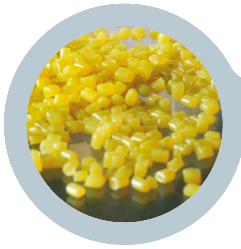
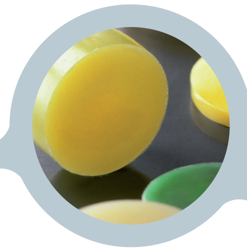


Polymer



Test sample

X-ray tube with efficient
tube head cooling

S8 TIGER

Lab Report XRF 99

S8 TIGER

The Analysis of Low Levels of Magnesium in Polyethylene and Polypropylene to Control the Polymerization Process

Introduction

In the polymerization process of PE and PP the Ziegler-Natta catalyst is commonly used for reaction enhancement. Catalyst systems of the Ziegler-Natta type are a mixture of reagents used in the production of polymers of the 1-alkenes type (α-olefins). Ziegler-Natta catalysts are typically based on titanium-magnesia and organometallic aluminium compounds, such as the undefined methylaluminoxane (MAO) or well defined triethylaluminium, $(C_2H_5)_3Al$. As the catalyst is very expensive (1000 US$/kg range) it is not wishful spending it rapidly. The efficiency of the catalysts must be optimized to maximize the output of polymer with a given amount of the catalyst. In order to monitor the catalyst performance the analysis of magnesium in polymers is an important application. The aim is to achieve the best accuracy and precision at lowest concentration levels of Mg.

One standard analytical technique for this application in general is ICP-OES. As this is based on a time consuming preparation using hazardous chemicals in combination with high argon gas consumption and the calibration is required day by day, other efficient analytical techniques such as wavelength dispersive X-ray fluorescence spectrometry (WDXRF) are preferred.

This application report will demonstrate that very low levels of Mg can easily be analyzed by means of the wavelength dispersive X-ray fluorescence spectrometer S8 TIGER 4K. Bruker AXS' modern sequential WDXRF spectrometer S8 TIGER applies an X-ray tube with up to 170 mA current at full 4 kW power. It proves to be an optimal solution for the enhanced accurate and precise analysis of light elements in extreme low concentrations.

Instrument

The S8 TIGER is the most versatile sequential wavelength dispersive X-ray fluorescence spectrometer. Equipped with an end window X-ray tube with Rh-target and a 10 position beam filter changer the excitation conditions can be easily adjusted to achieve optimum results. For the analysis of heavy elements up to 60 kV and up to 4 kW excitation power are optimal. To further improve the analysis of traces a broad selection of up to nine different beam filters is available to suppress e.g. Rhodium tube lines and to improve the peak-to-background ratio. With up to four collimators, up to eight installed analyzer crystals and two detectors the S8 TIGER can be adjusted for each element to match the required resolution and sensitivity.

Figure 1: X-ray tube of the S8 TIGER with low temperature tube head

High performance X-ray tube

The S8 TIGER is equipped with a high intensity X-ray tube for enhanced sensitivity. This allows to achieve very low detection limits and a very good reproducibility. In contrast to conventional X-ray fluorescence spectrometers the X-ray tube of the S8 TIGER is specifically designed reducing the heat dissipation to the sample. The heat produced in the tube head while generating the X-rays is efficiently conducted to the cooling water circuit. This is beneficial for the analysis of hydro carbon based samples such as polymers and oils. Stress and damages of the samples, especially of valuable standard samples, are reduced, therefore measurement times can be prolonged in order to achieve lower detection limits or samples can be analyzed several times.

Measurement and Calibration

The measurement was performed with an S8 TIGER 4K applying 23 kV and 170 mA, an XS-55 crystal which has a 2d value of 55 Å and a 0.46° collimator. These parameters ensure to achieve high resolution giving the advantage that the crystal fluorescence of Si and W is nicely separated from the analyte's (Mg) energy. The crystal fluorescence derives in WDXRF from the radiation of the crystal by the tube's Rhodium lines.

Four background positions were defined next to the peak position in order to correct the overlay of Aluminium, which is present in the samples shown in figure 2. The Al signal comes from the co-catalyst. Moreover, using the additional background positions, the analysis of Mg in PE and PP could be combined in one calibration where only Polypropylene based standards were available.

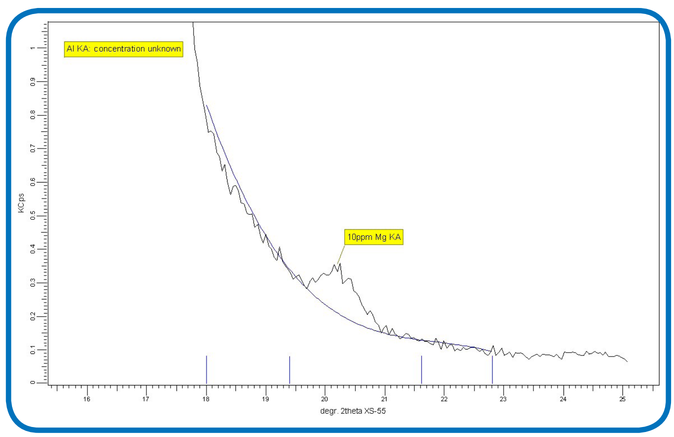


Figure 2: Polyethylene sample with 10 ppm Mg beside a high Al concentration

The S8 TIGER is calibrated using 12 factory standards. The standard deviation of the calibration is excellent with 0.2 ppm. The calibration curve is shown in figure 3, the calibrations details in table 1.

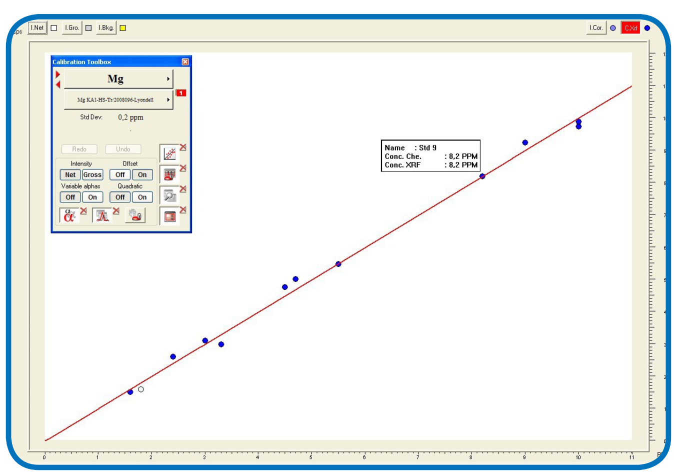


Figure 3: Calibration curve of magnesium in polyethylene at a very low concentration level

Table 1: Calibration table

Standard Name	Chemical Concentration (ppm)	XRF Concentration (ppm)	Absolute Deviation (ppm)	LLD (ppm)
Std 1	1.8	1.7	-0.1	0.2
Std 2	1.6	1.6	0.0	0.2
Std 3	2.4	2.7	0.3	0.2
Std 4	3.0	3.1	0.1	0.2
Std 5	3.3	3.0	-0.3	0.2
Std 6	4.5	4.7	0.2	0.2
Std 7	4.7	4.9	0.2	0.2
Std 8	5.5	5.4	-0.1	0.2
Std 9	8.2	7.9	-0.3	0.2
Std 10	9.0	8.9	-0.1	0.2
Std 11a	10.0	9.5	-0.5	0.2
Std 12a	11.0	11.5	0.5	0.2

Results

The accuracy of the method was evaluated with the analysis of two factory samples. Sample 1 contains 5.3 ppm, and sample 2 with 1.5 ppm Mg (reference values were obtained with ICP). The XRF results perfectly fit to the ICP values, the deviation is 0.3 ppm for sample 1 and 0.1 ppm for sample 2.

To test the precision the two samples were analyzed alternated, the results of the 10-fold repeatability test are shown in table 2. A precision of 0.1 ppm is obtained for both very low concentration ranges.

Table 2: Repeatability test

	Sample 1 Mg (ppm)	Sample 2 Mg (ppm)
Measurement 1	5.5	1.8
Measurement 2	5.7	1.6
Measurement 3	5.6	1.7
Measurement 4	5.4	1.5
Measurement 5	5.6	1.8
Measurement 6	5.7	1.7
Measurement 7	5.8	1.6
Measurement 8	5.7	1.5
Measurement 9	5.7	1.6
Measurement 10	5.4	1.6
Average	**5.6**	**1.6**
Standard Deviation	**0.1**	**0.1**

Conclusion

The analysis of very low levels of magnesium in polyethylene and polypropylene is accurate and reliable with the S8 TIGER. The achieved detection limits are very low with 0.2 ppm. It can be easily used to realize savings on catalysts costs giving early warnings in case of catalyst losses. In contrast to ICP-OES XRF is the perfect analytical tool due to its easy operation, quick sample preparation and simple integration into the plant quality and process control regime.

Authors

Pol de Pape
Dr. Kai Behrens
Bruker AXS, Karlsruhe, Germany

www.bruker.com

Bruker AXS GmbH
Karlsruhe, Germany
Phone +49 721 50997-0
Fax +49 721 50997-5654
info@bruker-axs.de

Bruker AXS Inc.
Madison, WI, USA
Phone +1 (800) 234-XRAY
Phone +1 (608) 276-3000
Fax +1 (608) 276-3006
info@bruker-axs.com