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Title:
Analysis of Dynamar Polymer Processing Additives in Polyolefins Using X-ray Fluorescence Spectrometry

Intro:
The concentration of Dynamar™ Polymer Processing Additive (PPA) products in polyolefins, at let-down (ppm) and masterbatch levels (%), can be determined using X-ray fluorescence spectrometry (XRF). This analysis requires the preparation of calibration standards which are used to develop calibration curves. Samples are readily analyzed by comparison to the calibration curves. Examples of specific analysis for fluorine and barium, applicable to Dynamar FX 9613, FX 5920A and FX 5920B, are shown.

Date Published: April, 1998

# Dynamar™
## Polymer Processing Additives
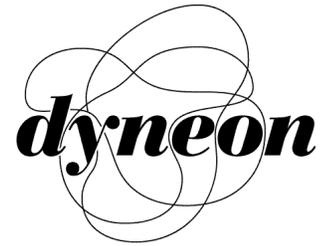
*dyneon*

## Analysis of Dynamar Polymer Processing Additives in Polyolefins Using X-ray Fluorescence Spectrometry

## Introduction

The concentration of Dynamar™ Polymer Processing Additive (PPA) products in polyolefins, at let-down (ppm) and masterbatch levels (%), can be determined using X-ray fluorescence spectrometry (XRF). This analysis requires the preparation of calibration standards which are used to develop calibration curves. Samples are readily analyzed by comparison to the calibration curves. Examples of specific analysis for fluorine and barium, applicable to Dynamar FX 9613, FX 5920A and FX 5920B, are shown.

## Preparation of Calibration Standards and Samples

A series of calibration standards which contain the same additive formulation as the unknown samples to be analyzed are prepared. Typically, a PPA masterbatch is diluted to concentration levels covering the range of interest. The actual PPA concentration in the calibration standards can be determined by Parr Bomb analysis for fluorine content.[1] The PPA must be uniformly dispersed throughout the standards and samples.[2] It is important that the calibration standards and samples have the same thickness. This can be controlled by using a standard size shim and compression molding the samples under identical conditions of temperature, pressure and time.

Polyolefins will degrade with continued exposure to x-rays. The degradation rate will be dependent on the excitation parameters (x-ray flux and measurement time). Consequently, it is advisable to prepare the calibration standards in sufficient quantity to allow preparation of new specimens periodically.

## Analysis of Standards and Unknowns

One or more specimens is cut from each calibration standard and inserted into the spectrometer. The intensity of the x-ray line of interest is determined and the intensity is plotted versus the actual concentration of the standards to establish a calibration curve. (If multiple specimens are measured for each standard, either an individual intensity or the average intensity value may be used for the calibration curve.) The concentration of PPA in unknown samples is subsequently determined by comparison of the measured x-ray intensity to the calibration curve.

The calibration curve should be updated, or a "check standard" should be measured regularly to allow compensation for drift in the spectrometer. Because the fluorine content of typical Dynamar use-levels is very low, the accuracy of the calibration curve is critical to insure the correct analysis of unknown samples.

[1]Dynamar Technical Information, Parr Bomb Analytical Method for Determining Total Organic Fluorine Concentration in Polyethylene.
[2]Dynamar Technical Information, Optical Microscopy Method for Dispersion Analysis in Polyolefins.

## Analysis of Dynamar™ FX 9613 and FX 5920A
(See Example 1)

The concentration of FX 9613 and FX 5920A can be determined using a wavelength dispersive x-ray spectrometer which has been configured to measure fluorine. Analyzing conditions are selected to optimize this measurement for the particular spectrometer. Typically, a layered synthetic microstructure (LSM or "multilayer") is used in conjunction with a flow proportional counter. Because of the low fluorine concentration in let-down samples, it is critical to perform a background measurement and appropriate background correction to the gross peak intensity.

The use of a stable inorganic compound such as NaF to determine the location of the fluorine peak and the appropriate angles for the background measurements is recommended. Because typical use levels of Dynamar are at part per million levels, a fluorine peak will probably not be observable during a step scan. The determination of fluorine typically cannot be done using an energy dispersive XRF spectrometer or a bench-top XRF system.

Work completed by our laboratory to date indicates that the same calibration curve appears to be usable for both FX 5920A and FX 9613 in LLDPE. Plot the concentration of fluorine (not FX 9613 or FX 5920) in the calibration standards against the x-ray intensities. A simple calculation, as shown in Example 1, can be done to convert weight percent fluorine to FX 5920A or FX 9613.

## Analysis of Dynamar™ FX 5920B
(See Example 2)

In FX 5920B, barium sulfate has been added at a specific level (10%) to serve as a tracer for analysis by XRF. Either an energy dispersive (ED) or a wavelength (WD) XRF spectrometer can be used for this analysis. The PPA concentration is calculated based on the measured barium sulfate content. Laboratories with bench-top XRF systems should consult their manufacturer to determine if their system has the appropriate configuration to perform this analysis.

The analyzing conditions are selected to optimize this measurement for a particular spectrometer.

- For wavelength dispersive instruments, a LiF200 crystal coupled with a flow proportional counter is an appropriate choice for the Ba-L$\alpha$ line. A LiF200 crystal coupled with a scintillation counter is appropriate for the Ba-K$\alpha$ line.

- For an energy dispersive spectrometer, either the Ba-L$\alpha$ or the Ba-K$\alpha$ line can be measured. If the sample also contains Ti, there will be severe peak overlaps between the Ti K-series lines and the Ba L-series lines. In this instance, it may prove advantageous to use the Ba-K$\alpha$ line for the analysis.

A second option is to measure sulfur and use this to calculate barium sulfate and the PPA concentration.

The concentration of FX 5920B can be determined using the barium or sulfur intensities only if there are *no* other sources of the selected element in the sample.

Care must be taken to set the measurement conditions appropriately if other additives are present. The need for inter-element corrections for absorption/enhancement effects was *not* studied. This will be dependent on the presence/concentration of other elements in a particular formulation of polyolefin.

| Example #1 | **Analysis of Dynamar™ FX 9613 and FX 5920A Concentrations in Polyethylene Using Wavelength Dispersive X-ray Fluorescence Spectrometry for Fluorine** |
|---|---|

This is a method for determining the concentration of Dynamar Polymer Processing Additive (PPA) in Linear Low Density Polyethylene (LLDPE). The method is broadly applicable for any laboratory equipped with a wavelength dispersive X-ray fluoescence spectrometer which is configured for the analysis of fluorine.

**Equipment**
A Rigaku model 3270 3-kW Sequential X-ray Spectrometer equipped with a Machlett OEG-76 Rhodium anode end-window x-ray tube was used for the method development and analysis. The spectrometer was designed to hold eight analyzing crystals which were coupled with either a flow proportional counter or a scintillation counter. The system was controlled by the vendor's software.

**Sample Preparation**
Calibration standards were prepared by melt mixing together known amounts of a Dynamar PPA masterbatch in an LLDPE resin using a laboratory Haake melt mixer. The cooled mixture was chopped and ground. The XRF specimens were prepared by pressing the ground sample between two sheets of polyester film using a ten mil thick circular shim. The samples were preheated for two minutes at 300°F, and then pressed for one minute at 20,000 psi. (Note: It is important that the standards and samples have the same thickness.)

**Measurement Parameters**
The measuring conditions and integration time must be optimized for a particular spectrometer. The conditions listed below represent appropriate choices for the Rigaku 3270 spectrometer.

- X-ray tube excitation conditions: Measurements were made using settings of 40 kV-75 mA and 50 kV-50 mA.

- X-ray tube filter: none used.

- Measurement area: 30 millimeters in diameter.

- Attenuator: 1 to 1 (Change as necessary to remain in appropriate intensity range so that linearity of detector electronics is not exceeded.)

- Primary Collimator: coarse Soller slit to maximize intensity, rather than resolution.

- Crystal: RX-35
  These devices are commonly referred to as layered synthetic microstructures (LSMs) or multilayers. The RX-35 is a W-Si construction with a measured 2d spacing of 58 angstroms at the Mg-Kα line.

  Individual spectrometer manufacturers have their own identification system for multilayers. The RX-35 is an OVONYX brand multilayered x-ray reflector made by:
  OSMIC Inc.
  1788 Northwood Drive
  Troy, Michigan 48084, 248-362-1290

**Example #1**
(continued)

- PHA window: 100-300

- Fluorine Peak Position: Using the RX-35 multilayer
  Peak: 37.00 degrees $2\theta$
  Background 1: 35.00 degrees $2\theta$
  Background 2: 39.00 degrees $2\theta$

  Note: Because of the low fluorine concentration, it is important to perform a background measurement to correct the gross peak intensity. Peak positions for other multilayers must be calculated for the particular 2d spacing of the crystal.

- Measurement time: 100 seconds (optimize for spectrometer and desired counting statistics.)

- Detector: Flow proportional counter (and associated Soller slit), using P-10 gas (90% argon, 10% methane).

**Analysis**
Three specimens were cut from each pressed film calibration standard. The specimens were inserted in sample holders and analyzed for the net fluorine x-ray intensity using the measuring conditions outlined above. The net intensities of the three specimens were subsequently averaged.

Separate specimens of each standard were analyzed using the Parr Bomb method to determine the fluorine content. The average x-ray intensities were plotted against the percent fluorine values determined by the Parr Bomb analysis to establish a calibration curve. Excellent linearity was observed; copies of representative curves are attached.

**Discussion**
The use of a stable inorganic compound such as NaF to determine the location of the fluorine peak and the appropriate angle(s) for the background measurement(s) is recommended. Because typical use levels of Dynamar are on the order of several hundred ppm, a fluorine peak will probably not be visible during a step scan. The approximate peak location for fluorine can be calculated for a given multilayer using the equation:

$$n\lambda = 2d \sin\theta, (n = 1).$$

The wavelength of the fluorine K$\alpha$ line is 18.3200 Angstroms. Calculate theta times 2 to obtain the correct angle.

**Example #1**
(continued)

**XRF Calibration Curve for FX 9613
Two Energy Configurations**
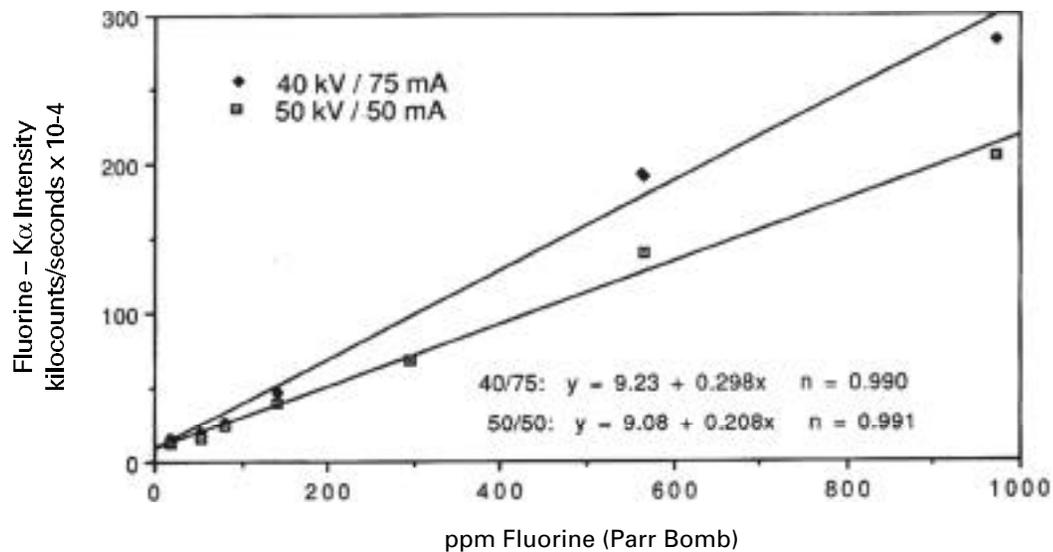


FX 9613 = 59.3 ± 1.3% Fluorine

$$\text{PPM FX 9613 (unknown)} = \frac{\text{ppm Fluorine (Calibration Curve)}}{0.593}$$

**XRF Calibration Curve for FX 5920A
Two Energy Configurations**
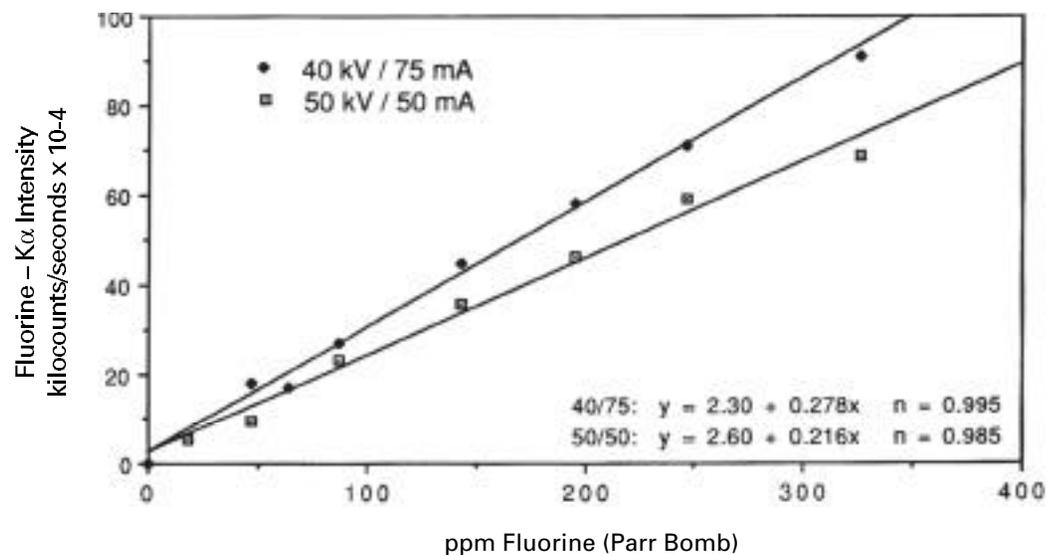


FX 5920A = 19.75 ± 2.65% Fluorine

$$\text{PPM FX 5920A (unknown)} = \frac{\text{ppm Fluorine (Calibration Curve)}}{0.1975}$$

| **Example #2** | **Analysis of Dynamar™ Polymer Processing Additive FX 5920B Concentration in Polyethylene Using X-ray Fluorescence Spectrometery** |

This is a method for determining the concentration of Dynamar Polymer Processing Additive (PPA) FX 5920B in Linear Low Density Polyethylene (LLDPE). In FX 5920B, barium sulfate is added at a specific level as a tracer for analysis by X-ray Fluorescence Spectrometry (XRF). PPA concentration is calculated based on the measured barium content. The barium concentration can be rapidly determined using either an energy dispersive (ED) or a wavelength dispersive (WD) XRF spectrometer. Laboratories with bench-top XRF systems should consult their manufacturer to determine if their system has the appropriate configuration to perform this analysis. (Please note: Analyzing PPA products which do *not* contain $BaSO_4$ requires measurement of fluorine, either by Parr Bomb or by WD-XRF. Fluorine cannot be measured by ED-XRF or bench-top XRF systems at this time.)

**Equipment**

A Rigaku model 3270 3-kW Sequential X-ray Spectrometer equipped with a Machlett OEG-76 Rhodium anode end-window x-ray tube was used for the method development and analysis. The spectrometer is designed to hold eight analyzing crystals which are coupled with either a flow proportional counter or a scintillation counter. The system is controlled by the vendor's software.

**Sample Preparation**

Calibration standards were prepared in a Haake melt mixer by compounding barium sulfate into LLDPE at a 10% level. The level of the concentrate was then verified using a gravimetric ashing procedure. This concentrate was then diluted to levels covering the range of the samples to be analyzed. Standards and samples to be measured were prepared in a Wabash press at 300°F, one minute preheat, followed by two minutes at 20,000 psi. Samples were pressed between two sheets of polyester film using a 10 mil thick shim. (Note: It is important that the standards and samples have the same thickness.)

**Measurement Parameters**

The measuring conditions and integration time must be optimized for a particular spectrometer. The conditions listed below represent appropriate choices for the Rigaku 3270 spectrometer.

X-ray tube excitation conditions: 50 kV-50 mA

X-ray tube filter: none used

Measurement area: 30 millimeters in diameter

Attenuator: 1 to 1 (Change as necessary to remain in appropriate intensity range so that linearity of detector electronics is not exceeded.)

Primary Collimator: coarse Soller slit

Crystal: LiF200 coupled with flow proportional counter

PHA window: 100-300

**Example #2**
(continued)

Ba-Lα line was used:
Peak position: 87.17 degrees 2θ
Background 1: 86.00 degrees 2θ
Background 2: 88.50 degrees 2θ

Measurement time: 100 seconds (optimize for spectrometer and desired counting statistics)

Detector: Flow proportional counter (and associated Soller slit), using P-10 gas (90% argon, 10% methane)

**Analysis**
A single specimen was cut from each calibration standard. The specimen was inserted in a sample holder and analyzed for the net barium x-ray intensity using the measuring conditions outlined above.

The net Ba-Lα X-ray intensities were plotted against the percent barium sulfate values to establish a calibration curve. Excellent linearity was observed. A copy of a representative calibration curve is attached.

**Discussion**
The Ba-Lα line and the combination of LiF200-flow proportional counter were selected for the analysis because this provided the best sensitivity for our spectrometer. This choice will be instrument dependent.

A second option would be to measure sulfur and use this to calculate barium sulfate and PPA concentration. We obtained similar and satisfactory data for sulfur.

Care must be taken to set the measurement conditions appropriately if other additives are present (antiblocks, acid neutralizers and pigments, for example). The need for interelement corrections due to absorption/enhancement effects was *not* studied. This will be dependent on the presence/concentration of other elements in a particular formulation of polyethylene.

Energy dispersive instruments: If the sample also contains Ti in excess of catalyst levels, there will be severe peak overlaps between the Ti K-series lines and the Ba L-series lines. In this instance, it may prove advantageous to use the Ba-Kα line for the analysis. The thickness of the sample must be closely controlled in this instance to avoid intensity variations due solely to film thickness.

**Example #2**

(continued)

**XRF Calibration Curve for FX 5920B**



$$y = 0.60692 + 61.902x \quad R^2 = 0.984$$

*Ba-Lα Intensity (kcps)* vs *ppm BASO₄*
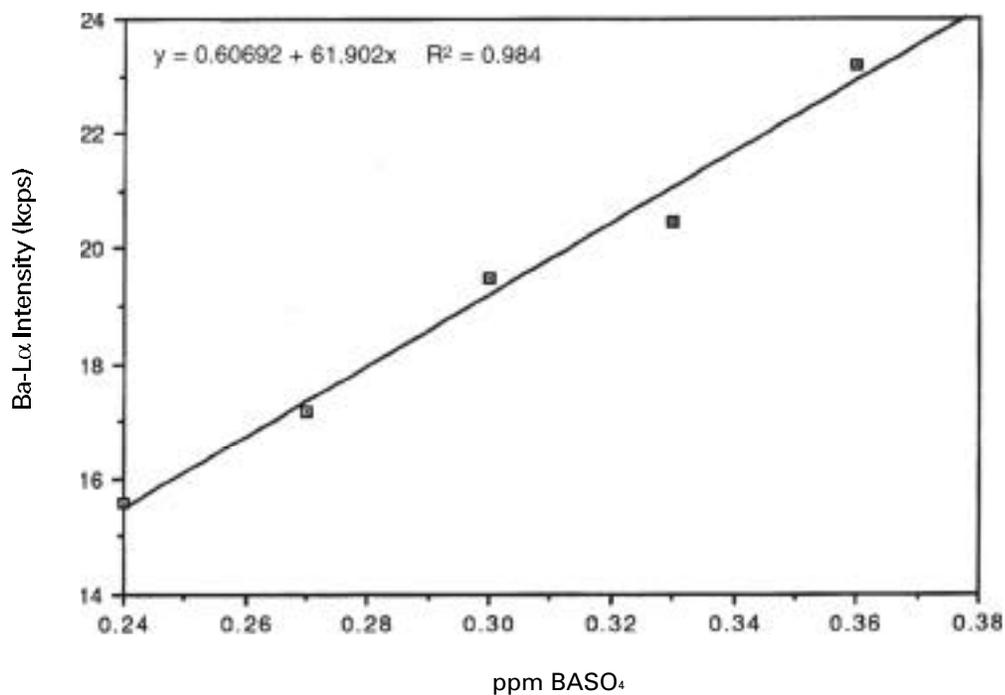
FX 5920B = 10 ± 2% BaSO₄

PPM FX 5920B (unknown) = $\dfrac{\text{ppm BaSO}_4 \text{ (Calibration Curve)}}{0.10*}$

*Or value of BaSO₄ listed for a particular lot in the Certificate of Analysis (divided by 100%).
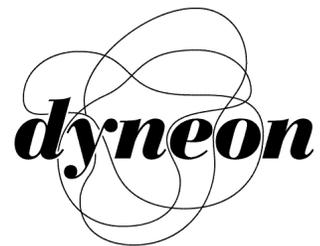
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