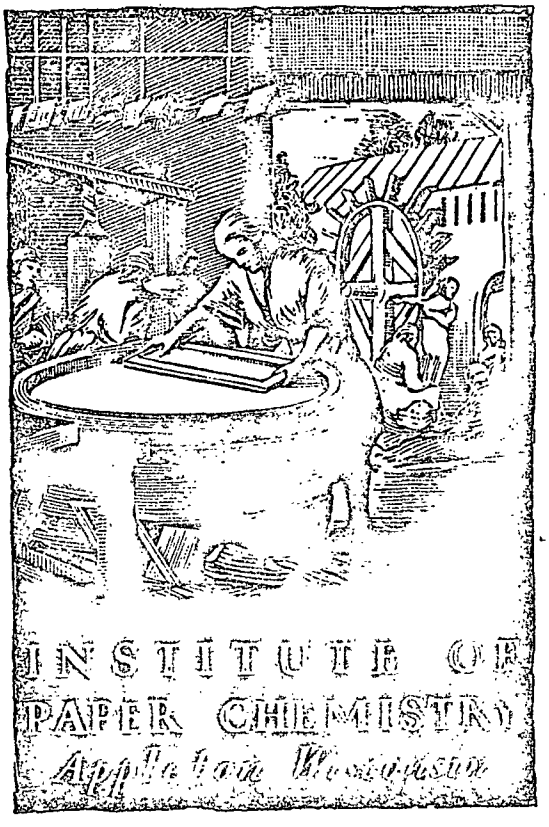

METHODS FOR THE DETECTION AND MEASUREMENT OF TOXIC COMPONENTS OF KRAFT PULP MILL WASTES

Project 1140

Progress Report Two
to
National Council for Stream Improvement

October 28, 1946

THE INSTITUTE OF PAPER CHEMISTRY
APPLETON, WISCONSIN

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SUMMARY

Methods for the detection and measurement of sulfides, mercaptans, resin acid soaps, and alkalinity are described. The methods are feasible, and do not require an unreasonable amount of time or equipment.

Data obtained in the application of the methods to sewer analyses of several kraft mills are presented.

Suggestions for the collection and correlation of data in a regular routine sewer analysis are made.

INTRODUCTION

The immediate effects of pulp and paper mill waste waters on a stream may be classified into two general categories--first those wastes which cause oxygen depletion in the stream and, second, those which behave as poisons to fish and other aquatic forms. Although ordinary kraft pulping wastes may contain moderate amounts of oxygen-depleting materials it is generally understood that their principle polluting effect is found in the toxic substances which are formed during the pulping process.

The toxic effect of kraft waste components on fish has been studied (1-5). Experiments made at The Institute of Paper Chemistry(6) have indicated that a considerable number of compounds toxic to fish may be found in these wastes. The studies were made on sewer contents of a mill pulping jack pine exclusively. The Institute's data are summarized in Table I.

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(1) Cole, Arch E., Sewage Works J. 7, No. 2: 280 (1935).
(2) Bergström, Hilding, Svensk Papperstidn. 42:223-228 (1939); C.A. 33:6591.
(3) Bergström, Hilding, and Vallin, Sten, Medd. Statens Undesöken-Försöksants Sötuattenfisket, Kgl. Lantsbruksstyrelson No. 13. 1937. C.A. 34: 2597: B.I.P.C. 10: 448.
(4) Ebeling, G., Vom Wasser 5: 192-200 (1931); C.A. 26: 2262.
(5) Hagman, Nils, Resin acids and fish mortality. Finnish Paper and Timber J. 18: 32-34, 36-38, 40-41 (1936).
(6) The Institute of Paper Chemistry, Project 970. Final Report, June 13, 1944.

TABLE I

A SUMMARY OF THE MINIMUM LETHAL CONCENTRATIONS OF TOXIC SUBSTANCES FOUND IN KRAFT PULP MILL WASTE LIQUORS(1)

Compound	Minimum Lethal Concentration, p.p.m.
Sodium hydroxide	100.0
Sodium sulfide	3.0*
Methyl mercaptan	0.5
Hydrogen sulfide	1.0
Sodium sulfhydrate	0.5
Crude sulfate soap	5.0
Fatty acids (sodium salt)(from sulfate soap)	5.0
Resin acids (sodium salt)(from sulfate soap)	1.0

* When this figure is expressed as sulfides ($S^{=}$), as in Tables VI and VII, it would be 1.2 p.p.m.

(1) Test fish used in these studies were local species of minnows.

These data indicate that, as far as fish are concerned, the most dangerous compounds are the sulfides, mercaptans, and the soaps or components thereof. Having established the minimum lethal concentrations of these substances to fish, it appeared desirable to design methods by which they could be detected and evaluated in the sewers. That is the purpose of the present investigation.

It is noted that technical personnel of the several Wisconsin kraft mills have in times past directed their attention to this problem and have accumulated a considerable number of data. These people have generously made these data available to the Institute, which, in addition, has enjoyed their close co-operation in the present investigation. Appreciation is expressed to Dr. M. L. Downs of the Thilmany Pulp & Paper Co., Mr. R. A. Nugent and Dr. T. A. Pascoe of the Nekoosa-Edwards Paper Company, Mr. Carl Moe of the Stevens Point Pulp & Paper Co.,

Mr. Gust Enderlein of Mosinee Paper Mills Company, and Mr. J. A. Extrom and Mr. Kermit Olson of the Tomahawk Kraft Paper Company.

METHODS AND PROCEDURE

DETERMINATION OF SULFIDES AND MERCAPTANS

An examination of the literature indicated that the most promising method for determining sulfides and mercaptans would be the use of a potentiometric argentimetric titration in highly alkaline solution such as that described by Tamele and co-workers(1), Lykken and Tuemmler(2), and more recently by Borlew and Pascoe(3). These investigators used higher concentrations than those involved in the present problem; however, in the opinion of Dr. T. A. Pascoe(4) this difference would not prevent successful application of the method.

It may be noted that sodium sulfide, sodium sulfhydrate, and hydrogen sulfide need not be determined individually, because the composition with respect to those constituents is determined completely by the pH value of the solution. At pH values in the neighborhood of 8.0 to 8.5, the chief component will be the sulfhydrate.

In order to test the applicability of the potentiometric method when dealing with low concentrations of sulfide and mercaptan, a number of titrations were carried out in which the concentrations

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(1) Tamele and co-workers, Ind. Eng. Chem., Anal. Ed. 8: 16(1936); 13: 619(1941).
(2) Lykken and Tuemmler, Ind. Eng. Chem., Anal. Ed. 14: 67(1942).
(3) Borlew and Pascoe, Paper Trade J. 122, No. 10: 31 (March 7, 1946).
(4) Personal communication.

of these constituents were in the range to be expected in mill effluents. As recommended by Borlew and Pascoe, the electrode system comprised a "Blue-point" high pH glass electrode and a silver-silver sulfide electrode.

The sulfide solutions were prepared by passing hydrogen sulfide into standard solutions of sodium hydroxide. The sulfide content was estimated by iodometric analysis. Aliquots of the strong solution thus prepared were diluted with boiled water just before use to minimize the oxidation which occurs in very dilute solutions of sulfides. Solutions of mercaptans were prepared by dilution of the pure materials with boiled water.

Table II shows the results of several potentiometric titrations when applied to low concentrations of sulfide and mercaptan, using a method which was essentially that developed by Borlew and Pascoe.

TABLE II

TITRATION OF SULFIDES AND MERCAPTANS BY THE POTENTIOMETRIC METHOD

Sulfide Added, p.p.m.	Found, p.p.m.	Error, %	Mercaptan Added, p.p.m.	Found, p.p.m.	Error, %
0.17	0.20	+18			
0.34	0.35	+ 3	3.3	3.0	-9
0.85	0.86	+ 1			
1.70	1.57	- 8	6.0	5.5	-8
2.40	1.90	-21			
3.0	2.40	-20			
4.0	3.5	-13	12.5	12.3	-2
4.8	4.3	-10			
15.0	14.1	- 6			

The positive errors for the sulfide at low concentrations are not in agreement with results previously reported. The errors may be

related to unsaturation of the solution with respect to silver sulfide and would be a relatively important factor only at low concentrations of sulfide. Otherwise, the values are similar to those reported by Kolthoff and Furman(1).

Despite the relatively large percentage error in certain of the titrations, it is believed that, in view of the very low concentrations, the method is entirely suitable for analysis of these constituents in mill effluents.

It was found that a purified sample of thidignin required no silver nitrate in the titration; hence, it may be concluded that thiolignins in sewer effluents will not cause error in the sulfide determination. Sodium thiosulfate is also without effect.

Colorimetric Methods For Sulfides

In the event that sulfides only are to be determined, there are available certain simple colorimetric procedures. These are useful also as a control check on the potentiometric method and as quick "spot" tests on effluents. A suitable method is a modification of the colorimetric sulfide test (Lauth's reaction) as outlined by Almy(2). The test can be carried out in a very few minutes and involves adding successively to 10 ml. of sample, 1 ml. of 1:1 sulfuric acid containing 7.5 g./liter p-aminodimethylaniline sulfate and two drops of 10% $FeCl_3$. The solution

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(1) Kolthoff and Furman, Potentiometric Titrations, 2nd ed., p. 170. John Wiley & Sons, Inc., New York, 1931.
(2) Almy, L. H., J. Am. Chem. Soc. 47: 1381(1925).

is mixed well and allowed to stand for two minutes. Then 10 ml. of NaH_2PO_4 (45 g./100 ml.) are added to decolorize the iron and the resulting color compared with standards.

It may be more convenient to use a La Motte sulfide test kit made up expressly for this purpose (supplied by LaMotte Chemical Products Company, Baltimore, Maryland).

When the colorimetric method is applied to a sample containing mercaptans alone, a permanent pink color is obtained, in contrast to the blue color obtained when sulfides are present. This pink color was first observed in analysis of mill effluents in which sulfides were absent. Further tests with pure mercaptan solutions showed that these were responsible for the color. It is possible that the test could be used for estimation of mercaptans in the absence of or after removal of sulfides, but this possibility was not investigated further. It is not believed that the color produced by mercaptans seriously interferes with the colorimetric sulfide test, because it is relatively much lower in tinctorial value.

Loss of Sulfides from Mill Effluents

In the course of preliminary tests, it was found that the apparent sulfide content of kraft mill effluents decreased rapidly when the sample was allowed to stand in the laboratory. To test this rate of loss, a sample from one mill was allowed to stand and frequent analyses were made. Results from these tests are shown in Table III.

TABLE III

RATE OF LOSS ON STANDING OF SULFIDES IN KRAFT MILL WASTES

Time	p.p.m.
1:33 P.M.	3.0
1:40 P.M.	2.0
1:50 P.M.	1.6
2:00 P.M.	1.0
2:05 P.M.	0.2
2:10 P.M.	0.0

In another case, a sample having a sulfide content of 75 p.p.m. at the time of collection was completely devoid of sulfides after 12 hours. In this case there were no intermediate analyses made and the time of complete loss may have been much shorter. The colorimetric test was found to be very suitable for following the decrease in sulfide content. The potentiometric method shows the same loss, as the two methods are in essential agreement.

The reason for this rapid loss of sulfides has not been established. However, it was observed that, after diminution of the sulfide content to zero, similar losses occurred after addition to the same effluent of a solution of sodium sulfide. Further, the same rapid loss occurred in completely filled bottles. This indicated that oxidation by air above the solution was not responsible, although the quantity of dissolved air may have been sufficient to account for the observed effects Also, it is not known whether the rapid loss of sulfides is characteristic of all kraft mill effluents.

The sulfides were found to decompose much more rapidly than the mercaptans. The latter are relatively stable upon storage.

Whatever may be the explanation of sulfide loss, it may be noted that a similar rapid loss after discharge of the effluent into natural waters would be of considerable significance in interpreting pollutional effect of the effluent.

The relatively rapid loss of sulfides means that the sulfide determination (by whatever method is used) must be made immediately after the sample is taken, if the true sulfide content in the sewer sample is desired. Large errors may occur if the sample is allowed to stand in the laboratory for even a short time before analysis, and on analysis of a composite representing several hours accumulation will be totally unreliable.

It was found that sulfide solutions are relatively stable in strongly alkaline solutions. If the solution is treated with enough strong sodium hydroxide solution to make it one normal in NaOH, the sulfide content remains unchanged for several hours as shown in Table IV. (This sample was a mill effluent.) This procedure is no disadvantage, since the potentiometric sulfide titration is performed in strongly alkaline solution, and is, therefore, to be recommended.

TABLE IV

STABILITY OF SULFIDE SOLUTIONS

Time, hrs.	Sulfide, p.p.m.	
	Stabilized in N NaOH	Untreated
0	1.8	1.6
0.75		1.2
3	1.8	0.3
5		0.0
6	1.7	
22	1.3	

Proposed Method for Sulfides and Mercaptans

In a 1200-ml. sample bottle are placed 200 ml. of a solution containing 48 grams of NaOH to stabilize the sulfides. The bottle is filled immediately after taking the sample from the sewer and is then set aside until after the titration for alkalinity.

The entire contents of the bottle are emptied into a 1500-ml. beaker, 4 ml. of concentrated NH_4OH are added, the "Blue-point" and $Ag\text{-}Ag_2S$ electrodes are immersed and the stirrer is started. The pH meter is turned on to "+MV" and, after the galvanometer needle has reached equilibrium, which may take as much as five minutes in the case of low sulfide content, the millivolt reading is recorded as "Initial EMF." The approximate total sulfide content can be estimated roughly from the value of the initial EMF. Reference may be made to Figure 1, which shows the relationship of initial EMF reading to total sulfide content as determined by titration. If the EMF value is below about 0.540 mv. and more than two minutes are required for the needle to come to equilibrium, it is advisable to titrate with 0.01 N $AgNO_3$. Above this value, 0.1 N $AgNO_3$ can be used. In the former case, 1 ml. increments are added and in the latter 0.2 to 0.5 ml. increments, at least until it is seen how rapidly the EMF changes. It is advisable to allow the galvonometer needle to come to equilibrium before subsequent additions of $AgNO_3$. In this work the standard used was: "until the drift is less than one division on the galvonometer scale in 10 seconds." As the end-point is approached, it is highly desirable to add small increments in order to determine more accurately the exact point of inflection. Tapping the electrodes after each addition is recommended.

Occasional wiping of the electrodes with cotton between titrations improves the sharpness of the end-point.

A plot of EMF vs. ml. $AgNO_3$ will usually give two inflections; the first represents sulfide and the second mercaptan (see Figure 2).

Sample calculation. The data given below are for a sample of effluent from one of the mills.

DETERMINATION OF SULFIDE AND MERCAPTAN

1000 ml. Sample 0.098 N $AgNO_3$, ml.	EMF, mv.
0.0	+0.585
0.5	0.585
2.0	0.583
5.0	0.575
6.0	0.565
7.0	0.557
8.0	0.545
9.0	+0.050
9.5	-0.020
10.0	-0.040
10.5	-0.180
11.0	-0.255
12.0	-0.280
13.0	-0.308

These data are plotted in Figure 2.

Examination indicates that the sulfide inflection occurs at approximately 8.6 ml. $2\ Ag^+ + S^= \longrightarrow Ag_2S$ (equivalent weight of $S^=$ = 16)

Hence, 8.6 x 0.098 x 16 = 13.5 p.p.m. sulfide

The mercaptan inflection occurs at 10.5 ml.

$Ag^+ + RSH \longrightarrow R^+ + AgSH$ (equivalent weight of CH_3SH = 48).

Hence (10.5 - 8.6) x 0.098 x 48 = 9 p.p.m. CH_3SH.

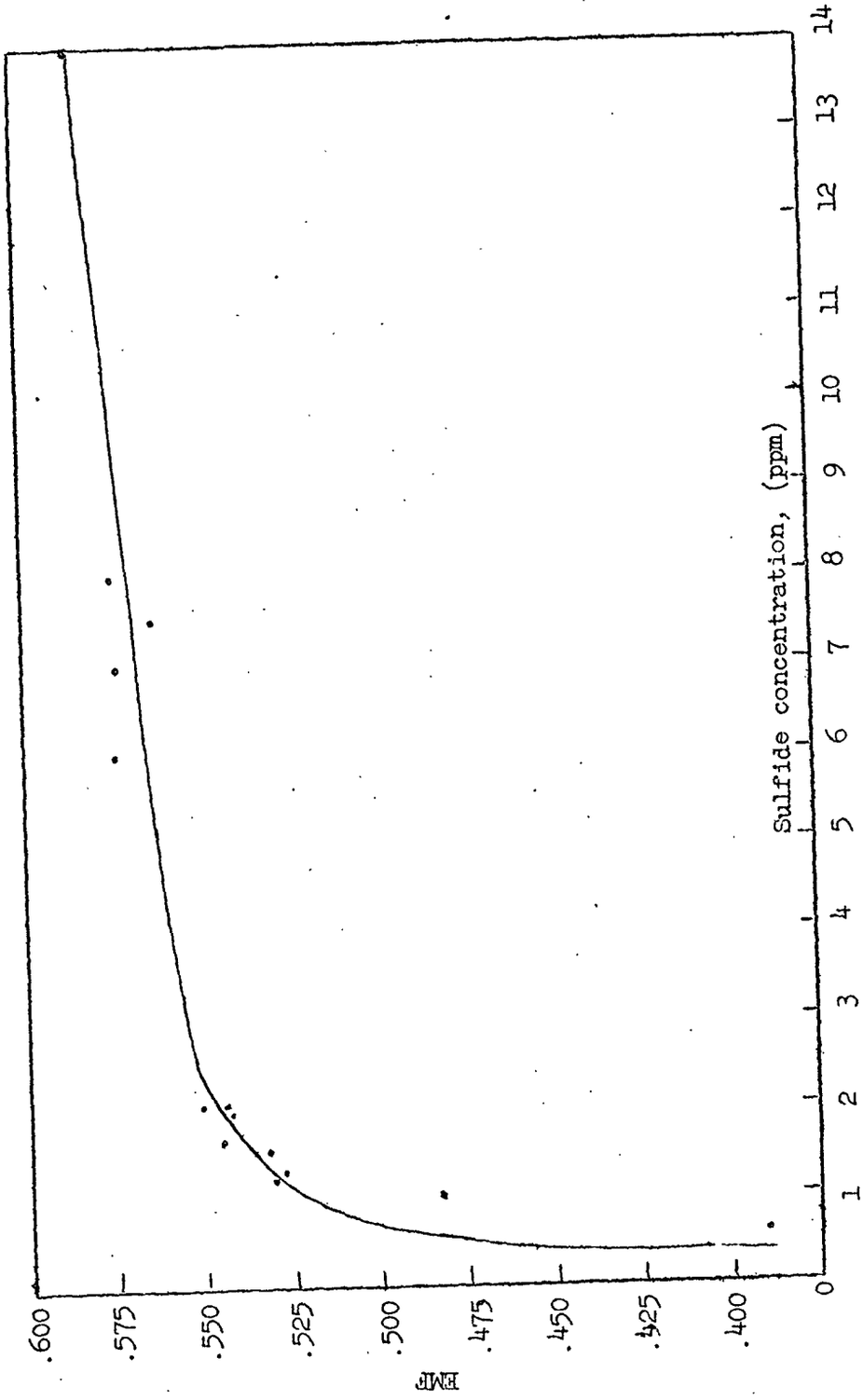

Figure 1

Relationship of Initial EMF Reading to Total Sulfide Content as Determined by Titration

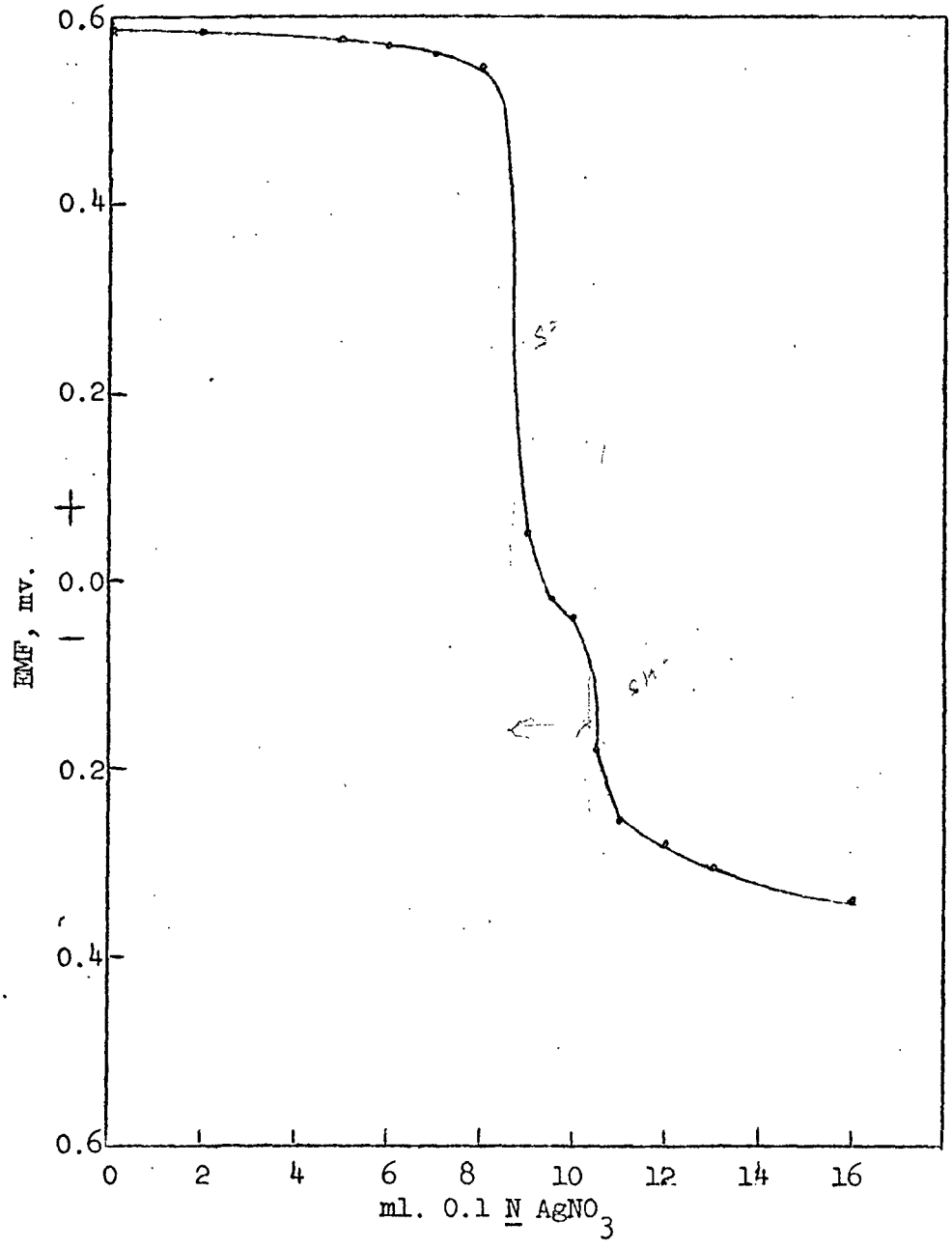

Figure 2

Typical Curve from Data for Sulfide Titration

RESIN AND FATTY ACID SOAPS

Conventional methods for analysis of soaps in materials of the type encountered in mill effluents would comprise acidification to convert the soaps to free acids and extraction of these acids by an organic solvent such as ether. Extractions of this nature are usually performed in a separatory funnel, although other procedures are available.

Subsequent estimation of the resin and fatty acids separately is quite feasible by well established methods involving selective esterification of the fatty acids, after which the fatty and resin acids can be separated in a fairly quantitative manner. Quantities of several grams are usually used in such procedures.

The time-consuming character of the conventional methods and the requirement of a considerable quantity of acids make them totally unsuitable for the present purpose, where the quantities are small and a relatively rapid test is desired. Therefore, a survey of other possible methods was undertaken. Unfortunately, there appears to be no alternative to extraction with an organic solvent.

Not many suggestions for simple and quick detection of fatty and resin acid soaps were found in the literature, but it was apparent that the detection and estimation of resin acid soaps is much more readily accomplished than are those for fatty acid soaps. The problem may perhaps be simplified on this basis, since the ratios of fatty and resin acids may be expected to vary within certain fairly well-defined limits. For example, in woods the ratios of the two acids will

probably not exceed the ratios of 1:3 to 3:1. In addition, available data on crude sulfate soap indicate that the ratio of fatty acid soaps to resin acid soaps is usually about 1:1, and certainly the amount of fatty acid soaps could not exceed five times the amount of resin acid soaps. From Table I, it will be found that the ratio of the toxicity limits for the two is 5:1. Thus it seems justifiable to use the rosin acid determination as the criterion for the amount of toxic material present. For example, if a mill effluent shows only 1 p.p.m. resin acid soap, then the fatty acid soap concentration could not exceed 5 p.p.m. and a nuisance condition would not exist, therefore, in the stream with respect to fatty acid.

The most promising method for the quick analysis of resin acids is that suggested in articles by Michel(1) and by Ebeling(2). It involves ether extraction of an acidified sample, evaporation to dryness, re-solution in chloroform, and treatment of the chloroform solution with strong sulfuric acid and acetic anhydride to give a pink or violet color, depending upon the resin acid concentration (the Liebermann resin reaction).

Of course it is possible to extract the effluent sample with ether, and to determine by evaporation and weighing the amount of ether-soluble material. This procedure would give a figure for the maximum possible content of resin and fatty acids. If the figure were sufficiently small, it might then be disregarded. The value would be too high,

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(1) Michel, Chem.-Ztg. 54: 182(1930).
(2) Ebeling, G., Wasser 5: 199(1931).

however, because the ether-soluble material would include nonacid material, as well as some water-soluble material (because the ether solution is saturated with water). An extraction of the residue thus obtained with dry ether, from which a purified fraction containing the fatty and resin acids would be obtained by evaporation, should yield a more reliable figure. Again, the acid content might be small enough to be disregarded.

The method given below represents an attempt to provide a quick field test for resin acids, which may serve as a means for obtaining an approximation of the resin acid content. It should be recognized that resin acids which do not give the test may be present (oxidized or polymerized acids). The possible toxic effect of altered acids has not been established, so that the relative validity of the total acid value, as compared with that giving the colorimetric test, cannot be stated at the present time.

Proposed Method of Analysis for Resin Acid Soaps-

The method involves the following steps:

1. Two hundred-fifty ml. of sample are acidified with 5 ml. of 1:1 sulfuric acid and extracted with one 60-ml. portion of ether and two 30-ml. portions of ether in a separatory funnel. The ether layer is allowed to separate for from 3 to 5 minutes before drawing off the water layer. In case emulsion difficulties are encountered, it is suggested that the clear water layer be drawn off after each extraction, and that the emulsified portions be separated from the clear ether layers. The combined emulsified portions can then be re-extracted with

two 25-ml. portions of ether. The combined ether extracts are evaporated almost to dryness on a steam bath (or asbestos-padded hot plate). Generally, there is a small amount of water dissolved in the ether and this remains. Attempts to evaporate it completely result in darkening of the resin acids, which should be avoided.

2. The evaporated residue is extracted with two 2-ml. portions of chloroform, which are then combined and placed in a 50-ml. separatory funnel. If the amount of water remaining after the evaporation is more than 0.2-0.3 ml., it should be separated from the chloroform layer in order not to dilute appreciably the 65% sulfuric acid.

3. Five ml. of 65% H_2SO_4 are added to the chloroform solution and the mixture is shaken vigorously. Then 1/3 ml. of acetic anhydride is added dropwise at the edge of the separatory funnel and just above the surface of the liquid. A pink or violet coloration at the interface is indicative of at least 2 p.p.m. resin soaps in the original sample.

If the color is strong, the entire procedure may be repeated, using a smaller sample--e.g., a 50-ml. portion of sewer sample. In this case, a color development shows at least 5 p.p.m. in the original sample. Table V shows the minimum original concentration of resin soap if a color develops when various amounts of sample are extracted. The table was established by applying the above method to a sample of tall oil, the resin acid content of which was known from a separate analysis.

TABLE V

Volume Extracted, ml.	Resin Acid, mg.	Minimum Concentration of Soap in Original Sample, p.p.m.
10	0.18	18
25	0.20	8
50	0.24	5
100	0.30	3
250	0.50	2
500	0.80	1.6

The data of Table V were obtained by determining the quantity of resin soap that had to be added to various volumes of water in order to develop a color after acidification, extraction with ether, evaporation, re-solution in chloroform, and addition of sulfuric acid and acetic anhydride. (In each case, the ether to water ratio was approximately 250 ml. to one liter for the first extraction, and 120 ml. per liter for the second and third extractions.) For example, it was found that, when 500 ml. of water were used, 0.80 mg. of resin soap had to be added before a color could be developed on the extract. On the other hand, with 10 ml. of water, only 0.18 mg. of resin soap had to be added. Inspection, then, shows that the original concentration for the large sample must have been: $\frac{1000}{500} \times 0.8 = 1.6$ p.p.m.;

for the small sample: $\frac{1000}{10} \times 0.18 = 18$ p.p.m., in order to obtain color development.

An alternative method involves the extraction of 5 to 10 liters of acidified effluent, evaporation of the combined extracts, extration of the dry residue with ether, filtration through a fine filter paper, and a second evaporation in a tared beaker. The total residue after

heating to constant weight on a steam bath is dissolved in ether to make either 100 or 250 ml. (in some cases where resin acid is higher, it may be necessary to make a still further dilution), depending upon whether the the residue is more or less than 0.500 gram. If the ether-soluble portion is less than 0.006 g./liter, it is not necessary to determine the resin.

The resin acid color estimation is made on a small (measured) portion of this ether solution in same manner previously described (evaporation and solution in chloroform, followed by addition of 65% sulfuric acid and acetic anhydride.)

In this case, however, the minimum detectable concentration is 0.16 mg. of resin acid. Just as it was necessary to add 0.18 mg. of resin soap when 10 ml. of water were extracted in order to obtain a color, it is necessary to use 0.16 mg. of rosin dissolved in chloroform or ether (without any extraction from water) in order to develop a color by the procedure already outlined. This figure is used to calculate the resin present in the original sample.

Sample calculation for resin acid soap. Ten liters of the sample were extracted with ether. Ether soluble = 0.524 gram = 52 p.p.m. The total residue was dissolved in ether and diluted to 250 ml. One ml. was evaporated and redissolved by extraction with two 2-ml. portions of chloroform; the color was quite strong; when 0.5 ml. was used, the color was persistent but faint.

Assuming this to be the limit, rosin acid soap = $\frac{250 \times 2 \times 0.16}{10}$ = 8 p.p.m. rosin acid soap.

ALKALINITY

Although the toxic effect of alkalinity is relatively less than that of sulfides, mercaptans, and soaps, the determination of alkalinity is so well recognized as a standard control procedure that its inclusion in this series of tests is suggested.

The minimum lethal concentration of sodium hydroxide has been established at 100 p.p.m. This concentration corresponds, in a solution of pure water at 25° C. and assuming unit activity of hydroxyl ions, to a pH of 11.4. It cannot reasonably be assumed that any pH values lower than this will not be inimical to fish life. Nevertheless, the measurement of pH can logically be included as a standard test in the examination of mill effluents.

Conventional methods of water analysis include "phenolphthalein" and "methyl orange" alkalinity, representing the titration to those respective end points. In the conventional analysis, the phenolphthalein titration represents the content of hydroxide and one half of the carbonate, and the additional titration to the methyl orange end point represents that required by bicarbonates. In the effluents at present under examination, there is the added consideration that approximately half the sulfide is neutralized at the phenolphthalein end point, whereas all of the hydrosulfide is neutralized at the methyl orange end point.

For control purposes, it may be considered quite adequate to define alkalinity in terms of the phenolphthalein and methyl orange

titrations. Of these, only that alkalinity represented by the phenolphthalein titration may be considered significant in terms of any pollutional effect.

In many effluents, the color is so dark that indicator titration is difficult or impossible. In such cases, the titration may be performed with the glass electrode pH meter, and the equivalent of the phenolphthalein end point taken as pH 8.3.

Proposed Method for Determination of Phenolphthalein Alkalinity.

A sample of mill effluent (300-400 ml., accurately measured) is titrated with 0.1 N HCl as soon as possible after sampling. The Beckman pH meter with Glass-Calomel electrodes is used, and agitation is carried out by slow stirring with the electric stirrer. The meter is standardized against a phthalate buffer(1) before using, and the initial pH reading is recorded as the pH of the solution. These pH values will generally be considerably higher than those obtained with daily composites, since the latter lose sulfide and take up carbon dioxide. The titration is carried out by adding small increments of 0.1 N HCl, and the end points are considered as pH 8.3 and pH 4.0. The amount of alkali neutralized at pH 8.3 is considered as "active alkali."

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(1) The stock solution contains 20.421 grams potassium acid phthalate per 500 ml.; 25 ml. of this, diluted to 100 ml., gives a solution whose pH is 3.98.

Sample analysis of a mill effluent: Sample light tan, turbid.

ALKALINITY TITRATION

Buffer = 3.98

300 ml. sample	
0.1 N HCl, ml.	pH
0.0	9.52
1.0	9 22
2.0	8.67
3.0	7.75
4.0	7.20
5.0	6.80
7.0	6.33
9.0	5.88
11.0	5.28
12.0	4.90
13.0	4.52
14.0	4.18
15.0	3.85

These data are plotted in Figure 3.

At pH 8.3, 2.5 ml. of 0.1 N HCl had been used, equivalent to 33 p.p.m. alkali as NaOH (2.5 x 0.1 x 40 x 1000/300 = 33).

Apparatus and reagents required for proposed methods

Beckman pH meter, Model G
Blue-Point Electrode
Silver-Silver Sulfide Electrode
Glass Electrode
Calomel Electrode
Separatory funnels
2000 ml., 500 ml., 50 ml.
Electric Stirrer
1200-ml. sample bottles

65% sulfuric acid
1:1 sulfuric acid
Ether
Chloroform
0.1 N HCl
0.1 N and 0.01 N $AgNO_3$
Acetic anhydride
Potassium acid phthalate

Other apparatus and reagents needed (beakers, burettes, etc.,) are generally part of the regular equipment of the laboratory.

All determinations can be carried out on a sample obtained by filling a twelve-quart pail.

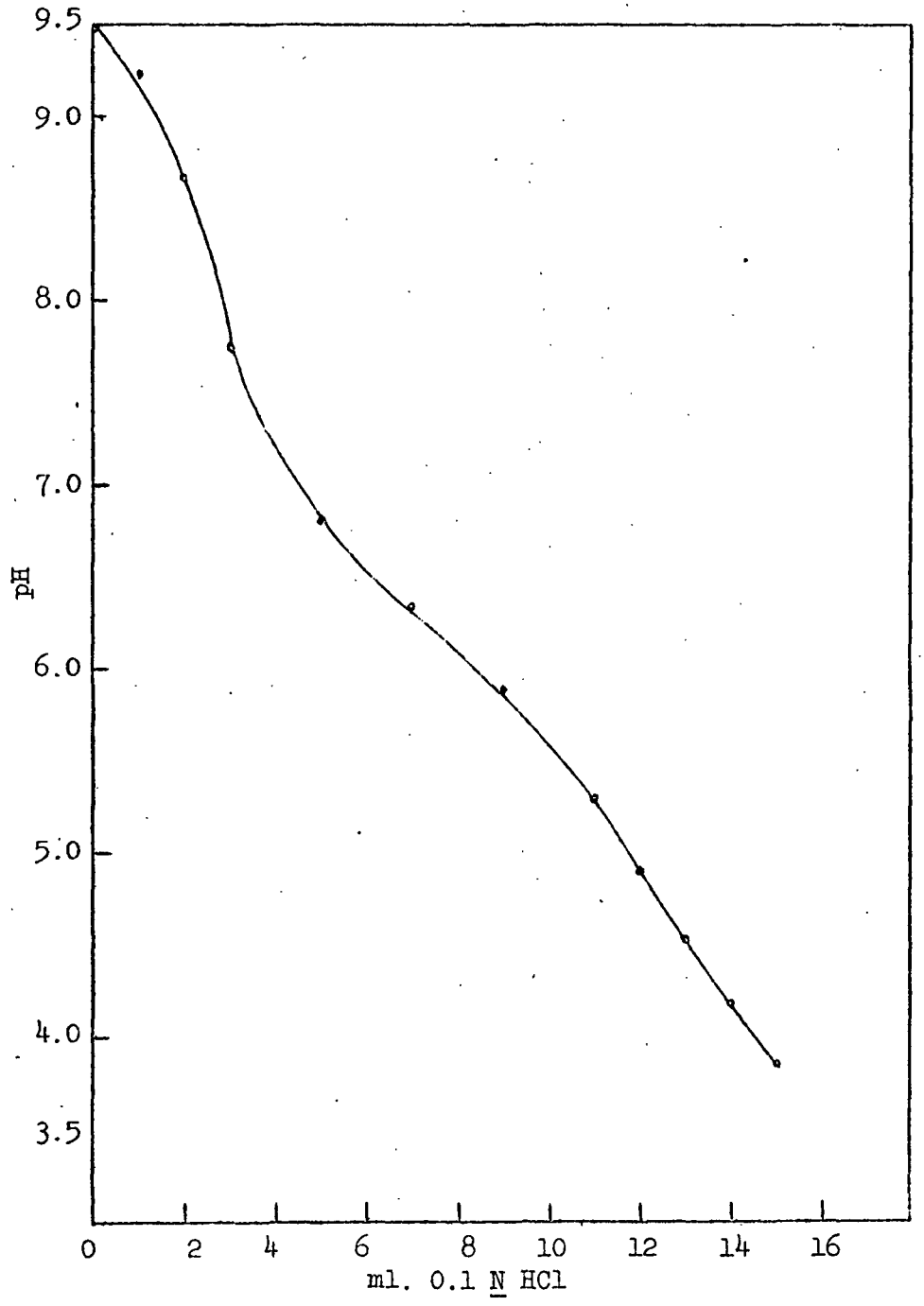

Figure 3

Typical Curve for Alkalinity Titration

Although the Beckman Model G pH meter was used in this work, any suitable vacuum-tube potentiometer will serve for the potentiometric titrations. The "Blue-point" and silver-silver sulfide electrodes are obtainable from National Technical Laboratories, South Pasadena, California.

RESULTS OF SURVEY OF MILL SEWERS

Two mill trips were made to a series of mills in Wisconsin, and the procedures outlined above were followed at each mill. The resin estimations on the second trip were carried out on the extract from ten liters of effluent. The data from these analyses and other pertinent information are shown in Table VI.

The analyses which resulted in the data shown in Table VI were made primarily to test the analytical methods described above, but there are a number of observations relating to the general problem of kraft mill wastes which can be made. It will be noted that there is considerable variation in amounts of all of the substances under consideration. Probably the most important cause of this variation is the fact that all samples taken were spot samples and, therefore, do not show the mitigating influence characteristic of a composite. Another cause for variation is to be found in the sewer arrangement of the mills; in some cases there were sewers carrying the pulp mill wastes only and in others the pulp mill wastes had been diluted with machine water above the point where the sample was taken. Although attempts were made to collect the test samples at as nearly the same representative point as possible, this could not always be done because of physical inability to reach the sewers at the desired place. Minor variations in the values

TABLE VI

RESULTS OF ANALYSES OF SEWER CONTENTS OF SEVERAL WISCONSIN KRAFT MILLS

Mill	Sewer	Time	Sulfide, p.p.m.	Mercaptan, p.p.m.	Active Alkali, p.p.m.	Ether Soluble, p.p.m.	Resin Soaps, p.p.m.	Sewer Flow, M gal./day	River Flow, M gal./day
I	Main	8/16/46 2:27 PM	1.5	6	6	--	1		
	Main	3:30 PM	7	18	20	--	--	11,600	2,592,000
	Main	8/28/46 9:40 AM	1.6	8	33	52	7		
	Main	10:37 AM	1.7	8	54				
II	Main	8/19/46 8:36 AM	1.6	6	26	--	2		
	Main	10:33 AM	0.3	6	8	--	--	3,900	3,000,000
	Main	8/27/46 2:42 PM	0.6	5	< 6	31	8		
	Main	3:15 PM	24	6	13				
III	White water	8/19/46 1:42 PM	0.9	3.5	72	--	2		
	White water	4:22 PM	0.0	1.5	20	--	--	868	
	White water	8/27/46 9:40 AM	0.6	2.5	26	87	20		
	White water	11:40 AM	7.0	12.0	86				242,000
	Evaporator effluent	8/19/46 2:52 PM	8	4.0	8	--	0		
	Evaporator effluent	4:24 PM	14	4.5	8	--	--	927	
	Evaporator effluent	8/27/46 8:36 AM	12	30	< 6	6.4	0.4		
	Evaporator effluent	10:22 AM	14	6	< 6				

TABLE VI (Continued)

RESULTS OF ANALYSES OF SEWER CONTENTS OF SEVERAL WISCONSIN KRAFT MILLS

Mill	Sewer	Time	Sulfide, p.p.m.	Mercaptan, p.p.m.	Active Alkali, p.p.m.	Ether Soluble, p.p.m.	Resin Soaps, p.p.m.	Sewer Flow, M gal./day	River Flow M gal./day
IV	Main	8/20/46 9:30 AM	1.4	2.4	20	--	1.5	6,360	
	Main	8/26/46 4:32 PM	1.0	25	9	18	1.6		
	Evaporator effluent	8/20/46 10:10 AM	79	8	0	--	--	212	1,800,000
	Evaporator effluent	8/26/46 7:05 PM	12	6	0	18	8		
	Barometric condenser	8/20/46 11:57 AM	0.0	0	0	--	--	818	
	Barometric condenser	8/26/46 5:50 PM	3.0	4.0	4	7	0.5		
V	Main	8/20/46 3:15 PM	5	8	33	--	Some		
	Main	4:20 PM	16	12	7	124	--	5,200	
	Main	8/26/46 9:43 AM	4	4.0	42	39	3.2		
	Main	12:05 PM	13	5.0					1,120,000
	Evaporator effluent	8/20/46 5:03 PM	16	12	7	--	--		
	Evaporator effluent	8/26/46 11:20 AM	13.5	9	2	112	33	1,000	
	Evaporator effluent	1:50 PM	10	--	--				
	Evaporator effluent	9/9/46 4:23 PM	--	--	--	163	36		

TABLE VI (Continued)

RESULTS OF ANALYSES OF SEWER CONTENTS OF SEVERAL WISCONSIN KRAFT MILLS

Mill	Wood Used	Salt Cake Make-Up, lb./ton	Pulp Capacity, tons/day	Water to Pulp Ratio, gal./ton	Dissolved Solids, tons/day	Treatment of Lime Sludge	Treatment of Tall Oil	Turpentine to Pulp Ratio, gal./ton
I	Jack Pine 60%, Hemlock 10%, Poplar 10%, Misc. 10%	280	138	41,000 (state) 32,500 (mill)	23	Burned	Burned	1
II	Jack Pine 85%, Poplar and Hemlock, 15%	250	155	24,100	6.5	Not stated	Not stated	1.7
III	Jack Pine, occasionally some Tamarack	300-350	32	68,800	4.1	Dumped	Burned	Only partially saved
IV	Jack Pine 2/3, Hemlock 1/6, Spruce 1/6	350	130	90,000	5.0	Not stated	Not stated	1.6
V	Jack Pine	360-370	97	44,000 (estimated)	13.8	Not stated	Burned	1.5-1.6

shown might also result from the type of wood used or in some process modification characteristic of a particular mill.

The data available on the evaporator effluents indicate that these wastes have higher contents of sulfides and mercaptans than the others. This is probably due to the higher volatility of these compounds. This sulfide problem may not be as serious as it appears, since, as has already been stated, the sulfide content drops very rapidly on standing.

At the time the sewer analyses were made, data on river discharge were also obtained and calculations were made to determine the concentration of the toxic components in the river, assuming total dilution. Data for these calculations are shown in Table VII.

It will be noted that the river dilution figures are given on the basis of total dilution. Their significance would depend on the speed with which the mill sewer contents would be dissipated in the stream and this, in turn, would depend upon the physical and other characteristics of the stream at the point and immediately below the sewer outfall. It has been observed that kraft wastes have a tendency to resist free mixing with the stream water; for that reason it is conceivable that toxic concentrations of the substances could exist for a considerable distance downstream.

DISCUSSION

In considering which method or methods were best adapted to achieve the objectives of this investigation, it became apparent that,

TABLE VII

SHOWING CALCULATED CONCENTRATIONS IN THE RIVER OF THE TOXIC SUBSTANCES, ASSUMING TOTAL DILUTION

Mill	All Sewers Combined p.p.m. Sulfides	Mercaptans	Resin Acid Soap	Concentration in River, Assuming Total Dilution, p.p.m. Sulfides	Mercaptans	Resin Acid Soap	River Discharge, c.f.s.	
I Highest	7.0	18.0	7.0	0.03	0.08	0.03	2600	Hudson
Lowest	1.5	6.0	1.0	0.006	0.025	--		
II Highest	2.4	6.0	8.0	0.003	0.008	0.011	3000	N. E.
Lowest	0.3	6.0	2.0	--	0.008	0.003		
III Highest	4.0	3.7	1.4	0.016	0.015	0.006	1800	St. Pt.
Lowest	1.2	2.9	1.4	0.005	0.012	0.006		
IV Highest	10.0	8.0	10.0	0.074	0.060	0.074	242	Massena
Lowest	4.0	2.0	1.0	0.030	0.014	0.007		
V Highest	16.0	12.0	8.0	0.084	0.063	0.042	1120	Fort Edward
Lowest	2.8	4.7	8.0	0.015	0.025	0.042		
				1.2	0.5	5.0		

for wide spread use in technical laboratories of the mills, the method must be (1) feasible, (2) as rapid as possible, and (3) must not require the use of apparatus not ordinarily available in mill laboratories.

The experience of Institute personnel in making the sewer surveys described above has adequately demonstrated the feasibility of the proposed methods. Furthermore, it has been determined that the complete proposed analyses can be made in a period not exceeding two hours and, as the analyst becomes familiar with the procedures, this time may well be reduced.

In the matter of apparatus, the use of a pH meter may be a problem in some laboratories. Although a Beckman (Model G) was used in the present work, it has been pointed out that any vacuum-tube potentiometer can be used. The various types of electrodes are readily obtainable if the pH meter is available. The rest of the items listed above are ordinary equipment and should present no problem.

The data presented in this report indicate that, on the basis of the "spot" samples taken, there are times when the concentration of toxic substances exceeds the minimum lethal concentration (to fish) and there are times when it does not. The weaknesses of the "spot" sampling method are apparent and, before recommendations are made in the matter of waste treatment, it is desirable that much more extensive data be available. To this end, it is suggested that each mill institute, as a part of its regular control testing procedure, regular sewer analyses as described herein. It would be desirable that this testing program be maintained over a period sufficient to demonstrate the amounts

of toxic compounds in the sewer under all possible conditions of production and mill operation. The data from the sulfide-mercaptan-resin acid soap analysis, coupled with certain information available from routine mill control tests in the mill, would be useful in formulating whatever remedial plans seemed desirable. In order to facilitate the collecting of these data, there is appended a tentative form sheet for tabulating the data. It is suggested that copies of these data sheets be forwarded to the co-ordinator of the Aquatic Biology project of the National Council for Stream Improvement at The Institute of Paper Chemistry.

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