

Quickly Analyzing Thermoplastic Road-Marking Material for Titanium Dioxide

FHWA Publication No.: FHWA-HRT-20-031

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Handheld x-ray fluorescence (XRF) spectrometers are easy to use, require no operator skill, and deliver data quickly. A cup with a thin, transparent plastic membrane bottom holds the sample. A typical handheld XRF spectrometer is shown in figure 1, and an XRF cup is shown in figure 2. With these tools, it is possible to determine the titanium dioxide (TiO_2) content of thermoplastic road-marking materials in a just a few minutes with no sample preparation.

The composition of thermoplastic road-marking materials is governed by AASHTO M247, *Standard Specification for Glass Beads used in Pavement Markings*, and AASHTO T250, *Standard Method of Test for Thermoplastic Traffic Line Material*.^(1,2) These materials often consist of a resin binder (either alkyd or hydrocarbon resin), glass beads to enhance light reflection at night, a white pigment (TiO_2) to add brightness, and calcium carbonate as an inert filler to lower cost. The resin binder and glass beads are shown in figure 3 and figure 4, respectively.

The specification of AASHTO T250 is given in table 1.

AASHTO T250 provides a test method in which a sample of material is placed in a muffle furnace at 540 °C (1,004 °F) to burn off the resin binder.⁽²⁾ The calcium carbonate filler is then dissolved from the residue with 18 percent hydrochloric acid. The resulting insoluble residue is classed as a reflective optic.

Since the thermoplastic road marking material is a heterogenous mixture, the analysis for TiO_2 is challenging. It was theorized that the powder components (TiO_2 and calcium carbonate) could be encouraged to the bottom of the sample by shaking and tamping, thereby creating a more homogeneous material. Both the resin binder and glass beads have a larger particle size than the powder components, so they would gravitate toward the top of the XRF cup. The powder at the bottom would consist mostly of TiO_2 and calcium carbonate—as well as any dust particles from the resin binder and glass beads.

This theory was tested with three 1-gallon samples of thermoplastic road-marking compound. To eliminate the possibility that the contents of the cans that contained the samples settled in transit, the contents were stirred with a large palette knife. After stirring, 10 random samples were taken from each can and placed in XRF cups. The cups were closed and the vent holes on the lids were covered with tape. The cups were then shaken and tapped on a bench 20 times to consolidate the powder at the bottom of the sample and remove air voids, as shown in figure 5-A and figure 5-B.



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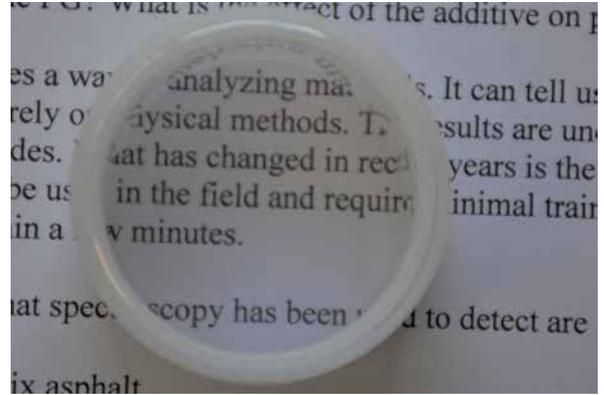
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Figure 1. Photo. Handheld XRF spectrometer.



Source: FHWA.

Figure 2. Photo. XRF cup.



Source: FHWA.

Figure 3. Photo. Resin binder.



Source: FHWA.

Figure 4. Photo. Glass beads.



Source: FHWA.

Figure 5. Photos. XRF cups containing compound before and after shaking.



Source: FHWA.

A. Compound before shaking.



Source: FHWA.

B. Compound after shaking.

Table 2 shows that the analysis results for TiO₂ content of the 10 samples were consistent. The results only apply to the powder at the bottom of the cup and do not reflect the overall TiO₂ content of the materials.

Component	Percentage
Resin binder	18 minimum
Glass beads	30–40
TiO ₂	10 minimum
Calcium carbonate	42 maximum

Sample	Reference 18-007	Reference 18-003	Reference 18-005
1	26.03	20.58	26.65
2	25.41	20.97	27.80
3	26.02	21.40	29.08
4	25.26	20.54	28.78
5	25.35	22.67	25.62
6	25.54	21.19	27.49
7	25.45	20.45	28.88
8	25.49	19.78	26.46
9	26.08	20.23	29.42
10	25.79	22.91	27.87

Handheld XRF spectrometers detect the presence of elements in a material. A detector in the spectrometer, which produces voltage, collects the fluorescence from a sample. To accurately measure a sample, the voltage of the detector must be set up and correlated to what is being measured. This set up is done by calibrating the instrument using a known material or set of calibration standards.

Many handheld XRF spectrometers are programmable, and some come preprogrammed to measure certain elements or sample types. Some spectrometers are designed for a specific application but are often expected to work with a wide range of materials. Results can vary widely depending upon the instrument, program, and application. The handheld XRF spectrometer used in this experiment was programmable and came equipped with a variety of programs. To illustrate this ability, a sample of thermoplastic road-marking compound was tested using different programs, which are shown in table 3.

Results depend on how and for what type of sample the program was written. The manufacturer can provide information on how their instrument should be set up for the application in mind.

To ensure accuracy, the instrument should be calibrated with something as close as possible to the samples and ranges to be measured. For this experiment, blends of TiO₂ (from 10 to 30 percent in increments of 1 percent) with calcium carbonate were used. The calibration had an R² value of 0.997396 and a standard deviation of 0.394 percent. These values were a good indication that the TiO₂ analyses were realistic. This procedure was called thermoplastic road-marking paint 1, or TRMP1.

Program	TiO ₂ Percentage
Geoexploration	0.0004
Geomining	5.10
Limestone	22.743
Precious metals	85.219
Cement	36.256
Gypsum	6.168

Reference	Supplier	TiO ₂ Percentage
19-012	One	8
19-014	One	9
19-013	One	10
19-015	One	11
19-011	Two	8
19-017	Two	9
19-021	Two	10
19-020	Two	11

A State department of transportation (DOT) supplied samples of known TiO₂ content for testing, the results of which are shown in table 4.

The samples shown in table 4 and the TRMP1 procedure were used to obtain calibration curves for the reference samples received from a State DOT. Each sample was placed in an XRF cup then shaken and tamped on a bench to encourage the powder components to the bottom of the cup. The powder contained TiO₂ and calcium carbonate filler plus any dust particles from the resin and glass beads. TiO₂ is reported as powder TiO₂ since only the powder at the

bottom of the XRF cup was measured, not the whole sample. The results are shown in table 5.

Table 5. Calibration measurements of tamped thermoplastic blends.

Reference	Supplier	Actual TiO ₂ Percentage	Powder TiO ₂ Percentage
TSA1/90/1	Two	8	29.24
TSA1/90/8	Two	9	31.29
TSA1/90/2	Two	10	37.60
TSA1/90/3	Two	11	41.64
TSA1/90/4	One	8	31.35
TSA1/90/5	One	9	25.50
TSA1/90/6	One	10	28.38
TSA1/90/6	One	11	33.97

The actual TiO₂ content measured using the TRMP1 procedure was plotted against the known TiO₂ content of the reference samples received from a State DOT. The results are shown in figure 6.

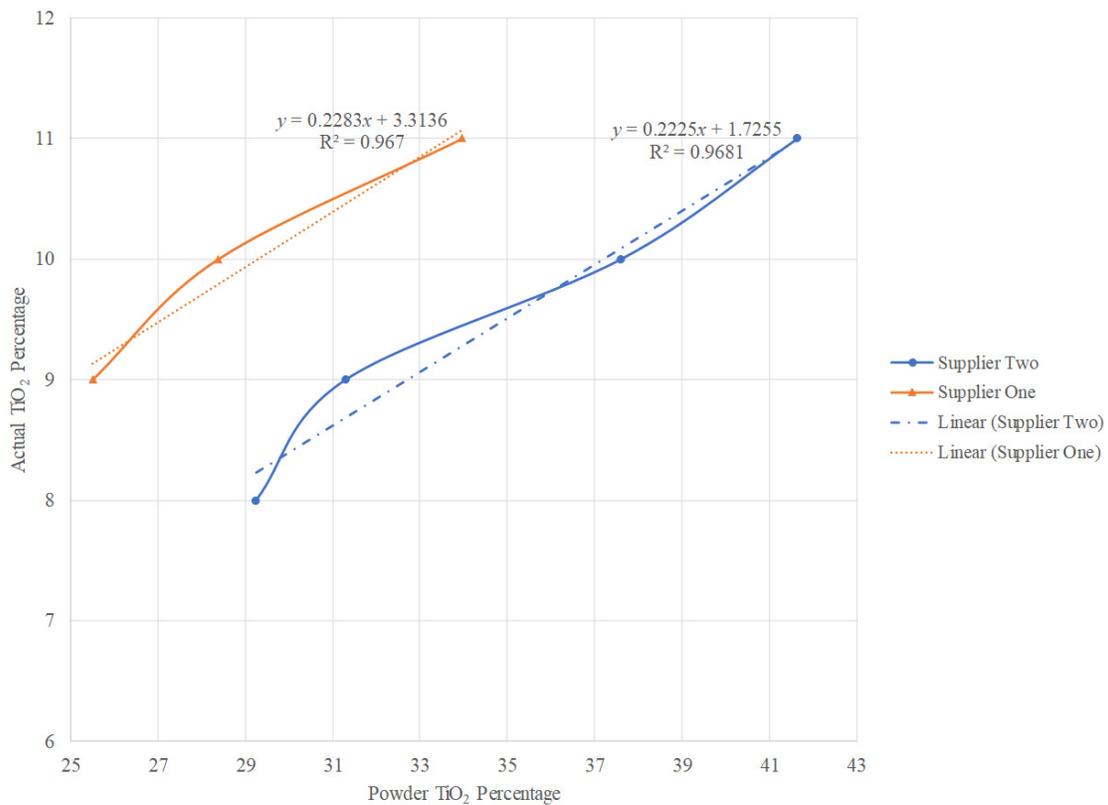
The samples from both suppliers are in agreement. The correlations have R² values of 0.967 for supplier one and 0.9681 for supplier two. The regression equations are $y = 0.2283x + 3.3136$ for supplier one and $y = 0.2225x + 1.7255$ for supplier two.

As figure 6 shows, calibrations are specific to a given formulation. Materials from different suppliers have different regression equations. The equations are formulation-specific and not interchangeable.

During the Take Our Daughters and Sons to Work Day at Federal Highway Administration’s Turner-Fairbank Highway Research Center (TFHRC) in April 2019, children ages 10 to 13 were invited to analyze random samples from the 1-gallon sample of supplier one (reference sample 18-007). The children took the samples themselves and carried out the measurements. To analyze the effect of shaking and tamping the cup, they took before and after measurements of the samples. Then, using the regression equation for supplier one, the children calculated the actual TiO₂ content. The results are shown in table 6.

Gravimetric analysis of reference sample 18-007 showed a TiO₂ content of 9.02 percent. Although some refinement is necessary, results show that the method works. If the signal from the handheld XRF spectrometer is strong enough, it may be possible to measure the material through the plastic bag. An alternative technique is to use Raman spectroscopy, which can “see” through plastic packaging materials.

Figure 6. Chart. Plot of actual TiO₂ versus powder TiO₂ content.



Source: FHWA.

Table 6. Measurements from Take Our Daughters and Sons to Work Day.

Operator	XRF Measurement Powder TiO ₂ Percentage		Calculated TiO ₂ Percentage
	Before Shaking	After Shaking	
Calli K.	24.28	25.26	9.08
Adelade K.	20.93	25.39	9.11
Walter G.	23.07	23.96	8.78
Aracely J.	20.77	25.60	8.06
Kyle C.	22.18	26.62	9.39
Bryce M.	23.59	25.59	9.16
Lyllie H.	23.81	24.22	8.84
Asher M.	23.50	25.35	9.10
Ayden B.	23.03	24.14	8.82
Elizabeth L.	23.52	25.90	9.23
Terry Arnold, TFHRC	22.28	24.88	8.99
Terry Arnold, TFHRC	22.63	25.15	8.93
Terry Arnold, TFHRC	20.50	24.59	8.95
Average	—	—	8.95
Standard deviation	—	—	0.32

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REFERENCES

1. AASHTO (American Association of State and Highway Transportation Officials). 2018. *Standard Specification for Glass Beads Used in Pavement Markings*. AASHTO M247. Washington, DC: AASHTO.
2. AASHTO (American Association of State and Highway Transportation Officials). 2005. *Standard Method of Test for Thermoplastic Traffic Line Material*. AASHTO T250. Washington, DC: AASHTO.

Researchers—This study was performed by Terence S. Arnold (HRDI-10) in the Turner-Fairbank Highway Research Center chemistry lab.

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Availability—This TechBrief may be obtained online at <https://highways.dot.gov/research>.

Key Words—Titanium dioxide, TiO₂, thermoplastic road-marking, x-ray fluorescence, XRF.

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