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SPECTRO ANALYTICAL INSTRUMENTS

X-ray fluorescence analysis of polymers

Introduction

Nowadays, plastics are used in all areas of our lives. Be it as packaging, in automobiles and above all in the electrical, electronics and toy industries. The properties of the plastics are very different, from extremely rigid to extremely flexible, everything is possible – and in the most diverse colors.

These properties are achieved by blending additives to the raw polymer. During manufacturing the concentration of many additives in the polymer can be controlled by the element content. Substances of interest are e.g. fillers (talc, chalk and limestone [$CaCO_3$], kaolin, feldspar ...), dyes (rutile or anatase [TiO_2], ZnO, ZnS, Fe_2O_3 ...), stabilizers (Ca and Zn compounds, CuI, KI, KBr ...) and flame retardants (bromine compounds, organo-phosphorus and inorganic flame retardants ...).

It is also often necessary to prove that a part made of plastic complies with legal requirements. The more well-known regulations here are the directive on the restriction of the use of certain hazardous substances in electrical and electronic equipment (RoHS), the directive on packaging and packaging waste and the directive on end-of-life vehicles ELV.

X-ray fluorescence analysis (XRF) as an analytical method for instrumental analysis is established as a fast method of accurate elemental analysis and screening of completely unknown samples. The advantages here are in particular the speed of the analysis as well as the low requirements for sample preparation.

There are fundamentally two different methods of XRF; wavelength dispersive (WD-XRF) and energy dispersive (ED-XRF).

Traditionally, in many cases WD-XRF is used in process control and ED-XRF (especially portable systems) for screening analysis. However, this has changed with new generations of devices: ED-XRF devices can offer comparable performance characteristics as WD-XRF systems, depending on the equipment.

On the one hand, ED-XRF is distinguished by the simultaneous multielement detection, but also by the low thermal load on the sample. ED-XRF devices are available in a wide range of handheld systems, from portable to laboratory instruments.

Depending on the task, the analyzers are also differentiated according to the sample surface under test. If individual particles are to be localized in a plastic (for example from abrasion) on a sample surface in a failure analysis, analyzers with a small excitation spot (microanalysis on a scanning electron microscope, micro-XRF) are suitable.

For process control, however, traditionally larger sample areas (2 to 10 mm) are investigated.

Analytical Principle

X-ray fluorescence analysis is an analytical method for identifying the different chemical elements contained in a substance and determining their quantity. For this purpose, the substance is excited to emit element-specific radiation, the spectral composition of which contains this information. Figure 1 shows this schematically.

In ED-XRF, the X-ray fluorescence radiation is detected with the aid of a semiconductor detector and the signals are further processed into a measurement spectrum. The principle is shown in Figure 2. The information in the spectrum is used to determine element concentrations in the sample.

Sample Preparation

The preparation of the sample is important for an accurate analysis. In order to achieve optimal results with the analysis, the samples should be in the form of pellets, produced by injection molding or compression molding. The same can also be achieved with homogeneous materials by examining a part of the sample with a sufficiently good sample surface when using the XRF device.

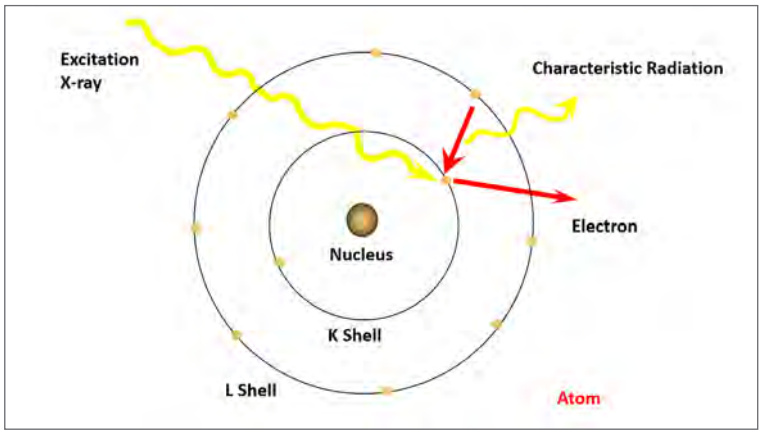


Figure 1: Principle of X-ray fluorescence

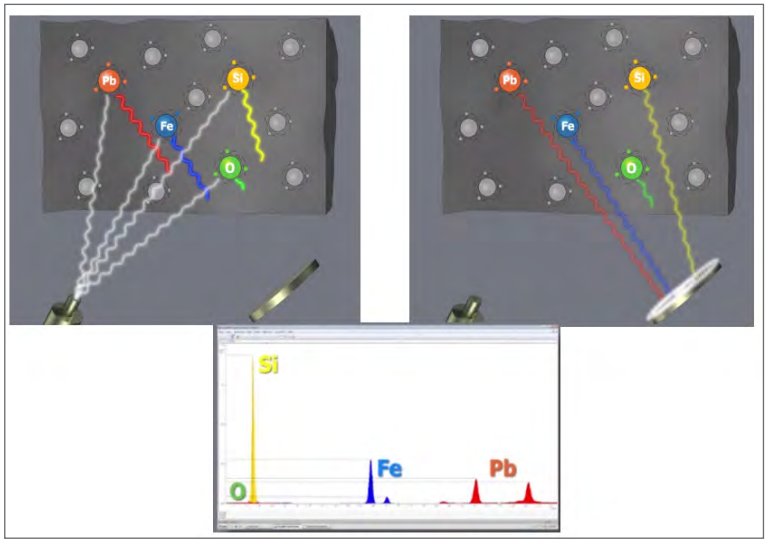


Figure 2: Principle of ED-XRF

For a fast screening analysis, it may be sufficient if the sample is present as a granulate or as a powder after a grinding.

Figure 3 shows measurement spectra recorded with the SPECTRO XEPOS using the HAPG polarization crystal for a granule sample of the BCR 680 material compared to a pellet produced by the compression molding process. The differences in the spectra are clearly visible, especially for the elements with low atomic numbers such as S and Cl.

Since fluorescence radiation of higher energy can also be detected from a greater depth of the sample, the thickness of the sample plays a role for the accuracy of the analysis of the concentrations of elements with a higher atomic number. This is irrespective of whether the sample is examined as granulate, fine powder or pellet. In order to reduce the effect, the device software can consider other parameters from the spectrum (backscatter information) or the specification of sample mass and sample diameter. For a screening analysis this is usually sufficient; for process control, samples of the same shape and thickness should be used for calibration.

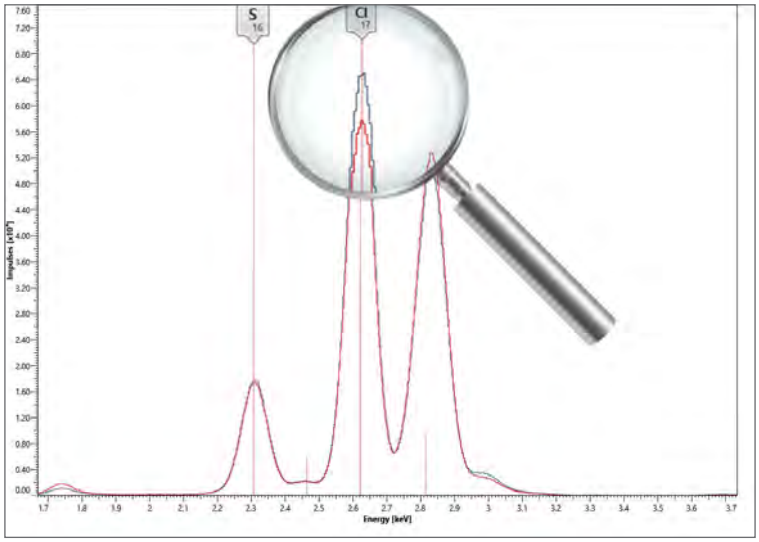


Figure 3: Measurement spectra, taken with HOPG polarization crystal for a pellet sample (shown in blue) and a molding pellet (shown in red)

The effect is caused by the fact that the excitation radiation is absorbed by the sample matrix when entering the sample and the generated fluorescence radiation is absorbed as it emerges from the sample. Since the excitation radiation is a higher-energy radiation, the effect is smaller than that of fluorescence radiation. The intensity I_0 generated in the sample is absorbed along the path d by the sample of the density ρ. The mass attenuation coefficient μ is dependent on the energy of the fluorescence radiation. This results in the following formula:

$$I = I_0 * \exp(-\mu * \rho * d)$$

If the value for the intensity I is determined for a thickness at which the fluorescence intensity was absorbed by 63% (1/e), you can determine a value which is generally referred to as “attenuation length”. Figure 4 shows the value of the “attenuation length” for the example of a polypropylene matrix and a take-off angle of 45 degrees for the fluorescence radiation of different elements with different atomic numbers.

As you can see from the graph (Figure 4), the escape depth of the fluorescence radiation is

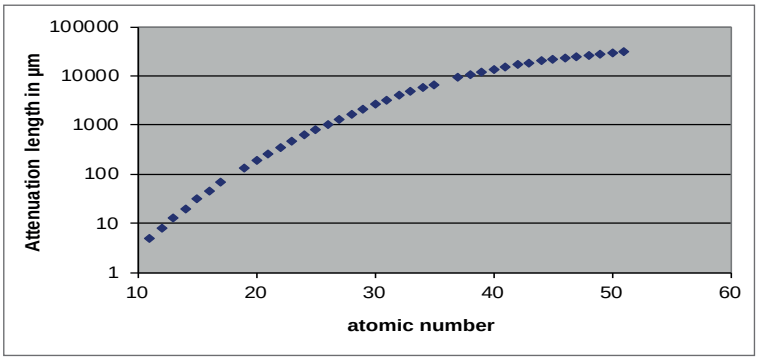


Figure 4: Escape depth of fluorescence radiation of different elements in a polyethylene matrix

very much dependent on the atomic number of the element (more precisely on the energy of the fluorescence radiation). If, for the detection of the element Na, the intensity is obtained from a depth of a few µm, this value for the element Cd is in the range of 2-3 cm in a polymer matrix.

Figure 5 shows measurement spectra recorded with the SPECTRO XEPOS for two pellets of different thicknesses. The differences in the spectra are clearly visible, especially for the elements with higher atomic numbers such as Br and Pb.

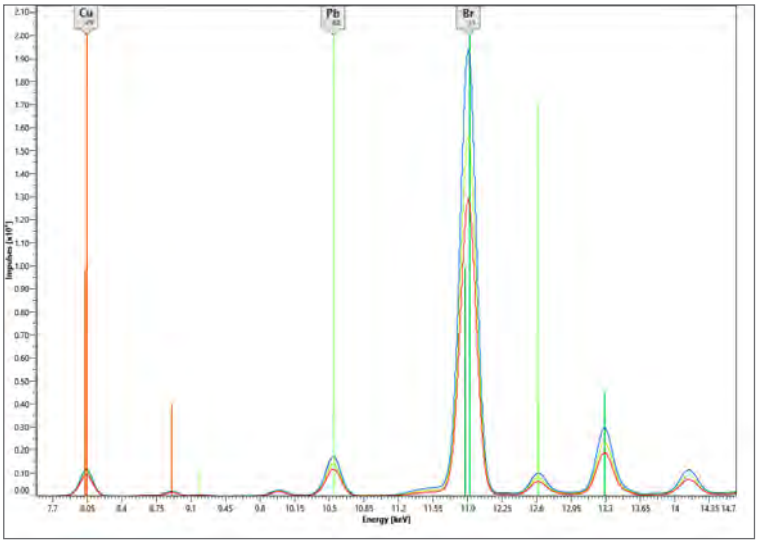


Figure 5: Measurement spectra for two molding pellets of different thickness (thick sample shown in red, thin sample shown in blue)

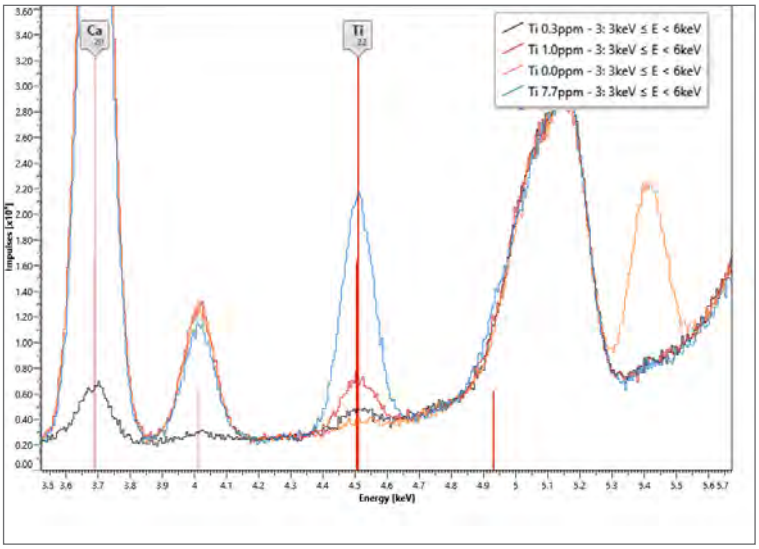


Figure 6: Measurement spectra recorded for four plastic compacts with different Ti contents (0, 0.3, 1.0, and 7.7 mg/kg), measuring time: 150 sec

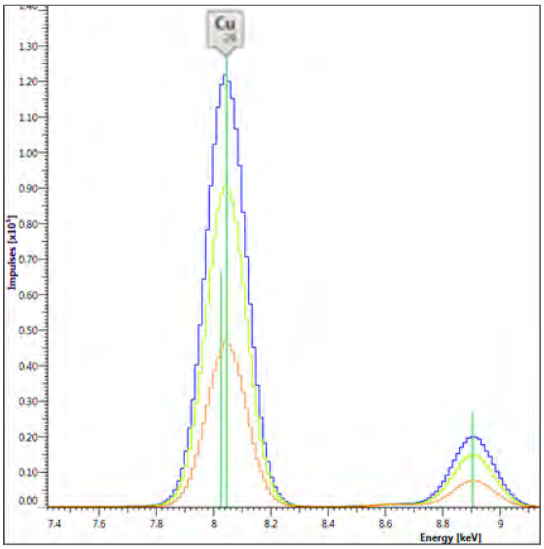


Figure 8: Measurement spectra recorded for three polyamide samples with Cu contents between about 1.6 and 5%

Analytics

For accurate analysis of the samples, a method that has been calibrated with revised standards is used. These standards should include a matrix comparable to the unknown samples, and the pellets should be of comparable size and thickness.

If low contents are examined in polymers, a calibration is often used which assumes a linear relationship between intensity and concentration. Other elements in the sample or higher contents can be taken into account by corresponding correction terms. Figure 6 shows measurement spectra recorded with the SPECTRO XEPOS for four plastic pellets with different titanium contents.

The detection limit for Ti in such a plastic matrix is <0.1 mg/kg. Comparable low detection limits are achieved for other important elements, too.

In many cases, the concentrations of the elements to be analyzed tend to be in the % range. The following example shows the analysis of Cu in polyamide in which copper iodide was added as a stabilizer.

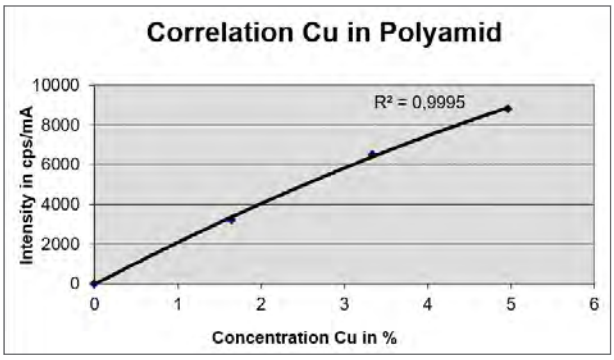


Figure 9: Calibration for Cu in polyamide

	Copper content in %
Sample R01	1.635
Sample R02	1.638
Sample R03	1.638
Sample R04	1.637
Sample R05	1.642
Average	1.638
Std dev (standard deviation)	0.002

Table 1: Precison of a repeat measurement of Cu in polyamide

With the measured intensities, the XRF spectrometer can be calibrated and a good reproducibility and accuracy of the analysis can be achieved.

The concentrations of other stabilizers (e.g., Ca

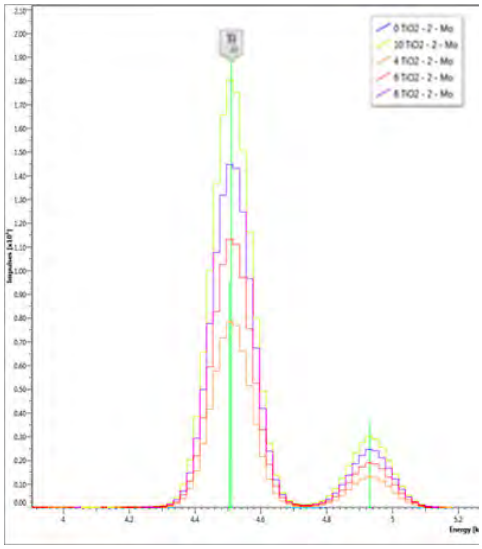


Figure 10: Measurement spectra recorded for ABS samples with different TiO2 contents

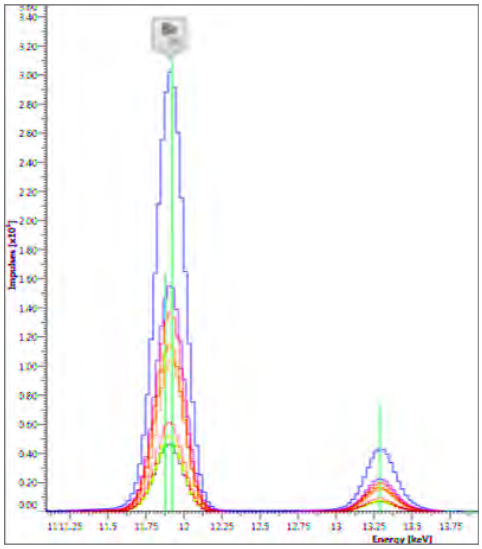


Figure 12: Measurement spectra recorded for polystyrene samples with different Br contents

and Zn compounds, KI, KBr ...) in plastics can be analyzed in the same way.

Also, the contents of dyes, e.g. rutile or anatase (TiO2), ZnO, ZnS, Fe2O3 ... can be determined by X-ray fluorescence analysis of the elements Ti, Zn, Fe ... Figure 10 shows the analysis of TiO2 in ABS. Of course, the TiO2 content could also be determined indirectly by incineration. However, if there are fillers in the ABS, for example, then this method does not give an accurate statement.
With the measured intensities, the XRF spectrometer can be calibrated and a good reproducibility and accuracy of the analysis can be achieved.

An additional example is the analysis of Br from brominated flame retardants. The method corresponds to that described above. The spectra in Figure 12 show measurements of polystyrene samples with different Br content. With the measured intensities, the XRF spectrometer can be calibrated and a good reproducibility and accuracy of the analysis can be achieved.

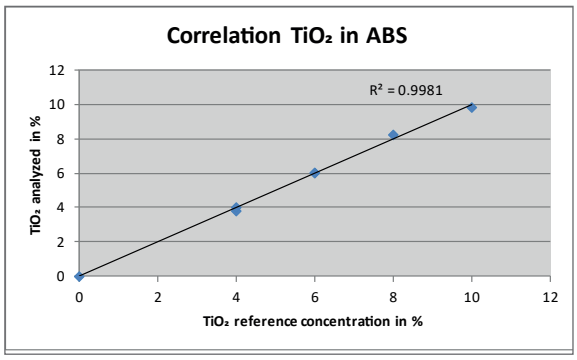


Figure 11: Calibration for TiO_2 in ABS

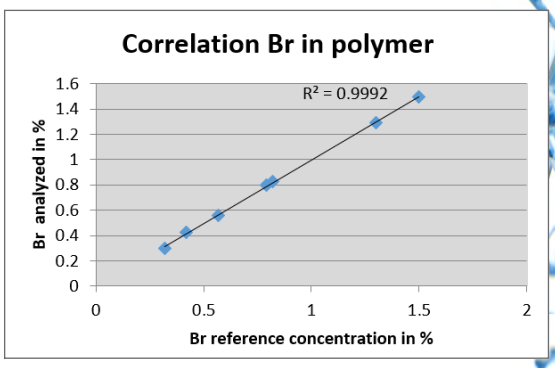


Figure 13: Calibration for Br in polystyrene

Fast Screening Analysis

For a fast screening analysis, methods with automatic matrix correction considering fluorescence and scattering, so-called TurboQuant methods are suitable.

Today, one of the most important applications for fast screening analysis is the screening of plastics for the detection of regulated substances (e.g., RoHS: *DIRECTIVE 2002/95/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of January 27, 2003 on the restriction of the use of certain hazardous substances in electrical and electronic equipment and DIRECTIVE 2011/65/EU OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL of June 8, 2011 on the restriction of use of certain hazardous substances in electrical and electronic equipment (amended version), ElektoG, AltfahrzeugV, VerpackV*). In test methods of international institutions such as IEC (IEC 62321-3-1) and ASTM, XRF is described as the method of choice for a fast screening analysis.

For this purpose, it is particularly important to achieve correspondingly low detection limits for the relevant elements in order to have sufficient safety that the limit values are undershot even at short analysis times. Figures 14a, b, and c show measurement spectra of the European reference materials ERM RC 680 m and 681 m in comparison.

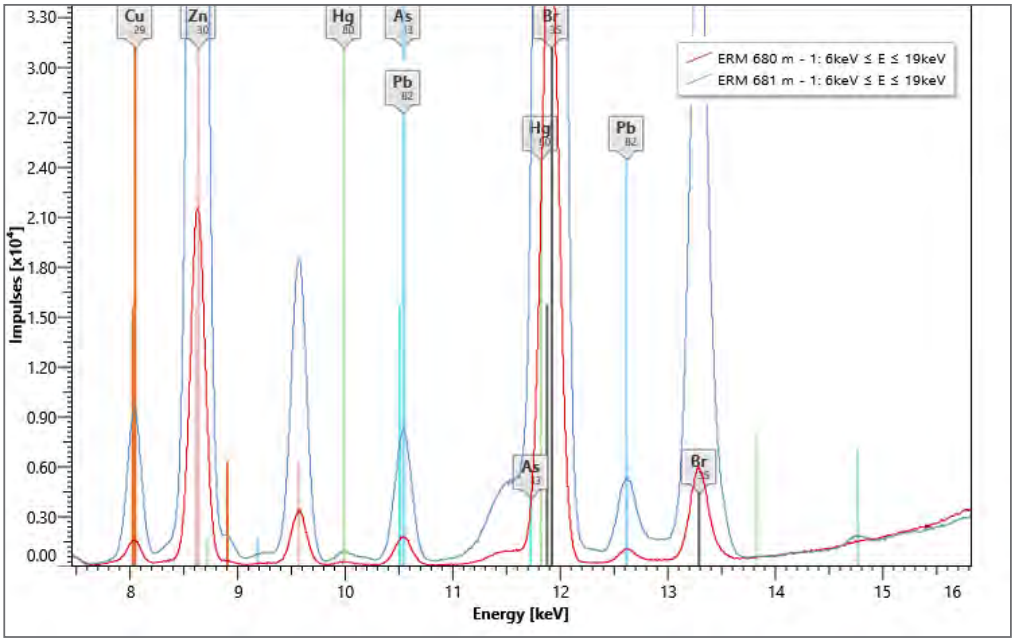


Figure 14a: Comparison of measurement spectra of the samples ERM EC 680m and 681m for the elements As, Hg and Pb

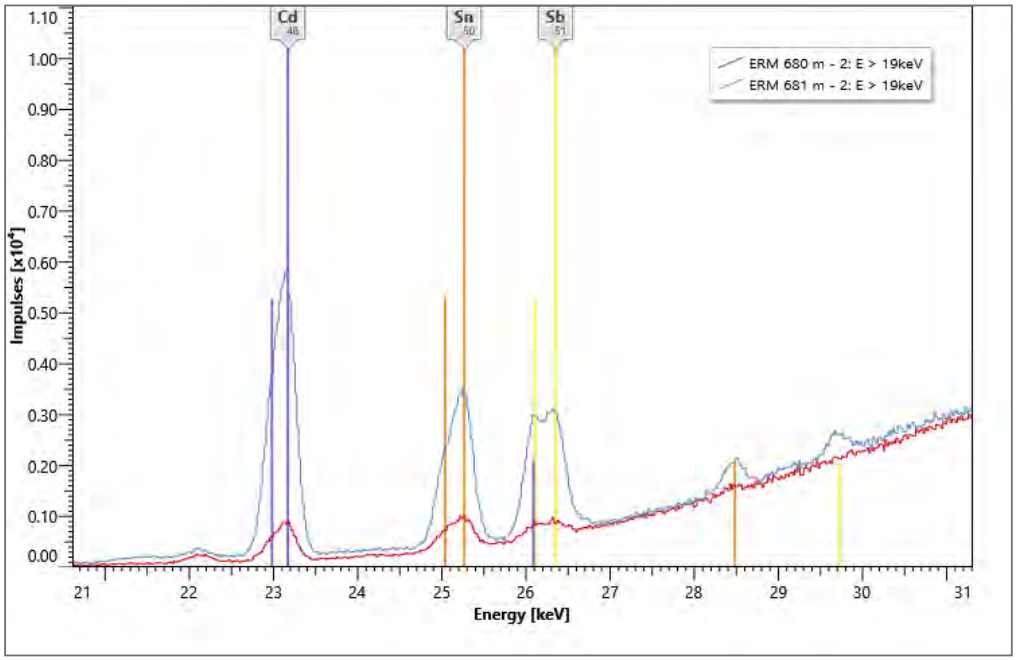


Figure 14b: Comparison of measurement spectra of the samples ERM EC 680m and 681m for the element Cd

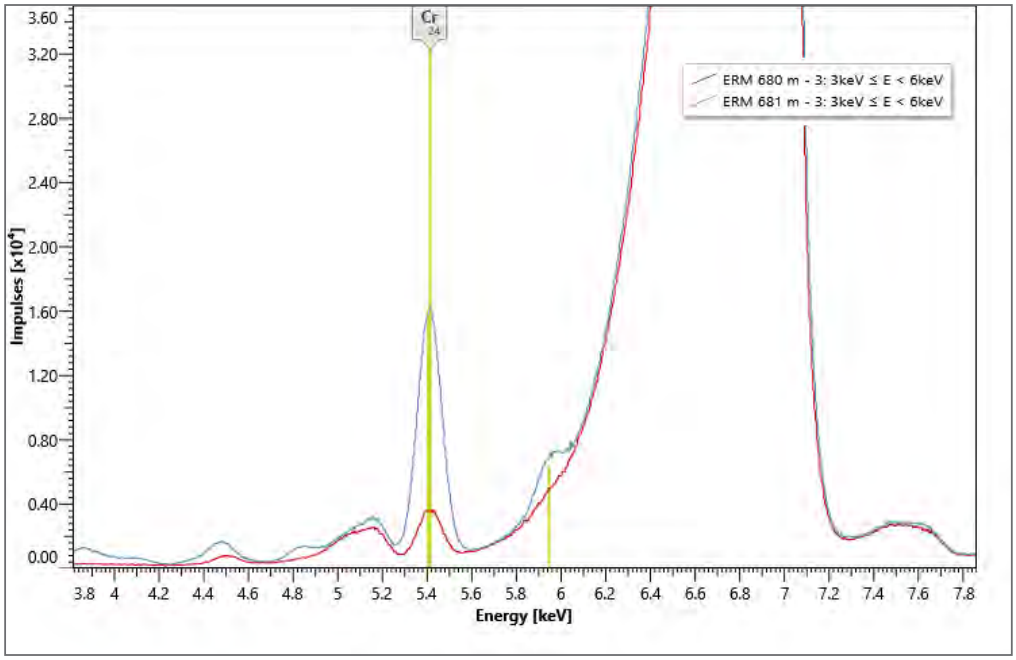


Figure 14c: Comparison of measurement spectra of the samples ERM EC 680m and 681m for the element Cr

Table 2:

	Cr in mg/kg	Zn in mg/kg	As in mg/kg	Br in mg/kg	Cd in mg/kg	Sn in mg/kg	Sb in mg/kg	Hg in mg/kg	Pb in mg/kg
Analysis 1	9.3	201.0	5.2	189.1	20.8	19.7	9.4	3.2	11.2
Analysis 2	9.4	200.6	5.1	189.1	21.2	20.0	10.0	2.7	11.4
Analysis 3	9.4	201.3	5.2	190.3	21.5	20.7	9.2	2.5	11.4
Analysis 4	9.4	201.3	5.2	189.2	21.1	20.4	10.0	2.9	11.4
Analysis 5	9.4	201.3	5.1	189.9	21.6	20.8	10.0	2.5	11.2
Analysis 6	9.4	200.8	5.3	189.2	21.4	20.4	10.2	2.9	10.8
Analysis 7	9.3	201.6	5.0	189.8	20.9	20.2	9.7	3.1	11.9
Analysis 8	9.3	201.5	5.1	189.1	21.2	20.2	9.5	2.6	11.5
Analysis 9	9.3	201.0	5.2	189.4	21.6	20.4	9.2	2.7	11.5
Analysis 10	9.5	201.2	5.2	189.4	21.4	20.3	8.9	2.9	11.5
Average	9.4 ± 0.1	201.2 ± 0.3	5.2 ± 0.1	189.5 ± 0.4	21.3 ± 0.3	20.3 ± 0.3	9.6 ± 0.4	2.8 ± 0.3	11.4 ± 0.3

Table 2 shows the results of a 10-fold repeat measurement of the sample ERM 680m with a total analysis time of 10 min per sample using the SPECTRO XEPOS HE.

Failure Analysis

For failure analyses (for example in the case of debris particles on a plastic surface), XRF devices with a small excitation spot and a mapping function can be used. The test sample is positioned on a movable sample table and the sample is then "scanned". While doing this, mapping images are created as shown in Figures 15 through 17. As an example, a "spiked sample" was examined here. The total mapping time for an examined area of 1.6 × 2.8 cm was about 40 minutes. When looking at the measurement spectra

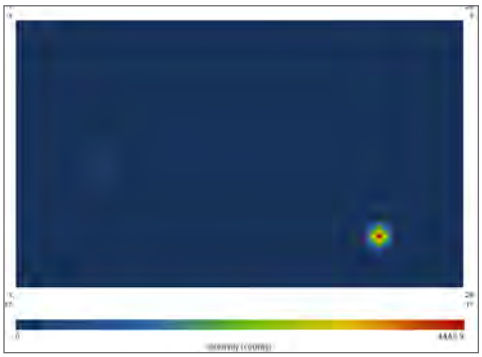


Figure 15: Distribution image of Cr on a plastic surface caused by abrasive particles

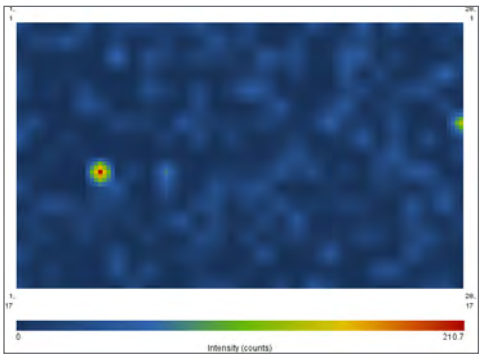


Figure 16: Distribution image of Ni on a plastic surface caused by abrasive particles

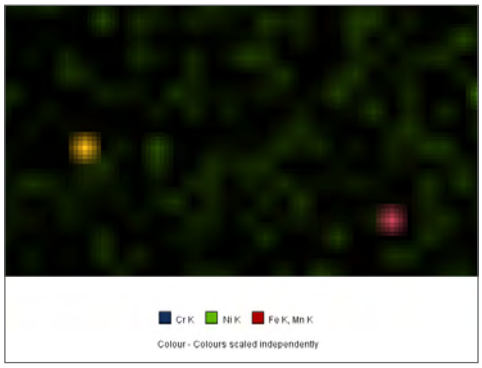


Figure 17: Superimposed distribution images of Fe, Cr and Ni on a plastic surface caused by abrasive particles

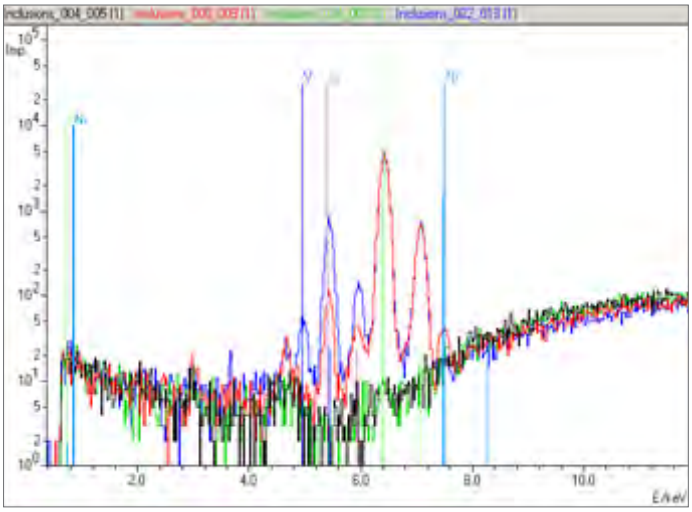


Figure 18: Spectra taken at two locations of the sample containing a particle

at the two points, recorded with a longer measurement time, the differences in the element composition become clear.
If the detected points are then subjected to a quantitative examination, the following results are obtained.

Summary

	1.8550		1.2379	
	Specification	Point analysis	Specification	Point analysis
Fe in %		94.55		87.59
Cr in %	1.5 - 1.8	1.7	11.0 - 12.0	9.95
Ni in %	0.85 - 1.15	1.65		<0.01
Mo in %	0.15 - 0.25	0.18	0.6 - 0.8	0.20
V in %	-	0.08	0.9 - 1.1	1.23
Mn in %	0.4 - 0.7	0.64	0.15 – 0.45	0.41

Table 3: Results of analyzes of “spiked” abrasive particles on a plastic sample

In the characterization of element content in polymers, XRF has proved to be an excellent analytical technique.

When preparing samples for an XRF analysis, a number of parameters must be considered. These include the sample shape, the sample surface and sample thickness. When calibrating the analyzer, the sample matrix must be observed. The selection of the right analytical system depends on the analytical tasks.

For trace element determinations, a high sensitivity to detection is required; the resolution of the spectrometer may be

important if many elements are present in the sample (due to possible line overlaps), and the device´s software should provide corresponding calibration models for large concentration ranges. High precision is, of course, essential for high accuracy.

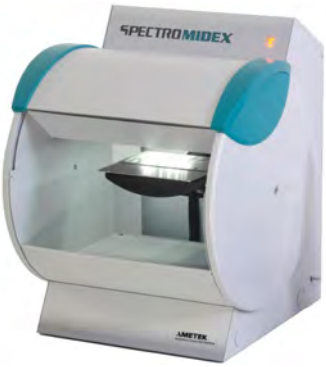
In addition to process control, XRF is also suitable for rapid screening of samples to monitor regulated substances.

For the detection of abrasion particles and their quantitative analysis, XRF systems with a small excitation spot and a mapping option are suitable.

The following table gives a good overview of which XRF system is suitable for which application:

Application	Best suited	Well suited
Compliance Screening	SPECTRO XEPOS (XEP05HE)	SPECTRO XEPOS, SPECTROSCOUT, SPECTRO xSORT SPECTRO MIDEX
(F), Na…Cl in polymers	SPECTRO XEPOS (XEP05C, XEP05P, XEP05HE)	SPECTRO XEPOS (XE-P05D), SPECTROSCOUT, SPECTRO MIDEX
Traces of K-Mn in polymers	SPECTRO XEPOS (XEP05P, XEP05HE)	SPECTRO XEPOS (XEP05D, XEP05C)
Process control of elements in the range of atomic numbers 19…92	SPECTRO XEPOS (all versions)	SPECTROSCOUT, SPECTRO MIDEX
Analysis of inclusions, element mappings	SPECTRO MIDEX	



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