X-RAY FLUORESCENCE SPECTROSCOPY
IN PLASTICS RECYCLING

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X-Ray Fluorescence Spectroscopy (XRF) is applied to the analysis of plastics encountered in the recycling of durable goods. XRF can detect Cl, Br, Sb, Ti and other elements that are found in plastics. XRF has several positive features such as relative ease of use, fast sample preparation and analysis, minimal re-calibration, a broad range of detectable elements and a broad concentration range for analysis. XRF is thus suited for real-world plastics recycling environments. Examples of qualitative and quantitative analysis illustrate a few applications of various XRF instruments in plastics recycling.

Background

Compared with other materials, the recycling of plastics can be technically demanding for a variety of reasons. Among these, full identification and characterization of collected plastics can be a formidable challenge. One must be able to characterize a wide variety of plastics containing a wide range of additives, frequently from unknown sources. Techniques such as chemical analysis[1] and infrared spectroscopy[2, 3] can be used to determine the type of plastic with reasonable certainty. These techniques are less useful when looking for additives in the plastics.

In this study, X-ray fluorescence (XRF) is evaluated as a method to determine the types and quantities of certain additives in engineering thermoplastics plastics from end-of-life durables. XRF allows a recycler to look for certain chemical elements that are commonly found in these additives. Among the elements of particular interest are Cl, Br, Sb and Ti. These elements, which are frequently found in pigments and flame retardant additives, are quantified using calibration curves created from plastic standards. Other elements present in many post-use plastics (e.g. Pb, Cd, Zn, Si, S, P, Ca and Fe) are also analyzed qualitatively or semiquantitatively. A distinguishing feature of this study is that it is part of a larger comparative evaluation of several different XRF instruments in a real-world plastics recycling environment.[4]

Introduction to X-Ray Fluorescence Spectroscopy

X-Ray Fluorescence is a spectroscopic technique which is useful in identifying the presence and amount of many elements.[3,5] Many XRF instruments can detect all elements heavier than sodium, and some can even detect elements as light as boron. This means that XRF is useful for inorganic materials, metals and inorganic or halogen-containing additives in polymers.

The principle of XRF is shown in Figure 1. The sample is bombarded with X-rays which are high enough in energy to extract a K or L electron from many atoms. Electrons from a higher energy shell then fill the vacancy. If an L electron falls into the K orbital, K_α radiation is emitted. K_β radiation is emitted if an M electron falls into the K orbital. The slightly different energies of these two events leads to paired peaks for K_α and K_β. The K_α peak is at slightly

lower energy and significantly greater intensity than the K_β peak.   L and M peaks also occur as groupings of several nearby peaks. L and M peaks occur at progressively lower energies and intensities than the K peaks. Such peaks are important for detection of heavier elements, however.

The energies of K, L (and M) peaks are characteristic of the particular element and independent of the matrix, so one can identify which elements are present in the sample based on the peak energies observed. These characterisitic peak energies increase with increasing atomic weight and are higher for K than L peaks.

As an example of qualitative analysis, consider the XRF spectrum in Figure 2. The spectrum is plotted as an intensity (in counts per second (for a given channel)) as a function of energy (in keV). Note the K_α and K_β peaks for Cl, Ca and Ti. The peak energies for these elements are always the

Figure 1: X-ray fluorescence of an atom. Incident X-rays extract a K level electron. Either K_α or K_β radiation is emitted, depending on whether the vacancy in the K shell is filled by an L or M electron.
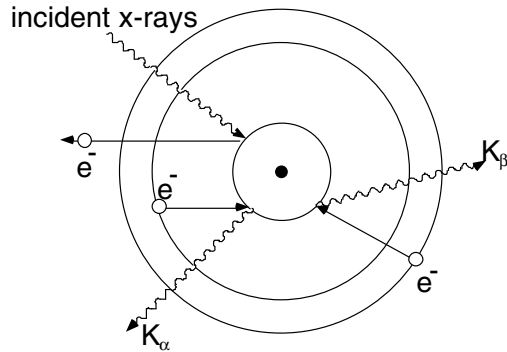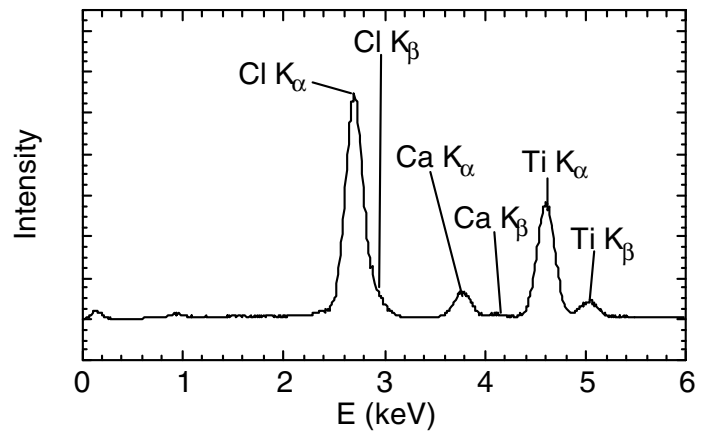
Figure 2: XRF spectrum of a plastic sample. Peaks at 2.6, 3.7 and 4.5 keV are $K\alpha$ peaks for Cl, Ca and Ti, respectively.

same, so the computer software (or the XRF operator) can qualitatively determine the composition of the sample. The spectrum alone does not tell us how much Cl, Ca and Ti are present in the sample, though.

Unlike energies, the intensities of the characterisitc peaks are strongly dependent on the matrix. This means that several standards in a matrix similar to the unknown matrix are required in order to quantify the element.

Some software can calculate quantitative information from spectra if the composition of the matrix is known. This method, which is known as fundamental parameters, is generally only semi-quantitative. Calibration using standards is required for reliable quantitative information.

Incident X-rays exciting the atoms can come from either an X-ray tube or an X-ray isotope source. The X-ray tube emits a wide spectrum of radiation and is capable of exciting a wide range of elements. Most XRF spectrometers employ an X-ray tube. The X-ray isotope source, on the other hand, emits a narrow spectrum of X-rays that can only excite a narrow range of elements. X-ray isotope sources are useful when only a particular element is sought, as in certain quality control or sorting applications.

The manner in which the X-rays of different energies are gathered distinguishes the XRF spectrometer as either wavelength dispersive (WDXRF) or energy dispersive (EDXRF). In WDXRF, a particular wavelength of the fluorescent X-rays is focused by a crystal onto the detector. The entire spectrum is collected as the crystal is rotated. WDXRF gives a very high resolution spectrum and allows for very low limits of detection, but these instruments are slower and more expensive than EDXRF instruments.

EDXRF instruments are able to distinguish the energies of incident X-rays. A given X-ray photon initiates a propagating event in the semiconductor (or gas-filled) detector. The degree of propagation depends on the incident energy, so the event is assigned to a certain channel based on that degree of propagation. Due to some variation in channel assignments, the peaks found in EDXRF are broader than those for WDXRF. The detection limits are also higher for

EDXRF. The significantly lower price of EDXRF instruments, however, justifies their use in many applications where ppm or lower detection limits are not necessary.

The detection of certain elements can be optimized by controlling a combination of X-ray voltage, X-ray current, filters, measurement atmosphere, time, target (for tube systems) and X-ray source (for isotope source systems).

Since detectors are only able to handle a certain quantity of X-rays photons, detection is improved if the only energy reaching a detector is energy close to that of the element of interest. Filters can be used to block the lower energy X-rays from the sample. This allows one to isolate the higher energy (higher atomic weight) elements. The amount of energy cut off and the energy where this cut-off occurs varies depending on the type and thickness of the filter used.

One can also isolate lower energy elements by setting the voltage to something less than the maximum voltage. This allows excitation of only the lighter elements (and L and M lines of heavier elements). With isotope source systems, the use of alternate sources has the same effect as decreasing the voltage for X-ray tube systems.

Another way to better observe the lighter elements is to make the measurement atmosphere inert and more transparent to X-rays. Argon, which is present in air at a concentration of 0.934% by weight, has K_α and K_β peaks around 3 keV. These peaks can partially overlap with the Cl peaks and also dominate the signal going to the detector. Also, the components in air (N_2, O_2 and Ar) absorb the characteristic energies of low atomic number elements. By replacing the air with He or placing the sample under vacuum, one can improve the detection of lighter elements.

A schematic of a typical EDXRF spectrometer is shown in Figure 3. X-rays from the X-ray tube (or isotope source) are passed through an optional filter and onto the sample. The sample may be in air, or perhaps under helium or vacuum to improve detection of lighter elements. X-rays from the sample then travel to the detector, which is cooled either electrically or with liquid nitrogen, depending on the detector type. The signal from the detector is then processed by the electronics and sent to the computer, which also controls the X-ray tube. XRF spectra can then be analyzed qualitatively and/or quantitatively using software in the computer.

In order to see the utility of XRF in the analysis of recycled plastic samples, several examples are discussed below. The various conditions and generic instrument type for the examples are given. A list of manufacturers supplying the instruments is given in the Appendix.

Black Toner Cartridges

In recycling, one might hope that all plastics in a given application with a given color would be the same. If this were true, one could sort plastics by color for a given product type. A closer look at black toner cartridges, however, shows a wide variety of plastic types and additives.

Figure 4 shows the spectra from two different toner cartridges at at conditions appropriate for lighter (condition A) and heavier (condition B) elements. Phosphorous is detected in the PC/ABS toner cartridge, suggesting the presence of a phosphorous-based fire retardant. The HIPS-FR toner cartridge contains a number of elements, including Br, Sb and Fe (other metals can be detected when the spectrum is plotted on a larger scale). Br (~10%) and Sb (~3%) are present in amounts typical of fire retardant materials.

Figure 3: Schematic of a Typical EDXRF Spectrometer. X-rays from the X-ray tube (or isotope source) pass through an optonal filter on their way to the sample (which may be in air, He or vacuum). X-rays from the sample then travel to the detector, which is cooled either electrically or with liquid nitrogen. The signal at the detector is then processed by electronics and sent to a computer or microprocessor.
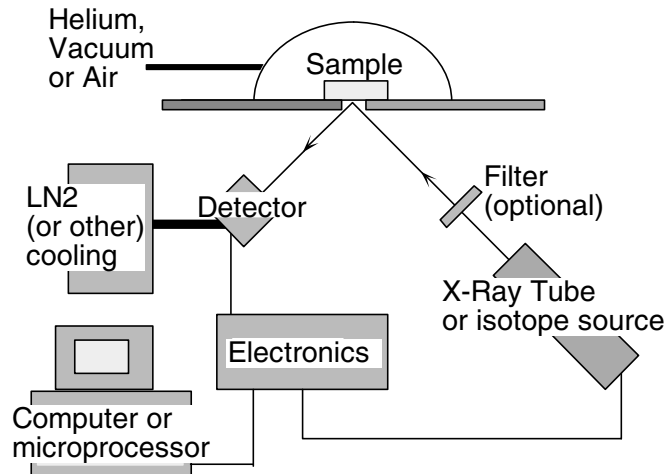

Figure 4: XRF Spectra of Black Toner Cartridges. Tests were conducted using an instrument with a pin-diode detector and a Rh target. Condition A utilized an X-ray tube voltage of 10 kV, a current of 50 µA and a Kapton filter. Condition B utilized an X-ray tube voltage of 25 kV, a current of 40 µA and a silver filter. Peaks at 2.7 and 3.0 keV are due to the Rh target and Ar, respectively. The broad peak between 3 and 10 keV is scattering from the source.
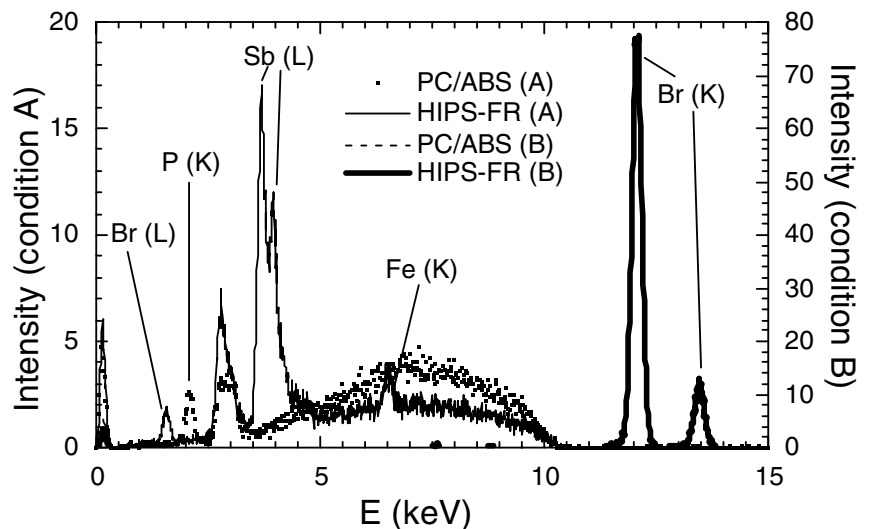
These results for the two toner cartridge materials show that a variety of additives may be present in plastics from similar applications. Other toner cartridges are also of different nominal plastic type and with different additives. XRF is a relatively quick method to determine which types of additives are used.

Blue Automobile Interior Trim

XRF is used to detect and determine the amount of Cl and other elements in a blue plastic used in automotive instrument panels and door panels. Figure 5 shows spectra obtained for the unknown sample using conditions A (lighter elements) and B (heavier elements). There

is a large amount of Cl and smaller amounts of Ca, Ti, Fe, Ni, Cu, Zn and Pb. The amount of Cl is quantified using instruments from four participating manufacturers. The average amount of Cl measured by the four instruments is 27±4%. Fundamental parameters calculations on three of the instruments give an average Cl concentration of 24±1%. Results from inductively coupled plasma spectrometry (ICP) measurements give a Cl concentration of 19.0%. Such a concentration for Cl indicates that the material is likely a blend of ABS and PVC.

ABS Automobile Plastic

XRF is used to determine the amounts of heavy metals in an ABS-rich plastic sample separated from a mixed plastic stream from end of life vehicles. Figure 6 shows that Cd, Pb, Hg and Se are present in the sample. The amounts of these elements based on fundamental parameters calculations are given in Table 2. For comparison, the concentrations determined using ICP are given.

Table 2: Concentrations (weight %) of Trace Metals in ABS Automobile Plastic

element	Cd	Pb	Hg	Se
Fundamental Parameters	540	310	590	280
ICP	1800	130	280	<80

This example shows that one can use XRF to look for (and even quantify within a factor of two or three) heavy metals in plastics. Even though such metals are not in common use today as additives in plastics, it is important for plastic recyclers to have the ability to look for such regulated elements that may have been used in plastics 10, 20 or even 30 years ago.

Figure 5: XRF Spectra of Blue Automobile Interior Trim. Tests were conducted using an instrument with a pin-diode detector and a Rh target. Condition A utilized an X-ray tube voltage of 10 kV, a current of 50 μA and a Kapton filter. Condition B utilized an X-ray tube voltage of 25 kV, a current of 40 μA and a silver filter. Peaks at 2.7 and 3.0 keV due to the Rh target and Ar are hidden by the Cl peak at 2.6 keV.
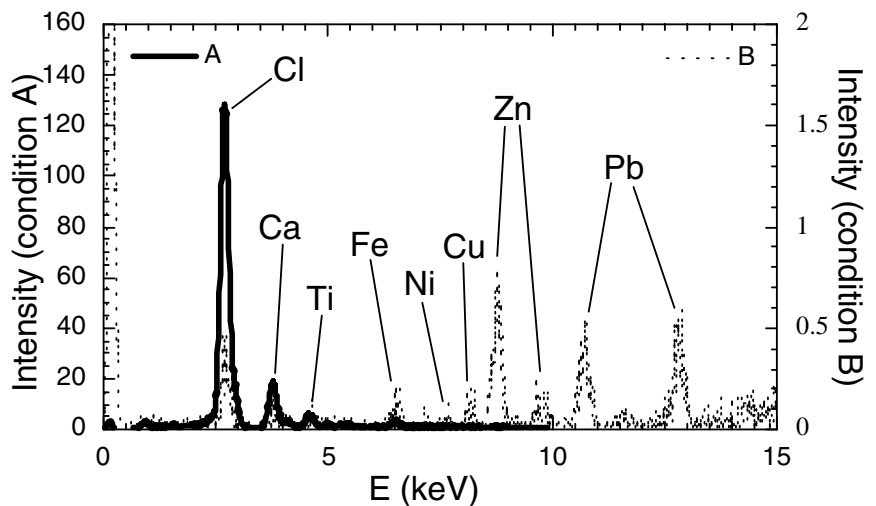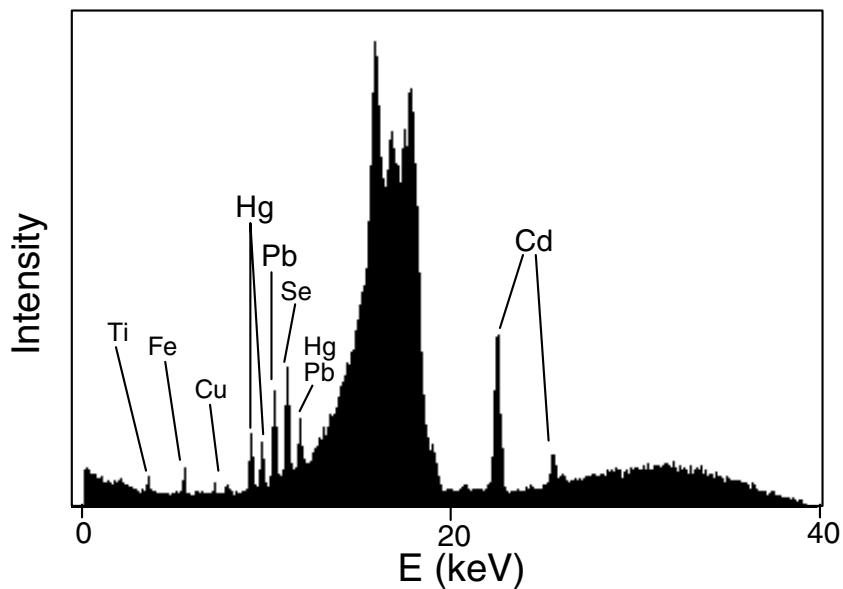

Figure 6: XRF Spectrum of ABS Automobile Plastic. Tests were conducted using an instrument with a Si-Li detector and a Rh target. The condition used was 45 kV with a current of 84 μA. A molybdenum filter was used. The large peaks from 15-20 keV are due to the Mo filter.

Conclusions

XRF spectrometry is a tool for detecting the presence of most elements heavier than Mg. The technique allows for relatively quick qualitative and quantitative analysis of certain elements that are common in recycled plastics. The previous examples have demonstrated the use of XRF to look for PVC (Cl), flame retardants (Br, Sb and P), or regulated heavy metals (Pb, Hg and Cd). Reflecting market conditions, it is expected that most recyclers of engineering plastics (and buyers of recycled plastics) could benefit in many ways from having access to on-site XRF analysis.

Appendix: Participating Instrument Manufacturers

company	U.S. office	phone	internet
Jordan Valley AR	Austin, TX	(512)973-9229	jordanvalley.com
Kratos Analytical	Chestnut Ridge, NY	(914)426-6700	kratos.com
Niton	Bedford, MA	(800)875-1578	niton.com
Oxford Instruments	Concord, MA	(800)447-4717	oxinst.com
Philips Analytical	Natick, MA	(508)655-1222	analytical.philips.com

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