Title: Feasibility of Analysis and Screening of Plastics for Heavy Metals with Portable X-ray Fluorescence Analyser with Miniture X-ray Tube

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Abstract

Metals and metal compounds have been used for many years in the manufacture of plastic products. The metallic compounds added to plastics although encapsulated in polymer matrix are usually not chemically bound to polymer molecules and consequently can gradually be released to environment over the service life of a plastic made object.

Similarly, when disposing of plastic waste either by incineration or by placing it in a landfill, toxic metals released from plastics can enter atmosphere or leach into soil. Environmentally responsible handling of plastics requires monitoring of potentially toxic elements in plastics during their production, recycling and disposal operations.

In this paper we report on application of a small, lightweight (1.5 kg), battery operated portable X-ray fluorescence analyzer for in-situ analysis and screening of plastic for toxic metals.

Introduction

Elements such as lead, cadmium, chromium, mercury, bromine, tin and antimony are or have been added to polymers as pigments, fillers, UV stabilizers, and flame retardants. Typically these elements are added as compounds which often do not chemically bond with molecules of plastic but rather create a suspension in solid plastic polymer. Therefore, in time they may potentially dislodge from plastics matrix. The finer the particles of added compound the easier it is for them to be removed. A visible symptom of such process is hazing on the surface of some plastics caused by migration of bromine from the bulk of material to its surface. The PVC based plastics contain considerable amounts of chlorine which, when released, facilitates leaching of metals into environment. This creates serious health and environmental problems since most of these elements have been identified as toxic to humans. Specifically, since so many toys and other objects of common use are made of plastics, they pose particular danger for small children. The initiatives undertaken to correct this growing problem target maximum allowable concentrations of toxic metals in plastics, and ultimately aim at their complete elimination from production.

The first regulations that specifically target heavy metals in plastics were introduced in mid nineties by European Community. European Community, “Packaging Directive” - EC-Directive 94/62/EEC, [1] regulate the total amount of metals such as Cd, Cr, Hg and Pb in plastic packaging materials to less than 100 mg/kg. Another EU Directive, 91/338/EC [2], sets the maximum allowable concentration of cadmium in plastics used for consumer goods at 100 mg/kg. In the US, the “Proposition 65” introduced in California banned cadmium from use. Separate effort is directed at proper handling of plastic waste. Specifically, European Council Directive 2002/96/EC on waste electrical and electronic equipment (WEEE) [3], mandates removal from such waste all plastic containing brominated flame retardants, all mercury containing components, batteries, etc.
FEASIBILITY OF ANALYSIS AND SCREENING OF PLASTICS FOR HEAVY METALS WITH PORTABLE X-RAY FLUORESCENCE ANALYZER WITH MINIATURE X-RAY TUBE

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The effective enforcement of such regulations requires that sensitive and reliable methods and instruments be readily available for responsible parties. For example, given the amount of imported goods crossing borders every day, the task of customs inspectors to effectively inspect the goods is possible only with a small, portable, easy to operate analytical tool(s) that can quickly identify and quantify prohibited elements in plastic products.
Over the last decade, small, lightweight Field-Portable XRF analyzers (or FPXRF) have become indispensable tools for accurate and rapid in-situ analysis and identification of alloys in metals production, fabrication and recycling. A second major use of these instruments has been in soil screening and analysis for heavy metals [4]. The problems encountered when attempting XRF analysis of plastics are in many ways similar to those that had to be addressed in analysis of soil. Therefore, the use of portable XRF analyzer to measure the concentration levels of metals in plastics seems to be a natural extension of its already tested capabilities for soil analysis.

The Principle of XRF Analysis

X-ray fluorescence analysis is based on the phenomenon of the emission of x-rays by the atoms of a sample when excited by an external source of radiation. If a gamma- or sufficiently energetic x-ray from an isotope or x-ray tube impinges on an atom of the sample material, it may eject one of the inner shell electrons of the atom. The vacancy created is almost instantaneously (in less than 10⁻⁸ sec.) filled by one of the electrons from the higher energy shell. The energy difference between the two energy shells involved in the process is emitted in the form of x-ray radiation. We call this radiation a characteristic x-ray because its energy is specific and unique to each atom. By being able to measure the energy and intensity of the characteristic x-rays, we realize qualitative and quantitative aspects of XRF analysis.

X-ray fluorescence spectrometry has long been recognized as a major analytical tool, originally in the wavelength dispersive (WDXRF), and later also in the energy dispersive (EDXRF) version. There probably is no metallurgical facility without at least one WDXRF spectrometer. The speed, reliability and truly nondestructive character of the XRF method make it suitable not only for laboratory applications, but especially for field and plant use. However, the successful expansion of x-ray fluorescence analysis from laboratory to plant and field environments was made possible only by the recent availability of portable XRF analyzers. Several critical factors have contributed to this, namely:

- the availability of small, sealed radioisotope sources to excite the characteristic x-rays of the sample;
- the availability of small, room temperature, high energy resolution detectors;
- the availability of powerful microprocessors; and
- the availability of compact, high capacity, rechargeable batteries to make the instrument independent of the AC power.

In particular, developments in microprocessor technology have made it possible for portable, battery-operated x-ray analyzers to perform in real time complex analyzes of the x-ray spectra from the sample, followed by sophisticated data processing; a task previously assigned only to off-line computers. The portable, microprocessor based x-ray analyzers have been a real breakthrough by combining speed and truly nondestructive character of analysis (the instrument being brought to the sample and not otherwise) with an expert identification/sorting software. Most recently, another technological breakthrough - the development of a miniature, low power x-ray tube - improved the performance of portable XRF analyzers and made them even easier to use. Replacing the isotope with an x-ray tube not only improves the instrument’s sensitivity and analytical range, but also makes it easier to transport and overall safer to operate because no x-rays are emitted from the x-ray tube once the power to the instrument is turned off.

Experimental

The Analyzer

The portable analyzer used in this work is shown in Figure 1. It is an ergonomically designed hand-held, lightweight (1.5 kg), environmentally sealed, battery operated unit. It employs a miniature, low power x-ray tube as the source of sample excitation. The end-window, transmission anode tube operates
at 38 kV of High Voltage and 20 μA of current. A high resolution silicon p-i-n diode detector (energy resolution better than 230 eV) is used to detect and register characteristic x-rays from the sample. The instrument is powered by a rechargeable Li-ion battery which sustains its operation for up to about 8 to 10 hours. A proprietary operating system controls all the functional blocks of the analyzer. The operator communicates with the analyzer via a built-in touch screen display with an intuitive user interface. The front end (nose) of the analyzer is a flat plate with a small 10 by 20 mm rectangular window sealed with polyimide foil. This plate provides a repeatable means of sample presentation for analysis. The measurement of solid, extended samples is performed by pressing the nose of the instrument against the analyzed object and pulling the trigger. Alternatively, to measure bulk samples such as powders or pellets, the instrument may be put into a special stand which accepts sample cups filled with bulk material as shown in Figure 2.

The primary result of the measurement is an x-ray spectrum of the sample. It is the information extracted from the spectrum that is then converted into qualitative and quantitative data of the elemental concentrations in the sample. Examples of x-ray spectra from a sample of plastic measured with the analyzer described above are shown in Figure 3. In this case, the sample has been a handle of a screwdriver. The two spectra shown, marked with black and yellow color, represent the black and yellow areas of the handle, respectively. The yellow spectrum reveals the presence of lead (two major peaks at 10.5 and 12.6 keV) in the yellow sections of the handle. The integral of any lead peak is a measure of the lead content.

Figure 1. Portable X-Ray Analyzer, Niton Model XLt-794

Figure 2. Portable X-Ray Analyzer measuring bulk samples in special stand. Also shown are sample preparation accessories.
Figure 3. An example of an x-ray spectrum of plastic object, here the HDPE handle of a screwdriver. Note that lead, titanium and chromium are present in the yellow sections of the handle. It appears that yellow sections are painted with paint containing titania and lead chromate pigment. Antimony is present in plastics. A relatively thin layer of yellow paint does not absorb antimony x-rays. This example illustrates excellent identification capabilities of the XRF Method.

Analytical Approach

In order to test the capabilities of the analyzer, a number of polymer-based samples of known compositions were procured. These samples were prepared from PVC and PE resins by adding to them antimony, bromine, titanium, chromium, mercury, cadmium and lead. The concentrations of additives were varied to imitate the concentration ranges encountered in real polymers. While concentrations of heavy metals were maintained between 0 to 1000 mg/kg, the other elements were allowed to reach several percent levels. It is worth noting that there are very few polymer based certified materials available, and those that do exist are prepared in polyethylene medium only [5, 6].

The XRF analysis is known for the so called matrix effects which are manifestation of interaction of x-rays with the medium they pass through. In any analytical method, one expects the measured signal from a given element to be proportional, preferably linearly, to the element’s concentration in the sample. In XRF analysis this relation is generally nonlinear for two reasons. First, the element itself absorbs its own characteristic x-rays when its concentration in the sample increases. Second, the presence of another element in the sample also increases the absorption of x-rays from the analyte in question. For example, two samples, each containing 5% iron in a polyethylene matrix will produce different intensities of iron if one of the samples will additionally contain, say, 10% titanium. Should we not be aware of this fact, we might infer a false conclusion about the iron concentration in samples from the iron intensities alone. In the past a number of methods (empirical, semi-empirical and mathematical) have been proposed to correct for these effects.

Based on earlier experience it has been determined that the best analytical approach to plastics analysis using XRF is the method of fundamental parameters (FP). This method utilizes the fact that the measured x-ray intensities of the elements in a sample can be fully described by a complete set of mathematical equations. The equations tie together the physics of the interaction of x-rays with matter and sample composition. These equations can only be solved by iterative methods which require considerable speed and computing power. The alternatives to the FP-based method are a classical
empirical calibration, or the so called Compton normalization (CN) method. The empirical calibration has the advantage of being the most accurate of all methods. However, its serious disadvantage is the requirement of availability of an extensive set of analyzed samples with compositions as close as possible to those of unknown samples. Given the number of various plastic materials, this requirement is practically impossible to satisfy. The CN method, while being less demanding on the availability of standards, is not capable of handling wide concentration ranges encountered in the analysis of plastics. An excellent, in depth discussion of the calibration methods mentioned here can be found in reference [7].

Results

Accuracy, Precision and Minimum Detection Limits

All samples used in this study were measured for 200 sec each. Samples prepared from PE or PVC resin were made into solid discs of 31 mm diameter, and at least 6 mm thick for PVC and 13 mm thick for PE. Additional samples collected from various sources were all at least 4 mm thick and covered the rectangular (10 by 20 mm) measuring window of the probe. Some samples were available only as 3 mm pellets. These were placed in 31 mm diameter by 20 mm high sample cups (Chemplex Industries).

Figure 4 shows measured data plotted against certified values for lead in PE and PVC samples. As can be seen, the Compton Normalization (CN) method cannot handle high levels of bromine, which often is present at up to 20% concentrations in some plastics. Similarly, higher concentrations of antimony pose problems for the CN method as shown in Figure 5 for cadmium. On the contrary, the Fundamental Parameters Method (FP) handles interferences quite well. Note also, that the FP Method automatically accounts for the type of plastic matrix, while the CN Method is not reliable in this respect.

![Pb in PVC and PE Plastics](image)

**Figure 4.** Measured v/s certified concentration of lead in PVC and non-PVC matrices. These data include samples of lead in a pure matrix and in matrices containing up to several percents of Ti, Br, and Sb, as well as up to 1000 mg/kg of Cd and Cr.
Cd in PVC and PE Plastics

Figure 5. Measured vs certified concentration of cadmium in PVC and non-PVC matrices. These data include samples of cadmium in a pure matrix and in matrices containing up to several percent of Ti, Br, and Sb, as well as up to 1000 mg/kg of Pb and Cr.

In summary, Figures 4 and 5 show consistently more accurate analysis with FP than with CN. Of particular note is the excellent ability of the algorithm to compensate for Br and Sb over a wide range of concentrations; the slopes and R² factors are close to 1.0 in all cases.

The instrument Minimum Detection Limits (MDL) were determined from the series of replicate measurements of samples with low and high concentrations of interfering elements but low (below 100 mg/kg) or zero concentrations of the analytes. Three standard deviations, as calculated from the appropriate series, is a measure of the MDL for a given analyte. These are reported in Table 1. The MDL and precision data for lead and cadmium appear satisfactory. That is not the case for chromium. In order to improve the chromium performance of the analyzer it will be necessary to make minor hardware improvements in the front end of the instrument. In any case, the present precision and MDL can be improved by extending the measurement time per sample. For each fourfold extension of the measurement time a twofold improvement in precision and MDL may be expected.

Table 1. Minimum Detection Limits (MDL) and precision data for Cd, Pb and Cr in plastics. All data in mg/kg. and for measurement time of 120sec per sample.

<table>
<thead>
<tr>
<th>Matrix</th>
<th>Parameter</th>
<th>Cd</th>
<th>Pb</th>
<th>Cr</th>
</tr>
</thead>
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<tr>
<td>PE</td>
<td>MDL interf. free</td>
<td>&lt;25</td>
<td>&lt;10</td>
<td>&lt;80</td>
</tr>
<tr>
<td></td>
<td>MDL at 5% Br</td>
<td>&lt;75</td>
<td>&lt;20</td>
<td>&lt;120</td>
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<td></td>
<td>2 sigma prec. interf. free</td>
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<td>&lt;10</td>
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<td>2 sigma prec at 5% Br</td>
<td>&lt;50</td>
<td>&lt;20</td>
<td>&lt;80</td>
</tr>
<tr>
<td>PVC</td>
<td>MDL interf. free</td>
<td>&lt;25</td>
<td>&lt;10</td>
<td>&lt;150</td>
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<td></td>
<td>2 sigma prec. interf. free</td>
<td>&lt;25</td>
<td>&lt;10</td>
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</tr>
<tr>
<td></td>
<td>2 sigma prec at 5% Br</td>
<td>&lt;75</td>
<td>&lt;20</td>
<td>&lt;120</td>
</tr>
</tbody>
</table>
The Issue of Sample Thickness

Figure 6 below illustrates how well the FP code automatically takes into account the effects of the thickness of the plastics. (Plastics are weak absorbers of x-rays so that the mean scattering distance of detected x-rays, and therefore the intensity of the detected x-rays, depends on the thickness).

Samples of the same composition of Cd and Pb were fabricated in thicknesses of PE and PVC ranging from about 2 mm to almost 30 mm. No interfering elements were added to these samples.

The graphed data show that for samples with thicknesses greater than 5 mm, the FP method is capable of correcting for thickness in samples of both PVC and PE. The relative variation of the results within the same series of data is less than 10% for sample thicknesses greater than 5 mm. It is worth to note that these data represent the most unfavorable results for a single heavy metal in pure PE or PVC matrix. For real samples, which routinely contain significant amounts of Ti, Br, and Sb, the curves would be expected to flatten at much smaller thickness than shown in Fig. 6.

The best approach when dealing with thinner or smaller plastic objects is to transfer them to a measuring cup in an amount sufficient to build up to a layer of at least 5 mm thick.

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Screening of Plastic Waste for Brominated Flame Retardants

Screening is understood as an analysis with somewhat relaxed accuracy requirements. Field-Portable X-ray Analyzers have for years been used for *in situ* screening of soil for metallic contaminants at or below $10^2$ mg/kg levels [8]. It appears that a similar approach can be successful in screening the waste from electric & electronic equipment (WEEE) for bromine, or any other elements that are present in plastic at about 500 to 1000 mg/kg levels or higher. Figure 7 shows fragments of x-ray spectra of samples of styrene butadiene (SB) plastic scrap containing varying amounts of brominated flame.
retardant. The spectra show two characteristic bromine x-ray peaks, $K_\alpha$ at 11.907 keV (taller peak), and $K_\beta$ at 13.296 keV (smaller peak). Included with SB samples is the spectrum of certified reference material, BCR-680, that contains 808 mg/kg of Br.

**Bromine in Styrene Butadiene**

![Graph showing spectra of styrene butadiene with various levels of brominated flame retardant added.](image)

Figure 7. Spectra of styrene butadiene with various levels of brominated flame retardant added.

The observed sample-to-sample differences between the magnitudes of peaks of the same series ($K_\alpha$) are very distinct, and by measuring them one can not only verify the presence or the absence of bromine in a sample, but even indicate the concentration level of retardant. For such a screening/sorting operation, the instrument can be set to not report the measured concentration of bromine, but to display whether the bromine content of a sample is greater than the predetermined level or not. As a matter of fact, an experiment was performed with some 70 samples of WEEE to screen them for the presence of brominated flame retardant. In each case the instrument positively identified bromine in the measured sample after only 1.5 sec of measurement time. Even a sample of certified reference material, BCR-680, containing merely 808 mg/kg bromine, was identified in such a short time.

**Summary Conclusions**

We have tested the usefulness of the Field-Portable X-Ray Fluorescence Analyzer in the analysis of plastics and plastic waste for heavy metals such as cadmium, lead and chromium. The results obtained with specially fabricated polymer standards, and with samples of plastic scrap, prove that the fundamental parameters method is very effective in handling the vast diversity of types of plastics and their compositions. It also has been shown that the FP method developed for the analysis of plastics is insensitive to sample thickness variations above about 5mm of sample thickness. The precision and MDL data indicate that the instrument can be used for testing of plastic made products and materials for compliance with pertinent regulations.
Demonstrated instrument ability to quickly sort or screen analyzed plastics for major elements, specifically for brominated flame retardants, makes it a very useful tool in high reliability separation of post-consumer plastic waste.

Our present work is focused on improving performance for chromium, and on further improvements to the FP algorithm to make the analysis more accurate and robust. At this point it is worth to note that a major factor affecting the accuracy of analysis is the homogeneity (or the lack of) of analyzed material. This fact is quite often overlooked, resulting in erroneous interpretation of measured results. In order for the measured results to be representative of the sample composition, the latter must be homogeneous. This applies to all analytical methods. It has been our experience that often the reference analyses were completely wrong, most likely because of improper sampling for ICP analysis.

Acknowledgements

The results reported here are the fruits of a team effort. It is, therefore, the author's privilege and pleasure to thank and acknowledge his tireless coworkers, Stephen Shefsky for his excellent work on FP algorithm, Mike Dugas for his relentless efforts in programming the actual instrument and Ewa Piorek of Modern Analytical Techniques for production of polymer samples.

References


Key Words

X-Ray Fluorescence Analysis, XRF, FPXRF, plastics, environmental pollution with metals.