRACTION

Element	Factor 1 (Soil)	Factor 2 (Sea salt)	Factor 3 (Lead)
Fe	0.98	-0.02	0.08
Si	0.98	-0.03	0.12
Al	0.97	-0.05	0.10
Ti	0.96	0.03	0.13
K	0.89	0.41	0.04
Ca	0.86	0.46	0.08
Zn	0.72	0.16	-0.13
Cl	-0.08	0.96	-0.08
Br	-0.02	0.90	0.20
Na	0.04	0.87	-0.09
Mg	0.52	0.78	0.11
S	0.32	0.77	0.27
Pb	0.10	0.13	0.97

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