MICRO-XRF

Analysis of small particles with micro-XRF

Application Note # XRF 452

Introduction

It is often necessary to analyze small particles as their chemical composition provide important information on their origin. For example, it is possible to determine the state of an engine by analyzing the wear debris in the engine oil, as this debris stems from the parts with the highest abrasion. The identification of debris particles allows to determine the corresponding engine components and their amount allows to judge whether their replacement is required. Particle inclusions in plastics influence the performance of this material and are caused typically by contamination, e.g. produced by the manufacturing machinery or the environment. Their analysis allows reduction of contaminants by using appropriate precautions.

This report describes particle identification by elemental analysis with micro-XRF, using the two examples described above. Here the elemental composition of particles can be compared directly with potential particle sources.

The samples

The analyzed samples were wear debris from an engine and particle inclusions in plastics. The aim was to identify the particles both by qualitative methods such as positive material identification or spectrum matching as well as by quantification. Isolated particles from both the engine and the plastic material were prepared on paper, respectively on adhesive film to reduce the influence of the sample matrix. The embedded particles were measured directly within the plastic material.

Instrumentation

The analysis was performed with the Bruker M4 TORNADO. This instrument is equipped with the following features:

- Large vacuum sample chamber,
- Fast X-Y-Z TurboSpeed stage,
- Effective excitation of fluorescence by a high brilliance X-ray tube combined with X-ray optics for concentration of tube radiation to spot sizes down to < 25 µm,
- Detection of fluorescence radiation with silicon drift detectors (SDD) providing highest count rates.

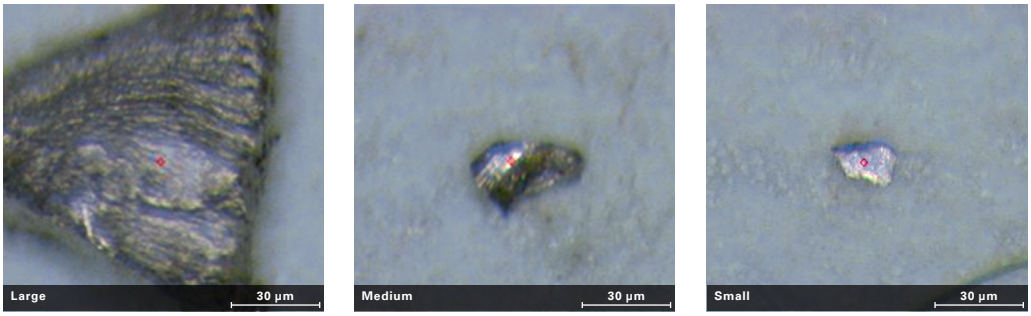


Figure 1
Wear debris of same composition (steel) but of different size

Wear debris from an engine

Particles were collected from engine oil, cleaned and filtered on paper. Two different types of particles could be identified. Three particles of a low-alloy steel of same composition but of different sizes are depicted in Figure 1. They were analyzed with a spot size of 25 µm. Their spectra are displayed in Figure 2. It can be seen that the main peaks of the spectra are the same, as expected, but that the spectral background differs. This is due to the penetration of excitation radiation through the small particle and scattering on the sample support. The spectra are displayed in a logarithmic intensity scale to better show also the low scatter intensities.

Independent of the spectral background the quantification results are similar as displayed in Table 1. These results allow secure identification of the particles.

Another particle type was analyzed to consist of mainly aluminum (Al). For Al alloys, which have to be measured in vacuum, identification is possible, too, as can be seen in the spectra contained in Figure 3, but for these Al samples in general the spectral background is higher because of the lighter matrix.

The quantification results for the Al alloys are summarized in Table 2. They show that the compositions of the first three samples are very similar but the composition of the fourth sample differs, in particular in its heavy element traces (red). It can therefore be concluded that this particle is from a different Al alloy than the other three.

These results show that even the identification of light element alloys is possible by quantification, too, although it is less reliable. Due to the irregular shape and surface of samples the quantification results for light elements, such as Al and Si, are not very consistent. Nonetheless, positive identification of the particles is unambiguously possible using minor and trace element concentrations of heavier elements.

Another method for the fast identification of materials is the spectra matching. Here either complete spectra or spectrum intensities are

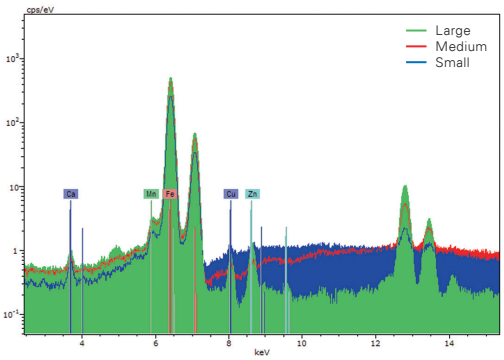


Figure 2
Spectra of the three particles depicted in Figure 1

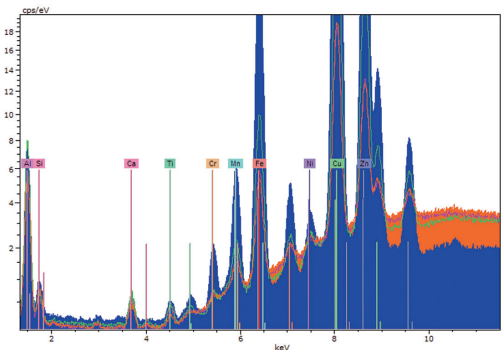


Figure 3
Spectra of different Al alloys

Quantification of particles

Element	Mn	Fe	Cu	Zn
Large (green)	0.49	98.7	0.32	0.45
Medium (red)	0.54	98.6	0.46	0.43
Small (blue)	0.50	99.2	0.16	0.14

Table 1
Quantification results of the three particles in wt.%

compared with reference spectra. The result is a ranking of materials which are similar to the analyzed material. The necessary spectrum library with reference spectra of all expected materials can be generated. This method is very fast and does neither require peak identification nor the calculation of quantification.

Table 2
Quantification results of Al alloys in wt.% with differences in the composition of sample 4 (red)

Quantification of Al particles									
Element	**Al**	**Si**	**Ti**	**Cr**	**Mn**	**Fe**	**Ni**	**Cu**	**Zn**
Large (green)	87.3	8.8	0.09	0.05	0.17	0.64	0.07	1.78	1.14
Medium (red)	87.6	6.7	0.07	0.04	0.21	0.83	0.09	2.72	1.73
Small (blue)	82.9	13.4	0.05	0.03	0.13	0.58	0.06	1.81	1.09
Small (blue)	79.2	7.3	0.06	0.19	0.56	2.27	0.18	6.54	3.86

Inclusions in plastic

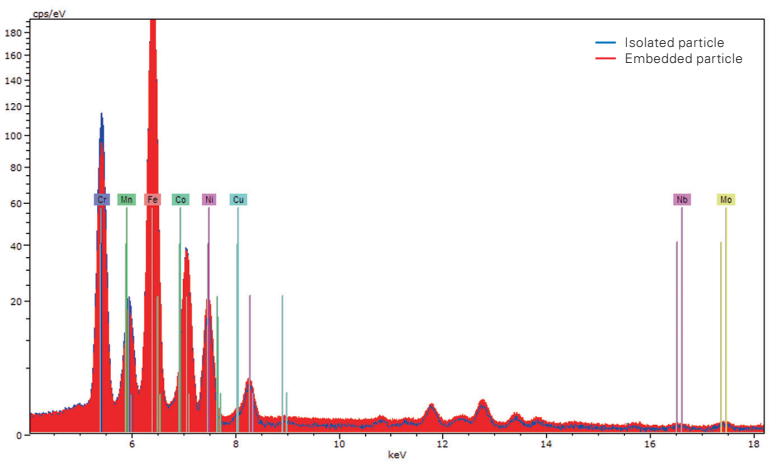
The analysis of inclusions in plastics (Figure 4) differs to wear debris of engines, because embedded particles cannot be separated from the plastic matrix easily for analysis. Therefore it is easier and faster to perform the measurement directly on the plastic. Here the measured intensity is influenced by the strong scattering of tube radiation on the plastic as well as by absorption of particle radiation in the material. For this reason, the correct identification of an embedded particle is a demanding analytical task.

The spectra of an isolated particle and an embedded particle of the same composition (stainless steel) are shown in Figure 5. The spectra are normalized to Fe and look very similar. Two main differences remain: the scattering on the plastic increases the spectral background which can be seen in the energy range from 8 keV to 16 keV, and secondly, the absorption of the fluorescence radiation of the inclusion in the plastic reduces the Cr intensity and enhances the intensity of elements which are heavier than Fe. But not only the spectra of these particles are similar also the quantification results are comparable as can be seen in Table 3.

Even in case of very similar alloys it is possible to distinguish between different alloy types due to different concentrations of minor or traces elements. This is illustrated in Table 4 with two low-alloy steels which have only small differences in Cr and Ni content (factor 0.5 and 1.4 respectively, marked red). Particles consisting of these alloys were also prepared in a plastic film.

Figure 4
Inclusion of a small particle in a plastic film

Figure 5
Spectra of an isolated (blue) and an embedded particle (red) of the same composition



Quantification of isolated and embedded particles								
Element	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Nb**	**Mo**
Reference	18.5	0.6	70.9	0.1	9.0	0.2	0.1	0.1
Isolated particle	19.1	0.9	70.3	0.0	8.2	0.2	0.1	0.1
Embedded particle	16.6	0.9	71.3	0.3	9.9	0.2	0.1	0.1

Table 3
Quantification results of an isolated and an embedded particle in comparison to their given element concentrations in wt.%

Quantification of isolated and embedded particles								
Element	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Nb**	**Mo**
Reference	0.6	0.7	96.5	0.0	1.2	0.1	0.0	0.1
Isolated particle	0.6	1.2	96.3	0.6	1.1	0.1	0.2	0.1
Embedded particle	0.6	1.0	94.7	0.8	1.4	0.1	0.3	0.2
Reference	0.3	0.7	96.4	0.0	1.7	0.1	0.0	0.2
Isolated particle	0.3	1.1	96.5	0.0	1.5	0.1	0.0	0.1
Embedded particle	0.2	1.0	95.7	1.0	1.5	0.1	0.1	0.2

Table 4
Quantification results of low-alloy steel particles (both isolated and embedded) with similar concentrations, compared to their given concentrations in wt.% which clearly identify the material by their trace components (red)

Conclusion

With micro-XRF it is possible to analyze isolated small particles as well as particle inclusions in light materials such as plastics or glass. The concentration of the excitation radiation to small spot sizes allows to analyze even smallest sample volumes.

Although quantification is influenced by effects resulting from particle surface and size, as well as by absorption effects in case of embedded particles, even smallest particles can be safely identified by their trace and minor element content.

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