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DETECTION OF LIGNOSULFONATE RETARDER IN
CEMENT SUSPENSIONS AND PASTES

BY

E. G. SWENSON AND T. THORVALDSON

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DETECTION OF LIGNOSULFONATE RETARDER IN CEMENT SUSPENSIONS AND PASTES*

BY E. G. SWENSON¹ AND T. THORVALDSON²

SYNOPSIS

The problem of detecting the presence of the lignosulfonate type of retarder or plasticizer in hardened cement paste is investigated by a spectrophotometric method based on ultraviolet absorbance measurements of aqueous extracts. The interaction of hydrating portland cement and lignosulfonate salt, whether in water suspension or in hardened paste, results in the disappearance of the characteristic 280 m μ maximum of the original lignosulfonate and the appearance of two new maxima at wavelengths of 245 and 350 m μ . This change is attributed to alkaline hydrolysis, with the formation of vanillin. The experimental results are discussed in relation to the qualitative and quantitative aspects of the method in detecting lignosulfonates in portland-cement products.

A lignosulfonate salt is the basic ingredient in certain commercial admixtures for concrete which are used primarily as plasticizers and retarders (1,2,3).^{3, 4} Despite their extensive use for many years, little or no published information is available on the nature of the interaction between lignosulfonate and cement, on the response of different cements, particularly to overdosage, or on methods of determining the presence or absence of such admixtures in concrete.

* This paper is a contribution from the Division of Building Research of the National Research Council of Canada and is published with the approval of the Director of the Division.

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³ The boldface numbers in parentheses refer to the list of references appended to this paper.

⁴ E. W. Scripture, U. S. Patents Nos. 2,081,642 (1937); 2,127,451 (1938); 2,169,980 (1939); and 2,229,311 (1941).

Field problems frequently require analysis of concrete to determine the nature or quantities of original ingredients. At best, such analyses are approximate, owing to the nature of cement and aggregate, but they are nonetheless of practical importance. Detection of the presence of certain admixtures may also present difficulties.

In an investigation of a field problem carried out by the authors, it became necessary to determine the presence or absence of a lignosulfonate retarder in a faulty concrete, and this led to the experimental work described in this paper. Following preliminary studies which indicated that direct tests for lignosulfonate were apparently doomed to failure, a possible method was explored which is based on spectrophotometric determination of absorbance curves in the ultraviolet for water-soluble products of interaction between lignosulfonate and hydrating cement.

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PRELIMINARY OBSERVATIONS

Lignosulfonate salts are lignin derivatives from waste sulfite liquors of the wood pulp industry. They are normally obtained by neutralization of the lignosulfonic acids, are variable in composition, and contain impurities. The lignosulfonate salt is considered to be a colloidal electrolyte which ionizes in solution to give metallic cations (usually calcium or magnesium) and lignosulfonate anions, the latter being positively absorbed by the cement particles in aqueous medium. It has been postulated that this phenomenon accounts for the dispersing effect which such substances apparently have on cement particle (3).

The detection and quantitative determination of a lignosulfonate salt in set cement paste and concrete presents difficulties. Although it was found by the authors that the usual qualitative test for lignin (chlorination with subsequent addition of sodium sulfite (4)) gave a distinctly positive result when 0.1 mg of a commercial lignosulfonate product was present, negative results were obtained with aqueous extracts of set cement pastes to which a larger quantity of the soluble lignin salt had been added. This suggested that the radical of the lignosulfonate molecule or ion responsible for the production of the color in this test was modified or destroyed in portland cement - water systems.

It was also found that mixtures of portland cement and the same lignosulfonate salt, when shaken with water, developed alkalinity much more slowly than similarly treated mixtures of cement and water. This may be due to adsorption of the lignosulfonate anion or molecule on the surface of the cement particle. Attempts to recover the lignosulfonate salt from hardened cement pastes by extraction with various solvents were not successful.

Zeisler's method for methoxyl deter-

mination (5) presented difficulties when applied to cement pastes containing a small amount of lignosulfonate. Authoritative advice indicated that modification of the conventional procedure which would be required to test such combinations was likely to produce questionable results. It is possible, however, that this method may be adapted to such determinations.

Ultraviolet spectroscopy has been used for some time in studies on the structure of lignin and its derivatives (6,7) but no published results appear to be available on the use of this method for detecting lignosulfonates in portland-cement products. For dilute aqueous solutions of two lignosulfonates used commercially as plasticizers and retarders for concrete, two maxima are found in the absorbance curve, one at a wavelength of about 205 $m\mu$, the other at about 280 $m\mu$ (absorbance is the negative logarithm of p/P_o , the ratio of the radiant energy of the transmitted light to that of the incident light). For detection of "lignin substances" this method appears to be extremely sensitive (8).

The sample of commercial calcium lignosulfonate retarder used in most of the spectrophotometric tests was subjected to paste and mortar tests to ensure that its influence on setting and hardening accorded with claims made for such admixtures. Dosages varying from $\frac{1}{20}$ to 10 times the prescribed or normal dosage were used. Results showed that this lignosulfonate product was typical of this class of dispersing and retarding agent.

MATERIALS AND METHODS

The main test sample of lignosulfonate was a commercial preparation derived from sulfite liquor and used very considerably as a plasticizer and retarder in concrete. A second commercial admixture containing lignosulfonate as a basic ingredient, and used very widely in prac-

tice, was found to give essentially similar absorbance curves in the ultraviolet region covered in the following experiments. Several samples of type I cement from five different plants were used.

The lignosulfonate salt dissolved or became colloiddally suspended in water with no residue left. The cement pastes were made as thin "pats" on Lucite or bakelite plates. After curing for 1 day they were partly broken and stored in beakers in a desiccator over water. They were ground to powder just prior to aqueous extraction for analysis.

The reaction vessels, used for shaking the cement with the lignosulfate solution, and the extraction vessels, in which the powdered pastes were shaken with water, were made of different materials in order to eliminate any possible influence of the container on absorbance values. Some were steel, lined with pure silver or gold foil and sealed with a suitable cap and clamp; others were polyethylene bottles with caps of the same material. Results of many experiments showed that no significant difference in absorbance values could be detected when using any of these materials. Mechanical shaking was used to keep the cement particles dispersed.

The aqueous extracts were clarified by high-speed centrifuging before absorbance measurements were made. This method gave more consistent results than filtering. When extracts were "cloudy" they were centrifuged again, but standing for 1 day permitted settlement of such suspensions.

The dosage of lignosulfonate used in most of the experiments was approximately that recommended for this material, 0.125 per cent of the weight of the cement. This is designated as a "normal" dose, N , and higher doses are designated as multiples of N .

Two Beckmann spectrophotometers were used, with hydrogen lamps and paired silica glass cells. The DU instru-

ment was hand-operated; the DK1 was an automatic recording instrument. With the first unit the absorbance of the test solution was measured against redistilled water, and the blank for the particular cement used was determined separately. With the automatic unit, the measurements were made directly against a blank which consisted of a similarly treated sample of cement, the absorbance of the blank being automatically deducted from the absorbance of the test sample.

The absorbance of the blank cement-water suspension and of the extract from the blank cement-water pastes was very low in the region of 240 to 400 $m\mu$ and gave a smooth curve over this range (bottom curve of Fig. 2). Since the results obtained in these studies on cement-water-lignosulfonate systems had a high dependence on time of contact, the blank values were not always deducted from the test values.

Absorbance curves for saturated solutions of lime, gypsum, and mixtures of both were very similar to those for cement blanks, being of about the same order.

ULTRAVIOLET ABSORBANCE STUDIES

Dilute Solutions of Lignosulfonate:

Figure 1 gives typical absorbance curves for two very dilute aqueous solutions of the lignosulfonate retarder (0.002 and 0.004 per cent). They show a very steeply sloping shoulder in the 220 to 240 $m\mu$ region, a minimum at 260 $m\mu$, and a characteristic maximum at 280 $m\mu$. Beer's law is applicable both on the basis of relative total absorbance and on the basis of the relative difference (280 maximum minus 260 minimum). While there was a definite maximum in absorbance at about 205 $m\mu$, readings at wavelengths below 215 $m\mu$ were not consistent and were considered unreliable since the ce-

FIG. 1.—Ultraviolet Absorbance of Dilute Aqueous Solutions of a Commercial Lignosulfonate Product.

ment blank also showed high absorbance in this region.

The absorbance curves of dilute solutions of the lignosulfonate remained es-

entially unchanged on standing at 23 C for up to 3½ months in glass bottles. For example, the absorbance values of the 260 mμ minimum and 280 mμ maximum

FIG. 2.—Change in Absorbance of Lignosulfonate Solution with Increasing Time of Contact with Portland Cement.

for a 0.005 per cent solution were, respectively, 0.33 and 0.41 after 2 days' standing, and 0.32 and 0.39 after 3 months' standing. For a 0.018 per cent solution, the corresponding values were 0.91 and 1.26 at 1 day's standing and 0.97 and 1.27 at $3\frac{1}{2}$ months' standing. The same was true for solutions stored in polyethylene bottles.

No significant changes occurred in the absorbance curves when the solutions were shaken in glass, polyethylene, or metal tubes for long periods of time. Partial neutralization of a dilute solution with HCl, boiling, or a combination of the two, did not alter significantly the absorbance values at the 260 $m\mu$ minimum or the 280 $m\mu$ maximum. Aeration of the solution appeared to lower the absorbance values slightly, especially at the shorter wavelengths. This may have been due to the difficulty of equalizing the pressure of water vapor in the air stream and the vapor pressure of the solution. The readings at 0 C were slightly lower than those at 25 C (order of 0.01 for wavelengths between 230 and 290 $m\mu$ and of 0.005 for longer wavelengths). None of these altered the position of the minimum at about 260 $m\mu$ or the maximum at about 280 $m\mu$.

Suspensions of Cement in Lignosulfonate Solutions:

Figure 2 gives absorbance curves for suspensions of 10 of type I cement in 50 ml of 0.025 per cent lignosulfonate solution. This represents a "normal" dosage of retarder (0.125 per cent of the cement by weight), but also represents an extreme condition where a large excess of the liquid phase is present. The time of shaking was varied from 5 min to 6 days, and measurements of absorbance were made immediately after centrifuging. The curve for a pure lignosulfonate solution of 0.025 per cent concentration (not

shown) is in accord with Beer's law when compared with the curves in Fig. 1.

It is observed that the 5-min contact between the lignosulfonate solution and the cement has materially changed the character of the absorbance curve from that of the pure lignosulfonate solutions (compare with Fig. 1). Calculation by Beer's law indicates that over 90 per cent of the radical or group responsible for the increase in absorbance at the maximum of 280 $m\mu$ has disappeared from the liquid phase. Such a rapid change would explain the failure of the sodium sulfite color test referred to earlier.

It is also observed that, with increasing time of contact between the cement and the lignosulfonate, the characteristic maximum of the latter at 280 $m\mu$ has shifted slightly to a higher wavelength of about 290 $m\mu$ and is finally replaced by a minimum, or "trough," at this point. The shift of the 280 $m\mu$ maximum to about 290 $m\mu$ has been observed for lignin products when strong alkali is present (7). At the same time the "shoulder," which began to develop at 230 to 245 $m\mu$ on 5-min contact has further developed into a new minimum at about 230 $m\mu$ and a new maximum at about 245 $m\mu$. In this region, however, the over-all absorbance shows a rapid decrease with time of contact. Concurrent with these changes was the development of a new maximum, at about 350 $m\mu$, which increased with time of contact up to 6 days.

Not shown in Fig. 2 are corresponding curves for 24 hr and 12 days of shaking. The 24-hr curve fits in with the other curves, as expected, but the 12-day curve (the lower dotted curve in Fig. 3) shows an over-all absorbance slightly lower than the 6-day curve, even at the new 245 and 350 $m\mu$ maxima. This "recession" in the absorbance curves for cement-lignosulfonate-water systems, after long contact with excess liquid phase,

was also found for paste extracts (see next section).

Similar experiments were carried out using four times the "normal" dose of lignosulfonate, that is, 10 g of type I cement shaken with 50 ml of 0.100 per cent lignosulfonate solution. The absorbance curves were similar to those obtained with the normal dose samples, but the time for the reaction to run to completion was longer. At 9 days' shak-

characteristic maximum at $280\text{ m}\mu$ is modified by the presence of the hydrating cement so as to destroy its absorption of light of that wavelength. Concurrently, two new maxima of light absorption gradually appear, one at about $245\text{ m}\mu$, the other at about $350\text{ m}\mu$. It is possible that the maximum of absorption for lignosulfonate observed at about 205 to $210\text{ m}\mu$ also undergoes change, but the only experimental evi-

FIG. 3.—Absorbance Curves for Aqueous Extracts from Aged Cement Pastes Containing Lignosulfonate Retarder.

NOTE.—4 month old pastes; 12.5-g powdered samples; extraction with 47.5 ml water; N, normal dose (0.125 per cent) lignosulfonate; dotted curve, 12-day old suspension.

ing, the $260\text{ m}\mu$ minimum and the $280\text{ m}\mu$ maximum had completely disappeared, with a new minimum absorbance of 0.15 at about $300\text{ m}\mu$. The maxima at $245\text{ m}\mu$ and $350\text{ m}\mu$ gave absorbance values of 0.40 and 0.44 respectively, as compared with 0.10 and 0.13 for the 6-day run of the normal dose sample (Fig. 2). At longer shaking times with the $4N$ samples, these maxima increased and then subsided as for the N samples.

It would appear from these and other experiments that the radical of the lignosulfonate that is responsible for the

dence available indicates increased absorbance in this region during the growth of the maxima at 245 and $350\text{ m}\mu$. The addition of solid CaO to a dilute solution of calcium lignosulfonate produced short-term changes in the absorbance curve similar to those produced by the addition of cement.

Water Extracts from Hardened Cement Pastes:

In the experiments discussed in the preceding section, an excess of the aqueous phase was always present during the interaction of cement and lignosulfo-

nate. This would represent one extreme or limiting condition not normally present in concrete except in the first hour or two in the plastic state. A large number of experiments were carried out on aqueous extracts of hardened cement pastes which would represent the other limiting condition where the liquid phase would be limited mainly to adsorbed films on solid surfaces during most of the period of "interaction."

Figure 3 shows typical absorbance curves for aqueous extracts from 4-month-old cement pastes with "normal," N , and twice normal, $2N$, doses of lignosulfonate retarder. The amount of extracting liquid used was such that concentrations of dissolved materials would be comparable with the solutions used in the preceding section. These results were obtained on the DU hand-operated instrument, with distilled water as a blank.

These curves are strikingly similar to the 12-day dotted curve for the cement-lignosulfonate-water suspension in Fig. 3 and to the curves in Fig. 2. The maxima at 245 and 350 $m\mu$ are increased with longer shaking times up to about 11 or 12 days but tend to recede slightly for longer shaking times (as with the suspensions). The $2N$ curve has a higher maximum than the N curves, but the differences are not proportional to original concentrations of the lignosulfonate. From these and other experiments, it appears to be quite definite that there is a considerably greater build-up of the molecules or radicals responsible for the maxima at 245 and 350 $m\mu$ in the paste than in the cement-solution suspension. It is conceivable that normal curing of paste made with a limited amount of mixing water (as for normal consistency requirements) provides a condition more conducive to degradation of the original lignosulfonate and to the stability of the new product or products.

At younger ages of paste, results were obtained similar to those for the cement-lignosulfonate solution suspensions, but again with a greater build-up of the new maxima at 245 and 350 $m\mu$. Table I gives absorbance values from cement-lignosulfonate pastes after curing periods varying from 6 to 67 days. These were obtained with the KG-1 automatic instrument and with the blank deducted. Original samples were made up separately. The maxima show a general tendency to increase with time of curing up to 67 days. Comparison with Fig. 3 (with

TABLE I.—ABSORBANCE OF AQUEOUS EXTRACTS FROM PASTES CONTAINING LIGNOSULFONATE, AFTER VARYING INTERACTION PERIODS.

M cement; "Normal" dosage of lignosulfonate

Interaction Conditions		Absorbance, p/P_o , at maxima and minima			
Paste Curing, days	Shaking Time, days	Minimum 225 to 230 $m\mu$	Maximum 245 $m\mu$	Minimum 270 to 300 $m\mu$	Maximum 350 $m\mu$
6	2	0.13	0.15	0.05	0.22
9	11	0.18	0.21	0.07	0.33
22	11	0.12	0.20	0.06	0.35
67	11	0.20	0.28	0.10	0.48

a different cement) would indicate, however, that no appreciable additional build-up of the peaks can be expected. The minimum or "trough" at about 290 $m\mu$ shows only a slight increase in absorbance with increasing curing time. The minimum at 225 to 230 $m\mu$ shows a fluctuation which is not unexpected in view of its nearness to the high absorbance range for the blank.

At still younger ages of paste, with only 1 or 2 days' shaking time, absorbance curves were obtained on the extracts which resembled closely that shown for the 6-hr suspension in Fig. 2. The characteristic 260 $m\mu$ minimum and the 280 $m\mu$ maximum for the original lignosulfonate were still prominent; the

245 $m\mu$ maximum had only begun to develop at a relatively high absorbance in the short wavelength region, and the 350 $m\mu$ maximum had developed only to a small extent.

Further experiments with varying curing periods, in the order of 2 days, and with varying shaking periods, for 1 to 6 days, produced absorbance curves show-

TABLE II.—ABSORBANCE OF AQUEOUS EXTRACTS FROM PASTES INVOLVING 3 CEMENTS, 2 LIGNOSULFONATE CONCENTRATIONS, AND 2 AGES OF PASTE.

Period of extraction by shaking with water, 10 to 11 days

Cement Type I	Ligno-sulfonate Dosage	Age of Paste, days	Absorbance, p/P_0 , at maxima and minima			
			Minimum 225 to 230 $m\mu$	Maximum 245 $m\mu$	Minimum 270 to 300 $m\mu$	Maximum 350 $m\mu$
B.	N	22	0.07	0.18	0.05	0.39
		67	0.21	0.31	0.09	0.56
	3N	22	0.46	0.65	0.23	1.06
		67	0.54	0.73	0.25	1.16
M.	N	22	0.12	0.20	0.06	0.35
		67	0.20	0.28	0.10	0.48
	3N	22	0.39	0.55	0.18	0.88
		67	0.48	0.66	0.21	1.16
P.	N	22	0.16	0.21	0.06	0.29
		67	0.17	0.23	0.06	0.37
	3N	22		0.57	0.18	0.86
		67	0.46	0.63	0.19	1.10

ing the gradual disappearance of the original lignosulfonate and the gradual build-up of the new product of interaction. These also showed that the build-up of the new product was favored by the paste condition as compared with the shaking of anhydrous cement with excess water. The rate of disappearance of the original sulfonate appeared, however, to be slower for the pastes than for the suspensions at very short periods of contact.

In Table II, absorbance maxima and

minima are recorded for extracts from normal, *N*, and thrice-normal, *3N*, dose cement pastes made with three different type I cements and taken at two paste ages, 22 days and 67 days. The cements are from three different plants, and the only significant difference in composition is the low alkali content of the *P* cement as compared with the high alkali contents of cements *M* and *B*. All shaking times were 11 days, and all readings were made in the KG-1 automatic unit with the blanks deducted. All samples are separate preparations.

It may be seen that over-all absorbance has increased with the longer curing period, with higher maxima at 245 and 350 $m\mu$. The increase in these peaks going from *N* to *3N* dosages is not uniform for the three cements and is not proportional to the original lignosulfonate concentrations. The "trough" at about 270 to 300 $m\mu$, which was quite flat for the *N* samples, showed with the larger dosage a definite rise at about 290 $m\mu$ to the higher wavelengths, suggesting residual amounts of unaltered lignosulfonate in the extract. For *9N* samples (not recorded), inconsistencies were even greater and unchanged lignosulfonate higher, with a definite hump at 280 $m\mu$. It appears that only a limited amount of lignosulfonate will react with a given amount of cement under these conditions of test. It might be added that microscopic evidence for unaltered lignosulfonate was found in aged pastes originally of high lignosulfonate content.

The stability of these products in solution after extraction appears to be high. In Table III are given the values for minima and maxima in the absorbance curves for an *N*-dose paste for progressively longer periods of standing of the extract (up to 13 days). No significant change occurred. The paste had been cured for 6 days at 100 per cent relative humidity, followed by 2 days of shaking.

Table IV shows that the speed and times of centrifuging within the ranges used had no appreciable effect on absorbance values.

Identity of the Reaction Product Giving Absorbance Maxima at Wavelengths 245 and 350 m μ :

J. M. Pepper, Professor of Organic Chemistry at the University of Saskatchewan, drew the attention of the authors to the similarity between the absorbance curves obtained above for the aqueous phase of cement-lignosulfonate-water systems and those for high pH aqueous solutions of vanillin. J. M. Pepper and his assistant, M. Siddiqueullah, then kindly made chromatographic analyses of three of our aqueous extracts which showed the very prominent typical absorbance maxima. One was produced by the interaction of lignosulfonate solution with type I cement (4*N*) for 6 months in a gold-lined steel tube; the second was an extract of a powdered cement-lignosulfonate paste (2*N*, cured over water for 6 months, then extracted for 6 months in a silver-lined tube); the third was obtained by shaking a type I cement from another plant with a lignosulfonate solution, *N*, for 24 hr in a Pyrex bottle and allowing the mixture to stand at 25 C for 2 months.

The liquids were acidified with HCl and extracted continuously for 24 hr with ether. The ether extracts were dried over anhydrous magnesium sulfate, then concentrated to small volume. All the extracts gave strongly positive tests for both the phenolic hydroxyl group and the carbonyl group.

The extracts were chromatographed on a Whatman No. 1 filter paper for 16 hr, using the developer petroleum ether: *n*-butyl ether: water (6:1:1, organic phase). Concurrently, authentic samples of vanillin and syringaldehyde were chromatographed. Only a trace of

syringaldehyde was present, but the position and density of the spots confirmed the presence of considerable amounts of vanillin in each sample of

TABLE III.—EFFECT OF TIME OF STANDING OF AQUEOUS CEMENT PASTE-LIGNOSULFONATE EXTRACTS ON ABSORBANCE VALUES.

Lignosulfonate dosage = *N* cement *M*
6 day moist-cured paste plus 2 days
aqueous extraction.

Age of Extract at Time of Measurement	Absorbance, p/P_0 , at maxima and minima			
	Minimum 225 to 230 m μ	Maximum 245 m μ	Minimum Approx- imately 290 m μ	Maximum 350 m μ
1 hr.....	0.13	0.15	0.05	0.22
2 days.....	0.14	0.16	0.05	0.22
8 days.....	0.13	0.15	0.06	0.23
13 days.....	0.14	0.16	0.05	0.23

TABLE IV.—INFLUENCE OF SPEED AND TIME OF CENTRIFUGING ON ABSORBANCE VALUES OF AN EXTRACT.

Cement *M* lignosulfonate dosage = *N*
9 days moist-cured paste plus 11 days
extraction time.

Speed of Centrifug- ing, rpm	Time of Centrifug- ing, min	Absorbance, p/P_0 , at maxima and minima			
		Minimum 225 to 230 m μ	Maximum 245 m μ	Minimum 270 to 300 m μ	Maximum 350 m μ
9450.....	20	0.16	0.21	0.07	0.33
14750.....	20	0.18	0.22	0.07	0.33
14750.....	40	0.17	0.21	0.07	0.33
15850.....	20	0.16	0.19	0.07	0.33

extract. Vanillin is an aromatic aldehyde of the formula

and is a degradation product of lignin.

It might be noted that a solution of pure vanillin at pH 10.75 has been found to be very stable at room temperature (9). The observation of a slight drop in

the absorbance of the two maxima, noted above for aged mixtures, was therefore probably due to reaction with other products in the mixture or to a decrease in the pH of the solutions.

The possibility that degradation products other than vanillin, such as aldehyde derivatives of lignin, might produce similar maxima at 245 and 350 $m\mu$ is not excluded (7).

SUMMARY AND CONCLUSIONS

Interaction between a calcium lignosulfonate salt and hydrating cement in an aqueous medium is very rapid, as shown by ultraviolet absorbance measurements in the range of 220 to 400 $m\mu$. This interaction is evidenced by the rapid disappearance of the characteristic 280 $m\mu$ maximum of the original lignosulfonate, followed by a new absorption system with maxima at about 245 and 350 $m\mu$. An alteration or degradation of the original lignosulfonate structure apparently occurs, the product of which possesses at least some degree of solubility in aqueous media of high pH (or containing calcium hydroxide).

The change in absorbance at these maxima with change in ratio of original lignosulfonate to cement do not show a direct proportionality, although the absorbance at the maxima is roughly proportioned at a given time to the original quantity of lignosulfonate. At greater ages there is some tendency to regression of the absorbance at the maxima.

Experimental evidence indicates a high stability of the product responsible for the absorbance maximum at 350 $m\mu$ and that its formation and stability are favored by a limited aqueous phase such as obtained in a hardened cement

paste under ideal curing conditions. This peak can therefore be used as a reliable indication of a lignosulfonate admixture in hardened portland-cement paste. The possibility that organic admixtures or adulterants might interfere with this determination was not investigated. The probability of any such material exhibiting a peak at this particular wavelength was considered very slight.

The two absorbance maxima which develop at wavelengths of about 245 and 350 $m\mu$ appear to be due to the alkaline form of vanillin resulting from alkaline hydrolysis of lignosulfonate.

Reproducibility of absorbance curves, under the conditions of test described, appears to be good. Absorbance values for the interaction product as well as for the original lignosulfonate were not affected significantly by certain deliberate variations in conditions of test.

In the present study, concentrations of lignosulfonate solutions and dosages in pastes covered only a range consistent with its use as an admixture in concrete. Experiments were also limited to a short wavelength range. It is possible that significant changes may occur at other wavelengths.

Despite these limitations and the possibilities of other methods, the experimental studies described provide a basis for a spectrophotometric method for determining qualitatively the presence of a lignosulfonate admixture in hardened portland-cement pastes. It is suggested that this method should prove equally effective for hardened mortars and concretes. Considerable further study would be required, however, to determine the influence of aggregate materials, organic adulterants, carbonation, and other factors.

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DISCUSSION

MR. W. G. HIME.¹—The authors are to be congratulated on their excellent work in the very difficult field of organic analysis. My comments are made in the hope that they will be helpful in future work designed to give detailed procedures for the determination of organic admixtures in concrete.

The authors' statement concerning the improbability of other organic admixtures or adulterants exhibiting a peak at the ultraviolet wavelength of vanillin may be misleading. According to Fig. 3, vanillin absorbs appreciably in the 240 to 260 $m\mu$ range and in the 335 to 365 $m\mu$ range. These ranges represent 25 per cent of the ultraviolet region.

Nearly all aromatic organic compounds and several aliphatic compounds possessing conjugated double bonds absorb in the ultraviolet region. In fact, most organic compounds, except for some of low molecular weight, absorb to some extent. It would not appear to be unlikely that many of these several thousand compounds, each absorbing over up to 25 per cent of the ultraviolet region, could interfere in the lignosulfonate (as its hydrolysis product, vanillin) determination.

It would appear that a quantitative determination must be preceded by a qualitative test. This may be by spectrophotometric means or perhaps as a colorimetric spot test. The authors describe a color test for lignin, but it is not applicable to the vanillin resulting from the alkaline hydrolysis of the lignin. A specific color test for vanillin would be of great value.

MR. E. G. SWENSON (*author's closure*).—Mr. Hime's comments on the paper are very useful, particularly in focussing attention on the limitations of analytical methods generally.

The limitations of the method described in the paper were early recognized by the authors. In suggesting the improbability that organic adulterants or admixtures would interfere with this method, the authors had in mind the improbability that the type of interfering substances mentioned by Mr. Hime would be found in mortars or concretes.

Analysts are well aware that even well-established methods will fail if certain interfering substances are present.

In the opinion of this author, the possibility of substances being present in mortar or concrete which would interfere with this method is very remote.

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