

APPLICATION OF INSTRUMENTAL METHODS
FOR EVALUATING HIGHWAY MATERIALS
First Progress Report: Determination of Amount
of "Plastiment A" Retarder in Hardened Concrete

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Progress Report On a Highway Planning and Research Investigation
Conducted in Cooperation with
The U. S. Department of Commerce--Bureau of Public Roads

Research Laboratory Division
Office of Testing and Research
Research Project 63 G-124
Research Report No. R-586

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State of Michigan
Department of State Highways
Lansing, November 1966

INFORMATION RETRIEVAL DATA

REFERENCE: Frederick, W. L. and Ellis, J. T. "Application of Instrumental Methods for Evaluating Highway Materials--First Progress Report: Determination of Amount of 'Plastiment A' Retarder in Hardened Concrete. Michigan Department of State Highways Research Report No. R-586. November 1966. Research Project 63 G-124.

ABSTRACT: A reliable colorimetric method for determining Plastiment A retarder in hardened concrete containing gravel, limestone, or slag aggregates has been developed which generally yields an absolute accuracy of ± 0.4 oz per sack of cement. Details of the method are given, and development of similar techniques is recommended for other retarders. The study resulted from instances of overdosage of retarder in bridge deck concrete. The analytical method will also detect omission of retarder that would result in early setting of concrete.

KEY WORDS: colorimetry, concrete admixtures, concrete bridge decks, retarders, spectrochemical analysis, water reducing agents.

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Introduction

Prior to 1961, set retarders were seldom if ever used in bridge deck concrete in Michigan. From about 1961 to 1963, "Plastiment A" (registered trademark of the Sika Chemical Co., Passaic, N. J.) was used on nearly all bridge projects when a retarder was specified. Since 1963, less expensive products have reduced its share to approximately 40 percent of bridge projects where retarders are used. Three out of four bridge deck pours are presently made with retarded concrete.

Two cases of defective bridge deck concrete, one in 1962 and another in 1963, were traced to addition of grossly excessive amounts of Plastiment A. During the investigation of these cases it was found that different brands of cement had varying susceptibility to set retardation by this product. Variation of retardation for different cements at constant retarder dosage has been reported in the literature (1). Generally, cements low in alkali oxides and tricalcium aluminate exhibit increased set retardation per unit of admixture addition. It was also reported that high quality concrete can be obtained from seriously over-retarded concrete mixes, provided the concrete is kept moist until setting occurs.

In view of the wide use of this particular retarder, its varying effects with respect to different cements, and in order to properly dispose of suspected cases of erroneous dosage it seemed advisable to develop a method for accurate determination of Plastiment A in hardened concrete. Other retarders would require the development of suitable methods on an individual basis.

The determination of Plastiment A was included in Research Project 63 G-124, which began in July 1964 in cooperation with the U. S. Department of Commerce--Bureau of Public Roads under the Highway Planning and Research Program. Because of the character of this project, in which a number of separate investigations are being carried on by instrumental techniques, it has been agreed that separate progress reports will be issued as individual phases are completed. This is the first in this series of progress reports.

Discussion

The investigation of a method for determining Plastiment A in hardened concrete was started late in September 1962 following an instance of defective concrete in the deck of an interstate highway structure in southwestern Michigan. One 5-cu yd load of concrete in one pour of this bridge had not completely set up seven days after it was placed. The concrete design called for addition of 3 fl oz of Plastiment A per sack of cement by hand at the transit mix plant. A core sample of the defective concrete crumbled into chunks with occasional patches of white powder on their surfaces. Preliminary chemical analysis and infrared spectral data showed the following:

1. Cement content was normal.
2. Adulterants such as sugar and form oil were absent.
3. The patches of white powder were carbonates similar to the limestone aggregate used in the concrete. The crystals apparently formed when the concrete eventually dried out.
4. The dried water extract of a powdered 140-mesh sample of defective concrete had an unidentified infrared absorption band near 9 microns.

This information and a literature report (2) on retarders led to investigation of excess Plastiment A as the cause of the defective concrete. Concrete specimens containing 0, 3, and 18 oz of retarder per sack of cement were prepared, using the same materials and mix design as in the bridge pour. The specimens containing 18 oz of retarder per sack of cement required seven days to attain final set.

Plastiment A was added to an alkaline solution of calcium chloride to test for the formation of an insoluble calcium salt of the organic acid that constitutes the active ingredient in this retarder. Chemical studies, infrared spectra, and information from the literature (3, 4) indicated that Plastiment A was a water solution containing 31.5 percent by weight of the sodium salt of a polyhydroxy carboxylic acid. No insoluble salt formed. This indicated that it would be possible to extract Plastiment A residues from concrete, which is rich in calcium compounds. Water extracts were obtained from the laboratory concrete specimens after they were ground to 140-mesh powder. Infrared spectra of these dried extracts showed that the laboratory specimen containing excess retarder enhanced an absorption band near 9 microns, as did the defective concrete.

An attempt was made to identify the 9-micron absorption band as characteristic of Plastiment A. The water extracts from the concrete samples were acidified and extracted with ether to separate the retarder organic acid from the soluble carbonates of the concrete. Infrared spectra indicated that the acid underwent changes during isolation that did not allow definite identification of the extracts as Plastiment A.

Since conclusive identification of the organic acid in Plastiment A was not obtained by infrared methods, a color test for this type of organic acid was investigated. The literature revealed a test (5) which produced a green fluorescent color when hydroxy-acids were heated with β -naphthol and sulfuric acid. No green color formed when water extracts of retarder-free concrete were tested, but a weak color formed when normal concrete containing this retarder was tested. A strong green fluorescent color was obtained with water extracts of the defective concrete and a laboratory control prepared with 18 oz of retarder per sack of cement. Visual color matching indicated that the defective concrete had received four to six times the design dose of retarder.

A second instance of retarder overdosage occurred in July 1963 on the deck of a Detroit expressway bridge. The design mix called for 3 oz of Plastiment A per sack of cement. In this case the initial set required approximately 26 hr during hot weather (92 F) with low humidity. Shrinkage cracks 4 to 6 in. in depth developed. The Plastiment A content of core samples from this bridge deck was determined by visual color matching, using the colors yielded by water extracts of a series of laboratory mixes containing 0, 3, 6, and 9 oz of retarder per sack of cement as standards. This concrete contained slag aggregate which interfered with the procedure and necessitated modification of the original method, as noted later. This procedure made it possible to classify the core samples in a certain range interval of the standards, but was less accurate and precise than desired. The over-retarded concrete samples contained approximately 6 oz of retarder per sack of cement, twice the design amount.

It was also found, with laboratory mixes, that the Dundee cement used in this bridge was much more sensitive to an excess of Plastiment A than Huron cement, which was used in comparison testing. Cement chemical composition, physical properties, and set retardation data are given in Appendix A. The Dundee values are for the Type 1A cement actually used in the Detroit bridge and in the laboratory. The laboratory Huron Type 1A cement did not undergo comparable analysis, but values are reported for averages of two samples of Huron 1A cement manufactured at about the same time.

In view of the lack of accuracy and precision of the preliminary method and the indicated differences in Plastiment A tolerance of various cements, it was decided to instrumentalize the measurement of the green color, and refine the method to yield accurate, more precise determinations of Plastiment A in hardened concrete. Accordingly, three series of concrete reference samples were prepared containing known amounts of Plastiment A, using limestone, gravel, and slag aggregates. These were used to establish calibration curves. Additional concrete samples containing Plastiment A in amounts different than the reference samples were prepared to serve as standard analytical samples.

An intensive study was carried out to find the optimum means of sample preparation, Plastiment A extraction, reagent stabilization, color development, and color measurement. The variables were then integrated into the following procedure, described in greater detail in Appendix B:

1. Crush and grind the sample to pass a 140-mesh sieve. Mix the ground material thoroughly to assure a representative sample.
2. Extract retarder from 15 g of the ground sample with hot water and filter the solution through medium paper.
3. Evaporate the water extract to dryness and extract the dry residue with hot alcohol to remove an interfering yellow color. The nature and cause of this yellow interference were not determined.
4. Take up the dried alcohol-insoluble material in a known volume of concentrated sulfuric acid. If the sample contains slag aggregate, filter this solution through an asbestos mat in a Gooch crucible.
5. Add an aliquot of the sulfuric acid solution to 3 ml of β -naphthol reagent in a test tube and heat in boiling water for 1 hr. A green color develops that varies in intensity with the retarder content.
6. Measure the absorbance of the green color at a wavelength of 595 millimicrons with a spectrophotometer such as the Beckman Model DU. Figure 1 shows the transmission curves for the green color obtained with concrete samples containing 0, 6, and 12 oz of Plastiment A per sack of cement. These curves were obtained with a recording spectrophotometer to facilitate location of the analytical peak, which is marked at 595 millimicrons.
7. Convert the spectrophotometer readings to ounces of retarder per sack of cement by use of a calibration curve (Fig. 2).

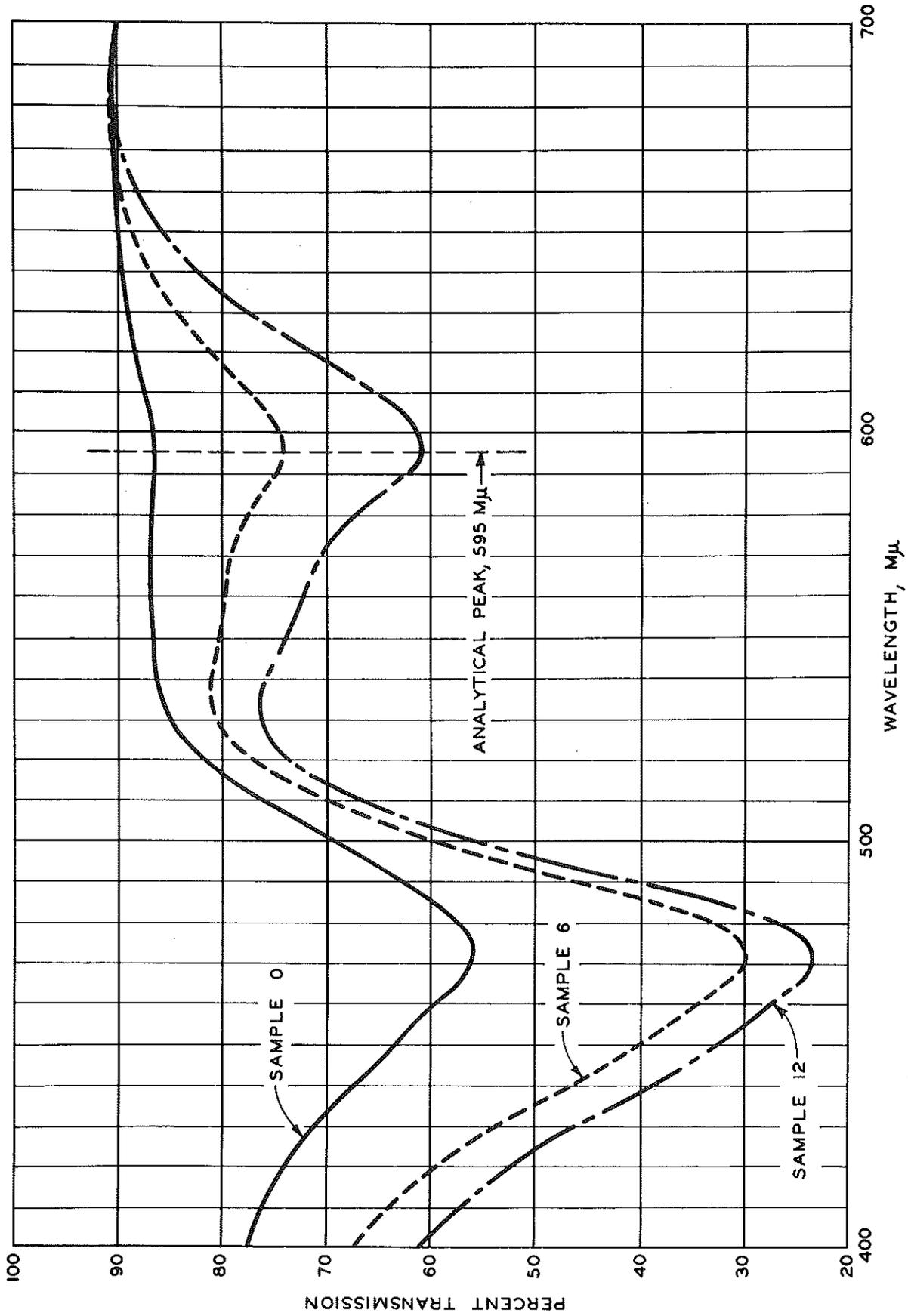


Figure 1. Transmission scans (using Beckman model DK-1A recording spectrophotometer) of the green color developed with extracts from concrete samples containing 0, 6, and 12 oz of Plastiment A per sack of cement. Vertical dashed line indicates peak used for analytical measurements.

In establishing calibration curves and determining the accuracy and precision of this method, three extractions of the reference mixes and standard samples for each aggregate type (limestone, gravel, and slag) were made and two aliquots from each extraction were taken for measurement. Thus, six color intensity (absorbance) measurements were made for each reference and standard sample. The three extractions were designated Series A, B, and C. The average of six absorbance measurements for each reference sample was used to plot the three calibration curves in Figure 2. The variation in calibration curves with aggregate type indicates that reference samples, prepared from the same materials as the unknown samples, are necessary for any Plastiment A determination. Calibration curves similar to those shown in Figure 2, fitted to the data points by the method of least squares, were used to obtain the data in Table 1. This gives the average retarder content for two aliquots in each series and compares the average of all three series with the known retarder content. The maximum deviation from the known value for any series is generally equal to or less than 0.4 oz per sack of cement. Two slag aggregate samples exceeded this deviation. The average of three determinations shows considerably less than 0.4 oz per sack of cement deviation from the known value in most cases.

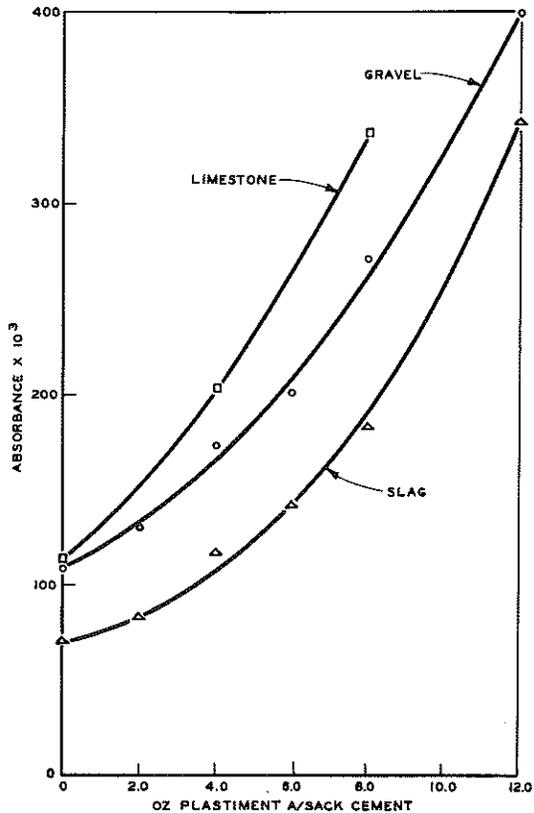


Figure 2. Typical calibration curves for the three aggregate types.

The effect of curing was investigated by crushing and grinding a portion of the samples just after initial set, while the remainder of the sample was given a normal seven-day cure. The gravel aggregate samples showed somewhat higher results after curing, but the limestone and slag aggregate samples were somewhat lower. The pre- and post-curing results are not sufficiently different to be a problem. The reasons for this difference were

TABLE 1
SUMMARY OF ANALYTICAL RESULTS

Sample*	Averages, oz/sack				Known Value, oz/sack	Maximum Deviation From Known Value, oz/sack	Deviation of Three Series Avg. From Known Value, oz/sack
	Series A	Series B	Series C	Series A, B, & C			
Gd	6.7	7.4	7.1	7.1	7.0	0.4	0.1
Gl	4.8	5.3	4.9	5.0	5.0	0.3	0.0
Gn	2.8	2.7	2.7	2.7	3.0	0.3	0.3
Gd _c	6.8	6.9	7.4	7.0	7.0	0.4	0.0
Gl _c	5.1	5.1	4.6	4.9	5.0	0.4	0.1
Gn _c	3.3	3.4	3.4	3.4	3.0	0.4	0.4
Sd	7.6	7.4	7.0	7.3	7.0	0.6	0.3
Sl	5.2	4.8	4.7	4.9	5.0	0.3	0.1
Sn	2.6	3.0	2.6	2.7	3.0	0.4	0.3
Sd _c	6.8	6.6	6.9	6.8	7.0	0.4	0.2
Sl _c	4.6	5.0	4.6	4.7	5.0	0.4	0.3
Sn _c	2.2	2.4	2.3	2.3	3.0	0.8	0.7
Ll	5.4	5.3	5.0	5.2	5.0	0.4	0.2
Ll _c	5.2	5.3	4.6	5.0	5.0	0.4	0.0

*Samples "G" prepared with gravel aggregate, "S" with slag aggregate, and "L" with limestone aggregate.

d, l, n are uncured standard mixes at initial set, containing known amounts of Plastiment A. d_c, l_c, and n_c are the same as d, l, n except that they were moist cured for seven days.

not investigated, but it was expected that the curing process might tie up the retarder and make it less extractable. Further aging of the ground concrete samples up to one year had no effect on the analytical results.

Summary

A workable, reliable colorimetric method for determining Plastiment A in hardened concrete has been developed which generally yields an absolute accuracy of ± 0.4 oz per sack of cement. This is quite acceptable considering that the procedure is complex and that all the variables in preparing, grinding, and sampling the reference and standard samples are included. A variation of ± 0.4 oz of Plastiment A per sack of cement from design dosage would have negligible effect. The minimum dosage recommended by the producer is 2 oz per sack of cement. Published information (1) indicates that the use of such water-reducing retarders results in rapid strength gain after initial set retardation, yielding concrete of higher quality than would be obtained using the same materials without retarder.

Determination of the Plastiment A content of hardened concrete would detect both overdosage and omission of this retarder. Overdosage causes prolonged retardation of set, while omission of some or all of the specified amount of retarder would cause unexpected early setting of the concrete during finishing. This analytical method, as developed, is not directly applicable to other retarders. It is quite likely that other retarders could be determined by the same general approach, but using different reagents and choosing the proper region of the visible-ultraviolet spectrum.

Recommendations

Since other retarders are finding increasing use on Michigan projects, they should be identified as to chemical type and their absorption spectra and possible analytical methods placed on file.

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Note

The opinions, findings, and conclusions expressed in this publication are those of the authors and not necessarily those of the Bureau of Public Roads.

APPENDIX A

Characteristics of Commercial Type 1A Cements in This Study

TABLE 1
CHEMICAL COMPOSITION OF
TWO COMMERCIAL TYPE 1A CEMENTS

Fraction Determined	Percent by Weight	
	Dundee	Huron
SiO ₂	22.1	21.0
Al ₂ O ₃	4.9	5.9
Fe ₂ O ₃	2.3	2.8
CaO	63.7	64.4
MgO	2.6	2.1
SO ₃	2.2	2.3
Loss on ignition	1.6	1.3
Na ₂ O	0.35	0.15
K ₂ O	0.77	0.92
Insoluble residue	0.08	0.14
<u>Calculated Compounds</u>		
C ₃ S (3CaO · SiO ₂)	48.9	52.4
C ₂ S (2CaO · SiO ₂)	26.5	20.7
C ₃ A (3CaO · Al ₂ O ₃)	9.2	10.8
C ₄ AF (4CaO · Al ₂ O ₃ · Fe ₂ O ₃)	7.0	8.5

TABLE 2
PHYSICAL PROPERTIES OF
TWO COMMERCIAL TYPE 1A CEMENTS

Property	Dundee	Huron
Autoclave expansion, percent	+0.06	+0.07
Specific Surface, sq cm per g	3198	3751

TABLE 3
TIME-OF-SET TESTS OF LABORATORY MORTAR MIXES*

Plastiment A Content, oz per sack of cement	Initial Set, hr to 500-psi needle pressure	Final Set, hr to 4000-psi needle pressure
<u>Dundee, Type 1A Cement</u>		
0	6	7
3	8	17
6	30	44
6 (Duplicate test)	33	47
12	65 (approx.)	123 (approx.)
<u>Huron, Type 1A Cement</u>		
3	7	13
6	10	21

*Data obtained using Proctor Needle Method (ASTM Designation C 403).

APPENDIX B
Experimental Procedure for Determination of
Plastiment A Retarder in Hardened Concrete

Details of Analytical Method

Crush a sufficient quantity of concrete (at least 10 lb) to assure a truly representative sample to about 1/4-in. pieces, split out a 1000-g sample, and grind it to pass a 140-mesh sieve. Take care not to lose the fine fractions during crushing and grinding. Dry the powder for 1 hr at 105 C and mix it thoroughly to assure uniform samples.

Weigh out 15 g of sample in a 250-ml beaker and add 20 ml of water, with stirring. Heat the resulting slurry on a steam bath for 15 min, stirring at 5-min intervals. Filter the sample slurry through fluted paper into a 100-ml beaker. When the residue retained in the filter paper has drained, wash once with 10 ml of water at 75 C. Allow 15 min for the washings to drain.

Evaporate the filtrate to dryness on a steam bath. Pour 10 ml of absolute ethanol on the dried residue and heat on a steam bath for 15 min, stirring at 5-min intervals. Decant the alcohol and repeat the process with 5 ml of alcohol, heated for 5 min. Discard the alcohol wash and evaporate the remaining alcohol from the insoluble residue.

Pipet 3 ml of concentrated sulfuric acid into the beaker. All sulfuric acid used in this procedure must be fresh and uncontaminated. Roll the beaker to contact and dissolve all the residue. Allow to stand 15 min, transfer to a test tube, and stopper the tube. Allow to stand for an additional 2 hr before proceeding.

Pipet a 1-ml aliquot of the sample solution into a test tube containing 3 ml of reagent,* stopper, and mix well. Heat this solution in boiling water for 1 hr. Remove the test tube from boiling water and cool to ambient temperature. Transfer the solution to suitable cells and measure the absorbance of the green color at 595 millimicrons with a spectrophotometer such as the Beckman Model DU, using reagent as a blank.

Calibration curves must be established by analyzing concrete prepared in the laboratory with known amounts of Plastiment A and the same materials used in the concrete in question.

Modifications for Slag Aggregate Concrete

Weigh out a 25-g sample of concrete powder. Extract with 30 ml of water and wash with 15 ml of water. After evaporating the extract to dryness and extracting the residue with alcohol, dissolve the alcohol-insoluble material in 5 ml of concentrated sulfuric acid. This solution is turbid and must be filtered to improve results. Allow the solution to stand up to 48 hr improves efficiency of filtration. Filter through a Gooch crucible fitted with a mat of sulfuric acid-washed asbestos. Transfer the filtrate to a test tube, stopper, and proceed as previously described.

* Reagent is 0.005 g of β -naphthol in 100 ml H_2SO_4 made up fresh every week.