

Nuclear Analytical Techniques for Detection of Rare Earth Elements

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Abstract: Nuclear analytical techniques with their broad band of applicability to almost all matrix types and their exceptional sensitivity to many elements are an indispensable tool for environmental research. Neutron activation analysis (NAA) appears to be an attractive technique for determining heavy metals and REEs present in environmental samples; soil, sediments, plants, water, air particulates, etc. NAA is frequently used to obtain data for geological materials. Usually this technique provides good results within a reasonable timescale. The accuracy and the limit of detection of the (REEs) data using INAA depends, however, strongly on the type of material analyzed and on the content of several interfering elements which provide either a high background or overall activity and therefore, may prohibit reliable analysis. Nuclear analytical techniques, such as instrumental neutron activation analysis (INAA), radiochemical neutron activation analysis (RNAA) and X ray fluorescence (XRF), which are generally considered as reference methods for many analytical problems, are useful as well. However, due to methodological limitations, they can, in most status, only be applied after pre-concentration and under special irradiation conditions. Finally, the purpose of this review is to cover firstly, short overview about rare earth element. The second part dealing with the nuclear analytical techniques in details with case study as application of the technique and the non-nuclear analytical techniques are also included.

Keywords: Rare Earth Elements, INAA, XRF, ICP-MS

1 Introduction

1.1 What Are The Rare Earth Elements?

The rare-earth elements (REE.s) are defined as a group of chemical elements composed of scandium, yttrium, and the lanthanides. The lanthanides are a group of 15 chemically similar elements with atomic numbers 57 through 71. They form a series of 17 chemically similar metals.

It typically occurs in minor amounts because of its smaller atomic and ionic size. The seventeen rare-earth elements are: scandium (Sc), yttrium (Y), lanthanum (La), cerium (Ce), praseodymium (Pr), neodymium (Nd), promethium (Pm), samarium (Sm), europium (Eu), gadolinium (Gd), terbium (Tb), dysprosium (Dy), holmium (Ho), erbium (Er), thulium (Tm), ytterbium (Yb), and lutetium (Lu) see Fig. 1.

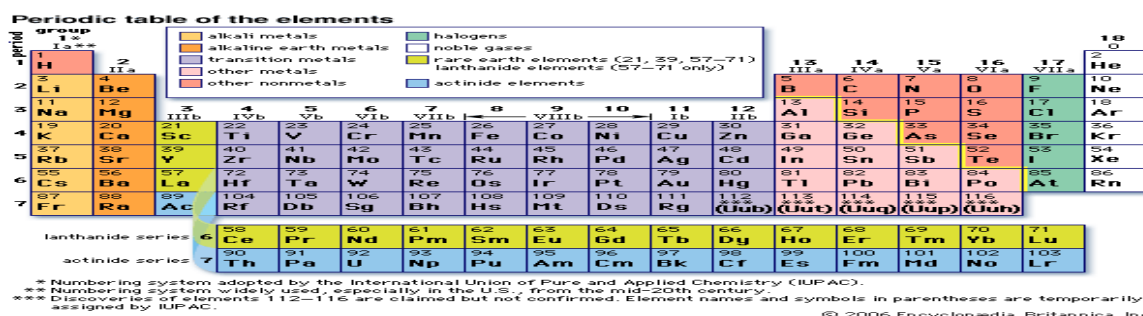


Fig 1. Periodic table of elements

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The rare-earth elements are not rare in nature. They are found in low concentrations widely distributed throughout the Earth's crust and in high concentrations in a considerable number of minerals. In addition, they are also found in many meteorites, on the Moon, and in the Sun. The spectra of many types of stars indicate that the rare-earth elements are much more abundant in these systems than they are in our solar system. Even promethium-147, which has a half-life of only a few years, has been observed in certain stars. Cerium is reported to be more abundant in the Earth's crust than tin, and yttrium and neodymium more abundant than lead [1-3].

The rare-earth elements are found as mixtures in almost all massive rock formations, in concentrations of from ten to a few hundred parts per million by weight. In general, it has been found that the more basic (or alkaline) rocks contain smaller amounts of rare earths than do the more acid rocks, and it is believed that as these molten basic rocks into the more acidic rocks, the rare earths are partially extracted into the more acidic rocks. Also, as this extraction takes place, the rare-earth elements of lower molecular weight (lanthanum, cerium, praseodymium, and neodymium) are taken up to a greater extent than the heavier elements [4-6]. The relative abundance of rare earths in the rocks on the Moon is of great interest because of what it is expected to reveal about how the Moon was formed [6-8].

The average content of rare-earth elements found in meteorites (chondrites) and in three types of common rocks is listed in the Table 1. It is now generally accepted that the relative values of the rare-earth elements in chondritic (granular) meteorites represent their overall relative abundance in the Cosmos. The elements with even atomic numbers are much more abundant than the odd-numbered elements. Such information, together with the relative abundance of their isotopes, is of critical importance to astrophysicists because it bears on theories of the origin of the universe and the genesis of the chemical elements.

Table 2 presents an overview of the rare earth elements in the earth crust, as described in references. The earth crust consists of the first 40 km of the earth divided in upper crust (0-20 km) and lower crust (20-40 km) [9-12].

1.2 Properties of the Rare Earths

- 1-The REEs are silver, silvery-white, or gray metals.
- 2- The metals have a high luster, but tarnish readily in air.
- 3- The metals have high electrical conductivity.
- 4- The REEs share many common properties. This makes them difficult to separate.
- 5- There are very small differences in solubility and complex formation between the rare earths.
- 6- The rare earth metals (REEs) naturally occur together in minerals (e.g., monazite is a mixed rare earth phosphate).
- 7- The REEs are found with non-metals, commonly in the 3+ oxidation state.

There is little tendency to vary the valence (Europium also has a valence of 2+ and cerium also a valence of 4+.) [13-15].

Table 1. Abundance of the Naturally Occurring Rare-Earth Elements in ppm [1].

Element	chondritic meteorite	North American Shales	Western American granites	Kilauea basalt
Y	1.800	35.00	31.00	----
La	0.300	39.00	49.00	10.50
Ce	0.840	76.00	97.00	35.00
Pr	0.120	10.30	11.00	3.90
Nd	0.580	37.00	42.00	17.80
Sm	0.210	7.00	7.20	4.20
Eu	0.074	2.00	1.25	1.31
Gd	0.320	6.10	5.80	4.70
Tb	0.049	1.30	0.94	0.66
Dy	0.310	----	-----	3.00
Ho	0.073	1.40	1.22	0.64
Er	0.210	4.00	3.20	1.69
Tm	0.023	0.58	0.53	0.21
Yb	0.170	3.40	3.50	1.11
Lu	0.031	0.60	0.52	0.20

Table 2. Overview of the rare earth element contents in the earth crust in ppm.

Z	Element	Lower crust [9]	Lower crust [10]	Upper crust [11]	Lower crust [12]
21	Sc	22	14	16	22
57	La	30	44	30	39
58	Ce	60	75	60	66.5
59	Pr	8.2	7.6	6.7	9.2
60	Nd	28	30	27	41.5
62	Sm	6	6.6	5.3	7.05
63	Eu	1.2	1.4	1.3	2
64	Gd	5.4	8	4	6.2
65	Tb	0.9	1.4	0.65	1.2
70	Yb	3	3.4	2	3.2
71	Lu	0.5	0.6	0.35	0.8

1.3 Application of Rare Earth Elements

The properties of the rare-earth elements in the form of their metals, alloys, or compounds or some combination are so varied as to make them valuable for many applications [16].

Use in Nuclear Technology

Europium, gadolinium, and dysprosium have large capture cross sections for thermal neutrons; they absorb large numbers of neutrons per unit of area exposed. These elements, therefore, are combined into control rods used to regulate the operation of nuclear reactors or to shut them down. Yttrium dehydrate is used as a moderator in reactors to slow down neutrons.

Certain rare earths are also used in shielding materials because of their high nuclear cross sections. Scandium metal is used as a neutron filter [1].

Use in the Glasses Industry

Glasses containing lanthanum oxide have very high refractive indexes and low dispersions. Such glasses are used in complex lenses for cameras, binoculars, and military instruments for the purpose of correcting spherical and chromatic aberrations. Rare-earth oxides often are added to glass melts in order to produce special glasses. Neodymium is added to some glasses to counteract the yellowish tint caused by iron impurities [1].

Use in the Metallurgical Industry

The addition of pure rare-earth elements to magnesium increases its high-temperature strength and resistance to slow deformation under prolonged use. This alloy also makes better castings if small amounts of zirconium or other metals are added, and such alloys are used in jet-engine and precision castings. The addition of small amounts of rare earth elements to aluminum has also been reported to give better casting [1].

Use in Television Industry

It has been found that if a small amount of europium (Eu_2O_3) is added to yttrium oxide (Y_2O_3), it gives a brilliant red phosphor. Color television screens utilize red, green, and blue phosphors. In the past, a zinc-cadmium sulfide was used as the red phosphor, but it was not completely satisfactory [1].

Other Applications

Yttrium - iron garnets are synthetic high melting silicates that can be fabricated into special shapes for use in microwave filters in the communications industry. The use of barium phosphate - europium phosphor in a sensitive X-ray film that forms satisfactory images with only half the exposure [1].

2 Nuclear Analytical Techniques for Rare Earth Elements

Nuclear techniques have become well-established important tools, complementary to non-nuclear methods. These nuclear analytical techniques provide a wealth of information some of which is difficult or impossible to obtain by other techniques. The type of information attainable as well their typical features are compared to those of non-nuclear techniques. The features are: (i) the underlying physically different basis for the analysis, (ii) isotopic rather than elemental determination, (iii) mostly

no effect of electrons and molecular structure, and (iv) penetrating character of nuclear radiation.

What Are Nuclear Analytical Techniques?

The Narrow Definition

Nuclear analytical techniques (NAT's) deal with nuclear excitations, electron inner shell excitations, nuclear reactions, and/or radioactive decay, e.g. instrumental neutron activation analysis (INAA), particle-induced X-ray emission (PIXE), and X-ray fluorescence (XRF). On the other hand, mass spectrometry does not involve ionizing radiation and consequently not directly considered as NAT's.

The Comprehensive Definition

In principle nuclear techniques are based on properties of the nucleus itself, to non-nuclear techniques which use properties of the atom as a whole, mentally as well as practically no sharp borderline can be drawn between nuclear, non-nuclear techniques. Mass spectrometry deals with ionized atoms, and rarely with the bare nucleus; however, the signal is determined by the mass differences of the nucleus. Some nuclear analytical techniques are not only based on nuclear properties, but on a combination of nuclear and electronic properties, either within a single technique, or within the two techniques.

PIXE as one of the varieties of ion beam analysis deals with electron shell ionization, and thus is formally a non-nuclear technique. However, since PIXE requires almost the same equipment as other varieties of ion beam analysis, PIXE is mostly incorporated in the domain of the nuclear physicist and practically it is considered here as a nuclear.

Whereas in non-nuclear techniques isotopes of the same element generally cannot be distinguished, in nuclear techniques they can, and actually specific isotopes are measured instead of elements, generally consisting of a mixture of two or more isotopes. Both nuclear techniques and isotope techniques will be comprised by the terminology "nuclear analytical techniques", abbreviated as NAT's.

Physical Basis and Classification of Nuclear Analytical Techniques

Nuclear parameters that serve as basis for NAT's are mass, spin and magnetic moment, excited states and related parameters, and probability of nuclear reactions. When dealing with a radioactive isotope, also the properties of a half-life and the types and energies of the emitted radiation are involved [17-20].

For trace quantities of different REEs the determination can be performed by

- 1) Instrumental Neutron Activation Analysis, INAA,
- 2) Radiochemical activation analysis, RNAA
- 3) X-Ray Fluorescence Spectrometry, XRF,

In the following, these techniques will be discussed in more detail

2. Instrumental Neutron Activation Analysis (INAA)

Many analytical methods have been developed to determine REE. In early days most basic gravimetric method [21] and polarographic method [22] was widely used. Some other modern instrumental analysis such as atomic emission method (AES) atomic absorption spectrophotometer (AAS) X-ray fluorescence) ion chromatography (IC) [23] was also selected. Recently, more powerful instrument induced coupled plasma mass has been used for trace samples [24]. In order to use these methods to analyze the REE, the samples must be in a form solution before it can be analyzed which process sometime becomes a burden if the sample is difficult to dissolve. Instrumental neutron activation analysis may be considered to be an ideal technique to solve this problem. In the following the instrumental neutron activation analysis INAA technique will be outlined in details

Method Description

Neutron activation analysis was discovered in 1936 when Hevesy and Levi found that samples contain rare-earth elements become highly radioactive after exposure to a source of neutrons. From this observation they recognized the potential of use measurement of the induced radioactivity to favour both qualitative and quantitative identification of the elements present in the sample. The NAA method is based on the detection and measurement of characteristic gamma-rays emitted from radioactive isotopes produced in the sample upon irradiation with neutrons [2]. The sample is first weighted into a plastic or quartz container and sealed. This step avoids the contamination of the material. It is then placed near the core of a nuclear reactor as a neutron source and irradiated for a suitable period of time. If a neutron approaches the nucleus of an atom, it may be absorbed. When this happens, the element will become a different isotope of the same element. This new isotope is sometimes unstable (radioactive) and decays by emitting gamma-rays [25-27]. Since neutrons activate the nucleus of an atom but not the electron shell, this method sees the total elemental content regardless of oxidation state, chemical form or physical location. Neutrons have no charge and therefore will pass through most materials without difficulty. This means that the center of the samples becomes radioactive as the surface. After the irradiation, the sample is allowed to decay, and then it is counted using gamma-ray spectrometers.

Typically, unknown samples together with standard materials of known elemental concentrations are irradiated with thermal neutrons in a nuclear reactor. After some appropriate decay period, high resolution gamma-ray spectroscopy is performed to measure the intensity and energies of the gamma-lines emitted. The position of each peak determines the energy of gamma ray (identifying the responsible element), and the area under the peak is proportional to its concentration [28-31].

The sequence of events occurring during the most common type of a nuclear reaction used for NAA, namely the neutron capture or (n,γ) reaction, is illustrated in figure (2). When a neutron interacts with the target nucleus via an inelastic collision a compound nucleus is formed in an excited state. Through emission of one or more characteristic prompt gamma-rays the compound nucleus will almost instantaneously de-excite into a more stable arrangement. In many cases this new configuration yields a radioactive nucleus which beta-decays and then de-excites by emission of one or more isotope characteristic delayed gamma-rays. This occurs at a much slower rate than the prompt emission according to the unique half-life of radioactive nucleus [32].

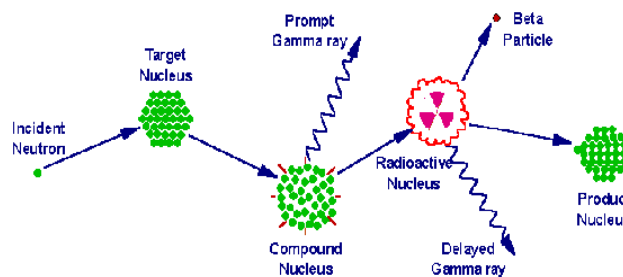


Fig 2. Illustration of the process of neutron capture by a target nucleus followed by the emission of beta-particles and γ -rays

Consequently, NAA is divided into two categories, with regard to the measurement time:

- (1) Prompt gamma-ray neutron activation analysis (PGNAA) where measurements take place during irradiation.
- (2) Delayed gamma-ray neutron activation analysis (DGNAA) where the measurements follow radioactive decay. The DGNAA is more common; thus when one mentions NAA it is generally assumed that the measurement of the delayed gamma rays is intended.

Applications of the INAA Technique

Neutron activation analysis is one of the most potent techniques for multi-element determinations. It has found diverse applications in studies requiring non-destructive analysis of samples and/or high sensitivity for the element of interest.

Neutron activation analysis techniques are widely used in

the scientific, engineering, environmental and industrial disciplines such as:-Biochemistry, Geological Science, Semiconductor Materials, Soil Science, Environmental Restoration, Epidemiology, Forensic Investigation , Archaeology, Air Filter Analysis and Water.

Advantages of the INAA Technique

Activation analysis measures the total amount of an element in a material regardless of the chemical or physical form and it has the following advantages [32].

- 1- Samples for NAA can be liquid, solid, suspensions, or glass. Samples do not need to be put into solution or to be vaporized (i.e. no pre-treatment).
- 2- NAA is a micro analytical method, only a few milligrams of samples are required.
- 3- NAA is a multi-element procedure. More than 30 elements can be measured simultaneously in a given sample gamma-spectrum without changing or altering the apparatus as necessary in atomic absorption.
- 4- NAA is fast in that for many elements, many samples can be irradiated at a given time and counted later on a given decay schedule.
- 5- NAA is non-destructive in that the integrity of the sample is not changed in any manner by prechemistry or the addition of any odd material before irradiation.
- 6- NAA is also totally unaffected by the presence of organic material in the sample, a significant problem in many types of conventional chemical methods.
- 7- A disadvantage of this technique concerns the time to complete a full analysis.

Sensitivities Available by INAA Technique

By neutron activation analysis technique, the sensitivities obtained is a function of the neutron cross section of the element, neutron flux, time of irradiation, resolution of the detector, matrix composition and the total sample size. Hence, increased neutron fluxes, optimized irradiation times and the advances in nuclear detector technology with respect to increased efficiency and resolution, have pushed the detection limits of most elements of interest to very low levels, often not readily achievable by other analytical techniques. Table 3 shows the estimated detection limit of rare earth elements in units of picograms for INAA using gamma ray spectrometry. Relevant nuclear data for the rare earth nuclides of interest are given in table 4.

Interferences in Measuring REE

In neutron activation analysis (NAA), the following three

Types of interfering nuclear reactions should be taken into account [35, 38]:

Table 3. Estimated detection limits for rare earth elements by using INAA and gamma-ray spectrometry for an irradiation with a neutron flux of $10^{13} \text{ n/cm}^2 \text{ .s}$ [33].

Sensitivity (picograms)	Elements
1	Dy, Eu
1-10	Lu
10-100	Ho, Sm,
100-1E3	Er, La, Sc, Tb, Tm, Yb
1E3-1E4	Ce, Gd, Nd
1E4-1E5	Y

1. Nuclides produced by (n, p) and (n, α) reactions on the other heavier elements which are often the same as the nuclide produced by the (n, γ) reactions.
2. Fission products of uranium which are the same as the radionuclides for the determination of some rare earth elements (REEs), zirconium, ruthenium and molybdenum
3. Daughter nuclides which succeed the (n, γ) reactions of different target elements and become the same as radionuclides of interest.

The isotopes ^{140}La , ^{141}Ce and ^{147}Nd commonly used in the activation analysis of the corresponding elements are also produced by fission of ^{235}U . For each of these radioisotopes an interference factor, defined as the activity produced by irradiating 1 μg of pure natural uranium divided by the activity produced by irradiating 1 μg of the chosen element, was determined. Tables 5-6 summarize the concentrations of the rare elements in some geological samples.

2.2 Radiochemical Neutron Activation Analysis (RNAA)

While instrumental neutron activation analysis (INAA) is more popular than RNAA (radiochemical neutron activation analysis). Owing to its simplicity, RNAA can determine much lower concentrations than INAA. Because the interferences from other radionuclides are reduced considerably. Whereas INAA involves only activation and activity measurement. RNAA also includes dissolution of the sample and chemical separation of the sample solution. In some cases, the interferences can be removed by decay (cooling) and INAA can be used.

However, in many cases the IRNs (indicator radio nuclides) are shorter lived than those of the interferences and in other cases the required decay time are too long to be practical. Owing to the chemical dissolution, separation and recovery

Table 4. Nuclear properties of the rare-earth nuclides [34].

Stable isotopes	Abundance %	Activation product	Half-life	γ -energy, keV	Detection limit, ppm
La-139	99.9	La-140	40.2 h	1596	0.2
Ce-140	88.5	Ce-141	32.5 d	145	0.3
Pr-141	100	Pr-142	19.13h	1575.3	6.2
Nd-146	17.2	Nd-147	11 d	531	0.09
Eu-151	47.8	Eu-152	13.3y	1408	0.03
Sm-152	26.7	Sm-153	47 h	103	0.17
Gd-158	24.84	Gd-159	18.5h	363.5	8
Dy-164	28.2	Dy-165	2.33 h	94.7	0.20
Ho-165	100	Ho-166	26.9 h	80.6	0.13
Tm-169	100	Tm-170	130 d	84.3	0.1
Yb-168	31.6	Yb-169	32 d	198	0.10
Tb-159	100	Tb-160	72.1d	86.8	0.01
Lu-166	2.6	Lu-167	161 d	208	0.01
Er-170	14.9	Er-171	7.5 h	308.3	8

Table 5. Rare Earth Elements analysis (ppm) of the tonalite, granodiorite, adamellite and monzogranite

Element	Tonalite	Granodiorite	Adamellite	Monzogranite
La	21.14	28.80	54.63	11.96
Ce	47.09	73.42	90.78	28.20
Pr	5.61	10.04	13.44	4.28
Nd	24.74	31.43	39.83	13.98
Sm	5.42	5.99	9.42	5.86
Eu	1.68	1.82	1.79	0.13
Gd	4.55	7.89	9.10	8.43
Tb	0.79	0.94	1.18	1.42
Dy	2.83	3.79	6.91	7.26
Ho	0.50	1.07	2.10	1.58
Er	1.68	2.26	3.33	8.22
Tm	0.26	1.36	1.07	0.56
Yb	2.03	1.90	5.18	6.23
Lu	0.22	1.78	1.31	1.51
\sum REE	118.54	172.50	240.08	99.29
Eu/Sm	0.31	0.31	0.18	0.025
(La/Lu) _{cn}	12.04	4.44	5.50	1.01

Table 6. Rare Earth Elements analysis (ppm) of the investigated syenogranite., rapakiv is yen granite and alkali feldspar granite.

Element	Syeno-granite	Rapakiv-Syeno-granite	Alkali Feldspar Granite
La	33.38	20.64	11.26
Ce	93.61	41.68	41.22
Pr	12.34	4.93	5.02
Nd	46.71	16.91	103.71
Sm	11.94	4.20	7.91
Eu	1.11	0.45	0.21
Gd	10.37	3.47	9.26
Tb	1.53	0.69	2.01
Dy	10.45	3.99	11.76
Ho	1.83	0.77	2.33
Er	4.79	2.44	6.04
Tm	0.67	0.39	1.23
Yb	4.42	2.75	8.04
Lu	0.73	0.47	1.22

Yield determination. RNAA involves more person hours and should be avoided when it is possible.

RNAA involves irradiation and counting as well as dissolution of the samples and separation of the dissolved samples into various groups. The dissolution step is much simpler than for other methods of analysis, because the final measurement in the determination of the radio nuclides formed by the irradiation. As the dissolution step is done after the irradiation is carried out, no contamination during the dissolution step can influence the final results. In addition, as the dissolution of the sample is done together with that of carriers, the danger of losing trace elements by adsorption is considerably lower. On the other hand, owing to the radioactivity of the irradiated sample, the dissolution, if performed many times, should be done behind lead shields. In principle every chemical separation that is used in any other analytical method can be used in RNAA. But since the separation very rarely involves a single element, an appropriate group of elements which do not interfere with each other is different for various determination methods. In some cases, even the separation into groups is not needed, and it is sufficient to remove the major interferences. An additional aspect which is different for RNAA with respect to all other determination methods is that in RNAA the final determination can be performed while the trace elements are absorbed into a separation column,

whereas all other methods require the elution of the trace elements from the column [39].

2.3 X-Ray Fluorescence (XRF)

The most popular methods for measuring rare earth, heavy

And toxic elements are atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP-MS). The need of exhaustive the sample preparation for AAS and ICP-MS has led to increasing interest towards energy dispersive X-ray spectrometry in environmental investigations. X-ray spectrometry, in its various forms is now a powerful well established technique for environmental analysis [40].

What is XRF Spectrometry?

XRF spectrometry is one of the oldest nuclear analytical techniques used for chemical composition analysis. XRF is a non-destructive multi-element technique capable for determining elements with atomic number $Z \geq 11$ (sodium) in different matrices. The samples to be analyzed require minimal or no preparation and the technique are regarded as non-destructive. Typical relative detection limits vary from 0.1 to 10 mg/kg, and in special configurations they can reach values as low as 1 $\mu\text{g}/\text{kg}$.

Advantages of XRF

- Extreme multi-element character for almost all elements
- High selectivity.
- Pure instrumental and non-destructive character.
- Much smaller number of spectral lines compared with Atomic emission methods, therefore.
- Less spectral interferences with respect to wavelength And qualitative element identification, following the sequence of the periodic system.
- Most suitable for element contents from 100 % to ca. 5 to 10 ppm.
- Good precisions of 0.1 to 1% for trace levels ca. $>5 \pm 5$ %

(h) Good speed, (i) ease of operation and (j) economy, and (k) automated analysis of large numbers of similar samples with help of sample changer.

(l) Almost independent from the molecular form of the element [6].

The main advantage of XRF technique over non- NATs is its de-excitation to the ground electronic state. The excitation of the atoms is achieved by means of a photo electric effect in which primary photons from an external source for example photons emitted by an X-ray tube or by radio isotope source illuminate the specimen and interact with inner atomic shell electrons. In this process an electron is expelled from its position in an atom, leaving a vacancy in the atoms shell. In a subsequent process the electronic configuration of the atom is rearranged, resulting in emission of the characteristic X-ray photons. The energy of the emitted photons is specific for the given element, and their intensity depends on the concentration of that element in the sample. The range of photon energies covered by the XRF technique from 1 to 50 keV for typical applications and may reach 150keV for specific applications. [41, 42].

Applications of XRF

X-Ray fluorescence is used in a wide range of applications including:

Research in igneous, sedimentary, and metamorphic petrology soil surveys mining (e.g., measuring the grade of ore).

Cement production.

Ceramic and glass manufacturing.

Metallurgy (e.g., quality control).

Environmental studies (e.g., analyses of particulate matter on air filters).

Petroleum industry (e.g., sulfur content of crude oils and petroleum products).

Field analysis in geological and environmental studies (Using portable, hand-held XRF spectrometers).

For investigations that involve bulk chemical analysis of major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) in rock and sediment, X-Ray fluorescence (XRF) is especially good-suited for these bulk chemical analyses of trace elements (in abundances >1 ppm; Ba, Ce, Co, Cr, Cu, Ga, La, Nb, Ni, Rb, Sc, Sr, Rh, U, V, Y, Zr, Zn) in rock and sediment - detection limits for trace elements are typically on the order of a few parts per million.

X-ray fluorescence is limited to analysis of

- Relatively large samples, typically >1 gram.
- Materials that can be prepared in powder form and effectively homogenized.
- Materials containing high abundances of elements for which absorption and fluorescence effects are reasonably well understood.

In theory the XRF has the ability to detect X-ray emission from virtually all elements, depending on the wavelength

and intensity of incident x-rays. However,

In practice, most commercially available instruments are very limited in their ability to precisely and accurately measure the abundances of elements with $Z < 11$ in most natural earth materials.

XRF analyses cannot distinguish variations among isotopes of an element, so these analyses are routinely done with other instruments.

XRF analyses cannot distinguish ions of the same element in different valence states, so these analyses of rocks and minerals are done with techniques such as wet chemical analysis or Mossbauer spectroscopy.

Various Techniques from XRF

An advanced EDXRF laboratory spectrometer utilizing a focused X ray beam has been used for the identification of individual particles. Micro beam XRF is a unique technique that can provide information on the distribution of elements within a heterogeneous specimen. This method is also suitable for the determination of elements in minute samples such as individual particles. EDXRF is a non-destructive and multi-element technique and can be applied to any kind of samples: liquid or solid (thick, intermediate or thin) and in many cases with sufficient sensitivity for the determination of many trace elements [43]. Field portable XRF (FPXRF) technology has gained widespread accurate in the environmental community as a viable analytical approach for field application due to the availability of efficient radioisotope source excitation combined with highly sensitive detectors and associated electronics.

FPXRF methodology provide a viable, cost and time effective approach for on-site analysis of a variety of environmental samples and offers some distinct advantages compared with conventional method that are been applied in the analysis of environmental samples [44-45].

Figure 3 shows schematic diagram of the arrangement of XRF spectrometer.

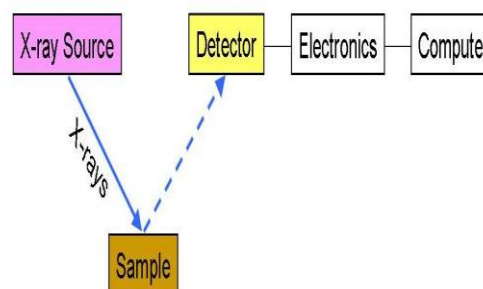


Fig3. Schematic arrangement of XRF spectrometer

3 Non-Nuclear Analytical Techniques for Rare Earth Elements

3.1 Atomic Absorption Spectrometry (AAS)

For many years both flame AAS (FAAS) and graphite furnace AAS (GFAAS) have been popular instrumental methods for the determination of the rare earth elements. Most applications involve separation and pre-concentration prior to AAS determination, because of the complex nature of interferences and the low concentrations of the analyses. Atomic absorption spectrometry is a method for elemental analysis in solution (mainly). It is very sensitive, can detect different elements down to a few ppb or less. Atomic absorption spectrometry (AAS) is one of the first modern commercial instruments for trace element analysis. Since its appearance, it became the working horse of analytical laboratories. There are hundreds of specific applications of thousands of references to articles in the literature concerning these applications. Atomic absorption spectrometry has many uses in different areas of chemistry [46].

Atomic absorption spectroscopy has become one of the standard methods for the analysis of trace elements in environmental samples, albeit one element can be analyzed at a time for each sample atomized. It measures the amount of light absorbed as a light beam is directed through an atomic vapor. External light emitting the spectral lines that corresponds to the energy required for an electronic transition from the ground state to an excited state is passed through the flame [6].

The flame gases are treated as medium containing free, unexcited atoms capable of absorbing radiation from an external source. Absorption occurs when the radiation corresponds exactly to the energy for a transition of the test element from the electronic ground state for an upper excited state. The absorption of radiation from the light source depends on the population of the ground state, which is proportional to the concentration of the solution sprays into the flame.

The absorbance is measured as the difference of the transmitted signal in presence and absence of the test element.

3.2 Inductively Coupled Plasma-mass Spectrometry (ICP-MS)

The coupling of inductively coupled plasma to mass spectrometry was first realized in the late 1970s. Since the development of ICP-MS, the potential of this technique for the determination of REEs in geological, biological and environmental samples has been clear.

ICP-MS is based on the vaporization, atomization and

ionization of a sample in plasma for subsequent mass spectrometric analysis. The plasma is a very efficient ion source and provides the technique with a high sensitivity allowing the determination of most elements at trace concentrations [6].

ICP-MS typically employs argon plasma. Argon is supplied through a torch with three concentric gas flows. The main gas flow provides Ar to the plasma, the auxiliary gas flow controls the position of the plasma and pushes it away from the torch, thereby preventing it from melting, and the central channel presents the sample to the plasma. The plasma is ignited by a short electric discharge and is maintained by an electromagnetic field generated by a copper load coil to which a radio frequency is applied. In the electromagnetic field, electrons are accelerated and their collision with Ar atoms and further collisions of Ar atoms results in the formation of a plasma [6].

Once introduced into the plasma, the sample is vaporized, atomized and ionized. The ions formed are then extracted into a mass spectrometer. Ion extraction is critical to ICP-MS with ions being transferred from high temperature and atmospheric pressure plasma into a mass spectrometer operating at room temperature and under vacuum. The interface is composed of two successive cones (the sampling cone and the skimmer) with millimeter orifices through which the ions are extracted from the plasma. After the interface, ions are focused through ion lenses and introduced into the mass filter where they are separated based on their mass-to-charge ratio (m/z) [6].

The most common mass filter is a quadrupole, which consists of four metallic or metallized rods suspended parallel to a central axis and with opposite pairs connected together. Direct current and radio frequency voltages are applied to each pair. The ions to be analyzed are introduced along the axis. For a given voltage, only ions with a specific m/z ratio will have a stable trajectory and emerge at the other end of the quadrupole, where they are detected.

Other mass filters used with an ICP include sector field and time-of-flight mass spectrometers. The sample can be introduced into the plasma as gas, micro droplets or solid micro particles. Different sample introduction techniques can be used for this purpose. When liquid samples are analyzed, a nebulizer has to be used to form the droplets. A range of nebulizers exists including pneumatic, ultrasonic and micro concentric, each one having its own advantages. In the case of solid samples, the sample is case of solid samples, the sample is converted to micrometer sized particles or vaporized. Laser ablation or electro thermal vaporization is examples of introduction techniques for solid samples.

Interferences in ICP-MS

Interference is a major problem in the determination of trace elements by ICP-MS. Two different interferences can be distinguished. Spectral interference, which occurs when several ions have the same or a similar mass to charge ratio and are not differentiated by the mass filter. Non-spectral interference or matrix effects. Spectral interferences can further be divided into three different types: isobaric overlap, polyatomic ions and double charged ions. The isotopic pattern of elements is well known and as a result, spectral interferences are easily predicted. An isobaric overlap occurs when two elements have isotopes of essentially the same mass. In principle, isotopic overlaps can easily be corrected using the isotopic pattern of the interfering element and the signal of one of its isotopes, providing that it is not subject to interference.

Reactions in the plasma and ion extraction can lead to the formation of polyatomic ions, including argues and oxides, and double charged ions. Ar, O and N are the dominant ions in the plasma and may combine with each other or with other elements to form polyatomic ions. The mass-to-charge ratio of these ions is half the ratio for single charged ions and therefore, interference might occur if an element has to be determined at this mass-to-charge ratio. Online matrix separation was performed using an ion chromatographic column coupled to ICP-MS using a micro concentric nebulizer and a cooled spray chamber. Off-line matrix separation was through ion exchange. For both approaches, quantification was by isotope dilution mass spectrometry (IDMS). The method is based on spiking the sample with a solution, which has an altered isotopic pattern. This avoids recovery problems in the matrix separation and provides a highly precise quantification method [47-49].

Comparison between Analytical Techniques for Rare Earth Elements

Table 7 summarizes the potentials data of different methods. However, it should be noted that these comparison refer mostly to the ideal case (i.e. the absence of any interfering element and assuming optimum experimental conditions).

Essentially, they can be used only for comparison of the different methods. In practice, one has to consider such factors as the nature of the matrix, interference from simultaneously present REE, problems of the pretreatment and incidental chemical separations, time consumption, the achievable accuracy, the given conditions and the cost factors arising from all this. Nevertheless, activation analysis may be the most frequent choice for the solution of analytical problems, as it is the case for the REE. The degree of accuracy of XRF is still less good as e.g. in INAA but for most applications rather acceptable.

Table 7. Comparison of analytical characteristics of INAA and other analytical techniques for element determination. --- = poor, +++ = excellent

Characteristics	INAA	Others
Sensitivity	+/-	ICP-MS +++
Absence of blank	+	LA-ICP, AAS +
Non-destructive	+++	LA-ICP, AAS, XRF +
No chemical matrix effects	+++	ICP, AAS, XRF -
Multi-element	+	ICP +
Accuracy, Metrological principles	+++	ICP, AAS +
Physically Independent	+++	XRF ++
RNAA for removal of interferences	+	ICP, AAS ++
Determination of chemical yield in RNAA	++	ICP, AAS --

4 Conclusions

Nuclear analytical techniques have been applied in many fields of science. Using instrumental neutron activation analysis technique INAA to determine the rare earth elements provides good results within a reasonable timescale. INAA offers sensitivities that are superior to those attainable by other methods of the order of parts per billion or better. In addition, because of its accuracy and reliability, INAA is generally recognized as the reference method of choice when new procedures are being developed or when other methods yield results that do not agree.

Radiochemical separation has a number of benefits including the ability to add a stable tracer, which also acts as a carrier.

Energy-dispersive XRF (ED-XRF) is widely used in environmental and industrial applications because is applicable to a wide range of elements over a large dynamic range. However, the use of total reflection XRF (TXRF) is increasing, particularly because it has the advantage of being more sensitive than ED-XRF, allowing for ultra-trace analysis. The degree of accuracy of XRF is still less good as e.g. in INAA but for most applications rather acceptable.

As in many cases nuclear techniques might not be available or might not be sufficiently sensitive, other non-nuclear techniques, such as atomic absorption spectrophotometer (AAS), or inductively coupled plasma mass spectrometry (ICP-MS) are also used.

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