COMMERCIAL APPLICATIONS OF X RAY SPECTROMETRIC TECHNIQUES

D. WEGRZYNEK
The IAEA Laboratories,
Seibersdorf,
Austria
D.Wedgrznek@iaea.org

1. INTRODUCTION

In the 21st century, the X-ray fluorescence (XRF) technique is widely used in process control, industrial applications and for routine elemental analysis. The technique has a multielement capability capable of detecting elements with $Z \geq 10$, with a few instruments capable of detecting also elements with $Z \geq 5$. It is characterized by a non-destructive analysis process and relatively good detection limits, typically one part per million, for a wide range of elements.

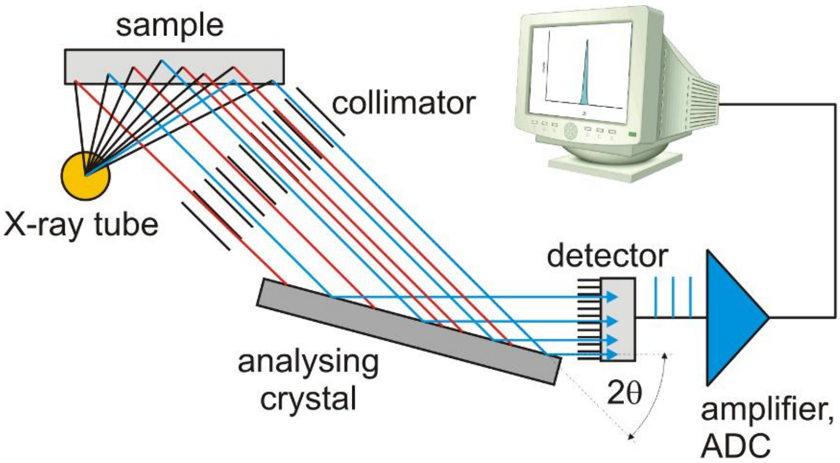

Fig. 1. Scheme of a wavelength dispersive X-ray fluorescence spectrometer.

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

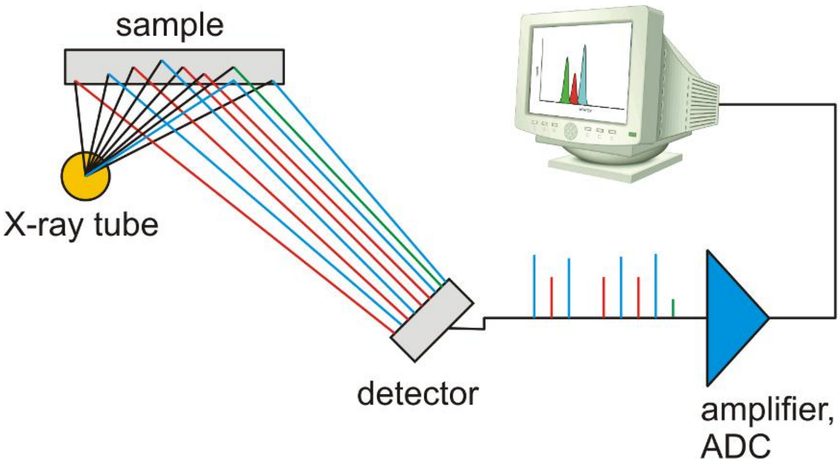

Fig. 2. Scheme of a wavelength dispersive X-ray fluorescence spectrometer.

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

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

Below are some industrial and routine applications of XRF techniques [1]:

— Elemental analysis in mining and minerals:
  - Na, Mg, Al, Si, S, K, Ca, and Fe in cement, clinker, and raw meal;
  - Na, Mg, Al, Si, K, Ca, and Fe in lime, limestone, dolomite, sand or glass;
  - Mg, Al, Si, Ca, Ti and Fe in kaolin and other clays;
  - Al, Si, Ti, and Fe in bauxite;
  - P, S, Ca and Fe in phosphate rock and fertilizer;
  - Na, Mg, Al, Si, and Fe in cement wallboard;
  - Ca and S in gypsum;
  - Determination of method detection limits (MDLs) for trace constituents in coal fly ash;
  - Trace Ca and V in silica;

- Qualitative and quantitative analysis of garnet;
- Compositional analysis of SiO_2 and TiO_2 in superconductors, TiO_2 and zircon materials, feldspar, alumina and silica;
- Portland cement and building materials
- Water-borne deposits and boiler scale;
- Coal and coal products;
- Silicate and phosphate rocks, clay, diatomites, zeolites, gypsum, limestone, lime and sludges;
- Fluorspar and related by-products;
- River sediments; and
- Ti and Pb ores, sinter and slag;

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

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

— Metallurgical analysis:
- Jewellery;
- Compositional analysis of Fe-based, Al-based, Co-based and U-based alloys; Ferrous and Ni-based alloys and finished parts; powder alloys; precious metal alloys; bronze; phosphorus bronze; brazes; and
- Steel and stainless steel analysis;

— Plastics and polymers:
- Zinc in polystyrene and other polymers;
- Bromine and antimony fire retardants in styrofoam and plastics;
- P, Ca, Ba, Zn in polymers;
- Silicones in polymers;
- Sulphur in polyurethane;
- Mg, Al, Si, Fe in fibreglass;
- Plastics compounding;
- Chlorine in rubber and plastic;
- Sorting PVC from other plastics;
- Trace P in plastic;
- Si in Plexiglas;

- Fe in extruded pellets;
- Cl in polyethylene;
- F in polycarbonate;
- Ti in polyethylene powder; and
- Trace Ti, Al, Mg in polymer film;

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

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

— Environmental:
- Lead in paint;
- Air filter analysis;
- Soil screening and analysis;
- On-site and stack air monitoring;
- Waste water;

- Tissue samples;
- PCB's in soil;
- Particulate matter on air filter pads;
- Pb, Cu, Hg in soils;
- Trace elements in soil, water, ashes; and
- Matching and quantitative analysis of waste streams;

— Wood treatment:
- Chromium, copper, and arsenic treatment (CCA) in wood and solution;
- ACZA, an alternative treatment to CCA, contains ammonium, copper, zinc and arsenic, in wood and solution;
- ACQ, a preservative containing ammonium, copper and quaternary ammonium, in wood and solution;
- Pentachlorophenol in wood and solution;
- Zinc borate treated wood and solutions;
- 3-iodo-2-propynyl butyl carbonate (IPBC) treated wood and solutions; and
- Bromine wood treatment;

— Pharmaceutical:
- Bismuth in anti-diarrhoeal medication;
- Calcium and magnesium in antacids;
- Zirconium, and aluminium in deodorant;
- Selenium in shampoo;
- Lead in bone and blood;
- Calcium in dietary supplements;
- Chlorine in toothpaste;
- Zinc in cold treatments;
- Metals in vitamin tablets and supplements;
- Iodine in sterilization products;
- Silver nitrate on medical products;
- Hazardous metal analysis in pharmaceuticals; and
- Silicone on condoms;

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

— Forensics
- Matching of glass fragments or paint chips;
- Bullet residue analysis;
- Metal and soil analyses;
- Qualitative analysis of explosion by-products;
- Trace metals in human tissue; and
- Analysis of starting materials of methamphetamine synthesis;

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

Tables 1 and 2 list some applications of laboratory and portable XRF analyzers based on radioisotope excitation [2]. The first applications of portable XRF analysers were in mining and mineral prospecting. Since then, the range of the commercial applications has been expanded significantly.

TABLE 1. TYPICAL COMMERCIAL APPLICATIONS OF RADIOISOTOPE BASED XRF ELEMENTAL ANALYSERS

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

TABLE 2. ON-LINE APPLICATIONS OF XRF/A ANALYSIS SYSTEMS

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

2. REFERENCES

[1] JORDAN VALLEY AR, INC., http://www.jordanvalley-apd.com/topapplications.htm.

[2] Handbook of X-Ray Spectrometry, 2nd Edn, VAN GRIEKEN, R.E., MARKOWICZ, A.A., Eds, Marcel Dekker, New York (2002) 1016 pp.