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BOOK OF ABSTRACTS

INTERNATIONAL CONFERENCE

***NUCLEAR ANALYTICAL
METHODS IN THE LIFE
SCIENCES***

Organized by the



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CHALLENGES OF APPLICATIONS OF NUCLEAR ANALYTICAL METHODS IN THE LIFE SCIENCES

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A survey is given of the various properties of nuclides which may serve as a base for NAM's (nuclear analytical methods). The characteristics of NAM's are outlined, particularly for use in the life sciences, against the background of non-nuclear analytical methods. General feature of NAM's is that excitation and de-excitation signals penetrate through matter, often enabling non-invasive measurement. Moreover, the signals are not - or at least not much - influenced by the matrix composition of the sample and/or by the physico-chemical state of the analyte, thus minimizing signal biases. Another feature of NAM's is that isotopes (stable as well as radioactive ones) of the same element being chemically identical, may be distinguished as nuclides, enabling particular techniques, for instance tracer and isotope dilution techniques. Sometimes NAM's provide unique information which cannot be obtained by other methods. However, in cases where NAM's give similar information, they may be used as reference method, due to its physically different base and the above-mentioned minimization of biases.

Important NAM's for application in the life sciences are: Nuclear magnetic resonance (NMR), Mössbauer spectrometry, Rutherford backscattering (RBS), instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA), various prompt nuclear reactions, proton-induced X-ray emission (PIXE), isotope dilution analysis (IDA), radioimmunoassay techniques (RIA), analysis via isotope effects and a variety of radiotracer techniques. A number of typical applications in the life sciences are presented, illustrating that NAM's do not only provide valuable information on amounts or concentrations of elements, but also on physico-chemical forms, spatial distributions, structures, and/or kinetics of elements and/or compounds.

Most times NAM's require considerable investments for equipment, supporting facilities, and also specialized staff. Therefore, facilities for NAM's generally have to be shared by groups of researchers, or NAM's have to be performed at centralized nuclear facilities. Full exploitation of the potentials of NAM's requires intensive cooperation and mutual understanding between researchers from the field of the life-sciences and the staff of centralized nuclear facilities. Possibilities to promote this cooperation and also to stimulate dissemination of knowledge on the potentials of NAM's to possible interested researchers are discussed.

Analytical Applications of Guided Neutron Beams in the Life Sciences

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A neutron guide is a reflecting channel which transports a beam of neutrons from the reactor to an experiment. The efficiency of a guide is inversely proportional to the temperature of the neutron source, so that most guided beams are associated with reactor cold sources. The term "cold" usually is applied to neutrons with a wavelength greater than 4 Å, which implies an energy less than 5 meV and subsonic velocity. The experimental advantages of cold neutrons have been well documented. Because cross sections are generally inversely proportional to the velocity, neutrons from a moderator at 30 K give a threefold higher reaction rate per target atom than those from a room-temperature source. By bending the guide or by filtration, the beam can be made entirely free of fast neutrons and gamma rays; as a result, the gamma ray background for prompt-gamma activation analysis (PGAA) is low, especially at low energy. Moreover, because the shielding can be made compact, induced radiation from the sample can be detected with much better geometric efficiency than with traditional beams, and thus the sensitivity for PGAA and related techniques is higher.

Recent advances in focusing neutron optics will lead to greatly increased flux density in neutron beams.¹ Capillary lenses, made up of hundreds of thousands of microguides, are especially promising. A gain of nearly an order of magnitude in flux density, condensed to a spot less than 1 mm in diameter, has been demonstrated with a first-generation lens; the theoretical limit in gain and spot size is very much better. A neutron microprobe appears within reach in the near future.

The first use of cold neutrons for PGAA was reported in 1973, but not until 1986 were modern large Ge detectors applied and the first permanent instrument installed at Jülich. A guided beam of thermal neutrons has been in use for a decade at Kyoto for analytical support of neutron-capture cancer therapy. More recently, cold-neutron PGAA has become established at NIST, and on cold and thermal beams at the JRR-3M reactor in Japan. Other instruments are under construction at Cornell, the University of Texas, and Budapest; a station at the Dhruva reactor in India is also planned.

The large amount of hydrogen in most biological materials causes a special problem for neutron beam techniques. The thermal scattering cross section of a free hydrogen atom is 20.5 barns. If the hydrogen is bound into a heavy molecule the cross section is four times higher, and for cold neutrons the cross section is tripled again. As a result, cold neutrons have a 50% probability of scattering after penetrating only 0.7 mm of carbohydrate or protein, and 0.4 mm of water. It has been known for ten years that this scattering affects accuracy for PGAA with a thermal neutron beam. The potential analytical bias has been controlled in practice by matching standards to the samples, but the problem remained poorly understood until recently.² The bias vanishes for spherical samples.

In addition, the background for certain elements (including B, N, and H itself) increases when neutrons are scattered from the sample into the surrounding parts of the apparatus. As a further complication, cold neutrons gain energy by scattering in a room-temperature sample, thereby decreasing the capture probability.³

These difficulties are most effectively avoided by measuring element ratios. The approach is similar to the classical k_0 standardization method of neutron activation analysis, with the important difference that the element chosen for the standard must be an intimate part of the sample. The fact that the reaction rate depends on the nature of the sample is inconvenient for analysts (and their customers) who are accustomed to units of grams of analyte per gram of sample, but in many cases the elemental ratio in fact the desired result. Recent examples from our own work include the determination of trace hydrogen in intact gas-turbine compressor blades (where the sample mass was ill-defined) and the analysis of major components in substituted C₆₀ derivatives (where the stoichiometry was to be determined).

Analytical uses of guided neutron beams seem sure to increase in the future. Work in progress at several laboratories on multilayer supermirrors suggests that the collection efficiency of neutron guides may be improved by as much as a factor of ten. A committee of the U. S. National Academy of Sciences recommended in 1984 that a new-generation Advanced Neutron Source be built for materials science research; a recent study has reinforced that recommendation. The ANS will be a 330 MW heavy-water reactor, with a peak thermal flux density $\phi = 7.4 \times 10^{15}$ n/cm²s, and more than 30 m³ of reflector with $\phi > 10^{14}$ /cm²s. On completion in 2002, the ANS will have 29 thermal, hot, cold, and very cold neutron beams, serving 48 neutron scattering, fundamental physics, and analytical chemistry instruments. The latter comprise two low-background cold-neutron PGAA stations and a neutron depth profiling station, each with $\phi > 10^{10}$ n/cm²s, seven pneumatic tubes, and associated laboratories to accommodate visiting users.⁴

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SIMULTANEOUS CYCLIC AND PROMPT NEUTRON ACTIVATION IN LARGE LANDFILL AND SEWAGE SAMPLE ANALYSIS

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Abstract

Land disposal of solid wastes has been practiced for many centuries, but it is in recent times that great concern has been expressed with respect to problems connected with the contamination of soil and the environment from industrial and domestic waste⁽¹⁾. The burial of millions of tons of refuse may result in serious environmental consequences; most notably groundwater pollution. On the other hand the wide usage of sewage-based fertilizers on agricultural lands is also of great interest, since the presence of trace elements including heavy metals in these fertilizers may have adverse effects on plants if allowed to accumulate in soils. Hence, the question arises whether what is actually buried in the landfills or covers agricultural land presents the potential to threaten the environment and human health.

Knowledge of elemental concentrations is essential in order to identify or establish the source of pollutants, and various studies have been carried out to determine these concentrations in order to assess potential hazards. Among the different analytical techniques employed, neutron activation analysis (NAA) offers a number of advantages in being multi-elemental, sensitive and having few sources of systematic errors, which means that high accuracy is attainable^(2,3). It is the objective of this work to investigate the use of prompt as well as cyclic neutron activation in bulk landfill and sewage sample analysis for monitoring studies.

The facility available incorporates an oscillating 1.85×10^{11} Bq (5 Ci) Am/Be isotopic neutron source which allows during each cycle period, the collection of both prompt gamma-rays emitted during irradiation and delayed gamma-rays emitted post-irradiation⁽⁴⁾. The neutron facility and the gamma-spectroscopy system (comprising a high resolution Ge(Li) detector) are controlled by computer to achieve reproducible timing parameters. The data collected are loaded onto a mainframe computer and analysed using a modified SAMPO program.

Since the absolute method was used in the analysis, it was necessary to optimise all the parameters in the so-called "activation equation", in particular the absolute efficiency of the detector for irregular shaped voluminous sources. A Monte-Carlo technique was adopted to calculate absolute efficiencies and also to choose the proper position of the detector with respect to the neutron source in order that the best elemental sensitivities can be achieved.

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Enhanced sensitivity for the determination of selenium by INAA

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Selenium commonly is assayed through its long-lived ^{75}Se isotope (half-life 120 days) produced in reaction of neutron capture $^{74}\text{Se} (n,\gamma)^{75}\text{Se}$. Low abundance of ^{74}Se (0.9%) is balanced in the reaction rate by relatively high neutron cross section of 52 barns for thermal neutrons. Hence, Se can be detected by NAA down to the pg range. However, this "interference free" sensitivity is not always reached in instrumental NAA. The most intense gamma lines of ^{75}Se , those at 136.0keV (emission probability of 59.0%) and 264.7keV (59.2%), often used for Se evaluation, interfere with those at 136.2keV of ^{181}Hf (half-life of 42.4 days) and 264.1keV of ^{182}Ta (115 days). The line at 279.5keV (25.2%) corresponds with that at 279.2keV of ^{203}Hg (46.6 days), and the line at 121.1keV (17.3%) with that at 121.8keV of ^{152}Eu (13.3 years). The magnitude of these interferences is particularly high in geological and environmental materials, and usually can not be corrected. Also in biological materials these interferences may make determination of Se less reliable. The line at 400.7keV is interference free, however its low emission probability (11.6%) limits their applicability to the cases with low compton background.

We employ the gamma line at 400.7keV with enhanced counting rate. The physical phenomenon that the gamma decay occurs from the same level via three branches, directly to the ground state, and via lines at 121.1keV and 279.5keV, and 136.0keV and 264.7keV in cascades, may contribute to the 400.7keV line in a true coincidence summing. The rate of the effect depends first of all on solid angle in a source-detector configuration. We use a well type detector to increase the rate of the summing effect (large solid angle). Experimental data show that with this arrangement the enhancement factor equals approximately 40.

Main disadvantages of the method are an increase in input count rate and pulse pile-up losses, an increase in the compton background under the peak, and worse resolution. However, employment of new amplifier technology is minimizing the adverse effects of high count rates. Thus far we have used high quality conventional amplifiers with proper calibration for pile-up/life time correction up to about 40kHz detector input count rate. The preloaded filter amplifier technology developed by Westphal (1) increases significantly the throughput, i.e., minimizes pile-up, and maintains good detector resolution at high count rates. Its implementation will further improve the measurements.

In the standard analytical procedure, samples of approximately 0.2 g in mass, closed in ampoules made of ultra-pure quartz, are irradiated with thermal neutrons (flux $\sim 7 \cdot 10^{13} \text{ s}^{-1} \text{ cm}^{-2}$) for 0.5h to 24h. After a decay period of 4-6 weeks, gamma spectra of the samples are recorded with the spectrometric system. Counting time is 4-8 hours. The spectra are evaluated with the program GAMANAL from the IAEA software package GANAAS. Peak area is corrected for pile-up and other losses with the semi-empirical

function of the ADC dead time. The sensitivity for selenium is in the one picogram range with possibilities for the detection of lower amounts.

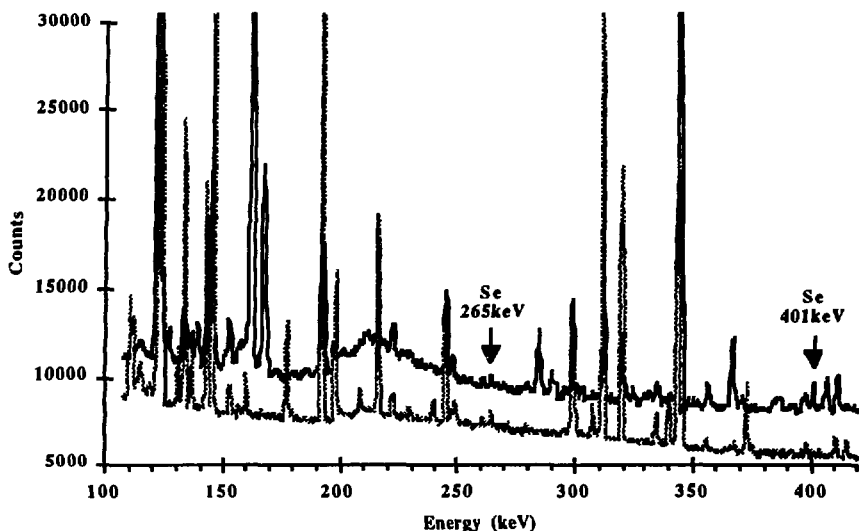


Figure 1 Gamma spectra of 0.2 g samples of brown coal ash, recorded with two different HP-Ge detectors at 70,000s counting time. The lower spectrum was recorded with a closed-end detector (28% relative efficiency, FWHM 1.8 keV at 1.3 MeV), the upper spectrum was collected 4 months later with a well-type detector (20%, 2.2 keV). Selenium can be quantified only in the latter measurement.

The increased sensitivity by using the 401keV line has made it possible to instrumentally determine selenium in a coal ash material (Figure 1). This material originated from the Kansk-Achinsk basin and is distributed as a test material, code ZUK-1, for intercomparison. The concentration of selenium is 0.7 mg/kg.

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APPLICATION OF NUCLEAR ANALYTICAL TECHNIQUES USING LONG LIFE SEALED TUBE NEUTRON GENERATORS

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Long life sealed tube neutron generators appear very attractive when used in research and industrial systems, for a large number of reasons. The first one is related to the deuterium-tritium or deuterium-deuterium fusion spectrum : the very sharp neutron energy spectrum makes any selective nucleus excitation possible, either at 14 MeV or at 2.5 MeV. The second reason is due to the high neutron output level of sealed tubes, associated with the on/off character of such generators : the neutron output in a wide range (10^7 - 10^{11} neutrons/second or more) may be considered without any excessive radiological arrangements due to tritium hazard or to a continuous activation of the installation. A third interesting feature for analysis is due to the pulsed mode at frequencies up to 10 kHz, which is not possible from radioisotopic sources or nuclear reactors. Using the pulsed mode, more selective excitations of material under examination are possible and, by means of synchronized detection techniques, prompt gamma-ray spectra due to either inelastic or capture interactions can be distinguished leading to better signal to background ratio and more powerful analysis. Another possibility is the activation of very short period elements (between 100 μ s and 100 ms, or more). In order to take advantage of these properties for versatile applications, long life neutron generators were designed and realized in transportable versions. Tests show useful lifetime equal or greater than thousand hours, depending upon the tube type and the selected neutron output.

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For on site real time process control, high energy neutrons, through their capability to penetrate deeply into materials, enable the dosing of a significant volume of materials in a short time, depending on the nature of the elements being sought. In aluminium production, an analyzer located at the output of a fluorated alumina silo enables short time neutron activation analysis of the bulk material for production. Its goal is to give a feedback signal related to Fluorine and Sodium content with an accuracy of 0.1 %. On line elemental analyzers for other bulk materials such as coal or cements may be designed with a pulsed neutron generator. An accurate determination of Calcium, Silicon, Aluminium, Iron, Oxygen, through a combination of gamma lines detected from activation and from prompt capture mechanisms was recently reported. In glass production, neutron analysis of Silicon, Oxygen and other elements could be completed at two points in the production line, at raw material entry and in the mix. In steel production, a continuous analysis of Iron, Calcium, Silicon and Aluminium is also of great interest.

The use of prompt neutron/gamma or neutron/neutron techniques is well established with 14 MeV neutron generators in the areas of geochemical exploration (oil and gas logging) and of environmental monitoring. These techniques are often more effective than the delayed activation techniques.

For radioactive waste containers survey, the most sensitive detection method for alpha emitters dispersed in a large matrix is based on triggered fission reactions by short neutron pulses. It is now possible to detect 1 mg of ²³⁹Pu in a 200 liters container, in less than 15 minutes.

Neutrons may also be used to detect hidden materials such as explosives in luggage, or in parcels. In these cases, a combination of prompt and delayed neutron/gamma techniques is proven powerful. The detection method is strongly linked to detection time, neutron output, object size, and elements to be detected.

For environmental monitoring, the neutron generator can allow the determination, in continuous mode, of the airborne pollutants. The neutron generator can emit simultaneously fast neutrons to determine for example cadmium and mercury elements, and thermal neutrons for chlorine and arsenic elements.

These few examples are included in a larger range of applications, based on spectrometric studies, on detection, or on imagery, for process control, non destructive testing, and analysis.

Optimization of irradiation conditions for gamma activation techniques of biological and environmental samples using a very high power electron accelerator

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Introduction

Gamma activation techniques (GAT) are well established for trace analysis [1] and radionuclide production. For high sensitivity of non-destructive photon activation analysis especially at environmental or biological samples, and high activity output, resp., a very high power electron accelerator is likely to be applied. Though using GAT the thermal load of the samples are lower as compared with other activation techniques (e.g. neutron activation with a reactor) some serious heating problems may arise because about 30 % of the beam power is transported by bremsstrahlung and partly absorbed in the sample, i.e. at the BAM 35-MeV LINAC at 30 MeV and 100 μ A about 1 kW. Therefore during such experiments an intensive sample cooling is necessary, but due to the low thermal conductivity of water and organic samples, the more effective the smaller the samples. On the other hand a highly sensitive analysis without preconcentration of traces [2] should be done at rather large samples. Therefore in some cases it is more efficient to keep the photon flux density just at an uncritical level, depending on the samples properties, by applying a limited beam power or an irradiation position far downstream from converter.

The PHOTAC code for calculating activity output

For quantitative estimation of the activity output and sensitivity as a function of the irradiation conditions the code PHOTAC [3] has been applied. It takes into account the electron energy and beam profile, the sample distance, sample composition, sample volume and form of the irradiation vessel (diameter, length). PHOTAC is based on the Monte-Carlo data of Tanaka et al. [4] for the photon flux density, which yet has been fitted in a rather rough way ($1/k^2$ -approximation) in the region of the Giant Resonance peak of the activation cross section function. PHOTAC has been confirmed recently by experiments at the BAM LINAC for 17 MeV, 25 MeV, and 30 MeV respectively, using potassium iodate solutions of different volumes located at different distances and irradiated together with Ni and Cu monitors. PHOTAC has been confirmed to represent the measured activities in the mean of almost 500 samples from 21 irradiations to about 20 % with a standard deviation of 30 % with maximum deviation of about 50 % mostly due to the mentioned rough approximations applied yet in PHOTAC. Some results will be shown. (More detailed results will be published elsewhere; an improved approximation is under development).

Optimizing the irradiation conditions using PHOTAC

Using PHOTAC different geometrical arrangements which might be useful for overcoming heating problems has been calculated and compared quantitatively for the activity output. The following problems has been studied:

1) Activating high volume water samples:

Ultratrace analysis of heavy element of environmental water samples should be done without preconcentration (which might be disturbed due to organic complexants [2]). The form of the

cylindrical sample vial (up to 5 liters) has been optimized using PHOTAC. The optimum diameter-to-length ratio for a given volume as a function of beam properties and sample position is shown and discussed from the viewpoint of the sensitivity. Roughly spoken diameter and length of the sample container should be chosen nearly equal.

2) Heating-up of water samples

Most serious heating problems appear at the the beam axis in the near-target-partition of the vial. There the water tends to boil especially in large containers, as the thermal conductivity of water is low; so the convection should be supported by an effective cooling of the outer surface. By using internal standard a boiling near the entrance window might be tolerated in the case of trace analysis of water samples, but the sensitivity is reduced. Calculations by PHOTAC show an activity reduction up to 30 % in the case of an almost empty central cylinder of 2 cm diameter due the boiling. The alternative way of using a small flow chamber (e.g. 0.5 l) more easily to be cooled and presenting only a part of the sample to the bremsstrahlung irradiation combined with a cyclic sample pumping [2] leads to a rather strong reduction of the activity output and of the sensitivity.

3) Heating up of organic samples

During instrumental trace analysis of organic samples having a very low thermal conductivity and resistance the sample might be irradiated off-axis and should be rotated during the irradiation giving a strongly reduced activity and sensitivity.

4) Heating-up of cryogenic and gas samples

A typical example for this problem is the production of iodine-123 by the photonuclear reaction $^{124}\text{Xe}(\gamma, n)^{123}\text{Xe} \rightarrow ^{123}\text{I}$. To yield an activity output of some 100 GBq a sample mass of about 20 g highly enriched Xe-124 must be positioned in a very condensed form, i.e. as an cryogenic or as a gas sample, at a very small distance from the bremsstrahlung converter target. PHOTAC calculations show that although the density of the cryogenic sample is higher by a factor of 3 (about 3 g/cm³) as compared with a high pressure gas target (maximum density about 1 g/cm³), a gas target should be preferred due to the low thermal conductivity of the cryogenic Xenon preventing an effective cooling and demanding a drastically reduction of the beam power. Because in the case of gas target the electrons may be allowed to strike the gas sample the thin walled sample cell can be positioned extremely nearby the converter target (distance about 5 mm compared to 15 mm in case of cryotarget) thus compensating for the lower density of the gas target. Numerical result will be given.

Conclusions

Some problems using very intensive bremsstrahlung fields at a high power electron accelerator are discussed. In estimating the influence of geometrical conditions and beam parameters upon the activity output the simulation of the activation process by the PHOTAC code was a very helpful tool to find out the best choice.

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NUCLEAR ANALYTICAL TECHNIQUES IN ENVIRONMENTAL STUDIES

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ABSTRACT

Nuclear Analytical Techniques have made a significant contribution to environmental research - among all the specialized analytical methods available to meet the special needs of the environment in this present day awareness of global change - and nuclear techniques will probably continue to play a particularly important role in the future. This is stated however, while acknowledging another observable trend, that is the demise of some research reactors and accelerators which have been used in the past for applied nuclear techniques and applications.

A cursory review of several notable environmental applications of nuclear analytical methods indicates that there are some attributes of these methods which, while not unique or distinctive in themselves separately, overall, combine to make nuclear methods of considerable use in the environmental field. These features include:

- (i) sensitivity combined with reliability and accuracy with a relative freedom from the need to establish empirical corrections,
- (ii) selectivity and relatively little matrix and interelemental interference,
- (iii) non-destructive analytical capability in a wide variety of *environmental sample matrices, eg. soils, sediments, biota and biological specimens,*
- (iv) multielemental capability for a range of 25-40 trace elements of environmental importance, and
- (v) reference and standardization techniques useful for round-robin analytical comparisons and calibration of analytical reference materials.

In addition, nuclear-based analytical techniques are particularly useful for meeting certain needs of current environmental studies: they are readily adapted to environmental pathways studies involving the tracking of trace components from their emission sources through to a range of receptor sites and living species via airborne-, water- or sediment-borne processes and food-chain pathways to biota to fowl and animals and to humans. Nuclear methods, particularly neutron techniques can readily handle the variety of environmental specimens involved in elucidating path-

ways, target species and organs in living systems. Further, recent developments in several laboratories have demonstrated that nuclear techniques can be applied to speciation studies which are essential in the assessment of environmental toxicology. Probably more future research will need also to examine synergism among contaminants and multielemental methods can be useful to help reveal any such effects.

Another requirement of some environmental investigations is to be able to deal with large sample suites. Quite apart from the task of monitoring well-identified contaminants and their routes to human exposure, which is mostly a role for regulating agencies, there is a need in some environmental research to make repetitive measurements at trace levels of ppm to ppb and lower in large sample collections of more than 100 samples. Because nuclear techniques can often be performed instrumentally and non-destructively, they can be carried out semi-routinely with the aid of robotic and software devices. Examples of nuclear techniques in the life sciences are extant in which in excess of 5000-10000 data points are involved.

In this paper, environmental studies in the life sciences are presented which illustrate the several ways in which nuclear-based analytical methods have proved to be very useful and important:

A combination of radiotracer and neutron activation techniques are being used, in this laboratory, to assess the potential environmental toxicity of residues from incineration of solid wastes in hospitals and in domestic waste treatment plants. In some related studies to identify hazards to local residents arising from district incinerators, INAA and PIXE analyses of suspended air particulate matter have been carried out and have revealed significant local elevations of Ni, Cd, Pb, Cr, Sb, As and halogens.

Contaminated industrial soils and dredge spoils have been used recently to create land spits in and outside the Toronto harbour for wildfowl use and for certain recreational uses. However, the fact that these land masses have been created with soils and sediments contaminated with metals and organics indicated that measurements should be made of the fate of toxics deposited in the lake in this manner. INAA has been performed on sediment layers being dredged, on exposed shoreline material compared to land-locked disposal pits, and on off-shore muds and waters. By SLOWPOKE INAA a total of 35 trace elements have been measured, including rare earth patterns.

These and other published researches can demonstrate the value of using nuclear techniques in environmental studies particularly when solids difficult to dissolve for conventional instrumental analyses, are involved.

USE OF NUCLEAR ANALYTICAL TECHNIQUES IN BIOENVIRONMENTAL STUDIES

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Bioenvironmental studies remain to be one of the most important field of applied analytical chemistry for long period and will remain in future. There is a number of problems because of very wide ranges of concentrations (from wastes to background levels) of great number of components to be determined in very broad row of types of samples to be analysed. This is a reason for nuclear analytical methods to be used beside of many other analytical techniques. At present time more than 50% of nuclear analytical studies deal with bioenvironmental investigations (MTAA-8) while decades ago high purity materials technology and geology were the main field of nuclear analytical techniques application.

The first period of nuclear analytical methods usage in bioenvironmental sciences could be characterized as a "pure analytical" while these methods were used for determination of samples composition in competition with other non nuclear methods.

Later the outstanding advantages of these methods were used for more detailed description of systems to be studied (elements speciations, spatial distribution, etc.).

Present period, in our opinion, not only develops approaches of previous periods but considers the bioenvironmental processes more widely and is focussed on their dynamics combining various nuclear techniques.

There are studies carried out in this direction by many researchers (including within the frames of IAEA CRPs) on role of coal in environment contamination. These studies include determination of coal and products of it's combustion composition, their interaction with wet precipitations and surface and ground water.

Similar studies were carried out during last years on pesticides (including dioxins) behavior in environment, on the atmospheric processes (system soil - dust - airborne particulate matter - vapor/gas - rain/snow), on the role of solid wastes, dynamics of environment and human health, etc.

Besides the determination of composition of bioenvironmental samples and elements speciations in them, the above named studies could give new view on biospheric processes and are important evidence of outstanding and growing importance of nuclear analytical methods in bioenvironmental sciences.

STUDIES OF INCINERATOR ASHES AND ITS ENVIRONMENTAL EFFECTS USING RADIOANALYTICAL TECHNIQUES.

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Incineration is commonly used in many cities for the management of solid wastes. Municipal wastes, hospital wastes and a variety of other wastes are routinely handled this way. While the waste volume is considerably reduced, the ash concentration of heavy metal toxins such as cadmium, mercury, selenium, arsenic and others are considerably increased and that poses a real environmental hazard. Many elements e.g. cadmium, arsenic, are loosely bound to the incinerator ash and are therefore easily leached into the water systems by rain or other natural processes. Incineration has therefore become a matter of great public concern.

We have studied solid waste incineration ashes using neutron activation and radioisotope techniques. The incinerators ashes studied include municipal refuse incinerator ash, coal fly ash and hospital incinerator ash. We have used batch extraction as well as sequential extraction techniques to study the leaching and speciation of toxic and other elements in these ashes. Various leaching media such as water, acid and other chemical complexes were used. The results of these experiments have suggested better methods of handling the wastes and the ashes.

Total Elemental Concentrations: The incinerator ashes contained high concentrations of cadmium varying from 17 mg / Kg in the case of fly ash to as high as 563 mg/kg in the case of municipal incinerator ash. Arsenic varies from 6 mg/Kg in hospital incinerator ash to 106 mg/Kg in the case of municipal incinerator ash. Mercury varied from 1 mg /Kg in the case of coal fly ash to 7 mg/Kg in municipal incinerator ash. Selenium varied from 13 mg/Kg in hospital incinerator ash to 50 mg/Kg in municipal incinerator ash. The pattern is generally similar with many other elements. The municipal incinerator ash, in particular, has high concentration of many elements thereby posing a significant environmental health hazard.

Leaching properties: The ash samples were air dried and homogenized to a 200 mesh size. They were then extracted with an acetate buffer at a pH of 5 for 18 hours using the United States Environmental Protection Agency procedure. 1g sample and 20 mL buffer were used. It was found that cadmium was leached from refuse incinerator ash to 76% while 14% was leached from sewage incinerator ash. This poses a significant health hazard since the cadmium in these ashes are released into localized water systems. 15% Hg was leached from the coal fly ash while 7 % was leached from refuse incinerator ash.

The kinetic studies of the leaching process showed that most of the elements are leached within the first few minutes to an hour and the rest of the leaching may take up to 200 hours. The extent of leaching also depended on the particle size of the ash. The lower the particle size the higher was the extent of leaching. These results suggest that the toxic elements are localized on the surface rather than in the interior matrix. Our results indicate that elements with low boiling point e.g. Cd, As, Hg, Se are localized on the surface of the matrix whereas those with high boiling points e.g. As and rare earths are located in the interior of the matrix. This has been confirmed by our experiments using the scanning electron microscope. In these experiments we have found that the smaller particles which are formed in the flue gases contain cadmium and other light metals on the surface. The heavier particles which are components of the bottom ash contain a core matrix of the refractory elements. This suggests that the low volatile elements are vaporized in the incineration process and then condense on the matrix particles as they rise towards the cooler levels of the stack.

Solidifying solid waste ashes: An important aspect of incinerator ash management is the solidification of these wastes so that the toxic elements are fixed to the matrix thereby rendering them non-leachable. We have studied many methods of chemically fixing of these elements. A method that is being studied is fixing these ashes in asphalt. Preliminary results appear promising.

Management of incinerator input: In many situations e.g. hospital wastes containing biological wastes, incineration process cannot be avoided for a variety of reasons e.g. the lack of effective alternative process and the lack of funding for changeover of the system within a short time. In these instances, the legitimate concerns of the hospital waste managers and the community must be addressed. Here a careful inventory of the waste is very useful. Our studies show that among the municipal or hospital wastes, the components that contain the most cadmium are common plastic items such as colored containers. If ordinary items such as bottles, plastics, colored containers are not added or removed and the waste strictly restricted to essential wastes which have to be incinerated due to biological contamination, the level of cadmium in the hospital incinerator ash and the air can be minimized. Another possibility is to acid or water wash the ashes for an hour by which up to 75% of the cadmium content are leached out. The rest of the solid waste containing the non-leachable residuals can then be sent to landfill sites.

Thus careful understanding of the distribution of toxins among the waste contents and the control of these is essential. Similarly careful control of the conditions to minimize leaching is also important. Procedures of fixing the toxins will also help us minimize environmental contamination.

METAL DETERMINATION BY EDXRF IN LICHENS: A CONTRIBUTION TO POLLUTANTS MONITORING.

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Lichens are useful indicators of atmospheric pollutants because they take up and accumulate high concentration of heavy metals.

In this study several samples of *Evernia prunastri*, collected in a mountain zone (Alpago-Belluno, North Italy), were placed in urban and high industrialized sites. In these, there were not growing lichens.

The amount of Cr, Mn, Fe, Ni, Cu, Zn and Pb was determined by EDXRF spectrometry in secondary target excitation mode and with the thin film approach.

Lichens were exposed in 14 different locations by means of special little traps (15*15*1.5 cm, with mesh of 1 cm²), from May 1992 to April 1993. Twelve sites were around a steel plant at different distances from it and the others in urban sites. Every two months samples were collected from thalli, to verify the influence of exposition time on metal accumulation. Each specimen was dried at 50°C for 24 hours and stored in closed bags in the dark.

The suitable samples for EDXRF were obtained by acid digestion of 200 mg of lichen in closed Teflon vessel, using a microwave oven. Targets were prepared by pipetting 300 µl of the solution onto a Mylar film and dried. Calibration was performed by means of NBS standard reference material n.1571.

An increase of metal concentration from the beginning to the end of the experiment was noted in all sites.

The most appreciable accumulations were found in those sites closer than 500 m from the steelworks where the ending concentrations were between ten and forty-fold the initials. Otherwise lichens exposed in urban and in places farther than 500 m from the factory, showed element concentrations about three to ten-fold the baseline.

In urban sites a significative increase of lead values was measured, as near cross-roads as lower traffic sites.

The washing procedure, employed for some samples, influenced the concentration of all the elements apart from Pb, as previously verified on *Pseudevernia furfuracea*.

NAA BIOMONITORING OF ENVIRONMENT WITH MOSSES AND PINE TREE NEEDLES

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In the recent years *Hylocomium Splendens* mosses and pine tree needles have become widely acknowledged biomonitors of air pollution with heavy metals. They rather exactly reflect pollution of environment with heavy metals and the REE transport through the air. It is shown that many of heavy metals (*V, Fe, Mn, Cu, Zn, Mo, Zr, Sn, Cr, Ni, W, Hg, Cs, Co, Ta, Ag, Sb, Sr, Au, Th, Ru, U*), REE's (*La, Ce, Nd, Sm, Gd, Yb, Eu, Lu, Tb*) as well as some non-metals (*Cl, Br, I, Se*) are well determined by NAA using resonance neutrons. The experimental data on the distribution of the above mentioned elements over a moss stem for "fine" and "coarse" stem fractions are given. On the basis of these results, the reasons for 10-15% inhomogeneity of the element distribution in powdered samples are discussed. Recommendations on moss sampling for activation analysis are given. For the given type of moss and pine tree needles the data on the detection limits of the mentioned set of elements are compared to those of original concentrations for resonance and thermal neutrons separately. As an example the data are given on heavy metals and REE pollution in some regions of Kola Peninsula, Moscow District, Norway, caused by Nickel mining, phosphorus fertilizers plants, etc. The results obtained are compared with the analogous element concentrations in adjacent soils. The investigations were carried out at the IBR- 2 reactor of FLNP JINR.

STUDIES ON HUMAN EXPOSURE TO ENVIRONMENTAL LEAD
IN TANTA, EGYPT USING EDXRF

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To assess human exposure to environmental lead in Tanta city closed to the agricultural high way , the concentrations of lead were determined by energy dispersive X-ray fluorescence technique in blood , water , grains , roadside vegetation (trefoil) and soil . The geometric mean blood lead concentration in non-smoking adult males , 89 ug / l was higher than the 67 ug / l reported for residents of some European or Chinese cities . Lead concentrations in different bodies of water has been studied , as well as guinea corn , soil and vegetation were also lower than values for similar environmental samples from the USA , Western Europe or China .

Lead concentrations in roadside soil and the trefoil increased with daily traffic volume and decreased exponentially with distance from the agricultural high way.

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THE BEHAVIOUR OF CHEMICAL ELEMENTS IN PLANTS AND SOILS

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The studies of trace elements in biological systems have become the subject of numerous investigations last years. NAA is one of the wide-spread techniques for study the peculiarities in behaviour of many chemical elements in environment.

In our research the accumulation of elements in soils and plants as well as redistribution of elements between different organs of plants were studied.

500 samples of plants and soils were collected during 5 years in different cities and countries in Russia. The weather conditions, species of plants, time of sampling etc. were noted in detail.

INAA with thermal and epithermal irradiations was used for determination the elemental compositions of plants and soils. The total number of determined elements was 40.

The NAA results were treated by means of different methods of multivariate statistics. Mean concentrations of chemical element and standard deviations were calculated; relationships between elements in different organs of plants and soil were studied too. Factor and discriminant analyses were used for explanation the behaviour of chemical elements in different biological systems.

It was found that urban soil is absolutely new formation now. It consists of soil itself and different debris. Urban soils are polluted by many heavy metals in comparison with rural ones. While, it may be supposed that soil is large reservoir for accumulation of toxic elements. In many cases direct correlation between trace elements concentrations in the soil and trace elements concentrations in the plants is absent.

It was shown that considerable changes in the relationships between chemical elements in urban plants in comparison with rural ones take place. For example, in leaves of urbanplants the Rb/Cs ratios are smaller than the rural ones. While the Sr/Ca ratios in urban leaves of plants are larger than in rural leaves of plants.

The behaviour of chemical elements in soils and plants is different. So, significant positive correlations between Eu and La, Tb and Sm are observed in soils and plant roots. On the other hand, correlations between these elements in plant leaves are absent.

At last, in plants (especially in green part of plants) clear positive Eu anomalies are observed. Whereas no Eu anomaly in both urban and rural soils was observed.

APPLICATION OF NUCLEAR METHODS IN THE STUDY OF SELENOPROTEINS

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Tracer techniques and neutron activation analysis (NAA) have been used in the detection and identification of selenoproteins and in the investigation of their distribution in the tissues of the rat. ^{75}Se with a high specific activity produced from enriched ^{74}Se by long-term irradiation with thermal neutrons was used as the selenium tracer. Selenium analysis was carried out either by instrumental NAA via $^{77\text{m}}\text{Se}$ or ^{75}Se , or by quantitative determination of the ^{75}Se tracer. In addition ultracentrifugation and chromatographic and electrophoretic methods were applied for subcellular fractionation and protein separation.

A procedure was developed for the optimum in vivo-labeling of the selenium compounds by administering a small amount of ^{75}Se -selenite to extremely selenium-depleted rats. By separating the labeled tissue homogenates using SDS-polyacrylamide gel electrophoresis more than 20 selenium-containing proteins or protein subunits were detected. Differences in their distribution among tissues and subcellular compartments suggest that they are part of several metabolic pathways of the element and that they might have different biological functions.

By double-labeling with ^{75}Se and ^{125}I and quantitative determination of the tracer distribution in the protein and protein fragments it was shown that a 27 kDa selenoprotein was identical to the subunit of the type I iodothyronine deiodinase. This compound, which has a key role in thyroid hormone metabolism, was thus identified as a new selenoenzyme containing one selenium atom per molecule in its active center. Other selenium compounds, such as a 34 kDa protein with a possible function in the testis, are at present under investigation.

Information on the tissue levels of the newly found selenoproteins was obtained in experiments in which extremely

selenium-depleted rats were replenished with labeled selenium. In a comparison with the tissue selenium levels determined by NAA it was shown that the tracer distribution corresponded to the distribution of the element in selenium-adequate rats and could therefore be used for quantitative selenium analysis.

In similar repletion experiments differences in the bio-availability of selenite and seleno-methionine were found. The rise in the tissue selenium levels observed with high selenium intake was shown to be mainly due to non-specific incorporation of the element into a large number of proteins. The levels of the specific selenoproteins seem to be homeostatically controlled and cannot be further increased by additional selenium supplementation.

SPECIATION OF TRACE ELEMENTS IN BIOLOGICAL MACROMOLECULES USING NUCLEAR AND BIOANALYTICAL METHODS

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Metalloprotein species are generally characterized by one of the three following techniques: (1) isolation of the protein followed by the measurement of its biological (enzymatic) activity; (2) incorporation of a radioactive tracer into experimental animals and subsequent measurement of the tracer activity in the isolated protein; and (3) purification of the metalloprotein followed by the determination of the metal in it by a suitable analytical method. The first technique is more suitable for confirming the presence or absence of a known enzyme. Although the second technique is widely used, the question remains whether a short-term exposure to a radiotracer could label all the proteins of that element to the same natural proportion. Additionally, problems are presently encountered in many laboratories regarding experiments with animals and in disposal of the radioactive remains of the animals. We have selected the third technique for studying metalloprotein species in the subcellular fractions of bovine kidneys.

A number of bioanalytical techniques are being used in our laboratory to separate and purify biological macromolecular species according to their size, charge, mobility, affinity to certain chemicals, etc. The techniques include: dialysis, pH variation, ammonium sulphate precipitation, cation and anion exchange chromatography, hydroxylapatite chromatography, chromatofocusing, gel filtration, electrophoresis, isotachopheresis, isoelectric focusing, etc.

The ideal analytical technique for measuring trace elements in proteins must satisfy several requirements. These include high precision, excellent accuracy, sensitivity of pico- to nanogram amounts, multielement specificity, linear range of several orders of magnitude, sample sizes of a few milligram quantities, none or very little interference from the major components of proteins and buffers, ability to analyze solid as well as liquid samples, preferably nondestructive analysis so that the samples can be reanalyzed by other methods and for other components, and fair rapidity for high sample throughput. Neutron activation analysis (NAA) is ideally suited for both qualitative and quantitative measurement of trace elements in biological macromolecules.

Dialysis experiments show that in all subcellular fractions >90% of Ca, Cd, Cu, Fe and Zn, and between 75 and >90% of Mg, Mo, S and Se remain bound to

macromolecules. Further separations and purifications reveal the presence of several metalloproteins and protein-bound trace elements in nuclei and supernatant fractions, and some of them have not yet been reported in the literature. These include cadmium-binding proteins (MW 13 000, 32 000, and >300 000 daltons), zinc-binding proteins (MW 27 000, 89 000, 260 000, and >300 000), copper-containing protein (MW 30 000), and arsenoprotein (MW 27 000). An unusual enrichment of about 75% of Se in the nuclei fraction attracted much of our attention for in-depth studies over the last several years. Three new selenoproteins (MW 30 000, 70 000, and 80 000) have been found in the nuclei fraction. Details of the methodologies and results will be presented.

RECENT DEVELOPMENTS IN NUCLEAR ANALYTICAL TECHNIQUES IN METAL TOXICOLOGY STUDIES

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The aims of the JRC activities on Trace Metal Exposure and Health Effects consist essentially in establishing, on a scientifically sound basis, dose-effect relationships in view of preventing potential health hazards from exposure to trace metals. To achieve this goal, two topics linked to each other, are being investigated: (i) trace metal levels in human tissues of EC population; (ii) metabolism and biochemical effects of trace metals.

The first topic is addressed, on one side, to establish baseline values in general population as the fundamental parameter for the assessment of the biological effects of trace metal exposure on humans. On the other side the determination of trace metals in body fluids and tissues of individuals exposed professionally or individuals poisoned accidentally as well as of pathological cases has provided meaningful information on etiological power of some elements and on their potential role in the induction processes of some diseases.

For the development of the second topic, studies on the metabolism and on the biochemical effects of trace metals are required, these being performed both in vivo on laboratory animals and by in vitro studies including toxicity testing as alternative to animal testing.

This paper summarizes recent achievements on the JRC metallotoxicological studies related to the environmental and occupational exposure of trace metals as carried out by neutron activation analysis (NAA) and radiochemical techniques in combination with ET-AAS, ICP-AES, ICP-MS and EPR techniques.

Trace metal reference values in body fluids and tissues of general population as baseline values for clinical / toxicological assessment studies The EURO TERVIHT (Trace Element Reference Values in Human Tissues) project is aimed at establishing and comparing trace metal reference values in tissues from inhabitants of the European Community. 46, 35 and 26 metals were determined in urine, blood and serum, respectively, of Italian subjects. In urine Si, Rb and B were the only elements for which reference ranges were in the order of milligrams per litre level (2.9 - 12.1, 0.28 - 4.1, 0.49 - 3.2 mg L⁻¹, respectively) in blood the highest reference ranges were for Zn (4.1 - 7.5 mg L⁻¹), Rb (0.9 - 4.15 mg L⁻¹) and Cu (0.87 - 1.64 mg L⁻¹); in serum for Zn (0.59 - 1.21 mg L⁻¹) and Cu (0.6 - 1.37 mg L⁻¹).

The influence of wine, mineral water, beer, tea and coffee as possible dietary factors influencing the experimental ranges of trace metals determined was also considered. An increase of the total dietary intake to an extent greater than 10 % was estimated for Ag, B, Ba, Li, Sb, V (mineral water); B, Ba, Co, Mn, Ni, Rb, Sb, Tl, V (wine); Co, Mn, Ni (tea); Rb (coffee); V (beer).

Identification of biological specimens as indicators of metal exposure in occupationally exposed workers The HAMBHIT (Hard Metal Biomonitoring In Human Tissues) project is aimed at determining hard metals (e.g. Co, W, Ta, Cr, Ti, Ni, Mo) in tissues of occupationally exposed workers. Major findings concerning the significance of possible indicators of Co exposure are : (i) blood and urine cobalt (BCo and UCo) are variable parameters and their use as possible indicators of exposure, particularly in pathological cases, is questionable. A decrease in urinary excretion of Co was observed with an increasing period at work (ii) pubic hair and toenail cobalt (HCo and NCo) represent suitable specimens as indicators of Co exposure but they do not seem good indicators of Co accumulation in the body (iii) analysis of cobalt in bronchoalveolar lavage is useful from a qualitative point of view, to prove that an exposure occurred, after that the subject was removed from work (iv) multielement neutron activation analysis of Co, Ta, W in microsamples of lung tissue (open lung or transbronchial biopsy) collected for clinical purposes is an excellent method to prove hard metal exposure.

Animal testing Vs. alternative in vitro testing Radioisotopes with very high specific radioactivity mainly produced at the JRC Ispra cyclotron have been used in vivo on laboratory animals and in vitro toxicity testing (as alternative to animal testing) to study metabolic pathways and toxicological effects of low doses of trace metal compounds.

Detoxification mechanisms of metal toxicity (by ^{73}As , ^{74}As and ^{76}As radiotracers):

(i) Methylation is the detoxification mechanism for inorganic arsenic in mammals. However, in mice the methylation is linear with the dose of inorganic As administered from 0.2 to 7.5 mg As/Kg b.w., while in the hamster and rabbits the formation of dimethylated As in urine is depleted at exposure of 5 mg As/Kg b.w. This suggests that different animal species would have different limits of capacity in As biomethylation, which should be taken into account before establishing an animal model. (ii) The reduction of V^{5+} to V^{4+} is a mechanism of detoxification for vanadate ions in mammals. ^{48}V radiotracer and Electron Paramagnetic Resonance technique were used to investigate the bioreduction of ^{48}V -vanadate ions in BALB/3T3 cell lines. The biotransformation of the toxic pentavalent V to tetravalent was proved to be glutathione-dependent as showed by the depletion of this latter in the cell. In this case, an increased cytotoxicity and morphological transformation frequency due to vanadate exposure was observed.

Influence of the chemical forms of trace metals on their metabolism:

Pharmacokinetic experiments by double-labelling with ^{124}Sb and ^{125}Sb radiotracers have been carried out in rats exposed to $0.1 \mu\text{g Sb/rat}$ as $^{125}\text{Sb}^{3+}$ or $^{124}\text{Sb}^{5+}$ species. 80 % of the Sb^{5+} form was excreted via urine during the first day after treatment and 1 % in the feces. In contrast only 5 % of the Sb^{3+} form was found in the urine while 40 % was excreted via feces. In the blood and liver the Sb^{3+} species show higher levels than Sb^{5+} confirming the different metabolic pathways of the two chemical species.

Biotransformations: Double-labelled experiments with $^{201}\text{Tl}^{+}$ and $^{204}\text{Tl}^{3+}$ radiotracers simultaneously administered to rats in equimolar concentrations ($1 \mu\text{g/Tl/rat}$) showed that the ratio $^{201}\text{Tl} / ^{204}\text{Tl}$ in tissues resembled to 1. This confirms that the two Tl species follow similar metabolic pathways which suggests the existence of a biochemical conversion of the two species to a single one.

A similar approach has been used in studying the in vivo biotransformations of As^{3+} and As^{5+} in mice ($0.1 \mu\text{g As/Kg b.w.}$ of each compound) and in BALB/3T3 cell lines. The distribution of the two radiotracers among plasma components, liver and kidney cytosols as well as the supernatant fraction of BALB/3T3 cells suggests that a biotransformation to a single chemical form occurred in these in vivo and in vitro experiments.

Detection and determination of metalloprotein species by nuclear techniques

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Trace element studies in biological samples have long been of great interest. The sophistication of these studies has increased in recent years, from the emphasis of determining elemental concentrations in various whole organs, tissues, and body fluids to making these determinations in smaller and smaller subunits, first in various cellular components, and at present of elements associated with biological macromolecules, or trace element speciation. For instance, research on selenium and selenium-containing macromolecules has been extensive since the time selenium was established as an essential element and that its presence is necessary for the prevention of several diseases. Numerous studies on the metabolism and effects of this element have been carried out, especially with glutathione peroxidase, where selenium was identified as being the active biological component of this enzyme. Due to the small amounts of the fractions available for investigations, and generally low selenium concentrations in tissues the conventional and nuclear analytical techniques are still substituted by radiolabelling. In the studies involving selenoproteins, radiolabelling has played an invaluable role in locating possible new selenoproteins and selenoenzymes, and confirming their identification. However, it is not always convenient, or even possible, to introduce radiolabelled compounds to man, animals, or tissues being studied. New analytical techniques with high specificity and sensitivity are needed.

Because of their sensitivity, nuclear techniques are suitable for determining the biological macromolecule-associated elements after performing a biochemical separation. Especially their application for simultaneous determination of trace elements in a large number of separated proteins as they are obtained by polyacrylamide gel electrophoresis (PAGE) may be appropriate. This is accomplished without destruction of the sample matrix by dissolution, etc., and so keeping the spatial information of the separation. The combination of polyacrylamide gel electrophoresis and neutron activation analysis (PAGE-NAA) for the determination of elements associated with proteins has previously been demonstrated (1,2), specifically in the analysis of separated phosphoproteins. Here, the proteins contained in non-radioactive samples were first separated by PAGE, then subjected to neutron activation, autoradiography and subsequent quantification of the phosphorus. Other nuclear techniques can also be employed in the determination of elements associated with biomolecules. The method of PAGE-PIXE has also been used in the analysis of iron and nickel-containing proteins (3).

The emergence of high intensity X-ray beams with the prospects of focusing may make the development of an appropriate probe technique possible. At present, we are studying the application of energy-dispersive X-ray fluorescence (EDXRF) for the analysis of selenoproteins, which have first been separated using PAGE. These tests have been done with glutathione peroxidase from bovine erythrocytes. The separated proteins on the gel were then

visualized by a non-specific protein stain, Coomassie Brilliant Blue. Two bands at approximately 22 kDa and 24 kDa were identified as monomeric plasma glutathione peroxidase and the subunit of the cellular glutathione peroxidase. Sections in 2 x 10 mm strips, including the bands of the separated proteins and the areas around them, were excised from the gel and analyzed with XRF, using a polarized beam. The primary excitation source was a molybdenum anode, at 50 kV, 20 mA, and the secondary target was single crystal molybdenum, providing a back reflection through an angle of 90°, resulting in a polarized beam. The beam had an area of 10mm², exciting approximately 5mm² of the sample.

The amount of selenium determined in each band was about the same (1ng•mm⁻²), indicating that the amounts of sub-cellular and plasma glutathione peroxidase were approximately equal in this preparation. The equal amounts of selenium were independently confirmed with neutron activation analysis and the total amount found was in agreement with the applied quantity. The current sensitivity of the XRF instrument is at the ng-level corresponding to about 0.1nmol of the protein, an amount encountered in routine applications.

The use of plane polarized x-rays for excitation reduces significantly the scattering process, thus lowering the background, compared to conventional EDXRF. Additional improvements will be implemented by tailoring the physical size of the X-ray beams to the physical dimension of the protein when separated by the PAGE procedure, namely a fine line of 8mm length. An instrument with such properties can be used to scan a protein track on a gel along the molecular weight axis and thus quantitatively associate trace elements with the molecular weight of the protein.

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STUDY OF LOW SELENIUM ENVIRONMENT IN CHINA BY INAA AND MOSSBAUER SPECTROMETRY

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The low selenium regions are widespread in China, exhibiting a Se-deficient belt running from northeast toward southeast. In this work we emphasize to study the low selenium environment at Exi Autonomous Prefecture, Hubei Province, just located in the middle of this belt. Geographically, it belongs to the northern subtropical zone and the soil there is of weakly acidic yellow and brown type. The rarity of severe cold in winter and of intense heat in summer, heavy fog and high humidity are characteristics of the local climate. In geological tectonics, it belongs to the Tertiary Upwarped District of the Neocathaysian Tectonic System, which is formed from erosional landform. The soil-forming source rock is brown sandstone.

We used neutron activation analysis (NAA), τ - τ coincidence spectroscopy, nondispersive hydrogen flame atomic fluorescence spectroscopy (NADFS) and Mossbauer spectrometry (MS) to determine the Se contents of the soil and botanic samples in this Prefecture, a well-known Keshan disease region.

The Se contents in the soil samples range from 0.075 to 0.18 mg/kg with the average 0.13 mg/kg, while in the maize from 0.001 to 0.018 mg/kg with the average 0.0099 mg/kg, being lower by factors of 31.8 and 19.2, respectively, compared with those in the normal Se districts. In addition, the Se contents of the soil samples in this region are comparable with the Se level of the Chinese Se-deficient belt, while the maize there contains lower Se content. It implies that part of Se in the Exi soil does not exist as a bioavailable species.

In order to decipher the formation of low Se environment, we used MS to study the Fe-57 Mossbauer spectra of the low-Se and normal-Se soil samples. The former consists of a paramagnetic central dual peaks and ferromagnetic six-line spectrum, considerably different from the MS spectrum of the normal soil. It indicates an anoxic environment. In addition to the Fe(+3) species, the compounds containing low valence iron, e.g. goethite, etc. also exist. The REE pattern obtained by NAA further confirms the reductive soil environment.

VANADIUM LEVELS IN URINE AND CYSTINE LEVELS IN NAILS AND HAIR OF EXPOSED AND NORMAL PERSONS

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There is continuing interest in the biological functions and metabolic roles of vanadium, because the element has been reported to be essential trace element for chicks and rats, speculations appeared as to whether vanadium could also be essential for man, the element is released in large quantities to the environment, mainly by burning oil, and there are also well known sources of occupational exposure to vanadium [1]. Therefore, the assessment of possible effects of vanadium on human health should be considered. In occupational health, vanadium levels in blood, serum, urine, hair, and nails were discussed as possible indicators of exposure to vanadium [1,2]. However, the sensitivity of the particular tests is not very well known and the reported base-line levels ("normal" values) of vanadium in blood, serum or urine vary widely from 0.24 to 31 ng/ml for urine and from 0.031 to 800 ng/ml for blood and/or serum, presumably due to analytical difficulties involved. Contradictory findings were also reported on decreased cystine levels in fingernails of exposed workers [3].

As an extension of our previous small scale study on vanadium determination in blood and hair of normal and exposed persons [2], vanadium levels in urine and cystine levels in nails were studied in this work. The tissues and/or body fluids were collected from 54 occupationally exposed workers of a vanadium pentoxide production plant, where occupational exposure limits for vanadium in workplace air were exceeded at several workplaces. One small control group (C 1) was formed by 10 administrative workers of the plant, while another control group (C 2) consisted of 21

workers of a research institute where no occupational exposure to vanadium occurs. Using RNAA with proven accuracy at the ultratrace level [2], the following urine vanadium levels in ng/ml were determined:

Subjects	Range	$X_a \pm SD$	$X_g \pm SD$	Median
Exposed group	3.02-762	71.2 \pm 132.7	30.1 \pm 3.46	32.8
Controls C 1	1.05-10.7	3.51 \pm 2.96	2.76 \pm 2.00	2.24
Controls C 2	0.066-0.489	0.224 \pm 0.096	0.203 \pm 1.61	0.215

The mean urine vanadium value in the control group C 2 is one of the lowest reported. Since the necessary precautions to minimize sample handling and to avoid contamination on urine sampling and since the accuracy of vanadium determination by the RNAA procedure employed was proved by concurrent analysis of suitable reference materials, this finding supports the recent conclusions [2,4] that, similarly to blood and/or serum analysis, the lowest end of the reported values is probably correct, i.e. mean values in the range of 0.2 to 0.8 ng/ml of vanadium in urine of occupationally non-exposed persons. The sensitivity of vanadium levels in urine and blood as a measure of exposure to vanadium is discussed using our previous results for blood vanadium [2], as well as results of cystine determination in nails and hair obtained in this work.

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IODINE AND SOME OTHER TRACE ELEMENTS OF THYROID GLAND :
STANDARD AND DISEASE

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An important part of iodine deficiency in etiology of goiter and thyroid cancer is well known. However, recently the information appeared that deficiency or excess of some other body trace elements may result in thyroid diseases.

Contents of 16 chemical elements (Ag, Br, Ca, Cl, Co, Cr, Fe, Hg, I, K, Na, Rb, Sb, Sc, Se, Zn) in normal thyroid gland and with different thyroid nodular destructions were estimated by a complex of instrumental neutron activation (NAA) and X-ray fluorescent analysis (XRF) [1]. Autopsy and operation material was used for it. Operation material was obtained during surgical treatment of 91 patients, among them there were 33 operated on the occasion of thyroid cancer, 11 on the occasion of adenoma and 47 on the occasion of nodular goiter. Samples for analysis were taken both from a destruction focus (goiter) and from surrounding apparently intact tissues (paranodular tissue). Diagnoses of an every patient were verified according to histological data, and results of clinical and dynamic observation of the patients during some years. Intact thyroid glands were taken from 50 human corpses perished suddenly as a result of an accident. The patients' age ranged from 15 to 77 years.

The most considerable changes between the element contents for a standard and diseases were found for native iodine. Thus, mean iodine concentrations in a destruction focus for thyroid cancer, adenoma and nodular goiter were 32 ± 5 , 174 ± 38 and 344 ± 4 μg in g of wet tissue, respectively. A iodine content of intact thyroid gland is approximately 20 times higher than that of destruction malignant tumour. The highest iodine concentrations in paranodular tissue were found as a rule for malignant tumours. Mean iodine concentrations in paranodular tissue for cancer, adenoma and nodular goiter were 960 ± 91 , 527 ± 138 and 640 ± 66 $\mu\text{g/g}$, respectively.

Statistical analysis showed a high informational ability of both absolute and relative values of iodine concentrations in destruction focus for differential diagnostics of its benign or malignant nature [2]. A high informational importance of an absolute iodine concentration value was the basis of a new method for differential diagnostics of thyroid cancer and benign tumours. Samples of puncture biopsy weighing approximately 3 - 5 mg were used for elemental analysis. Special methods of NAA and XRF developed for such analysis possess a high productivity (time for a single element estimation averages approximately 5 - 10 min) and can be completely automatized [3, 4]. Low traumaticity (goiter puncture with thin needle), high informativity (accuracy, sensitivity and specificity), expressness and availability of XRF make it possible to recommend it as a method of diagnostics for mass examinations of goitre-

-carriers, within the goiter endemic regions in particular, for the purpose of exposure of patients with increased risk of goiter malignization.

A high informational importance found for iodine concentration ratio of destruction focus to paranodular tissue was used to develop a non-invasive method and equipment for thyroid cancer diagnostics based on in vivo XRF [5]. In such variant the method can be used as an additional test firstly for patients for whom radionuclide methods of examination are contra-indicated (children and pregnant women). By present in Russia small series of equipment for in vivo thyroid iodine XRF have been produced and are now being tested in the largest hospitals of country.

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TRACE ELEMENT ANALYSIS OF TISSUES OF HUMANS AND RATS

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To quantify systemic effects and to study a possible cancerogenic influence of corrosion products of metallic prostheses, element concentrations in tissues of deceased humans, who had carried hip joints consisting of CoCr-alloys, as well as tissues of WISTAR-rats of an animal experiment were determined by means of neutron activation analysis. The analysed rat samples are from a normal cohort of WISTAR-rats from a study in which particles of alloys that are commonly used for prostheses are implanted into rats to study possible induction of cancer.

Lyophilized samples (30 - 50 mg) of pancreas, spleen, kidney, liver etc. were irradiated for 20 h in the FRG-1 at Geesthacht ($\Phi_{th} = 4 \cdot 10^{13} \text{ n s}^{-1} \text{ cm}^{-2}$). Selfmade standards were irradiated with the samples. NBS-SRM 1577 Bovine Liver, NBS-SRM 1571 Orchard Leaves, NBS-SRM 1549 Milk Powder and GHENT-Serum (Human Serum) have been used in order to control the analytical procedure. Purified Suprasil AN which was also used as sample containers has been analysed as blank values.

Determination of chromium at naturally occurring levels in biological materials requires very low detection limits (and dust-free conditions during sampling). To this purpose a radiochemical separation technique which includes extraction of Cr(VI) into tribenzylamine/chloroform and reextraction into alkaline aqueous solution has been improved. Without time-consuming precipitation of BaCrO₄ the detection limit has been decreased (to values like 1 ppb) by elevation of decontamination by a factor up to 1000. Coprecipitation of ⁶⁵Zn(OH)₂ is shown as the reason for this result. Yield determination of each sample was carried by ICP-AAS measurements. The accuracy of the radiochemical procedure has been proved by analysis of NBS-SRM 1577 Bovine Liver.

The correction for ⁵⁴Fe(n,α)⁵¹Cr-interference has been calculated from the results obtained from irradiated high-purity iron.

Results. The radiochemical separation technique described by Greenberg and Zeisler¹ has been improved by changing the concentration of the alkaline solution used for reextraction from tribenzylamine from 2 mol/dm³ to 0.4 mol/dm³. Gammaspectroscopic measurements as well as simulation-experiments with solutions of ZnCl₂ showed an increase of decontamination for ⁶⁵Zn of a factor 1000 effected by this change.

For NBS SRM 1577 Bovine Liver a mean value of (66±10) ng Cr/g has been determined.

As example for the analysed organs of WISTAR-rats, Table 1 shows the results for chromium determination in pancreas.

The observed concentrations below 20 ppb for Cr and below 1 ppb for Sc as well as antimony concentrations below 15 ppb show that the analysis of chromium was not affected by mineral dust.

Table 1: Chromium concentrations [ng / g dry weight] in pancreas of WISTAR-rats.

Sample	ng Cr / g
A2	18.3±2.3
B1	< 16.9
D1	19.1±2.0
E1	13.0±1.8
F1	8.0±1.4

Table 2 shows chromium concentrations of the liver of 5 deceased human implant (made of CoCr-alloy) bearers (Pat. A, B, C, D, K) in comparison with "normal" values determined by Lievens et al.² and Michel et al.³.

Table 2: Chromium in human liver of implant bearers (CoCr-alloy) compared with "normal" values [ng / g dry weight].

Sample	ng Cr / g
Pat. A	< 10.4
Pat. B	< 67.9
Pat. C	101 ± 45
Pat. D	19.6 ± 6.7
Pat. K	1404 ± 93
"Normal"	6.9 - 34.5 (n=5) Lievens et al. ²
"Normal"	< 14 (n=4) Michel et al. ³

For patient K chromium-concentration in liver is enhanced by nearly two orders of magnitude. Because the liver has not been in contact with the implants (hip and knee, respectively), this shows that implants of CoCr-alloys can cause burdenings in the whole organism.

For patient K also enhanced levels of Co and Mo were found in the liver. This patient shows also burdenings in lymphatic tissue. Concentrations observed for Sb and Sc prove that the results are not affected by mineral dust.

For spleen, kidney and heart Co and Cr-concentrations were also determined.

Conclusions. The determined concentrations of Cr and Co are reliable because handling under dust-free conditions has been proved. Systemic effects of joint prostheses made of CoCr-alloys have been demonstrated by observing Co and Cr enrichments in various organs of deceased implant bearers. The new radiochemical separation technique simplifies determination of chromium at naturally occurring levels in biological materials so that reference levels for possibly enhanced values can easily be obtained.

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DETERMINATION OF TRACE ELEMENTS IN HUMAN LUNG SAMPLES

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Neutron activation analysis has been applied to the determination of trace elements in lung samples. A detailed study of the elemental composition profile of tissue samples collected from smokers is of great interest in order to provide additional information on the effect of tobacco smoking on the lungs.

Tissue samples were obtained from seven smokers and six non-smokers classified according to information provided by their closest relative. As an internal control a sample was collected from one child dead by intrauterine events.

Samples of lung tissues and lung hilum lymph nodes were obtained from autopsies and submitted to cryogenic homogenization, lyophilization and sterilization using a ^{60}Co source. Precautions were taken during this preparation step to avoid contamination.

The analytical method used for the determination of trace element concentrations was the instrumental neutron activation analysis. Lung samples and environmental and biological reference materials were irradiated together with the synthetic standards of elements in the IEA-R1 swimming-pool type research reactor and after adequate decay periods, gamma ray measurements were carried out using a Ge(Li) detector.

Irradiations of 30 min under a neutron flux of $3.7 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ were performed to determine Cl, K, Mn and Na and longer irradiations of 16 hours under a flux of $10^{13} \text{ n cm}^{-2} \text{ s}^{-1}$ for the determinations of Br, Cr, Cs Fe, Hf, La, Rb,

Sb, Sc, Se, Th and Zn.

Results of replicate determinations in a lung tissue sample showed a good reproducibility of the method for most elements analysed with relative standard deviations lower than 10.5% . Also the accuracy of the method was evaluated by analyzing IAEA Animal Muscle H-4, NIST Bovine Liver 1577a, IUPAC Bowen's Kale and NIES Vehicle Exhaust Particulates and their results showed in general a good agreement with published values.

Although a considerable inter-subject variability was observed, the elemental analysis results for non-smokers were within the range reported in the literature except for the Cl and Hf. Results obtained for lymph nodes could not be compared since literature published data for this type of tissue are scarce.

Sb levels in lung tissues were significantly higher in smokers in comparison with non-smokers. Lymph nodes presented the same behaviour observed for lung tissues. This finding indicates that hilum lymph nodes may due to their physiological function of draining and clearance of exogenous material, be used as indicator of elemental composition profile in lungs.

The analysis performed for stillborn tissue revealed either lower levels of most elements when compared to those obtained from adult non-smokers, or in some case they were not detected. (Work supported by CNPq and FAPESP from Brazil)

A STUDY ON CHILDREN'S CONDITION THALASSEMIA USING NEUTRON ACTIVATION ANALYSIS AND OTHER TECHNIQUES

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Two of the most devastating blood diseases , in terms of cost of treatment as well as human suffering, are homozygous β thalassemia(HBT) and sickle cell disease(SCD). These are the most common single gene disorders in the world. According to WHO estimates, by the year 2000, about 7% of the world population will be carriers for one of these diseases. At present over 200,000 children are born annually who will be affected by these diseases. Most of the affected children in the Third world die within the first decade of life. In North America, The Hospital for Sick Children in Toronto manages the largest program for patients with thalassemia and its program for sickle cell anemia is one of the largest on this continent.

These two disorders of human hemoglobin suffer from such anemia that, after the first year of life, monthly red cell transfusions are necessary for survival. But this, in turn, leads to body iron loading which itself is fatal and , again for survival, has to be removed by daily chelation therapy. Thus monthly blood transfusions and lifelong, cumbersome irritating subcutaneous, daily overnight infusions of desferroxamine are essential. The cost of this therapy has restricted its usage to a small portion of these patients in developing countries. A search for an easier oral therapeutic agent is now underway.

The careful management of these patients under transfusion and chelation therapy have increased the life expectancy of these patients to the second decade. This has brought on concerns of other secondary effects when these patients survive many years. One of the concerns is their bone status since bone formation is intimately connected with blood and bone marrow. Since many of these patients are susceptible to osteopenia and fractures associated with it we began a study of their bone mineral status.

In this study we have followed 50 patients with an average age of 24 years (range 15 to 49 years). All, except seven of them, have been under transfusion. We have measured their liver iron content and also their bone mineral status. The bone status of these patients have been measured using in-vivo neutron activation analysis (IVNAA) and dual energy x-ray absorptiometry(DEXA).

We wanted to determine which of the two techniques is appropriate and accurate. The IVNAA using thermal neutron activation of ^{48}Ca to ^{49}Ca in the bone is an established direct method of estimating bone mineral status. In this work we have considered this technique as the gold standard. It takes about an hour to complete, give only total body status and the radiation dose to the patient is of the order of 3.5 mSv. The DEXA, on the other hand, is a relatively new technique based on x-ray attenuation. It takes less than half hour to complete, gives site specific data e.g. lumbar and femur data, and the radiation dose is under 0.1 mSv. The data from these two techniques have shown very interesting results.

Calcium Bone Index(CaBI), a measure of bone mineral status determined by IVNAA, correlates poorly with Lumbar spine data and somewhat better with Femoral neck data obtained using the DEXA method. It should be noted that in IVNAA the bone mineral content measured is normalized to body size by dividing it by height raised to power 3, whereas the DEXA gives bone density(BMD) which is bone mineral content (BMC) in grams per square cm.

The correlation coefficients are improved if only the patients under 21 years of age are considered and especially if the lumbar spine bone mineral content is divided by height raised to power three, similar to data from IVNAA. This indicates that BMC divided by height to power 3 is a better indicator of bone mineral status than BMD usually given. The body size normalization is relevant and necessary up to the age of 21 years but beyond that there is no height dependance since height does not change significantly .

For patients with CaBI under 0.8 (normal range 0.8 to 1.2), the liver iron content is higher than in patients with CaBI greater than 0.8. Patients under 21 years of age have lower liver iron content than older patients. Patients under transfusion have lower liver iron content than those not under treatment.

These results suggest that IVNAA is a more accurate technique than DEXA for measuring the bone status of these patients. Lower age and treatment with transfusion corresponds to lower liver iron content and also to higher bone mineral content in the normal range. It therefore appears that, patients who are long survivors, can develop osteopenia which needs to be monitored and treated.

ELEMENTAL BONE COMPOSITION OF RATS FLOWN IN BIOSATELLITE "COSMOS-2044"

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The problem of mineral metabolism violation under weightlessness is continuing to remain one of the most important issues from the point of view of the impact of weightlessness on the living organisms activity in the conditions of a space flight. It has been experimentally established that in rats exposed to real or imitated weightlessness, osteoporosis and inhibition of bone post traumatic regeneration devepole. It is supposed that at the same time the process of bone tissue mineralization breaks down. The method of neutron activation analysis that we use permitted determination of the content of 16 elements in 6 structurally different skeleton sections of the rats which have been subjected to experimental fracture of fibula 2 days before the 14-day space flight or "tail suspension" in the antiorthostatic position. The investigations were carried out at the IBR-2 reactor of FNLP JINR. Analogous bones of the animals kept in the conditions of a vivarium and the space ship model served as reference. The analysis had shown that the concentration of the elements varies in a large range from fraction to fraction remaining similar in the bone tissues of same localization. In general the behaviour of the concentration of elements in different samples in the conditions of weightlessness and "tail suspension" did not change. The changes observed are determined by the biological role of the elements and by the morphological functional peculiarities of the bone tissue. The factors of the space flight exert a modifying influence on the process of bone post traumatic regeneration.

TOMOGRAPHIC TECHNIQUES USING RADIATION PROBES FOR ELEMENTAL ANALYSIS IN BIOMEDICAL RESEARCH

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Tomography in its two main modes of application, transmission and emission, using a variety of radiation probes has been proven over the past two decades as an invaluable tool for both diagnosis and radiotherapy treatment planning in a hospital environment. More recently it is becoming established as a powerful technique for nondestructive evaluation in industrial applications where information about either the structure or the dynamic function of a system is required. However, although x-ray and gamma-ray transmission tomography have been used for the determination of elemental composition of tissues in terms of the distribution in a selected plane of photon linear attenuation coefficients (a function of atomic number and density) as for example in osteoporosis where bone mineral content is obtained, tomography as an analytical method has not been fully exploited. It is therefore intended in this paper to suggest possibilities of nondestructive analysis using tomographic techniques employing neutrons, photons (for x-ray fluorescence) and positrons as probes.

We have developed potentially useful techniques with neutrons as probes for materials characterisation which combine the principles of reconstructive tomography with instrumental neutron activation analysis (INAA) so that elemental concentrations in a section through a specimen can be mapped. Neutron induced gamma-ray emission tomography (NIGET) where either prompt or delayed gamma-rays are detected has been used in studies of different biological matrices.

It will be shown how quantitative information about the induced radionuclide concentration distributed in a specimen can be obtained when compensation for scattered gamma-rays is taken into account and the capabilities of the technique will be illustrated using ^{75}Se and a spatial resolution of 1mm. The combination of gamma-ray emission tomography with time differential perturbed angular correlations (TDPAC) will be discussed in connection with ^{75}Se , as the possibility of determining both the location and the molecular environment of the radionuclide arises. Reference will be made to research carried out on brain function and other studies using a small diameter positron emission tomography (PET) system and how detector developments in this area are making the prospects of elemental analysis using tomography particularly exciting.

NOVEL METHOD FOR DETERMINATION OF SUBPICOGRAM QUANTITIES OF ^{239}Pu BY COMBINATION OF NEUTRON-INDUCED AND PHOTOFISSION

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It is impractical to determine subpicogram quantities of ^{239}Pu by α -spectrometry because of too low an activity. In principle, even a much higher sensitivity can be achieved through neutron activation with the registration of induced fission events. To make use of it in ecology and life studies, one must chemically isolate the plutonium fraction from the analysed sample; only 10^{-6} or even less of the uranium originally present in the sample is allowed in the Pu fraction because ^{235}U also gives fission events, which cannot be told apart from those due ^{239}Pu . We have proposed to check the plutonium fraction for uranium contamination making use of photofission. The ratio of the numbers of photofissions and neutron induced fissions is more than 100 times larger for natural uranium compared with ^{239}Pu in the same conditions. With the microtron MT-24, a fluence of γ -quanta by 10^3 - 10^4 larger than the thermal neutron fluence allows one to find whether the uranium content in the plutonium fraction is low enough.

Some samples of soil from different regions of Ukraine and Russia were treated to obtain plutonium fractions in nitric acid solution. The isolation of the Pu and its decontamination from uranium were done with the use of extraction chromatography with quaternary amines. Chemical yields of Pu were measured using ^{236}Pu tracer. The evaporated concentrate was put in contact with a PETP (lavsan) foil as a track detector of fission fragments and was bombarded with thermal neutrons (fluence 10^{15} cm^{-2}). Then the plate in contact with another foil was irradiated with γ -quanta (10^{20} cm^{-2}) at the FLNR microtron MT-24. The foils were chemically etched and searched for fission fragment tracks. At present, the minimum detectable amount of ^{239}Pu is about $10^{-13} \text{ g Pu per gram of soil}$. There are seen several ways how to further increase the sensitivity.

Neutron and Gamma Activation Analysis of Microelements with Using of Compact Electron Accelerator MT-25

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Compact electron accelerator MT-25 is the basic set up of the FLNR for microelements analysis [1]. The main characteristics are: the energy of electrons: $10\div 25$ MeV; the electron beam current - $20\div 30$ μA ; the fast neutron flux - 10^{12} 1/s, the thermal neutron flux - 10^9 1/s.

The instrumental methods of determination of Pu, U, Th, Pb, Tl, Mg, Au, Ag, Pt, It in the environmental objects with using the MT-25 were developed. The determination limits of the elements varied from 10^{-4} up to $10^{-6}\%$. The technique of the preliminary selective isolation of microelements and subsequent neutron and gamma activation analysis were also developed. Special attention was attracted to the analysis of nobel elements. The methods, which include the aqua regia [2], microwave plasma [3] decomposition of geological samples and subsequent recovery of Au, Pt and Pb with solid extractants based on the TBP and TOPO were proposed. The limits of determination in this case were $10^{-6}\%$ (Au) and $10^{-5}\%$ (Pt). The analysis of several kinds of coals and ashes was also carried out for determination of the concentration and behaviour of microelements [4].

At the analysis of biological objects good results were obtained for determination of nitrogen. A method of estimation of protein concentration in the cereals and leguminous was proposed [5].

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Determination of Heavy Metals in Humic Substances by Instrumental Photon Activation Analysis

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A systematic investigation of the basic interactions of microcomponents in natural systems is necessary for a better understanding of geochemical processes in a region under the influence of man-made pollutants.

Humic substances comprise a class of biogenic, organic substances in water and soil and have different roles in the environment. They are complexing agents or sorbants for pollutants and naturally occurring substances, and also a precursor of toxic substances in natural processes.

We have investigated a series of groundwater samples from a drinking water region near the Elbe river in Saxony. One specific feature of this region is that residual pollution was found from a chemical factory (explosives) destroyed during the Second World War. The aim of our studies was to characterize the path of pollutants of heavy metal ions stably bonded on water humic acids. Therefore, the humic substances were isolated by adsorption on XAD-amberlite. The contents of humic acids was approx. 0.03 - 0.10 mg per liter of water.

The pure humic substances were prepared with an internal standard and irradiated at the Leipzig microtron and the Berlin linac with 22 resp. 30 MeV photons. We determined 22 elements by γ -spectrometry. An enrichment could be stated for the determined heavy metals especially for Pb, Hg and Cd in the polluted area in comparison with the other. Out of the investigation of the path of pollution follows: the migration of the heavy metal ions does not take place in the direction to the river but further towards inland. This result emphasizes the necessity of further investigation of organic pollutants in this context.

Photonuclear reaction yield ratios in tissues used as an index of abnormality.

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The purpose of this work is to establish whether it is possible to use photonuclear activation ratios (PAR) as an indication of the relative concentration of carbon , nitrogen , oxygen and potassium in the body of patients who have undergone high energy photon (or even electron) therapy, with sufficient accuracy so as to monitor changes in the concentrations of a few percent. PAR is defined as the ratio of the saturation activity per target nucleus of one element relative to another.

Since the activated photoproducts of carbon, nitrogen, oxygen and potassium are all positron emitters which on annihilation emit photons of identical energy (511keV), effects of sample size, self absorption and counting geometry cancel out when the photonuclear activation ratio is utilised. Hence the simplest and most reproducible scheme is to use an analysis which will give a unique PAR from a single irradiation.

A FORTRAN computer programme which was previously written to calculate the bremsstrahlung spectra from medical linear accelerators was modified to simulate the perturbation of the concentration of constituents of a tissue. The concentrations of the major elements were changed and their photonuclear reaction yields were then calculated.

A correlation between the ratios of their yields and the relative concentrations was drawn in order to establish a relationship between the photonuclear activation ratios and the changes in the concentrations of the constituent elements. This will lead to a method for distinguishing abnormal from normal tissues and may allow the monitoring of changes in elemental levels as radiotherapy progresses.

EFFECTS OF TARGET TEMPERATURE ON ANALYTICAL SENSITIVITIES OF COLD NEUTRON CAPTURE PROMPT γ -RAY ACTIVATION ANALYSIS

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It has been shown that neutron scattering by hydrogen affects the element sensitivities of thermal neutron capture prompt γ -ray activation analysis (PGAA)¹. Neutron scattering can present problems in the analysis of biological materials which often contain percent levels of hydrogen. For thermal neutron PGAA using a beam of neutrons, the effects of neutron scattering are a function of the target size, shape, and macroscopic scattering cross-section. These effects can be accounted for using a monoenergetic model of neutron scattering (one in which the energy of the neutron does not change) within the sample². Experiments and calculations have shown that the effect is particularly pronounced for relatively thin, highly hydrogenous targets^{3,4}. Sensitivities (counts \cdot sec⁻¹ \cdot mg⁻¹) for elements in this type of target may be enhanced by as much as 17%. Monte Carlo calculations show good agreement with experimental results; that is, the observed enhancements are quantitatively accounted for by this model⁴. It was also demonstrated experimentally and by Monte Carlo calculations that the use of spherical targets minimizes the effects of neutron scattering, also indicating that the effect is largely the result of elastic scattering and of the geometric properties of the target⁴. For thermal neutron scattering by hydrogen in these targets, there does not appear to be a significant change in the average energy of the neutron.

Similar PGAA experiments were performed using a guided beam of cold neutrons at the Cold Neutron Research Facility at the National Institute of Standards and Technology to determine the effects of neutron scattering by hydrogen on cold neutron PGAA sensitivities⁵. Identical targets were measured in both the thermal and cold neutron PGAA facilities; the results were very different. For thin liquid targets (15 x 15 x 2 mm³), thermal neutron PGAA sensitivities increased with increasing H content but decreased with increasing H content for cold neutron PGAA. For a series of solid targets of constant H concentration and varying thickness, similar trends were observed for the cold and thermal neutron PGAA sensitivities but sensitivity decreases were much greater when using cold neutrons.

One significant difference between the two PGAA facilities is that in the thermal neutron facility, the temperatures of the target (room temperature) and the neutrons (about 300 K) do not differ as markedly as they do in the cold neutron facility (60 K

neutrons). It is not surprising that there is not a significant change in the average energy of the neutrons from scattering within the sample in the thermal neutron facility, since a thermal neutron interacting with a room temperature target should be just as likely to gain as to lose energy. (The neutron beam at this facility is well thermalized.) However, for a cold neutron interacting with a room temperature target, there is a much greater probability for a scattered neutron to gain energy. An increase in the average energy of the neutrons, or spectral hardening, would result in lower effective neutron absorption cross-sections and therefore, lower sensitivities.

As mentioned previously, while sensitivity increases were observed with increasing hydrogen using thermal neutron PGAA, cold neutron PGAA of the same targets showed decreased sensitivities. To determine whether the observed sensitivity decreases are the result of spectral hardening, two cold neutron PGAA measurements were made on each of several hydrogenous targets. The first measurement was made on the target at room temperature and the other on the same target cooled under vacuum to liquid nitrogen temperature. Element sensitivities were monitored during the cooling down and warming up periods. For thick targets, sensitivities increased significantly with decreasing temperature. For example, sensitivity for H in a 0.53-cm thick, 850-mg disk of tris-hydroxymethyl-aminomethane (which contains 78 mg of H), increased by 25% upon cooling to liquid nitrogen temperature.

These results indicate that the observed decrease in sensitivity is due in part to spectral hardening and in part to the geometric and scattering properties of the target. Results indicate that for hydrogenous targets, the portion of the sensitivity decrease due to neutron warming may be eliminated by keeping the target temperature as close as possible to the effective Maxwellian temperature of the neutron beam. The remainder of the effect, that due to the geometric and scattering properties of the sample cannot be eliminated in this way. Using thermal neutron PGAA, effects of scattering were minimized by using spherical targets. Further experiments are in progress to determine whether the combination of target cooling and the use of spherical targets will minimize the effects of scattering on analytical sensitivities of cold neutron PGAA. Results from these and the experiments on disk-shaped targets will be presented.

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COMPREHENSIVE RNAA OF Cd, Co, Cu AND Ni USING ^{109}Cd , ^{57}Co AND REACTOR- PRODUCED ^{67}Cu AS RADIOISOTOPIC YIELD MONITORS

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"Comprehensive neutron activation analysis (NAA)" was defined by Heydorn¹ as a method where a characteristic indicator is determined after a radiochemical separation, followed by determination of the chemical yield of the separation. Chemical yield determination is often most easily and accurately performed by measurement of a suitable radioisotopic tracer, if available. However, as in the case of cadmium and cobalt, even when tracers with appropriate properties exist i.e. ^{109}Cd , ^{57}Co , in practice this is often not done.

In the present work, as well as using ^{109}Cd as a radioisotopic tracer for cadmium (via $^{115\text{m}}\text{Cd}$ - $^{115\text{m}}\text{In}$), and ^{57}Co for cobalt (via ^{60}Co) and nickel (via ^{58}Co from $^{58}\text{Ni}(n,p)$), the chemical yield for copper (via ^{64}Cu) was determined for every sample aliquot using ^{67}Cu tracer produced by reactor irradiation of zinc from the $^{67}\text{Zn}(n,p)^{67}\text{Cu}$ reaction. A simple procedure for production and purification of ^{67}Cu in tracer quantities is described, based on irradiation of ZnO and anion exchange separation of copper from zinc in 2M HCl. Although in this irradiation ^{64}Cu is produced in initially much greater amounts than ^{67}Cu , due to its longer half life (62 hours as compared 12.7 hours for ^{64}Cu), after 10 days decay, the ^{64}Cu content is less than 2 %.

The procedure for simultaneous determination of Cd, Co, Ni and Cu is based on the dithiocarbamate extraction method of Dermelj et al.². Use of yield tracers enables better control of the separation procedure and produces more accurate values. The usefulness of the method was shown by results for biological certified reference materials.

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NEUTRON ACTIVATION ANALYSIS OF BIOLOGICAL SAMPLES AT THE
RADIOCHEMISTRY DIVISION OF IPEN-CNEN/SP

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Determination of trace elements in biological samples has attracted much attention lately, accompanying the development of increasingly sensitive analytical techniques as well as due to improvements in knowledge on the role of trace elements in living organisms.

At the Radiochemistry Division of IPEN-CNEN/SP, neutron activation analysis (NAA) is being extensively applied to study biological samples. Recent studies have been performed in collaboration with other research institutions, universities and medical clinics.

Determination of trace elements in extracts from Brazilian medicinal plants has been carried out to study their role in relation to medicinal effects or their toxicity (1).

Human head hair has been analyzed with the aim of using the concentrations of trace elements as an indication of nutritional or health status of human subjects.

Mercury has been determined in head hair from Brazilian populational groups in order to detect contamination due to the consumption of fish (2).

Human lungs from smokers and non-smokers collected in autopsies have been analyzed so as to obtain normal levels of elements in hilum lymph nodes and lung tissues as well as to know whether there is any correlation between trace elements in these tissues and smoking habit of the subjects (3).

Analysis of Brazilian snake venoms from the species Bothrops and Crotalus has been carried out, to study the role of metals in their toxic action and in the biochemical characterization of snake species for further contribution to antivenim serum production (4).

Toxic and other elements were analyzed in Brazilian foodstuffs, such as bread, milk powder and rice (5,6) as well as in gelatine samples (7). NAA was also applied to analyze five varieties of corn obtained as a result of studies developed to increase nutritional value of the protein contained in this foodstuff (8).

To validate our analytical procedures biological reference materials provided by NIST, IAEA, NIES, IUPAC and SHINR have been analyzed. The reference material has been chosen, when possible, to be sufficiently similar to the matrix and to have an elemental concentration of the same order of magnitude as the one to be analyzed.

Irradiations of biological samples and synthetic standards have been performed in the IAEA-R1 nuclear reactor using neutron fluxes from 10^{11} to 10^{13} n.cm⁻².s⁻¹. Adequate conditions for irradiation, decay and counting have been chosen based on half-life of the nuclide of interest. Ge(Li) or hyperpure Ge detector have been used for gamma ray measurements.

Elements such as Al, As, Br, Ca, Cl, Co, Cs, Fe, K, Mg, Mn, Na, Rb, S, Sb, Sc, Se, V and Zn have been determined by instrumental method of neutron activation analysis (INAA). However some elements of great biological interest such as As, Cr, Cd, Hg, Sb and Se could not be determined by INAA due to interference of predominant radionuclides such as Na-24, P-32, Br-82 and K-42 in the gamma ray spectra. In these cases, radiochemical separation techniques have been used for the isolation of the elements of interest(5-7,9). (Work supported by FAPESP and CNPq from Brazil and IAEA).

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SUBSTOICHIOMETRIC DETERMINATION OF COPPER BY ISOTOPIC DILUTION ANALYSIS IN BIOLOGICAL AND ENVIRONMENTAL SAMPLES

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Traces of copper play an important role in biological and environmental samples. Copper deficiency may lead to the impairing of taste and its toxic effect is the main cause of Wilson's disease.

A rapid and simple method for the determination of Cu in biological and environmental samples by isotopic dilution analysis employing substoichiometric solvent extraction of Cu(II) with dithizone in carbon tetrachloride has been developed. The method can be used for always extracting the same amount of copper from solutions of different concentrations.

The optimum pH range for the separation was tested and the extraction was complete in the pH range 2 to 7. Above and below this pH range the extraction is not quantitative. The reproducibility of the substoichiometric extraction was checked using increasing amounts of Cu(II) labelled with ^{64}Cu , an aliquot of the organic phase was measured and the plot of the activity against the concentration of Cu(II) showed an increase in activity until the ratio of copper concentration to dithizone was 1:2 after which it remained constant.

In the analyses even if a large excess of metals which form extractable complexes with dithizone, such as Hg, Mn, Ag, Se, In, Bi, Co, Ni, Cd, Zn, Pb, Sn and Sb does not interfere when iodide is present and the separation is made using a substoichiometric amount of dithizone. The precision and the accuracy of the method was tested using reference materials. A good agreement was achieved between the results found and those reported in the literature. The procedure was applied to determine copper in several kinds of matrices.

ADVANCED SHORT-LIVED NUCLIDE NAA WITH APPLICATION IN THE LIFE SCIENCES

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Neutron activation analysis has already been established as a suitable method especially for the assay of trace and minor elements in various materials. Because of its sensitivity it is particularly useful for trace element determination in biological material where the available quantities are often limited¹. Proper sampling and sample preparation is important to avoid contamination because of the small quantities involved. Long-time activation, decay and counting allow the analytical laboratory to be far from the neutron activation facility which is usually a reactor or an accelerator, and reduce matrix interferences from short and medium-lived nuclides, but are time-consuming and restrict the analytical capability to long-lived nuclide determination². Short-time measurements increase the analytical throughput and broaden the analytical range, since in this case short and medium-lived nuclides can be analysed, even in the presence of long-lived nuclides, if the concentration of those is not too high, or sometimes if epithermal neutron activation is used. The analytical system for short-lived nuclide activation has already been described³, showing that the measurements have to be performed at the reactor or other neutron activation site because the waiting time has also to be short. However, the main problems are then the optimization of the count rate throughout the counting period, to avoid dead-time losses, pulse pile-up effects and background interferences at the extreme high and low rates, respectively, as well as the limitation of the counting period because of the rapid radioactive decay, leading to low counting statistics and thus to low accuracies and sensitivities of the techniques. In order to overcome these problems, besides the instrumental Loss-Free-Counting System developed at the Atominstitut in Vienna⁴, a new technique has been introduced, by which the rapid count rate decay is compensated by counting geometry variation during the counting period⁵. This is achieved by approaching the sample holder to the radiation detector with a not necessarily constant but repeatable speed for calibration purposes. The compensation is not anticipated to be complete, since the decay is exponential while the radiation variation at the detector is inversely proportional to the square of the distance between the detector and the sample. However the count rate does not have to be constant, but only between certain limits, to avoid the above mentioned distortions, as long as the measurements are repeatable, for comparison with the calibration standards. It is obvious and has been tested that in this way the counting time can be prolonged considerably, practically

at least four times. Thus also the necessary cyclic activation can be reduced to a few cycles to obtain the minimum counting statistics for good results. The reduction of the number of cycles is important, since the plastic sample containers cannot withstand many cycles without damage, due to irradiation and repeated shocks at the pneumatic transfer tube terminal close to the reactor core. Several techniques are being tested to achieve the proper slow movement of the sample holder for radioactive decay compensation. Tests have shown that the use of a piston driven by controlled air or even oil pressure is not adequate for such low speeds. Therefore a mechanical system consisting of a slow motor with variable frequency and a converter of the rotary to linear movement is envisaged to be used, since its repeatability seems to be more reliable.

The operation of the whole analytical system and the data processing is being automated by a programmable logic controller and by proper computer software to facilitate the analysis, so that it can be performed even by non-specialists with some guidance. Thus even laboratories far away from the irradiation facility can use the short-lived nuclide analytical laboratory by just sending their samples to the facility which will then be in the position to make the measurements for them.

There is a number of essential trace and minor elements with short-lived radioisotopes, besides the medium and long-lived ones, which are of interest in biological materials, such as F, Sc, Ge, Se, Rh, Ag, Sb, Er, Hf, W, Pb and Al, Ti, V, Cu, Rb, Rh, Pd, Gd, Dy, Ir with radioisotope half-lives in the second and a few minute range, respectively. An important element in biological material is selenium, whose short-lived $^{77}\text{Se}^m$ isotope has a half-life of 17.5s, while its long-lived isotope ^{75}Se has a half-life of 120d. It is obvious that the measurement of the short-lived nuclide will provide a much higher throughput, which is important in biological and environmental research where often a large number of samples have to be analyzed for sufficient sampling statistics. Some biological samples are being analyzed at our laboratory in the framework of intercomparison runs for standardization. Special emphasis will be given to the short-lived nuclides in order to test the new techniques of neutron activation analysis.

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The Characterisation of Rhino Horn and Elephant Tusk using the Technique of Neutron Activation Analyses

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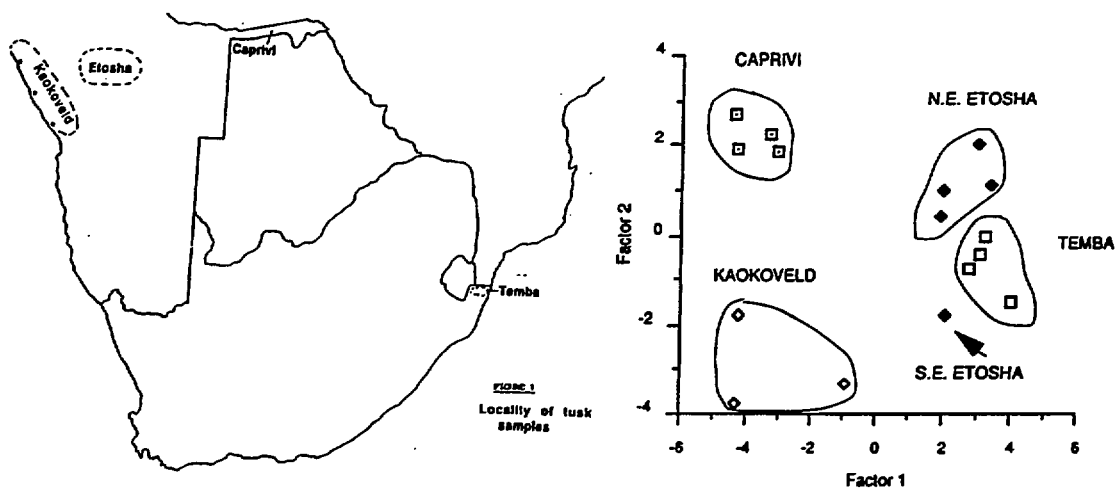
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One of the difficulties in controlling the poaching of endangered species such as elephants and rhino that are hunted for their tusks and horn respectively, is tracing the illegal tusk and horn found in the open market back to its origin. In addition, now that some countries are planning to market culled ivory it has become necessary to distinguish between legal and illegal ivory, and to be able to identify the source of ivory whenever necessary.

Various techniques which involve the measuring of different isotopic ratios (eg. C, N and Sr) in samples of ivory and horn, in order to distinguish between elephants or rhino from different localities have been investigated. The technique makes use of the fact that the isotopic ratios of these three elements vary from region to region because of the variation of vegetation, climate and geology. These elements are all absorbed into the plant life and are incorporated in the diet of the animals, finally to be reflected in their tissue. Thus, the chemistry of the ivory or horn might directly reflect conditions in the source region. Although these techniques have had limited success, even these ratios cannot uniquely characterise the different populations of elephants and rhino in all cases, as overlap in the values of the ratios was found for individuals from different environments. Apart from the elements mentioned above, there are numerous other trace elements that may be absorbed into tusk and horn via the dietary processes of elephants and rhinos. Like the elements mentioned above, it is suggested that the trace elements also reflect local vegetation, climate and geology, and that if sufficient number of trace elements can be determined they may act as useful parameters which could uniquely characterise the source region.

In this study we are attempting to develop an additional technique using Neutron Activation Analysis (NAA) which might be able to more accurately identify the source region of ivory and horn, based on their trace element compositions. NAA is a highly sensitive technique for the simultaneous determination of a number of trace elements in small samples. The method allows the selective determination of trace elements in parts per million and parts per billion (ppm and ppb) range. Up to date we have been able to determine up to 9 elements in samples of ivory and up to 15 elements in horn samples. Analyses were performed on both ashed and raw samples. A pilot study on samples of tusk from four different regions (See Fig. 1) has shown that we get some interesting and significant differences in the trace element content between the four regions shown in Fig.1. Although no single chemical parameter can uniquely distinguish samples from a particular region, by combining these elements using statistical programmes such as factor analysis, we can clearly separate samples from different regions (see Fig.2). Similar results have been obtained from our analyses of rhino horn. In this study we hope to analyse and characterise both ivory and tusk from throughout Southern Africa.

FIGURE 2



Factor Analysis of Tusk Samples from Four Regions

DEVELOPMENT OF OPTIMAL TECHNIQUES FOR NEUTRON
ACTIVATION ANALYSIS OF HUMAN HAIR COMPOSITION.

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Determination of human hair composition could be used for solving of some problems in life sciences. Its composition correlates with environmental contaminations, status of inhabitant health and distribution of some human diseases. Complex of analytical techniques were worked out for neutron activation analysis of human hair. It was created by software and information system for development of activation techniques with optimal characteristics (1). The complex includes set of techniques. Some of them provide the most sensitivity for some elements, and other ones minimize time of analysis or irradiation time. Some of them provide maximum multielementence. Analytical techniques were realized by nuclear reactor with flux $2 \times 10^{15} \text{ n}/(\text{cm}^2 \cdot \text{s})$. Possibilities of this reactors for solving this analytical problem were analyzed. The created techniques were tested and used for determination of NA, CL, K, CA, MG, FE, CO, ZN, AS, SC, SE, BR, MO, CD, SB, I, CS, LA, W, AU, HG and other elements in hair samples.

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HAIR TRACE ELEMENTS IN KIDNEY DIALYSIS PATIENTS BY INAA

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ABSTRACT

As a consequence of continued blood dialysis procedures, some kidney disorder patients tend to exhibit changes in trace electrolytes and other elements in their blood serum. There has been speculation that patient deterioration in some cases is somewhat similar to dementia for which the possible role of aluminum is being considered. This INAA study of trace elements (T.E.) in the head hair of patients and controls was conducted to assess whether hair T.E. monitoring, including for Al, might provide corroborative information on such abnormalities as they develop in dialysis patients.

Scalp hair samples were collected from kidney patients (n=54) undergoing periodic dialysis (some of more than 10 years' duration) and, from healthy control subjects (n=50) residing in Toronto. The sex distribution was similar but the controls, while covering about the same age range, were much younger on average than the patients.

INAA was performed, with and without cadmium shields, on 0.1-0.3 g hair specimens that had been washed three times with ether and alcohol, by 3-5 min irradiations at 5×10^{11} thermal neutron flux. The accuracy of these INAA hair analyses was assessed by reference to two hair powder standards: a Chinese homogenized hair sample prepared by the Shanghai Inst. for Nuclear Studies and the NIES-5 (Japan) standard hair. After making some corrections for epidermal and fast neutron interference with Al (described below), the agreement found in this work with the reported values for the hair standards for Al, P, S and Ca content ranged from 1 to 8%.

In most reactors, interference with Al from P(n, α) or Si(n,p) contributions to ^{28}Al intensity can be appreciable. By comparing hair samples activated with and without 0.75 mm Cd shields it was determined that slight corrections for P interference of 3 and 19%, respectively had to be made to the Chinese and Japanese hair standards, whereas Si interference was not detectable. Similarly, corrections for hair P content ranging from 0 to a maximum of 29% were found for the patients' and controls' hair.

A summary of the INAA results for hair Al, P, S and Ca is given in the table together with some measurements of serum levels of Al and phosphate in the same patients. While there are obvious differences in the median concentrations of Ca and P between patients and controls - none was expected for S, a major constituent of the keratin component of hair structure -it was surprising not to observe any increase in hair Al similar to that observed for P. Ca decrease correlates with the observed evidence of bone disorders in dialysis patients.

TABLE:
Hair and Serum Concentrations of Dialysis Patients & Controls

	<u>Dialysis Patients</u> (n=54)		<u>Healthy Controls</u> (n=50)
	<u>Hair</u>	<u>Serum[†]</u>	<u>Hair</u>
Al	6.6(1.6-29)	520(200-3200)	7.5(2.4-28)
P (PO ₄) [†]	289(63-2150)	1.82(0.9-3.5)	199(100-480)
S	5.1(3.7-6.6)	-	4.5(3.9-5.5)
Ca	592(104-5000)	-	880(140-4500)

Correlations of these hair and serum concentrations with clinical information for the patients such as: duration of dialysis, ranging from 0.1 to 25 years; type of medication; age; sex was examined and some variation in P and Al with these variables was significant. Multivariant statistical factor analysis using STATGRAPHICS software was also performed using the above hair and serum concentrations and the clinical data for each patient. Four factors or groupings of variables were found relating hair and serum aluminum, phosphorus and hair sulfur to length of dialysis and administration of medication to some extent. The significance of these findings to effects of prolonged dialysis and the potential value of hair INAA for such studies, are discussed in this paper.

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Determination of Sodium-to-Calcium Ratio in Mouse Femora by INAA

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ABSTRACT

Within the scope of the study of the heteroionic exchange in the bone mineral, the sodium-to-calcium ratio was established in femora of 55 male ICR mice. The purpose of the work was to establish the precision of the method as well as biological variations since the authors intend to investigate the sodium-to-calcium ratio on pathophysiological models in the future with a special regard to the osteoporosis. The resulting mean value was of 0.02516 ± 0.00053 . The small standard deviation indicates that the ratio is not subject to considerable individual variations. The accuracy of the method was checked with the reference bone sample IAEA H-5. The results obtained exerted a good agreement with the certified sodium and calcium concentrations.

Index Entries: bone, bone mineral, calcified tissues, calcium, femur, mice, neutron activation analysis, sodium.

KINETICS OF ELEMENTAL CONTENT CHANGES OF BONE TISSUE OF MICE DURING EVOLUTION UNDER HYPOKINETIC STRESS

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To investigate the mechanisms of mineral metabolism violation following hypokinesia it seems attractive to perform comparative study of peculiarities of the mineral elemental content in the sections of a skeleton, which perform different functions. The instrumental neutron activation analysis allowed us to determine concentrations of 13 elements in the tissues of the bones, including the tibiae, accomplishing both supporting and dynamic functions, the parietal bone, being practically immovable and the ectopic bone of mice, which was newly formed under kidney capsule in the place of singene spinal cord implantation. Distinct difference in the elemental content of the examined bones with respect to reference ones were observed. The dynamics of the mineral composition change under the influence of 3 week hypokinesia developing in mice, cooped up in little space pens, was examined also. The elements kinetics in the course of hypokinesia is offered to be conditionally divided into four types of reactions. The progressing demineralization due to loss of *Ca, P, Mg* and *Fe* is accompanied by the compensatoric inclusion of *Sr* in a bone tissue. During evolution under hypokinetic stress the trace element concentration (*Zn, Cr, Ru, Rb, Br, Co, Sb*) changes significantly. Their role is the mobilization of activating elements at different stages of the general adaptation syndrom. The similar dynamics of the elemental composition of functionally different bones of a skeleton evidences for some systematic character of osteoporosis at limited mobility. The investigations were carried out at the IBR-2 reactor of FLNP JINR.

Simulation and Optimisation of cyclic activation analysis of short-lived isotopes with 14 MeV neutron generator.

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Abstract

A program of simulation and optimisation is developed for the case of cyclic activation analysis of short-lived isotopes with 14 MeV neutrons. The background line under the photopeaks of interest is simulated using the Zykowski model. The reliability of the latter is checked on real conditions with a geological standard sample " Soil5" provided by IAEA. Optimal experimental conditions (timing parameters, number of cycles) are determined and corresponding lower detection limits are calculated. A systematic study of short-lived isotopes with half live lower than five minutes is done for Soil5 and the results are discussed.

URANIUM DISTRIBUTION AND CONTENT MEASUREMENTS
BY THE FISSION TRACK METHOD IN SOME CRUSTACEA
OF *MYSIDACEA* SPECIES

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ABSTRACT

The presence of the inclusions in certain *Mysidacea* species is investigated in order to correlate their presence with some specific properties of *Mysidacea* crustacea /1/. To this end the Uranium distribution and content were analysed using the fission track micromapping technique described in /2/.

Two crustacea of *Mysidacea* species, i.e. a) *Javanisomysis gutzui* Băcescu, 1992 and b) *Mesopodopsis slabberi* Van Bened, 1861 were analysed. These crustacea specimens were sampled: a) in 1991, in Nord West Sea, 35 Km offshore Djakarta near Pari island, 0,5 m depth and b) in 1949, from the Black Sea Shore at the mouth of Saint George Branch of Danube River Delta, 30-50 m offshore, 2-3 m depth. Immediately after sampling the crustacea were put in ethylic alcohol, 72 per cent.

An Uranium fission track micromapping was obtained in a muscovite track detector for each analysed samples in the following way: the dried crustacea sample put sandwich with two slices of muscovite track detector is bombarded by thermal neutrons. The fission fragments from the neutron induced fission of Uranium in analysing sample are registered by trails in the muscovite track detectors during the neutron irradiation. After neutron irradiation the muscovite detectors are etched in order to visualize the trails by tracks. The neutron irradiations were performed in the

VVR-S nuclear reactor, Bucharest, at the thermal neutron fluences of $4 \cdot 10^{14}$ n.cm⁻². The etching conditions used by us were: FH Λ 38 per cent, 4 hours at room temperature /3/.

The obtained Uranium fission track micromappings were studied by optical microscopy. A stereomicroscope Wild M 7 S was used for the Uranium distribution studies and a binocular Zeiss Jena microscope for details and Uranium content determinations.

The SL-1, IAEA, Viena Seibersdorf Laboratory Certified Reference Material was used as reference material in content measurements.

The obtained experimental data led us to conclude:

- For all the investigated crustacea samples, a quite uniform Uranium distribution was found and any Uranium inclusions do not observed;

- The Uranium contents were found in the following concentration ranges: (1.19 \pm 0.18) ppm \pm (3.38 \pm 0.51) ppm for the *Javanisomysis gutschui* Băcescu, 1992 and (1.90 \pm 0.29) ppm \pm (4.65 \pm 0.70) ppm for the *Mesopodopsis slabberi* Van Bened, 1861.

Aknowledgements. The authors are indebted to Academician Prof.dr.Mihai BACESCU of the Natural History Museum of Bucharest who give us the samples, and for usefull discussions.

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ADVANTAGES OF USING THE " z_0 - METHOD"
IN CPAA APPLICATIONS

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The "Without Standard Method" (WSM) was recently presented in [1,2] as a new, practical way in the elemental analysis of materials by CPAA [1] and by NAA [2] techniques, by which reduced uncertainty contributions in evaluating the weight - fractions of the elements composing the complex matrix of an investigated sample can be realized; it is mostly useful in assaying low (trace) - level elements in alloys prepared by industrial, technological procedures.

It was shown in [2] that the NAA-WSM theoretical equations [2] include the " k_0 - k" parameters, as defined by Simonits et al. [3], so their use provides an advantage in applying the method and in optimizing the calculations and the experimental procedures [4].

In the paper, new parameters denoted by " z_0 " and " z " - with similar significances - are defined for the CPAA field, starting from some relations demonstrated in [1], in which the nuclear activation relations are basically described by experimental Radionuclide Activation Yield (RAY) data.

The expression defining the parameter " z_0 " is a ratio of general nuclear reaction and decay data, quite similar to that of the " k_0 " term, established by formulae specific to the NAA field; the nuclear parameter " z " - mostly characterizing the technical performances of the user's spectrometric equipment is dependent on " z_0 " by a formula perfectly identical to that correlating the k_0 and k terms.

By introducing these two new nuclear parameters and by developing special computing codes for calculating tables of

numerical "z₀ data" for various types of CP induced reactions on elements of interest for various applications one may realize great practical advantages in every CPAA experiment, either conducted by the Without Standard Method or by the classical Method employing Internal Standards, as well.

The correctness of introducing experimental RAY data instead of the usual calculation formulae [5] and the dependence of the "z₀ - z" parameters on the type and energy of the accelerated ion beams are discussed.

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**A GRAPHICAL METHOD
FOR OPTIMISING THE NAA AND CPAA EXPERIMENTS
BY FUNCTIONS USING THE " k_0 " AND " z_0 " PARAMETERS**

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A graphical method allowing for precised experimental evaluations of the elemental concentrations in samples investigated by NAA and CPAA techniques is presented.

The method operates in two steps and consists in optimising the experimental measurements, i.e., the analyses of the complex and variable γ -ray spectra of the samples activated by neutron or charge particle induced reactions; that means to find out - by the first step - the optimum cooling time intervals after irradiation, when the intensities of the full energy peaks of the elements of interest (especially: low-content elements) attain the maximum counting statistical levels by relative comparison with the other γ -ray peaks simultaneously present in the spectra and with the background level; by the second step the effective quantitative evaluations are performed just during these "optimum" cooling time intervals previously established.

This method involves the definition and use of two functions: $K_0(k_0, t)$ and $Z_0(z_0, t)$ dependent on the cooling time t and on the parameters k_0 [1] and z_0 [2]; generally, each of these terms characterizes a certain nuclear "activation - decay" line comprising: the stable isotope of the investigated element - the nuclear activation channel - the γ -ray emitting isotope - the γ -ray selected for analysis.

By employing libraries containing general nuclear reaction and decay data, numerical values of the k_0 (NAA)

and of the z_0 (CPAA) parameters for various elements and "radioactivation - decay" lines and by developing a special computing code by which theoretical $K_0(k_0, t)$ and $Z_0(z_0, t)$ functions can be rapidly calculated and graphically represented along of a temporal abscissa established by the user it is possible to finally construct in a simple mode the "time - map" of the γ -ray spectrum for any combinations of elements composing target matrices.

So, the "optimum" cooling time intervals allowing to perform measurements with the highest experimental precision will be graphically determined for each target and type of nuclear activation process (type of bombarding particles, incident energy, etc.).

This graphical method is particularly useful for the analysis of trace and impurity elements at low and very low levels, as are the cases of the compound matrix materials prepared by industrial, technological procedures and of some elements producing isotopes with short half-life times.

Applications of this graphical-optimisation method for thermal neutron and proton activation reactions, based on the code OPTIGRAPH - developed in a first form at the IAP-Cyclotron Laboratory - are presented.

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**DETERMINATION OF LEAD AND BROMINE IN ENVIRONMENTAL
SAMPLES BY XRF AND ATOMIC ABSORPTION ANALYSES**

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A series of 70 environmental samples were collected near the city of Tanta , Egypt, by means of filter combinations . The filters, containing the < 5 μm particle size fraction , were analyzed for Lead and Bromine. In a novel calibration procedure , standards were prepared by drying fine precipitates of lead molybdate and silver bromide on to filters. Such standards were evidently free from bromine loss during analysis and storage , and more accurately represent real samples than conventional solution - impregnated filters. Elemental loadings in the range 0.1 - 10 μg could be measured. Inhomogeneous efficiency of detection across the surface of samples was noted , and was accounted for by applying correction factors obtained from an intercomparison of XRF and atomic absorption analyses.

PRECISION OF THE STRONTIUM/CALCIUM RATIO DETERMINATION OF
CORAL SAMPLES BY RADIOISOTOPE INDUCED X-RAY FLUORESCENCE

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For many years now isotopic studies (1) and more recently elemental studies (2) of coral skeletal have been investigated for determining sea-surface temperatures. This climatic data is very important for validating climate models since the ocean temperature is a function of other climatic variables, for examples, atmospheric temperature and moisture, cloud cover, atmospheric and oceanic circulation patterns.

In the studies of marine sediments by isotopic oxygen ratio, the interpretation of the results have been hindered by the lack information of the fluctuations in the oxygen isotopic ratio in the ocean, which is a function of rainfall and evaporation effects. Such studies have concluded that the tropical sea-surface temperatures were between 0° - 2°C less than the present during the last glacial maximum about 18000 years ago (3). But other estimates based on elevation of past mountain snow lines indicated that the tropical sea-surface temperature were about 3° - 6.5°C lower.

The early works using the Sr/Ca ratio were performed by atomic absorption spectrometry with about a $\pm 3^{\circ}\text{C}$ precision for 2σ , mostly due to the measurement precision. This poor precision is inadequate for evaluation of seasonal or long-term ocean temperature variation. While recently, the Sr/Ca ratio in corals (2) determined by isotope dilution mass spectrometry has been shown as a promising method for the determination of past sea-surface temperatures with an excellent precision of less than 0.1°C .

In this work, we shall present and discuss our results on estimating the precision of different methods employing radioisotope induced X-ray fluorescence with different excitation sources. In the case of simultaneous determination of strontium and calcium in the same sample, the errors in weighing the sample and its geometry in respect to the excitation source and detection system are eliminated. Errors due to the difference in the matrix effects (mainly absorption) within the same sample can be minimize by employing thin samples (4). The instrumental and statistical errors can be minimize by using long counting times. Finally, it should be noted that these methods by radioisotope induced X-ray fluorescence are very simple and economical in respect to isotope dilution mass spectrometry.

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DETERMINATION OF K, Ca, Zn, Cu, Fe IN TUNA - IAEA-350
SAMPLE BY X-RAY FLUORESCENCE TECHNIQUE

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Abstract

This work is a contribution of our Laboratory to the intercalibration exercise on trace metals in marine biota organized by the International Atomic Energy Agency (IAEA). The determination of k, Ca, Zn, Cu, Fe in tuna-fish sample by X-Ray Fluorescence (X.R.F) is described. The sample labelled Tune-IAEA-350 is provided by the Agency.

The standard addition method is used to measure the concentration of these elements. Pure titanium and Cobalt were chosen as internal standards.

Dry ashing method is also used to reduce the background of organic bulk. A drastic change of the peak to background ratio is observed, but the concentration values are slightly affected.

Our results are in good agreement with those obtained by other participating laboratories.

THE ACCUMULATION AND DISTRIBUTION OF HEAVY AND TRACE METALS IN SOME LOCALIZED MARINE SPECIES

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Neutron activation analysis (NAA) technique and hydride generation atomic absorption spectrometry (HGAAS) were used in the determination of heavy and trace metals in some localized marine species collected from 12 chosen locations along a coastal area in the vicinity of an industrial zone. The elements As, Co, Cr, Hg, Sb and Zn were determined by NAA while Cd, Cu and Pb by HGAAS. Marine samples were first dissolved and homogenized by microwave heating under controlled conditions to prevent loss of volatile elements. To overcome problems normally encountered in marine sample analysis, a separation procedure involving the isolation of the matrix elements from the elements of interest present in samples collected from a marine environment was done by preconcentration using Chelex-100, a chelating resin, in the ammonium form. The standard used in the determination of percentage volatile elements retained using microwave heating was *Lobster Hepatopancreas TORT-1* supplied by NRCC while *Coal Ash (1632A)* supplied by IAEA was used in the activation process. The efficiency of the separation column was determined by running known standards prepared by dissolving the nitrate salts. Percentage retention of the elements of interest in the resin column was obtained by working out the difference in the concentrations before and after elution at a controlled pH. Marine samples used in this study were blood clam (*Anadara granosa*), swimming crab (*Portunus pelagicus*), green mussle (*Perna viridis*), sulcata swamp cerith (*Terebralia sulcaia*) and kuruma prawn (*Panaeus japonicus*). Results of this study indicated that the concentrations of Hg and Pb were 1.329 $\mu\text{g/g}$ and 4.74 $\mu\text{g/g}$ respectively, exceeding the maximum permissible level recommended by the ministry of health for some marine species. Swimming crabs and green mussels were identified as marine species capable of accumulating high levels of heavy metals in their tissue. The distribution of heavy and trace metals bearing marine species was mapped using elemental concentration data obtained from this study. This, could in turn be used as a basis for tracing the source of marine contamination due to industrial activities. The suitability of the recommended procedure in the analysis was also discussed with particular reference to marine samples.

SOME IMPROVEMENTS IN THE QUALITY OF NAA PROCEDURES AND THE RELIABILITY OF THE RESULTS

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Neutron activation analysis (NAA) is a mature technique and dramatic developments either in equipment or in procedures are not to be expected. Improvement in the quality of the results provided by NAA is therefore mainly to be achieved by painstaking attention to detail and careful checking of individual phases of the procedure, and by eliminating known sources of error which are nevertheless sometimes overlooked or ignored.

Examples of such checks and error avoidance include regular quality control analyses and participation in well-designed intercomparisons, frequent control of standards, critical assessment of peak evaluation software, avoidance of processing of standards (ie. their misuse as yield monitors), and ensurance of isotopic exchange as early as possible in radiochemical procedures.

Two other approaches are suggested which can be rewarding in terms of increased accuracy. The first is a general exploitation of the possibilities offered in NAA for self-validation of results for a particular determinand by the use of independent isotopic reactions, and/or the use of both instrumental and radiochemical modes, in order to obtain two independent sets of analytical information in parallel. Such an approach is particularly appropriate in certification of reference materials or when accuracy and confidence in the data must be maximized, but is rarely performed within the same laboratory.

The second is careful attention in RNAA to determination of chemical yield, which should be measured on every sample aliquot individually. The use of radioisotopic tracers is certainly one of the simplest yet best methods in this respect, and possibilities for extending the range of isotopic tracers applied in radiochemical procedures to include some less frequently used ones is discussed. Examples are given, including the tracer isotopes ^{231}Pa (for Th via ^{233}Pa), ^{103}Pd (for Pd via ^{109}Pd), ^{67}Cu (for Cu via ^{64}Cu), ^{108}Ag (for Ag via $^{110\text{m}}\text{Ag}$), $^{113\text{m}}\text{Sn}$ (for Sn via $^{117\text{m}}\text{Sn}$), ^{204}Tl X-rays (for Tl via ^{202}Tl), ^{235}U (for U via ^{239}U) and ^{238}Np (for U via ^{239}Np), $^{81\text{m}}\text{Se}$ from isotopically enriched ^{80}Se (for Se via ^{75}Se), and others.

RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS (RNAA) AS COMPARED TO INDUCTIVELY COUPLED PLASMA MASS- SPECTROMETRY (ICP-MS) FOR THE ANALYSIS OF NORMAL HUMAN SERUM

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The study of trace and ultratrace elements in human serum has attracted the interest of many scientists in the clinical and the analytical field. The composition of serum gives in fact a picture of the metabolic activities and it is readily available. Although its composition is largely organic it has a salt content equivalent to about 9 g NaCl/l. Since the concentrations of trace elements ($< 10 \mu\text{g/ml}$) but also of a number of ultratrace elements ($< \text{ng/ml}$) are of potential interest, for their determination analytical methods are required that allow multielemental analysis, ultimate sensitivity, high selectivity and optimum precision as well as accuracy. An additional requirement is the minimization of blank values, implying the reduction of contamination during sample preparation, handling and measurement. The two methods that at present probably best satisfy these requirements are radiochemical neutron activation analysis (RNAA) and inductively coupled plasma mass-spectrometry (ICP-MS).

The advantages of RNAA for the detection of ultratrace elements are well known, besides sensitivity, freedom of contamination after irradiation, high precision only determined by counting statistics and the accuracy nearly independent of the matrix composition. It was generally recognized that it is the method of choice for Sc, V, Mn, Co, As, Se, Rb, Mo, Ag, Cs and Sb. It gives reliable results for Cr, Fe, Cu, Zn, Br, Sr, I and Hg. It lacks however sensitivity for elements such as B, Li, Al, Ni, Cd, Sn, Ba, Tl, Pb and Bi in normal human serum. The ultimate sensitivity of NAA is in general only obtained when radiochemical separations are performed after irradiation. Only a few elements (Co, Se, Br, Rb, Sb, Cs) can be determined in a purely instrumental way. In general multielement analysis is possible. Radiochemical separation schemes, using for example inorganic retention media such as acid aluminium oxide, hydrated antimony pentoxide and hydrated manganese dioxide, have been developed that allow the determination of 13 elements (Ag, Co, Cr, Cs, Fe, Hg, Rb, Sb, Sc, Se, Sn, Sr and Zn) after a long irradiation at a high neutron flux of 150 mg lyophilized serum. Together with the elements giving rise to shorter lived isotopes (V, Mn, I, Br, As) more than 15 elements can be determined by RNAA in normal human serum. A nuisance is of course that liquid samples must be freeze-dried and that most of the results come only available after 1 month. Its major trump is still its ability to produce accurate results for example in certification campaigns of reference materials. When the second generation biological reference material (lyophilized serum) was produced a few years ago, certification was for many elements largely based on RNAA results.

Mass-spectrometry for inorganic element determination, especially when coupled to an inductively coupled plasma (ICP-MS) for volatilization, atomisation and ionization has a series of very interesting features : amenable to liquid and solids; low detection limits; the atoms themselves are measured not some emitted or absorbed radiation; in principle simple line spectra; high precision; the availability of isotope ratios (application of IDMS). However generally only a quadrupole mass spectrometer is used, instead of a more expensive double focussing magnetic spectrometer, implying that spectral overlaps from isobaric, molecular ions or doubly charged ions cannot be resolved. The sensitivity is typically 2 to 3 orders of magnitude better than for ICP-AES. In the absence of spectral interferences detection limits range from 0.5 to 50 ng/l depending on the degree of ionisation and the abundance of the isotope measured. In human serum a number of spectral interferences due to molecular ions formed with Ar, O, C, S, Cl, Na, K and Ca, often limit the attainable detection limits for elements with atomic mass between 12 and 80. Matrix interferences such as clogging of the orifice or the nebulizer, ionizing suppression or space charge effects can be compensated for by dilution at the expense of the detection limits, by matrix matching or by standard addition. By a simple 5 or 10 times dilution with 0.14M ultrapure HNO₃ and by correction for interferences and blanks using a simulated synthetic serum solution it was possible to determine accurately the trace elements Mg, Fe, Cu, Zn, Rb and the ultratrace element Co. No corrections were needed for the determination of the trace elements B, Li, Br and Sr and for the ultratrace elements Mo, Cd, Sn, Sb, I, Cs, Ba, Pb and Bi. The accuracy can be excellent if the calibration is applied properly and if blanks are subtracted and the precision can be as good as 2 to 5% since always an internal standard is used with an atomic mass close to the one of the analyte element. For several of these elements the values certified in the second generation reference material could be confirmed. For a number of these elements however. Very few results for normal human serum have been published. Many of the earlier published concentration data are orders of magnitude higher. Although in principle the whole mass range can be scanned in less than 200 ms, typically a limited mass range (± 50 mass units) will be scanned a few hundred times in one minute so that 2 to 5 elements together with the internal standard are measured simultaneously. The simple preparation is limited to the addition of the internal standard and the 5 to 10 times dilution of the serum. Disadvantages are, owing to spectral overlap with molecular ions, the insufficient sensitivity for elements such as V (³⁵Cl¹⁶O), Cr (⁴⁰Ar¹²C), Mn (³⁷Cl¹⁸O, ³⁹K¹⁶O), Ni (²³Na³⁵Cl), As (⁴⁰Ar³⁵Cl) and Se (⁴⁰Ar⁴⁰Ar). The application of chemical separations or electrothermal volatilization can however largely solve these problems. Se and As were in this way already accurately determined in human serum. Thus in total more than 20 elements can be determined in normal human serum without preconcentration.

IRMM-International Measurement Evaluation Programme (IMEP) IMEP-3: Trace elements in a synthetic and a natural water

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IRMM is conducting on a regular basis an "International Measurement Evaluation Programme" (IMEP) aiming at the establishment of the real "State-of-the-Practice" (SOP) in measurements of toxic and life-essential elements. These programmes provide photographic pictures of the SOP and offer certified ("definitive") values with conservative uncertainties obtained by means of an "isotope-specific" measurement technique: Isotope Dilution Mass Spectrometry (IDMS). These certified values are directly traceable to the mole, our SI unit for amount of substance, in the shortest possible transparent way. Thus field laboratories are given the opportunity to realise the comparability of their measurements across borders because their measurements are traceable to a common basis.

The main characteristics of the IMEP programmes are:

- Providing "State-of-the-Practice" pictures for the assay of a given toxic or life-essential element in a given matrix. It is not primarily intended to perform the evaluation of a particular method, nor is it intended to demonstrate "State-of-the-Art" (SOA) or ultimately achievable, optimum performance.
- Providing a certified value with a provable total uncertainty, smaller than the interlaboratory spread.
- Officially guaranteed **coded participation**; individual results are only decoded to the participant concerned.
- Reporting of results in **graphical display**.
- Limited frequency; to be discussed with participants.
- Participants work under **normal working conditions** with choice of the measurement methods, procedures and instrumentation at their discretion.
- **Conclusions** from graphical display to be drawn by participants for themselves; assistance is only given if requested and then only after the measurement round.

The earlier IMEP rounds were on lithium in human serum (IMEP-1) and on cadmium in polyethylene (IMEP-2). The results of IMEP-3: trace elements in a synthetic and a natural water are presented.

Water is a matrix of environmental importance: quality control in drinking, ground-, river and treated waste water, and of political importance: border crossing pollution of rivers and seas, scarceness of drinking water.

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Good analytical measurement capability for water analysis is of highest importance because measurements will determine the official quality and use of the water. In IMEP-3 70 laboratories participated, mainly from Europe, but also from India and China, analyzing 10 different elements (B, Ca, Cd, Cu, Fe, K, Li, Pb, Rb, Zn) in a synthetic and a natural water using 8 different analytical techniques. These results, with special emphasis on the element cadmium, will be discussed. The graphical displays will indicate values in ascending order, values arranged by methods, experience of the participating laboratories, calibration errors etc.

COMPARATIVE STUDY OF METHODS FOR DETERMINING LANTHANIDE ELEMENTS IN BIOLOGICAL MATERIALS BY USING NAA, HPLC POST-COLUMN REACTION, AND ICP-MS

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INTRODUCTION The use of lanthanide elements has been increasing in the fields of both traditional and ultramodern industries. The elements belonging to the lanthanide group have not been studied much in regard to health effects or analytical procedure in biological materials. We tried to measure lanthanide elements in various organs of mice. The concentrations in liver were determined by three methods, NAA, HPLC post-column reaction, and ICP-MS. The results were within acceptable range.

MATERIALS AND METHODS Male mice were purchased at 5 week old and housed in a climatic chamber. After a week each mouse received a single intravenous injection with one of the elements. The chloride compounds of yttrium (Y), lanthanum (La), cerium (Ce), neodymium (Nd), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), and ytterbium (Yb) were used. The dose of 25 mg element/kg body weight was administered. At 20 hours after the injection the animals were sacrificed and organ specimens were removed.

Analytical procedure:(A) NAA--The lyophilized liver samples were powdered by grinding. Then samples of about 100 mg each were weighed accurately in polyethylene bags and sealed by heating. Irradiations were carried out with appropriate standard samples in a IEA-RI nuclear research reactor. The detailed conditions are listed in Table 1. The radioactivities were counted by an ENERTEC hyperpure Ge detector coupled to an EG & G Ortec 4096 channel pulse height analyzer connected to a Monydata PC 200 Plus microcomputer.

(B) HPLC post-column reaction--an aliquot of the liver samples, 20 to 100 mg, was digested by simple wet ashing technique using nitric acid and perchloric acid. After heating at 100 to 120 C for 1 to 2 hours then at 200 C for about one hour, the remaining amounts were dissolved with 0.5% nitric acid. This solution was passed through an ion exchange column (Shim-pack IC-CI) installed with HPLC (Shimadzu LC 6A). 0.05 to 0.2 mol/L 2-hydroxybutyric acid (pH 4.4) was used as a mobile phase. The eluents were reacted with Arsenazo III to develop color. The optical density at 655 nm was detectable for all lanthanide elements which we tried at 2.5 ng of the detection limit. When 2, 6-pyridinedicarboxylic acid was used as a reaction reagent, Eu, Tb, and Dy were measured by fluorometry at the detection limit 0.1 to 1.0 ng.

(C) ICP-MS--0.5% nitric acid solution after digesting liver samples was applied to ICP-MS (Yokogawa PMS-200). The detection limits were 0.02 ng element/ml.

RESULTS AND DISCUSSION The analytical results were scattered in a relatively small range. The ratio, HPLC/ICP-MS and INAA/ICP-MS are shown in Table 2. The results by HPLC post-column reaction and ICP-MS coincided well. It may be considered that the reason for this is that the applying sample solutions were divided into two after the digestion. On the other hand the samples for INAA were prepared separately from the same liver specimens. It was not clear whether the difference in the distribution of the elements inside liver exists or not. As a point for further investigation, we have to compare the individual standard solutions.

Table 1 Experimental conditions and nuclear data

Element	Irradiation time	Neutron flux	Decay time	Radioisotope measured (half life ; gamma ray energy(keV))
La	30 min	(a)	1d	¹⁴⁰ La(40.27h ; 1597)
Ce	30 min	(b)	4d	¹⁴¹ Ce(32.5d ; 145.4)
Nd	8 h	(c)	6d	¹⁴⁷ Nd(11.1d ; 91)
Sm	30 min	(a)	1d	¹⁵³ Sm(47.1h ; 69 and 103)
Eu	3 min	(a)	1h	^{152m} Eu(9.35h ; 841)
Gd	30 min	(a)	4h	¹⁵⁹ Gd(18h ; 363)
Tb	30 min	(b)	11d	¹⁶⁰ Tb(73d ; 298)
Dy	30 min	(a)	19h	¹⁶⁵ Dy(2.36h ; 634)
Ho	10 min	(a)	20h	¹⁶⁶ Ho(26.9h ; 80 and 1378)
Er	15 min	(a)	1d	¹⁷¹ Er(7.8h ; 308)
Yb	30 min	(a)	15h	¹⁷⁵ Yb(101h ; 396)

(a) $2.67 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$ (b) $1.54 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$ (c) $10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$

Table 2 Comparison with the results analyzed by three methods

Element	HPLC/ICP-MS		INAA/ICP-MS	
	MEAN	CV(%)	MEAN	CV(%)
Y	0.98	5.1	-	-
La	0.93	9.1	1.01	6.9
Ce	0.97	7.3	0.68	13.8
Nd	0.91	3.5	0.68	2.9
Sm	0.97	4.5	0.72	13.5
Eu	1.01	2.6	1.14	14.3
Gd	1.17	2.0	0.82	4.3
Tb	0.95	2.2	1.37	3.9
Dy	1.06	2.6	1.08	12.8
Ho	1.00	2.5	0.86	11.1
Er	1.01	1.6	0.63	20.4
Yb	0.94	3.7	1.44	3.7

n = 4~5

INTERCOMPARISON OF TECHNIQUES AVAILABLE AT INETI IN THE ANALYSIS OF TWO IAEA CANDIDATE RESEARCH MATERIALS

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Multielement plant analyses are routinely performed for monitoring purposes, mapping and risk assessment. In such applications, relevant information is commonly obtained by studying an organism used for monitoring (the monitoring organism). In recent years, a variety of different biological materials, including lichens, have been suggested for use as biomonitors of environmental pollution. However, the control of analytical quality in this field is hampered by the non-existence of suitable reference materials.

Under contract with the IAEA, the epiphytic lichen *Evernia prunastri* was collected to prepare a multielement lichen reference material for environmental purposes. The choice of an epiphytic lichen is experimentally justified by its metal uptake and retention from the atmosphere and not from the soil on bark substrate. In previous publications,^{1,2} it was demonstrated that the homogeneity of the material is better than 5% for samples of ≥ 100 mg, except for K (13%) and Ba (8%). The homogeneity test was performed for the minor elements K and Na, and for the trace elements Sb, As, Br, Ba, Ce, Cs, Cr, Co, Fe, La, Mn, Rb, Sc, Sm, Th and Zn using the k_0 -standardized INAA.

Under the intercomparison run on trace and minor elements in this candidate research material (the IAEA-336 research material) which is presently going on, six analysis groups of the National Institute of Engineering and Industrial Technology (INETI) have given their collaboration. The following techniques/methods were used:

Laboratory	Technique/method
1	INAA
2	INAA
3	PIXE
4	PIXE
5	XRF
6	AAS,Flame ICP-ES

The elemental concentrations for Al, Ba, Br, Ca, Cl, Cr, Cu, Fe, K, Mg, Mn, Na, P, Rb, Se, Si, Sr, Th, Ti and Zn were determined at least by three laboratories; for Ce, Co, Cs, Hf, Hg, La, Lu, Nd, Pb, S, Sb, Sc, Sm, Ta, Tb and Yb by two laboratories and for Ag, Ni, U and V by one laboratory. The results obtained by the different laboratories are compared and their complementarity is discussed.

As a quality control, the IAEA cabbage research material (the IAEA-359 research material) was also analysed by each laboratory. The results are compared with the approximately estimated values of some elements given by the IAEA: Ca, Cd, Cr, Fe, K, Mg, Mn, Na, Ni, Pb and Zn.

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USE OF A ROBOTIC SAMPLE CHANGER IN CERTIFICATION OF SEVERAL BIOLOGICAL REFERENCE MATERIALS BY INAA

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ABSTRACT

Trace element certification of reference materials requires the highest possible accuracy and precision from an analytical laboratory. Counting of the irradiated samples is a crucial aspect of the analytical process for instrumental neutron activation analysis (INAA) [1]. The National Institute of Standards and Technology (NIST; formerly the National Bureau of Standards (NBS)) has been certifying biological Standard Reference Materials (SRMs) for over twenty years using neutron activation analysis. During that time a variety of automatic sample changers have been available which can be used together with instrumental and/or radiochemical neutron activation analysis to increase productivity. In many cases the results obtained using automatic samples changers has been less than perfect, often with malfunctions and breakdowns adding to the difficulties. Recently, the NIST Nuclear Methods Group has obtained a computer controlled robotic sample changer (RSC) which has provided extremely reliable operation for the past year, and which has been used to provide certification data for two botanical reference materials, SRM 1573a, Tomato Leaves and SRM 1570a, Spinach.

DESCRIPTION OF THE SAMPLE CHANGER

The sample changer is the Tracerlab Model ASC-50, obtained from a company in Germany [2]. The basic system construction is as follows: the sample changer itself, which moves both vertically (more than one meter) and horizontally (up to six meters) along a highly stable fixed transport frame; a universal sample holder which is capable of firmly holding (with attachments) the seven different sample containers we specified (ranging from a 50 ml polyethylene bottle to the often used "2/5 dram" polyethylene vials to a 54 mm diameter polystyrene Petri dish); a 50 sample magazine; and a pc-clone controller system. This controller system is then connected to a pulse height analyzer (PHA) through a communication cable.

The reproducibility and reliability of the changer system was evaluated through (1) the counting of 15 irradiated foils activated under conditions so that they all received identical neutron exposure, and (2) by comparing results from four different botanical SRMs, two counted manually and two counted on the RSC.

For the foil evaluation, 15 identical thin iron foils were irradiated for one hour in the RT-4 pneumatic tube facility of the NBSR for a total neutron fluence of $7.3 \times 10^{16} \text{ n} \cdot \text{cm}^{-2}$. The foils were then separated and placed in separate plastic Petri dishes and then into different RSC sample holders. The holders were placed into positions 1-15 of the magazine, and the counting procedure initiated. These foils were counted at approximately 5 cm from the detector.

For the botanical SRM results, the INAA certification analyses for long halflife elements in the two SRMs using the RSC (SRM 1573a, Tomato Leaves, and SRM 1570a, Spinach) [3]

were initiated using an identical procedure to that used previously for two similar botanical materials (SRM 1515, Apple Leaves, and SRM 1547, Peach Leaves) [4]. The only difference was that for the Apple and Peach Leaves the samples were counted with manual positioning of the samples on an upward looking Ge detector using a fixed geometry, while for the Tomato Leaves and Spinach the RASC was used to position the samples above the upward looking Ge detector.

RESULTS AND DISCUSSION

Results of the foil evaluation gave an uncertainty of 0.52 % relative (ts/\sqrt{n} at the 95 % Confidence Interval) for the 15 foils using the 1099 keV peak of the ^{59}Fe iron matrix, and an uncertainty of 0.63 % relative (ts/\sqrt{n} at the 95 % Confidence Interval) for the 1332.5 keV peak of a ^{60}Co component of the foil. For the ^{59}Fe , with $s = 0.95$ % together with counting statistics of 0.3 % establish that for these foils all other sources of uncertainty are less than 0.9 % at the 5 cm counting geometry used.

For evaluation of results obtained using botanical materials, two different measurements were used. First, a ratio of the average observed uncertainty to the uncertainty expected from counting statistics was examined, using the relative standard deviation of the mean for five elements (cobalt, iron, rubidium, scandium and zinc). This ratio was very similar for the four SRMs, averaging about two percent relative. Second, the observed average relative standard deviation of the mean was calculated for the same five elements, which was 1.10 % for the Apple Leaves, 0.95 % for the Peach Leaves, 0.47 % for the Tomato Leaves, and 0.53 % for the Spinach. This lower uncertainty for the two materials counted using the RSC is due partially to improved counting statistics from higher elemental concentrations in the Tomato Leaves and Spinach, as well as to longer average counting times allowed by the more efficient used of the detector by the RSC.

In conclusion, no significant decrease in counting accuracy and precision has been observed due to use of the RSC, and significantly improved counting efficiency has been obtained.

Disclaimer

Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedures. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

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**ACCURATE DETERMINATION OF COBALT TRACES IN SEVERAL
BIOLOGICAL REFERENCE MATERIALS**

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Newly devised, very accurate ("definitive") method for the determination of trace amounts of cobalt in biological materials was used for the analysis of several reference materials (IAEA A-11 Milk Powder, IAEA H-9 Human Diet, Bowen's Kale, IAEA H-8 Horse Kidney, IAEA V-10 Hay Powder, NBS 1571 Orchard Leaves, NBS 1570 Spinach, Versieck's Human Serum and some others). The method is based on combination of neutron activation and selective and quantitative post irradiation isolation of radiocobalt from practically all other radionuclides by ion exchange and extraction chromatography followed by γ -spectrometric measurement.

The accuracy and precision of the method are discussed and the significance of criteria which should be fulfilled in order to accept a given result as obtained by "definitive method" is emphasized. In view of the demonstrated very good accuracy of the method it is suggested that our values for cobalt content in those reference materials in which it was originally not certified, might be used as provisional certified values.

SUM and MEAN: Standard Programs for Activation Analysis

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Two well-tested programs have been in use for over a decade in the Nuclear Methods Group at NIST: *SUM*, to integrate difficult peaks in a gamma spectrum, and *MEAN*, to compute the best average of repeated measurement of a quantity. These programs illustrate the utility of standard software as tools to help perform accurate measurements. We define a standard program for this discussion as one which is widely available and widely used because it is reasonably easy to apply in a number of contexts. In an ideal standard program, well tested and publicly known algorithms are employed to produce results which are well understood, and thereby capable of comparison and discussion, within the community of users. Commercial computer-based gamma-ray spectrometry systems use standard programs for such common operations as peak finding and integration: if two workers use the same manufacturer's counting system, then they are probably processing their data in much the same way and their results can be compared.

SUM

The most basic operation in gamma-ray spectrometry is the identification of significant peaks in the spectrum and determining the position, net area, and uncertainty of the area of each peak. *SUM* was originally written because the commercial peak search program then in use in our laboratory calculated the uncertainty incorrectly. Channel numbers for each peak are entered by the user via the keyboard or mouse for the peak and baseline regions. All outputs to disk are in the appropriate formats so that *SUM* can be used in automatic command procedures. The original version was written for the Midas operating system in 1978, and later translated to VAX/VMS. Different versions of the program allow for the baseline to be adjacent to the peak region or detached. Definitions of terms and algorithms are documented in a five-page user's guide.

The *SUM* program gives better results than most automatic peak search programs in three cases: when counting statistics are poor, when they are very good, or when peak shapes are unusual (such as the β^+ annihilation or the boron capture gamma ray). Judicious use of the program can eliminate certain non-Poisson sources of error inherent in the peak search process.

When there are very few counts per channel, the eye of an experienced analyst, or judgment based on a standard with good statistics, can be better than an automatic program for detecting peaks and judging where their boundaries occur. A particularly good recent example of the shortcoming of a commonly used peak search program in our laboratory is the determination of iodine in the presence of the activation products of other halogens and manganese. For some samples the 443-keV iodine gamma ray appears as a small peak on a relatively large, locally smooth baseline. Using *SUM*, the precision of the

analysis was improved by nearly a factor of two, by showing experimentally that the optimum number of baseline channels was much greater than those the automatic program chose to use.

Manual selection of peak boundaries may also improve precision in the opposite situation: when there are a very large number of counts in the peak of interest. In a high-precision nuclear safeguards application, Greenberg¹ showed that the peak search process introduces excess non-Poisson variability into repeated counts of the same sample. The SUM program with nonadjacent baselines improved the precision by more than a factor of two, to about 0.02%, compared to a Gaussian fit.

MEAN

A fundamental operation in all of measurement science is to combine several measurements of a single quantity, generally with different uncertainties, to obtain the best value for the average and for its uncertainty. Before combining the individual measurements we want to test them for consistency, and perhaps reject outliers and re-average the remainder. The appropriate algorithm to perform the combination is a weighted mean, where the weight assigned to each point is inversely proportional to its estimated variance. The MEAN program performs this function.

The algorithms were taken from a standard textbook² and implemented in Fortran for Midas and VAX/VMS, and later transported to the Excel spreadsheet for Macintosh. In addition to weighted and unweighted means, the program displays the residual for each input point in native units and in standard deviations, computes six measures of uncertainty of the means, displays chi-squared and its probability, and offers the option of re-fitting the data set with an additional error added to each point. Comparing the observed standard deviation of the mean with that value expected a priori from the input precision (essentially a *t* test) helps detect unexpected sources of error. The computation is carried out to as many significant figures as the language allows. MEAN passes robustness tests which determine when roundoff becomes noticeable; this is generally important for precise numbers where differences are small. The statistical terms are defined and the algorithms are documented in a three-page user's guide. The program has been used for more than ten years to evaluate the results of analyses for certification of Standard Reference Materials.

These well-tested standard programs provide uniform definitions of terms and common algorithms for comparing measurements. Both are useful for exploratory data analysis, and as tools for adjusting measurement processes and interpreting their results. They have also proven to be useful teaching tools for new workers.

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NAA METHODOLOGY FOR THE CERTIFICATION OF EIGHT TRACE ELEMENTS IN A PLANKTON REFERENCE MATERIAL

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SUMMARY

Neutron Activation Analysis (NAA) methodology has been applied for the certification of eight trace elements (As, Co, Cr, Cu, Hg, Mn, Se, Zn) in a plankton reference material (CRM 414) prepared by the BCR of the Commission of European Communities. Among the 16 laboratories from 8 member states and the Joint Research Centre of Ispra which participated in this certification campaign was our Radioanalytical Laboratory of the Demokritos Center (1). INAA was applied for the determination of Co, Cr, Mn, Se and Zn in plankton. Arsenic, Cu and Hg were estimated in plankton by RNAA. Average concentrations ($\mu\text{g/g}$ dry weight) and standard deviations found in plankton for the 8 trace elements were as follows: As 6.29 ± 0.19 , Co 1.37 ± 0.05 , Cr 23.70 ± 0.56 , Cu 27.0 ± 0.88 , Hg 0.29 ± 0.02 , Mn 285 ± 4.1 , Se 1.62 ± 0.10 and Zn 114 ± 3.4 . All values found were in very good agreement with certified values.

EXPERIMENTAL

Bottles of plankton: Two bottles of plankton (CRM 414) were sent to us for analysis (BCR Project RM 370). Prior to analysis each bottle of plankton was shaken for 2 minutes for proper mixing. Portions from each of the two bottles of plankton were taken for analysis. To check the reproducibility of the NAA methodology used, as well as the homogeneity of the plankton samples, the analysis of plankton samples was performed 5 times.

Preparation of samples and standards for irradiations: Proper liquid standards of As, Co, Cr, Cu, Hg, Mn, Se and Zn were prepared. The concentration of these elements in standard solutions was as follows:

Mixed standard solution of Co, Cr, Se and Zn: Co 5 $\mu\text{g/ml}$, Cr 20 $\mu\text{g/ml}$, Se 5 $\mu\text{g/ml}$ and Zn 100 $\mu\text{g/ml}$.

Mixed standard solution of As and Cu: As 20 $\mu\text{g/ml}$ and Cu 40 $\mu\text{g/ml}$.

Mercury standard solution: 1 $\mu\text{g Hg/ml}$, and

Manganese standard solution: 100 $\mu\text{g Mn/ml}$.

Plankton samples weighing about 200 mg each were placed in polyethylene tubes (10x30 mm) for short irradiation or in quartz tubes (10x30 mm) for long irradiations. Aliquots of 0.5 ml of each of the standard solutions were pipetted into identical polyethylene or quartz tubes. The tubes were heat-sealed.

Irradiation: All neutron irradiations were carried out in the swimming pool type Reactor of the NCSR "Demokritos" using the rotation system. The thermal neutron flux as well as the irradiation, the decay and the counting time were varied depending on the trace elements under investigation and are given in Table 1.

Gamma ray-spectroscopy: A germanium detector (ORTEC) was used. The output signals were passed into a preamplifier (ORTEC) and spectroscopy amplifier (ORTEC). The Ge detector system was connected with a 4096 channel pulse height analyser (Canberra model 35/plus). System resolution was 1.69 keV and the peak Compton ratio was 59.1 for the 1332 keV of ^{60}Co . The efficiency of the Ge detector was 20%. The calibration of the multichannel analyser was done with a Europium-152 standard source. The analyser was coupled with an IBM AT Computer. The data was processed using the Canberra spectran AT V 3.0 software.

TABLE 1: EXPERIMENTAL PARAMETERS USED FOR THE DETERMINATION OF 8 TRACE ELEMENTS IN PLANKTON BY NAA METHODOLOGY

Thermal neutron flux $n.cm^{-2}.sec^{-1}$	Irradiation time	Cooling time	Methodology	Counting time	Elements determined
2.78×10^{12}	210 sec	2.5 h	INAA	180 sec	Mn
2.78×10^{13}	4 hours	21 d	INAA	30 min	Co, Cr, Se, Zn
2.78×10^{13}	7 hours	7 d	RNAA	60 min	Hg
2.78×10^{13}	5 min	20 h	RNAA	1000 sec	As, Cu

NAA METHODOLOGY

INAA (Mn and Co, Cr, Se, Zn)

The experimental parameters are given in Table 1. After counting the areas under the photopeaks of ^{56}Mn at 847 keV, of ^{75}Se at 264 keV, of ^{51}Cr at 320 keV, of ^{65}Zn at 1115 keV and of ^{60}Co at 1173 keV or 1332 keV of samples and standards were compared.

RNAA (Hg, As, Cu)

The determination of Hg in plankton was made by a RNAA (2). The radiochemical procedure is based upon the digestion of irradiated samples with $\text{HNO}_3/\text{H}_2\text{SO}_4$ in the presence of a Hg carrier. The resulting solution was made 10M H_2SO_4 -0.025M KI. Mercury was extracted as HgJ_2 into toluene and back-extracted into 0.034 M EDTA in 5% ammonia solution and the ^{197}Hg was counted. The chemical yield of Hg was estimated by a reactivation procedure.

The simultaneous determination of As and Cu was made by a modified RNAA method based on solvent extraction (3). The modification consists in using toluene as a solvent instead of benzene which is equally active but not toxic like benzene. The radiochemical procedure is based upon the digestion of irradiated plankton samples with HClO_4 - HNO_3 in the presence of Na, As and Cu carriers. The resulting solution was made 7M HClO_4 -1M HBr, and the As was extracted as AsBr_3 into toluene and back-extracted into water. Arsenic was precipitated as metallic As with sodium hydrophosphite, dissolved in HNO_3 , transferred to a 5 ml volumetric flask and the ^{76}As was counted.

The Cu in the aqueous phase was extracted as copper cupferronate into chloroform and back-extracted into concentrated ammonia solution. The Cu was precipitated as sulphide with 3% aqueous thioacetamide solution and the precipitate was dissolved in HNO_3 . The resulting solution was transferred to a 5 ml volumetric flask and the ^{64}Cu was counted. The chemical yields of As and Cu were estimated by reactivation procedures.

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APPLICATION OF SHORT LIVED RADIONUCLIDES IN NEUTRON ACTIVATION
ANALYSIS OF BIOLOGICAL AND ENVIRONMENTAL SAMPLES

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ABSTRACT

There are a number of elements of interest having only short lived radionuclides or isomeric states with half lives of less than one second, which are activated by reactor neutrons e.g. B, Li, Pb, and some with half-lives in the second and minute range -- F, Y, Al, V, Cl --, which can be used for NAA. Cl, Se, and Na have short lived isomeric states which enable a fast determination or a fast correction of side reactions. By means of a removable ${}^6\text{Li D}$ -converter, which doubles the fast flux but at the same time shields the thermal neutrons, it is possible to activate biological and environmental samples up to 30min, without a long delay before measurement as the main activities of Na-24, K-42 Cl-38, Al-28 are a factor of about 30 reduced. I - measurements are easily performed using activation with converter by I-128.

Examples given :

B by B-12 in urin

Li by Li-8 in higher fungi

Pb by Pb-207m in streetdust

Se by Se-77m in biological standard reference materials

F by F-17 in contaminated grass

I by I-128 in pets food

halogens in water of fumaroles

V by V-52 in environmental samples (lichen)

Al by Al-28 with P - correction in lichen

TXRF is a practical complementary method which enables the determination of a number of additional elements as shown on the analysis of lichens in which Ti, Rb, Sr, Cu, Zn, Fe, Ni, and Pb were determined by this method.

USE OF k_0 -NAA IN THE LIFE SCIENCES

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The applicability and usefulness of k_0 -based NAA in the analysis of biological and environmental samples is evaluated from the following examples:

- instrumental multi-element NAA of NIST SRM 1633a coal fly ash, performed independently at the INW and the KFKI;
- radiochemical NAA of Versieck's reference human serum, and - herewith associated - the development of practical correction procedures for neutron induced reaction interferences [$^{54}\text{Fe}(n,\alpha)^{51}\text{Cr}$; $^{44}\text{Ca}(n,\gamma;\beta^-;n,\gamma)^{46}\text{Sc}$];
- determination of the lanthanides in environmental materials (plant leaves, lichens) near a Portuguese coal-fired power station, which led to the introduction of the Westcott-formalism and to the use of a low-energy photon detector in the k_0 -standardization method.

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NEUTRON ACTIVATION ANALYSIS FOR THE DETERMINATION OF TRACE ELEMENTS
IN BIOLOGICAL MATERIALS

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Over the last 30 years, neutron activation analysis grew up to an extremely powerful analytical technique for trace element determinations. It started as a single-element technique when only Na(Tl) detectors were available but with the advent of high-resolution Ge(Li) detectors or, more recently, high-purity (HP) Ge detectors and associated multichannel analyzers it became a really multi-element technique. Moreover, the introduction of mighty computers for data processing greatly increased its applicability in current analytical practice.

Neutron activation analysis has some considerable advantages for the biologically oriented trace element researcher. An invaluable one is its relative freedom from contamination. Indeed, pre-irradiation sample preparation can generally be kept to a minimum whereas sample mineralization and chemical separations of elements of interest - if necessary - can be postponed till after the end of the irradiation when extraneous additions from reagents and laboratory equipment do no longer affect the final result. Another advantage is the great sensitivity for many biologically interesting elements. Neutron activation analysis is a flexible technique that permits to calculate the optimal irradiation, waiting, and counting times. In addition, a choice may be made - at least within certain limits - between different neutron fluxes. To push up the sensitivity, a detector may be chosen with an as great as possible counting efficiency. Other virtues are that the relation between the concentration of an element and the measured signal are nearly matrix independent and that radiochemical separations can be carried out in optimal conditions by post-irradiation carrier addition. An interesting aspect of instrumental neutron activation analysis is its non-destructive character which is unique among all analytical techniques.

Of course, neutron activation analysis also has its disadvantages and limitations. In general, it is expensive when compared to other techniques. There has been a time that this aspect did not prove a deterrent to the extensive application of the technique but this is no longer the case and straws in the wind indicate that the aspect "cost" will assume an even increasing importance in the future. Furthermore, in a reactor building and in a radioanalytical laboratory several safety regulations must be strictly observed. Most biological samples contain large amounts of sodium, chlorine, or other matrix elements which, after irradiation, form nuclides emitting considerable radioactivity. An further hindrance to the use of neutron activation analysis - especially in clinical practice - is the low sample throughput and the sometimes very long delay between the collection of a sample and the calculation of the final result.

The foregoing discussion of the advantages and disadvantages of neutron activation analysis explains why, in the biological sciences, the technique was infrequently used for routine purposes but played an exceptionally important role in the certification of numerous reference materials, especially those with the lowest trace element levels (1,2), as well as in the establishment of the normal concentrations of many "difficult" trace elements in several body fluids and tissues (3). It is largely thanks to neutron activation analysis that, at present, it has been settled that the normal concentrations (mean values) in human blood plasma or serum of healthy, environmentally or occupationally unexposed individuals are, approximately - 0.060 ng/ml for vanadium, 0.15 ng/ml for chromium, 0.55 ng/ml for manganese, 0.10 ng/ml for cobalt, 1.0 ng/ml for arsenic, 0.60 ng/ml for molybdenum, 0.075 ng/ml for cadmium, 0.60 ng/ml for tin, 0.75 ng/ml for cesium, and 1.0 ng/ml for mercury.

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**Doppler Broadening as a Supplementary Tool for
Analytical Utilization of
High Resolution Prompt Gamma-Ray Spectroscopy**

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Elemental analysis based on prompt gamma-rays following nuclear interactions induced by neutrons and charged particles has developed considerably over the last 30 years¹⁾. All possible interactions can be roughly divided into three main types of processes: radiative capture, inelastic scattering and rearrangement nuclear collisions. Because of kinematics, residual nuclei are always produced in the motion. In typical nuclear interactions they can be produced with the velocity up to $v/c \sim 1\%$, where c is the velocity of light, and afterwards they can be stopped in target material in a time shorter than $\sim 10^{-12}\text{s}$ ²⁾. The slowing down time of nuclei depends on the nature of the target medium.

If the photon is emitted by a nucleus during its motion, its energy E_γ is shifted with respect to the energy E_γ of a photon emitted from a nucleus at rest. This *Doppler energy shift* is proportional, to first order in v/c , to E_γ and to the projection of relative nucleus velocity v/c into the direction of photon emission. The sign of energy shift depends on the sign of this velocity projection; the shift does not take place at nucleus the velocity of which is perpendicular to the direction of emission. A real measurement does not involve the disintegration of a single excited nucleus but, of a whole set of excited nuclei moving in different directions and at different velocities. The photon energy shift in an individual event of emission leads in this case generally to the *Doppler shift and broadening of the measured spectral line*. An energy distribution of the measured photons depends on the distribution of velocity projection (at the moments of photon emission) into the direction of photon emission (determined by the position of a photon detector). A velocity distribution of nuclei can be estimated from the kinematics of the interaction (from the momentum conservation law diagram³⁾) and from the slowing down process. If the *lifetime of the gamma emitting state is comparable with the slowing down time*, a gamma photon can be emitted by the nucleus during its flight and the *Doppler shift and broadening will be observed*. Both Doppler effects depend significantly on energy of incident particles, on energy of reaction Q and on the rest masses of particles and nuclei which take part in the process. Importance of the detector resolution for the observation of the Doppler broadening is illustrated by Jolie et al.⁴⁾. The most pronounced Doppler effects can be expected in the nuclear

interactions induced by fast particles on light target nuclei if residual nuclei promptly decay with a very short lifetime τ (shorter than 10^{-12} s). This situation often occurs in $(n, n'\gamma)$, (n, γ) , $(n, \alpha\gamma)$ processes induced by fast neutrons and in (p, γ) , $(p, p'\gamma)$, $(p, \alpha\gamma)$, $(p, n\gamma)$, (α, γ) $(\alpha, n\gamma)$ nuclear processes realized on accelerators, as well.

In case of analytical utilization of prompt gamma ray spectroscopy, energy interferences can arise from the observation of unresolved gamma lines and from the observation of identical gamma lines of different origin. The identical lines are connected with the decay of identical residual nuclei produced in different processes on different target nuclei, as demonstrated by the following list of proton induced nuclear processes: $^{A-1}(Z-1)(p, \gamma)^AZ$, $^AZ(p, p'\gamma)^AZ$, $^{A-1}(Z-1)(p, n\gamma)^AZ$, $^{A+3}(Z+1)(p, \alpha\gamma)^AZ$. Thus, also the velocity distribution of residual nuclei will be different. In this way, the Doppler effects, if observed (if gamma decay of short living excited state takes place), as well as lineshape of Doppler modified spectral line will be different and may serve as a complementary and unique analytical information about the origin of some observed spectral lines and may be very useful for solving some special spectral interference problems. Since the Doppler modification of spectral line depends on the angle of observation, the experiment can be cultivated by the measurements with detector placed in two positions with respect to the incident beam direction (e.g. in the beam direction and perpendicular to the beam direction).

The general differences between radiative capture, inelastic scattering and rearrangement nuclear reaction induced by protons are described from the viewpoint of resulting differences in spatial velocity distribution of recoiled nuclei. The main differences between Doppler modified lines in these processes are explained. Some experimental examples of the Doppler modified lineshapes are exhibited⁵⁾. Special attention is devoted to the determination of light elements (Li, Be, B, C; N, O, F; Na, Mg, Al, Si; P, S, Cl) where some groups of interferences exist between the proton induced gamma-ray lines^{1,6)}. Recommendations how to utilize an observation of Doppler phenomenon for routine solution of interference problems are given in the contribution.

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PIGE studies on fluorine in Polish clays and kaolins (technological and environmental approach)

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Fluorine belongs to very harmful elements to the natural environment. The determination of this element using classical methods of chemical analysis is rather complicated. On the contrary, some physical methods are useful for this purpose. Measurements by use of the PIXE method, which is very convenient for some light elements (B,F,Li,Na) have been carried out in the Institute of Nuclear Physics in Cracow. The beam of protons, accelerated to the energy of 2.6 MeV in the cyclotron C-48 strikes sample, prepared in the form of pressed pellet. During 2 years of studies the measurement conditions were and detection limit of fluorine was lowered from 100 ppm to 30 ppm. At present the measuring line of the new installed van der Graaf accelerator allows RBS and PIXE/PIGE measurements simultaneously, thus we are able to get an information about the content of trace elements and also deep-profiling of the sample at the same time.

Our investigation was focused on the analysis of fluorine in Polish clays and kaolins. The majority of clays studied are used in ceramic industry for the production of bricks. They are represented by clay rocks of different age and show distinct variability of mineral composition. In the majority of samples the content of F in raw material varies from 500 to 900 ppm. After firing of clays in 1200°C, the content of F decreased rapidly - in most cases below 100 ppm. Taking into account the temperature of firing bricks (ca 1000°C), the global emission of the fluorine in production of bricks has been determined (Fig.1). The obtained data are comparable with the emission of this element by metallurgical plants (mainly of aluminium) and by chemical industry (production of phosphate fertilizers).

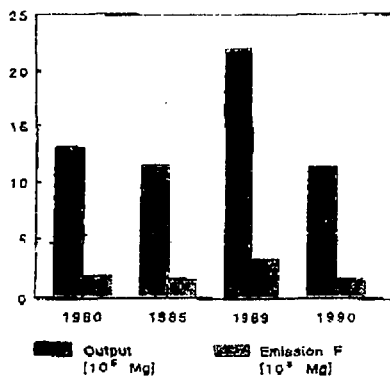


Figure 1. Estimated total fluorine emission in Poland caused by brick industry in the years: 1980, 1985, 1989, 1990

Fluorine is also liberated during firing of washed kaolins, which are the most important components of porcelain bodies. Washed kaolins contain mainly ca. 400 ppm of F, therefore fluorine emission during production of clays is lower in comparison with the brick industry.

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**THE RADIOANALYTICAL LABORATORY AT PELINDABA:
APPLICATIONS FOR ENVIRONMENTAL AND HEALTH MONITORING**

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Various techniques are applied at the radioanalytical laboratory of the Atomic Energy Corporation of South Africa to assist in various scientific fields, especially environmental and health monitoring. Analytical techniques include instrumental neutron activation analysis (INAA) with γ -ray and delayed neutron counting (DNC), as well as α -spectrometry, gross α/β -counting and liquid scintillation counting. A variety of matrixes are analyzed, including water (both suspended solids and liquid fractions), soil, airfilters, plant material and urine for personnel monitoring.

Specific analytical techniques discussed in more detail, include the following:

1. Semi-cyclic activation for the determination of fluorine in vitamin mixtures

Vitamin supplements, administered to women during pregnancy, are subjected to strict regulations. Among others the limit for fluorine per capsule is less than 30 micrograms.

NAA offers a quick and cost-effective method for analysing fluorine, but interfering radionuclides resulting from the matrix elements, such as magnesium, manganese and sodium, cause a serious loss of sensitivity. Since radiochemical separation techniques are labour intensive and therefore expensive, a semi-cyclic activation method was evaluated.

The laboratory operates an automatic pneumatic rabbit system (RINGAS) for the analysis of short-lived radionuclides by neutron activation. This system has a minimum irradiation time of one second

and minimum delay time of eleven seconds, allowing the analysis of such short-lived radionuclides as fluorine-20 with a half-life of twenty seconds.

The RINGAS-system was not designed for cyclic activation analysis, since each sample has to complete the full cycle of irradiation, cooling and counting before the next sample can be analyzed. The semi-cyclic activation analysis was performed by analysing twenty separate samples and accumulating the individual spectra, thereby enhancing the fluorine-20 peak in respect of the interfering radionuclides. The sensitivity for fluorine determination was thereby greatly enhanced. The specific gain of semi-cyclic activation is both in its signal/background (due to long-lived nuclides) and its relatively large sample analyzed.

2. Radium and uranium analysis in urine samples from decontamination workers

Decommissioning of acid- and uranium plants at South-African gold mines has led to the need for monitoring contract workers employed at these plants for possible contamination from uranium and its decay products. These radioelements are present in great quantities and the dusty conditions cause great concern for internal contamination by inhalation.

The proper regulatory body in South Africa requires strict control of workers by monitoring urine samples on a regular basis and has set the observable lower limits as low as 0,72 mBq/l and 8,2 mBq/l for uranium-238 and radium-226 respectively. Special analytical procedures had to be developed to meet the demands for these ultra-low limits.

Samples are homogenized by ashing, since uranium shows a preference for the protein present in urine. Sub-samples are then analyzed for uranium by direct neutron activation and delayed neutron counting. Radium is determined by dissolution and co-precipitation with barium and subsequent alpha-spectrometry counting on a low-background instrument.

The application of reversed phase chromatography for the neutron activation analysis of cobalt.

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High performance liquid chromatography (HPLC) has proven to exhibit certain intrinsic advantages which have been explored for multi-element radiochemical separation in this laboratory(1,2). The separation and the (on-line) chemical yield determination step are performed in one single run by using HPLC, thereby avoiding any long lead times and intrusion of an independent method for yield determination. The ruggedness of the method for practical purposes has been demonstrated by its application to radiochemical neutron activation analysis of cobalt in certified biological reference materials(3). The validity of the concept was evaluated by verifying the constancy of the ratio between two measured signals of the processed samples - the UV absorbance of the separated metal compound and the radioactivity signal of ^{60}Co . Variations or losses of the radioactivity are reflected in the UV response. Hence correction between the corresponding signals is perfectly rational(3).

In this presentation, we discuss additional results achieved by this method of trace cobalt contents in various biological and botanical reference materials. Where possible, comparison is made between the instrumental and the radiochemically obtained results of the same sample.

To briefly summarise the protocol, after irradiation and addition of excess cobalt carrier, the cobalt and other minor matrix components were converted into diethyldithiocarbamate (DDTC) complexes. The complexes were then subjected to reversed phased chromatography. The UV absorbance of ^{59}Co -DDTC was registered and the eluted fraction measured for ^{60}Co activity by gamma ray spectrometry. The separation was performed on a semi-preparative column.

The figures obtained for a number of CRMs were in close agreement with the certified or indicative values. Results (refer table) of NIST SRM 1577A Bovine Liver for Co, processed over a time interval of several months, were $215 \pm 17 \mu\text{g}/\text{kg}$ after yield correction. The yield corrected values obtained for botanical materials like NIST SRM 1515 Apple Leaves and NIST SRM 1574 Peach Leaves were $101 \pm 6 \mu\text{g}/\text{kg}$ and $77 \pm 9.5 \mu\text{g}/\text{kg}$ respectively. The corrected results for Bowen's kale had a similar trend, the results improved from $67 \pm 11 \mu\text{g}/\text{kg}$ to $63 \pm 4 \mu\text{g}/\text{kg}$. But the results of other CRMs like BCR CRM 274 Single Cell Protein and IAEA A11 Milk Powder, which have a cobalt content on the lower $\mu\text{g}/\text{kg}$ level did not give satisfactory results. The reason for this is yet to be assessed but most probably it seems to be cross contamination in the column. Overall, the yield correction using UV absorbance signal simultaneously with the HPLC separation is a useful concept improving the precision of the radiochemical neutron activation analysis. The UV

absorbance signal of $^{59}\text{CoDDTC}$ over a period of several months remained almost consistent within 15 to 20%, indicating that the separation with HPLC does not deteriorate over a period of time and that the solvent extraction of CoDDTC as a preconcentration step is adequately reproducible. Thus, although grosso modo the yield can be controlled between 80 to 100%, individual samples each need yield correction for accurate results. Since in one chromatographic run both the separation of several metal complexes and their yield are determined simultaneously, the necessity of an extra elemental technique is obviated.

Advantages and pitfalls of this scheme will be discussed with the results of several CRMs.

Reference Materials	Yield corrected results	Uncorrected results	Certified values
NIST SRM 1577A Bovine Liver	215 ± 17	229 ± 38	210 ± 50
NIST SRM 1515 Apple Leaves	101 ± 6	97 ± 12	Not certified
NIST SRM 1574 Peach Leaves	77 ± 9.5	64 ± 30	Not certified
Bowen's kale	63 ± 4	67 ± 11	63.2 ± 11

* All values in $\mu\text{g}/\text{kg}$.

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7

DETERMINATION OF ALUMINUM AND PHOSPHORUS IN BIOLOGICAL
MATERIALS BY REACTOR ACTIVATION ANALYSIS USING GERMANIUM AS
INTEGRAL FLUX MONITOR AND COMPARATOR

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The increasing need for fast and reliable determinations in reactor activation analysis led to the use of simple methods of standardization. Thus, for instance, multiisotopic comparators have been successfully used, as they allow the simultaneous measurement of both the thermal and epithermal components of the reactor spectrum by irradiation of a single element. However, the analysis can also be influenced by the fast neutrons of the reactor. One of the examples of this situation occurring in biological materials is the determination of aluminum based on the $^{27}\text{Al}(n,\tau)^{28}\text{Al}$ reaction, which is interfered by phosphorus, through the threshold reaction: $^{31}\text{P}(n,\alpha)^{28}\text{Al}$. On the other hand, since the capture reaction on phosphorus leads to pure β^- emitter ^{32}P , the (n,α) reaction offers an interesting possibility for its assay.

Determination of aluminum and phosphorus in biological materials has been carried out by the authors through measurement of ^{28}Al , after two irradiations at the RA-6 reactor (Centro Atómico Bariloche), in the undisturbed and the epicadmium spectra. Germanium was used as comparator and integral flux monitor, through the reactions: $^{74}\text{Ge}(n,\tau)^{75}\text{Ge}$ and $^{76}\text{Ge}(n,\tau)^{77}\text{Ge}$, for the thermal and epithermal components, and $^{72}\text{Ge}(n,p)^{72}\text{Ga}$, for the fast component. The constants necessary for the calculations involved in flux measurements, i.e. k_0 factors and resonance integral to cross-section ratios for the production of ^{75}Ge and ^{77}Ge , and the fission neutron averaged cross-section of the threshold reaction, had been determined in previous works ^{1,2}.

Samples and hyperpure germanium slices were sequentially irradiated, with and without cadmium cover, for 180 s, and after a short decay (40-50 s), the ^{28}Al peak at 1779 keV was measured for 300 s. Then the germanium standards were measured for ^{75}Ge and ^{77}Ge (half-lives: 1.3797 h and 11.30 h). Following the decay of ^{75}Ge , another measurement was performed for ^{72}Ga (half-life: 14.10 h). The contributions of aluminum and phosphorus to the ^{28}Al activity were easily calculated from the two-equation system obtained for the measurements after both different irradiation conditions.

The analysis of reference materials of biological origin showed reasonable agreement between the experimental results and the certified or recommended values. The precision of the data depends primarily on the statistical dispersion of the measurements: high contents of chlorine and sodium can affect the counting of the short-lived ^{28}Al

in the undisturbed spectrum. The detection of ^{72}Ga at the same conditions is sometimes difficult, especially for reactor positions with high thermal to fast flux ratios, because of the interference of ^{72}Ge . A simple radiochemical method for separation of gallium from germanium, developed in the course of the previous works, can be applied to remove this interference. All the parameters involved in the calculations, including the nuclear constants of the germanium isotopes previously determined, are known with good precision, with the only exception of the fission averaged cross-section of the $^{235}\text{P}(n,\alpha)^{28}\text{Al}$ reaction. The influence of the uncertainty of this datum on the final results has been also evaluated.

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Use of ^{191}Pt radiotracer for the development of enrichment procedures to detect natural levels of platinum in biological and environmental materials.

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Since the introduction of automobile exhaust catalytic cleaning, platinum has become a new environmental pollutant¹. This potentially new threat for human health has initiated research to develop analytical methods for Pt-detection at very low levels (<pg/g). As the usual analytical techniques such as graphite furnace atomic absorption spectrometry (GFAAS) and inductively coupled plasma-mass spectrometry (ICP-MS) do not reach such low detection limits, a preconcentration of Pt is mandatory.

For this purpose a Pt-radiotracer is a powerful tool to develop separation and preconcentration methods. This requires, however a very high specific activity (i.e. activity to mass ratio) as to create representative conditions. Ideally the radiotracer should have a sufficiently long half-life, and emit an energetic γ -ray (>300 keV). The ^{191}Pt radionuclide ($t_{1/2} = 2.96$ d and main γ -energy at 539 keV) is best suited for this purpose. Two methods are used for the production of ^{191}Pt with high specific activity and radionuclidic purity: (1) via the $^{190}\text{Pt}(n,\gamma)^{191}\text{Pt}$ reaction by thermal neutron irradiation of a Pt-target enriched in ^{190}Pt in a high neutron fluence rate nuclear reactor and (2) via the $^{191}\text{Ir}(p,n)^{191}\text{Pt}$ reaction by proton irradiation of natural Ir in a cyclotron. In the latter case a liquid-liquid extraction with dithizone is applied to separate Pt from the Ir matrix². The production yield, the specific activity and the chemical and radionuclidic purity of both production procedures are compared.

At first the enrichment of Pt by liquid-liquid extraction was investigated. Using ^{191}Pt radiotracer, the solvent extraction behaviour of Pt(IV) from HCl medium with tributylphosphate (TBP), rubeanic acid in TBP and thenoyltrifluoroacetone (TTA) in n-butylalcohol/acetophenone has been examined. The effect of acidity, shaking time and Pt-concentration has been studied, as well as the subsequent backextraction. Optimum extraction recoveries were found when using 3 M HCl for TBP and 4 M HCl for TTA. 2 M NH_4OH yielded the best recovery (90%) for backextraction. In order to evaluate the procedure in the presence of a matrix, some biological and environmental materials were spiked with ^{191}Pt and the recovery of the radiotracer investigated along the different steps.

With a view to develop a hyphenated technique to detect cold Pt with ICP-MS, ion exchange chromatography offers the best possibilities. Trace amounts

of Pt (spiked with ^{191}Pt) were preconcentrated as bis(carboxymethyl)dithiocarbamate (CMDTC) chelates³, formed by adding solid CMDTC (1.2% (w/v)) to the sample solution, in 1.6 M H_2SO_4 , 0.3% KI and 0.03% ascorbic acid. After completion of the reaction the sample solution (7.5 ml) was pumped with a flow rate of 0.5 ml/min through a 123 μl micro-column (4 mm id, 1 cm length) packed with XAD-4 (50 -150 μm) as a hydrophobic sorbent. The column was washed with 1 ml 1 M H_2SO_4 . The adsorbed complexes were eluted in opposite direction (0.2 ml/min) with ammonia, containing CMDTC. 70-80% recovery was obtained in 300 μl eluting solution. The column was then washed and reactivated with 1 ml EtOH containing 1 M HNO_3 . Several parameters such as flow rate, size of the column, reducing agent and sample medium are under investigation.

It is the purpose to detect Pt in samples by ICP-MS measurement. In both procedures isotope dilution with non radioactive Pt is necessary. The ^{194}Pt spike added to the sample prior to digestion, will allow to correct for the variable overall yield.

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Chernobyl experience of the environmental
radiomonitoring in the forest

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About 40 tones of the spent fuel release resulted due to the Chernobyl accident.

The total activity of the fallouts is about $50 \cdot 10^6$ Ci radionuclides of iodine-131, cesium-137, strontium-90, plutonium-239, neptunium-239 at. el.

More then 23000 km² of the Russia, Ukraine, Belorussia were contaminated (density > 5 Ci/km²).

There were developed 21 observation points to study radionuclide migration in the forest ecosystem. This net-work covered different types of forest and furnished with information for the predict models testing.

The observable characteristics are total density of the radionuclides cesium and strontium per squar metre, the depth distribution, soluble or exchange form of the chemical components, contamination of the plants, trees, mushrooms.

Main results of three year monitoring are: the mobility of strontium is higher then that of cesium, 60-80% of total amount of cesium remains in the forest mat and continuously contaminates the top lie of the soil. The part of the soluble and exchange form depend on the distance and direction from the destroyed reactor. The time-dependency of the observable characteristics is discussed.

APPLICATIONS OF PIXE IN THE LIFE SCIENCES

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The big majority of papers claiming to use nuclear analytical methods in the life sciences reports trace analyses carried out by neutron activation analysis. Other techniques like charged particle activation (CPAA), prompt nuclear reaction analysis (NRA) or particle induced X-ray emission spectroscopy (PIXE) can only gradually "intrude" into the field. Among these ion beam techniques certainly PIXE is playing the leading role. One reason of this is that, during the last decade PIXE has been accepted, also by the analytical chemistry community, as a standard method [1]. Its multielemental character and the generally accepted fact, that PIXE is most suitable for analysis of trace elements of medium and high atomic number in a matrix composed of light elements, on the other hand, make PIXE to be most useful in environmental, biological and medical applications [2]. Taking into account, however, that the method requires an access to an accelerator operated by a specially experienced staff, routine bulk analysis of biomedical samples are definitely not the cases where PIXE could be the first choice to apply. The usefulness of bulk analysis in order to get information about the structural and functional role of trace metal ions, which should be the ultimate purpose of such studies, is rather uncertain. Location of these ions in a generalized sense is obviously necessary. The versatility of PIXE provides two different approaches, at least for this purposes. The application of micro-PIXE utilizing proton beamspot of the size about $1 \mu\text{m}^2$ or less promises unique perspectives to get elemental maps on the cellular level. A completely different strategy to speciate the trace metals of interest could be the combination of PIXE with appropriate biochemical separation techniques. In biochemistry or medicine, however, often only a very small amount sample material is available. That very advantageous feature of PIXE that sample volumes of $1 \mu\text{l}$ or less can be rather easily analysed with sensitivity in the ppm range offer unique possibilities for the technique. A convincing example could be the in situ PIXE analysis of the minute metalloprotein volumes concentrated in thin layer electrophoretograms [3].

The paper surveys the present status and trends of PIXE applications in the life sciences discussing the special advantages and limitations of the technique, as well.

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COMPARISON OF ABSOLUTE AND COMPARATIVE ANALYSIS IN DETERMINING THE DISTRIBUTION OF TRACE ELEMENTS IN HEART USING PIXE.

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In the trace element analysis of biological and environmental samples, two approaches may be taken. One approach involves the employment of a standard of well known composition, whilst the other relies upon an accurate data base and knowledge of the experimental configuration and parameters. These are known as comparative and absolute analysis respectively. In proton induced x-ray emission (PIXE) analysis, the comparative approach removes uncertainties in the detector efficiency, and to a large extent minimises uncertainty in both the proton ionisation cross-section and x-ray attenuation coefficients which would be present whilst performing absolute analysis. However, comparative analysis only guarantees concentration determination in samples for elements that are also found within the standard. In contrast, absolute analysis removes this reliance on standards for trace element determination and requires less experimental time.

Comparative and absolute analysis are compared whilst determining the distribution of trace elements in pigs heart using PIXE. Thirty one samples in total were extracted from at least 10 different positions in each of the three organs and freeze dried. These were homogenised, pelletised and mounted on an aluminium target plate for subsequent trace element determination by 2MeV vacuum PIXE analysis. During proton irradiation, x-ray spectra from a high resolution Si(Li) detector and Rutherford backscattering (RBS) spectra from a surface barrier detector were collected simultaneously. RBS spectra were used to determine the major element compositions of samples so that matrix self absorption effects could be calculated and thus trace element concentrations derived.

Comparative analysis was performed using standards of Bowen's kale and IAEA animal muscle (H-4), and concentrations derived with the aid of PIXAN, a PIXE analysis computer package [1]. Absolute analysis involved the use of a specifically developed program that relies upon accurate knowledge of ionisation cross-sections, x-ray attenuation coefficients and Si(Li) detector efficiency. Results from each approach are compared and differences discussed where they were found to occur. These compositions are then employed in assessing the degree of heterogeneity of this organ with respect to trace elements and deriving sampling factors. This information is essential if we are to perform successful trace element determination upon this organ.

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ANALYSIS OF MEMBRANE FILTERS AND THICK FLY ASH SAMPLES BY PIXE

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The possibility of the routine PIXE measurement of environmental samples has been tested at the INP in Řež. The new experimental arrangement [1] provides a low spectral background, well defined geometry and precise beam monitoring also in the case of nonconductive thick samples using the detection of backscattered protons on the thin nickel foil placed in the front of the sample (RBS monitor).

The PIXE setup built around the 3MV Van de Graaff accelerator was calibrated by the set of thin standards. Both the commercially available Micromatter standards [2] and own produced standards calibrated by RBS method were used. The new version of the computer program package PIXE-INP for spectra fitting and quantitative analysis was developed to simplify the analysis. The PIXE-INP code package is based on the digital filter background subtraction, nonlinear least-squares fitting with Gaussian line shape and fixed intensities for shell's multiplets, standard matrix correction for thick samples [3] and filter attenuation calculation.

All aerosol, fly ash, reference and standards samples were measured at 2.35MeV proton beam (5mm in diameter) under the same geometry and with proton current between 1-20 nA depending on the sample composition. Different filters were used to reduce appropriately intense low energy X-rays. The advantage of the aerosol samples collected on thin membrane filters (Nuclepore, Synpore) is that they do not need a special sample preparation. The exposed filters were fixed on the plexiglas frames and put into the sample holder inside a vacuum target chamber. Thick samples of fly ash and urban particulate matter required more preparation. They were in 1:1 ratio mixed with spec pure graphite and then palletized into a small pellets (12mm in diameter and 1-2mm thick). Some of thick samples were doped by yttrium to provide an internal standard.

The thin aerosol samples are very suitable for the PIXE method. It was shown that the Nuclepore filter is better than the Synpor one because the former one is thinner and less contaminated by trace elements. Among different X-ray attenuation filters which were tested, the 0.3mm mylar filter with 10% central hole seemed to be the most useful for such samples. On the other hand, the

thick fly ashes samples are a rather difficult for PIXE method namely because of complex X-ray spectra and significant matrix effect corrections. The grain size effects were observable for some samples too. Nevertheless, a good accuracy (about 10% for most of the elements) can also be achieved for such samples as was tested by analysis of pellets made of reference materials. The aluminum funny filter (0.2 mm thick, 1.5% area pin hole) appeared the most convenient for routine analyses of thick fly ash and urban aerosols samples.

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DETERMINATION OF OPTIMAL METHODOLOGICAL
VERSION OF NEUTRON ACTIVATION ANALYSIS.

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Neutron activation techniques used for solving ecological problems are needed to increase their accuracy and sensitivity. Optimal values of these characteristics are depended on methodical versions of analysis. The method to optimize methodical versions of analysis is developed in this work.

The method idea is in constructing of the grid covering of all interesting areas of analysis conditions, in simulating sample's gamma-spectra within knots of this grid, in elaborating and analyzing all possible versions of element content calculations.

The gamma-spectra simulation is based on rigorous calculations of a) the processes of activation and decay in total volume, b) the spectrum response function, c) the photo-peaks due to the birth of e^+ , e^- pairs. The resolution of gamma-spectra is determined by possibilities of using detector and GANAAS [1] software complex.

Forming the set of the methodical versions of the content analysis is based on elaborating the sensitivity matrix to determine all possible paths to include the interference contributions of any order.

The optimal methodical version corresponds minimum either analysis error or quantitative determination limit of element content calculated via the algorithm of ref. [2].

Suggested method is realized in codes for personal computer. Neutron activation techniques based on this approach are developed for some ecological objects. There were examples of the influence of the paths of calculations of interfering contributions and their values on the errors and quantitative determination limits of element's contents.

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INTERLABORATORY ANALYSIS OF IRM NSC-21 COMPOST VITAHUM

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Analyses of industrial composts represent an important task for many agricultural and hygienic laboratories including the laboratory of the University of Agriculture (UA). Since maximum admissible levels of heavy metals and other toxic elements are set for both composts and raw materials used for its production, the contents of the above elements should be periodically checked in these materials. Quality assurance of compost analysis is hampered by lack of an appropriate reference material (RM), because RMs of soils and sewage sludges do not provide good matrix and analyte level matches. Therefore, an internal RM of industrial compost denoted NSC-21 was prepared at the UA and an anonymous interlaboratory comparison was organized in which 11 Czech and 8 foreign laboratories participated on voluntary basis.

Approximately 3 kg of the industrial compost "Vitahum" were freeze-dried, ground, manually homogenized in a plastic bag, and sterilized by gamma-rays of ⁶⁰Co by a dose of 25 kGy. Homogeneity of the material was tested by determination of 17 elements by instrumental neutron activation analysis (INAA). The relative standard deviation (RSD) due to inhomogeneity amounted to 3-8 % for sample weights of 100 mg, the highest values (RSD 7-8 %) being observed for the elements Ce, Co, Cr, La, Sm, and Th which apparently originate from the mineral fraction of the compost. The participating laboratories were sent 25 g aliquots of the material and were asked to determine the elements of interest employing those analytical techniques in which they feel experienced for routine analysis of this kind.

Totally, 125 laboratory means (n) were obtained, most in the case of cadmium (22). In some laboratories, more than one method of either decomposition or measurement were applied. For other elements, the following numbers of laboratory means were received: Pb 17, Cr 15, Cu 15, Zn 11, As 11, Hg 10, Ni 9, Co 7, Mn 7, Fe 4. For many other elements (Al, Ba, Br, Ca, Ce, Cl, Cs, Eu, K, La, Mg, Mo, Na, P, Rb, Sb, Sc, Sm, Sr, Th, Ti, V, W) n 3 was obtained and no attempt was made to evaluate the content of these elements.

Nondestructive analysis (INAA) was employed only in one laboratory, all remaining laboratories used analytical techniques which involved sample decomposition. 35 laboratory means were obtained after preceding dry ashing, using both classical (in open system, on air and under atmospheric pressure) and modern versions (increased pressure of oxygen). In this number, the majority of Czech and Slovak laboratories is involved in which dry ashing in a stream of oxygen was carried out "in situ" and Hg trapped on gold amalgamator in the single-purpose atomic absorption spectrometer TMA-254 for Hg determination. Wet ashing under atmospheric pressure and pressurized wet ashing in various mixtures of acids (including microwave decomposition) was applied for obtaining 29 and 33 laboratory means, respectively. Not all laboratories used HF in their procedures for destruction of silicate fraction of the material. Ten laboratory means resulted from combination of some of the above mentioned decomposition methods, one laboratory mean was obtained after alkaline fusion with Li₂B₄O₇ and one after extraction by 2 mol.l⁻¹ HNO₃.

From measuring techniques, AAS in various modes (i.e. flame, flameless, cold vapor or hydride generation techniques) was most frequent (59 laboratory means), electrochemical methods provided 14 laboratory means, 17 laboratory means were obtained by neutron activation analysis (both instrumental and radiochemical mode), 22 by ICP-AES, 10 by ICP-MS and one by spectrophotometry.

In some laboratories, the accuracy of results was checked by concurrent analyses of certified RMs of various types (soil, sewage sludge, plant material, bovine liver).

Evaluation of the elements determined can be summarized as follows:

Group 1: Approximately normal, rather narrow distribution of results with good agreement of means obtained by various decomposition and measurement techniques - consensus value can be derived with the relative width of 95 % confidence interval (CI) < 15 % (Cd, Cu, Ni, Pb, Zn).

Group 2: Higher variability of results due to problems of sample decomposition and measurement techniques, unrecognized interferences, and/or small number of laboratory means - information value can be derived with the relative width of 95 % CI in the range of 20-30 % (As, Co, Fe, Hg, Mn).

Group 3: Typical bimodal distribution of results (Cr) due to significantly higher results obtained using HF on wet ashing, alkaline fusion, or instrumental analysis (INAA) as compared to procedures employing other decompositions mentioned above.

Table 1: Consensus and information values of element contents in IRM NSC-21 ($\mu\text{g}\cdot\text{g}^{-1}$)

Element	cons. value	95 % conf. int.
Cd	0.450	0.070
Cu	27.0	3.4
Ni	11.8	1.5
Pb	14.7	1.2
Zn	122	5

Element	inf. value	95 % conf. int.
As	3.77	1.11
Co	5.19	1.24
Fe (%)	0.96	0.28
Hg	0.078	0.016
Mn	442	108

Based on the results of this interlaboratory comparison, it can be concluded that analysis of industrial compost represents a difficult task even for laboratories that are supposed to analyze this type of material routinely. It follows from comparison of INAA results with proven accuracy, as well as from results obtained by other analytical techniques after sufficiently aggressive decomposition procedures (as concerns temperature of both dry and wet ashing and presence of HF in wet decomposition mixtures), that choice of appropriate decomposition method appears to be a crucial factor for obtaining accurate results for the majority of elements in industrial compost samples.

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IRMM REFERENCE MATERIALS FOR k_0 ACTIVATION ANALYSIS*

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The IRMM dosimetry reference materials programme was established to provide monitor materials for reactor surveillance and for dosimetry in materials testing applications, but includes materials specially prepared for k_0 -standardization of neutron activation analysis.

The element gold is well established as a comparator for k_0 -standardization, but because of its high cross-section for thermal, and especially for epithermal neutrons, significant self-shielding can occur. This can be overcome by dilution in a convenient matrix provided accurate concentrations and good homogeneity can be achieved. To this end, an alloy of composition Al-0.100%Au was prepared by levitation melting in 20g quantities. This crucible-less technique allows close control of alloy composition, and intense electro-magnetic stirring combined with a high solidification rate ensures good homogeneity on sample sizes appropriate for neutron irradiation. The foil and wire produced was subjected to homogeneity control by two independent laboratories using neutron activation, and the gold concentration was confirmed by induction-coupled plasma emission spectrometry. A certified gold mass fraction of 0.100 ± 0.002 wt% (2s) was established, which is valid for sample sizes > 10 mg. The reference material was allocated the number IRMM-530.

A more sophisticated approach is made with the development of the alloy Zr-0.01%Au-0.15%Lu. In this case the reactions $^{197}\text{Au}(n,\gamma)^{198}\text{Au}$, $^{176}\text{Lu}(n,\gamma)^{177}\text{Lu}$, $^{94}\text{Zr}(n,\gamma)^{95}\text{Zr}$, $^{96}\text{Zr}(n,\gamma)^{97}\text{Zr}$ and $^{90}\text{Zr}(n,2n)^{89}\text{Zr}$ enable the determination of all relevant neutron spectrum parameters: the Maxwellian neutron temperature, the epithermal fluence rate distribution factor α , and the thermal, epithermal and fast neutron fluence rates. Alloy preparation was carried out by cold-crucible levitation melting, with cold-rolling and recrystallization heat treatment to improve homogeneity. Foil samples were prepared and analyzed by activation analysis.

Other reactor neutron dosimetry reference materials available include high purity metals certified for interfering trace impurities, Al-Co alloys, and UO_2 and NpO_2 fission monitors in the form of high density microspheres. Fluence rate monitors are encapsulated in aluminium, stainless steel, quartz or vanadium.

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TRUE-COINCIDENCE CORRECTION WHEN USING AN LEPD FOR THE DETERMINATION OF THE LANTHANIDES IN THE ENVIRONMENT VIA k_0 -BASED INAA

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As part of a recent study of the environmental effects caused by the operation of a coal-fired power station at Sines, Portugal, k_0 -based instrumental neutron activation analysis (INAA) was used for the determination of the lanthanides in plant leaves and lichens¹. In view of the accuracy and the sensitivity of the determinations it was advantageous to make use of a low-energy photon detector (LEPD). This required the introduction of special procedures for efficiency calibration of the LEPD² and for correction for true-coincidence (cascade summing) effects^{3,4}. As to the latter, algorithms were developed taking into account γ - γ , γ -KX and γ -LX coincidences (with KX and LX originating from internal conversion or orbital electron capture), and computer codes were designed to define the relevant summing cascades of a measured gamma-ray in a decay scheme and to calculate coincidence correction factors (COI) for different counting geometries. In the present paper, a survey is given of these developments, and computed COI-factors are tabulated for the relevant low-energetic gamma-rays of the analytically interesting lanthanide radionuclides. Also the 140.5 keV line of ⁹⁹Mo/^{99m}Tc is included, molybdenum being the comparator chosen when counting with an LEPD.

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DETERMINATION OF THE TOTAL EFFICIENCY FOR POINT SOURCES IN VOLUME-SAMPLE GEOMETRIES IN GAMMA-RAY SPECTROMETRY

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Determination of the activity of volume samples in the presence of coincidence summing effects requires the knowledge of the total efficiencies of the gamma spectrometer as well as the peak efficiencies. The total efficiency is defined as the probability that the gamma ray is registered anywhere in the spectrum. In addition to scattering processes within the detector also scattering on the sample and detector shield contribute to the continuous part of the spectrum at energies smaller than the energy of the emitted gamma ray. It is the purpose of this contribution to show how the total efficiencies of point sources embedded in an absorbing medium may be assessed. These efficiencies enter the expressions which determine the count rates in the full energy peaks in the presence of coincidence summing effects.

It is supposed that the total efficiency of a point source emitting gamma rays with the energy E which is placed at the point \vec{r} in the interior of a shield within the volume occupied by the sample with attenuation coefficient μ may be written as a sum of three independent contributions

$$\varepsilon_T(E, \vec{r}) = \varepsilon_{TO}(\mu, E, \vec{r}) + \varepsilon_{SH}(E, \vec{r}) + \varepsilon_{SA}(E, \vec{r})$$

$\varepsilon_{TO}(\mu, E, \vec{r})$ denotes the total efficiency for gamma rays emitted by a point source embedded in a medium with attenuation coefficient μ and registered by the detector. It is approximated by

$$\varepsilon_T(\mu, E, \vec{r}) = \varepsilon_{TO}(E, \vec{r}) \frac{\varepsilon_P(\mu, E, \vec{r})}{\varepsilon_{PO}(E, \vec{r})}$$

where $\varepsilon_P(\mu, E, \vec{r})$ represents the peak efficiency of the point source, $\varepsilon_{PO}(E, \vec{r})$ the peak efficiency of the point source in the absence of the sample and $\varepsilon_{TO}(E, \vec{r})$ the total efficiency in the absence of the sample. This is not the intrinsic efficiency as introduced by Moens et al [1] since it refers to the whole detector and not just to the crystal. It is measured simultaneously with the peak efficiency $\varepsilon_{PO}(E, \vec{r})$ by the detector calibration procedure described in [2]. The peak efficiency in the presence of sample $\varepsilon_P(\mu, E, \vec{r})$ is calculated by use of a suitable detector model [2].

$\varepsilon_{SH}(E, \vec{r})$ is the probability for detection of gamma rays scattered on the shield. It is determined by measuring the total efficiency when the detector is in the shield. From that efficiency the total efficiency measured outside the shield is subtracted. That difference is attributed to the rays scattered on the shield. It depends on the inner dimensions of the shield and on the materials of the inner layers. Examples for an iron and two lead shields are presented. It is shown that at the achieved accuracy ε_{SH} may be considered to be independent on the position \vec{r} of the point source within the shield.

$\varepsilon_{SA}(E, \vec{r})$ represents the probability for the detection of gamma rays scattered on the sample. It is assessed by using a model in which the process of scattering and detection is decomposed in two independent steps. The probability for each step is calculated independently of the other. In that way the integration over the degrees of freedom of the scattering process is avoided. The probability is calculated as

$$\epsilon_{SA}(E, \vec{r}) = P_{SC}(E, H, R) \cdot P_{DET}(E_{SC}, r_{eff}, h_{eff}) \cdot \Phi_{OV}(\vec{r}, r_{eff}, h_{eff})$$

$P_{SC}(E, R, H)$ represents the probability that the gamma ray is scattered in the sample. It depends on the energy of the gamma ray, the radius of the sample R and on the thickness of the sample H . It is assumed to be independent on the point of emission of the gamma ray. It is approximated by the expression

$$P_{SC}(E, R, H) = \frac{\mu_{sc}(E)}{\mu_{tot}(E)} (1 - e^{-\mu_{sc}(E) \frac{RH}{R+H}})$$

where $\mu_{sc}(E)$ and $\mu_{tot}(E)$ denote the scattering and total attenuation coefficients in the sample material at the energy E .

$P_{DET}(E_{SC}, r_{eff}, h_{eff})$ represents the probability for the detection of the scattered gamma rays. It is calculated as

$$P_{DET}(E_{sc}, r_{eff}, h_{eff}) = \epsilon_{T0}(E_{sc}, r_{eff}, h_{eff})$$

the total efficiency of a point source placed at average distance h_{eff} from the detector at the average radius r_{eff} from its symmetry axis. The distances r_{eff} and h_{eff} are calculated as efficiency weighted averages of the distance and radius over the volume of the sample. The scattering energy E_{SC} is determined by the energy of the gamma ray E and the scattering angle. It is assumed that the scattered photon interacts with the detector in its geometry axis at the average penetration depth in the crystal for photons with energy E .

$\Phi_{OV}(\vec{r}, r_{eff}, h_{eff})$ represents a function which takes into account the fact that gamma rays emitted far from the detector have smaller chances to scatter in the area of considerable efficiency which is defined by r_{eff} and h_{eff} relative to gamma rays emitted within that area. It is calculated as

$$\Phi_{OV}(\vec{r}, r_{eff}, h_{eff}) = e^{-\mu_{tot}(E) \sqrt{(r_{eff}-r)^2 + (h_{eff}-h)^2}} \text{Min} \left(1, \frac{(2r_{eff})^2 + h_{eff}^2}{r^2 + h^2} \right)$$

The model was tested by measuring total efficiencies of point sources immersed in water. The contribution due to the detector $\epsilon_{T0}(\mu, E, \vec{r})$ was subtracted from the measured value and the difference compared with the calculated value $\epsilon_{SA}(E, \vec{r})$. Reasonable agreement between measured and calculated values was found.

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A PRELIMINARY STUDY OF ELEMENTAL BIOACCUMULATION ON PSEUDEVERNIA FURFURACEA THALLI EXPOSED IN URBAN AND RURAL SITES.

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Lichens have been regarded as suitable tools for monitoring the relative levels of atmospheric pollution, because their mineral nutrition is dependent on wet and dry deposition from the atmosphere.

In this study lichens were employed to examine and compare bioaccumulation of several elements (S, Ca, Cl, Fe and Pb) on a rural site (Isola Serafini, near Piacenza) and on an urban site (Redecesio, near Milan).

The experiment was carried out on *Pseudevernia Furfuracea* thalli exposed in special little traps inside Open Top Chambers (OTCs), from April to December 1991. All the OTCs were equipped with an air pollution monitoring system and a meteorological station, some of these were also fitted with air filters.

The values of S, Ca, Cl, Fe and Pb concentrations were measured by X-ray fluorescence analysis in secondary target excitation mode.

Every two months, lichens were collected and divided in two parts, one of which was washed in deionized H₂O; both parts were dried at 50°C for 24 hours and stored in closed bags in the dark.

Two grams of each specimen were ground and pressed into pellets with a diameter of 32mm. The system was calibrated using NBS standard reference materials.

Only an appreciable accumulation of Sulphur and Lead during the eight months of exposure was verified. On both sides the Sulphur behaviour is probably related to SO₂ increase in the air during the winter. The Pb content showed a wider increase in Milan than in Isola Serafini, presumably due to the heavy urban traffic.

At the end of the exposure period both elements showed higher concentrations on the urban than on the rural site.

The thalli washing procedure influenced the S amount but had no effect on Pb values. These results suggest that S is probably accumulated on the cortex surface, while Pb is stored beneath the cortex at the level of medulla.

HEAVY METALS IN *PARMELIA SULCATA* AND *INULA VISCOSA* COLLECTED IN THE NEIGHBOURHOOD OF A COAL-FIRED POWER STATION

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The toxic emission from coal-fired station have become the subject of growing concern since they may have health risks. The pollutants can be inserted into the air, the surface water, the soil and the groundwater.

Lichens are frequently used for monitoring purposes.^{1,2} Lichens receive their mineral nutrients as particulates and in solution by the interception of atmospheric and aquatic deposition, without the complication of absorptive function by the root systems of higher plants. These organisms also have the ability to accumulate metals to levels far greater than their physiological needs, understandable by their ion-exchange properties and by the fact that surface, structure and roughness facilitate interception and retention of particles. In addition, the absence of a well developed cuticle or similar wax minimizes any physical resistance to the diffusion of soluble minerals into the plants.²

Other plants are known to be metal accumulators.³ In this work, the species *Inula viscosa* was also studied as a biomonitor, because their leaves have a viscous layer which may difficult the fallout of the air particulates. Therefore, the foliar uptake may easily occur on the *I. viscosa* leaves.

The epiphytic lichen *Parmelia sulcata* and *Inula viscosa* leaves were collected in the neighbourhood of a Portuguese coal-fired power station (Sines coal power station), as monitors for heavy-metal air pollution. A study of the metal contents variability along 1991 and 1992 was performed. k_0 -Based instrumental neutron activation analysis (INAA) was applied.⁴ The heavy metals Cr, Fe, Co, Zn, As, Se, Ag and Hg, among others, were determined. Other elements which may be of interest were also obtained.

The deposition of particulates on *Parmelia sulcata* and *Inula viscosa* originated or in the fly ashes emitted into the air by the chimneys or in the coal and ashes deposits, was demonstrated by observing with the scanning microscope ash particulates on the *P. sulcata* samples and *Inula viscosa* leaves. The elemental concentration found in the *P. sulcata* along the months shows an accumulating process of elements in this lichen. The metal contents in *Inula viscosa* leaves is clearly enriched due to the laboration of the coal-fired power station. It is concluded that both *P. sulcata* and *I. viscosa* leaves are good air pollution biomonitors.

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Rb and Cs in spruce needles: levels, biodynamics and transfer factors.

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Rb and Cs have been determined in about 200 needle samples of Norway spruce (*Picea abies*). The range found was extremely high for Cs (3 - 28000 ng/g) and somewhat less for Rb (1 - 200 µg/g).

Instrumental neutron activation analysis of the ashed needles was used to determine these elements by the nuclear reactions $^{85}\text{Rb}(n,\gamma)^{86}\text{Rb}$ and $^{133}\text{Cs}(n,\gamma)^{134}\text{Cs}$ as follows :

Ashing : in order to reduce the sample volume, dry needles were ashed before irradiation at 500 °C for 10 h. No losses of Rb were induced by ashing, whereas losses of Cs were < 3 %.

Sample mass : 200 mg ash, corresponding to 3 g of dry needles.

Irradiation : 2.5 h at a thermal neutron flux of $2.2 \cdot 10^{13}$ n/s cm² ($= 2 \cdot 10^{17}$ nvt).

Counting : 7 h after a decay time of 10 to 30 days.

γ-Spectroscopy : 1077 keV for ^{86}Rb ($\tau = 18.6$ d) and 796 keV for ^{134}Cs ($\tau = 2.06$ y).

Sensitivity : all Rb values had a counting error < 2%. Very small Cs concentrations were at the determination limit (counting error 15% at 10 ng/g).

Great care was used to remove any surface contamination of the needles by soil and aerosol particles before the analysis. This was done by an appropriate washing procedure in order to measure the endogenous needle concentrations only. This step is very important for needle samples with low Cs concentrations, as the surface contamination is of the order of 10 ng Cs / g dry needles.

Each sample analysed consisted of an individual age class (normally from age class 1 to 5) from an individual tree. Eight different stations were sampled, taking from 5 to 9 trees at each station. The results were used to clarify the following points :

1. Concentration changes due to the needle age:

Rb and Cs both decrease with increasing needle age by about a factor of 3. The experimental data can well be described by the function $C_t = A + B \cdot e^{-\lambda(t-1)}$, where C_t is the concentration in needle age class t and A , B and λ are constants.

The elemental mass in the needle can therefore be represented by two components. The first one does not change with time, whereas the second one decreases each year by a constant factor. This decrease is caused by retranslocation of Rb and Cs from older to younger needles. The same form of biodynamic curves, although with other constants, was also found for other mobile elements (K, Mg, Cu, P, Cl).

2. Concentration changes due to soil characteristics :

The variation of the concentration among individual trees on a given station is very large (CV = 43% for Cs and 22% for Rb). Both elements are log normally distributed. A very large range is also found among the 8 station means (Cs 29 - 19000 ng/g, Rb 9 - 134 µg/g). Cs shows by far the largest variation of all 25 investigated elements. It is certain that these variations are due to the soil characteristics at the sites of the individual trees and of the various stations.

3. Correlation between Rb and Cs :

There is an extremely high correlation between log(Cs) and log(Rb). However this correlation is not linear, what means that the ratio Rb/Cs depends on the concentration. The ratio Rb/Cs varies from 8 at high concentrations to 300 at low concentrations. This effect can also be explained by soil properties.

4. The variation of the ratio Rb/Cs with the needle age class :

There is only a small change of about 20% in this value when going from age class 1 to age class 5. This clearly shows the close similarity of both elements as far as translocation, retranslocation and storage in the plant are concerned. In contrast, the ratio K/Rb in the same samples show much larger changes with time (by about a factor of 2), pointing to the fact that ⁸⁶Rb cannot be used as a tracer for K, as is sometimes assumed.

Determination by INAA of essential and toxic elements in SOIL
(S-SP, S-VM and S-MS, reference materials)

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This paper represent our contribution in the intercomparison run organized by the Institute of Radioecology and Applied Techniques of Košice-Slovakia on the new set of three soil reference materials.

In accord to the international classification of FAO the soil samples in question, belong to the Rendzina (S-SP), Futric Cambisols (S-VM) and Orthic Luvisols (S-MS) types.

The samples were collected in the neighbourhood of Rožňava, Košice and Prešov respectively, from 0 to 5^{cm} depth.

In total 33 laboratories of 14 countries using various analytical methods have participated in this intercomparison exercise.

We have reported the concentration values determined by instrumental neutron activation method at VVR-S reactor in Bucharest using a high resolution HPGe detector.

A number of 34 elements has been analyzed in our laboratory: Al, As, Ba, Br, Ca, Ce, Co, Cr, Cs, Dy, Eu, Fe, Gd, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tl, Th, Ti, U, V, Yb, Zn, Zr. Underlined elements have been identified in our laboratory only.

The certified values of 17, 15, 14 elements for S-SP, S-VM and S-MS samples respectively are given. In the Tables 1, 2, 3 our values

TABLE 1. - Certified values of elemental concentration in soil RENDZINA (S-SP)

Element	Concentration	Confidence limits	Accepted values limits	Our values (\pm st.dev.)
As (ppm)	14.00	12.60-15.30	10.42-16.33	13.47 \pm 1.81
Ba (ppm)	315	294 - 337	280 - 358	311.0 \pm 5.3
Ca (%)	6.34	6.09-6.59	5.78-6.70	6.52 \pm 0.13
Co (ppm)	15.6	14.4 -16.8	11.2 -19.8	15.3 \pm 0.2
Cr (ppm)	75.3	72.1 -78.4	60.3 -87.8	75.4 \pm 1.8
Fe (%)	3.73	3.55-3.92	2.82-4.49	3.79 \pm 0.12
K (%)	2.63	2.41-2.86	1.91-3.12	1.98 \pm 0.06
Mn (ppm)	734	700 - 768	594 - 866	669 \pm 20
Sb (ppm)	2.11	2.03-2.19	2.00-2.20	2.04 \pm 0.08
Sr (ppm)	274	264 - 283	232.3-292.0	232.3 \pm 1.5
V (ppm)	89.7	81.1-98.4	75.0-113.0	81.1 \pm 8.2
Zn (ppm)	119	112 - 125	92.2-153.5	150.3 \pm 2.9

for 12, 10, 9 elements analyzed in the corresponding samples are compared with the certified values. Our value for each element, as an arithmetic mean of three individual determinations, as well as the standard deviation of the mean is given in the last column of the tables.

TABLE 2. - Certified values of elemental concentration in soil ENTIC CAMBISOL (S-VM)

Element	Concentration	Confidence limits	Accepted values limits	Our values (\pm st.dev.)
As (ppm)	13.6	11.3 - 15.9	8.82-18.2	18.2 \pm 1.1
Ba (ppm)	582	548 - 616	524-657	593.7 \pm 19.9
Co (ppm)	15.4	14.1 - 16.6	11.6-19.0	17.4 \pm 1.2
Cr (ppm)	79.8	74.0 - 85.5	50.8-93.0	85.2 \pm 0.2
Fe (%)	3.73	3.56 - 3.89	3.16-4.30	3.98 \pm 0.06
K (%)	3.08	2.89 - 3.27	2.32-3.42	2.63 \pm 0.08
Mn (ppm)	897	853 - 942	716-1015	808 \pm 19
Sb (ppm)	4.58	4.35 - 4.81	4.35-5.00	4.46 \pm 0.14
V (ppm)	98.3	88.6 -108.1	83.3-122.0	88.7 \pm 6.5
Zn (ppm)	88.8	85.6 - 92.1	70.1-112.3	107.0 \pm 1.0

TABLE 3. - Certified values of elemental concentration in soil ORTHIC LUVISOLS (S-MS)

Element	Concentration	Confidence limits	Accepted values limits	Our values (\pm st.dev.)
As (ppm)	9.36	8.87 - 9.85	8.33-10.30	9.50 \pm 1.61
Co (ppm)	11.9	10.6 - 13.2	9.1 -18.7	12.5 \pm 0.2
Cr (ppm)	87.4	77.0 - 97.7	52.7-126.1	120.9 \pm 3.0
Fe (%)	2.70	2.59 - 2.81	2.16-3.19	2.81 \pm 0.04
K (%)	1.85	1.74 - 1.95	1.51-2.23	1.51 \pm 0.10
Mn (ppm)	910	876 - 945	822 -1096	833 \pm 19
Sb (ppm)	1.92	1.85 - 2.00	1.82-2.00	1.82 \pm 0.04
Sr (ppm)	107	91 - 123	70 - 152	110 \pm 37
Zn (ppm)	63.7	59.5 - 67.8	48.0-82.7	68.1 \pm 0.8

None of our reported results have been rejected. The values are situated inside of the accepted values limits and have been taken into account in overall mean calculation.

For the other elements analyzed non recommended values could be given.

**MINOR AND TRACE ELEMENTS IN MILK DETERMINED BY
NEUTRON ACTIVATION ANALYSIS**

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Milk is surely one of the most complete and essential food as a source of mineral nutrients for all alive beings. Many trace elements play an important role in growth and development and their deficiency can be responsible for many illnesses and syndromes.

This paper is a study of the elemental contents in several commercial milk powder samples of different proveniences (China, Czechoslovakia, Holland) in comparison to the commercial romanian milk powder as well as to the fresh cow milk collected in three industrial sites in our country. This study was aiming to put into evidence the quality of romanian milk concerning the essential element contents as well as of those of the toxic and pollutant trace elements.

The samples and standards (IAEA-153-milk powder and IAEA-155-whey powder) have been irradiated in a 2.10^{12} n.cm⁻².s⁻¹ flux of VVR-S reactor (short and long irradiation). The measurements have been carried out using a HPGe detector with high resolution.

The concentration of Al, As, Au, Br, Ca, Cl, Co, Cr, Cs, Fe, Hg, K, Mg, Mn, Na, Rb, Se, Zn have been determined and their comparative values are discussed.

DETERMINATION OF CERTAIN TRACE ELEMENTS IN CAMEL'S MILK BY NEUTRON ACTIVATION ANALYSIS.

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Natural milk samples were analyzed by instrumental neutron activation analysis for (Cs, Eu, Zn, Co, Se, Ir, Sb, Ta, Mn, and Fe). These samples were collected from different regions of Libya by co-operation with camel's research center in Tripoli. In our laboratories trace elements in human and milk powder samples have been, also determined using the (INAA) technique. The concentration level of the elements of interest within 10 % in agreement with values obtained for human and powder milk. The results of this investigation will be presented.

DETERMINATION OF LEAD IN DIFFERENT PLANTS AT TRIPOLI CITY BY PIXE ANALYSIS METHOD.

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Knowledge of heavy metals in air pollution is of considerable importance. This is true as the health of human populations may be seriously affected by the long-term exposure to low levels of toxic metals.

In recent years the utilization of neutron activation analysis (NAA) enable the concentration of trace elements in various matrices such as, plants, soil, geological, biomedical,...etc, samples to be determined. Unfortunately NAA can not be conveniently applied for the determination of some elements which are of great environmental importance such as, lead due to the necessity to have available special irradiation facilities for short-lived radionuclides.

Since the pioneering experiment on PIXE by Johansson et al. in 1970. Particle Induced X-ray Emission (PIXE) has came to existence as a mature technique for elemental analysis and was applied to a variety of research fields including environmental sciences.

Some plants, such as Cynolon (Dactylon), can serve as good indicator of air pollution caused by motor cars. Samples have been collected from different places along Tripoli's motor ways during 1989 - 1990 and were investigated for heavy elements with special emphasis on lead.

PIXE has been utilized for determination of lead in different tree leaves and plant species along the motor ways around Tripoli. Content of lead in Cynolon, which used as animal fodder as well as a ground ornament, was found 10-200 times more than the normal level (background). Results of the investigation of the various collected samples are also included.

STUDY OF TRACE ELEMENTS IMBALANCES IN AFFECTIVE DEPRESSION BY PIXE

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ABSTRACT

Trace elements imbalances have been reported in a number of neurological diseases including Alzheimer's disease¹, amyotrophic lateral sclerosis², and Wilson disease³. In the present work, trace elements levels in the blood of 23 patients suffering from affective depression (both in the manic and depressive phases) were compared with 40 normal subjects used as controls. Blood samples were collected and separated into erythrocytes and plasma components and lyophilized. Elemental analysis was carried out using the Proton-Induced X-ray Emission technique, involving a 2Mev Van de Graaf accelerator. Our results show a significant depression of Cu in both the erythrocytes and plasma of the mental patients relative to the controls. Zn was also depressed in the red blood cells, but was elevated in the plasma. In the erythrocytes, Fe, Ca and P were significantly depressed but S was elevated. K and Zn levels in the plasma also were significantly elevated. The possible biological implications of these findings, including a comparison of elemental ratios will be discussed in the full paper.

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Baseline Levels of Elemental Concentrations in Whole Blood Erythrocytes and Plasma of Nigerian Subjects

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Abstract

The necessity for the establishment of baseline levels for elemental concentrations in various tissues of man is well recognised. There is considerable interest in trace element concentrations in human tissues for a variety of reasons, including their perceived roles in health and disease, nutrition and environmental pollution. Before these could be meaningfully assessed, reliable baselines must first be established for 'normal' subjects. Several works have been published on the baseline elemental concentrations in blood or blood components from different regions of the world⁽¹⁻⁴⁾. However, for different populations, differences in local factors such as geochemical variability of the environment, dietary habits, culture and social habits would be reflected in elemental concentrations in blood.

In this pioneering effort on Nigerians, the arithmetic means, ranges and standard deviations for the concentrations of 25 elements detected in freeze dried whole blood, erythrocytes and plasma of 120 subjects drawn from different geographical regions of Nigeria are reported.

Elemental analyses have been carried out largely using INAA with both PIXE and graphite furnace AAS serving as complementary techniques. Our values compared with similar data published on Bangladeshi¹, European² and world wide averages³, show a general good agreement and some trends.

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A Comparative Study of Elemental Composition of Human Breast Milk and Infant Milk Substitutes

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Abstract

There has been a growing interest among international and governmental organisations such as WHO and UNICEF to encourage breast feeding of infants all over the world. It is estimated that more than 1.5 million babies die annually due to malnutrition. This nutritional deficiency is not just in the protein content but also in the essential trace and minor elements of importance to infant growth. It has been demonstrated through extensive animal experiments that there is a need for an adequate supply of essential trace elements such as Cu, Fe, Mn and Zn for growth and development of infants. Deficiencies of these elements have been known to result in poor growth, abnormal overall development, skin disorders, bone fractures and increased neonatal morbidity.

Human breast milk and its substitutes are usually the only source of food for infants during their early stages of life. It is therefore, essential that the breast milk and substitutes contain all necessary nutrients in adequate amounts. However, while deficiencies of trace elements are generally believed to be rare in breast fed infants, those infants that are fed on milk substitutes or infant formulas may experience deficiencies in essential trace elements.

In Nigeria, the economic situation in the country has resulted in parents feeding their babies with locally produced cereals particularly in the rural areas and these cereals are believed to be adequate in essential nutrients. The objective of this study was therefore, to investigate whether these locally produced cereals and the commercial infant milk products contain adequate levels of essential trace elements when compared with human breast milk.

Instrumental neutron activation analysis (INAA) and proton induced x-ray emission (PIXE) analysis were therefore used to determine the concentration of 15 minor and trace elements in 22 healthy and lactating subjects of Nigerian origin as well as from a number of commercial infant milk products and locally produced cereals.

DETERMINATION OF PLATINUM BY NEUTRON ACTIVATION ANALYSIS IN NERVE TISSUE FROM RATS TREATED WITH CISPLATIN

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Since the discovery of their anti-neoplastic properties, platinum co-ordination compounds like cisplatin and carboplatin have been increasingly used as chemotherapeutic agents. Cisplatin as the parent compound in this group is widely used for treating testicular and ovarian cancers and, to a lesser extent, head and neck tumours.

Unfortunately, the cytostatic efficiency of cisplatin is accompanied by undesirable side effects like nephrotoxicity and neurotoxicity. Recently, the medical research in the field of clinical oncology has been concentrated especially on neurotoxicity, which includes peripheral neuropathy and a number of more central neurotoxic phenomena. To understand neurotoxic effects we must know the distribution of platinum among different kinds of neural tissues.

Therefore, the purpose of this investigation is to identify the major sites of platinum accumulation in neural tissues following treatment with cisplatin. This special problem can be solved only by the use of a sensitive analytical method.

Because of its outstanding sensitivity and selectivity, radiochemical neutron activation analysis was used for the determination of traces of platinum in different neural tissues of Wistar rats.

The analytical method used for this purpose permits the determination of Au and Pt in biological materials and is based on neutron activation analysis with radiochemical separation of gold. The ^{199}Au daughter of ^{199}Pt is a favourable indicator for the determination of platinum in biological materials, where radiochemical separation is needed,



Adequate sensitivity for the determination of platinum requires a long irradiation time, as well as a high neutron flux density. However, the radiation decomposition of biological materials limits the duration of the irradiation. On the other side, the limit of detection for platinum is determined by the formation of ^{198}Au , from which the ^{199}Au indicator of Pt cannot be separated. Therefore, an irradiation time of 6 hours at approximately $4 \times 10^{17} \text{ n/m}^2\text{s}$ in the carbondioxide-cooled, rotating facility of the Danish DR 3 reactor was chosen as a compromise. These conditions give a modest radiation decomposition and an a priori detection limit for platinum of $\text{LD} < 0.01 \mu\text{g}$ for quantities of gold up to $< 0.17 \mu\text{g Au}$ [1]. After irradiation, complete decomposition of the irradiated materials is achieved by digestion with a mixture of hydrochloric, nitric and perchloric acids under strict temperature control in a modified Bethge digestion apparatus [2]. Before starting the digestion procedure an inactive Au-carrier solution with approximately 5 mg of Au is added to the sample.

The separation of gold from other radioactive species in the irradiated sample is achieved by electrolysis of a 1 M hydrochloric acid solution. The electrolytic deposition of gold on a niobium cathode over a period of 5 hours ascertains highest radiochemical purity with a complete elimination of the 159 keV γ -ray interference from ^{47}Sc , at a potential of 800 mV between a graphite anode and the niobium cathode. By the addition of carrier-free ^{47}Sc to non-irradiated BCR Reference Material No. 185 Bovine Liver, a decontamination factor of 1.58×10^7 was found at a chemical yield of 74 %, which corresponds to a separation factor of 0.85×10^{-7} . Therefore, interference from calcium could be disregarded [2].

The only significant interference comes from the second-order reaction of the naturally occurring gold in the sample matrix (double neutron capture):



Correction for this interference is based on the counting of a gold comparator for 24 hours, so that precision of the Pt determination for the tissue sample is not significantly affected. Increased sensitivity obtained by longer irradiation in higher neutron flux leads to greater Au correction.

The rat tissue samples used for this investigation included dorsal root ganglia and segments of medulla spinalis. In addition, samples of the kidney and a few blood samples were analysed using the same technique. Cisplatin was administered at 2 different dose levels 14 and 24 mg of cisplatin/kg rat. Altogether 2 tissue samples at the 14 mg level, 11 tissue samples and 2 blood samples at the 24 mg level were analysed for their content of gold and platinum.

The samples of the kidney and the blood showed the highest level of platinum, followed by the dorsal root ganglia, the posterior part of medulla spinalis and finally the anterior part of medulla spinalis (range: 0.06 - 8.90 ppm).

Chemical yields averaged 84 % and were determined individually by re-irradiating the separated sample together with a reference containing the same amount of gold as was added to the sample.

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Analyses of Elemental Absorption and Excretion on Mice Bearing Ascites Tumor

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ABSTRACT

The kidney and small intestine are related to the pathway of excretion and absorption of substance in body; while urine and feces are excrements as waste from body. According to their physiological function, they should play a role for elemental redistribution as suffering disease. In this work, the mice were induced by ascitic tumor with sarcoma-180. Samples (kidney, intestine, feces and urine) were sampled from the mice for different time during tumor growing period to investigate the kinetics of elemental distribution in body. The data of ingestion, drinking and body weight at the time of sampling were recorded. The contents of element in samples were analyzed by instrumental neutron activation analysis (INAA). Samples were irradiated by reactor neutrons and subsequently subject to direct analysis using high-resolution HPGe gamma spectrometer. There were fourteen minor and trace elements determined in these samples. The result shows that the elements of Na, Cl, Al, Cu, Br, and Se increase while Mn decreases in kidney with the growth of ascites tumor. There were, however, Na and K appeared to be in significant difference in small intestine at second and third stage of tumor growth, respectively. As regard to the possible correlation of the result of elemental analysis in feces and urine, the information of ingestion and changing weight to elemental transfer in different organ in body are analyzed and discussed.

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Table 1. Elemental concentration in kidney for tumored and normal mice groups

Element Group ^a		Growing Stage of Tumor			
		I ^b	II	III	IV
Na (%)	N	-	0.50 (6)	0.55 (8)	0.50 (5)
	T	0.60 (6) ^c	0.68 (7) ^{**}	0.69 (8) [*]	0.66 (5) ^{**}
Cl (%)	N	-	0.63 (10)	0.69 (7)	0.65 (7)
	T	0.76 (11)	0.80 (8) [*]	0.88 (7) ^{**}	0.87 (8) ^{**}
Hg (µg)	N	-	926 (185)	1039 (81)	860 (74)
	T	931 (21)	1075 (168)	1114 (103)	930 (73)
Al (µg)	N	-	4.98 (68)	3.54 (60)	3.11 (76)
	T	5.01 (112)	4.82 (115)	4.56 (5)	4.19 (28) [*]
K (%)	N	-	1.34 (4)	1.42 (6)	1.27 (11)
	T	1.35 (13)	1.45 (17)	1.51 (23)	1.32 (14)
Mn (µg)	N	-	8.23 (153)	5.23 (99)	5.85 (119)
	T	6.14 (82)	4.80 (146) [*]	3.49 (76) [*]	3.80 (89) ^{**}
Cu (µg)	N	-	48.7 (146)	49.5 (63)	30.8 (72)
	T	60.4 (182)	52.8 (89)	55.9 (72)	47.9 (115) ^{**}
Br (µg)	N	-	16.6 (28)	18.5 (60)	14.9 (19)
	T	21.9 (37)	23.7 (38) ^{**}	22.3 (48)	21.7 (31) ^{**}
Ca (µg)	N	-	274 (116)	185 (47)	212 (50)
	T	222 (62)	278 (90)	311 (77) [*]	239 (73)
Fe (µg)	N	-	222 (36)	283 (53)	242 (35)
	T	238 (14)	290 (58)	258 (39)	238 (50)
Co (µg)	N	-	0.19 (4)	0.30 (7)	0.26 (6)
	T	0.29 (12)	0.24 (7)	0.20 (8)	0.22 (3)
Zn (µg)	N	-	83.3 (108)	83.5 (56)	81.3 (36)
	T	78.4 (29)	78.5 (63)	83.6 (79)	92.7 (81)
Se (µg)	N	-	7.12 (104)	7.54 (109)	6.62 (46)
	T	5.75 (42)	6.85 (81)	8.75 (142)	10.2 (15) ^{**}
Rb (µg)	N	-	26.6 (42)	22.3 (31)	25.0 (22)
	T	22.7 (40)	19.8 (53)	16.8 (16)	26.3 (111)

^a : N=normal mice, T=tumor bearing mice

^b : I, II, III and IV stage means 1/4, 2/4, 3/4 and 4/4 period of life span (20 days) of tumored mice, respectively.

^c : the number in the parentheses indicates the uncertainty of the last digits of the mentioned values

^{*} : p < 0.05; ^{**} : p < 0.01 (t test)

CORRELATION OF ELEMENTAL CONTENTS IN CANCEROUS AND NORMAL BREAST TISSUE
WITH CLINICAL STAGE AND OF BLOOD BY NEUTRON ACTIVATION ANALYSIS

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The trace elements are increasingly coming under minute scrutiny due to their active participation in metabolic processes of the human body. Their role as activator or inhibitor of various enzymatic reactions leads to their enhancement or depletion at various sites of activity.

De Jorge et al. [1] first observed a significant rise in the concentration of Cu in tumors. Since then several workers [2,3] have reported correlation between Cu, P, Se and Zn contents of cancerous tissue of breast, stomach, liver etc. Schrauzer et al. [4] have reported alteration in the trace element levels in the blood of breast cancer patients. In continuation of earlier work reported from our laboratory [5], we have analyzed 30 paired samples of cancerous breast tissue and the blood of five normal healthy ladies. An attempt has been made to establish a variation profile of trace elements and the clinical stage of malignancy.

Experimental Methods : Paired samples of normal and cancerous tissues of the same individuals were collected after radical mastectomy at the Government Medical College, Nagpur. For statistical consideration of the successive clinical stages, 3, 15, 7 and 5 samples (total 30) were collected.

The samples were thoroughly washed first with cold and then with hot doubly distilled water to remove adhering blood and low melting fats. These were then dried in a closed chamber under IR lamp (80°C) so as to avoid charring. Completely dried samples were powdered in an agate mortar. The blood sample was drawn out in sterilized polyethylene syringe and heparin was added to avoid coagulation. These were also dried similarly and the wet to dry weight ratio was 4.1 ± 0.3 . These were irradiated in ^{60}Co Gamma Chamber-900 at a dose of 25 kGy. 20-30 mg each of samples and the standards (Bovine liver, Animal Muscle, Oyster tissue, lyophilized human serum and animal blood A-13) were packed in high purity Al foil (INDAL) and/or quartz ampoules. These were irradiated with thermal neutrons at 10^{12} - 10^{13} or $n\text{ cm}^{-2}\text{ s}^{-1}$ for 15m, 2h, 7h and 2d. Resultant activity was counted by high resolution gamma spectrometry. P was determined by beta counting of ^{32}P on a gas flow proportional counter using 27 mg cm^{-2} Al filter.

Results and Discussion : Elemental concentrations of 20 elements (As, Ba, Br, Cr, Co, Cu, Cs, Fe, Hg, I, K, Na, Mn, Mg, P, Rb, Sr, Sb, Se and Zn) were calculated using pure elemental standards and also SRM/CRM as comparators. Our values for SRM/CRM agree well with the certified values within ± 5 -10%. Ranges of concentrations for 12 elements in normal and cancerous tissue and blood of normal healthy ladies along with their mean \pm SD are listed in Table 1.

A perusal of data shows that Se concentration is enhanced to a maximum extent (by almost twofold) in cancerous tissue. Interestingly Fe and Cr concentrations are depleted by about one third. Other elements which show significant enhancement are As, K, Cl, Co, P, Na, Rb, Cu and Zn. When compared with blood, concentrations of Na, K, Cl, Br and Se are

higher, whereas those of P, Cu, Fe, Rb and Zn are lower. In a single case study of stage 2 pre- and post operative blood samples of the same individual has shown lowering of Se concentrations. The protective functions of Se are subject to numerous inhibitions from competing elements like As, Cu, Zn, etc.

Se and Zn have been found to play an important role in the malignancy of breast [3,4]. It has been observed that enhancement in Se concentration of the cancerous tissue is maximum (130%) at stage 3 whereas for Zn it is higher for stages 1 and 4. However, enhancement in Cu concentration shows a successive increase of 25 to 70% in stages 1 to 4. Correlation of Se/Zn and Cu/Zn concentration ratios with respect to the four stages in Fig. 1 show interesting trend. Cu/Zn ratio increases with the stage of malignancy, whereas for Se/Zn it remains relatively constant. It has been suggested that Se and Zn are antagonistic elements. It is observed that both elemental ratios are lower for the clinical stage 1 when compared to normal tissue. Financial assistance from the DAE, Govt of India is gratefully acknowledged.

Table 1 Comparison of elemental concentrations in Cancerous and Normal Breast Tissues with Normal Blood samples

Element	Normal (n=30) Range	Normal (n=30) Mean \pm SD	Cancerous Range	Cancerous (n=30) Mean \pm SD	Change %	Blood (n=5) Range	Blood (n=5) Mean \pm SD
Cl (%)	0.04-0.82	0.22 \pm 0.20	0.08-0.09	0.28 \pm 0.26	+27.3	1.22-2.13	1.54 \pm 0.31
K (%)	0.01-0.31	0.10 \pm 0.10	0.04-0.44	0.10 \pm 0.134	+81.6	0.52-1.22	0.85 \pm 0.24
Mg (%)	0.04-0.17	0.10 \pm 0.04	0.04-0.21	0.10 \pm 0.05	+3.0	0.08-0.13	0.10 \pm 0.02
Mn (%)	0.09-0.62	0.20 \pm 0.16	0.14-0.70	0.30 \pm 0.10	+48.5	0.66-1.61	1.05 \pm 0.32
P (%)	0.04-0.82	0.20 \pm 0.16	0.13-0.88	0.41 \pm 0.15	+44.4	0.16-0.27	0.23 \pm 0.03
Br (μ g/g)	2.0-53.6	17.3 \pm 11.7	0.1-60.8	10.7 \pm 13.7	+0.1	14.6-92.0	31.4 \pm 25.0
Cr (μ g/g)	0.25-5.03	1.73 \pm 1.55	0.25-4.40	1.21 \pm 1.29	-30.1	0.10-0.70	0.30 \pm 0.24
Cu (μ g/g)	0.76-97.0	16.5 \pm 15.9	1.11-82.0	28.0 \pm 24.1	+58.2	6.2-12.4	9.6 \pm 2.3
Fe (μ g/g)	19.8-552	89.9 \pm 136.6	10.0-337	69.1 \pm 74.2	-30.8	30.1-42.6	38.8 \pm 2.1
Hb (%)	0.1-13.3	6.3 \pm 4.8	0.3-20.4	8.1 \pm 6.6	+28.6	1.0-2.6	1.8 \pm 0.7
Se (μ g/g)	0.1-1.06	0.57 \pm 0.28	0.3-1.73	1.11 \pm 0.47	+94.7	0.8-3.3	1.80 \pm 1.13
Zn (μ g/g)	10.0-144	40.1 \pm 15.3	20.2-132	55.0 \pm 26.3	+38.2	11.0-20.0	17.0 \pm 7.3

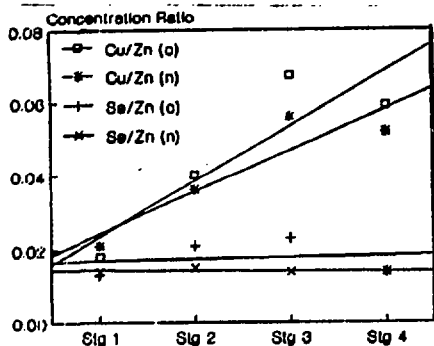


Fig. 1 Correlation of Se/Zn and Cu/Zn with the stage of breast cancer

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TRACE ELEMENT CONTENT IN BREAST WITH FIBROCYSTIC DISEASE

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The essentiality of some trace elements in cell metabolism has become well-established by a continuously increasing evidence in the last decade. As the trace elements act through different kind of mechanisms such as affection of cell permeability, activation or inhibition of enzymatic reactions, competition for binding sites, their role in etiology, pathogenesis and process of some diseases should be expected and must be studied.

As it is shown from literature, research interest has been focused mainly in the study of the role of trace elements in diseases of unknown etiology, high mortality, and high social - economical cost such as cancer, heart attack, neurodegenerative disorders etc.

Female breast, as the main and the unique food source at first months of human life as well as an organ with a risk of subsequent carcinoma, concentrated the special attention of researchers. One interesting study showed that calcium, rubidium and zinc are the most important trace elements for the distinction between malignant and normal breast tissues¹.

Benign breast disease or fibrocystic disease encompasses a wide range of histological lesions. Some are well defined entities but a large number of biopsies have a mixture of changes such as adenosis, epithelial hyperplasia, cyst formation, epithelial metaplasia and papilloma. Contrary to previously held views only a minority of lesions are now considered to carry an increased risk of subsequent carcinoma. This risk is further increased in patients with family history of breast cancer².

As far as we know there is no information in literature about trace element content in breast tissue with fibrocystic disease. In addition because there is a relation between this disease and cancer it could be interesting to know the trace element content in benign breast disease. Also it could be very interesting to study the role of this content in etiology, pathogenesis and process of the disease under investigation.

Therefore, in this work we determined the concentration level of cobalt chromium, iron, rubidium, scandium and zinc in breast tissues with histological reconfirmation of fibrocystic disease and we correlated statistically this content with the recorded lesions for each patient.

Breast tissue samples were collected from patients with mastographic and clinical symptoms suspected for benign breast disease.

The excised surgical specimens were immediately transferred to the pathology laboratory for histological examination. The pathologist removed an aliquot for trace element analysis when the macroscopical examination showed signs of fibrocystic disease which is reconfirmed microscopically. The histological report for each patient was recorded.

The removed tissues were lyophilized and then were analyzed by instrumental neutron activation analysis for the determination of chromium, cobalt, iron, rubidium, scandium and zinc.

Samples and standards were irradiated simultaneously at the rotation system of nuclear reactor of N.C.S.R. "Demokritos" in Athens, Greece, for 50 hours at a thermal neutron flux of $2.3 \cdot 10^{13} \text{ n} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1}$. After a 20 days cooling time samples and standards were measured for the radioactivity of the produced radioisotopes under investigation.

Statistical tests correlation coefficient, multiple correlation and analysis of variance were applied to the analytical data set and to histological lesions recorded for each sample.

The obtained results are discussed for trace element content in breast tissue with fibrocystic disease. In addition it is studied a) the intercorrelation between trace elements in breast tissue, b) the correlation between trace element and each histological lesion, c) the comparison of trace element content between fibrocystic disease normal and malignant tissue, d) the possible groupation of trace element content according to each histological lesion.

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ANALYSIS OF MERCURY AND METHYLMERCURY IN HAIR OF MALAYSIAN FISHERMEN BY NEUTRON ACTIVATION

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ABSTRACT

Being a peninsular state, fishing is an important industry in Malaysia, providing people with employment as well as supplying them with protein from the fish. Fish comprises about 70 % of the protein intake of the population, with consumption at about 100 g/d/person. The average mercury levels in commercial sea fishes marketed in Malaysia range from 0.08-0.46 mg/kg wet weight. With such a high intake of fish, it is apparent that fish is a possible source of non-occupational mercury exposure to the general population.

In this study 106 hair samples were collected from fishermen and their families residing in a fishing village in Pulau Pinang. Sample were also collected from another fishing village in Terengganu. For comparison purposes hair samples were obtained from non-fisherman group in Selangor. Hair sampling and washing were carried out in accordance with the IAEA protocols. Total mercury were determined by irradiating about 150 mg samples for 6 hours at a neutron flux of $3 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. After cooling for two weeks samples were counted for 1 hour or more and the mercury concentrations were determined via 279.1 keV photopeak of Hg-203 after correcting for 279.6 keV interference from Se-75. Total organic mercury (methylmercury) were analysed by neutron activation after radiochemical separation based on method developed by Kratzer et al. [1].

Results of the analysis for total mercury are shown in the Table 1. Data for total mercury were compared to other population groups in Selangor and Terengganu. The population group in Selangor consists of office workers but the consumption pattern of fish is similar to the group in Pulau Pinang. They take about 100 gram of fish per day. The mean values for the two groups are not significantly different. This shows that hair mercury levels depend on fish consumption pattern. The group in Terengganu consists of fishermen and their families. This group consumes fish twice a day at about 300 g/person/day which consists mainly of tuna which is preferred by this group. Tuna has been known to contain higher levels of mercury compared to other fishes.

Table 1. Total mercury in hair (mg/kg)

	Pulau Pinang	Selangor	Terengganu
Sample	106	45	33
Range	0.45-16.87	0.66-6.90	6.79-18.31
Arith. mean	3.61	3.01	12.08
Median	2.96	2.69	12.05
Geom. mean	3.49	2.95	11.69

The levels of mercury found in this study are similar to those reported by other workers for fish consuming population groups world wide. The concentration of methyl mercury is about 70-80 % of the total mercury which indicates that fish is the source of mercury in the hair analysed, as mercury occurs mainly as organic form in fish. Further discussion on the analysis of methylmercury in hair will be presented.

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Determination of total mercury and methylmercury in human scalp hairs by NAA, GC(EC) and SRXRF

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Hg is a toxic element to human-being and Hg pollution is still a problem in some regions of china. The human scalp hair can be used as a monitor of environmental pollution. In the framework of the IAEA Coordinated Research Project on assessment of environmental exposure to mercury in selected human populations as studied by nuclear and other techniques, We collected 1179 hair samples of the human populations living at the Second Song-Hua River district in northeast China, a typical Hg-polluted district. Also, the hair samples from 33 nursing women and their new-borne babies at the same district and from 27 pairs at Zhong-Guan-Chen, Beijing, as a control were taken. The analytical procedure of total-Hg and Me-Hg is mainly based on INAA and GC(EC), respectively. (see Fig.1) The in-house and external analytical quality controls were made. The INAA results indicate that most of 1179 hair samples contain low mercury, less than $5\mu\text{g/g}$. Only about 20 samples have high Hg contents. There is one sample containing the highest Hg, up to $113\mu\text{g/g}$. Thus, the Hg pollution is still present, even though it has been substantially reduced in comparison with the seventies.

Between the Hg contents in maternal and infant scalp hairs there is a significantly positive correlation. Further, the infant Hg levels exceed the maternal by 12%. Generally, about 80-100% of mercury in human scalp hair are present as Me-Hg species, which is able to penetrate the placental barriers and is accumulated in foetus. Our results that the Hg contents in maternal scalp hair gradually reduce during pregnancy support this mechanism. Thus, the conclusion can be drawn that the mercury harm has occurred at the early time of pregnancy.

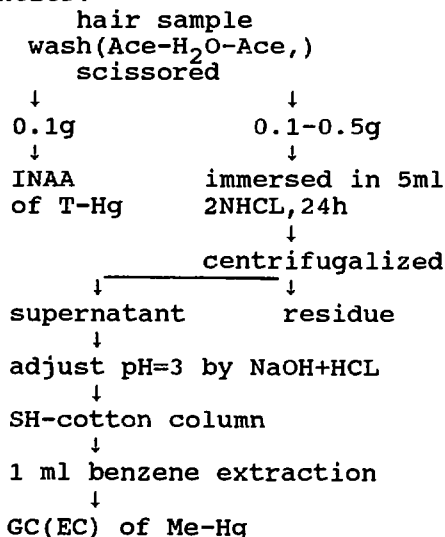


Fig.1. Analytical procedure of
T-Hg and Me-Hg

Forensic Analysis through Signal Intensity Comparison - A Case of Murder

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Summary

Paint residues taken from a small 10 oz. household hammer were taken and compared with a reference paint sample. The hammer had been used as a murder weapon. The reference paint sample was taken from a paint distributor owned by the prime suspect, a wall painter whose former mistress was the victim. By comparison of the respective residues the ownership of the murder weapon was to be confirmed. A sample as small as 0.6 mg (from the hammer) was available for the study. Instrumental photon activation with high (30 MeV) energy bremsstrahlung of an electron linear accelerator followed by gamma-ray spectrometry as well as low energy photon spectrometry was applied as an analytical tool. The conditions of the validity of the evaluation will be discussed. It was found that both paint samples originated from the same batch of paint with a high degree of probability which was a fingerprint for the murder within the meaning of the prosecution.

Radiotracer method in the study of environmental speciation and migration of contaminants

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Speciation and migration of contaminants in the environment have been extensively studied in the past two decades because they strongly affect the environmental and health effects of the contaminants. Considerable difficulties have been encountered in these studies due to the very low concentrations of contaminants and due to the complexity of environmental processes and systems. Some of these difficulties can be overcome using radiotracer method either in the laboratory or *in situ*. The paper illustrates possibilities of the use of radiotracer method for this purpose with several recent studies.

Principal advantages of radiotracer method in the study of speciation of contaminants in the environment lie in the easiness and sensitivity of tracing of radioactively labelled contaminant in separation or other process used in the speciation procedure, and in the possibility of application of methods avoiding shift of equilibria in the studied system (free-liquid electrophoresis, self-diffusion etc.). The advantages can be illustrated by the development of speciation procedure for mercury in human hair and by the analysis of complexation of cadmium in soil solution.

Radiotracer method was used for the development of separation of methylmercury from inorganic mercury in hair. First, the methylmercury was labelled with Hg-203 by isotope exchange in aqueous solution containing 0.15M nitric acid and 0.01M Ag. Then human hair samples were spiked with labelled methylmercury or inorganic mercury. Efficiency, selectivity and homogeneity of the labelling as well as the stability of speciation of the label were very good. The latter fact is due to the slow isotope exchange between methylmercury and inorganic mercury in hair. Further experiments have shown that the spiked hair samples can be dissolved in 0.2-1M NaOH or KOH without significant loss of mercury and change in the speciation of the label. The separation of methylmercury from dissolved hair was achieved by its extraction with benzene at pH 0.5-1 in the presence of 0.5M KI. Measurement of radioactivity of the extracts proved that the extraction was very selective.

Acidic forest soils (pH 4.0-4.8) were extracted with distilled water and the extracts were spiked with carrier free, cationic Cd-109. The spike equilibrated with cadmium present in the extracts and its speciation was studied using free-liquid electrophoresis, solvent extraction, centrifugation, dialysis and ultrafiltration. The results have shown that cadmium forms reversible complexes with fulvic acids leached from the soils. The complexes are negatively charged or neutral (as inferred from their

negative or very low electrophoretic mobility). The extent of complexation found using electrophoresis was higher than that determined by methods which disturb equilibrium in the analyzed system, like dialysis, solvent extraction and DPASV. Complexation capacity of the extracts for cadmium determined by the electrophoresis was also much higher than that determined with DPASV. It has been confirmed that the radiotracer method combined with the free-liquid electrophoresis is very useful for detection and characterization of labile complexes of trace elements in aquatic systems.

Radiotracer method also represents excellent tool in the research of migration of pollutants in surface and ground waters. The method is particularly suitable for the study of interaction of pollutants with solid phases in the waters and for obtaining data necessary for modelling the migration. The use of radionuclides greatly facilitates the study of mechanisms and laws of pollutant interaction with the solid phases by laboratory model experiments. Of special importance is the use of radiotracer method for the study of uptake and release of artificial radionuclides by suspended solids in surface waters because the predominant mechanism of these processes is the isotopic exchange with stable isotopes of the radionuclides.

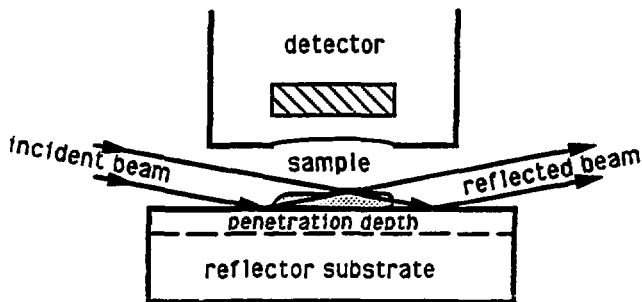
The latter possibility was recently demonstrated by the study of interaction of Cs-137 and Co-58 with suspended solids in a small river receiving waste waters from a nuclear power plant. Laboratory batch experiments identified the main factors affecting the interaction, which are important for the modelling of the migration of these radionuclides in the river. The results indicated that namely kinetics of the interaction should be properly considered in the modelling. Effects of other factors on the interaction can be taken into account either through quantified changes in kinetic or equilibrium parameters of the interaction or through variability of the parameters.

The weak point of applicability of many migration models for prediction of transport of pollutants in surface waters is the lack or low accuracy of certain input data for the model. Some of the data can be obtained or made more accurate by means of radiotracer method. Analysis of the migration of an artificially introduced (usually short-lived) or naturally present radionuclide in the system can greatly facilitate determination of the dispersion coefficients, sedimentation or resuspension rates etc. Radionuclides can also be used for verification of transport models. Recently we described the use of an accidental release of radiocesium into a stream for obtaining input data on the distribution of resuspendable sediments along the stream and on the mean coefficient of exchange of solid phase between suspended solids in water and bottom sediments. A simple migration model was proposed whose applicability for the studied system was corroborated using the data on the time changes of the distribution of radiocesium in sediments of the stream.

Use of Total Reflection X-ray Fluorescence Analysis in the Life Sciences
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Abstract:

Total reflection x-ray fluorescence analysis (TXRF), which is basically an energy dispersive technique (EDXRF) with a special geometry to excite the sample, has proved to be a powerful analytical tool. The sample preferably a thin film or layer on the flat and polished surface of a suitable reflector is excited by the collimated narrow primary beam at grazing incidence angle. Total reflection occurs at these conditions leading to efficient excitation of the sample by both the primary and the reflected beam doubling the fluorescence intensity and a drastic reduction of the spectral background. The lower limits of detection (LLD) in XRF have been improved by this technique and the extrapolated values are in the range of picogram for most elements. The various suitable x-ray sources as standing- or rotating anode x-ray tubes and also synchrotron radiation as the ultimate best source and their usefulness will be discussed. Modifying the spectral distribution of the source by different means e.g. multilayer structures to obtain monochromatic intensive primary radiation leads to extrapolated LLD of 170 fg for Mn. As in TXRF only a few μl of sample volume are required a concentration level in the range of pg/g (ppt) can be detected using instrumentation at laboratory scale. With standard detectors the range of elements which can be determined starts from Na upwards. The new generation of Si(Li) or HPGe with ultra thin windows enables the detection from C on, so also the light elements can be measured. A schematic of the experimental setup for TXRF is given below.



Applications of that technique in the life sciences will be given and results from measurements on environmental samples presented. A short treatment of the mathematical procedure to convert spectral data into concentration making advantage of some of the features of TXRF and the software support will be discussed.

RADIOANALYSIS OF WATER

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Radioanalysis of water

Radioanalysis makes a minor but indispensable contribution to water research and environmental monitoring. Three areas are conspicuous:

1 Chemical analysis.

1 Detection and measurement of transport phenomena.

1 Inventarisation of natural and water-made radioactivity.

Chemical analysis comprises both total concentration of (trace) constituents and their specification in terms of chemical state or distribution over various phases. Both activation analysis and radiotracer procedures are applied. Sampling, preconcentrations and storage make part of an analysis and radiotracers are often used in defining these steps. Measurement of homogeneity, chemical yield and gradual loss or contamination during storage are acknowledged tasks of the radioanalyst.

Neutron activation analysis (NAA) is used for validation of routine methods. For a varied set of elements, NAA is the method of choice: V, Sc, Br, the lanthanides, I and the precious metals.

The same holds for the speciation of inorganic Cr, As, Se and I.

Laboratory radiotracer experiments on the kinetics and equilibrium distribution of a microconstituent between two or more phases are indispensable in geochemistry and environmental science. This also holds for their use in leaching studies and the determination of the effective diffusion coefficient in (partly) wetted soils and waste dumps. In distribution experiments the essential step is phase separation prior to counting. In leaching studies the flow-pattern in the vessel or column is decisive. In both cases independent radiotracer experiments on these influencing factors are necessary.

Radiotracers are also used in pilot plant field experiments within institute or industrial premises. A few stable, well neutron activable, tracers are accepted for outside application. Stable isotopes analysis by mass spectrometry is preferred for large scale environmental studies.

Natural and man-made radioactivity in the environment is measured within the scope of monitoring programmes and to follow slow transport processes in soils and sediments.

Examples are met in the monitoring of actinides around nuclear waste deposits, the measurement of ^{137}Cs -movement in sediments and porewaters and in the estimation of erosion rates of top soils.

The balance-shifting between radioanalysis and other analytical methods seems to have come to a state of quasi-equilibrium. In trace element analysis and speciation, radiotracers are used for kinetic and yield measurements. Activation analysis is mostly applied as a reference method. In some long-range programmes it serves routinely.

Field radiotracer experiments are rare.

A growing occupation is found in environmental monitoring of natural and man-made radionuclides.

**Determination of antimony in natural waters
by preconcentration on a chelating sorbent
followed by instrumental neutron activation
analysis**

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The determination of antimony in natural waters is of interest to the environmental research due to the toxic nature of the element and its compounds.

The concentration of antimony in natural waters is very low (generally less than $0.1 \mu\text{g/l}$).

Very few analytical techniques are capable of determining such low concentrations and even the most sensitive ones require some preconcentration steps.

In this work a chelating sorbent- thionalide loaded acrylic resin (TBB) has been applied for preconcentration of antimony from natural waters. The sorption of antimony is carried out from 0.5 M hydrochloric acid solutions after reduction of Sb(V) to Sb(III) with potassium iodide. The determination of the retained antimony is carried out by neutron activation followed by gamma- spectrometric measurement of the activity of Sb-122 ($E=564 \text{ keV}$). The lower limit of detection is $0.023 \mu\text{g/l}$.

Water samples from the Vistula river as well as samples of well and tap waters were analysed.

TOXIC HEAVY METALS AND OTHER TRACE ELEMENTS IN FOODSTUFFS FROM DIFFERENT COUNTRIES: RESULTS FROM AN IAEA CO-ORDINATED RESEARCH PROGRAMME

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International Atomic Energy Agency (IAEA), Vienna, Austria, and participating institutes in 12 countries

Human growth and metabolism depend, basically, on a well balanced diet in terms of proteins, lipids, carbohydrates, etc. However, traces of inorganic elements also play an important role in various metabolic processes and their excess or deficiency may disturb normal biochemical functions of the body. Human exposure to these elements is mainly through the diet. A research study related to the determination and assessment of toxic heavy metals and some other, mainly essential, trace elements in foodstuffs has been carried out in twelve countries under the auspices of the IAEA. The main purpose of this Co-ordinated Research Programme (CRP) was to obtain comparative data on the existing elemental concentrations of potentially toxic elements in foodstuffs in various countries and to compare them with the maximum permissible levels specified in national legislation and international guidelines. The elements identified as having high priority for this study were arsenic, cadmium, chromium, lead, mercury and selenium. Also of interest, but of lower priority, were antimony, copper and zinc. The matrices of interest were foodstuffs which comprised together more than 50% of the average daily intake. Drinking water was also considered to be highly relevant and was studied by some participants. A detailed research protocol was issued by the IAEA for this CRP. It contains guidelines on the types of food to be collected, the minimum amount of each food to be sampled to obtain a representative analytical sample, how to prepare it for analysis, and procedures for analytical quality control and data evaluation. Emphasis was placed on the use of nuclear and nuclear-related analytical techniques. However, in cases where other, conventional, methods were considered more appropriate, their use was also encouraged. The techniques actually used by the participants were neutron activation analysis, both instrumental (INAA) and radiochemical (RNAA), anodic stripping voltammetry (ASV), inductively-coupled plasma emission spectrometry (ICP-ES), atomic absorption spectrometry (AAS), direct current plasma emission spectrometry (DCP-ES) and proton-induced X-ray emission (PIXE). Quality assurance was emphasized and the IAEA organized a number of external analytical quality control exercises to ensure that the analytical data produced by the laboratories was reliable. Through these procedures it was possible to detect some mistakes and correct for them. With only a few exceptions, participants reported that the concentrations of toxic elements in the analyzed foodstuffs complied with present regulations and guidelines. As regards essential trace elements, the results obtained from this study showed that these are present in variable concentrations depending on the type of foodstuff, the country and the season during which the samples were collected. A summary of the results obtained is presented in this paper.

Assessment of trace element levels in biological indicator organismal of the Environmental Specimen Bank of Germany.

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Abstract:

Assessment for heavy metal contamination of our environment can be performed only on the basis of "base line data". The evaluation of trace metal concentrations in "unaffected" samples is therefore mandatory. Undisturbed samples of the kind which are collected for Specimen Bank purposes from pre industrialized times unfortunately are not preserved. Hence the analysis of similar materials from rather undisturbed areas for comparison with ESB materials is the second best choice.

Bioindicator organisms with the ability to accumulate heavy metals from water air or soil being stored within the ESB represent not only the externally deposited elements into the compartment but also the biological metabolism of these elements depending on the sampling position. To enable the estimation of the influence of these factors a multielement approach (INAA) for fingerprinting was used. First results of various matrix types will be discussed.

Brown algae (*fucus vesiculosus*) from the North sea and the Baltic are compared to brown algae (*sargassum*) of the Indian Ocean. Zinc an essential element with various impact from anthropogenic sources is low in the *sargassum* samples by a factor of 20.

Mussel samples from the German Bight (*mytilus edulis*) have been compared with mussels (*mytilus galloprovincialis*) from the Adriatic coast near Sibenik, Kroatia (as a background area). Nickel in the samples from the Adriatic is low by a factor of 10, Au and Hg by a factor of 5, the rare earth elements, Sc, and Th by a factor of 2 compared to the North sea samples.

Provided that these elements are not reflecting different metabolic activity in the different species, the assessment of the burden with heavy metals in the North sea seems to be feasible. Comparisons of terrestrial plants are difficult because hardly any species with similar trace element behaviour exists which seems to be abundant in remote, tropical areas and in heavily industrialized Middle European climate. Investigations to identify comparable plant materials are still going on.

**INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF MARINE
MAMMAL LIVER TISSUES ARCHIVED IN THE NATIONAL
BIOMONITORING SPECIMEN BANK**

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The National Biomonitoring Specimen Bank (NBSB), located at the National Institute of Standards and Technology (NIST), is a collaborative project of several U.S. government agencies. The bank serves as a repository for human liver tissues, marine mammal tissues, bivalves, sediment samples, diet samples, and serum samples. For all of the projects, the specimens are collected according to specific criteria under carefully controlled and meticulously clean conditions. Aliquots of some of the specimens are used for real-time monitoring, and the remainder is banked for future analyses employing new analytical techniques, for long-term monitoring, or for use by other laboratories that require very specific sample types. As part of this scheme, concentrations of inorganic constituents for selected subsamples are measured by instrumental neutron activation analysis (INAA) at NIST.

The National Oceanic and Atmospheric Administration's National Marine Mammal Tissue Bank (NMMTB) and Alaska Marine Mammal Tissue Archival Project (AMMTAP) are two of the collaborative projects for which tissues have been analyzed recently. Liver tissues from nine pilot whales collected during a stranding of these animals on Cape Cod, Massachusetts and from eight beluga whales taken during native American subsistence hunts in Alaska were analyzed during the past year. Quantitative evaluation was usually possible for 18 of the 35 elements for which we assay. A summary of the results is presented in Table 1.

Pilot whale liver tissues from eight animals were analyzed. Concentrations for the electrolytes showed very little animal to animal variation. Concentrations for essential trace elements such as Zn and Cu also showed little animal to animal variation. Significant differences were observed for the elements with which toxic effects are associated, e.g. Cd, As, Hg. To determine whether these differences could be attributed to age differences the concentrations were plotted versus total length. (The ages for these animals were not available and the assumption was made that the total length of the animal would be an indication of the age of the animal.) Positive correlations were observed for Se, Ag, and Hg, but not for the other elements. This

finding indicates that Se, Ag, and Hg accumulate in the liver. These elements are also correlated with each other as are Mg and Cl, Zn and Mn, Co and Cd. Cesium is correlated with Mg, Mn, Zn, and As.

These correlations of the Se, Ag, and Hg concentrations with each other were observed in earlier AMMTAP data for six beluga liver tissues (1) and are also observed in the data presented here for eight additional livers. For the beluga liver tissues, no statistically significant correlations with total length were observed in previous data set; however when all of the data are combined ($n = 14$) there is a positive correlation with length for V, Se, and Hg. The correlations of Ag with Se and with Hg are not as strong for the beluga liver data as for the pilot whale. However, although no ages are available for these animals, other qualitative information suggests that all of the beluga whales were mature and probably older than the pilot whales so that length may not be as good an indication of age for the belugas. Vanadium concentrations in liver tissues of animals from the U.S. Arctic regions have been consistently higher than those from the U.S. northeast coast (1). Concentrations of V in pilot whales and harbor porpoise are generally close to or below detection limits whereas concentrations in beluga liver tissues range from 0.03 to 0.3 mg/kg and correlate well with total length ($r = 0.80$, $n = 13$).

Table 1. Results of INAA of pilot whale and beluga liver tissue.

Element	Pilot whale			Range	Beluga			
	Mean	±	Std Dev		Mean	±	Std Dev	Range
Na	1480	±	152	1263 - 1621	1307	±	187	961 - 1577
Mg	120	±	24	81 - 150	133	±	41	58 - 219
Cl	1810	±	196	1630 - 2228	1684	±	186	1384 - 1908
K	2192	±	306	1638 - 2635	2405	±	203	2061 - 2704
Ca	48	±	12	24 - 68	30.7	±	8.1	19 - 44
V				≤0.013 - 0.021	0.13	±	0.076	0.03 - 0.3
Mn	2.45	±	0.41	1.78 - 2.98	2.25	±	0.057	1.62 - 3.36
Fe	388	±	209	144 - 806	559	±	135	332 - 781
Co	0.012	±	0.003	0.0066 - 0.015	0.013	±	0.0036	0.0081 - 0.0212
Ni	0.038	±	0.013	0.0204 - 0.060				
Cu	2.83	±	0.81	1.13 - 3.8	14.57	±	8.89	6.89 - 40.7
Zn	38.2	±	7.65	28.3 - 51.1	25.84	±	5.06	20.9 - 38.53
As	0.454	±	0.332	≤0.4 - 1.17	0.198	±	0.15	0.0475 - 0.252
Se	12.8	±	9.2	1.59 - 28.5	19.54	±	17.98	3.99 - 75.52
					15.23	±	8.31	3.99 - 29.36
Rb	1.89	±	0.2	1.44 - 2.1	1.294	±	0.204	≤1 - 1.518
Ag	0.164	±	0.106	0.013 - 0.333	27.6	±	24.7	10.05 - 107.4
					21.53	±	9.41	10.05 - 40.69
Cd	8.48	±	3.14	2.78 - 14.28	2.074	±	1.072	≤0.75 - 3.65
Cs	0.006	±	0.002	≤0.002 - 0.010				
Hg	43.24	±	36.45	1 - 82.8				

1. P. R. Becker, S. A. Wise, M. M. Schantz, J. Koster, and R. Zeisler, National Institute of Standards and Technology Internal Report 4731, "Alaska Marine Mammal Tissue Archival Project: Sample Inventory and Results of Analyses of Selected Samples for Organic Compounds and Trace Elements".

CLIMATIC CYCLES INFLUENCING WOOD DENSITY IN AMAZONIAN TREES

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Trees like any live organism are influenced by environmental factors, such as soil and climatic conditions, being all the seasonal alterations recorded in the annual growth rings as differences in their width and density. The ring width representing the annual volumetric increment is a function of solar energy availability, soil water content, temperature and photoperiod. Then, the rings width and density analysis can provide important informations about local climatic variations¹.

At low latitudes the forest tree biomass production is extensively influenced by precipitation, since temperature remains almost constant throughout the year. The Amazon Basin, localized in the equatorial region, is characterized by isothermal conditions, with temperatures ranging from 24 to 28°C, because of the great amount of water stored in the atmosphere of about 35 mm compared with the world average² of 28 mm.

To identify the possible fluctuations of precipitation records in Amazonian region over last 500 years, samples of local trees were submitted to radial density analysis. For this purpose, wood samples having 20 mm of thickness were taken from the tree trunk at 130 cm height, dried to 8% dry weight equilibrium moisture point and directed to radial scanning by a 60 keV gamma from ²⁴¹Am. This densitometry by gamma ray attenuation system³ allows step-by-step determinations, with a 0.2 mm minimum step and a sensitivity better than 0.03 g.cm⁻³.

The density results were normalized as time function and filtered by statistical methods. It was possible to identify two climatic cycles, a shorter period of about seven years, in coincidence with Manaus pluviometric data from 1912 to 1991, and a large period with about 100-130 years (Figure 1).

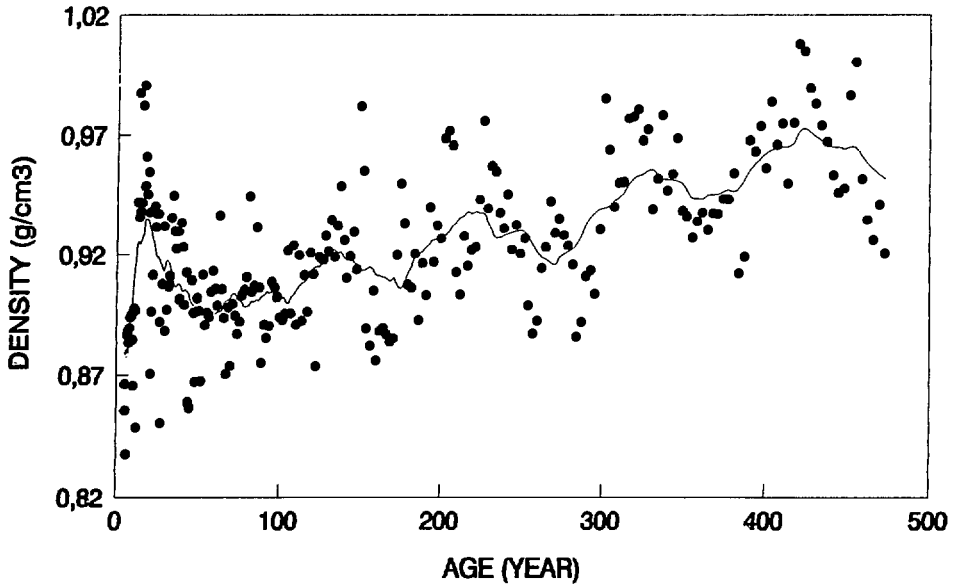


Figure 1. Radial wood density variation (g/cm^3) as time function. Sample of a "Jatobá" (*Hymenae sp*) tree felled in 1980, with an estimated age ranging between 480 and 720 years. Each dot marker is an average of 40 determinations and the curve is a smooth of such averages.

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Methodology and applications of neutron activation analysis in studies of Pt-based antitumour drugs

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Continuing our application of NAA in the development of new cytostatic platinum compounds /1, 2/, we performed cell culture experiments testing Pt complexes which differ from *cis*-(NH₃)₂PtCl₂ ("Cis") by substitution of the NH₃-groups by the bidentate ligands L₁ = *meso*-1,2-bis-(2,6-dichloro-4-hydroxyphenyl)ethylenediamine, L₂ = *meso*- or *d,l*-1,2-bis(4-fluorophenyl)ethylenediamine. Investigated complexes: Cis, *meso*-L₁Pt(H₂O)₂SO₄ ("*m*-2,6Cl₂-4OH-PtSO₄"), *meso*-L₂Pt(H₂O)₂SO₄ ("*m*-4F-PtSO₄"), *d,l*-L₂Pt(H₂O)₂SO₄ ("*d,l*-4F-PtSO₄").

The previously applied NAA procedure /1, 2/ has been modified in such a way that now only one irradiated sample is needed for the determination of Pt and of 11 biologically essential trace elements. The γ -spectroscopic detection limit (Critical Level /3/) for Pt is 20 pg. The increase in this detection limit due to the formation of ¹⁹⁹Au from gold is discussed (cf. /4, 5/). A procedure is described for the correction of the γ -spectroscopic data of ¹⁹⁹Au for that part which is caused by ¹⁹⁹Au formed in the mentioned interfering reaction. The limits of this correction are shown.

MCF-7 cells (hormone sensitive human breast cancer cell line) were treated with 5 μ mol/l (final concentration in culture medium) of the above mentioned Pt complexes. The Pt accumulation in the cells as well as in the DNA and the cytostatic or cytotoxic effect, respectively, were determined (Fig. 1 and Fig. 2). In the analyses of the DNA, the DNA mass per sample was between 0.3 and 0.6 mg and the Pt mass per sample was between 0.14 and 9 ng.

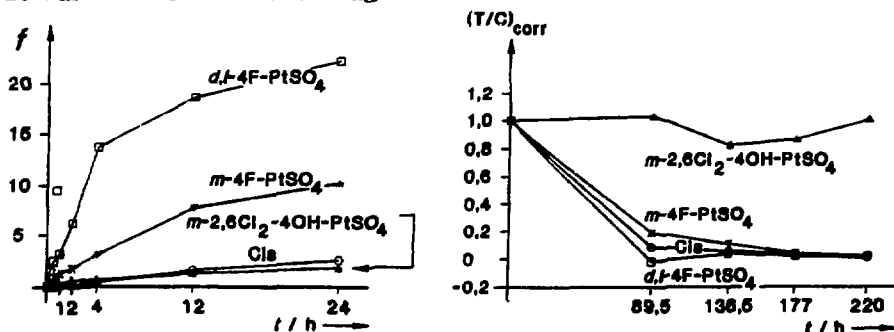


Fig. 1. Pt accumulation in the cells and anti-tumoral effect.

$$f = C_{Pt, cell} / C_{Pt, medium}$$

$$\text{Anti-tumoral effect} = (T/C)_{corr} = \frac{T_t - T_0}{C_t - C_0}$$

T = cell mass in the test culture, C = cell mass in the control
 $C_0 = C$ at $t = 0$.

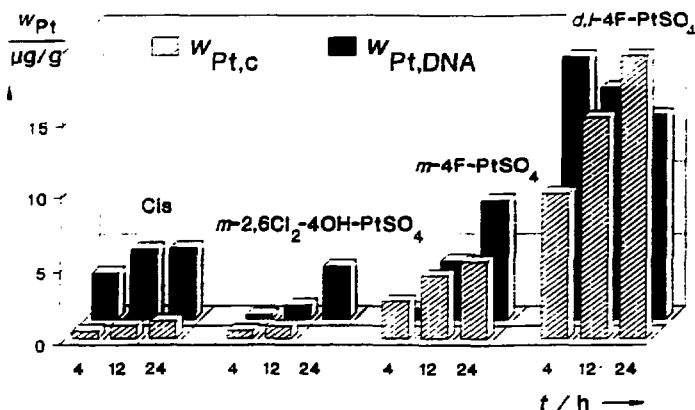


Fig. 2. Pt accumulation in the DNA compared with the Pt accumulation in the cells.

$$W_{Pt,c} = W_{Pt,cell}$$

As shown in Fig. 1, for the three Cis-analogs there exists a correlation between their cellular accumulation (f values) and their anti-tumoral effect [$(T/C)_{cell}$ values], whereas Cis exhibits a divergent behaviour. As expected, this divergency becomes lower when the Pt accumulation in the DNA ($W_{Pt,DNA}$ values, Fig. 2) and the anti-tumoral effect (shown in Fig. 1) are compared. However, the degree of the overall platinumation of the DNA is obviously not the only reasonable parameter to quantify the anti-tumoral effect.

All complexes were inactive against MCF-7 cells implanted into NMRI nude mice. Therefore, the bioavailability of the substances was determined by measuring the Pt concentrations in plasma ultrafiltrate after application of the maximum tolerated dose of 10 $\mu\text{mol/kg}$. Pt concentrations of 0.03 to 0.2 $\mu\text{mol/l}$ were found in the ultrafiltrates. These values are by one to two orders of magnitude smaller than the Pt concentration in culture medium (5 $\mu\text{mol/l}$).

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TRACE ELEMENT CONTENTS IN FOOD DETERMINED BY NEUTRON ACTIVATION ANALYSIS

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Advances in analytical methodology and sophisticated instrumentation introduced during the last few decades have certainly helped to bring about a breakthrough in the field of trace element research.. Using powerful analytical techniques, such as neutron activation, atomic absorption spectrophotometry and mass spectroscopy, researchers have demonstrated the presence in living systems and their food chain of a number of trace elements that were considered up till now as contaminants or accumulated material. The nutritional importance of trace elements has grown rapidly during the last fifty years mainly due to a better understanding of their biological functions. One of the basic requirements for nutrition research concerned with trace elements is the knowledge of exposure levels. From a public health point of view, it is important to assure the general population that the intake of all essential trace elements is adequate in the average, normal daily diet to meet the requirements. At the same time, the ideal diet should not contained more than the permitted levels of toxic heavy metals such as lead, cadmium and mercury. Except for occupational exposure, the major pathway through which the trace elements enter the human body is via the food chain. Information concerning the dietary intake of essential and toxic trace elements can be obtained by either direct or indirect methods. Only direct analysis of the actual food consumed during 24 hours can provide an accurate estimate of the dietary intake of both essential and toxic trace elements. Indirect methods are based on computation from standard food tables. Indirect methods may not provide satisfactory information concerning the concentration of certain trace elements such as chromium, copper and selenium.

Duplicate portion dietary sampling technique is a direct technique that is suited for the study of dietary intake of essential and toxic trace elements in a small, well-defined group in the general population of any country. Duplicate portion is a copy collecting while eating normally to represent all the solid food items and fluids consumed during a period of 24-hours. Employing this technique, we have investigated the dietary intake of a number of important minerals (sodium, potassium, calcium and

magnesium) and trace elements (chromium, copper, iodine, iron, manganese, selenium and zinc) in a limited number of well-defined population groups in India, Pakistan, Portugal, Russia and Sweden. We have also analyzed the contents of the toxic metals (lead, mercury and cadmium) in some of the 24-hour diets. All the elements were determined by both neutron activation analysis and atomic absorption spectrophotometry.

The results indicate that the intake of potassium, magnesium, copper, zinc and selenium in the diets of populations in affluent countries is below the current recommendations. The intake of toxic elements is within the permitted levels. Preliminary results from India and Pakistan indicate wide variations in the intake of some of the important trace elements such as copper, iron, zinc and selenium in different regions. The intake of lead in the urban areas in India and Pakistan is much higher than that found in the urban areas of central European countries. Trace element problems as a public health issue has a very low priority in developing countries. At the same time, both deficiencies and toxicities are fairly common in many of the developing countries. It is therefore essential to study the actual intake levels of essential and toxic trace elements in various populations in developing countries and to draw the attention of the authorities in order to take the necessary preventive measures. This paper will discuss the problems involved with dietary collection and the analysis of trace elements with special reference to the problems in developing countries.

PROGRAMMES OF THE IAEA UTILIZING NUCLEAR ANALYTICAL TECHNIQUES IN THE LIFE SCIENCES

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Nuclear analytical techniques continue to have an important role in programmes of the IAEA relating to human health, and in other life-sciences applications. This is despite the rapid advances that have occurred in some other, alternative, methods of analysis. During the period since the last Life Sciences Conference in this series, the IAEA has organized and provided support for seven pertinent Co-ordinated Research Programmes (CRPs). A major effort has been devoted to a study of dietary intakes of trace elements in 25 study groups in 16 countries. Neutron activation analysis (NAA) served as the reference analytical method for 14 of the elements of interest and as quality control check on a further 4 elements. NAA has also been used for the analysis of food samples collected as part of a study in three countries of the former USSR affected by the Chernobyl accident. The same accident stimulated interest in using ^{129}I to trace the distribution of fission products in the environment. The Agency's Laboratory has recently established an NAA procedure for determining ^{129}I in biological and other environmental materials and has applied it to a variety of samples, including some from the Chernobyl region. An effort is underway to establish a reference material with a recommended ^{129}I concentration. Other research topics that have utilized nuclear analytical techniques include environmental pollution associated with solid wastes, air pollution, and exposure to mercury in selected human populations. In this latter programme, interest centres on using human hair as a bioindicator of exposure to inorganic and methyl-mercury. A new research programme, due to start in 1993, will use NAA and other techniques to study trace elements in human bone; this is part of a comparative international study of osteoporosis using isotope techniques. Much of the IAEA's work in these fields is concerned with analytical quality assurance. In addition to preparing and distributing its own analytical quality control materials, the IAEA also maintains a database of biological and environmental reference materials for trace elements available internationally from any supplier. This database is currently being updated in a collaborative project with UNEP. Many of the materials in the database have been certified with the aid of NAA and/or are suitable for the quality control of measurements made by nuclear analytical techniques. New materials in preparation under the IAEA's own programme of Analytical Quality Control Services include a lichen reference material (for trace elements) and human hair (for total and methyl-mercury). An overview of all these programmes will be presented in this paper, and illustrated by representative data.

X-RAY ANALYTICAL TECHNIQUES IN ENVIRONMENT AND BIOLOGY

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We can see the increased application of nuclear and atomic analytical techniques in life sciences, special in environmental science and biology research. Often areas of the interest are pollutant monitoring, trace element analysis and microanalysis. The X-ray analytical methods have already stable position in this field of research, due to their nondestructive way of analysis, easy sample handling, and in the last time micro-beam application possibilities.

Purpose of the presented work is the critical comparison of the following analytical X-ray techniques: XRF (X-Ray Fluorescence), XRTR (X-Ray Total reflection), PIXE (Particle Induced X-Ray Emission) as well as SRXF (Synchrotron Radiation X-Ray Fluorescence). The priorities and the limitations of each method are given. The emphasis is putting upon an application in the environmental science as well as in the biology.

The discussion is focused on the specific features of each method, present status in the equipment offering by commerce, cost of the experimental devices. The criteria of the sample preparation, the flexibility of the measurement conditions, measurement time and other demands are also discussed.

The following analytical characteristics: the sensitivity, the detection limits, as well as the cost of the analysis are discussed. Finally results of the soil, plant and ash analysis as well as the possibilities of the application of the micro-beam in PIXE and STIM analysis in biological applications are presented.

THE PRESENT STATE OF PIXE SET UP AT CTU IN PRAGUE

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At Czech Technical University in Prague, in Ion Beam Laboratory of the Dept. of Physical Electronics, Faculty of Nuclear Sciences and Physical Engineering, an equipment has been built [1] and is operated for analyses with light ions with use of ion beam from Van de Graaff accelerator of Nuclear Centre of Charles University. It has a chamber devoted especially to PIXE analysis. In last two years development of PIXE methodology and improvements of the equipment for various applications of the method have been the main subject of program of the laboratory.

In the equipment proton beam enters the target chamber in vertical direction (downwards) with energy up to 2.5 MeV. Current on the target from some tenths to about 100 nA is used. The equipment allows the proton beam to be extracted from high vacuum to atmosphere and the analyses are performed both in high vacuum and with the external beam in an atmosphere of pressure from atmospheric one down to high vacuum level. External beam makes possible analyses of samples not compatible with high vacuum, removes problems of charging insulating samples and may be advantageous even in some other way. The favourable and expressive influence of enhanced gas pressure (N_2 , several Pa) at the target on quality of PIXE spectrum of insulating sample has been observed. Now it is exploited when insulating samples are analysed. In such a case the analysing proton charge is measured with the use of simultaneous RBS spectrometry of protons backscattered on the exit foil. Recently a study has been done of sample to detector position influence on X-ray detection efficiency to find an optimum detection arrangement and an improvement of sample holder manipulator was performed to secure well defined and reproducible setting the position of samples with regard to the beam. X-rays from samples are detected by a PGT Si(Li) detector, in front of which a removable absorber is used to reduce the intensity of selected part of spectrum and to stop backscattered protons. Signal from the detector is processed by MCA Canberra 40. Spectra collected are sent through a PC XT and LAN to a more powerful computer for evaluation. A set of programmes has been prepared both for measured data evaluation and also for calibration of the detection set up with the use of standard samples. Beside current evaluation of thin sample spectra, new programme prepared for thick target spectra evaluation is practically tested at present.

Besides routine analyses of solid aerosols on thin membrane filters (thin broad homogeneous samples), analyses of dry residues of evaporated drops (e.g. of solutions of mineralized biological materials) on thin foils are tested. Such small inhomogeneous thin samples need ion beam of

uniform current distribution, cross section of which covers completely the sample. Uniformity of ion beam is monitored by two mutually perpendicular wire probes crossing the beam in front of the target chamber. Thick sample spectra are also measured, but development of quantitative analysis of such samples in the laboratory has only started. In connection with this it should be mentioned that vertical external beam analysis of thick target presents unique conditions for liquid samples, as well as a liquid sample may be an ideal thick target.

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X-RAY AND GAMMA-RAY SPECTROMETRY SYSTEMS DEVELOPED AT THE NRI ŘEŽ

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A survey of properties of Si(Li) and HPGe Low Energy Systems produced at the NRI Řež is presented in the first part of the paper. In the second part, some results are presented which were obtained for measurement of high gamma-ray count rates, for beta-spectrometry, and for special purposes. The last part of the paper deals with special electronics for measurement of gamma radiation by means of scintillation detectors and photosensitive diodes.

^{236}Pu WITH HIGH RADIOCHEMICAL PURITY AS A TRACER FOR DETERMINATION OF ^{238}Pu AND $^{239,240}\text{Pu}$ IN THE ENVIRONMENT

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Standard radiochemical methods of the determination of plutonium in the environment require the addition of 0.1-0.3 Bq of an α -emitting tracer into the sample analyzed. The calculation shows that the purity of ^{236}Pu equal to 10^{-4} Bq/Bq of ^{236}Pu is the upper limit for the determination of the ^{238}Pu global fallout. The quantity of ^{238}Pu in the tracer with such impurity can be compared to those to be determined. The most isotopically pure ^{236}Pu was produced recently by the (d,n) reaction on highly enriched ^{235}U (99.747%) [1]. $^{238}\text{Pu}/^{236}\text{Pu}$ ratio was 5×10^{-4} Bq/Bq. For precise analysis the ^{238}Pu admixture should not exceed 10^{-4} .

The plutonium isotopic ratio is very important for the determination of the origin of plutonium in the sample investigated. The global fallout ratio of $^{238}\text{Pu}/^{239,240}\text{Pu}$ is estimated as 0.03-0.05 Bq/Bq. This ratio is much higher in cases of a nuclear fuel reprocessing plant release or an accident at a nuclear power station. The present work is aimed at the production of isotopically pure ^{236}Pu and at using it as a tracer for determination of plutonium in the environment.

^{236}Pu was produced by the ($\alpha,3n$) reaction on enriched ^{235}U (95%) at the FLNR, JINR. The target (5 mg/cm²) was irradiated by ^4He -ions with an initial energy of 35 MeV at a 40 μA beam current for 20 hours on the U-200 cyclotron. After "cooling" for 5 days, the irradiated uranium target was dissolved from its aluminium backing with 12 M nitric acid. Plutonium was reduced to Pu(IV) with sodium nitrite and the preliminary separation of Pu(IV) from uranium was carried out by the lanthanum fluoride method. Then plutonium was isolated from the residual uranium, other activation and fission products by using the anion-exchange chromatography. After the final chemical purification the total activity of ^{236}Pu was 50 kBq. The ratio $^{238}\text{Pu}/^{236}\text{Pu}$ was 2.0×10^{-2} Bq/Bq. To obtain higher purity of ^{236}Pu , the separation of Pu isotopes was carried out with the electromagnetic mass-separator ISOL-Facility YASNAPP-2 (LNP, JINR) [2]. The total activity of ^{236}Pu was 25 kBq indicating to $\approx 50\%$ efficiency of the mass-separation. The ratio of $^{238}\text{Pu}/^{236}\text{Pu}$ in the final preparation was lower than 10^{-4} Bq/Bq.

For the determination of plutonium in soils we used the standard method recommended by IAEA [3]. The samples were processed after the addition of 0.13 Bq of ^{236}Pu . Then plutonium content was measured by the α -spectrometry. The chemical recovery of ^{236}Pu was $81 \pm 6\%$. The concentrations of $^{239,240}\text{Pu}$ isotopes were found to be of the same order as those reported for the global fallout, the average meaning was about 0.34 ± 0.08 Bq/kg. The $^{238}\text{Pu}/^{239,240}\text{Pu}$ ratio also corresponded to the global fallout.

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**Distribution of Na, K, Rb and Radionuclide Cs-137
in Some Austrian Higher Fungi**

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The level of Cs-137 in 28 species of basidiomycetes collected and analyzed in the time between 1986 and 1992, after the Chernobyl accident, are reported. *Xerocomus badius* is found to accumulate Cs-137 (the median value of 58 samples is 3667 Bq/kg). The Cs-137 content of *Xerocomus subtomentosus*, *Rozites caperata*, *Scleroderma vulgare*, *Russula ochroleuca*, *Tylopilus felleus* and *Xerocomus chrysenteron* exceeded 600 Bq/kg. Some of these samples collected in August 1992 from one place on the same day were investigated for their Cs-134 and Cs-137 content as well as their Na, Rb, K, and Cs levels by applying neutron activation analysis. The results show a high correlation coefficient (0.80) between the contents of Cs-137 and Na but none between Cs-133 and K.

RADIOACTIVE CONTAMINATION OF FORESTS IN POLAND

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Our study is within the Polish Government programme investigating the forest radioactive contamination including the natural and artificial radioactivity, with particular emphasis on the Chernobyl component. Each of 404 forest inspectors was asked to collect and send us a set of samples containing two layers of forest litter: leaf (A₀) and humus (A₁), as well as leaves of blueberry, *Xerocomus badius* and other mushrooms samples. Approximately 350 sets were received, 280 of them with *Xerocomus badius* samples, which have been taken for gamma-spectrometric analyses first [1]. These measurements allowed us to choose the 120 regions with increased contamination levels for which whole sets of samples are being examined to detect radioactive gamma-emitters with use of low-background germanium gamma spectrometers. The specific aim of this analysis is:

1. Determination of the caesium isotope (Cs-137 and Cs-134) contamination levels, where the amount of Cs-134 makes possible deducing the Chernobyl component.
2. Search for other artificial long-lived gamma-emitters.
3. Determination of natural radioactivity (mainly K-40) in all samples examined.
4. Determination of caesium isotopes transfer factors (Tr) from litter to blueberry and various species of mushrooms.
5. Testing some models on Tr dependance.
6. Determination of average (relative to *Xerocomus badius*) ability to concentrate radiocaesium by various mushroom species.

The detailed analysis is still in progress, but we may already quote some of our initial results. Maximum observed concentration of caesium was found in samples from forest near Olesno (close to Czestochowa). Below we give the activities for Olesno samples (all in kBq/kg d.m.) corrected for decay to the 1.09.1991, the sampling date.

	Cs-137	Cs-134
leaf layer A ₀	3.30 ± 0.16	0.35 ± 0.01
humus layer A ₁	1.11 ± 0.09	0.11 ± 0.01
blueberry leaves	3.71 ± 0.09	0.37 ± 0.03
mushrooms:		
<i>Xerocomus badius</i>	121 ± 4	12.5 ± 1.0
<i>Leccinum scabrum</i>	17.5 ± 0.4	1.8 ± 0.1

The maximum value for cesium contamination in mushrooms other than *Xerocomus badius* has been found in *Paxillus involutus* sample originating from Mazurian Lakes district (Szczytno) and it is equal to 32 kBq/kg d.m. (Cs-137) and 3.0 kBq/kg d.m. (Cs-134). In many samples of litter (both A₀ and A₁ layers) the Sb-125 (T_{1/2}=2.73 y), Ru-106 (T_{1/2} = 368 d) and Co-60 (T_{1/2}= 5.27 y) isotopes were found. In some samples from N-E corner of Poland traces of the Ce-144 (T_{1/2}= 284 d.), Eu-154 (T_{1/2}= 8.59 y), Eu-155 (T_{1/2}= 4.68 y) were observed. All isotopes mentioned above have been reported as constituents of hot particles [2-4] , but now it has been found that they are evenly distributed throughout the sample.

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FOREST LITTER ACCUMULATION OF CAESIUM AND RADIO-CAESIUM IN SELECTED REGIONS OF POLAND

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The study aimed at further investigation of the samples of forest ecosystems, which were collected in 1991 from all woods in Poland [1]. In 20 samples (out of 345) of two upper layers of forest litter which revealed the highest radioactivity (Cs-137, Cs-134) and came from Upper Silesia (10 samples) and North East Poland (10 samples), the stable caesium was assayed by AAS preceded by microwave digestion. An attempt to detect any significant correlation between stable caesium and radiocaesium was made. Results were compared with those obtained for mushrooms from the same sites, where the statistically significant differences were observed. The influence of stable caesium content on transfer factor (from litter to mushroom) was studied.

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THE MEASUREMENT OF LOW CONCENTRATIONS OF Kr-85 IN ATMOSPHERIC AIR SAMPLES

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Data on Kr-85 atmospheric activity in Prague have been collected on regular basis in the Institute of Radiation Dosimetry since 1983. The method used for this purpose consists of pre-enrichment steps during which the atmospheric krypton is collected on activated charcoal at 77 K and purified by standard chromatography. The Kr-85 activity of the krypton fraction is measured by a low-level counter equipped by $\text{CaF}_2(\text{Eu})$ scintillation detector. With the conventional measurements the air volume of about 10 m^3 is treated and minimum detectable Kr-85 activity of $(10 \text{ mBq.m}^{-3} \text{ STP})_{0.95}$ is achieved.

The long-term trend of Kr-85 air concentration increased steadily over the investigated period 1983-1992 with the growth rate of $0.04 \text{ Bq.m}^{-3} \text{ (STP)}$ per year and reached of about $1.2 \text{ Bq.m}^{-3} \text{ (STP)}$ at present. This pattern reflects the dispersion of this radionuclide in the surface air of the middle latitudes of the Northern Hemisphere. The short-term variations of Kr-85 air activity with the amplitude of about 12% of mean annual value were found to be dependent on the season with the maximum occurring in spring. The occasionally registered spikes of Kr-85 indicated the passage of undispersed radioactive plumes originated in its main source regions i.e. in the regions of operating nuclear fuel reprocessing plants located in western Europe as well as in Russia.

NEUTRON ACTIVATION ANALYSIS OF TWO CRUSTACEA OF
MYSIDACEA SPECIES

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The Mysidacea species, Javanisomysis gutzui Băcescu - 1992 and Mesopodopsis slabberi Van Bened - 1861, by instrumental neutron activation method have been investigated. The first sample has been collected in 1991, 35 km offshore Djakarta near Pari Island, 0.5 m depth and the second one was sampled in 1949 from the Black Sea, 30 - 50 m. offshore of Saint George Branch of Danube River Delta, 2-3 m. depth.

The dried samples were irradiated at a 3.10^{12} n.cm⁻². s⁻¹ flux of the VVR-S reactor (short and long irradiations). The measurements have been carried out making use of high resolution HPGe detector.

The marine biological reference materials MA-M-2/TM (Mediterranean mussels - Mytilus galloprovincialis) and MA-B-3/TM (Baltic garfish - Belone belone) have been used.

The concentrations of Ag, Al, As, Au, Ba, Br, Ca, Cl, Co, Cr, Cu, Fe, Hg, K, La, Mg, Na, Ni, Rb, Sb, Sc, Se, Sm, Th, U, V and Zn in the two crustacea of Mysidacea species have been determined.

It has been concluded that:

- Se, Zn, Rb, Cu concentrations in the both samples are about the same;
- Sc, Mn, Fe, V concentrations are greater for the crustacea sampled from the Black Sea than those of the Indonesian Sea, of 5.9, 7.8, 8.3, 9.8 times respectively;
- Co, Cr and Ni, only in the Black Sea sample have been identified;
- Au content of (103 ± 7) ppb was found about four times more in Jawa sample than that of the Black Sea;

- Th and U were identified about three times more in the Black Sea samples, than in those of the Indonesian Sea;

- The toxic and pollutant elements as: Al, As, Hg and Sb have higher values in the Black Sea than in the Indonesian Sea.

In conclusion the higher mineralization of Mysidacea specie sampled from the Black Sea is explained by us due to the fact that at the mouths of Danube river delta is a great liquid and solid discharge mixed with the Black Sea water with a higher salinity.

In a previous paper 1 other marine species samples have been analyzed by INA method, but for the first time the crustacea of Mysidacea species were investigated.

Aknowledgements.

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**Study of Trace Elements in Rain Water
by Instrumental Neutron activation analysis**

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Element composition of rain water has been determined with use of instrumental neutron activation analysis. Solid water insoluble fractions were separated by filtration through membrane filters. Filtrates were dried and dry remains as well as solid fractions on filters were analyzed. Concentrations of 25 elements in samples obtained were determined. Enrichment factors as well as relations between element concentrations in soluble and solid fractions were calculated.

Changes of element concentrations in rain water in soluble and insoluble fractions during all sampling period were found. Element concentrations in solid fractions decreased during sampling period while element concentrations in soluble fractions were more constant. For elements found to be mainly in solid fractions this tendency to decrease of concentration in solid fractions was pronounced stronger than for elements prevailed in soluble fractions.

On the basis of data obtained conclusions about investigated elements speciations in atmosphere are drawn. These results are compared with our previous data obtained by investigation of element speciation in atmosphere by passive sorption method.

VARIABILITY OF LIVING ORGANISMS ELEMENTAL COMPOSITION

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The planing of analytical procedure could be simplified by knowing a priori of some regularities of studied samples composition (expected element concentrations, variability, etc.) This question is in a case of biological samples a part of wide general problem of living organisms tolerance to changes of elemental composition of their internal and external (environmental) media. This problem is for many years very interesting field of analytical technique, biogeochemistry, bioinorganic chemistry, etc. At present time the importance of such a study grows as the contamination of environment grows.

This study needs reliable data on elemental composition of living organisms. The outstanding progress in analytical technique (including the nuclear methods), and growing interest to Life Sciences allowed to accumulate reach enough data to try to describe quantitatively such phenomena as variability of elemental composition, elements toxicity, limitations of elements accumulation by organisms, etc. To describe these phenomena as a function of average elemental composition simple equations are proposed.

The significance of found regularities for determination of acceptable analytical accuracy and reproducibility, study of ecological limitations, and probable response of Life on growing pollutions are discussed.

MAPPING USING HUMAN BLOOD COMPOSITION DATA

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The mapping using INAA on the base of whole blood of inhabitants (2 700 samples) elemental composition (as well as hair composition) was made in Uzbekistan (CIS) and allowed to determine average concentrations of 15 elements (24 for hair). The results obtained were compared to regional medical statistics (data were given by Ministry of Health of Republic of Uzbekistan).

The correlations for various diseases were obtained. It was pointed out that for some elements the positive correlation with rate of cardiovascular diseases was observed, whereas the correlation was negative for rate of malignant neoplasms. The correlations obtained stipulated the study of correlations of whole human blood elemental composition with some diseases for groups of patients (cardiovascular diseases, some malignant neoplasms, urolithiasis). For such elements As Na, K, Cl, Co, Sc, Fe, Cu, Zn, Se, Br, Au, elevated concentrations for patients with cardiovascular diseases and decreased concentrations for patients with malignant neoplasms were observed. The correlations for human hair in general were opposite. The elemental composition of human blood seems to be statistically significant (P up to 0.84) diagnostic tool as well as factor characterizing the population health status and method for determining groups of risk.

The maps for human blood composition in comparison to those for human hair composition seem to be less significant in terms of regional contamination (probably due to more strong homeostatic protection of blood). On the other hand, specific changes of blood composition were detected for some occupational groups. Relationships of blood and hair elemental composition and their relative significance are discussed.

STUDIES ON ERYTHROPOIESIS IN BILHARZIAL HEPATOSPLENOMEGALIC
CASES AND RESPONSE TO SPLENECTOMY USING TRACER TECHNIQUE

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The presented study has been conducted in order to evaluate the impact of splenectomy on the haematopoietic activity in patients suffering bilharzial hepatosplenomegaly.

Results showed preoperative decrease in values of serum iron, haematocrit, $T_{1/2}$ for clearance and a parallel increase in the values of plasma volume, percentage maximum incorporation of radio ferric into circulating red blood corpuscles (R.B.C.'s).

Splenectomy in forty five days lapse of time resulted in amelioration of the decrease in values of haematocrit and clearance half life in blood and plasma.

Splenectomy on the other hand, aggravated the decrease in serum iron, however, splenectomy resulted in more increase in percentage maximum incorporation of ^{59}Fe into circulating red blood corpuscles (R.B.C.'s).

The obtained results permit conclusion that, the enlarged bilharzial spleen is mainly responsible for the enhanced phagocytosis of R.B.C.'s although, its role in inhibiting the bones marrow activity cannot be overlooked.

Comparison of chemical and extrinsic tag (⁵⁹Fe and ⁶⁵Zn) method on the in vitro bioavailability of Fe and Zn from food stuffs and human diets

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Iron deficiency anemia is widely prevalent in our population in spite of seemingly adequate intakes of dietary iron. The main reason for this could be due to poor absorption. Factors which influence iron absorption are primarily derived from food stuffs. The well identified inhibitors are phytates and tannins and promoters are ascorbic acid and some reducing agents. Iron and zinc tend to move together through the food chain, it is likely that factors which influence bioavailability of iron would also influence zinc. Detailed studies were planned to compare the estimation of in vitro ionisable iron and soluble zinc using chemical as well as extrinsic isotope (⁵⁹Fe and ⁶⁵Zn) tag methods in various food stuffs and human diets. Various food stuffs like cereals, pulses, vegetables were collected from the local market. Diet samples like beverages, breakfast, lunch, dinner etc. were collected from local hotels and restaurants. The diets were homogenised and lyophilised for analysis. Food stuffs were powdered and passed through a 1mm sieve and processed for analysis. Simulated digestion of the materials was carried out using standard procedure after appropriate concentration of ⁵⁹Fe or ⁶⁵Zn addition. Total iron and ionisable iron was estimated by colorimetry using bathophenanthroline reaction and using first derivative spectrophotometry. Total zinc and soluble zinc was estimated by Atomic Absorption spectrophotometer. The ⁵⁹Fe and ⁶⁵Zn counting was done using packard liquid scintillation counter. The results clearly indicated a good correlation between chemical and extrinsic isotope tag methods both for iron (r = 0.98) and zinc (r = 0.97) bioavailability in food stuffs as well as in the diets.

CADMIUM LOSSES ON WET AND DRY ASHING OF PLANT MATERIALS

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Cadmium is one of the most thoroughly followed elements in the environment and in the food chain owing to its high toxicity to organisms even in trace concentrations [1]. Therefore, highly accurate Cd determination is required in many environmental, biomedical and nutritional health-related studies.

Analytical techniques capable of low level cadmium determination in biological materials usually involve sample solubilization, decomposition and/or total mineralization which can be accomplished by various wet or dry ashing procedures. The complete Cd recovery on wet or dry ashing is thus a prerequisite for the accurate element determination by analytical techniques in which the Cd separation yield is not followed. Recently, employing a RNAA procedure, in which the Cd chemical yield is determined using ^{109}Cd radiotracer [2], for analysis of candidate NIST SRM-1573a Tomato Leaves (a renewal of SRM-157), we noted unusually low Cd yields (60-80 %). The losses seemed to occur on wet ashing. Therefore, we studied this problem in more detail for several wet ashing (in mixtures of H_2SO_4 , HNO_3 , HClO_4 , H_2O_2 , and HF at temperature 150-300 $^{\circ}\text{C}$) and dry ashing procedures (at temperature 450-900 $^{\circ}\text{C}$) using tomato leaves with the metabolized ^{109}Cd radiotracer. We also examined incorporation of the ^{109}Cd radiotracer into various parts of tomato plants.

In the tomato plants, the highest Cd accumulation was found in leaves (34.9 %), followed by roots (24.5 %), stem (24.1 %), stalks (15.9 %), fruit flesh (0.5 %), and seeds (0.1 %). Wet ashing procedures studied yielded solutions with some precipitates and/or residues, except for mixtures containing HF. In the absence of H_2SO_4 and HF in the decomposition mixtures, the residue was formed by

a siliceous material which retained only small amounts of Cd (up to 5 % of the Cd present) as followed from the measurement of ^{109}Cd and of other elements as it was found by INAA of the residue. The most appreciable Cd losses (30-40 %) occurred when H_2SO_4 was used on wet ashing, because CaSO_4 precipitated (as it was confirmed by INAA) which retained Cd and also by INAA measurable amounts of several elements, namely Al, Mg, Si, and Sr. Only small Cd losses (about 5 %) were observed on dry ashing in air in an open system at temperature not exceeding 500°C . However, the losses increased up to 30 % when the final ashing temperature was raised to 900°C .

It can be concluded that for the accurate determination of Cd traces in plants and other Ca-rich materials, the use of H_2SO_4 for wet ashing should be avoided if the Cd yield cannot be determined. For dry ashing, temperature should not exceed 500°C to guarantee that Cd losses from plant materials higher than 5 % will not occur. The use of decomposition and/or dissolution mixtures containing HF can be recommended for analysis of plant materials to dissolve the siliceous precipitate and/or residue formed after both wet and dry ashing modes to achieve the highest Cd yield, closely approaching 100 %.

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THE EXTRACTION OF URANIUM FROM ACIDIC SOLUTIONS BY TBP IMPREGNATED POLYURETHANE FOAM

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The content of radioactive nuclides in the uranium plants waste solutions must be kept as low as possible. A number of methods have been employed for removing small amounts of radionuclides. The use of polyurethane foam (PUF) in the separation of metals from aqueous solution was first demonstrated by Bowen and the field has been reviewed by Braun and Farag. Polyurethane foams are polyethers or polyesters crosslinked by amido - linkages and foamed with carbondioxide during the cross-linking. Polyurethane foams have been of interest as efficient sorbents for the separation, collection and concentration of trace amounts of metal ions.

The purpose of the present work was to investigate the sorption of U (VI) using polyurethane foam impregnated with tributyl phosphate (TBP) from acidic solutions. Plugs (4.5 cm diameter, 2.2 cm length, average dry weight 0.5500 ± 0.0020 g) were cut from sheets of polyurethane foam. Each plug prior to use was squeezed in 2 M HCl, washed with distilled water until free of HCl and squeezed dry. The foam plug was then rinsed with acetone and air dried overnight. The cleaned foam plug was soaked in a solution of TBP / cyclo hexane. Solution of uranium was prepared by dissolving $UO_2(NO_3)_2 \cdot 6H_2O$. Uranium was determined spectrophotometrically by the PAR method ($\lambda=510$ nm, $\epsilon=3.87 \cdot 10^4$ l /mol.cm).

The impregnated foam plug was equilibrated with standard uranium solution by automatically squeezing the plug of solution 40 times / min. 1.5 cm compression stroke. Preliminary experiments showed that equilibrium was established after 1.0-1.5 hours. The pH of uranium solution was adjusted to the desired value with HNO_3 / NH_4OH . The percentage extraction was found maximum between pH=6.00 and 7.00. It was observed that the extraction efficiency depends on the concentration of uranyl ions. The effect of different temperatures and contact times were also studied.

The uranium sorption capacity of foam increases with increasing TBP concentration.

Thus TBP impregnated polyurethane foam can be used for the absorption and extraction of uranium from dilute aqueous solution. It has been shown that the polyurethane foam can act as a cheap and readily available support material for the neutral organic extractant (TBP). The extraction mechanism is similar to liquid-liquid extraction.

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**INVESTIGATION OF URANIUM RECOVERY FROM DILUTE AQUEOUS
SOLUTIONS USING SILK FIBROIN**

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The silk which had a very important position over 4000 years period in life of humanity, is composed of the fibers of Larva secretion. The Bombyx mori silk is a material which have been studied in detail by different researchers. The amino acid units of fibroin protein that forms silk are linearly arranged. The amino acid and the peptide chain of the Bombyx mori silk fibroin has been shown as Gly-Ala-Gly-Ala-Gly-Ser-Gly-Ala-Ala-Gly-(Ser-Gly-(Ala-Gly) n)₈-Try sequence. There are some of investigations about the uptake of heavy metals Cu(II), Ni(II), Hg(II), Pb(II), Sn(II), (IV), Fe(III) from aqueous solutions using the silk mentioned. In this study, we investigated the recovery of uranium from aqueous solutions by using the silk fibroin .

First, the native silk was cut with scissors into short lengths (about 0.5 cm) . The coarsely shredded silk was degummed in 100 ml of solutions (pH=10) containing 0.5 g of soap and 0.05 g of Na₂CO₃ for 2 hours at about 100 °C. Native silk/solution ratio was selected as 2 g/100 ml. The degummed samples was washed thoroughly with deionized water, and air-dried. Thus, fibroin which was enclosed with sericin, is saved. The yield of degummentation which was found to be 76.31%, conforms to the literature values. The fibroin was then used for uranium uptake tests.

Then, by use of the standard uranium solutions, factors effecting uranium recovery, like; pH, uranium concentration, temperature, retention time and mixing rate were studied and the uranium uptake capacity of Bombyx mori silk fibroin was determined. The parameters investigated were as follows; pH=2-10, [U]: 10-500 ppm, temperature:25-60 °C and retention time 5-360 min. It has been found that it exhibits a maximum at pH=5, concentration of uranium 100 ppm, temperature 25°C, retention time 120 minute. Under this optimum conditions, the recovery efficiency of fibroin is found to be as 98% .

We also investigated elution of uranium from the loaded fibroin. For this purpose, different elution solutions were being tested. 1M CH₃COONH₄ was distinguished as the appropriate elution reactive. The optimum elution conditions were also determined and under these conditions the highest elution efficiency was obtained as 90 %. The uranium concentration in aqueous solution was determined spectrophotometrically by the PAR (4-(2-pyridylazo) resorcinol) method.

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Determination of Iodine in Drinking Water

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A recent medical investigation of the thyroid gland indicates the evidence of goiter in some area of Libya. To investigate this problem further, there is a need to determine the concentration levels of iodine in drinking water and food stuff with relation to the incidence of the endemic goiter. It is well known that iodine is essential for living organisms especially in the syntheses of thyroid hormones and that low iodine concentrations produce a high incidence of goiter. The main source of iodine in the south areas of this country is the drinking water. Whereas the people on the coast get their supply of iodine from seafood.

In this study drinking water samples have been analyzed for iodine levels using radiochemical neutron activation analysis technique. To determine the concentration levels of iodine in drinking water, this method is simple, fast and accurate. 2.5 ml of drinking water is pipetted in polyethylene capsule and 50 μ l of concentrated NH₄OH is added. The capsule is then sealed off and irradiated in a thermal neutron flux of 5 x10¹² n. cm⁻². sec⁻¹ for five minutes. The capsule is cooled in liquid nitrogen then opened and transferred into a separatory funnel containing 3 ml deionized water. The mixture is acidified with 20 μ l concentrated HCl followed by the addition of 5 ml of iodine solution in CCl₄ and shaken for at least one minute. The organic phase is transferred into a polyethylene test tube. Standard solution of iodine, prepared from KI, irradiated in the same way as the samples. Samples and standards were counted on a Ge(Li) detector and the peak area of the 442.7 KeV γ -ray from ¹²⁸I was integrated. The concentrations of iodine in the samples were calculated by comparison of the gamma peak areas between the samples and the standard.

Samples of water were collected from tap water and well water at different places in Tripoli city, Libya. Our preliminary results showed that, the concentration levels of iodine in drinking water revealed considerable regional differences, the area with higher iodine levels are near the coast and are decreasing as we move away from the coast. We are still investigating this further by analysing samples as far as 500 Km south of Tripoli. The possible links of iodine contents in drinking water with endemic goiter will be discussed.

Correlations Between Trace Element Levels in Headhair and Blood Components of Nigerian Subjects

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Abstract

Blood is well suited, by the nature of its distribution in all organs in the body, for use in assessing trace element burdens in human beings. Levels of essential trace elements are important in health and disease while those of elements of anthropogenic origin could be useful as indices of environmental pollution. Several works have been published on these subjects.

Hair is however, more easily and atraumatically obtained. It is therefore of interest to seek correlations between elemental levels in hair and blood in order to determine the extent to which results obtained using hair could be interpreted in terms of blood and body burden⁽¹⁻⁴⁾.

In this work, we have measured the concentrations of 22 elements in headhair and blood (whole blood, erythrocytes and plasma) using INAA technique. Correlations are then sought both between and within these using Pearson's product moment correlations and cluster analysis.

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Trace Element Composition of Headhair and Fingernails of Some Nigerians

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ABSTRACT

As part of our environmental monitoring and impact assessment program, we have been measuring baseline levels of elemental concentrations in various tissues in different groups of Nigerian subjects. In this paper we present the elemental concentrations measured by INAA for 30 elements measured in some or all headhair samples of 99 Nigerian subjects and 20 elements in the fingernails of some of the same subjects. Measurements of the skewness of the distribution of each element in both tissues confirm previous reports that many of them tend towards having a log-normal distribution⁽¹⁻³⁾. Thus their concentrations in the tissues may not be under any homeostatic control. The ranges of elemental concentrations together with the medians and the arithmetic and geometric means with their respective standard deviations are presented and compared with literature values for other populations^(2,3,4,5). Where significant differences ($p < 0.01$) have been found between paediatric subjects (age <15) and adults (age >15), or between different sexes, the different values have also been indicated.

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NUCLEAR AND TRADITIONAL METHODS FOR SOIL DETERMINATION IN SUGAR CANE INDUSTRY - VALIDITY OF SAMPLING PROCEDURE

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The soil carried as impurity in sugar cane supplies is of vital importance, occasioning losses in industrial efficiency and sugar recovery, and also increasing equipment wear rates. Several methods have been developed to measure soil level in cane, with reasonable accuracy and practicability, being used for industrial daily control, while others with accuracy as their principal characteristic are most preferred for technical researches.

Among the usual methods, emphasis may be given to two main types, the ash and separation methods, both presenting particular variations from one mill to another. The ash method estimates the soil level by the residual ash remained after a controlled incineration, while the separation method directly determines the soil amount manually withdrawn from the cane.

Nuclear methods have been developed, involving the measurement of elements present in much higher concentration in soil than in cane, such as iron and titanium¹, silicon and aluminium^{2,3}, and scandium⁴. Most of these methods have shown better accuracy when compared to the usual methods, however being more laborious and often requiring expensive equipments, nowadays avoiding their full application in routine control.

The mineral impurities in a sugar cane load are unevenly concentrated in some points, the sampling procedure therefore becoming a drawback for every method. Brazilian mills, in general, have been using an horizontal probe, with about 20 cm in diameter, which perforates each burden at three spaced positions, being the final sample a mixture of total extracted material. If more holes were done, the results would undoubtedly have much accuracy, but the sampling would take longer time to be accomplished. There must be a compromise between sampling and analysis methods, which means that the sampling process should be compatible with the attainable accuracy by the analytical method. It is not worthwhile concentrating efforts in increasing the accuracy of the analytical method if the sampling does not represent the load as a whole.

In this work, eighteen holes were done in three different loads, half for each side of the truck. The total portion of the hatch samples, approximately 10 kg each, were individually collected, disintegrated in a laboratory shredder and

handily homogenized before taking subsamples. Then, these materials were dried at 60°C, pulverized and analysed by either instrumental neutron activation and ash methods. The elements considered to ascertain the soil level by INAA were scandium, iron and thorium. The main idea was to verify the non-uniformity of mineral impurities distribution in the consignment and estimate the magnitude of errors occurred when different numbers of holes were taken, ranging from three to eighteen.

Results of both methods were compared in order to determine whether there is some real advantage in the activation over the ash method on account of sampling restrictions. In fact, noticeable variation was observed among the soil contents obtained for the eighteen analyses of a single consignment (Fig.1), pointing the need of an improved sampling procedure, if nuclear methods such as INAA have to be applied in cane quality control.

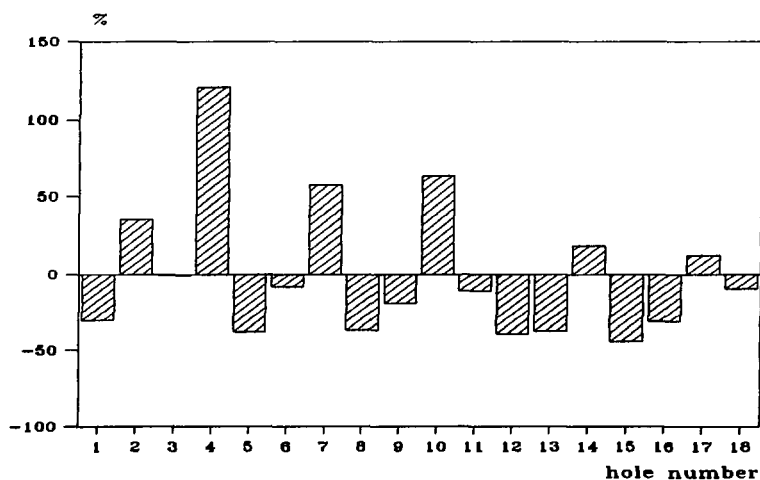


Figure 1. Soil content percent deviation from average of 18 samples of a single load.

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EVALUATION OF THE WASHING SYSTEM EFFICIENCY IN SUGAR CANE MILLS BY NEUTRON ACTIVATION ANALYSIS

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Towards high productivity of cane and its derivatives sugar and alcohol, the Brazilian agroindustry converted from manual to mechanical loading in the beginning seventies. The average soil levels in cane received at the sugar mill has shown a relatively sharp rise with a gradual upward trend since then. Moreover, as cane is burned while standing before harvest, sucrose exudates from its inner parts promoting more adherence of extraneous matter onto stalks. Soil in cane has an important impact on maintenance, operational costs and efficiency of the entire industrial process. Strategies have been explored for overcoming such adverse conditions, with substantial investments directed to the development and implantation of modern technology in the feeding sector of the production system.

Research approach to reduce soil levels in harvested cane therefore has been given high priority by sugar cane producers, addressing two main aspects of the soil-in-cane problem, by improving field and harvesting conditions so that soil intake is reduced and introducing a washing process. For this, huge amounts of water had to be promptly available followed by a special treatment process to reduce the organic and inorganic materials which are thoroughly incorporated into fed water. After several years, the present system was developed, which is the application of recycled water by means of aspersion at a rate of about $1 \text{ m}^3 \cdot \text{ton}^{-1}$ over the feeder tables.

The first aspect investigated in this work was the effectiveness of the washing operation in minimizing soil being carried together with stalks. Three different sampling times were accounted for by the first trial during the 1990/91 crushing season. At each time, four cane consignments from the same field area were sampled by the standard method of the Control Quality Payment. Briefly describing, it consists of each consignment material being composed by 3 hatch samples, which were disintegrated and well handily homogenized before taking representative subsamples for analysis. After passing through the washing system, the cane was conveyed upward into the shredder, from whose elevator material was taken at very short intervals composing the final prepared cane sample. A follow-up survey using only one consignment at each time was carried out to assess the accuracy and precision of the proposed method. In order to have a blank value, 15 kg of cane was randomly taken

from each load and carefully washed to remove all traces of soil. This clean cane was then grounded in a laboratory mill following the same process for all others industrial prepared cane, to achieve a high degree of sample homogeneity.

Instrumental neutron activation analysis was the nuclear analytical technique chosen for this work, with the elements Sc, Th, and Hf selected as soil tracers as described elsewhere^{1,2}. Most of these elements had their concentration highly reduced in a variable pattern after the washing operation, as can be seen in Fig.1. Consequently, on the basis of the differences between elemental concentration of integral and prepared cane, that is before and after washing, the feasibility of the method in ascertain the washing efficiency is demonstrated.

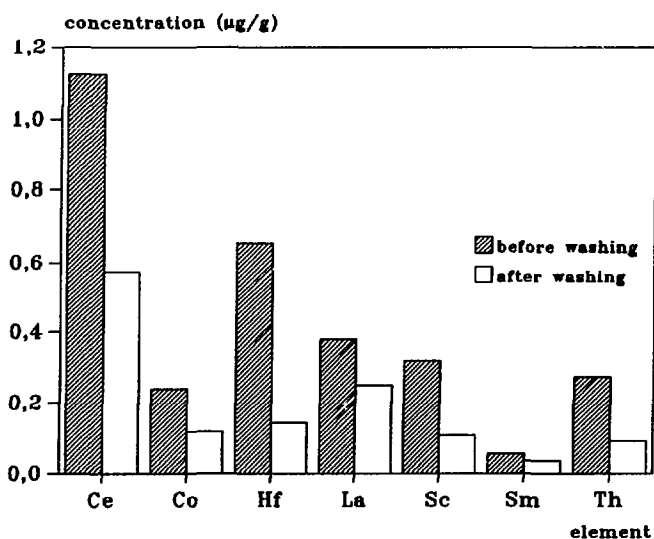


Figure 1. Trace elements concentration of sugar cane material before and after washing system.

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EFFECT OF ENHANCED BROMIDE INTAKE ON THE CONCENTRATION RATIO I/Br IN THE RAT THYROID GLAND

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Water solutions of potassium bromide in concentration of 10, 50 and 100 ppm Br were given to the groups (n=6) of young rats from the 22th till the 37th days of life. The control (n=6) group received bidistillated water. On the 15th day of the experiment the animals were killed by overdose of ether narcosis and the thyroid glands were collected. After lyofilization the samples were weighed and sealed in polyethylene foils. The determination of iodine was carried out by means of ^{128}I nuclide after short-time activation in nuclear reactor LWR-15 (Nuclear Research Institute, Řež) at power 8MW (irradiation time 1 min, decay time 4 or 15 min, measurement 10min). Bromine was determined in the same samples 10 days after short-term irradiation by means of ^{82}Br nuclide by 10 hours irradiation in a reactor core. Accuracy of determinations was assured by means of reference materials (Milk Powder NIST-SRM 1549 and Rye Flower IAEA-V-8).

From the results of the determination of bromine and

iodine in the dry weight of thyroid glands given in the table follows that with increased bromine concentration in the thyroid gland the concentration of iodine and also the ratio of concentrations I/Br decreases.

Concentration of Br in water (ppm)	T h y r o i d g l a n d		
	I (ppm)	Br (ppm)	I/Br
0	2475	27.6	89.7
10	2236	74.1	30.2
50	2154	321.1	6.7
100	1985	589.1	3.4

The weight concentration of 100 ppm Br in consumed water leads to the 32% atomic abundance of bromine in thyroid gland of experimental animals (related to the content of iodine and bromine). This result means that one bromine atom belongs to two atoms of iodine, while at the usual intake of bromine from the standard diet with the control group one atom of bromine belongs to 56 atoms of iodine (atomic abundance of bromine 1.7% only).

UPTAKE OF SILVER IN L-292 FIBROBLASTS MEASURED BY APPLICATION OF AG 110M

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Culture media for tissues contain many complexing agents as amino-acids and proteins. The effect of these substances on the uptake of Ag - ions into fibroblast cells was tested by adding glutamine. By application of Ag 110m as tracer it was possible to determine quantities between 1 and 10000 ng Ag in the tissue.

For the first setup, the concentrations of Ag in the culture media were 0.1, 1 and 10 $\mu\text{g} / \text{ml}$ to test the cytotoxic effect of the silver ions. To exclude the influence of radioactivity, we took the same tracer activity for all three Ag concentrations. The fibroblasts, 4 samples for each silver concentration, were incubated for 72 hours, then centrifuged and washed 3 times with fresh culture medium, which was also measured to prove that there was no soluble surface contamination left. The centrifuged cell residue was measured by γ - spectroscopy. The proliferation of the cells was examined by counting under the microscope and the silver uptake is normalized to 10^6 cells. The results showed for the lower concentrations no or neglectible influence on the proliferation. However, 10 $\mu\text{g} \text{ Ag} / \text{ml}$ were lethal.

The next step was the addition of glutamine to the culture medium. The procedure was the same as described before and it could be shown that the uptake of Ag into the fibroblasts was significantly higher in the samples with glutamine than in those without. The cytotoxic effects increased accordingly. This effect was not reproducible in all experiments. We conclude that the experiments should be carried on to quantify the influence of the complexing agent on the toxicity of metal ions and its threshold concentration.

A SURVEY OF TRACE ELEMENTS IN FRESH-WATER FISH AND RICE ALONG THE HAN-RIVER BY NEUTRON ACTIVATION ANALYSIS

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For the case study of environmental contamination, the Han River is one of the most interesting areas in Korea, because it flows through Seoul, the most urbanized and industrialized city. We have been investigating the river contamination non-periodically since 1973 by instrumental and/or radiochemical neutron activation analysis of crucians which reflect the water contamination directly in their bodies. In those previous investigations, we were interested in observing the variations of elemental contents as functions of sampling sites and years. The sixteen elements(Hg, Cd, As, Br, Cu, Cr, Rb, La, Cs, Na, K, Se, Hf, Fe, Zn and Co) were monitored at 10 sampling sites along the Han River. Our general results up to now can be summarized as follows:

- 1) The most upper part of the river shows the lowest contents of 16 elements in the 10 sampling sites and the similar values in three investigations. This fact could be explained by the fact that the site is least populated and have a small chance of contamination by industries and inhabitants.
- 2) Among the 16 elements, 7 elements of Na, K, Se, Hf, Fe, Zn and Co show similar contents regardless of the sampling site and year, which means these elements do not have any relation with environmental contamination.
- 3) The contents of the other 9 elements Hg, Cd, As, Br, Cu, Cr, Rb, La and Cs show systematic trends with the sampling sites and years: they increase as the river goes down and decrease as the sampling year come to the present. This trend is significant in the case of Hg, Cd and As. These results mean that the middle and lower part of the river, which had been seriously contaminated, have been decontaminated drastically but are still contaminated, especially by those three toxic elements.

In the practical point of view, rice is by far more interesting than crucian, because it is the major source of Korean nutrition. In this article, the result of our rice investigation is presented and compared with that of crucian to see if there is any correlation. The rice samples were collected from 7 sampling sites near crucian sampling sites in 1993. About 3 g of each rice sample was put into cleaned quartz tube and irradiated with two monitors of Co and Au at the rotary specimen rack of TRIGA Mark III reactor for 30 hours. The irradiated sample was counted three times after 2 days, 1 week and 1 month cooling, respectively. For Hg and Cd, chemical separation was performed when their contents are under the detection limit of instrumental analysis. The activity of each nuclide in the gamma-ray spectrum was calculated with PIAD(Peak Identification and Activity Determination) computer code. The content of each element in a sample was calculated by the single comparator method using the two monitors.

LEVELS OF SOME TRACE ELEMENTS IN SERUM OF PRAGUE
INHABITANTS MEASURED BY INAA

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Sera of random selected 240 persons of both sexes in the age of 6, 10, 13, 18-35, 36-49, and 50-65 years were analyzed by instrumental neutron activation analysis (INAA) for the purpose to assess state of some trace elements in Prague population, their sex and age differences and to compare their values with those of inhabitants of rural region of Central Bohemia.

Nonheme iron, zinc, selenium, rubidium, cesium and scandium were determined by the relative method of comparison with inorganic standards irradiated and treated under identical conditions. Quality assurance was checked by analyses of IAEA reference material H-4 (animal muscle) and reference human serum of the second generation (kind gift of prof. Versieck, Ghent, Belgium).

Analytical system for gamma-spectroscopy from Silena, Milano, consisted of multichannel analyzer MB 7329/S with coaxial HPGc detector (relative efficiency 34.6% and FWHM 1.87 keV for 1.33 MeV). Quantitative analyses of peaks were performed by the program Silgamma.

From the measured elements with demonstrated essentiality (Fe, Zn, Se) iron and zinc proved small but significant differences in serum of men in Prague and in the countryside of Central Bohemia. Selenium on the other hand proved age dependent changes and its concentration was one of the lowest in Europe in all analyzed groups. No differences were found between males and females. Age dependent changes of serum concentrations were also found in the case of rubidium. Statistical results will be tabulated and changes illustrated by graphs.

SEPARATION AND PURIFICATION OF A SELENOPROTEIN IN THE CYTOSOL FRACTION OF BOVINE KIDNEYS

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Studies on selenoproteins in the nuclei fraction of bovine kidneys have been reported in the literature from our laboratory over the last few years. The present paper, however, deals with the selenoproteins in the cytosol fraction of bovine kidneys.

Selenium in all samples and standards was determined *via* the 162-keV gamma-ray of its short-lived (half-life = 17.4 s) nuclide ^{77m}Se using the cyclic activation system of the Dalhousie University SLOWPOKE-2 reactor facility. The instrumental neutron activation analysis (INAA) method for selenium consisted of irradiations for 30 to 60 s at a flux of $5 \times 10^{11} \text{ n cm}^{-2} \text{ s}^{-1}$, decay for 10 s, and counting for 30 to 60 s depending upon the salt content of the sample. Gamma-ray spectra of the irradiated samples were recorded using an Aptec hyperpure Ge detector (FWHM of 2.08 keV at the 1332-keV photopeak of ^{60}Co , peak-to-Compton ratio of 35:1, and an efficiency of 10%) connected to a Nuclear Data ND-66 model 4096-channel pulse height analyzer.

The quality assurance program involved various steps including replicate analysis of elemental comparator standards and certified reference materials (CRM) on a routine basis, use of control charts, *etc.* Plasma grade selenium standard solution (SPEX) was used as comparator standards. The internal quality assessment control chart showed a variation of less than $\pm 5\%$ from the average for all values. A number of CRM from the U.S. National Institute of Standards and Technology, International Atomic Energy Agency, National Institute of Environmental Sciences of Japan, *etc.* Our values agreed within $\pm 5\text{-}7\%$ of the certified values. A detection limit of 3 to 5 ppb can be achieved for most samples.

A fresh sample of bovine kidney was minced and homogenized in 0.01M HEPES buffer at pH 7.4. Dialysis through bags of MWCO of 3 500 showed that $>95\%$ of selenium was bound to macromolecules. The kidney was separated to five subcellular fractions using a standard procedure. The purity of these fractions was evaluated by assaying specific activities of marker enzymes; lactate dehydrogenase was used for cytosol. The cytosol fraction was found to be quite pure and used as such. Hemoglobin was separated from the cytosol fraction prior to any further treatment of the fraction.

A sample of the cytosol fraction was concentrated using Aquacide, applied to an anion exchange column of DEAE-Sepharose, and proteins eluted by 0.3M NaCl. At least five protein peaks containing selenium were identified. The fractions from the most prominent peak containing the highest amount of selenium was further concentrated using Aquacide and applied to a gel filtration column. Polyacrylamide gel electrophoresis in non-denaturing as well as denaturing buffer systems and isoelectric focusing experiments were carried out to evaluate the purity of the selenoprotein and to determine its molecular weight and isoelectric point. Details of the various experiments done and results obtained will be presented.

ENERGY DISPERSIVE X-RAY FLUORESCENCE ANALYSIS APPLIED TO BIOMONITORING ON ALPS.

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ABSTRACT

In this paper we show the results of a research in progress at the Istituto di Fisica Generale Applicata - University of Milan on the natural and anthropic elements determination in biological indicators.

The analytical technique used is the Energy Dispersive X-Ray Fluorescence.

Mosses and lichens have been chosen for our monitoring because of their ability of absorbing metals directly from the atmosphere; in fact many authors point at this as the preferential exchange way with the environment in respect to the possible interchange with the substratum.

This kind of biomonitoring has also other advantages:

- the "bioaccumulation" make easier the identification of those pollutant elements which can be found in atmosphere in very low concentrations;
- the "bioindicator" gives a time-integrated measure and furthermore is possible to cover wide interesting areas without the high costs necessary for a conventional monitoring campaign.

These characteristics of mosses and lichens, besides the fact that they are greatly diffused in the investigated areas, lead us to use them for a preliminary pollution mapping on Alps and to verify the confidence of EDXRF applied to this field.

The samples, a hundred in total, have been picked up most on Alps (in Valmalenco and Valtellina) and on the hills around Como (pre-Alps); in addition a group of mosses was from the Monza park, near Milan.

Our experimental apparatus consists of an X-ray tube generator with a Rhodium anode and a Si(Li) detector with a Be-window (8 μm thick). We have calibrated the spectrometer in particular for the following elements: Mg, Al, Si, S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb using either standards from the Community Bureau of Reference either from the National Bureau of Standards.

The minimum detection levels, in the conditions chosen for the measurements, are of the order of few p.p.m. (part per million of dry weight) for trace metals.

Analyzing the whole data set we can observe that some of the detected elements have a natural origin as, for example, Mg, Si, Ti, K, Ca; while others are clearly due to anthropic pollution as S, Pb, Br, Ni, Zn.

It is also interesting the fact that elements with natural origin show nearly constant concentrations in different areas.

On the contrary, the anthropogenic elements concentrations vary going from urban zones, as the area near Milan and around Como, towards alpine ones where their levels appear to be lower increasing the altitude.

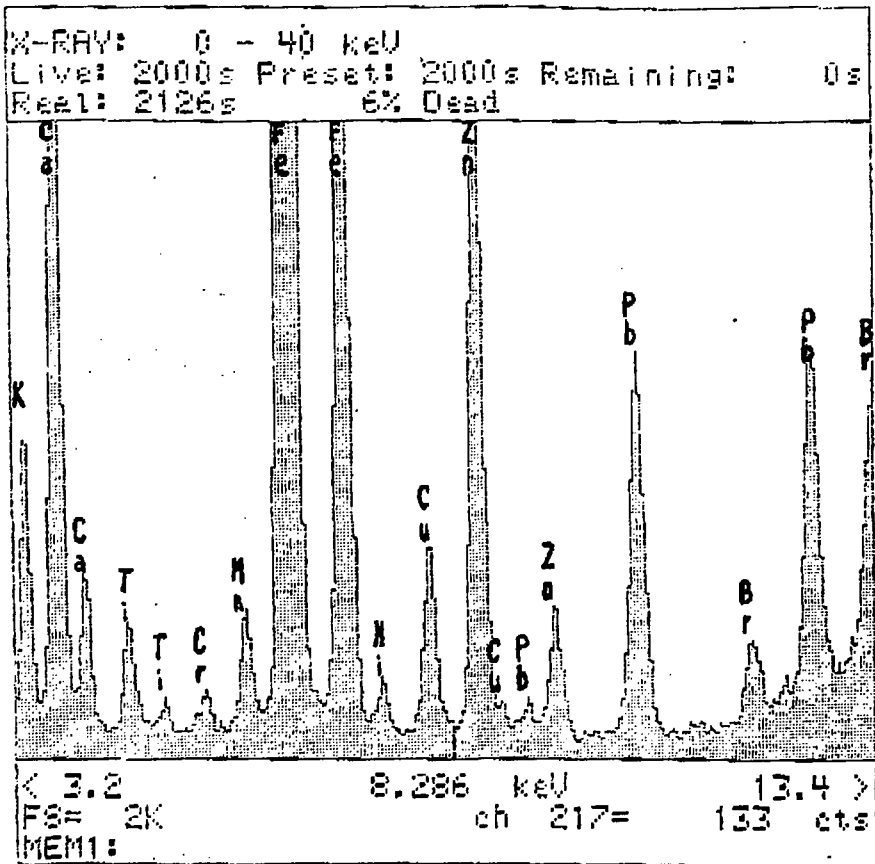


Fig. 1: Spectrum of a moss sampled on the hills around Como

A PC BASED COMPUTER PROGRAMME FOR QUALITY ASSESSMENT OF INAA RESULTS OF EMISSION AND AIR PARTICULATE SAMPLES

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The Quality Assessment (QAS) is overall system of activities to provide assurance that the Quality Control (QC) system works properly and effectively. QAS techniques are used to monitor the precision and accuracy of a system operating in a state of statistical control. Some QAS techniques can be applied only occasionally (e.g. participation in interlaboratory tests), but other can be used routinely (e.g. use of control samples, reference materials, etc.)¹⁻⁶.

QAS system for which the programme is designed is based on comparison of results of analysis of duplicate aliquots of suitable Certified Reference Material (CRM) analysed together with samples⁷⁻⁸. Such CRM is chosen to match matrix and analyte levels of samples as closely as possible. Usually, the following steps can be followed: sample preparation for irradiation, irradiation, preparation for radioactivity counting, counting and result evaluation. The result of CRM analyses are evaluated and compared with CRM certified values and their uncertainties and with control limits of the QAS based on previous determinations.

The reference material used as quality control material in each batch allows us to check batch to batch repeatability, the accuracy of results for the analysed batch and long-term stability of the analytical system. Computer programme enables to prepare the working file from the result file, compute all warning and control limits for tests, carry out the tests, produce protocols and store results into the database results of analyses. A control chart can be displayed in the graphic part of the programme together with box plot and frequency histogram, and also the control chart of range of duplicate determinations. The charts for up to 5 various analytical lines can simultaneously be displayed for "visualisation" of possible discrepancies. Generally, all results are stored and used for calculation of the limits. However, under certain circumstances it might be desired to make changes in the CRM or result databases. This can be done using the database manager.

The five following tests are done in the presented QAS programme: combined QAS, repeatability, robust statistics, accuracy and repeatability within batches. First four tests are used to check particular results of CRM analysis and their mean, the test one evaluates range of CRM replicates. The tests are based on the philosophy of control charts with control and warning limits.

Combined QAS test combines a check of repeatability and accuracy. It has been derived from the test used in the Health and Environmental Chemistry Group at the Los Alamos National Laboratory⁹. Warning and control limits are set to the 2σ , respectively 3σ distance from reference value. Sigma, here the " σ " represents standard deviation of the mean of previous determinations propagated by the uncertainty of the reference value. If no reference value is available, arithmetic mean of all previous results is used as the reference value. In this case the test has the same meaning as the **test of repeatability**.^{10,11}

The empirical distribution of control results of CRM analyses does not necessarily conform with normal distribution, because outliers can occur. In such a case **robust statistics**¹² is a more appropriate approach. In addition, this test can be used to define tolerance bounds from only 4 control results of CRM analyses stored. From these results *median* is calculated and warning limits are placed as the *first and third quartiles*. Control limits are derived from these values too.

Accuracy test check the difference between result and reference value with its uncertainty and statistic error of counting.

The **repeatability within batches** is tested by the evaluation of range of results obtained in the tested batch and mean ranges of previous results¹⁰.

The programme described is routinely used to assure the quality of analytical results especially for air particulate samples. For this purpose NIST SRM 1648 Urban air particulate is the most frequently used RM. The results of QAS tests approve that the analytical system works under statistical control.

The programme can be used for INAA of various materials. Its application for NAA with radiochemical separation is limited due to problems related to the chemical yield of separation, splitting of databases according various separation methods, etc.

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DETERMINATION OF TRACE ELEMENTS IN NORMAL AND DIABETIC WHOLE BLOOD BY NEUTRON ACTIVATION ANALYSIS.

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The concentration of 10 trace elements in samples of normal and diabetic whole blood were investigated by neutron activation analysis. These elements are Al, Co, Cr, Hg, Mg, Mn, Rb, Se, and Zn. Radiochemical methods were applied for separation of Al, Cu, Mg and Mn. The results are expressed in ppm and in agreement with reported values. Co, Cr, Se and Zn show lower values in diabetes than in the normal blood samples.

STUDY OF TRACE ELEMENTS IN BLOOD CANCER BY INAA

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ABSTRACT

Neoplastic tendency in a normal cell is directly influenced by changes in enzymatic activities within that cell, which in turn could be significantly affected by the trace element composition of the cell. Previous works using cancerous tissues and whole blood have shown that several elements such as Zn, Cu, Mn, Co, Se and Br are elevated while others including Fe, Cs, I and Sr are depressed within the cells of cancer patients. In the present work, we study the distribution of trace elements in both intracellular and extracellular compartments using blood obtained from 24 patients suffering from blood-related cancer, including Burkitts, Lymphomas, and CML. The samples were separated into the plasma and erythrocytes components and analyzed by Instrumental Neutron Activation Analysis for some essential trace elements. Elemental levels in the patients were then compared with values obtained from 70 normal subjects used as controls. Our results show that Br, K and Zn are significantly elevated in the erythrocytes of the cancer patients, relative to the normal controls while Fe is significantly depressed in the same blood component. In the plasma, Br is again significantly elevated in the patients while Fe and Zn are significantly depressed. These will be further discussed and compared with previous findings.