Natural Resources Canada
Ressources naturelles Canada
National Non-Destructive Testing Certification Body
Organisme de certification national en essais non destructifs

Operator of Portable X-Ray Fluorescence Analyzers (XRF)

Certification Information and Examination Preparation Booklet

Version 5
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Canada

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I. Foreword and Scope

Natural Resources Canada (NRCan) is a federal department that manages Canada's nationwide program for the certification of individuals performing non- destructive testing (NDT). The NRCan National NDT Certification Body (NDTCB), through CanmetMATERIALS, certifies individuals as part of the national NDT Personnel Certification Program.

The NRCan NDTCB has adopted the International Standard ISO 20807:2004, "Non-Destructive testing - Qualification of personnel for limited applications of Non-Destructive testing" with modification to form the basis for x-ray fluorescent (XRF) operator certification. The NRCan XRF operator certification program has been developed and implemented by NRCan NDTCB with the collaboration of Health Canada. Health Canada publishes Safety Codes that are incorporated by reference into the Canada Labour Code, which applies to federally regulated sectors. An Addendum specifically applicable to portable hand-held x-ray tube based open-beam XRF devices falls within the scope of Safety Code 32 and requires the user of a 'portable hand-held x-ray tube based open-beam XRF device' to be an NRCan XRF certified operator. XRF devices have applications as analytical techniques which (a) are repetitive or automated, and (b) fall within the scope of limited industrial NDT. An XRF certified operator is an individual who possesses a valid certification in the XRF NDT test method as administered by the NRCan NDTCB. The NRCan XRF certification program is comprised of radiation safety training and examination components that are based on industrial radiographic testing.

The NRCan NDTCB certification is a federal program aimed at providing unbiased certification services at a national level. To ensure that this objective is met, an Advisory Committee composed of individuals with knowledge of NDT methods advises NRCan NDTCB on the operation of its program.

This NRCan NDTCB XRF Examination Preparation Booklet contains information specific to the theory, use, maintenance, storage, and radiation protection and safety aspects related to portable handheld x-ray tube based open beam XRF analyzers.

Within the context of ISO 20807:2004, NRCan is the "certification body" and the certification scheme and guidelines set forth in this booklet shall supersede any other details within the generic certification standard where differences exist.

An operator must possess a basic knowledge of XRF theory and applications as well as the principles and practices of radiation safety regarding portable open beam XRF analyzers. Candidates are advised to engage in self-study prior to examination. Candidates are responsible for ensuring that they use the latest version of this booklet to prepare and guide them for XRF operator certification. This booklet may be revised periodically.

The NRCan NDTCB gratefully acknowledges all agencies, organizations, and individuals whose input, comments and suggestions helped in the preparation of this booklet, and the XRF Technical and Scheme Committee for their work in guiding and strengthening the XRF operator certification program. While care is taken to provide concise information, there may be errors or omissions. NRCan will not be held responsible for the accuracy of information presented; the reader is encouraged to consult the reference materials, the applicable Acts, Regulations and Safety Code or other subordinate references cited in the booklet. Under no circumstances will the Government of Canada be liable to any person or business entity for any direct, indirect, special, incidental, consequential, or other damages based on use of this booklet.

The NRCan NDTCB is committed to protecting your privacy whether you are an existing client or a new applicant. All personal information created, held, or collected by the Government of Canada is protected under the federal Privacy Act. Our office will ensure that collected personal information and any communications between the NDTCB and their clients or applicants are considered confidential, protected, and are for the exclusive use of the intended recipient to fulfill certification program requirements. Personal information is collected as stated in NRCan's Info Source (PAA 3.1.2 – Materials and Certification for Safety and Security - Bank Number: NRCan PPU 015), and the certified personnel's name, city and province of residence and certification status are made publicly available as a mechanism of effective certification status verification.

IMPORTANT NOTE: Users of XRF devices to which this booklet refers are advised to contact their appropriate federal, provincial, or territorial radiation protection authority for applicable rules of operation.

For certification information, please contact:
National Non-Destructive Testing Certification Body
CanmetMATERIALS, Natural Resources Canada, Government of Canada
183 Longwood Road South, Hamilton, Ontario, Canada L8P 0A5
Email: ndt-end@nrcan-rncan.gc.ca
Telephone: 1-866-858-0473
Website: ndt.nrcan.gc.ca

II. The National XRF Certification Program - Introduction

X-ray fluorescence (XRF) is a diagnostic Non-Destructive Testing (NDT) technique that can be used to detect and measure the concentration of elements in substances. Fluorescence is the phenomena of absorbing incoming radiation and re-radiating it as lower energy radiation. An example of fluorescence is the t-shirt that visibly glows when exposed to invisible ultraviolet light. Fluorescence occurs with certain minerals; when exposed to ultraviolet light, they fluoresce giving off visible light.

On an atomic scale, visible light fluorescence is caused by incoming ultraviolet light that ejects low energy electrons from the outer electron shells of atoms. The vacancies, left by the ejected electrons, are filled by electrons 'dropping in' from the outermost shells. This 'dropping in' releases a specific amount of energy in the form of visible light of a certain colour (energy).

In x-ray fluorescence, the same principle applies but the energy of the incoming radiation is higher. Instead of exposing a substance to ultraviolet radiation and observing visible light fluorescence, a substance is exposed to x-rays and fluoresces giving off low energy x-rays.

On an atomic scale, x-ray fluorescence is caused by incoming x-rays that eject high energy electrons from the innermost electron shells of atoms. The vacancies, left by the ejected electrons, are filled by electrons 'dropping in' from outer shells. This 'dropping in' releases a specific amount of energy in the form of a characteristic x-ray.

The discrete energies of fluorescent x-rays are characteristic of the energy levels of the electron shells in the element. These energy levels are different for each element.

Thus, by analyzing the energies of the spectrum of fluorescent x-rays emitted by a substance, one can determine what elements are present, and their concentration in the substance. This information may be sufficient to identify the substance.

To competently use portable XRF analyzers, candidates must understand how an XRF analyzer works, how to operate it, potential sources of measurement error, and general XRF applications. To safely use portable XRF analyzers, candidates must understand the dangers of x-rays, know the fundamentals of radiation protection, and apply safe XRF work practices in accordance with the applicable regulatory requirements.

III. Levels of XRF Certification and Examinations

All questions in the examinations are based on the materials in this NRCan NDTCB Examination Preparation Booklet for Portable X-ray Fluorescence Operators.

Note: Practical examination and experience are not required components for XRF certification.

There are two levels of XRF operator certification:

Level 1

A certified Level 1 operator is qualified to perform XRF operation of portable hand-held open-beam devices.

The Level 1 examination has one part.

Level 1 Exam: 30 multiple choice questions on basic knowledge of XRF radiation safety, theory and application.

- 10 questions on theory and application and;
- 20 questions on XRF radiation safety

The maximum time allowed is 90 minutes. Passing grade is 70%.

Level 2

In addition to the responsibilities of a Level 1 XRF operator, the Level 2 operator is qualified to provide the accepted formal XRF training for certification purposes.

Holders of Level 2 certification may be:

- manufacturer's representatives;
- company employees, who train other personnel within the same company, the same premises, or the same project.

The level 2 examination consists of the Level 1 examination plus an additional Level 2 examination. The applicant must pass both level 1 and level 2 examinations to become level 2 certified.

Note: Holders of a Level 1 XRF operator certification only need to pass the Level 2 examination to qualify as a Level 2.

Level 2 Exam: 30 multiple choice questions on more detailed or advanced theoretical knowledge on XRF analysis technique, radiation safety and equipment, and stakeholder responsibilities.

The maximum time allowed is 90 minutes. Passing grade is 70%.

Examination Process

- The XRF **written paper-based examinations** are for first examination attempts only for initial and recertification candidates. They are only administered by a Special XRF Examination Centre (SXEC) authorized by the NDTCB.
- A valid and completed NRCan Examination Admittance Form is issued by an SXEC before the start of an examination and must be included with the submission of the completed examination to the NRCan NDTCB.
- Candidates should always contact and confirm with the examination administrator beforehand to ensure that their examination can be properly administered on the day/time of the examination.
- Admittance forms are valid for one (1) examination attempt. In the event a candidate is unsuccessful with an examination, the candidate must apply to the NRCan NDTCB for re-examination by submitting a retest application.
- Re-examination attempts must be scheduled and taken through the online electronic system.
- **Online written examination** authorizations are provided to candidates by email when an initial XRF application is received unaccompanied by an examination and is processed or when a re-examination application is processed.

  Note: Candidates can view unofficial examination results immediately after completing the exam when using the online examination system.

  Please visit the NRCan NDTCB website at http://ndt.nrcan.gc.ca for more information.
- It is the candidate's responsibility to ensure that they have met all the requirements prior to the examination. Please refer to section IV. for the requirements.
- The NRCan NDTCB is not responsible for the individual coordination of examination scheduling and specific availability of services.

  Note: Other than the official NDTCB examination location at the NRCan CanmetMATERIALS facility, all other examination centers are owned and operated as separate organizations from NRCan NDTCB and are only providing the proctoring of examination services on behalf of the NRCan NDTCB certification program.

Examination Fees

There are two specific payable fees associated with the candidate's examination:

1. **NRCan NDTCB Application and Examination Fees**

   These fees are paid to the NRCan NDTCB and cover the cost of the NDTCB to process applications, grade exams, maintain files, communicate, and provide the examination and other support services warranted of the certification process.

   Please visit the Fees for XRF Analyzer Operator Certification page on the NRCan NDTCB website at http://ndt.nrcan.gc.ca for the current NRCan NDTCB fee information.

2. **Examination Centre Proctoring Fee**

   This fee is paid to the Examination Centre and covers the physical proctoring of the examination process at the Examination Center or remote facility, and handling of the associated examination requirements.

The network of NRCan Examination centers is implemented to offer the candidates flexible and convenient options across Canada. The NRCan NDTCB suggests examination fees to the Examination Centers to promote consistency; however, the Examination Centers may reasonably adjust their fees to suitably cover their specific operational requirements that may be present in their region or facility.

IV. Requirements for Certification, Renewal and Recertification

IMPORTANT!

- All the latest forms and application requirements are available on the NRCan NDTCB website http://ndt.nrcan.gc.ca Quick Downloads: NDT Certification Body Forms and Guides page.
- Payment of fees does not complete or guarantee the application and examination process. Examinations will not be processed until full completion, verification, and NRCan approval of application, required fees and requisites are met.
- It is the responsibility of the XRF operator to be aware of their XRF certification expiration date. As the date of expiration approaches, it is the responsibility of the candidate to apply to NRCan NDTCB for renewal or recertification.
- NRCan will not notify the XRF operator that it is time for renewal or recertification.
- Applicants must be the age of majority in the province which they reside, at the time of certification.
- Payment of fees does not complete or guarantee the application and examination process. **Examinations will not be processed until full completion, verification, and NRCan approval of application, required fees and requisites are met.**

Initial XRF Certification

To be eligible for initial XRF certification, the candidate shall:

1. submit a completed NRCan application form for XRF certification.
2. submit a completed NRCan photograph identification form accompanied by two passport photos as described in section 4 on page 2 of the application form.
3. submit a completed NRCan identification verification form.
4. provide a completed NRCan Training Declaration .
5. submit a completed NRCan XRF vision test report form.
6. submit a signed NRCan code of conduct.
7. pay the application fee. The current fee schedule is available on the NRCan NDTCB website.
8. pass the initial certification qualification examination(s).

Renewal of XRF Certification

As the date of expiration of the initial certification approaches (no more than 6 months before the expiry date), or after recertification, the certified individual may apply for renewal. Renewal is required five (5) years from the last certification expiry date.

To apply for renewal of XRF certification, the individual shall:

1. submit a completed NRCan application form for XRF renewal.
2. submit a completed NRCan XRF form of continued satisfactory work activity.
3. submit a completed NRCan XRF Vision Test Report.
4. submit a signed NRCan Code of Conduct.
5. pay the renewal fees, which are payable to the NRCan NDTCB. The current fee schedule is available on the NRCan NDTCB website.

If an individual is renewing past their certification expiry date, a late renewal fee is required**.**

If more than 365 days have passed since the date of expiration, renewal is not an option only recertification.

Recertification of XRF Certification

Upon completion of each second period of validity (5 years after renewal, or following a significant interruption of work activity, a new certificate is required.

To apply for recertification of XRF, the individual shall:

1. submit a completed NRCan XRF application for recertification.
2. submit two passport photos as described in section 4 on page 2 of the XRF application.
3. submit an NRCan XRF training declaration.
4. submit a completed NRCan XRF vision test report.
5. submit a signed NRCan code of conduct.
6. pass the recertification examination/s.
7. pay the application fee. The current fee schedule is available on the NRCan NDTCB website.

Recertification extends the validity for five (5) years from the date of recertification.

V. Training Requirements and Curriculum for XRF Operators

Training Requirements for XRF Operators

The accepted formal training is to be provided by an XRF Level 2 certified personnel, with the following conditions:

1. All training must be provided with the proper demonstration and physical presence of a portable handheld x-ray tube based open beam XRF device that is RED Act compliant.

2. Training shall be provided by XRF Level 2 personnel, who may be:
    - A representative of a manufacturer of such an XRF device or of an Accepted Training Organization;
    - A company's employee, for the purpose of training other personnel within the same company, the same premises, or the same project.

3. Failure to comply may result in unacceptability of the training for certification.

All training must be attested to in writing by the XRF Level 2 certified training instructor and the candidate. The completed training declaration must be provided to the NDTCB included with the application. The following minimum training hours are suggested:

- 1-hour minimum - demonstration and practice in using the portable analyzer to make accurate and safe measurements
- 1-hour minimum - demonstration and practice in the safe set up, handling, operation, general maintenance and storage of the analyzer
- 3-hour minimum - overview of the subject materials that are contained in this XRF booklet

Note:
Examination questions are based on materials contained in this XRF booklet. In order to pass the XRF examinations, the 3-hour overview training must be supplemented by candidate's self-study of the materials.

The candidate is encouraged to engage in a period of self-study of the material in this booklet prior to the 3-hour overview training and the writing of the examination(s).

Curriculum for XRF Operators

The recommended training subject materials in the XRF booklet are as shown.

SUBJECT

1. Fundamental properties of matter
2. Types of radiation
3. Process of XRF
4. XRF analyzers
5. Sources of Error
6. XRF Analyzer Operation
7. XRF Applications
8. Interaction of radiation with matter
9. Biological effects of radiation
10. Radiation Detection
11. Safe XRF work practices
12. Applicable Canadian Standards Regarding XRF devices

Formal update training for renewal or recertification purposes should also follow the curriculum expectations as outlined above.

Notes:

In this booklet, there are sections denoted by 'Examples' which are intended to help the candidate /XRF operator better understand the subject matter.

Certain sections are also designated as "***Recommended for Level 2"***. The materials in those sections are required for Level 2 certification only. Level 1 examination will not include materials in those sections.

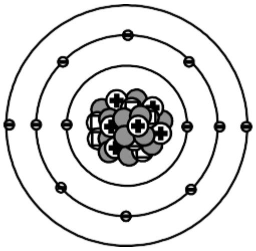
VI. THEORY

1. Fundamental Properties of Matter

1.1 Atoms, elements, molecules, and compounds

The physical world is composed of key materials called ***elements***.

Element: A basic chemical substance that cannot be divided into a simpler substance (E.g. hydrogen, oxygen, sodium, chlorine, etc.).



The basic unit of every element is the ***atom***. Although microscopic, each atom has all of the chemical characteristics of its element.

Atom: The smallest portion of an element that exhibits all the chemical properties of that element. It consists of two parts (i) a central nucleus, composed of protons which are positively charged and neutrons which are particles that have no charge; and (ii) electrons which are negatively charged particles orbiting around the nucleus (shown in the adjacent diagram).

All substances are made from combinations of atoms. Atoms from the same element may combine to form ***molecules*** of that same element. In other cases, atoms from different elements may combine to form molecules of a new substance.

Molecule: The smallest particle of a substance that retains the physical and chemical properties of that substance. A molecule consists of one or more atoms of one or more elements.

Example: The element hydrogen (H) does not like to exist as one atom but combines with a second hydrogen atom to from a molecule of hydrogen gas H_2.

Example: The smallest particle of water (H2O) that can exist is a molecule composed of two atoms of the element hydrogen and one atom of the element oxygen.

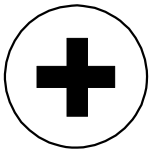
Compound: A pure substance composed of two or more elements that are chemically united in a fixed and definite proportion by weight.

Example: Water (H_2O) is a compound formed by the chemical union of two atoms of the element hydrogen (H) and one atom of the element oxygen (O). Thus,
2H + O yields H_2O.

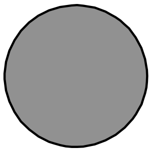
1.2 Atomic particles - properties of protons, electrons, and neutrons

Parts of the Atom

Just as all things are composed of atoms, atoms are made up of three basic particles called ***protons***, ***neutrons***, and ***electrons***. Together, these particles determine the properties, electrical charge, and stability of an atom.



Protons:
- Are found in the nucleus (centre) of the atom.
- Have a positive electrical charge.
- The number of protons in the nucleus determines the element.
- The number of protons in the nucleus is called the atomic number.

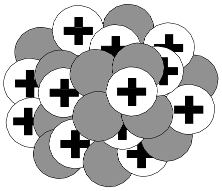


Neutrons:
- Are found in the nucleus of every atom except Hydrogen (H).
- Have no electrical charge.
- Mass is slightly greater than a proton.

Electrons:
- Like planets around the sun, electrons rotate around the nucleus in precisely spaced orbits termed shells.
- Have a negative electrical charge.
- Determine chemical properties of an atom.
- Mass is small, only 1/1840 that of a proton.

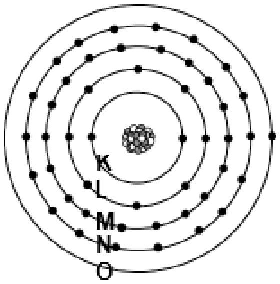
1.3 Atomic structure

The structure of the atom has two main parts: The ***nucleus*** and the ***electron shells*** that surround the nucleus.



Nucleus:
- Is the centre of an atom.
- Is composed of protons and neutrons.
- Produces a positive electrical field.
- Makes up nearly the entire mass of the atom.

Protons and neutrons in the nucleus are bound tightly together by nuclear forces.



Electron Shells:

- Encircle the nucleus of an atom at fixed distances of different discrete energy levels, the inner most shells having more energy.
- Have a specific number of electrons.
- Produce a negative electrical field.
- Are the principal controls in chemical reactions.

Electrons (-) are held in orbit by their electromagnetic attraction to protons (+) in the nucleus. Like planets around the sun, electrons circle around the nucleus in precisely spaced orbits termed shells.

The distance between shells is different for each element. The energy of an electron varies inversely with distance from the nucleus. Electrons in the inner shell (K) are more tightly bound by the nucleus and have greater energy than electrons in outer shells (L, M, N, O and P).

Each electron shell has a maximum capacity of electrons that it can support: For example K shell has 2 electrons; L shell has 8; M shell has 18 etc.

Each element has a unique set of electrons orbiting in shells of different energy.

The unit of energy used at the atomic scale is the electron-volt (***eV***).

1 eV = the energy that an electron acquires in passing through a potential difference of 1 volt.

Since this is a very small unit of energy, one often observes the use of larger units:

keV = thousand electron-volts

MeV = million electron-volts

1.4 Atomic number and mass number

Each element has a specific number of protons in its nucleus. This is called the atomic number, and is denoted by Z. The ***Atomic Number*** can be used to uniquely identify the element.

Atomic Number (Z): The number of protons in the nucleus of an atom.

Mass Number (A): The sum of the number of protons and neutrons in the nucleus.

Atomic Weight: The average weight of the mass numbers of the ***isotopes*** in an element.

Isotopes: Atoms of an element having the same atomic number (similar chemical behaviour) but different mass numbers (different number of neutrons).

2. Types of Radiation

Radiation consists of invisible waves or particles of energy that can have a health effect on humans if received in too large a quantity. There are two distinct types of radiation: ***non-ionizing*** and ***ionizing***.

Ionization:

- The dissociation, or break up, of a molecule into constituent electrically charged atoms (ions).
- The process of removing electrons from a neutral atom.

Ions may have a positive or negative charge. An atom that loses electrons is called a positive ion, and one that gains electrons is called a negative ion. Ions are highly reactive in a chemical sense and seek to achieve a state of neutral charge by combining with oppositely charged ions. When ions from two different elements combine, a chemical reaction occurs and a new compound is created.

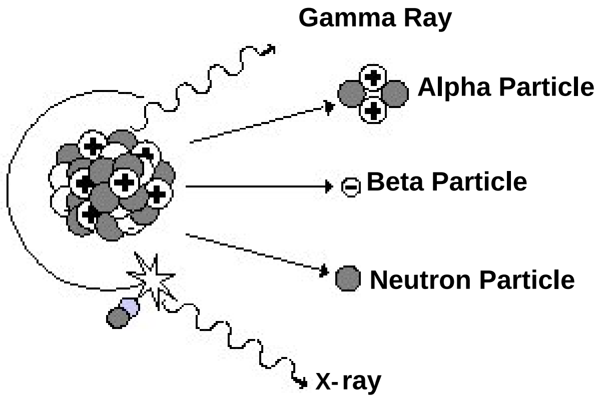
Non-ionizing Radiation: Non-ionizing radiation does not have the energy needed to ionize an atom that is, to remove electrons from neutral atoms. Non-ionizing radiation includes radio waves, microwaves, light, etc. (see the diagram in section 2.1) Although this radiation can cause biological damage, like burns, it is generally thought to be less hazardous than ionizing radiation.

Ionizing Radiation: Ionizing radiation has enough energy to ionize an atom (>4 eV).

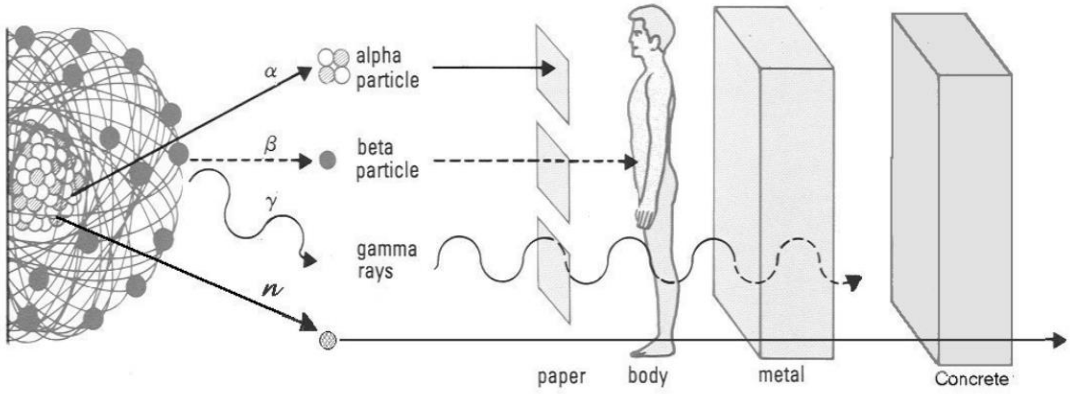
Ionizing radiation is a health concern as it can alter the chemical structure of living cells. Chemical changes can impair the normal functions of cells. Sufficient amounts of ionizing radiation can cause hair loss, blood changes, degrees of illness and death.

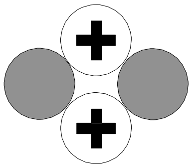
Four types of ionizing radiation are:

- Alpha Particles
- Beta Particles
- Neutron Particles
- Gamma rays or x-rays (XRF analyzers)



The penetrating power of the four radiation types varies significantly.





Alpha particles:

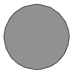
- Have a large mass, consisting of two protons and two neutrons
- Have a +2 positive charge and are emitted from the nucleus of certain radioactive materials.
- Ionize by stripping away electrons (-) from other atoms.

Range:	Alpha particles travel about one to two inches in air.
Shielding:	Stopped by a piece of paper or the outer layer of the skin.
Hazard:	Not an external radiation hazard but a potent internal hazard.

Beta Particles:

- Have a small mass and a negative charge (-), same as electrons.
- Are emitted from the nucleus of certain radioactive atoms
- Ionize other atoms by ejecting electrons (-) from their orbits.

Range:	Beta particles travel about 10 feet in air.
Shielding:	Stopped by a few millimetres of plastic, glass, or metal foil.
Hazard:	A short-range external radiation hazard to the skin and eyes. If ingested/inhaled, beta radiation may pose a hazard to internal tissues.



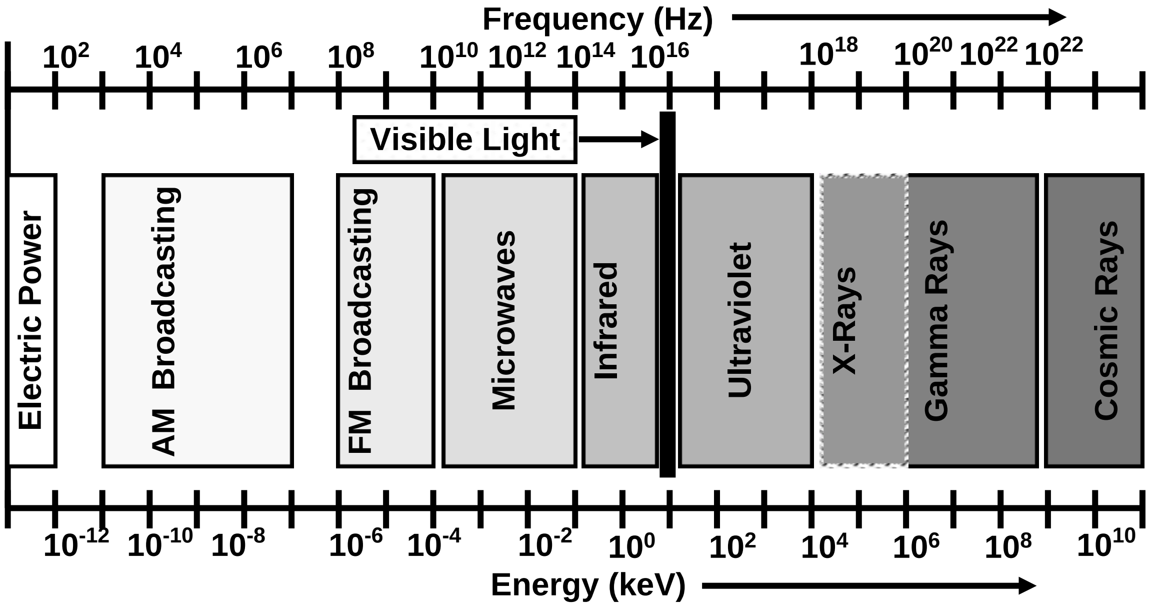
Neutron Particles:

- Are produced by the natural decay process of some radioactive elements, as well as in a nuclear reactor or particle accelerator.
- Can split atoms by fission, forming two or more unstable atoms that decay creating ionizing radiation of the alpha, beta and gamma type.
- Neutrons can also be absorbed by some atoms (fusion) resulting in creation of a possible radioactive atom dependent on the absorber.

Range:	Neutrons travel several hundred feet in the air.
Shielding:	Highly penetrating, requires thick shielding material to stop. Best shielding materials are rich in hydrogen (water, concrete or plastic).
Hazard:	Primarily an external hazard due to its long range and penetrating ability.

2.1 Electromagnetic spectrum

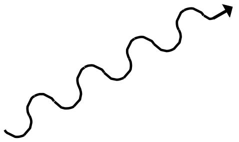
The electromagnetic spectrum is a term used to describe the entire frequency range of all electromagnetic waves and their energies - from 60 Hz electric power through high-energy cosmic rays.



Recall that **ionization requires about 4 electron volts of energy**. That energy level is reached as one moves into the ultraviolet region and beyond, into x-rays and gamma rays.

2.2 Penetrating radiation: x-rays and gamma rays

X-rays and gamma rays are electromagnetic waves or photons of high energy that have no mass or electrical charge.



Gamma or x-ray

Range: Because x-rays and gamma rays have high energy and no charge or mass, they are highly penetrating and can travel quite far.

- For low energy (~40 keV) XRF radiation, range in air is about 3 metres.

Shielding: X-rays and gamma rays are best shielded by use of dense materials, such as lead, steel or concrete.

There is no observable difference between x-rays and gamma rays. The fundamental difference between x-rays and gamma rays is their origin. X-rays originate from the acceleration of electrons near atomic nuclei while gamma rays originate from the radioactive decay of the atomic nuclei.

2.3 X-ray Sources

There are two types of x-rays, created in two different processes:

- **Bremsstrahlung:** continuous energy spectrum, process = acceleration of electron
- **Characteristic:** single energy line, process = electron shell transition

2.4 Bremsstrahlung x-rays

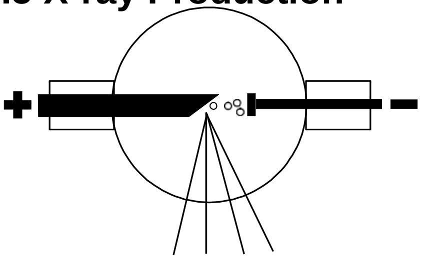
Bremsstrahlung is the German term for “braking” and was originally used to describe the unknown penetrating radiation (x-rays) released when high-speed electrons were stopped by sudden impact with a metal target. *Bremsstrahlung* or "braking" radiation can occur in a purposely-designed x-ray tube or in a material when high-speed electrons are suddenly slowed down or change direction.

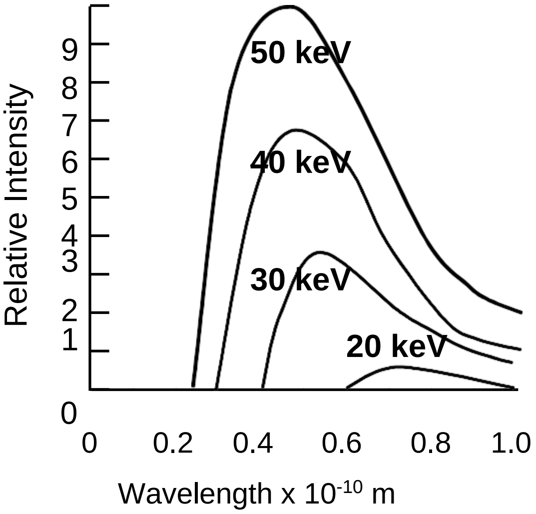
When a charged particle *accelerates* within the field of a nucleus, it emits electromagnetic radiation.
Acceleration = any change in speed [faster or slower] or direction.

2.5 X-ray Production

A modern industrial x-ray tube consists of a ceramic container that is under vacuum. It is comprised of an anode and a cathode. Electrons are emitted by a filament configured in a cathode. When a high voltage is applied across the anode terminal maintained at a positive potential (+) and the cathode terminal at negative potential (-), the electrons are accelerated to hit a target embedded in the anode.

These electrons transfer most of their energy to the target material in the form of heat (~97%), and the remainder of the energy is converted to x-rays as the electrons decelerate near the nuclei of atoms. It is the rapid deceleration of the electrons that generates ***Bremsstrahlung*** - ***a spectrum of x-rays.*** These x- rays have a range of energies of which the maximum corresponds to the maximum kilovoltage (kV) applied across the x-ray tube. The adjacent figure shows for example the x-ray energy spectrum for an x-ray tube operating at 20, 30, 40 and 50 kV.





X-ray energies from a tungsten target bombarded at various voltages.

For efficient x-ray production, the target must be a high atomic number material. Often tungsten is the target material used, but chromium, silver, molybdenum etc. are also utilized. The anode should be a good heat conductor in order to remove the heat generated by the impact of the electrons onto the target. The heat can be removed by air, water, or oil medium. Typically, x-ray tubes are comprised of a beryllium window to allow low energy x-rays to escape. Filters added in the path of the x-ray beam modify the x-ray energy spectrum.

An XRF analyzer operating at 40 kVp (kilovoltage peak) will emit x-rays having a range of energies up to 40 keV.

Current passing through an x-ray tube determines the intensity of the x-ray beam; the higher the current more x-rays are produced. Typical XRF analyzers operate with x-ray tube currents in the range of up to a few hundred microamperes.

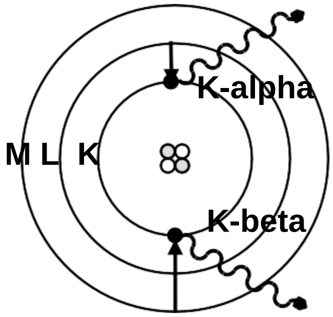
Depending on the operational parameters, the radiation output at the window surface of an XRF analyzer can reach 2000 Roentgen/hour.

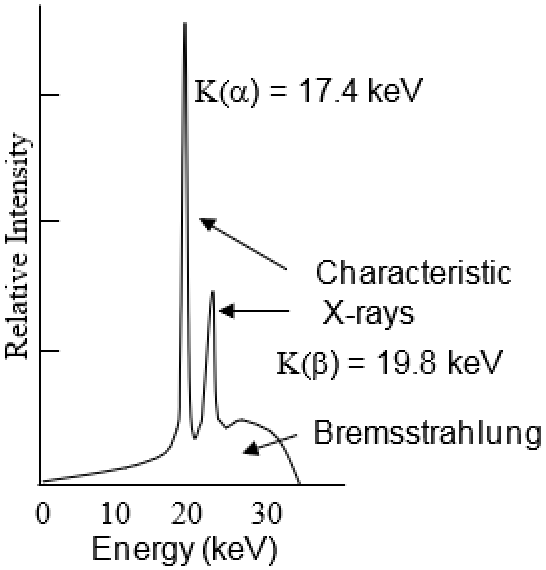
Please check your XRF device manual or verify with the manufacturer regarding the operational specifications and radiation outputs of the XRF device.

2.6 Characteristic x-rays

When certain elements are bombarded with electrons, superimposed on the Bremsstrahlung x-ray radiation are x-ray lines of energy that are unique to or “*characteristic*” of those elements.

Characteristic x-rays: X-rays emitted from electrons during electron shell transfers.





X-rays from a molybdenum target bombarded at 30 keV

High-speed electrons and Bremsstrahlung x-rays can eject electrons from the inner shells of atoms. These vacancies are quickly filled by electrons dropping down from higher-level, outer shells, as the atoms attempt to regain stability. When this happens, '***characteristic* x-rays**' are emitted, having precise energies associated with the difference between the energy level of the outer and inner electron shells of the atom.

The emission of characteristic x-rays is the foundation for x-ray fluorescence analysis.

In the XRF method, important sources of x-rays are electron movements within the atoms of elements. When an electron moves from an outer electron shell to an inner electron shell, an x-ray of precise energy is emitted. The energy of the **characteristic** x-ray is **equivalent to** the difference in energy levels between the two electron shells.

The distance between electron shells is different for each element. Thus the energy level of each electron shell, and the difference in energy between the shells is different for each element. That is why these x-rays are termed characteristic - characteristic of the element that emitted them.

(Recommended for Level 2: Rest of Section 2)

Special terminology describes x-rays emitted in electron shell transitions, for example, K-alpha:

- The 1st letter (K, L, M, N or O) is the shell into which the electron moves.
- The 2nd letter (alpha [α] or beta [β]) describes the shell of origin of the electron. α = next outer shell. β = next-next outer shell.

K-alpha = electron dropped into the K shell from the L shell
K-beta = electron dropped into the K shell from the M shell
L-alpha = electron dropped into the L shell from the M shell
L-beta = electron dropped into the L shell from the N shell

As an example, the table below shows the energies of characteristic x-rays emitted by common alloy elements in steel.

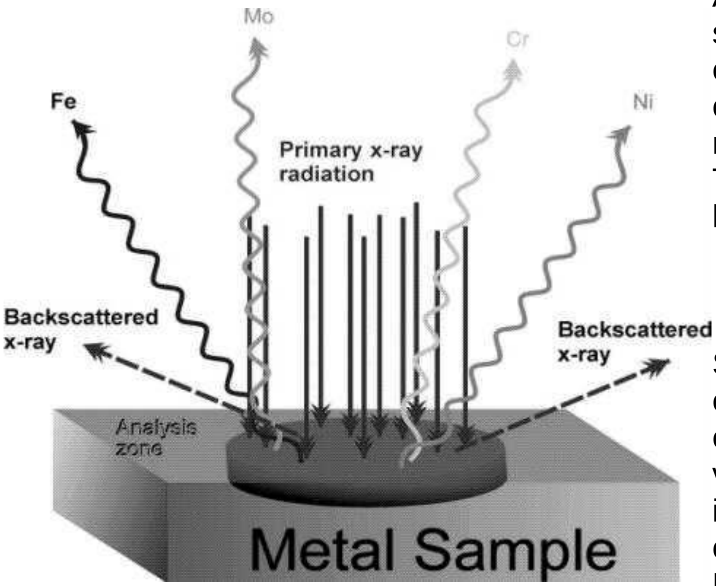
Example: Some materials and their Characteristic X-ray Energies in keV

Element	Symbol	Atomic number	K-alpha	K-beta	L-alpha	L-beta
Vanadium	V	23	4.95	5.43	0.51	0.52
Chromium	Cr	24	5.41	5.95	0.57	0.58
Manganese	Mn	25	5.9	6.49	0.64	0.65
Iron	Fe	26	6.4	7.06	0.70	0.72
Cobalt	Co	27	6.93	7.65	0.78	0.79
Nickel	Ni	28	7.47	8.26	0.85	0.87

Each element can be distinguished by the different energies of the two characteristic x-rays coming from the K-shell. Notice for a given element, there is about a 500-eV difference between the K-alpha and K-beta lines.
However, when many of these elements are present in an alloy, it can be a challenge to separate and identify certain closely spaced energy lines.

E.g. Chromium (Cr) K-beta (5.95 keV) and manganese (Mn) K-alpha (5.9 keV)

3. The Process of X-ray Fluorescence

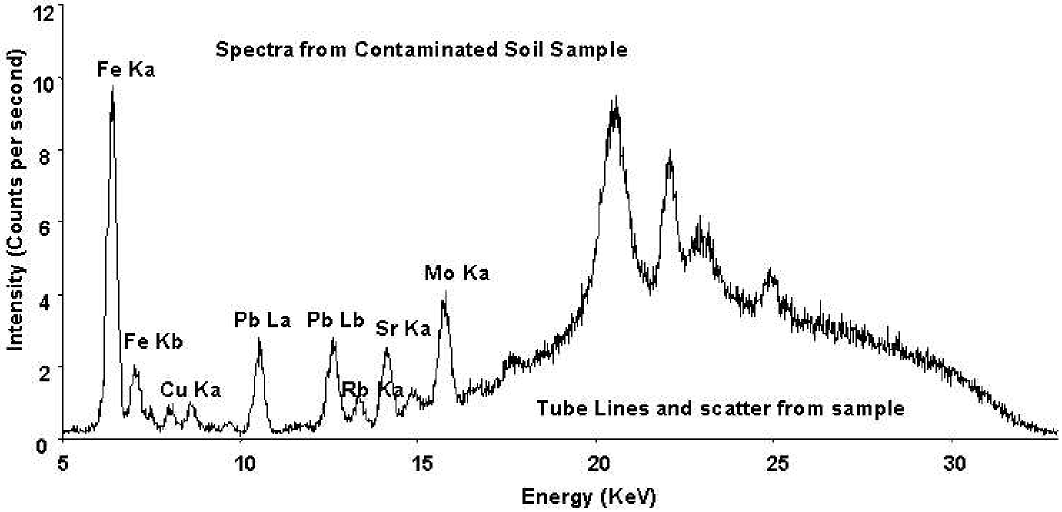


An XRF analyzer bombards the atoms of the sample with x-rays. This creates a shower of electrons, Bremsstrahlung x-rays, and characteristic x-rays, including backscattered x-rays from the sample and underlying material. These backscattered x-rays may present a health risk.

[Recommended for Level 2: remainder of Section 3]

Some of the x-rays collide with K and L shell electrons of the sample atoms, ejecting electrons from their atomic orbits. This leaves vacancies in the K (or L shell) that are immediately filled by electrons transiting from outer L, M, or N shells of the affected atom. Each electron transition emits a characteristic x-ray (fluorescence photon); this x-ray has an energy equal to the energy differences between the two shells for the specific atom.

Since the electron shells have the same fixed energy levels in all atoms of the same element, each similar electron transition emits an x-ray of the same discrete energy. Thus when electrons are ejected from atoms of the same element, the emitted x-rays are identical. These x-rays can be detected and the quantity of K shell and/or L shell x- rays measured will be proportional to the number of atoms of the particular element or elements present in the sample.



The figure above is a typical XRF Energy Spectrum (Intensity versus Energy) showing the concentration (Intensity) of various elements detected in a soil sample. The characteristic x-rays from several elements are clearly visible. The greater the peak height, the greater the concentration of that element.

3.1 Characteristic X-ray Energies of the Elements

The table below shows characteristic x-rays of some selected elements

For Example: Some elements and their Characteristic X-ray Energies in keV

Element	Symbol	Atomic number	K-alpha line	K-beta line	L-alpha line	L-beta line
Hydrogen	H	1	0	0	0	0
Carbon	C	6	0.282	0	0	0
Neon	Ne	10	0.851	0.86	0	0
Sodium	Na	11	1.04	1.07	0	0
Magnesium	Mg	12	1.25	1.30	0	0
Silicon	Si	14	1.74	1.83	0	0
Calcium	Ca	20	3.69	4.01	0.34	0
Copper	Cu	29	8.04	8.9	0.93	0.95
Zinc	Zn	30	8.63	9.57	1.01	1.03
Molybdenum	Mo	42	17.48	19.63	2.29	2.4
Tin	Sb	50	25.27	28.5	3.44	3.66
Gadolinium	Gd	64	42.6	49.3	6.06	6.71
Tungsten	W	74	59.31	67.23	8.39	9.67
Bismuth	Bi	83	77.1	87.34	10.84	13.02
Uranium	U	92	98.43	111.29	13.61	17.22

This table reveals several important facts:

- K-lines are much more (~7X) energetic than L-lines from the same element.
- As the atomic number Z rises, the characteristic x-rays have higher energy.
- Measurement of light elements (Z<12 Mg) is difficult due to the absorption of the low energy characteristic x-rays (<2 keV) in air, and therefore they do not effectively reach the detector.
  E.g. portable XRF can't do carbon.
- To measure high Z elements (Uranium 92), use the L-lines and an x-ray tube that produces ~ 20-40 keV x-rays.
- Overall, an x-ray tube that produces 20 to 40 keV x-ray energies should give good results.

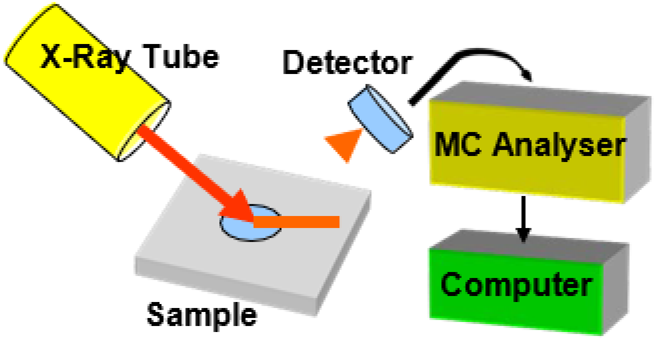
An x-ray source can excite characteristic x-rays only if the source x-ray energy is greater the energy of the characteristic x-ray emitted. **Energy in > Energy out**

XRF Summary:

The energy level of each fluorescent x-ray is characteristic of the element excited. Thus, by analyzing the energies of the x-rays emitted, one can determine what elements are present in a sample. Further, by analyzing the intensity of the x- rays emitted, one can determine the relative amount of each element present in a sample. In 'alloy analysis', one can compare the analysis to the known composition of several alloys and make a positive identification of the alloy.

4. XRF analyzers

4.1 Basic Components



An XRF analyzer consists of four basic components:

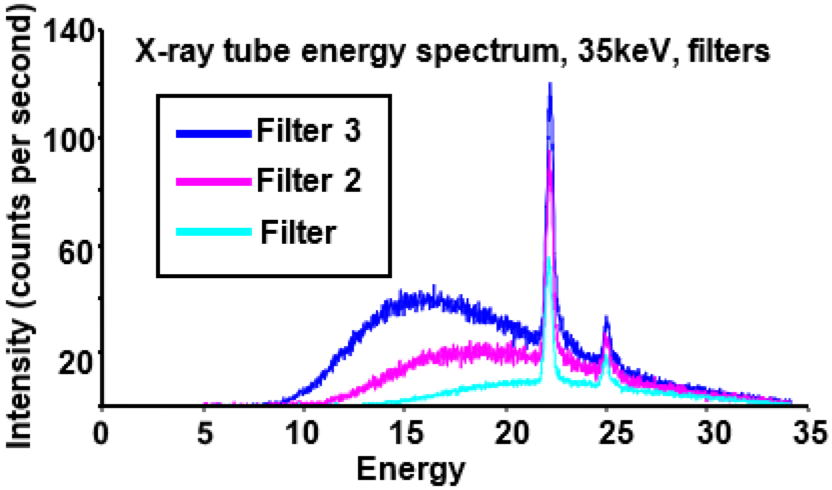
- Miniature x-ray tube
- X-ray detector
- Multi-channel analyzer
- Computer

X-rays from the x-ray tube interact with the sample thereby producing fluorescent x-rays that are ‘characteristic’ of elements in the sample. The fluorescent x-rays are detected by a detector and the signals are converted to voltage pulses. A multi-channel analyzer categorizes the voltage pulses into a fixed number of quantized (digital) energy values and counts the number of times each energy value occurs. The output is an energy spectrum counts per second versus photon energy in keV. A computer takes the data from the multi-channel analyzer, adjusts the data for several factors, and calculates the sample chemistry from the ‘adjusted’ energy spectrum.

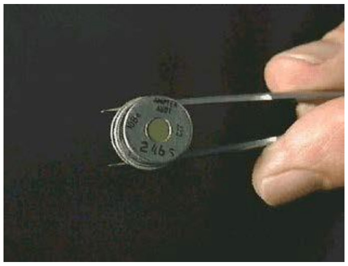
4.2 X-ray tube

The x-ray tube used in portable x-ray fluorescence analyzers equipment is miniaturized, about 20 mm in diameter and operates at about 15 to 50 kV maximum with a current of 2 to 200 micro- amperes. Small as it is, the x-ray tube can produce rather high x-ray outputs (~ 2000 R/h) at the face of the instrument window.

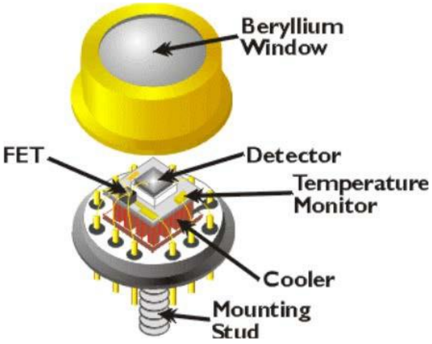
Various filters may be placed in the primary beam to alter the output energy spectrum as illustrated in the next figure.



4.3 X-ray Detection



The x-ray detector used in portable x-ray fluorescence analyzers is miniaturized,~8 millimetres in diameter. The detector features a beryllium (Z=4) window to allow transmission of low energy x-rays - without the creation of additional characteristic x-rays.

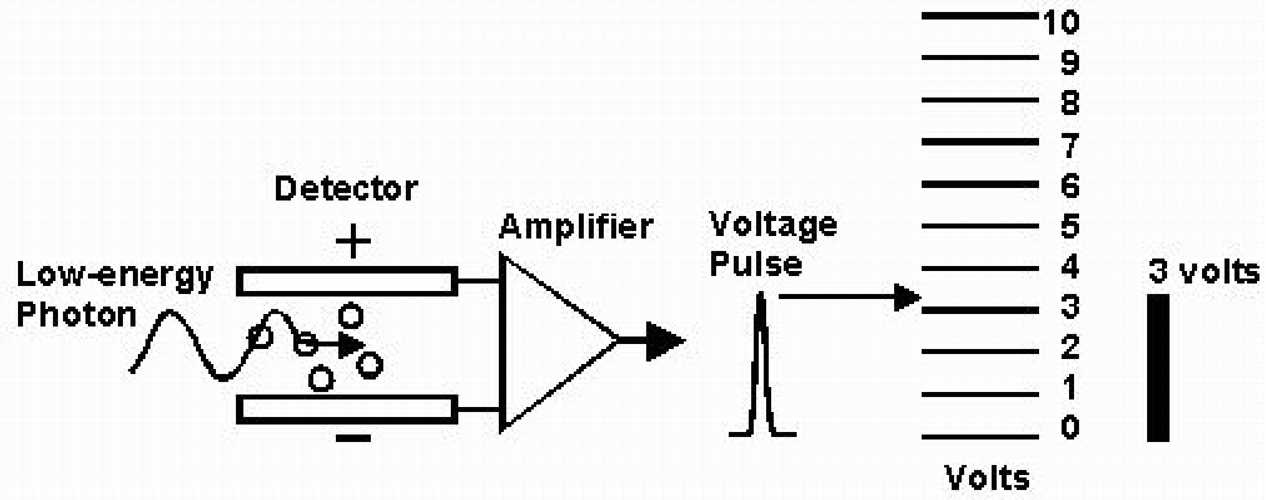


The solid- state detector reduces background electronic noise by operating at low temperature via a peltier cooler.

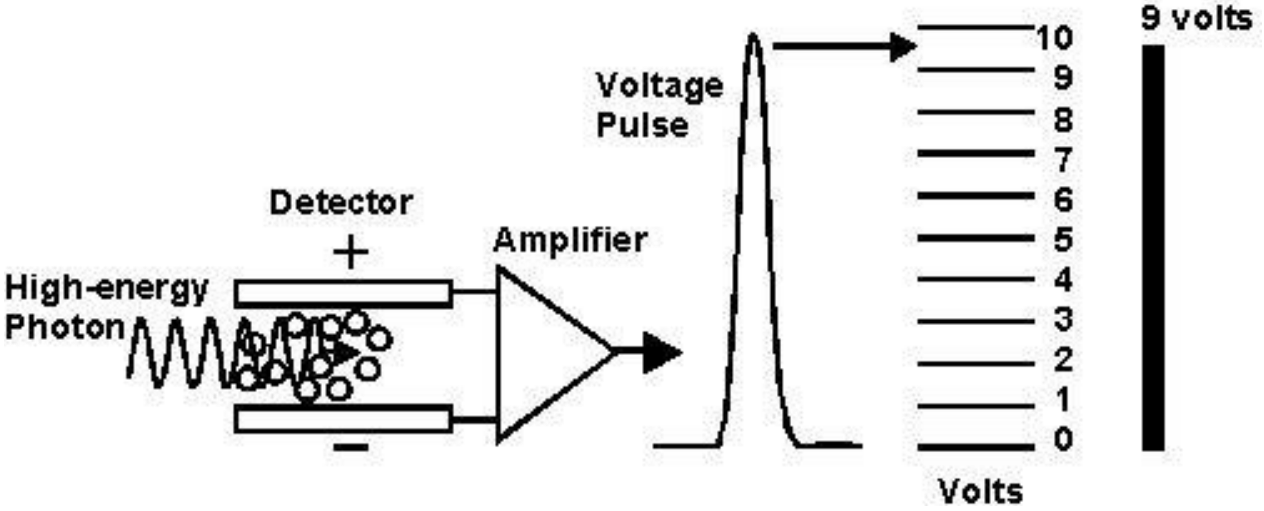
(*Recommended for Level 2: Rest of Section 4.3*)

The x-ray detection process involves the following steps:

1. Conversion of x-ray photon into electrical charges
2. Accumulation of total charge and conversion to voltage pulse
3. Amplification so that pulse height in volts is proportional to x-ray energy



An incoming x-ray photon enters the detector and begins to release a number of electrical charges. A high voltage applied across the detector causes these charges to move to sides of the detector where they create a small voltage change that is amplified and output from the detector. With time, the x-ray photon passes deeper into the detector, releasing more charges while losing energy until the photon is finally absorbed. In this process, the detector output voltage goes from near zero background to some maximum peak voltage and back to background in a very short time - creating a voltage pulse. A high-energy photon will release more charges than a low-energy photon, creating a larger voltage pulse from the detector.



The peak height of the voltage pulse is proportional to the energy of the x-ray photon. The detector outputs a series of voltage pulses of height proportional to the energy of the x-ray photon that struck the detector. Knowing the energies of the characteristic x-rays from each element, the pulse heights can be used to identify the elements that are present in the substance under investigation.

Detection is a statistical process. Thus, there is some variation in the height of pulses observed from photons of identical energy.

Example: One observes pulse heights of 9.7 and 19.5 volts. This corresponds to K-alpha for zinc at 9.6 keV and K-alpha for molybdenum at 19.6 keV.

Consider a zinc sample with no molybdenum present. It is possible that two photons of energy 9.7 keV from zinc could strike the detector at almost the same time. This would produce a single pulse of height = 9.7 + 9.7 = 19.4 volts. This would make it appear that the sample contained molybdenum.

Note too that a detector processes thousands of x-rays per second.

The detector must have a fast response time so that each X-ray photon is detected individually.

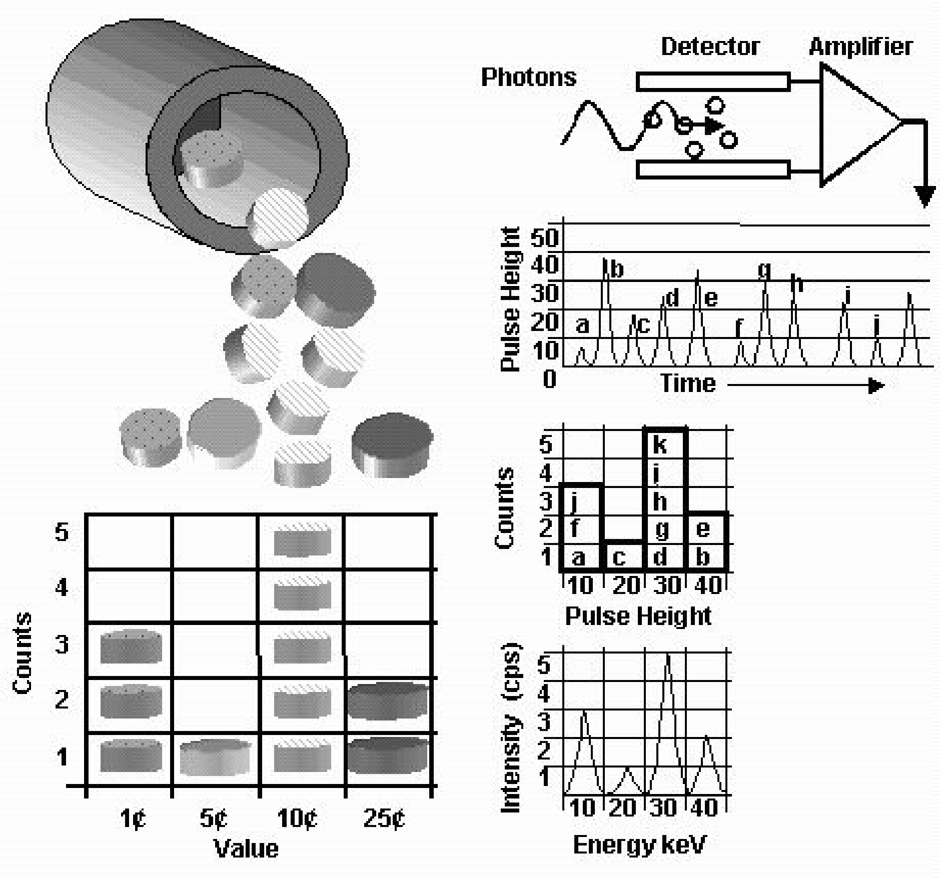
4.4 Multi-Channel Analyser

Simply put, a multi- channel analyzer is an electronic sorter; it sorts the energies of the characteristic x-rays into energy bins. This information is then processed with the use of appropriate software and the data are displayed on the XRF user screen (or output).

(Recommended for Level 2: Rest of Section 4.4)

The nature of electron-shell transfer fixes the energy of a characteristic x-ray. To identify the elements present in a substance, the pulse height from each x-ray photon striking the detector must be recorded for analysis.

The intensity of a characteristic x-ray depends on the number of identical electron-shell transfers occurring. The greater the concentration of an element, the greater is the occurrence of the x-rays with the same energy or pulse height. To determine the concentration of the elements present in a substance, the number of times the same pulse height occurs (counts) must be recorded for analysis.



The multi-channel analyzer sorts and counts voltage pulses. As shown in the figure, the process is similar to counting pocket change. A person takes each coin in turn, determines its value (sorting), then drops the coin into the appropriate value box (1¢, 5¢, 10¢ or 25¢) and increases the count of that value box by one. The multi-channel analyzer takes each voltage pulse in turn as it arrives from the detector, determines its pulse height in volts (sorting), then increments the count of the appropriate voltage box by one. This creates a chart of counts (y-axis) versus pulse height in volts (x-axis).

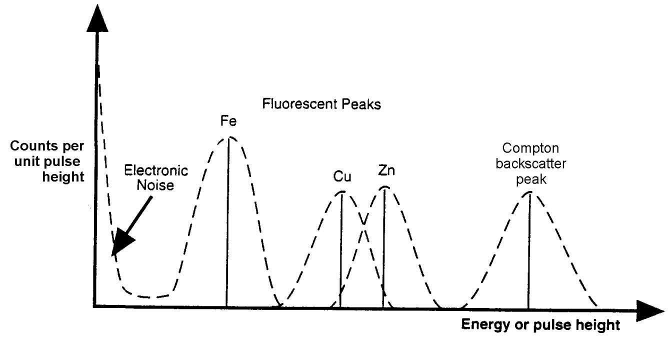
The x-ray energy spectrum: Pulse height denotes x-ray photon energy (keV). Counts denote intensity of photon radiation. To compare charts, the counts are normalized to an interval of one second, and the y-axis becomes counts per second (cps).

Challenges - Energy Spectrum

In practice, the production of an x-ray energy spectrum is not so simple because of:

- Bremsstrahlung radiation from the x-ray tube and scattered electrons
- low-energy background from light elements
- widening of the pulse caused by the detector
- variations in pulse height and count rate caused by statistical processes
- overlapping of pulses from different elements
- matrix absorption effects

Spectral Resolution



The statistics of the detection process cause pulse height to vary randomly about a mean value. The detector converts each narrow x-ray energy line into a wider bell-shaped voltage pulse a couple of hundred eV wide. Spectral overlap occurs when two peaks are not completely resolved – a problem with elements of adjacent atomic numbers such as Cu and Zn.

The two energy pulses overlap, forming two humps instead of two clearly separated lines. The analyser, having divided the energy spectrum into a fixed number of slots (1024, 2048, etc.), must assign the two humps to a number of different energy slots - instead of just two. This limits the resolution of the XRF system. Resolution of the XRF system is also dependent on the energy level measured.

4.5 Computer

The computer is an integral part of the XRF instrument. The computer has several functions:

- to control the x-ray tube, detector and multi-channel analyser
- to calculate and apply corrections to the energy spectrum
- to display details of the chemistry of the sample
- to identify the alloy by comparing the sample's energy spectrum to a library

Eliminating spectral interference due to background and overlap

(Recommended for Level 2: Rest of Section 4.5)

After accumulation of an energy spectrum by the multi-channel analyzer, the first step is the mathematical elimination of background and spectral peak overlap.

Background interference arises from gamma ray and x-ray backscatter and the low- energy tail associated with each energy pulse. This background interference is a result of an imperfect detection process and is proportional to the peak causing it.

Calculations on spectral peak overlap are made during instrument calibration using spectra taken from reference standards (standard reference materials or site-specific standards).

Calculating Concentrations

After obtaining net x-ray intensities, the second step is to convert the net intensities to element concentrations. This is done in a mathematical process (algorithm), using empirical coefficients and linear and/or polynomial multi-parameter regressions.

Calibration is achieved by measuring many reference standards of accurately and precisely known element concentrations. The microprocessor inside the analyzer calculates the correction factors for each element.

Intensity Concentration Relation

The concentration (C) of the elements in the sample is directly proportional to the x-ray intensity [I] (in counts per second) in the energy spectrum.

$$I = N/t = k \times Io \times C$$

Where:
I = X-ray Intensity (counts per second)
N = Net count (after background and overlap subtractions)
t = Measurement time (seconds)
k = Constant (detector/sample geometry, cross-section, matrix)
Io = Original x-ray intensity
C = Weight fraction of the element

Matrix Absorption Coefficient

The presence of an element with a much higher (or lower) x-ray absorption coefficient than the rest of the sample can alter the apparent intensity from a target element - even though the concentration (C) of the target element has not changed. This can cause an error in the estimated concentration of the target element.

Calibration

The purpose of calibration is to calibrate for the elements' energy scale

- XRF analyzers come with factory calibration
- User may also perform calibration if they maintain the factory calibration conditions
- Some XRF analyzers use an internal reference to maintain/verify factory calibration
  - Entire recalibration of energy scale is automated
  - Stable electronics and detector allow days or weeks between recalibration
- Use a 'check sample' provided by factory to verify accuracy of calibration/results

5. Sources of Error

5.1 Systematic and Random Errors

All errors may be classified as either systematic errors or random errors.

Systematic errors (Bias)

Systematic errors are due to bias in the measurement system - consistently producing either too low a value or too high a value. Systematic errors can be reduced by calibration and careful procedures.

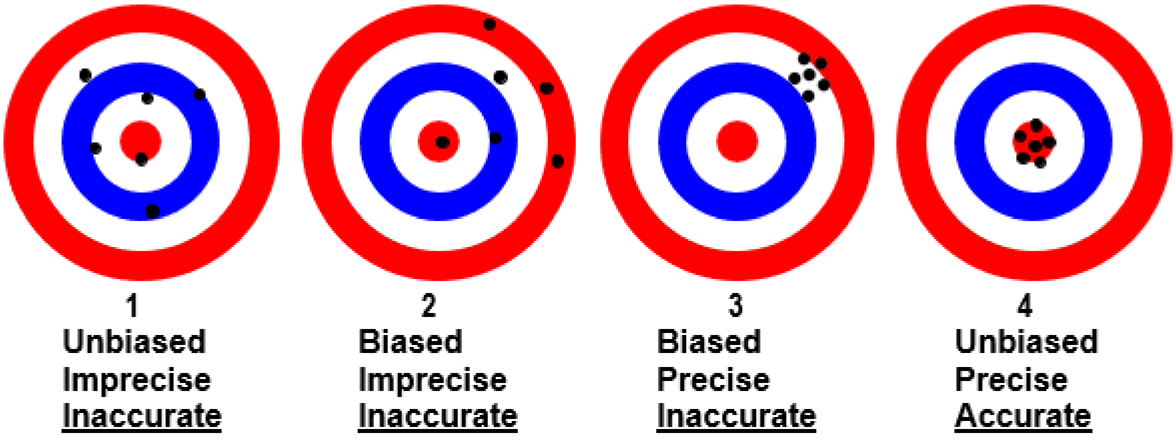
Random errors (Imprecision)

Random errors are due to uncertainty (imprecision) in the measurement system - randomly producing a statistical variation, either too low or too high, about the true value. Random errors can be reduced by averaging results of repeated measurements.

5.2 Accuracy, Precision, and Bias

For the measurement to be accurate, it must be both unbiased and precise.

There is confusion about the terms precision, accuracy, and bias in measurements. The figure below illustrates the relationship between bias, precision and accuracy.



Bias

Bias is due to systematic errors such as a change in voltage since calibration or wrong calibration constants would introduce a constant error into each measurement. Bias can be reduced by calibration and carefully following established measurement procedures.

Example: In the figure, 2 and 3 show a bias toward the upper-right. This can be fixed by applying a correction factor toward the lower-left.

Precision

Precision is a measure of the agreement among a group of individual measurements. (How close repeat measurements are to one another.)

> **Example:** In the target figure, 3 shows values that are precise ('agree' with one another) but are not accurate (close to the true value).

XRF Precision is influenced by random factors such as:

1. statistical nature of the x-ray tube emission process
2. statistical nature of the sample's x-ray absorption/emission process
3. statistical nature of detection process
4. unpredictable variations in substrate/matrix effects

One through three above occur because the x-ray fluorescence process is random; atoms in samples are excited randomly. The detector processes thousands of counts per second. Typical readings are several seconds long. Since the data set is large, statistics can be applied. For such a process, precision increases with the square root $\sqrt{N}$ of the number (N) of measurements.

- 4 X the number of measurements yields $\sqrt{4}$ = 2X the precision
- 100 X the number of measurements yields $\sqrt{100}$ = 10X the precision
- 10000 X the number of measurements yields $\sqrt{1000}$ = 100X the precision

For XRF, as the number of counts increases, the uncertainty in the result decreases. Thus, the operator can increase precision by increasing the measurement time.

> **Practical Application**
> Low levels of Manganese (Mn) in a stainless steel can be difficult to detect and can sometimes be missed in a short test.
> In contrast, Molybdenum (Mo) gives good readings even with short test.

Accuracy

Accuracy is a measure of how close the measured value is to the true value.

Error (E) = Measured value (M) - True value (T)

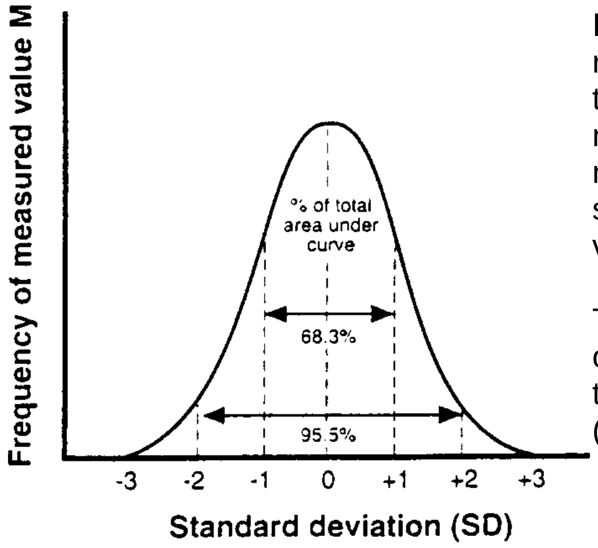
The True value (T) can never be determined with absolute certainty. In the real world, the best approximation of the True value is the arithmetic mean (**precision** $\alpha \sqrt{N}$) of a number of measurements, but only if systematic type errors (**bias**) can be corrected or reduced to a negligible value.

XRF accuracy is influenced by factors such as:

- the quality of reference standards used in the calibration
- the calibration procedure
- the duration of the measurement

Standard Deviation (SD or σ) (Recommended for Level 2: Rest of Section 5.2)

The random error in repeated measurements is often expressed in terms of Standard Deviation SD, where 1 standard deviation is referred to as Sigma (σ). Therefore, it is important that the XRF operator has some basic knowledge of this concept.



In any measurement process, if we take repeated readings of a quantity 'x', there will be a spread in the measured values. Plot the number of times each measured value occurs (Y-axis) against the measured values (X-axis). We will obtain a bell-shaped (Gaussian) curve centred about the mean value $\bar{x}$ (average).

To specify error, we are interested in the magnitude of the deviation (spread) of measured values about the mean value. This is termed standard deviation (SD).

Reference

Standard Deviation $\sigma = \sqrt{\sum(x_i - x)^{-2} / (N-1)}$

$\sqrt{\;}$ = math symbol for square root

$\sum$ = math symbol for summation

$\bar{x}$ = mean over 'i' measurements = $\sum x_i / N$ $x_i - \bar{x}$ = deviation of the i^{th} value of x from the mean $\bar{x}$

N = number of readings

Relative Standard Deviation RSD %
RSD % = $(\sigma / \bar{x})$ x100

The "68.3 – 95.5– 99.7" Rule

- 68.3% will be within ±1σ of mean
- 95.5% will be within ±2σ of mean
- 99.7% will be within ±3σ of mean

Example:
Suppose the concentration of nickel in a sample is specified as 2.5±0.2.
This means that σ = 0.2. Thus: 68.3% of values are from 2.3 to 2.7.
95.5% of values are from 2.1 to 2.9.
99.7% of values are from 1.9 to 3.1.

Limit Of Detection (LOD)

The limit of detection is the level of concentration at which the presence of an element in a sample can be detected above background.
LOD = 3 σ as measured on a test blank.

Limit of Quantization (LOQ)

The limit of quantization is the level at which the concentration of an element in a sample can be quantified.
LOQ = 10 σ as measured on a test blank

Example of RSD, LOD and LOQ

Measured concentration of lead in a sample is specified as 104 ppm with a standard deviation of 10 ppm.

This means:

Mean $\bar{x}$ = 104 ppm, σ = 10 ppm, Relative SD % = σ / $\bar{x}$ x 100 = 9.6%

LOD = 3σ = 3 x 10 ppm = 30 ppm

(Lead content of sample must be at least 30 ppm or 30/104 x 100 = 29% to be detected.)

LOQ = 10 σ = 10 x 10 ppm = 100 ppm

(Lead content of sample must be at least 100 ppm or 100/104 x 100 = 96% to be quantified.)

6. XRF Analyzer Operation

6.1 Using the XRF analyzer – General

An XRF analyzer is usually delivered to the user fully calibrated. Therefore it can be used for daily work without any major preparation. However, calibration accuracy is vitally important, so it is wise to verify calibration on test standards or check samples before starting analysis. An operator can improve the accuracy of the results by keeping the probe on a clean representative sample during the entire measurement.

Errors from counting statistics are a main source of error in most analyses. A longer reading may provide the precision needed to identify more elements in the sample.

An XRF analyzer is operated through a control program. Using this program the user can:

1. Select the mode of operation
2. Make the measurements
3. View spectra
4. Save results and/or spectra

To make a measurement, place the analyzer nose on the sample and press the trigger. Be sure that the proximity sensor on the nose of the instrument is activated or the measurement will not start. A warning light indicates the x-ray tube is generating x-rays.

Make sure that you keep the analyzer nose on the sample during the entire measurement.

The XRF analyzer should be operated according to manufacturer's instructions regarding the use of the device. Make sure that safe operating procedures are being followed while taking measurements.

6.2 Advantages of Portable XRF

Some advantages of the portable hand-held XRF device in NDT test method include:

- Completely Non-Destructive
- Fast results
- Portable and easily transported to job sites
- Minimum set up and calibration required
- Delivers qualitative and/or quantitative multi-element analysis
- Wide range of application
  - Alloy determination / chemical analysis
  - Soil analysis
  - Mineral analysis

6.3 Typical Limitations of Portable XRF

There are some limitations that exist with the test method and the user should consult the device manual or contact the manufacturer.

- Very difficult to detect elements lighter than Atomic Number Z = 12, Magnesium (Mg) e.g. lithium (Li), beryllium (Be) boron (B), carbon (C)
- Minimum detection limits is in the parts per million (ppm) range
- XRF is a surface/near surface technique
- Analyzer only measures the portion of the sample directly in front of window
- Analyzer measures ALL material in front of analyzing window
- Many carbon steels may be difficult to identify

6.4 Typical Analyzer Features *(Recommended for Level 2: Rest of Section 6)*

1 – Libraries (for alloy analysis)

Stored in memory are one or more libraries or look-up tables such as:

- Manufacturer's library: all common Fe, Ni, Co, Ti, and Cu based alloys/elements
  - e.g. many hundreds of alloy grades may be found in a typical library
  - user may add, delete, rename, or modify the manufacturer's alloy library

- Users library: users may generate their own custom library (multiple libraries)
  - e.g. load only the alloys relevant to the current project

2 – Instrument parameters and calibrations

Hidden from the user, but stored in memory are instrument dependent factors, calibration references and correction algorithms for:

- Excitation cross-section of the elements
- Geometry of the tube/detector
- Matrix effects
- Variable tube voltage and/or x-ray filters

3 - Displays

Portable analyzers may incorporate a visual screen that may be able to display:

- Chemical results (concentration of each element) and grade identification
- A graph of the energy spectrum - cps of each energy line in the sample
- Details of library in use, mode in use, etc.

4 - External Connections

Portable analyzers may incorporate software and hardware to permit:

- Data logging - storing thousands of measurements in removable memory
- Sending of XRF analyzer information to an external computer. e.g. spread sheet
- Sending of external computer information to the XRF analyzer. e.g. library, factors

6.5 Testing Modes

Most portable XRF manufactures offer a variety of analytical modes. The names will vary from one manufacturer to the next. These names may relate to the function of the mode (e.g. Soil or Alloy Analysis) or refer to the calibration method used. Consult your operator manual for further information on available modes.

Common analysis methods include:

1.	Fundamental Parameters	- mining samples and alloys
2.	Compton Normalization	- soil samples
3.	Spectral Matching	- alloy analysis
4.	Empirical	- precision matrix matching

Fundamental Parameters

The fundamental-parameters calibration is a "standardless" calibration. Fundamental-parameters calibration relies on the known physics of the spectrometer's response to pure elements to establish the calibration theoretically. Built-in mathematical algorithms are used to correct for matrix effects. A fundamental-parameters calibration is performed by the manufacturer, but the analyst may be able to adjust the calibration curves (slope and y-intercept) on the bases of results of analyses of check samples.

‘Fundamental parameters’ is typically used for analysis of mining samples and alloys. Alloy software packages often include an alloy grade library containing a series of alloy min/max specifications. After the chemistry calculations are preformed, the software searches the library to produce a grade match to the calculated chemistry.

The fundamental-parameters method is well suited for applications that require analysis of proprietary or uncommon alloys, for monitoring chemistry of tramp elements, or for monitoring chemistry during processing. The fundamental-parameters method is also ideal for obtaining an average chemistry of turnings, especially mixed turnings. (Turnings = usually metal shavings/cuttings from a lathe.)

Compton Normalization

The sample matrix affects the way in which source radiation is scattered by the sample. Compton backscatter (Section 8.2) is proportional to total Light Element Content (LEC) in the sample and is directly related to the intensity of the Compton peak. The Compton normalization method of calibration consists of the analysis of a single, well- characterized standard in order to store the intensity of the Compton peak. In use, Compton peaks in the spectra of samples are normalized to the ‘standard’ Compton peak. This approach reduces problems with matrix effects that vary among samples.

Compton normalization is similar to the use of internal standards in analysis for organic analytes. Compton normalization is used primarily for soil samples (low concentration).

Spectral Matching

The spectral-matching method compares the x-ray spectrum from the sample to many x-ray spectra previously stored in the analyzer memory. The closest match is displayed along with a number indicating the quality of the match.
e.g. Stainless Steel, SS 316, 98%
Spectral-matching is primarily used for alloy analysis. This method is used to quickly (3 seconds) match a test sample against known alloy spectra stored in analyzer memory. Analyzers may be shipped with factory-installed libraries, or the operator may create custom library entries by testing a known alloy and storing its signature in the library.
Spectral matching may also be used to produce precise chemistry information if assay information is stored. Chemistry may be extrapolated from a single point value stored for a matching alloy, or by extrapolating between minor differences in reference samples.

Empirical Calibration

The empirical calibration method uses a series of calibration standards to establish calibration parameters. The instrument response to known analytes is measured and used to create calibration curves. Empirical calibration is effective because the samples used closely match the sample matrix. The standards should contain all the analytes of interest and interfering analytes. Empirical calibrations can be installed by the manufacturer and some analyzers permit the user to create their own calibration curves. Empirical calibration may be used for any type of samples provided sufficient standards are available.

Note: Manufacturers of portable XRF analyzers offer a variety of analytical methods that may combine some of the features described above. Consult your operator manual for further information on available modes.

7. XRF Applications

The three main applications of portable XRF analyzers are:

- Alloy determination / chemical analysis
- Soil analysis
- Mineral analysis

7.1 Alloy Determination / Chemical Analysis

By far the greatest usage of portable XRF analyzers is for determining the alloy under examination and in obtaining a chemical analysis of the constituent elements of samples.

Consult the device manual and/or the manufacturer on how to perform specific tasks.

Alloy Sample Considerations

Sample Preparation - General

The sample surface should be clean of dust, corrosion, oil etc. The analysis is done on the surface of the sample, so the surface must be representative of the whole material. If the sample is flat and clean (no rust, oil, dirt etc.), no sample preparation is necessary. If the sample surface is dirty it should be cleaned. Contamination on the sample surface will have the greatest effect on light element analysis (Ti, V, Cr). Dirt and oil can be simply cleaned from the surface with a cloth. Rust, paint and coatings should be removed by grinding the sample surface.

Alloy – Error Reduction

Measurement errors set the limit of detection for the elements being measured.

- Analyzer only detects surface of sample directly in front of analyzer window. If concentration is higher/lower on surface particles, analyzer will read accordingly
  - Clean or remove any surface metallic dust, corrosion, oxide layers (rust, aluminum oxide, anodizing - grinding), coatings (paint) or films (plastic, oil, etc.)
  - Shot-blasting to clean may itself leave residue from pellets on/in the surface.
  - Metallic plating on the surface, will dominate the reading from the substrate.
- Readings can be affected by the presence of other elements in sample (matrix).
- Readings on non-homogenous samples will represent that portion of the sample.
- Large ‘chunky’ sample pieces cause voids between pieces.
- If sample is undersize (does not cover aperture) try to obtain larger specimen. e.g., instead of single wire strand, measure on the wire spool.
  Follow manufacturers' recommended procedure for analysis of small parts.
- Read-through: x-ray will penetrate thin samples and read from what is below.
  - Be careful how you support lath/drill turnings and powders.
  - Don't place a thin aluminum sample on a steel desk - lots of Fe!

Problem Samples - Solutions

- Painted, coated surfaces - analyzer measures the paint/coating plus the sample.
- Surface treatment - hardening processes, shot peening - change surface chemistry.
  - Painted, coated, chromed, treated surfaces, can be ground to remove top layer.

- Non-homogeneous samples - how to measure?
- Welds - weld metal, heat-affected zone - have different chemistry than parent metal.
- Small samples
  - If many small pieces exist of the same material (turnings, powders, etc) analyze multiple pieces at the same time.
- Hot surfaces
  - Work on hot surfaces may require a hot surface adapter from the manufacturer.

7.2 Soil Analysis

XRF has application to analysis of soil for determining metal contamination.

- High levels (several hundred ppm); quick screen <30 seconds
- Near detection limits; 60 second or longer test

Soil Sample Considerations

Soil type, heterogeneous sample, particle size, element concentration distribution, moisture, depth and area profiles. Don’t test in-situ soil with standing water on top of it.

Lab Work: A few samples sent to a laboratory may yield almost perfect analytical data that is non-representative of site.

Field Work: Many samples are read in the field and the data is more representative of site. However, there must be a proper site characterization strategy to yield good site characterization results (e.g. EPA Method 6200).

Types of Sampling

- Direct (in-situ): field-screening technique, no sample preparation performed.
- Indirect: bagged samples - field-screening technique, no sample preparation.
- Indirect (ex-situ): analytical grade accuracy using prepared samples that are dried, ground, sieved and mixed.

Soil - Error Reduction

- Calibration instability or long-term drift: minimize by regular calibration.
- Chemical matrix effects: minimize by Compton normalization calibration.
- Physical matrix effects such as particle size, moisture: minimized by drying/grinding.
- Sample presentation errors such as non-representative material in measurement area, re-entrant surfaces: minimize by clearing & levelling soil measurement surface, or intrusive sampling followed by sample preparation procedure.

7.3 Mineral Analysis

XRF has application to analysis of minerals to determine concentration.

- Prospecting and exploration
- Mining: concentration of metals in drill core, ore samples, directly on rock face
- Plant process: Check concentration of metals through the refining process (Alloy check: ensure correct alloy grades in process piping and machinery)
- Determining metal content in slag

Prospecting and Exploration

- For screening/prospecting, it is sufficient to show regions of increased concentration
  - in-situ testing provides screening level data
  - calibration factors not necessary but may improve accuracy
- For accurate assays, preparation in field can improve data quality
  - XRF cannot be used to prospect for gold, silver or low levels of any precious metals; limits of detection are in the range of ~75-150 ppm in soil/rock matrices.

Mining Applications

- Drill Core
- Ore Grade control - open cut
- Blast hole cuttings

Mineral Sample Considerations

- Samples must be representative of material being analyzed
  - samples measured “in-situ” require multiple location, short-shots (10-20 seconds)
  - intrusive samples in plastic bags require several locations, short-shots
  - finely ground (~20 um is optimum) representative, homogenous samples in x-ray cups can be measured for long periods (few hundred seconds)
- Precision/accuracy depend on sample preparation and presentation to XRF window
- Lab quality data is achievable but sample must often be dried and ground <150 µm

Mineral – Error Reduction

- Non-representative samples
- Spatial extension errors (geo-statistical errors)
- Lack of homogeneity
- Variable particle size
- Bulk density changes
- Porosity (especially rocks, etc)
- Significant moisture changes
- Referee analysis errors
- Lack of sufficient specimen quantity
  - for cups, fill to max possible
  - in plastic baggies, measure with about 40 mm depth

In mineral analysis, empirical correction factors are sometimes necessary.

- The matrix of geological samples can vary greatly. Samples can exist as oxides, carbonates, sulfides, etc
- Significant amounts of water, light elements, may exist in industrial processes
- Slag & waste products contain C, P, S, etc. in addition to metallic elements
- Light element variations may affect x-rays from target elements (light matrix effects)

Example: Light Matrix Effects - effect of matrix on Copper (Cu) readings

Actual Copper Conc.	Matrix	24.96	Ratio
XRF Reading	Cellulose	26.38	1.06
	SiO_2	23.36	0.94
	$CaCO_3$	20.32	0.81

Type of matrix, not concentration, affects calibration factors

- Calibration factors are valid for wide concentration range
  Example: In Zinc/Oxygen samples, Zinc varies from 2-60 % and oxygen varies from 40-98 %, yet the same calibration factor applies. However, if samples consisted of Zinc/Aluminum, a different calibration factor would likely apply

Calibration Factors

- **<u>Refer to your manufacturer's literature</u>**
- Calibration factors can be set for a single element, or a suite of elements.
- Changing calibration factors for one element will not affect other elements being measured.
- Multiple calibration factors may be stored simultaneously.
- The entire procedure can take as little as 10-15 minutes (depending on number of calibration samples used).
- Process needs only be done once if sample type remains constant (empirical calibrations must be redone periodically).

7.4 Obtaining Quality Data

(Recommended for Level 2: rest of Section 7.4)

In order to obtain quality data using portable XRF analyzers, the operator should apply one or more of the following strategies.

Performance Based Measurement Systems

This is a systematic planning approach that requires operator to establish goals and data quality needs that answer the following questions:

1. What is the purpose of this analysis? (Why are we doing this?)
2. How will the data be used? (What decisions will it support?)
3. How good does the data quality have to be to support the decision?

Sampling Analysis Plan

The plan for analyzing sample should answer the basic questions:
1. Why are we doing this project?
2. What is the regulatory driver?
3. How will the data ultimately be used?
4. Will the ultimate decision be risk-based or technology based?

Data Quality Objective - Process

1. State the problem
2. Identify the decision
3. Identify inputs to the decision
4. Define the study boundaries
5. Develop a decision rule
6. Specify limits on decision errors
7. Optimize the design for obtaining data

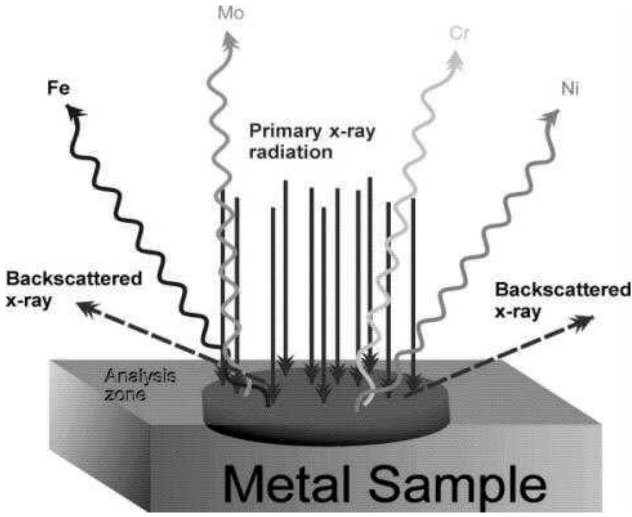
8. Interaction of Radiation with Matter

8.1 Ionization

Ionization is the dissociation (or break up) of an atom or a molecule into positively or negatively charged ions (ion pairs) or electrons. It can also be thought of as the process of removing electrons from a neutral atom. Since x-rays and gamma rays can ionize matter, they are often called ionizing radiation.

Ionizing radiation is a safety concern due to its potential to alter the chemical structure of living cells. These changes can alter or impair the normal functions of a cell.

8.2 Radiation interaction with matter



Process of x-ray fluorescence

An XRF analyzer bombards the atoms of a metal sample with x-rays. This creates a shower of free electrons, Bremsstrahlung x-rays and characteristic x-rays. Note that backscattered x-rays from the sample and underlying material are also produced and can present a health risk.

(Recommended for Level 2: Rest of Section 8.2)

X-rays and gamma rays lose energy to atoms by three main processes:

- Photoelectric absorption (low energy)
  50 eV to 0.1 Mev
- Compton scattering (medium energy)
  1 keV to 1 Mev
- Pair production (high energy)
  >1.2 Mev) [not applicable to XRF]

Photoelectric absorption

An incoming low energy x-ray photon is totally absorbed. Some of its energy is used up to eject an orbital electron (30 to 50 eV) and the remainder of its energy imparts speed to the electron. The moving electron then loses energy by causing further ionization.

Compton scattering

At higher energy, an incoming x-ray photon transfers only part of its energy to ejecting an orbital electron and imparting speed to the ejected electron. That photon now has a lower energy and is scattered in a direction different from its original path; it is called a Compton scattered x-ray.

One high-energy x-ray may trigger off an entire shower of free electrons and x-rays. E.g. the ejected electrons may change direction/speed in passing close to an atom - creating Bremsstrahlung x-rays. The ejected electrons, Compton scattered x-rays and Bremsstrahlung x-rays may eject other electrons from inner atomic shells, causing emission of characteristic x-rays as outer-shell electrons drop into the vacancies. Such processes repeat with decreasing energy until the energy of the emitted electrons or x-rays is too low to cause further ionization.

8.3 Unit of radiation exposure – Coulomb/Kg and the Roentgen

The unit of measure for intensity of x-ray radiation is based upon the ability to produce ionization in air. The electrical charge (coulombs) is deposited per kilogram of air.

Roentgen: Unit of exposure to x-rays or gamma rays having energies < 3 MeV.
One roentgen = 2.58×10^{-4} coulomb per kilogram of air.

8.4 Attenuation of electromagnetic radiation

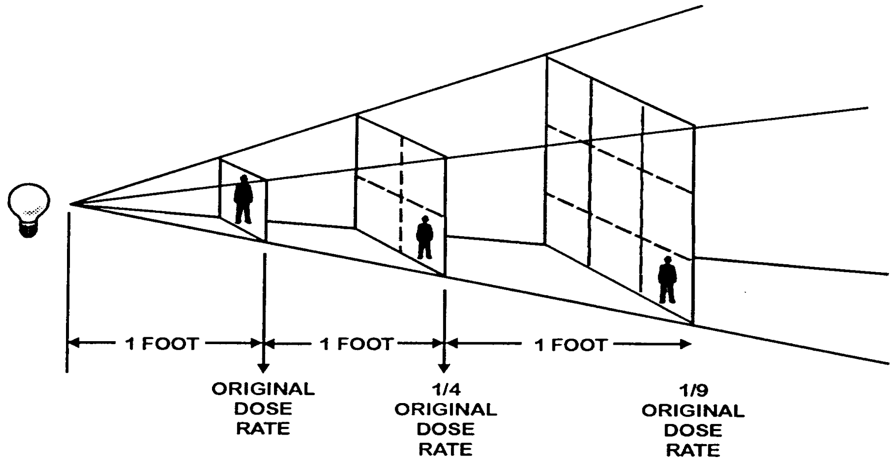
Radiation loses intensity in passing through material. The greater the energy (keV) of the x-ray or gamma ray, the greater is the penetration into material. The greater the density of the material, the less is the penetration.

- For XRF applications, the operator should be aware that low energy (<50keV) x-ray radiation can penetrate and pass through thin samples.

Inverse-square law for distance

Radiation loses intensity with distance from the radiation source. For a point source of x-rays or gamma-rays, the intensity of radiation is inversely proportional to the square of the distance from the source.

- Doubling the distance reduces the intensity to 1/4 of the original value.
- Tripling the distance reduces the intensity to 1/9 of its original value



Sample Calculation:
An XRF analyzer has an intensity of 24 mR/h at a distance of 1 metre, what will be the intensity at two metres? Ans: 6 mR/h

The inverse square law does not work well with a large source or multiple sources at close distances, or with low energy sources in an enclosed room where the low energy x-rays can scatter off the walls. In these cases, the intensity does not decrease as rapidly with distance from the source as the inverse-square law would suggest.

9. Biological Effects of Radiation

9.1 Absorbed dose units: Gray and Rad (any material)

Dose: the energy absorbed per unit mass caused by exposure to ionizing radiation.

Rad: Unit of **R**adiation **A**bsorbed **D**ose (for any material)
One rad = 100 erg of energy absorbed per gram of material.

Gray: International Standard (SI) unit for measurement of radiation absorbed dose.
One gray = 10,000 erg of energy absorbed per gram of material.
1 gray (Gy) = 100 rad or 1 rad = 10 milligray

Dose rate: the rate at which energy is absorbed per unit mass (e.g. gray/h or rad/h) caused by exposure to ionizing radiation.

9.2 Dose equivalent units: Sievert and Rem (Biological Effect)

Dose equivalency relates radiation dose (in rads) to biological damage in humans. The damage sustained depends upon the type of radiation.

Dose equivalency: The product of dose and a radiation weighting factor. In 1990, the ICRP proposed using the term ‘equivalent dose’ instead of dose equivalent, and weighting factor instead of quality factor.

The weighting factor is based on the radiation's ability to cause biological damage.

Radiation Type	**Weighting Factor**
X-ray, Gamma ray, beta	1
Neutron (Fast)	10
Alpha	20

Equivalent dose is expressed in units of ***rem*** (**R**oentgen **E**quivalent **M**an)
The rem is used to specify equivalent dose and is equal to the dose in rads times the radiation weighting factor: **rem** = rad x radiation weighting factor.
For x-rays, 1 rem ~ 1 rad for soft tissue

In view of the1990, ICRP proposed terminology "equivalent dose":
The product of dose and a radiation weighting factor expressed in ***Sieverts***.
1 Sievert (Sv) = 100 rem

Overview: The term "dose" applies to absorption in any material while equivalent dose applies strictly to human tissue. However, when dealing with x-rays and gamma rays for which the Weighting Factor = 1, it is common in the workplace to use the expression 'dose' to describe how much absorbed radiation a person has received in millisieverts or mrem.
e.g. "How much dose did you get?" "I received three mrem."

Conversions:

Dose:	1 gray (Gy) = 100 rads	or 1 rad = 10 milligray
Equivalent Dose:	1 Seivert (Sv) = 100 rem	or 1 rem = 10 milliseiverts

Biological Damage Factors

Biological damage factors determine how much damage living tissue receives from radiation exposure, and include:

- Total dose: the larger the dose, the greater the biological effects.
- Dose rate: the faster the dose is received, the less time for the cell to repair.
- Type of radiation: the more energy deposited the greater the effect.
- Area exposed: the more body area exposed, the greater the biological effects.
- Cell sensitivity: rapidly dividing cells are the most vulnerable.
- Individual sensitivity to ionizing radiation:
  a) developing embryo/fetus is the most sensitive.
  b) children are the second most vulnerable.
  c) the elderly are more sensitive than middle-aged adults.
  d) young to middle-aged adults are the least sensitive.

9.3 ICRP radiation dose limits

ICRP: International Commission on Radiological Protection

Dose Limits for General Public in a year:
Whole body Effective dose: ....100 mrem, 1 mSv
Equivalent dose to the skin or extremity .... 5 rem, 50 mSv
Equivalent dose to the lens of the eye.. 1.5 rem, 15 mSv

Dose Limits for a Radiation Worker in a year:
Whole body Effective Dose: .... 2 rem, 20 mSv
Equivalent dose to the skin or extremity ....… 50 rem, 500 mSv
Equivalent dose to the lens of the eye equivalent............................... 2 rem, 20 mSv
A pregnant worker (during gestation period)..Effective dose............100 mrem, 1 mSv

These dose limits do not include medical and natural background ionizing radiation exposures.

In general, the larger the area of the body that is exposed, the greater the biological effects for a given dose.

9.4 Natural background radiation

We live in a radioactive world and always have. We are continually exposed to sources of radiation from our environment, both natural and man-made. The average person in North America receives about 365 millirem (mrem) of radiation per year.

Most radiation exposure comes from ***natural sources*** (about 300 mrem per year).
The four major sources of natural background radiation are:

• Cosmic radiation (sun and outer space)	30 mrem/yr
• Terrestrial radiation (soil, rock, uranium, thorium)	30 mrem/yr
• Internal sources (drinking water, food e.g. K-40 from bananas)	40 mrem/yr
• Radon gas in homes	200 mrem/yr

The rest of radiation exposure comes from ***man-made sources*** (65 mrem per year).
Man-made sources tend to be x-ray and gamma ray radiation.
The four major sources of man-made radiation exposures are:

• Medical radiation (chest/dental x-rays, CAT scans, radiotherapy)	53 mrem/yr
• Atmospheric testing of nuclear weapons (radioactive fallout)	1 mrem/yr
• Consumer products (burning fuel, smoke detector)	10 mrem/yr
• Industrial uses (x-rays)	1 mrem/yr

9.5 Organ radio-sensitivity - Radiation damage/repair

Cell Sensitivity

The human body is composed of over 50,000 billion living cells. Groups of these cells make up tissues, which in turn make up the body's organs. Some cells are more resistant to radiation damage than others.

The most sensitive cells are those that are rapidly dividing, and that is why exposure to a fetus is so carefully controlled. Radiation damage and repair depends on cell resistance and level of exposure.

9.6 Symptoms of radiation injury

- reduced white blood cell count
- hair loss
- nausea
- increased temperature
- fatigue
- vomiting
- loss of the exposed body part

9.7 Acute radiation exposure and somatic injury

Acute and Chronic Doses of Radiation

Acute Dose

An acute dose is a large dose of radiation received in a short period of time that results in physical reactions due to massive cell damage (acute effects). The body can't replace or repair cells fast enough to undo the damage right away, so the individual may remain ill for a long period of time. Acute doses of radiation can result in reduced blood count and hair loss. Recorded whole body doses of 10 rem to 25rem have resulted only in slight blood changes with no other apparent effects.

Radiation Sickness

Radiation sickness occurs at acute doses greater than 100 rem. Radiation therapy patients often experience it as a side effect of high-level exposures to singular areas. Radiation sickness may cause nausea (from cell damage to the intestinal lining), and additional symptoms such as fatigue, vomiting, increased temperature, and reduced white blood cell count.

Acute Dose to the Whole Body

Recovery from an acute dose to the whole body may require months. Whole body doses of 500 rem or more may result in damage too great for the body to recover from. Mean Lethal Dose (MLD) = 500 rem

Acute Dose to Part of the Body

Acute dose to a part of the body most commonly occurs in industry (use of x-ray machines), and often involve exposure of extremities (hand, fingers, etc.). Sufficient radiation doses may result in loss of the exposed body part. The prevention of acute doses to part of the body is one of the most important reasons for proper training of personnel.

Chronic Dose

A chronic dose is a small amount of radiation received continually over a long period of time, such as the dose of radiation we receive from natural background sources every day.

Chronic Dose versus Acute Dose

- Chronic = small radiation dose over a long time
- Acute = large radiation dose in a short time

The body tolerates chronic doses better than acute doses because:
- Only a small number of cells need repair at any one time.
- The body has more time to replace dead or non-working cells with new ones.
- Radical physical changes do not occur as with acute doses.

Genetic Effects

Genetic effects involve changes in chromosomes or direct irradiation of the fetus. Effects can be ***somatic*** (cancer, tumours, etc.) and may be ***heritable*** (passed on to offspring).

- **Somatic Effects**

  Somatic effects apply directly to the person exposed, where damage has occurred to the genetic material of a cell that could eventually change it to a cancer cell. It should be noted that the chance of this occurring at occupational doses is very low.

- **Heritable Effects**

  This effect applies to the offspring of the individual exposed, where damage has occurred to genetic material that doesn't affect the person exposed, but will be passed on to offspring. To date, only plants and animals have exhibited signs of heritable effects from radiation.

9.8 Personnel monitoring for tracking exposure

We cannot detect radiation through our senses. Special devices are needed to detect and record radiation exposure. These devices are required by law to be worn by radiation workers and personnel operating x-ray equipment in order to monitor and record their occupational doses. These devices are commonly referred to as ***dosimeters***, and the use of them for monitoring is called ***dosimetry***.

9.9 ALARA (As Low As Reasonably Achievable) concept

While dose limits and administrative control levels try to ensure very low radiation doses, it is the goal of the ALARA program to reduce ionizing radiation doses to a level that is As Low As Reasonably Achievable (ALARA).

ALARA is designed to prevent unnecessary exposures to employees, the public, and to protect the environment. It is the responsibility of all workers, managers, and safety personnel alike to ensure that radiation doses are maintained ALARA.

Three basic practices to maintain external radiation ALARA:

- **Time**
- **Distance**
- **Shielding**

Time

The less time you are exposed to ionizing radiation, the smaller the dose you will receive.
Reduce dose by limiting the time spent in a radioactive area.
The effect of time on radiation can be stated as: Dose = Dose Rate x Time

Example: If 1 hour of exposure time results in 20 mrem of dose, then 1/2 an hour would result in 10 mrem of dose.

Distance

The further you are from the source of ionizing radiation, the smaller the dose you will receive. Reduce dose by maintaining the maximum possible distance from the radiation source.

For x-rays and gamma rays, the effect of dose on distance can be determined by the ***inverse square law. In simple cases, one can perform quick approximate calculations by remembering that:***

a) doubling the distance from the source reduces the dose or dose rate to 1/4
b) tripling the distance from the source reduces the dose or dose rate to 1/9

Sample Calculation:
If the dose rate from a source is 2 mrem/h at 3 metres, what would be the dose rate at 1 meter? Ans: 9 x 2 mrem = 18 mrem/h

Shielding

The more material between you and ionizing radiation, the smaller the dose you will receive. Reduce dose by placing dense shielding material about the radiation source. Shielding is considered to be the most effective method of reducing radiation exposure.

The shielding ability of a material is proportional to its density (mass per unit volume) and depends upon the energy of the ionizing radiation.

> Which is the best shielding material, lead, steel or aluminum?
> Answer: Lead because it has the highest density.

10. Radiation Detection

10.1 Instruments for radiation detection and measurement

Several instruments are used for detection and measurement of radiation dose and dose rate. Recall that dose is a measure of energy per unit mass caused by ionizing radiation. The underlying principle of operation for all these instruments is ionization.

These instruments include:

- Ionization chambers (survey meters)
- Geiger-Mueller tubes
- Pocket dosimeters
- Film badges (photographic film)
- Thermoluminescence detectors (TLD’s)
- Optically stimulated luminescence dosimeters (OSL)

Ionization Chamber

The Ionization chamber is the simplest type of detector for measuring radiation. It consists of a sealed cylindrical chamber containing air with a wire running through its centre length with a voltage applied between the wire and outside cylinder. When radiation passes through the chamber, ion pairs are created and electrons are collected on the wire. The resulting charge is used as a measure of the exposure received. The measurement is only 30-40% efficient, as radiation can pass through the chamber without creating enough ion pairs for proper measurement.
Most survey meters use ionization chambers.

Geiger-Mueller Tube

The Geiger-Mueller (GM) tube is very similar to the ion chamber but is much more sensitive. The voltage applied between the wire and outside cylinder is so high that even a very small number of ion pairs will yield a large number of electrons that are detected. Thus, a GM tube can detect and measure very small amounts of beta or gamma radiation. However, a GM tube is prone to overload in high radiation fields.

Pocket Dosimeter

The pocket dosimeter is a specialized miniature version of the ionization chamber. It is basically a small quartz-fibre electroscope. The chamber is given a charge of static electricity, which it stores like a condenser. As radiation passes through the chamber, ion pairs reduce the stored charge in proportion to the amount of radiation received, and the quartz-fibre indicator moves across a measurement scale. A pocket dosimeter is charged and ‘zeroed’ by the operator using a charging station.

Film Badge [Rarely used today]

The film badge is a light tight case that contains photographic film. The film will darken in proportion to the amount of radiation received (dose). The degree of film darkening is determined by dosimetry service.

Thermoluminescence Detector (TLD) & Optically Stimulated Luminescence Dosimeter (OSLD)

TLDs and OSLs are small badge-like devices that use materials in the form of crystals, which can store free electrons when exposed to ionizing radiation. These electrons remain trapped until the crystals are read by a special reader or processor; crystals that utilize heat to release the trapped electrons are referred to as thermoluminescence detectors (TLD) and those that use light are called optically stimulated luminescence detectors (OSLD). As a result of such treatment, the electrons are released and the crystals emit light which can be measured and related directly to the amount of radiation received (dose).

10.2 Personnel monitoring

Personnel monitoring devices are utilized for recording and controlling exposures to ensure occupational dose limits are not exceeded.

Whole body monitoring

For external whole-body dose monitoring purposes, typically a TLD or OSLD whole body dosimeter is used to measure both shallow and deep penetrating radiation doses. They are worn on the clothing closest to the body either at the waist or chest level and yield effective doses to the whole body from penetrating radiation. The measured dose this device records is used as an individual's legal occupational dose.

Extremity monitoring (Finger ring)

Personnel monitoring devices worn on the extremities or near the skin yield equivalent doses from low-penetrating radiation. A finger ring- type dosimeter contains a TLD or OSLD dosimeter. The measured dose this device records is used as the worker's legal occupational extremity exposure.

In the case where personnel monitoring is necessary when using a portable hand-held x-ray tube based open-beam XRF device, an extremity dosimeter should be worn on the finger that is likely to incur the highest risk (from the scattered photons attributed to the analytical measurement activities).

10.3 Survey instruments

Survey meters are typically used for monitoring an area when ionizing radiation is present.

For XRF operation, the survey meter should be capable of detecting photons greater than 5 keV.

For operators of XRF analyzers, a survey meter has the following applications:

- To detect the presence of scatter radiation in the vicinity of the operator’s hands.
- To verify the presence of x-rays passing around or through small or thin samples.
- To determine if radiation is passing through a tabletop (and striking the legs of the XRF operator) or passing through partitions or walls into occupied areas.
- To assure the public adjacent to an XRF-test area that no undue radiation is present.
- To determine if radiation leakage is present in the event of damage to the XRF analyzer.

Thus, an XRF operator should acquire and use a survey instrument at the job site when necessary for any of the preceding applications .

Calibration of the survey instrument should be performed once a year, or when it is serviced or repaired.

10.4 Radiation survey reports

Radiation scatter profiles or reports should accompany the device at time of purchase. The equipment owner should keep that on record.

As an example, some radiation values are shown below.

Typical XRF Analyzer Radiation Survey Results (mR/h)

Analyzer	With Sample	Sides Contact	Top Contact	Trigger Contact	In Beam Contact	In Beam 1 metre
1	Yes	10	10	-	5	
	No	5	5	-	450	20
2	Yes	0.1	0.1	0.1		
	No	0.1	0.1	0.1	28,000	24
3	No	0.1	0.3	0.12	2,000	3

11. XRF Safe Work Practices

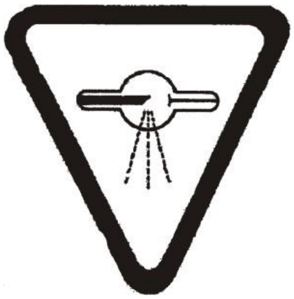
11.1 Knowledge of the XRF analyzer

The highest dose rates are at the beam port of the XRF analyzer. Avoid placing hands or portions of the body in the beam path. The XRF operator must be thoroughly familiar with the safety features and manufacturer's recommended operating procedures for the specific XRF analyzer that he/she will be using.

11.2 XRF labels

Warning labels must be in place on the XRF analyzer.

a) a label bearing the X-radiation warning symbol.
b) labels stating:



CAUTION – X-RADIATION This equipment produces
High Intensity X-radiation when Energized.
To be operated only by Qualified Personnel

c) a label setting out details of the model and manufacturer
   (i) the name and address of the manufacturer,
   (ii) the model designation,
   (iii) the serial number,
   (iv) the date of manufacture, and
   (v) the country of manufacture.

11.3 XRF Operator Responsibilities

The XRF Operator should refer to Section 12.0 of this document.
Portable hand-held x-ray tube based XRF devices present an open beam, which means no part of the human body is prohibited from being in the primary radiation and the use of engineered safety controls is somewhat limited. Nonetheless, they appear convenient for carrying out elemental or chemical analyses of materials, components or systems in situ by industry. By procedure, the XRF work analyses are performed when such devices are brought to the location of the test material, are hand-held by the operator, and are activated to provide a high intensity primary beam that bombards the test material at very close range. Mitigation of the hazards is necessary. Thus, XRF NDT work not only must address radiation safety based on NDT industrial radiography, but also require strict adherence to administrative measures in order to reduce the likelihood of radiation accidents and unintentional exposures. The owner of a portable hand-held x-ray tube based open-beam XRF device is directly and ultimately responsible for its management, control and applications, and any delegation to another individual does not relieve the XRF device owner of these responsibilities.

At any XRF NDT jobsite or facility where the XRF device is hand-held or presents an open beam for the intended application, the XRF certified operator has a responsibility to:

1. carry on his or her person appropriate proof of identification and XRF operator certification whenever XRF NDT work is being conducted;
2. provide the owner of the XRF device appropriate evidence affirming identification and certification;
3. perform, prior to use, safety and functional checks of the XRF device and survey meter, ensure they are safe to use and, if they are defective, not use them;
4. keep unauthorized personnel away from the immediate vicinity of the XRF NDT work area while taking measurements (a minimum distance of 1.0 metre is recommended);
5. wear, where required by a regulatory authority or specified in operational procedures, extremity dosimeters appropriately on the hand(s) and finger(s), that are likely to incur the highest risk, and ensure that the worker permissible limits regarding these tissues or organs as indicated in Section 9.3 of this booklet are not exceeded (such dosimeters must be supplied by a dosimetry service provider which is approved by the Canadian Nuclear Safety Commission in accordance with its regulations);
6. when necessary, use an appropriately calibrated and functional survey meter to ascertain, establish or confirm radiation levels are within 20% of those provided by the manufacturer of the XRF device, such as, might be the case for which (i) the radiation shielding or performance of the XRF device is suspect for reasons related to design, damage or malfunction, or (ii) during XRF measurements, when radiation levels in the immediate work area are in question, and ensure relevant documentation of such actions is retained (the survey meter photon detection threshold should be 5 keV; the survey meter must be calibrated by a national standards calibration ionizing radiation laboratory, or a laboratory that has been accredited by a national standards laboratory to perform such calibrations; calibrations are to be done at several photon energies to cover the range of photon energies generated by the XRF device; frequency of calibration is once a year or after the meter has been serviced or repaired; records of survey meter calibrations must be kept at the facility; additional information on survey meters is provided in Appendix II of Safety Code 32);
7. keep radiation exposure to himself or herself and allied personnel ALARA;
8. notify the owner of the XRF device of any known or suspected abnormal radiation exposure to any person, provide the necessary details and maintain a record of such notification;
9. supervise, as delegated by the owner of the XRF device, any individual in training for XRF operator certification;
10. when necessary and as delegated by the owner of the XRF device, supervise students in an educational or vocational institution who are required to use the device as part of a course curriculum, after they have received safety training specific to the device intended for use;
11. follow all protection and safety rules established by the owner of the XRF device for the XRF NDT work and for the device itself;

12. secure the XRF device when it is in your custody, and not allow any unauthorized individual to use it; and
13. where applicable, when XRF NDT work is to be carried out at a client's facility, brief the client appropriately in respect of the safety issues relevant to such work, and unsure that the work is carried out safely.

Students assigned XRF NDT work at a facility or job site (i.e., field work) for which
(a) the XRF device must be in the hand-held or open-beam mode for the application, and
(b) direct supervision by an XRF certified operator is neither practical nor warranted and must have NRCan XRF certified operator certification, before using the XRF device for such work.

XRF NDT Work using a Closed Beam System

There are situations in which a portable hand-held x-ray tube based open-beam XRF device is manufactured, assembled or integrated by the manufacturer into a closed beam system to carry out XRF NDT work. A closed beam system that comprises such an XRF device as the ionizing radiation source must comply with the requirements specified in the applicable RED Act Regulation (Schedule II, Part XIV Analytical X-ray Equipment).

In a case where such an XRF device is configured and operated in a closed beam system, the user would not require NRCan XRF operator certification since the XRF NDT work does not require the XRF device to be in the hand-held or open- beam mode for the application.

11.4 Use of time, distance, and shielding to reduce radiation exposure

Whenever practical, the primary beam of radiation shall be directed away from occupied spaces. The XRF operator should perform his work in such a way as to promote ALARA concepts (time, distance and shielding):

- Minimize the exposure time,
- Maximize the distance from persons to the source of radiation, and
- Shield persons from the radiation.

Radiation safety tips for using XRF analyzers

- Do not allow anyone other than a certified XRF operator to operate the analyzer.
- Be aware of the direction that the primary beam (x-rays) travel.
- Avoid placing any part of your body (especially the eyes or hands) near the x-ray beam port to adjust the instrument during operation.
- Allow no one closer than 1 meter during operation of the analyzer.
- Never defeat safety devices on analyzers such as sensors, switches, indicators, etc.
- Wear appropriate dosimetry as might be required by the regulatory authorities or in operational procedures
- The XRF operator is responsible for the security of the analyzer.

  - Never leave the analyzer unattended when in use.
  - When in use, the analyzer should be in the operator's possession at all times (i.e. either in direct sight or a secure area).
  - Always store the instrument in a secure location when not in use

Small Samples

Small samples that do not cover the measurement window entirely are potentially risky because part of the primary beam may not be attenuated by the sample. To eliminate this risk, some XRF analyzers have a protective safety cap or test stand designed to completely enclose a small sample Use it.

Thin Samples

Radiation from the x-ray tube can penetrate test samples depending on their thickness and atomic number. The following table gives some ideas of the relative x-ray intensities after 40 keV radiation has passed through various thicknesses of aluminum and iron sheets.

Aluminum Sheet		Iron Sheet	
Thickness (mm)	Relative Intensity (%)	Thickness (mm)	Relative Intensity (%)
0	100	0.0	100
1	46	0.1	23
2	26	0.2	9
4	11	0.4	2.1
10	1.5	1.0	0.08

From the preceding data in order, to absorb 90% of the radiation, aluminum samples must be 4mm thick while iron samples (because of their higher atomic number than aluminum) would require a thickness of 0.2 mm. More importantly,
because of radiation transmitted through the test samples and the resulting scattered radiations, in practice, it is not safe to measure samples:

- while holding them in your hand.
- while sitting at a desk - radiation may go through the desktop and strike your legs or other body parts.

11.5 Owner Control of XRF analyzers when not in use

The owner of the XRF analyzer is responsible for the safe keeping (under lock and key) of XRF analyzers under his authority.

- When not in use, always keep and store the analyzer in a secure area.
- Keep the key separate from the analyzer.
- Maintain records to keep track of all XRF analyzers owned and the operators assigned to use them and where they were used.

In Case of Emergencies

- **Lost or Stolen:** Notify the appropriate regulatory authority (HRSDC Labour Program or the appropriate provincial or territorial jurisdiction) as soon as possible. In addition, contact the police and the manufacturer.
- **Accident**
  The first step is to turn off the analyzer and:
  - **remove the battery pack and**
  - **other power sources (e.g. disconnect line power).**

Minor Damage: If any hardware item appears to be damaged, even if the analyzer remains operable, contact the equipment owner for advice immediately. The equipment owner is to contact the manufacturer for advice as soon as possible.

Major Damage: If the analyzer is severely damaged, immediately contact both the manufacturer and the regulatory authority ((HRSDC) Labour Program or the appropriate provincial or territorial jurisdiction).

12. Applicable Canadian Standards Regarding XRF devices

12.1 Radiation Emitting Devices (RED) Act

Health Canada is a regulatory authority for radiation emitting devices and is responsible for administering the Radiation Emitting Devices (RED) Act and its Regulations.

The RED Act governs the sale, lease or importation of radiation emitting devices in Canada. Manufacturers, distributors and importers of radiation emitting devices are responsible for ensuring that their products comply with the RED Act and the applicable RED Act regulation before they are sold, leased or imported in Canada. RED Act Regulations prescribe specific safety standards governing the design, construction and function of radiation emitting devices.

XRF devices are radiation emitting devices. They determine elemental composition or examine the microstructure of materials, are classed as analytical x-ray equipment, and are regulated under the RED Act as well as Schedule II, Part XIV Analytical X-ray Equipment. These documents may be consulted at the following web sites:

http://laws-lois.justice.gc.ca/eng/acts/R-1/index.html
http://laws-lois.justice.gc.ca/eng/regulations/C.R.C.,_c._1370/index.html

12.2 Canada Labour Code

Human Resources and Skills Development Canada (HRSDC) Labour Program is the regulatory authority responsible for administering and directing compliance with the Canada Labour Code (CLC) and associated Regulations in the Public Service of Canada, as it is in the rest of its jurisdiction, i.e., in the position of regulator of both occupational health and occupational safety.

Safety Codes are incorporated by reference into the CLC which applies to federally regulated sectors nationally. Safety Codes prepared by Health Canada set out requirements for the safe use of x-ray equipment. They are intended primarily for the instruction and guidance of persons employed in Federal Government departments and agencies, as well as those that fall under the jurisdiction of the Canada Labour Code.

An Addendum specifically applicable to portable hand-held x-ray tube based open- beam XRF devices falls within the scope of Safety Code 32. Safety Code 32 applies to analytical x-ray equipment. The owners of radiation generating equipment are ultimately responsible for the radiation safety of their equipment.

The Canada Labour Code and Safety Codes may be consulted at the following websites, respectively:

http://laws.justice.gc.ca/en/L-2/sor-86-304/text.html. http://www.hc-sc.gc.ca/ewh-semt/pubs/radiation/index-eng.php

Facilities under provincial or territorial jurisdiction may be subject to requirements specified by their jurisdictions. Users should contact the relevant authorities in their jurisdiction for details of regulatory requirements of individual provinces and territories. Website for provincial/territorial radiation protection authority contact list:

http://www.hc-sc.gc.ca/ewh-semt/radiation/fpt-radprotect/members-membres-eng.php

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END OF BOOKLET

NOTE: All the latest forms and application requirements are available on the NRCan NDTCB website http://ndt.nrcan.gc.ca

IMPORTANT NOTE: Users of XRF devices to which this booklet refers are advised to contact their appropriate federal, provincial, or territorial radiation protection authority for applicable rules of operation.

For certification information, please contact: National Non-Destructive Testing Certification Body
CanmetMATERIALS, Natural Resources Canada, Government of Canada website: ndt.nrcan.gc.ca
Telephone: 1-866-858-0473
Email: ndt-end@nrcan-rncan.gc.ca