

ELEMENTAL ANALYSIS AND CHEMICAL-COMPOSITION-BASED MATERIAL SEPARATION AND BLENDING

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Abstract

The need for elemental analysis and chemical-composition-based material separation will be demonstrated for scrap metal alloys, including aluminum alloys.

Sorting of a few known alloys in the manufacturing scrap stream will be compared to the batching of a secondary alloy from an unknown mixture of post-consumer scrap.

The capabilities of LIBS, XRF and PGNAA (neutron activation) for quantitative elemental analysis will be compared.

The analytical capability requirements of process control and high-speed sorting will be contrasted.

Examples of successful sorting applications using each of the three technologies will be discussed.

Introduction

Recent years have seen an unprecedented explosion in developments in technologies related to sensors and sensor-based process control and sorting. Particle sorters are using a variety of sensors to identify and sort ores, coal, glass cullet, metal scrap, plastic scrap, plastic bottles, electronic waste, as well as foodstuffs, including grains, nuts, fruit and vegetables. Online elemental or molecular analysis is finally penetrating industrial markets and is being adapted to particle-sorting applications. This paper compares the three leading elemental analytical techniques applicable to metal particle online analysis and gives examples of successful industrial applications.

Need for Elemental Analysis and Chemical-Composition-Based Material Separation

Recycling of metals requires separation of metal scrap from non-metal and then sorting the metals by at least parent metal categories. This in most cases can be done by bulk-density and magnetic separations followed by visual inspection. Bulk material separation technologies are usually lower cost and higher throughput than the particle sorting circuits. When that is the case, there is no need to develop particle sorters for these applications. The exception in these early stages of recovery is removal of residual metals from the nonmetallic residue, which usually contains nonmagnetic stainless steel, insulated metal wire and small Al grain as main metal contaminants of the nonmetallics. There are further opportunities for the particle sorters to separate nonmetallic components, but in all these cases these separations do not and need not involve online elemental composition analysis

At this time with rapidly expanding demand for all metals in Asia, the scrap metal recycling market can consume all the parent metal separated scrap without further upgrading. Hence there is no envi-

ronmental or immediate global recycling system need past what is already currently accomplished in Asia by handsorting.

There is a growing interest in US and EU to stem the flight of the industry and manufacturing base to Asia. Since, handsorting of shredded scrap in the West is not economic, and handsorted scrap from Asia is not sold back to the West, all the scrap that is to be used in the West is a candidate for automated separation by parent alloy and further upgrading. Chemical-composition-based separation is justified by the use of the metal scrap value-added alloys.

There is a world of difference between sorting out parent metal groupings and sorting alloys within these groups. In most cases, the parent metal can be identified by external appearance or some other physical attribute, a fact that enables the Chinese handsorting "technology"; even poor sensors can identify concentrations in the 80-98% range. Sorting among alloys of the same metal is much more challenging (5x – 200x harder). Table 1 shows that comparison. Most particle sorting is based on measuring the major alloying element concentrations. There is little chance to obtain sufficient precision and sensitivity to determine trace elements online with single shot analysis. The trace elements can be found for the batch average composition determined in process stream analysis mode rather than during the single shot/single particle sort.

Table 1: Difference between parent metal identification and measurement of alloying element concentrations

Typical concentrations		
Parent metal	Major alloying elements	Trace elements
(balance)	(min and max)	(max only)
80% - 98%	0.5% - 20%	0.01% - 1%

Sorting of Manufacturing Scrap and Batching of a Secondary Alloy from Post-Consumer Scrap

New and old scrap segregation poses different challenges. The sorting of new scrap is a problem of separation of a few known alloy types, each with its own well-defined market and composition. The sorting of old scrap is a problem of trying to make the highest value product out of a large number of alloy types of unknown composition.

Manufacturing Scrap feed contains a small number of alloys of well-known composition. There is a need to identify the elemental fingerprint of each of these alloys. There is no need for quantitative analysis to segregate these alloys for closed-loop recycling.

Alloy Identification

Analytical instruments operated in a qualitative mode give a spectral signal characteristic of the material being analyzed. If there is only a few known alloys mixed in the feed, one can compare the wavelength or energy spectra for the known alloys and identify them by a statistical correlation or neural-network procedures. Since the composition variation within a single alloy batch is usually much smaller than the precision of a single non-contact analysis, assigning the known composition to a particle that was identified through qualitative fingerprinting is the preferred method of obtaining the composition of a new scrap particle. This method breaks down when the scrap feed contains a large number of alloy variants of a priori unknown compositions. This is the case for post-consumer scrap.

Sorting of Post-Consumer Scrap

Post-consumer scrap feed contains a large number of unknown alloy compositions. The objective is to make the largest quantity of value-added secondary alloy by batching of this secondary alloy from post-consumer scrap. There is a need to analyze the elemental composition of each piece. Quantitative elemental analysis is required.

Quantitative Elemental Analysis

Quantitative analysis relies on much more careful analytical procedures to measure the intensity of collected radiation as a function of wavelength or energy, eliminate or correct for instrumental factors, and, through de-convolution of the spectrum, extract the signal for each alloying element of interest separately. This signal is then compared with elemental concentration calibration curves to determine the concentration of each of the elements. In most cases, multivariate chemometric procedures are used to account for interaction and matrix effects.

Non-Contact Industrial Analytical Methods

In industrial particulate process stream control and particle sorting applications, it is impractical to contact each particle that needs to be analyzed. Successful analytical methods direct a flux of energy at the material and analyze the radiation emitted by the material in response to the incoming energy flux. In general, the material energy absorption and re-emission processes are resonant in nature. The material most efficiently interacts at the frequencies or energies that match the vibration energies of the molecules or electron transition energies of the atoms. The molecular bond vibrations absorb and radiate in the infrared part of the spectrum at a 10-20 μm wavelength, corresponding to an energy of 0.124-0.062 eV.

NIR absorption spectra, which look at overtones of these vibrations in the 0.9-2 μm spectral window, are the basis of qualitative identification and sorting of polymers and plastics. Solid metals do not form molecular bonds that exhibit infrared spectra, and one needs to look at the electron transitions of the individual atoms. The outer shell valence electrons have electron transition energies in the 1.5-8 eV energy range, which span the visible through UV parts of the spectrum from 800 down to 160 nm. The shorter wavelengths are so efficiently absorbed by oxygen that remote analysis in air becomes impractical until one comes to the energies of the inner K, L and M shell electrons of 1-60 keV.

Below 1 keV, absorption by air and the alloy matrix is so strong that the M lines are not observed for transition metals, and only K are observed for lighter metals ranging from Mg to V. Below Mg,

which fluoresces at 1 keV, there is no useful remote XRF analysis in air atmosphere, and most industrial applications of XRF focus at elements of the atomic number of 17 (chlorine) and above. As the x-ray photon energy is increased, the atmosphere and the alloy matrix materials become more transparent making bulk analysis of the particles more practical. With the inner shells, however, we run out of the electron transitions that provide the characteristic fluorescence emissions.

The next set of shorter emissions comes from the nuclear reactions. These γ -ray emissions accompany absorption of thermal neutrons into the nuclei of the material producing unstable radioisotopes that after short delay decay with emission of α or β particles and energy in the form of γ -rays. Both prompt and delayed γ -rays have energies in the range of 1-7 MeV. All light and transition metals are quite transparent to the photons of such high energy enabling true volume analysis of the entire particle or a large portion of a bed of particles on a conveyor belt. Three industrially implemented methods of non-contact particle or process stream analysis are based on irradiating the materials with and detecting radiation in the different portions of the spectrum: laser-induced breakdown spectroscopy (LIBS), x-ray fluorescence (XRF) and prompt gamma neutron activation analysis (PGNAA). The bulk portion of this paper will be devoted to comparing and contrasting these methods and discussing their successful industrial applications.

LIBS

LIBS uses a high-power pulsed laser to deliver a burst of focused ablation pulses to the material surface spot, cleaning it and then vaporizing and ionizing a sample from this surface spot to generate a bright and quite reproducible plasma spark. The light emitted from the spark is characteristic of valence shell electronic transitions of both neutral atoms and ions in the plasma, and falls in the UV-VIS portions of the spectrum. The spectrum of the collected light from the plasma spark is used for the determination of the elemental composition of the plasma, which can be correlated to the local particle surface composition.

XRF

XRF uses a high-voltage, 20-50 kV, 20-50W x-ray tube to generate a collimated or diverging beam of broadband bremsstrahlung x-rays to illuminate the surface of the particle or the process stream. These incident x-rays have sufficient energy to knock out the inner shell electrons from the atom; characteristic fluorescence x-rays are emitted when the electrons from the L and M shells drop into the K shell electron hole. The fluorescence photons are detected by a solid-state photo cathode detector that produces a current pulse proportional in size to the energy of the incident x-ray photon. This detected pulse size-photon energy proportionality is the basis of the energy dispersive analysis. The pulses are sorted by size and counted by a multichannel analyzer that produces a histogram of all photon energies detected. The energy is characteristic of the elemental emission line and the deconvoluted peak integral can be converted to the alloying element concentration by a suitable multivariate calibration procedure.

PGNAA

Prompt gamma ray neutron activation analysis uses a flux of thermal neutrons from a ^{252}Cf radioisotope source to diffuse into the particle, or, more often, a bed of particles, passing through the sensor on a conveyor belt. Some of the thermal neutrons are captured by the alloying element atom nuclei, producing an unstable isotope. The neutron capture process is accompanied by a release

of a high-energy characteristic γ -ray. The atmosphere and the materials tested are transparent to the γ -rays; these γ -rays are usually detected by a NaI scintillator that converts the γ -ray energy into a light pulse of intensity proportional to the incident γ -ray energy. The light pulses are detected by a photomultiplier tube (or tubes) whose current output is again fed into a multichannel analyzer for energy dispersive analysis.

Illumination Sources

Pulsed Laser

A pulsed laser used for LIBS is usually a Q-switched Nd:YAG or Nd:YFL giving <10 ns 50-300 mJ pulse. The output of these lasers is monochromatic at 1064 and 1048 nm respectively. These lasers are sometimes frequency doubled, tripled or quadrupled to improve the ablation pulse coupling the material surface. The upper limit on the pulse peak power that can be used is the formation of air sparks above the surface at the dust particles crossing the beam. The laser is focused and at a wavelength that is not absorbed by the atmosphere so the concentrated energy can be delivered to the material surface from large distances. However, the requirement for generation of the plasma spark makes this a surface composition analysis in a small, usually <1 mm diameter, spot.

X-Ray Tube

Radioisotopes or x-ray tubes can be used as sources of x-ray illumination for x-ray fluorescence analysis. The radioisotope sources are used predominantly in small handheld analyzers for positive material identification in scrap yards or in industrial maintenance applications. X-ray tubes are used for higher output sources for radiography or elemental analysis.

An x-ray tube used for XRF analysis of transition metals consists of an electron gun, focusing coils and an anode target held at a high accelerating voltage of usually 20-50 kV. The accelerating voltage determines the upper limit of the x-ray photon energy emitted by the gun. The majority of the x-ray photons are produced by the process of deceleration due to the high-energy electrons passing through the electric field of the nucleus of the atoms of the anode target. This process produces a broadband continuum x-ray spectrum - bremsstrahlung. The number of x-ray photons emitted in that spectrum grows exponentially with the difference between the incident electron energy and the emitted x-ray energy. Superimposed on this continuum spectrum are the discrete characteristic fluorescence emission lines of the anode target material. On the low energy end, the emitted x-rays are quickly re-absorbed by the tube materials and by the atmosphere so that the low-energy limit of the observed x-rays mainly depends on the type and thickness of the output window material filtering the outgoing x-ray flux. The electron beam current determines the overall brightness of the source. This brightness is limited by the ability to remove heat from the anode to prevent it from melting. The x-rays in the 20-50 keV energy range cannot be conveniently focused. They tend to diverge in all directions and are typically collimated to a <120-degree cone diverging from the electron beam focus spot on the anode. Without additional source collimation, such a source illuminates the surface of the particles like a floodlight. The depth of penetration of incident radiation coming from a 50-kV tube into the particles is substantial, ranging from 10's of μm for transition metals and several 100 μm for light metals, but since the fluorescence x-rays for transition elements are typically <10 keV, the escape depth from the material is much smaller and one gets an average surface analysis.

Radioisotope Neutron Source

Radioisotope neutron source is used industrially for the prompt γ -ray neutron activation analysis. The isotope used is ^{252}Cf . It is an element manmade through irradiation of Pu in a nuclear reactor. Pu mutates sequentially to Am, Cm, and ^{252}Bk , which then decomposes through β decay into ^{252}Cf . With this pedigree, it is no wonder that in spite of being produced as a byproduct of plutonium enrichment, it is being sold as probably the most expensive industrially used element at $\$60 \times 10^{12}$ per tonne. Fortunately the ^{252}Cf has a relatively stable half-life of 2.64 years, giving it sufficient activity and stability as an industrial radioisotope source. ^{252}Cf decays through both a particle decay to ^{248}Cm (96.02% of the time) and by spontaneous fission (3.08% of the time). The spontaneous fission results in production of 2-3 fast ($\sim 2\text{MeV}$) neutrons in addition to fission product atoms and energy in the form of γ -rays. In a radioisotope source, these fast neutrons are slowed down (moderated) to the moderator temperature. The moderator used in these radioisotope sources are carbon atoms in plastic radioisotope housing. These thermal neutrons then diffuse out of the source with its characteristic speed of 2.2 km/s into the process stream particle bed. ^{252}Cf produces exceptionally high neutron fluxes with a sufficiently long half-life to be useful as an industrial neutron source. Such a source produces 170 million neutrons per second per microgram of ^{252}Cf . A typical industrial source used for analysis of material on a conveyor belt may contain 100-200 μg of ^{252}Cf and have a total output of $1.7\text{-}3.4 \times 10^{10}$ thermal neutrons per second. Radiation shielding is only partially effective in reflecting the neutrons, so that only a portion of them diffuse into the volume of the particles to be analyzed.

Interaction of Incident Radiation with the Analyzed Metal

LIBS

In the case of a focused, pulsed laser beam at a monochromatic wavelength between 250 and 1500 nm, or photon energy between 0.8 and 6 eV, peak power densities that can be delivered to the surface are limited by the dielectric breakdown of air that is facilitated by dust particles. Typically, 10-30 MW of power is delivered for <10 ns to a target spot of <1 mm diameter. Hundreds of mJ of energy delivered to such a small spot in the first few ns ablate, vaporize and ionize the metal from the surface of the target spot. Ionization strips the valence electrons from the metal atoms producing a highly reflective, dense electron cloud. The latter part of the ~ 10 ns laser pulse interacts with this electron cloud, mainly reflecting from and not getting to the surface. Plasma is generated and heated to 10-20,000 degrees K, initially emitting mainly blackbody broadband radiation. After $\sim 1 \mu\text{s}$ of cooling time, the characteristic optical emission lines begin to dominate the emission spectrum as the electrons and ions recombine, emitting photons characteristic of the particular electronic transitions. These emitted photons are just the right energy to re-ionize the neighboring atoms of the same metal and thus are strongly self-absorbed. This leads to limiting of the intensity of emission as the alloying element concentration increases, and, in the case where the emitting plasma is non-isothermal, can actually lead to peak reversal, where absorption in the cooler outer portion of the plasma dominates the emission from the hotter inner portion of the plasma. Eventually all the re-ionized ions return to the ground neutral state so the main effect of self-absorption is to expand the time duration of the fluorescence pulse. The duration of such pulses varies widely depending on the overall size of the spark and the alloying element concentration. Heavily self-absorbing lines from a 100-mJ spark can fluoresce for 100-150 μs . The emitted spectral line

energies correspond mainly to ionization energies of the various valence electrons and thus tend to lie in the 1-10 eV range, which converts to the spectral range from vacuum UV to NIR.

Basically LIBS provides the spectrum of the vapor phase plasma derived from a small spot on a surface. The correlation of this measurement with the bulk material composition can be in question in the case of surface contamination, surface coating, surface segregation, or targeting of micro-constituents with a size range of >100 μm . If one has a sufficient time, the analysis can be spot cleaned by laser ablation. In the case of particle sorting, however, the analysis is practically limited to a single laser pulse burst per particle and pre-cleaning is limited to the number of ablation pulses that can be packed into that single burst.

XRF

Broadband x-rays produced by an x-ray tube can be collimated and filtered, or discrete wavelengths can be selected from it by diffraction, but all these methods effectively throw away the unused portion of the x-ray energy. Since XRF depends on the incident x-ray photons knocking out the inner shell electrons, broadband illumination is usually used. The incident x-rays are attenuated as they interact with the alloy atoms; the low energy x-rays are absorbed near the surface while the more energetic ones reach deeper under the surface. However, fluorescence x-rays are less energetic and are readily absorbed by the surrounding material so that only those close to the surface have a chance to escape into the air and can proceed to the detector. The $1/e$ escape depth, the thickness of material that allows 37% of the energy to escape, depends both on the x-ray energy and the absorbing matrix. Light metal x-rays can escape only from a top μm of a transition metal matrix, whereas transition metal x-rays can escape from $\sim 100 \mu\text{m}$ of light metal alloy. This leads to two notable effects. XRF is a technique suitable for determination of average surface composition of the metal and is still susceptible to surface segregation of the alloying elements. The organic surface contamination and coatings are much more transparent to the x-rays so that XRF is much less susceptible to errors due to organic surface contamination. However, the higher atomic number components of the pigments in surface coatings do figure prominently in the XRF spectra. Qualitative XRF analysis indicates the presence of the alloying elements and estimates their relative abundance from the peak areas. Alloy identification through rank correlation or neural network with an alloy standard spectrum is possible. However, for quantitative analysis, one needs to deal with and correct for instrumental calibration, particle geometry, surface texture and matrix effects. In the microanalysis area, x-ray fluorescence analysis is done qualitatively on a fracture surface in an electron microscope, but for quantitative analysis in an XRF microprobe, a flat polished sample is required to be positioned in precise alignment to the electron beam source and the nearby x-ray detector. Under industrial particle sorter conditions with unprepared particle surface, random surface orientation, and substantial distance to the detector, only partial success in the quantification of the alloying element concentration measurements can be expected.

PGNAA

Thermal neutrons carry no electrical charge and hence do not interact with the electric fields of either electrons or nuclei. Direct collision between the neutron and the nucleus is necessary to have a chance of neutron capture reaction. Since all matter is mainly empty space, the probability of such a collision is small and neutrons can penetrate into the material to quite large depths and can effectively activate the entire volume of the material under analy-

sis. Once the collision between the neutron and a nucleus takes place, the capture probability of a thermal neutron flying around at room temperature at 2200 m/s depends on the neutron capture cross-section of the nucleus. These captured cross sections vary by 7 orders of magnitude over the periodic table with a gradual trend of increasing cross section with increasing atomic number. Deuterium, helium, beryllium, carbon and oxygen have particularly low capture cross sections, making them suitable as moderators that slow down but not absorb the neutrons, but difficult to detect by PGNAA. On the other hand, hydrogen-1, boron-10, sodium-23, chlorine-35 and cadmium-113 have very high cross-sections, making PGNAA particularly sensitive to these elements.

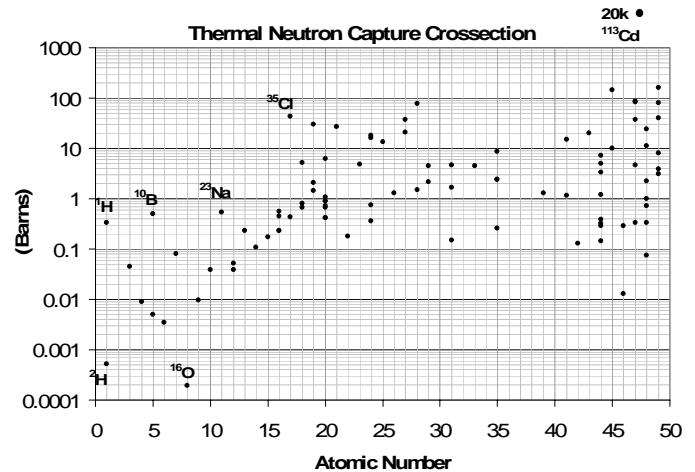


Figure 1: Thermal neutron capture cross section

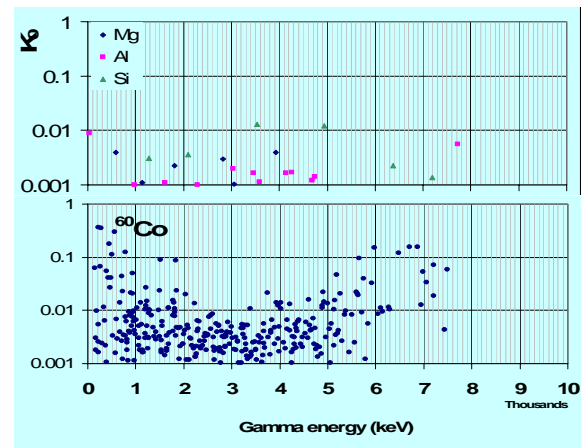


Figure 2: Relative γ -ray production cross section k_0

Neutron absorption reaction is accompanied by prompt release of energy in the form of γ -ray photons with energy ranging between 30 keV to 10 MeV. The intensity of a particular γ -ray spectral line is thus proportional to the product of the isotopic concentration, isotopic neutron capture cross section and the cross section for the production of the γ -ray of this energy. These high-energy photons have low probability of interacting with either electrons or nuclei of the material and hence tend to leave material unhindered. Each point in the volume analyzed radiates in γ -rays in all

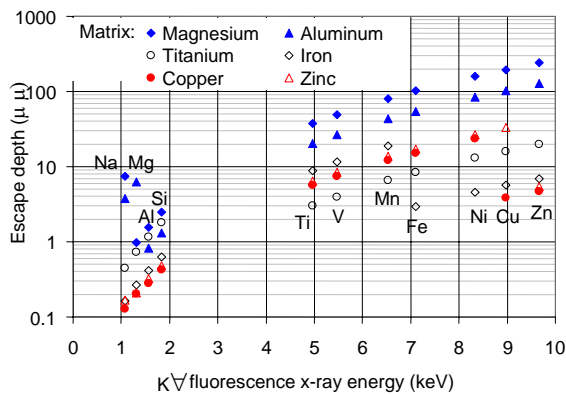


Figure 3: X-ray attenuation by metal alloys

directions. The ones that are detected are within the solid acceptance angle of the detector. That angle decreases as the source point moves away from the detector, so in spite of the fact that the γ -ray generation can be made reasonably uniform within the analyzed volume, the material closer to the detector has more influence on the measure material composition. This becomes important if there is composition stratification within the particle bed. This can easily happen on a conveyor belt if there is a particle size distribution that is correlated with the particle composition.

Matrix Effects

Matrix effect is a term much misused by spectroscopists. It tends to be used to encompass anything that causes the concentration measurement in one medium to differ from a measurement of the same concentration in another medium.

In LIBS there can be several reasons for matrix effects to be observed. The ablation efficiency of a particular elemental alloy component can be affected by surface segregation, formation of refractory intermetallic microconstituents, and a relative melting point and volatility of the alloying element and the parent metal. It is surprising there is not more trouble caused by these effects in sampling the metal by the ablation pulse for analysis as gaseous plasma. The plasma itself depends critically on its “matrix,” the gaseous atmosphere, especially its pressure and composition. Intensities of lines measured in the background of air plasma differ drastically from those measured in the background of nitrogen, argon or helium plasma. It was recently reported that hydrogen could be successfully analyzed in He atmosphere, whereas it did not show expected fluorescence lines in either air or argon. This was attributed to the very high mobility of the protons in the plasma. In argon or air, these protons escaped the confinement of the shock wave and did not participate in the ion-electron recombination reactions that lead to spectral emission. In contrast, in low atomic number He, the mobility difference was insufficient to let the protons escape and they, as expected, fluoresced on recombination with the plasma electrons.

The ions and atoms in high concentration in the plasma can absorb the photons emitted by the fluorescing ions and atoms. The magnitude of this effect depends on the parent metal type, the concentrations of the major alloying elements and on the wavelength of the particular alloying element spectral line.

Spatially and time-resolved LIBS spectroscopy has clearly demonstrated that there is segregation of ionic and atomic species and temperature within the plasma volume and that this distribution evolves in time. Theoretically, the concentration of a particular element is a sum of concentrations of all ionic species of that ele-

ment existing within the measurement volume at a given point in time. However this is a very difficult measurement to accomplish in a small plasma volume that grows and evolves on a ns- μ s time scale. Typically the light intensity is integrated over the selected spectral and temporal windows and the resulting measurement is calibrated against certified standards. It is easy to see how sampling the light from only a portion of the plasma or selecting different time and spectral windows for the various spectral lines can lead to apparent matrix effects. Chemometric, multivariate calibration procedures allow the calibration to account for some of these effects if they are reproducible from measurement to measurement. In particular, multivariate calibration is good in performing spectral deconvolution of the data if one element affects more than one measurement window.

In XRF the main source of matrix effects is the differential absorption of the various fluorescence x-rays by the composition of the alloy matrix. The variation of the photon x-ray escape depth with its energy and the parent metal atomic number clearly leads to calibration-curve dependence on the alloy composition and leads to a need for multivariate calibration procedures.

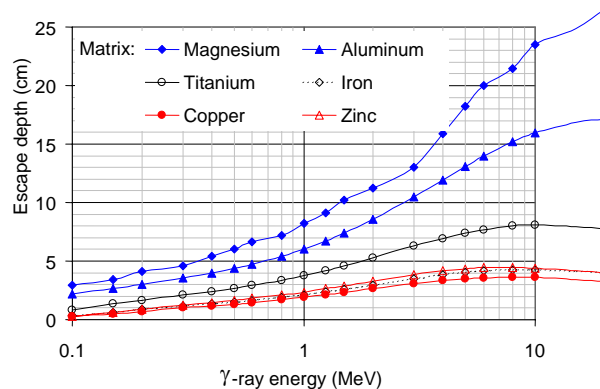


Figure 4: γ -ray attenuation by metal alloys

In PGNA the neutrons affect each nucleus individually and the resultant γ -rays tend not to interact with the surrounding material and later with the atmosphere between the material and the detector. This minimizes the analyte-matrix interactions. There can be some apparent inter-element interactions between the various γ -ray spectral peaks due to line interferences. These again can be accounted for through multivariate calibration procedures.

Interaction of Emitted Radiation with Atmosphere and Collection and Transmission Optics

In remote non-contact analysis, radiation emitted from the sample passes through and can be selectively scattered or absorbed in the atmosphere or later in fibers or waveguides directing the radiation to the detectors.

LIBS

The ultraviolet light is absorbed by both air and by fused silica at wavelengths below 200 nm. This limits the standoff that can be used between the material and the light collection optics and, later, the length of the UV-grade optical fiber that can be used to bring the collected light to the spectrometer entrance port. For gasses the absorption is both pressure and temperature dependent so the ambient temperature needs to be controlled for most reproducible results. The gas in air that absorbs at longest wavelengths

(120-180 nm) is oxygen. Hence, the UV light collection can be enhanced by purging the collected light beam path and the spectrometer with either nitrogen or inert gas.

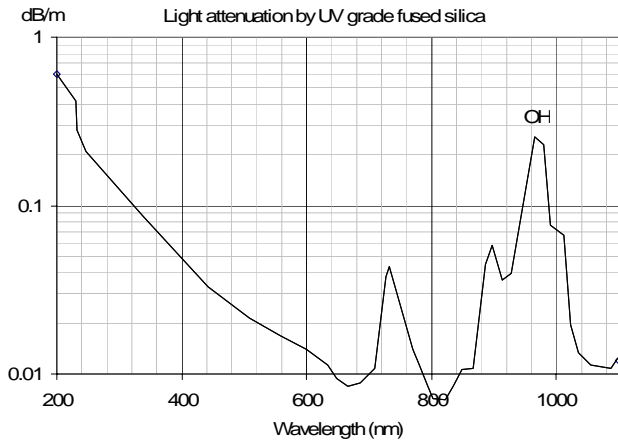


Figure 5: Light attenuation by UV-grade silica

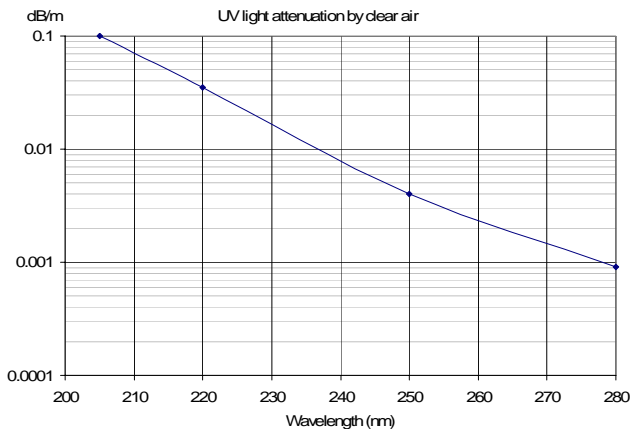


Figure 6: UV light attenuation by clean air

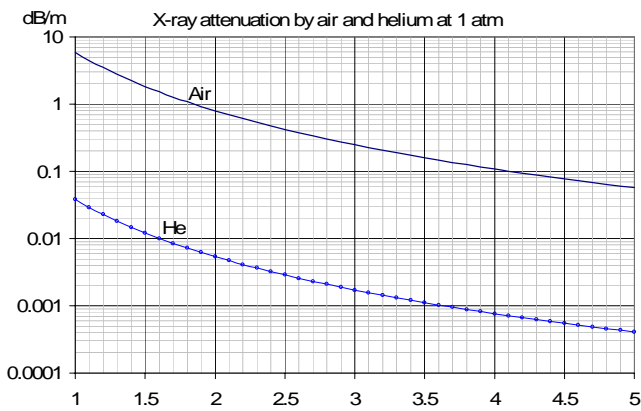


Figure 7: X-ray attenuation by air and helium

XRF

The low-energy x-rays of 1.5 keV and less are absorbed very efficiently by either nitrogen or oxygen or any higher atomic number gasses. Hence, to enhance the detection of the x-ray fluorescence from light metals, one needs to minimize the material-detector

distance. Helium is the only nonflammable gas that absorbs significantly less x-rays than air, but its use is not practical for non-contact analysis in industrial particle sorting applications.

PGNAA γ -rays are not absorbed to any measurable extent by air.

Radiation Detectors

LIBS uses a high-resolution polychromator to simultaneously direct the photons of different wavelengths to different detectors. For stationary analysis, echelle spectrometers use coarsely ruled diffraction gratings at a high angle of incidence to produce many overlapping diffraction orders, then separate these diffraction orders in an orthogonal direction by using a prism. This image of the entire spectrum is then projected onto a rectangular array image intensifier that is usually coupled to a CCD/CMOS array detector. Such a system is time gated through the image intensifier with a nanosecond resolution. The overall analysis speed is limited by the readout speed of the high-resolution array detector, which with 12- or 16-bit digitizing can take a few seconds. Such a system is adequate for process stream composition monitoring where an analysis at a few-second interval is more than adequate. For particle-sorting applications, systems capable of 50 analyses per second have been designed and implemented. These systems use Rawlings Circle polychromator monitoring light output at particular fixed spectral line locations. The light leaving the spectrometer exit slit is detected by a photomultiplier tube, with the output of the tube connected to an analog gated integrator. The integrated signal is then digitized. Such a system in a micro-analytical mapping application was able to map the concentration of a dozen individual elements simultaneously, performing individual spot analyses at 2 kHz – 500 μ s per analysis. This is actually possible since each plasma spark lasts only \sim 100 μ s, the analog signal gating and integration is simultaneous with the spark, and the remaining 400 ms gives plenty of time to sequentially digitize and read out a dozen integrated numbers.

XRF At x-ray energies up to 25 keV, a solid-state photodiode as a radiation detector is used. A photodiode produces a current pulse in response to each photon that strikes it. The current pulse is proportional to the photon energy. These pulses are sorted by size by the multichannel analyzer. In order to be able to resolve each pulse individually, the x-ray fluorescence flux has to be low enough that the pulses do not overlap; if they do overlap, they are counted as a single photon with higher energy. The time resolution of a pin detector varies with the detector size. A larger detector area means more x-rays are detected, but at a cost of the time resolution. A 25 mm², 500- μ m thick Si-PIN diode has a current pulse time resolution of approximately 10 ns. Since the x-ray photons arrive at random times in order to keep the peaks non-overlapping in time, \sim 10% “duty cycle” is typical giving a limit of \sim 10 million photons per second. In order to be detected, the x-ray photon has to reach the detector and then interact with the Si semiconductor in a photoelectric interaction. At the low x-ray energy limit, the photons are attenuated by the atmosphere and then by the Be window; at the high energies, the x-ray photons pass through the detector without the photoelectric interaction. A typical Si-PIN detector efficiency curve is shown in Figure 8.

PGNAA At γ -ray energies between 0.1 and 10 MeV, a scintillation detector is used. A single crystal thallium-doped sodium iodide crystal – NaI(Tl) – converts the invisible γ -rays to visible light photons inside of the scintillation crystal. NaI(Tl) produces

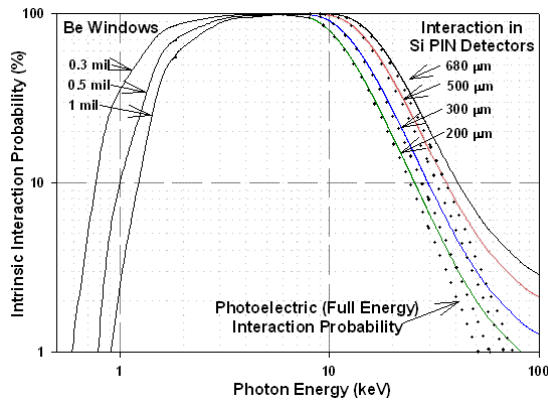


Figure 8: Typical Si-PIN diode detection efficiency as a function of x-ray photon energy (Amptek)

40,000 420 nm photons per each 1 MeV in the γ -ray-detected photon. The light pulses are converted to electric pulses and amplified by a photomultiplier tube bonded to the crystal. The pulse output of the PMTs is fed into an MCA for digitization and sorting into energy channels.

At the γ -ray energies, the materials are quite transparent and a substantial thickness of NaI is required to ensure that the γ -rays are efficiently detected. Fortunately at these high photon energies, Compton scattering and nuclear pair production add to the photoelectric process for gamma ray capture and detection. Figure 9 shows that the three processes give over 60% detection efficiency for a 76-mm thick, 76-mm diameter NaI(Tl) crystal. The NaI fluorescence pulses have a decay constant of 23 μ s (to 1/e), significantly slower than the Si-PIN diode, and limiting the practical throughput to ~4 million of individual pulses per second. Additionally there is persistent phosphorescence giving an afterglow of 8% after 1 ms and 4% after 2ms. The high intensity pulses need to be detected and separated this persistent background by the MCA.

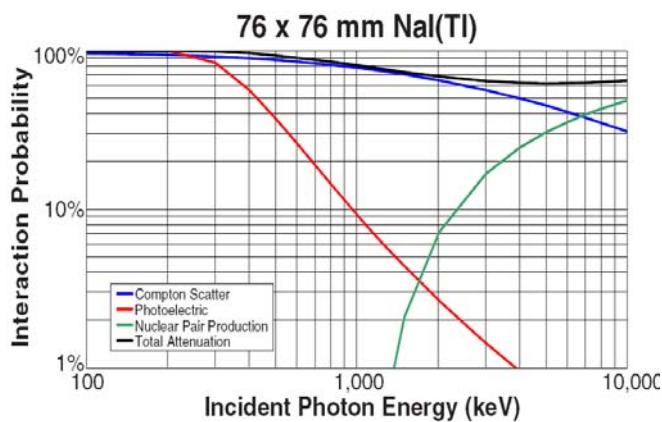


Figure 9: NaI(Tl) scintillating detector efficiency as a function of the γ -ray energy

Energy-Dispersive Multichannel Analyzers

Each of the pulses coming from either an Si-PIN diode or the scintillator PMT is amplified and then digitized, sorted by size and counted in each histogram channel. These functions are performed by multichannel analyzers, which, using multiple A/D converters, can process up to 4 million pulses per second, which

matches the maximum output of the scintillator crystal. In process stream composition control applications, where minutes of integration time are available, ED-MCA systems can provide excellent counting statistics. In particle-sorting applications, however, particle throughputs of 10-50 Hz are common. This limits the integration time to 20-100 ms and the total counts of 80,000-400,000 photons. A resolution of 0.1% would correspond to a count of 80 to 400 photons, and if these were Al, at 1.5 keV less than 10% (8-40) of these would get through the air atmosphere, and the absorption in the Be window to be lost in the noise. An increase in the source intensity is not an option as this would lead to overlap (sum) peak generation. Practically, the ED detectors are limited to lower throughput sorting and are the systems of choice for handheld ED-XRF analyzers for scrap yards and positive material identification in maintenance of oil rigs and chemical plants.

To get a high particle throughput, LIBS marries a very high brightness plasma spark with a wavelength dispersive spectrometer that splits the photons simultaneously and directs them to multiple monochromatic PMT detectors. The PMT output undergoes analog integration in a multichannel gated integrator, which is then digitized.

Analytical Capability Requirements

Product certification requires both high precision and high accuracy in the composition measurement. There is, however, plenty of time for calibration, standardization and replication. The elemental analysis technologies discussed here do not pretend to attempt to displace the traditional product composition certification laboratories.

In process control one can trade off accuracy for sensitivity as following trends and staying within process control limits is important in this case. Continuous monitoring permits replication and averaging to access and improve on the precision of individual measurement. In the process control approach, one trades off the ability to sort the feed for the ability correct for feed composition variations through process adjustments, hardener additions, or dilution of alloy-segregated scrap with prime metal.

Feed characterization. Determination of an average composition of a batch enables feed blending, which can accomplish some of the same goals as material batching through sorting without the need for high-speed analysis and diversion of individual particles. In this application, a material stream or a portion of a material stream is analyzed on line. The elemental concentrations are integrated over the entire material batch to give a measurement of the batch composition. With the knowledge of the average compositions of the feed batches, one can blend the input to achieve stable process control and consistent product without the need for high-speed sorting. One can also identify and separate higher purity batches or batches with a high level of a particular element to use them to batch higher value alloys.

High-speed elemental-composition-based sorting is justified by maximizing the fraction of the feed that can be batched into the high-value alloy. For post-consumer scrap, accuracy of the calibration is desired for the quantitative analysis, but the precision requirements in the individual single shot/single particle analyses are quite relaxed. With 20-g average weight of a piece, it takes a million particles and million analyses to make up a typical 20-tonne truckload batch, and the standard error of the batch average

analysis is then 1000 times more precise than the standard deviation of the individual particle analyses.

In the case of manufacturing scrap, where the feed consists of a mixture of a few known alloys, one needs to focus on some key identifying features of the raw analytical spectra. Based on this information, one can then separate the known alloys and confirm the composition by analyzing a few pieces off line on a laboratory or handheld spectrometer. The manufacturer's certified composition in such a case is known and sufficient to represent the product batch composition.

Examples of successful sorting applications using PGNAA

Thermo Electron Corp. has been developing markets for industrial PGNAA analysis for over a decade. In solid particle streams, they developed a cross-belt analyzer in which the ^{252}Cf neutron source is located below the belt and an array of NaI scintillation detectors monitors the γ -ray output above. These units were first used in coal-fired power plants for in-feed composition and blending control of coal fuel. The analysis helps predict the quantity and the composition of ash and determines the moisture and sulfur content of the coal. Prompt elemental analysis of inbound materials allows the power plants to reject shipments that do not meet the coal contract specifications. Feed blending and off-spec material rejection constitute grand macro-scale sorting of crushed material.

There is a similar application of PGNAA cross-belt analyzers in the cement industry for control and blending of cement kiln feed. In this case knowledge of the elemental composition of the raw materials leads to improved control of the cement product chemistry and additionally to greater throughput and reduced energy consumption per clinker tonne. It also extends quarry life by maximizing the use of lower cost and lower quality materials and avoiding kiln upsets. In total there have been 225 PGNAA cross-belt analyzers installed in cement kilns around the world since 1984.

In the scrap metal industry, steel shredder operators use PGNAA cross belt analyzers, produced by Thermo Electron and marketed by Gammatech, to certify the low-copper content of shredded copper product. Each of these shredders outputs more than 200,000 tons of steel shred. A new application developed just this year involves the use of the cross-belt analyzers at aluminum secondary smelters for the control and blending of scrap feed to secondary remelt furnaces. In this application the PGNAA feed batch analysis and least-cost feed blending competes directly with LIBS high-speed alloy-sorting technology.

XRF

It was already mentioned above that either radioisotope or x-ray mini tube powered hand-held analyzers are the tools of choice for scrap yard handsorting and scrap grouping. Austin AI is adapting this technology to automated particle sorting systems. Austin AI claim to have delivered prototype systems for detection of transition metal alloying elements in shredded aluminum scrap destined for wrought alloy applications. This system is limited to less than 10 particles per second per detector line by the previously discussed constraints of ED-XRF technology. Austin AI also delivered a system for inspecting whole wheels for foreign metal contaminants including lead balancing weights, copper in valve stems, and chromium surface plating with each wheel weighing between 5 and 10 kg. A 10-tonne per hour throughput requires that the inspection be completed in 2-4 seconds per wheel.

LIBS

The Austin AI, US XRF technology system will compete directly with the LIBS sensor elemental composition. The Al-alloy sorting technology developed by Huron Valley Steel is capable of sorting up to 50 particles per second per sensor and is able to deal with particles that are distributed randomly on the belt. HVSC has an industrial Al-alloy scrap sorting line in Belleville, Michigan, which has been continuously operating since 2004, sorting out and batching selected wrought alloys from Al scrap separated from non-ferrous metal concentrate produced by steel shredders.

Laser Analytical Systems in Germany has produced a robot-based automated part-LIBS elemental analysis, sorting and marking system that certifies the alloy composition of pipefittings for the chemical plant and oil industry. The high liability associated with the fitting failure due to material misidentification justifies the 100% inspection of each fitting sold into these applications.

Laser Detect Systems in Israel industrially installed LIBS elemental analysis sensors over conveyor belts in phosphate mines. Although the analysis is limited to a single line on the conveyor belt, they find that the batch average from such analysis correlates very well with the compositions back calculated from the eventual plant output data. In this application, the LIBS sensor is an alternative to PGNAA that is lower cost and less burdened with association with nuclear fission and radiation hazards, whether real or imagined.

Summary and Conclusions

The three elemental analysis methods applicable for non-contact online analysis each have their strengths.

PGNAA is mechanically simple, robust, surface-state independent and gives direct measurement of the volume average concentrations least susceptible to matrix effects. PGNAA cannot target individual particles and is too slow for particle-sorting implementations. It is a method best suited to batch analysis and least-cost blending strategies. PGNAA carries with it the stigma and hazards involved in handling fissile radioisotopes.

XRF requires the lowest capital investment and has a long history of both qualitative and quantitative elemental analysis of transition metal elements. XRF gives an average analysis of the surface of the metal scrap particles. This analysis can look through organic surface coatings of contaminants. XRF is well suited for the separation of parent transition metals, but is not well suited to non-contact quantitative analysis of light metal elements ($Z < 16$).

LIBS is the fastest and most versatile of these three elemental analyses methods. It is sensitive for both light and dense metal elements. Wider industrial adoption is hindered by the relatively high capital cost of the equipment required for single-shot-per-particle sorter implementation.

Feed batch elemental analysis by PGNAA and blending accomplish part but not all of the justification for a single-shot-analysis-per-particle sorter.

All three methods are beginning to be used for upgrading post-consumer Al scrap.

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