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FURTHER STUDIES ON THE MEASUREMENT OF ORGANIC  
(COLOURING) MATTER IN NATURAL WATERS

by

John Ungar\* and J. F. J. Thomas\*\*

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SYNOPSIS

Measurements of organic colouring matter in water were made using visible and ultra-violet absorption spectra, fluorescence, and oxygen consumption from acid permanganate. These methods all have serious limitations. Measurement of the absorption at 425 m $\mu$  of colour of buffered water is preferable to direct determination of Hazen colour scale. The ultra-violet absorption method is considered superior to the oxygen-consumption-from-permanganate test as a means of measuring organic colouring matter. Some comparison of fluorescence measurements with other methods of measuring organic colouring matter is also reported.

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\*Former Scientific Officer, Industrial Waters Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, now Manager of Technical Services (Laboratories), Ionac Chemical Company, a division of Pfaunder-Permutit, Inc., Birmingham, N.J., U.S.A.

\*\*Head, Industrial Waters Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

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NOUVELLES ÉTUDES RELATIVES À LA MESURE  
DES MATIÈRES ORGANIQUES (COLORANTES)  
PRÉSENTES DANS LES EAUX NATURELLES

par

John Ungar\* et J. F. J. Thomas\*\*

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RÉSUMÉ

On a procédé à des mesures des matières colorantes organiques que contient l'eau en ayant recours au spectre d'absorption visible et ultraviolet, à la fluorescence, ainsi qu'à la consommation d'oxygène à partir du permanganate acide. Ces procédés comportent tous de sérieuses restrictions. La mesure de l'absorption à 425 m $\mu$  de couleur de l'eau à mélange tampon est préférable à la détermination directe de l'échelle de teintes Hazen. Le procédé d'absorption ultraviolette est supérieur, croit-on, à l'essai de consommation d'oxygène à partir du permanganate en tant que moyen de mesure des matières colorantes organiques. De plus, les auteurs comparent quelque peu la méthode de mesure de la fluorescence avec d'autres procédés de mesure des matières colorantes organiques.

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\*Ci-devant chargé de recherches à la Section des eaux industrielles de la Division du traitement des minéraux, Direction des mines, ministère des Mines et des Relevés techniques, à Ottawa, M. Ungar est maintenant directeur des Services techniques (laboratoires) à l'Ionac Chemical Company, filiale de la Pfaunder-Permutit, Inc., Birmingham, N. J., U. S. A.

\*\*Chef, Section des eaux industrielles, Division du traitement des minéraux, Direction des mines, ministère des Mines et des Relevés techniques, Ottawa, Canada.

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## INTRODUCTION

A large proportion of the surface waters of Canada are coloured, some very highly. This colouring matter must be removed from waters used for many industrial and domestic purposes. The World Health Organization proposed, in its International Standards for Drinking Waters (1), that the permissible limit for colour in potable water should be 5 units on the platinum-cobalt (Hazen) scale, 50 units being considered excessive. Many industrial users demand less than 5 Hazen units of colour in process water.

Chemical analyses\* of many of the highly-coloured surface waters from uncontaminated areas, especially waters very low in total mineral content, show an excess of cations when an ionic balance is attempted. Further, waters from different regions of Canada, although having the same visible colour, react differently to methods of colour removal such as chlorination and coagulation; some of these waters also lose colour when exposed to sunlight during storage in glass, while others do not. These and other phenomena, presumably related to the colouring matter in the water, have for some time been under study in the Industrial Waters Section's laboratories. Of major interest are methods of measuring and classifying the coloured waters from various regions of Canada, particularly as to:

- (1) their reaction to conventional colour removal methods, including chlorination;
- (2) their reaction in the ionic balance of a water analysis, that is, knowledge as to whether the colouring matter is in solution or is present as a colloid; and
- (3) the corrosivity or corrosion-inhibiting nature of the colouring matter.

Once a satisfactory means of classifying various coloured waters is found, studies designed to identify the specific material causing differences in the reactions of coloured waters may be considered.

The technical literature on the colour and/or organic matter of natural waters is quite extensive, but no attempt will be made at this time to summarize the subject. It is generally agreed that the materials colouring natural surface waters are organics of a general class known as humic and fulvic acids. Free acids are present as well as salts of these acids and other organic compounds, and some of the differences in the reactions of coloured waters have recently been shown to be due to whether the free acid or a salt is present (2). Some difference of opinion still exists, however, as to the relative amounts of these materials present in solution and as

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\*By the Industrial Waters Section, Mineral Processing Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada.

colloids. Further clarification of the reactions, properties and structures of the materials causing colouration of water is needed.

In late 1959 and in 1960, preliminary studies (3) were made on several highly-coloured Canadian surface waters, in an attempt to measure more accurately the amount of colour and to show, if possible by simple test, differences in the behaviour of coloured water from different areas of Canada. This study, which was very limited in scope, gave the following indications:

1. Direct titration of organic acids, even those in highly-coloured waters after hydrogen ion exchange, is not feasible unless the colouring matter is first concentrated. (The risk of loss or change in the colouring matter by the usual concentration methods, such as evaporation, is great.)

2. Present methods of measuring colour--e.g., visible spectrum absorption, ultra-violet absorption, and oxygen consumption from permanganate--have some serious limitations.

3. Storage of a coloured water can affect the amount or nature of the colouring matter present or measured.

4. Treatment of a coloured water on a suitably-prepared, strongly-acid exchange resin causes little or no change in the colour, but this treatment does appear to improve the efficiency of colour absorption on strong-base anion-exchange resins and on activated carbons.

5. Some colour appears to be removed from waters by weak-base anion exchange, after suitable pretreatment.

6. Removal of colour by several types of activated carbons was not an efficient method.

7. Calcium ion appears to be complexed or ionically balanced by organic acids in those coloured waters which are shown by normal chemical analyses to have an excess of cations. A simple measurement of the exact amount of such acids or complexed compounds is not yet possible.

This report outlines further studies carried out during late 1960 and in 1961 on the measurement and classification of colouring matter. Much of this work was directed to confirming the findings outlined above.

#### MEASUREMENT OF COLOUR FROM THE VISIBLE SPECTRUM

Visible comparison is a simple, arbitrary method commonly employed to measure the colouration of water. Thiessen and Engelder (4) stated that all humic acids are coloured and are almost completely transparent to red and yellow light, become less transparent to light of decreasing wavelength, and are practically opaque to blue and violet light. Hale (5), Van Beneden (6, 7) and Berg (8) all used colour intensity measurements as

an estimate of humic acid in water. Freytag (9) gives a mathematical treatment of changes in light absorption by humic acids at wavelengths of 472 and 664 m $\mu$  in relation to changes in colour concentration.

Hazen developed a standard scale (10), using varying amounts of platinum and cobalt salts to which water colour is compared. Such a method of measurement assumes all colour in water to be identical in nature and hue and to match the standards. It is known, however, that a breakdown of colour in waters from various regions into the Lovibond standards (primary colours) produces considerable differences in the shades and ratios of such primary colours.

### Experimental

Several Hazen standards ranging from 0 to 500 colour units were examined in 10-mm cells in a Beckman DK-2 recording spectrophotometer. Three highly-coloured surface waters, a treated Ottawa River water, and a highly-coloured surface water after hydrogen ion exchange, were also examined under the same conditions.

Some ultra-violet spectral curves were also obtained on the same waters, using a Beckman DU spectrophotometer and 100-mm cells.

One of the highly-coloured river waters was also examined for light absorption at 455 m $\mu$  and 300 m $\mu$  after various periods of glass storage in daylight.

### Discussion

Figure 1 shows that the Hazen colour standards have minimum transmittance (maximum absorption) at about 455 m $\mu$ , and a minor transmittance peak at 430 m $\mu$ , when very high colours are studied. There is little difference in the absorption at 425 m $\mu$  and 455 m $\mu$ , especially at Hazen colour units of 100 and below. Below 425 m $\mu$ , transmittance decreases with decreasing wavelength in the visible range. Figure 2 shows that the Hazen colour standards up to 500 units follow Beer's law when measured at 455 m $\mu$ .

Figure 3 shows that the spectral curves of several natural and treated waters differ from those of the Hazen standards. There is considerable difference in all coloured waters between the transmittance at 455 m $\mu$  and 425 m $\mu$ , the transmittance being lower at the latter wavelength. These naturally-coloured waters show a peak transmittance at about 735-740 m $\mu$ ; the transmittance decreases thereafter as the wavelength increases.

Figure 3 also confirms the effect of pH on colour intensity as originally pointed out by Hale (5), i. e., a decreasing pH decreases the visible colour (increases transmittance). Treatment of Malartic River sample II



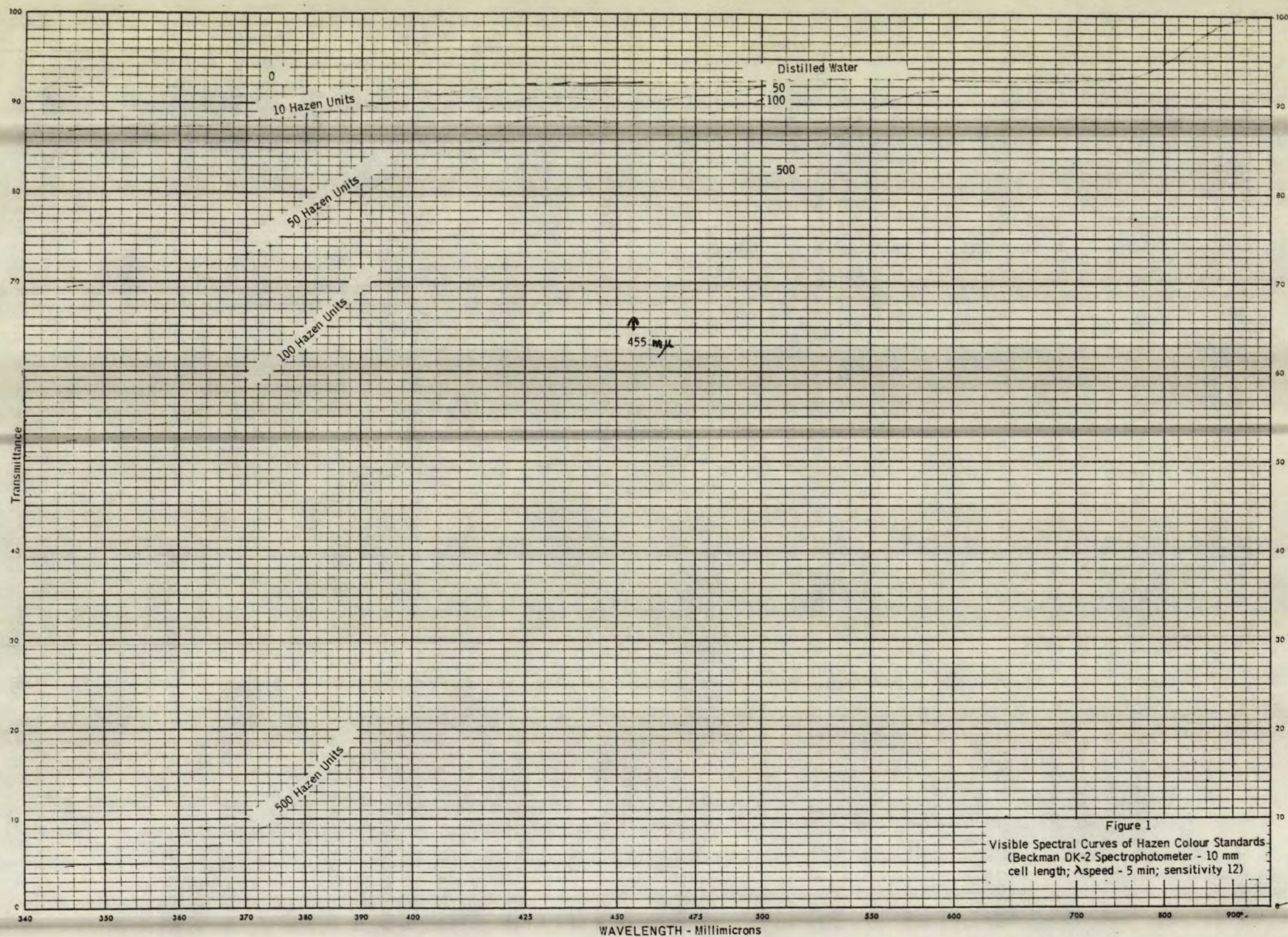
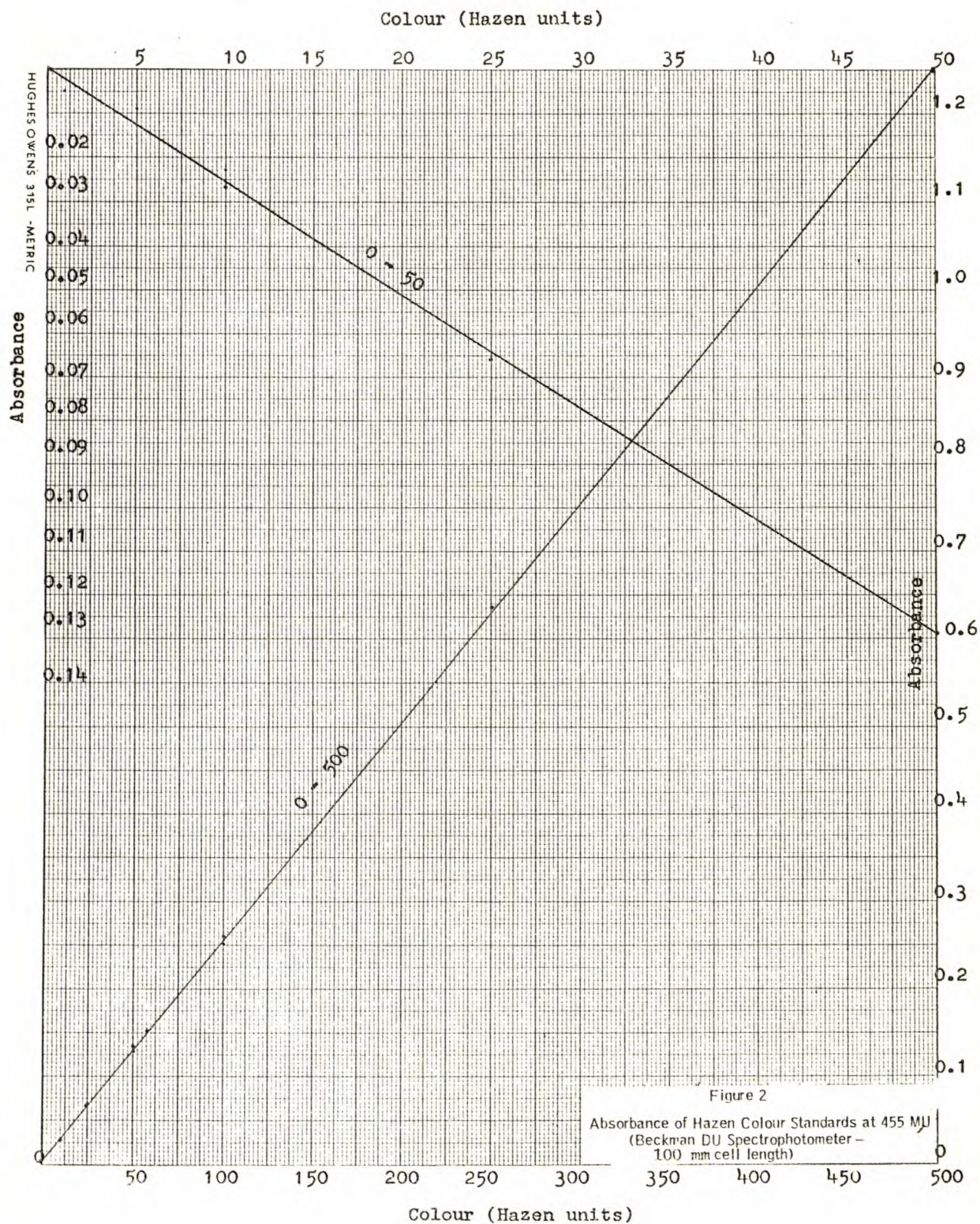
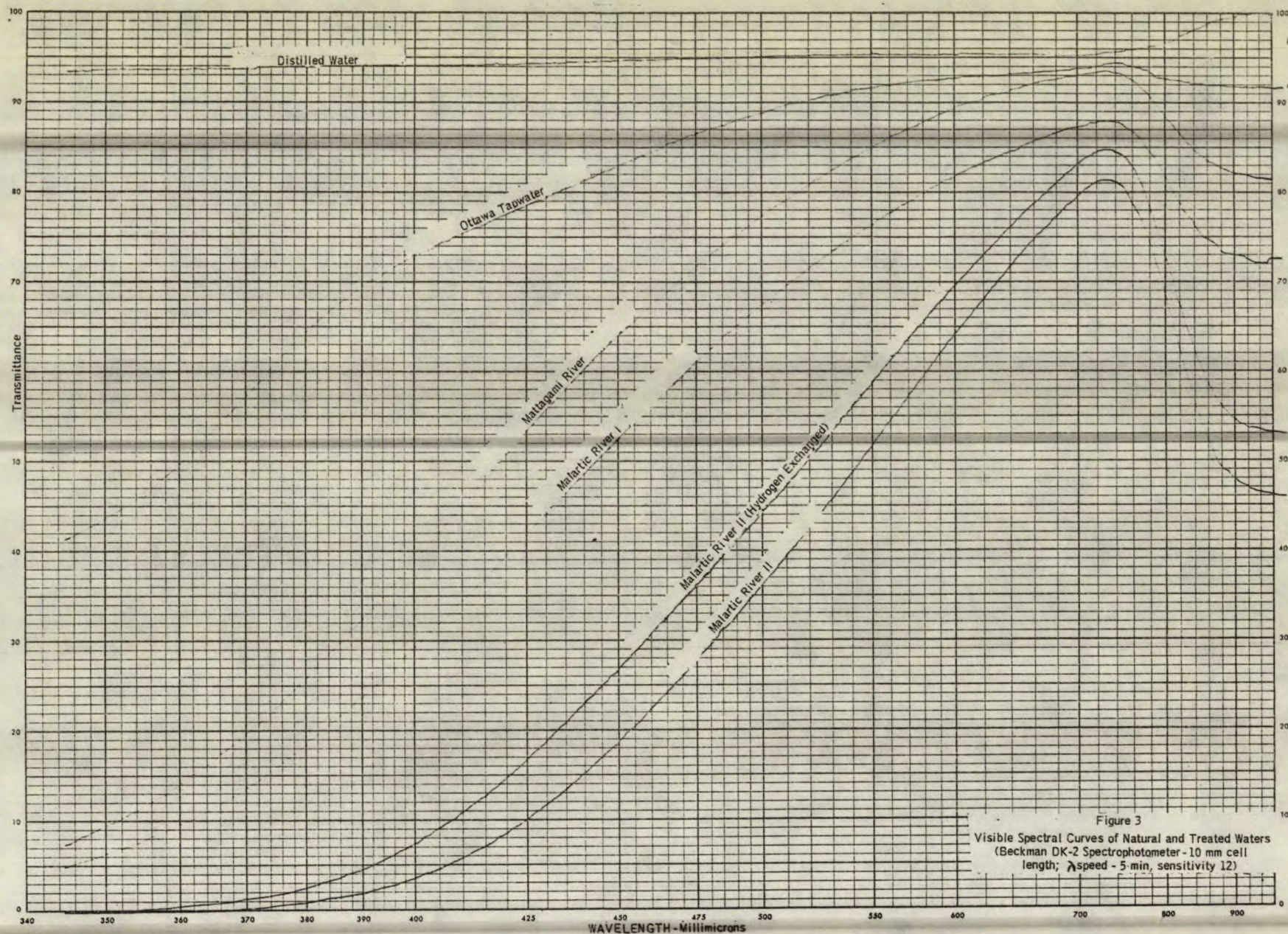


Figure 1  
Visible Spectral Curves of Hazen Colour Standards  
(Beckman DK-2 Spectrophotometer - 10 mm  
cell length;  $\lambda$  speed - 5 min; sensitivity 12)











by hydrogen ion exchange (decrease in pH) increased the transmittance of the water. Table 1 further illustrates the effect of pH on several coloured waters. A study of the transmittance on the ultra-violet region (250-350 m $\mu$ ) of a wide variety of waters adjusted to pH 4 and pH 8 further confirmed an increase in transmittance at lowered pH. However, the increase varied with different waters and the wavelength of measurement.

TABLE 1

Effect of pH on Absorbance\* of Naturally-coloured Waters

Water	After Filtration	After Hydrogen Ion Exchange (decreased pH)
A	0.074	0.059
B	0.024	0.022
C	0.039	0.028
D	0.023	0.020
E	0.054	0.043
F	0.145	0.120
G	0.150	0.125

\*Beckman DU spectrometer with 100-mm cell length at 455 m $\mu$ .

The samples studied in Table 1 were filtered prior to hydrogen ion exchange to remove turbidity. Neither oxygen consumption (from KMnO<sub>4</sub>) nor ultra-violet light absorption showed any change in the organic matter concentration resulting from filtration and hydrogen ion exchange. Columns of sulphonated polystyrene bead resins served as the hydrogen ion exchangers; these resins were always fully regenerated, then rinsed with distilled water until all free acid was removed and the distilled water showed no pick-up of organic matter from the resin.

Figure 4 shows clearly the effect of storage on the visible colour of Malartic River water exposed to daylight and sunlight. A decrease in colour results, a change noted previously on a number of waters. With some highly-coloured waters the change is quite marked and formation of a brown, amorphous precipitate of a flocculent nature accompanies the visible colour fading. Somewhat similar changes in colour upon storage were noted when measurement was carried out in the ultra-violet range (300 m $\mu$ ).

The effect of turbidity or suspended matter on visual measurements of colour is well known. When turbidity is present the measured colour is called "apparent" colour: "true" colour can be measured only if all turbidity is removed or, as suggested by Palin (11), when allowance is made for the



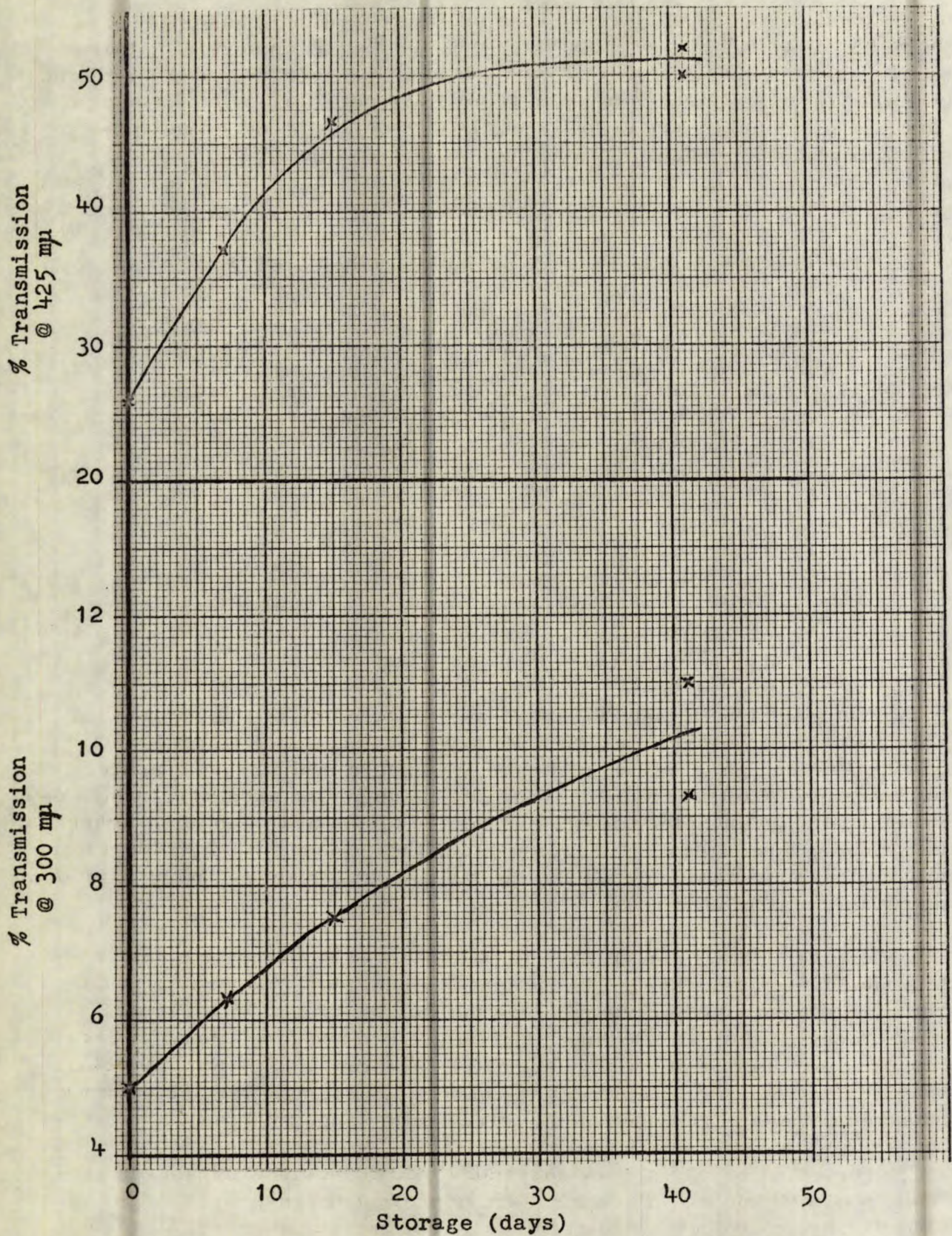


Figure 4 - Change in Ultra-violet and Visible Light Transmission of Malartic River Water on Storage.



effect of turbidity by differential measurements at 425 m $\mu$  and at 570 m $\mu$ .

These brief studies confirm that the generally-accepted Hazen standards do not truly measure natural colouring matter in water, because these standards have a somewhat higher absorption at 455 m $\mu$  than at 425 m $\mu$ , whereas most waters have a higher absorption at 425 m $\mu$  than at 455 m $\mu$ . Measurement at 425 m $\mu$  would give greater accuracy when comparing the colour of different waters; also, commercially available filter photometers are usually supplied with 425-m $\mu$  filters and not 455-m $\mu$  filters. Whether or not all coloured waters from various regions of Canada show peaks at the same wavelength is not yet known. Most of the waters studied to-date have generally similar transmittance or absorbance curves, although some significant variations are noted.

Since pH greatly influences colour, true comparisons and measurements of coloured waters can be made only at a standard pH. It would therefore be advisable to demand that all colour measurements and comparisons be made after hydrogen ion-exchange treatment. Such treatment would also tend to remove the effect of turbidity; if any remained, it could be corrected for by Palin's method.

Since colour in waters is also affected to varying degrees by storage, some relationship to storage duration and conditions must also be considered.

#### MEASUREMENT OF COLOUR BY ULTRA-VIOLET ABSORPTION

Thiessen and Engelder (5) in 1930 studied the ultra-violet spectrum of humic acid, and Buswell and Dunlop (12) in 1942 suggested that it be used for detecting organic matter in water. Fuchs and Kohler (13) developed this method in 1956-57 for the quantitative measurement of organic matter, and, later, Wilson (14) reported that he obtained characteristic absorption spectra with fulvic acids in water. These acids showed a steady increase in absorbance as the wavelength decreased from 700 to 200 m $\mu$ . No absorption peaks occurred within this range, and absorption is very intense in the ultra-violet. Fuchs, in his study of humic acids in both the visible and ultra-violet range, found that they could be determined quantitatively at very low concentrations by measurement in the ultra-violet range. He further reported that in very dilute solutions the concentration and absorption appeared to follow the Beer-Lambert law. Wilson (14, 15) applied Fuchs's method to characterize moorland water phragmites and peat extracts, measuring the absorption in 40-mm cells between 350 and 220 m $\mu$ . A comparison of his results with those of Fuchs showed that they were quite similar but not identical. He also showed that the ultra-violet spectra of humic acids in moorland waters, in a coagulated municipal water, and in an eluate from a fouled anion exchange resin, were similar. The peat extract, although showing a curve of somewhat different shape, still gave no absorption peaks.

The ultra-violet absorption method as a measurement of organic colouring matter in water also has its limitations. Fuchs and Kohler showed that sugars and acids such as formic, acetic, citric, and oxalic absorb light at 220 m $\mu$  but, for all practical purposes, are transparent at 300 m $\mu$ . Anions such as sulphates, chlorides, phosphates, etc., are transparent between 200 and 400 m $\mu$ , even in molar concentration. While nitrites and nitrates do interfere in this range, there is virtually no absorption above 250 m $\mu$  at concentrations below 10 mg/l. Wilson in his studies (14) reported that 5 ppm NO<sub>3</sub> gave an apparent fulvic acid concentration of only 0.1 ppm. Hoather and Rackham (16) actually propose absorption measurement at 210 m $\mu$  for nitrate determinations in water, correcting for interference of inorganic matter in low concentrations by differential absorption measurements at 210 and 275 m $\mu$ .

Hydrolysis products, such as those from aluminum, chromium and the heavy metals, especially iron (solutions of ferric chloride and ferric sulphate), even at great dilutions, were also found by Fuchs and Wilson to interfere. These cationic interferences can be eliminated by strong acid cation-exchange as outlined below.

Both Fuchs and Wilson reported interference by silica as an almost negligible factor. Wilson reported slightly higher readings at pH greater than 6.0, but below this value pH had little effect in the ultra-violet range.

### Experimental

Ultra-violet spectral curves were obtained for the same Ottawa, Malartic and Mattagami River waters studied over the visible light range using the same instrument - a Beckman DK-2 spectrophotometer with a cell length of 10 mm. The effect on the ultra-violet absorption of pure nitrate solutions alone, and when added to highly coloured waters, was also checked with the same instrument.

A series of coloured lake waters from northern Ontario, as well as a number of waters from other parts of Canada, was studied in a similar manner with the DK-2, or on the Beckman DU instrument in 100-mm cells, to determine their absorption in the ultra-violet range (210 to 340 m $\mu$ ).

### Discussion

Figure 5 shows a relatively steady decrease in transmittance of the several coloured waters as the wavelength decreased from 340 to 220 m $\mu$ . It will be noted that the Malartic River II sample, after hydrogen ion exchange (lowered pH), did show a small decrease in colour (increase in transmittance). No explanation can be given as yet for the cross-over at about 296 m $\mu$  in the spectral curves for the Malartic River I and Mattagami River waters.



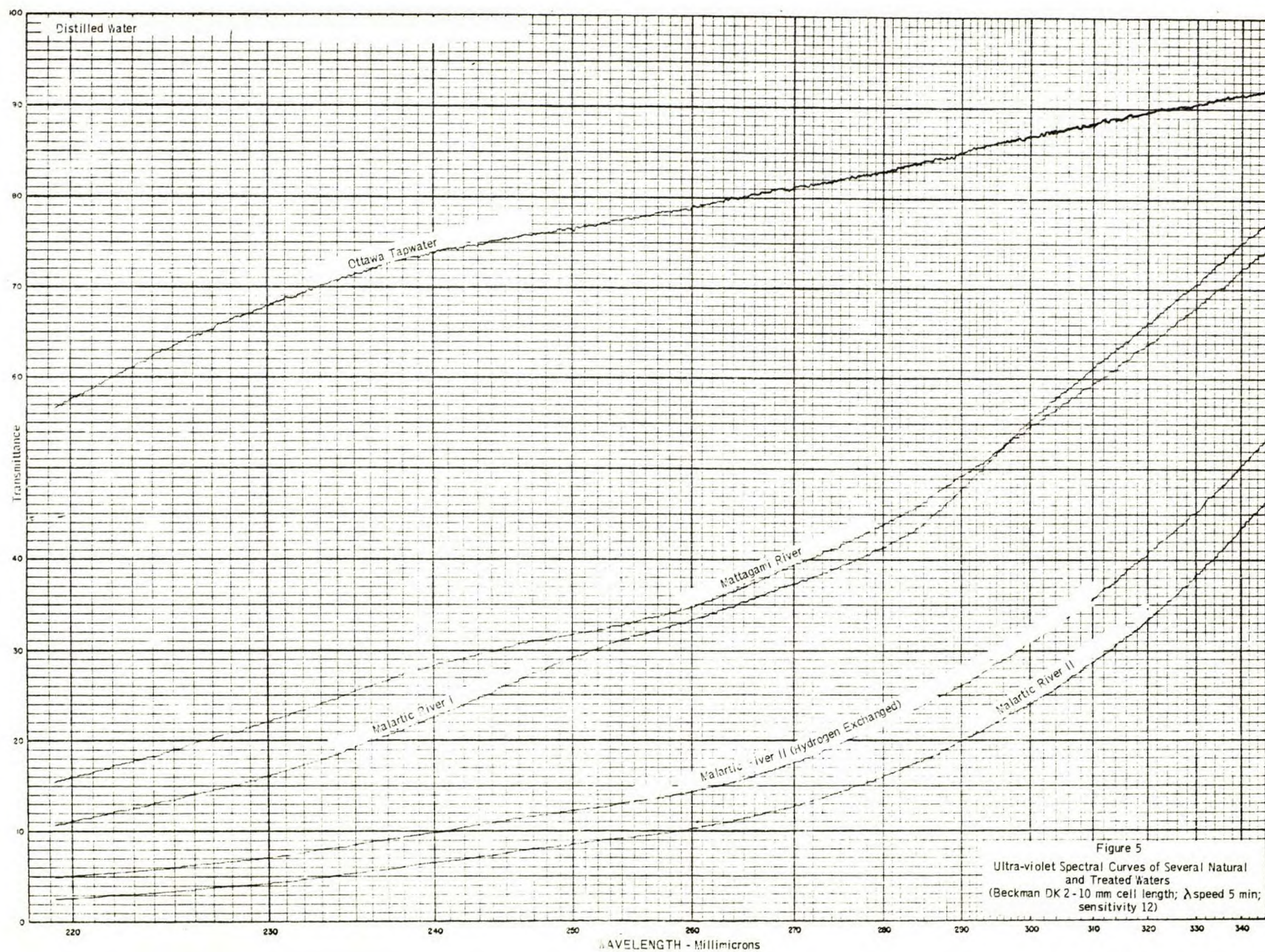


Figure 6 shows a similar decrease in transmittance with less-coloured lake waters from northern Ontario, studied on the Beckman DU instrument. Some variations in certain curves are noted. In general, this work on Canadian waters confirms the findings reported by others on waters in the United States, Europe, and Great Britain.

Figure 7 shows the effect of pure nitrate and of ferrous and ferric solutions in the ultra-violet absorption spectrum. Also included are curves showing the effect of 1 ppm ferric ion on the spectrum for Malartic River II water over the range from 340 to 270 mμ. The absorption of pure nitrate solutions at 300 mμ is negligible. Table 2 shows that while pure nitrate solutions do have a small measurable absorption at 300 mμ, using a 100-mm cell and a Beckman DU spectrophotometer, the same amounts of nitrate added to relatively highly-coloured waters increase the absorption negligibly.

TABLE 2

Nitrate Ion Effect in Ultra-violet Absorption

Sample	Absorption at 300 mμ*						
	Nitrate (ppm NO <sub>3</sub> )	0	1	5	10	50	100
Distilled water		0.0	0.25	-	0.125	-	-
A		1.03	-	-	1.05	-	1.06
B		0.67	-	0.67	-	0.69	-
C		0.46	-	0.41	-	0.49	-

\*Beckman DU spectrophotometer, 100-mm cells.

Ferric ions do affect absorption but are readily removed by passing the water sample through an acid-regenerated, strong acid cation-exchange column of the polystyrene-sulphonic acid type. The column must first be rinsed with distilled water until no traces of organic matter bleed from the resin; this can be checked by measuring the ultra-violet absorption of the distilled water before and after passing through the column.

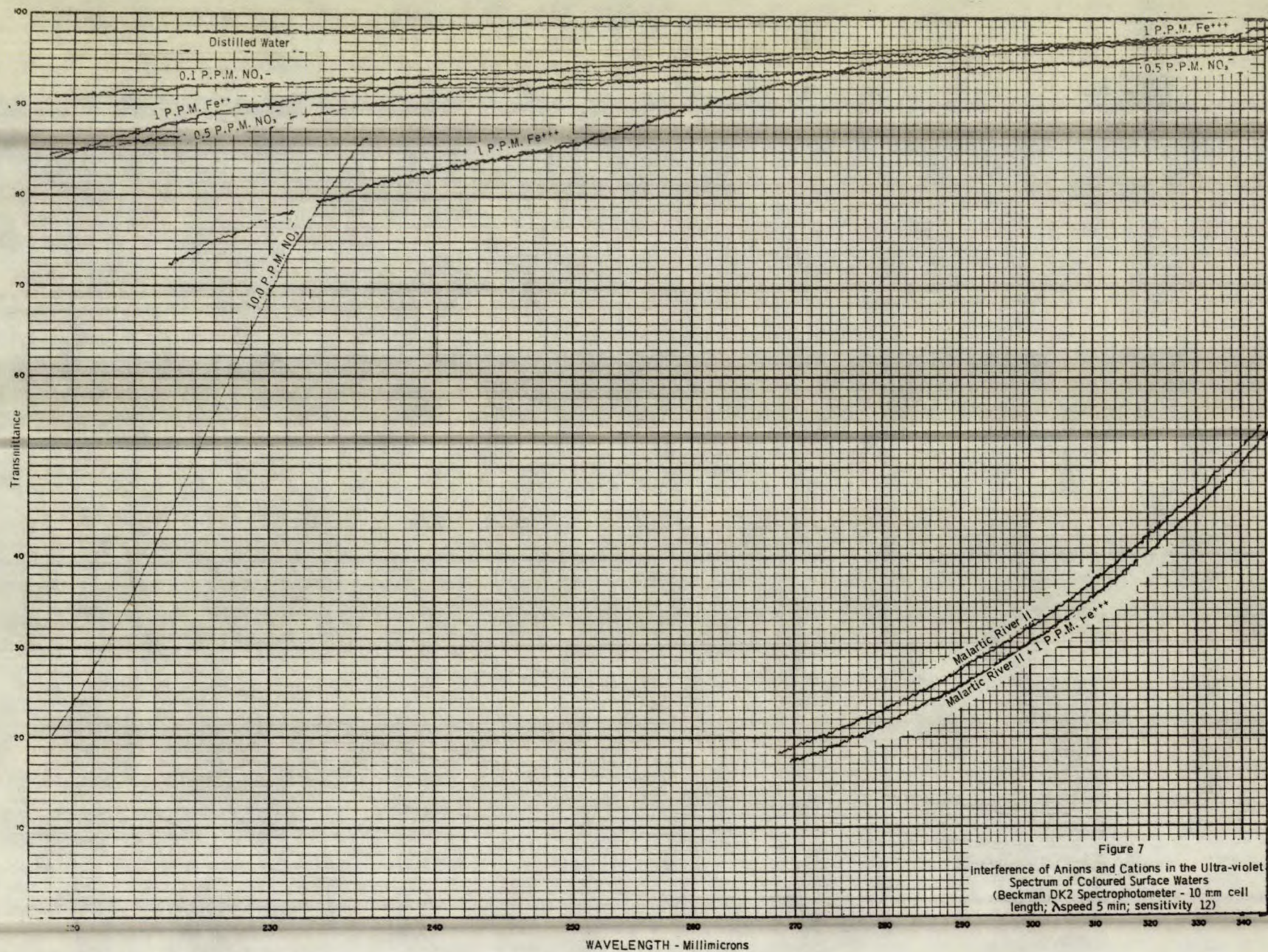
Work reported elsewhere (17), comparing the ultra-violet absorption and Hazen colouration of a number of lake waters (0 to 30 Hazen colour units), showed very little correlation although there was a general trend to increased absorption with increasing Hazen colour.

Hoather and Rackham (16) said that, for low organic matter, absorption at 275 mμ = 4. The highly-coloured Malartic River II water absorption at 210 mμ











gave a ratio of 1:2, but the less-coloured Ottawa River water gave an approximate ratio of 1:3.5.

Ultra-violet absorption at about 275 m $\mu$  appears to be a useful tool for estimating organic matter, provided the interfering ions are removed by ion exchange. The relationship between actual visible colour and the ultra-violet absorption measurement in a river must be determined before the ultra-violet measurement can be said to measure colour directly.

#### MEASUREMENT OF ORGANIC COLOURING MATTER BY THE OXYGEN CONSUMPTION TEST

Another widely-adopted method of measuring colouring matter in water involves the consumption of oxidizing agents by the organic matter; it is assumed that all colour is caused by organic matter and that all organic matter causes colour.

Some workers employ the Biochemical Oxygen Demand (BOD) test using permanganate, but the "oxygen consumed from acid potassium permanganate" test has been used under various test conditions by many as a simple, arbitrary test for organic matter in uncontaminated natural waters.

In Britain (18, 19), the absorption of oxygen from acid permanganate over a 4-hour period at 27°C is used, while in Europe (20), as a rule, the water with acid and permanganate is brought to the boil and then simmered for 10 minutes. In North America (10), permanganate oxidation for 30 minutes at 100°C is the common test. Oxidation using ceric sulphate has been stated (21) to be more satisfactory than permanganate, dichromate (1, 19, 22), and chlorine or its compounds (23, 24).

Windle-Taylor (24) suggests that for a potable water supply an oxygen absorption figure of 0.5-1.0 mg/l after 4 hr at 27°C is satisfactory, but that amounts greater than 4 mg/l for a peaty water, and greater than 2 mg/l for other types of water, indicate organic contamination. The permanganate test has also been used for the measurement of residual quantities of humic acid or its salts after coagulation (25), and for the determination of organic colloids in waste waters before and after activated carbon treatment and filtration (26). Hissel (27) measured humic acid by determining oxygen consumption from acid permanganate, and Van Beneden (6, 7) also estimated the concentration of humic acids by essentially the same test. Since about 1954 the Mines Branch's Industrial Waters Section laboratory has been measuring the consumption of oxygen from  $\text{KMnO}_4$  by surface waters collected in connection with countrywide surveys on water quality.

This test has serious limitations, especially as a measure of organic matter. Various types of organic compounds show considerable differences in their respective permanganate consumption: one report (28) lists the potassium permanganate consumption of some organic compounds (referred to 1 gram of the compound per litre of water) as follows:

<u>Compound</u>	<u>Potassium Permanganate</u>
(1 g/l)	(KMnO <sub>4</sub> ) - mg/l
phenols	9666
tannic acid	3530
humic acid	219
urea	6
acetic acid	5

The permanganate consumption, moreover, depends on several other conditions, such as time and temperature; indeed, some organic compounds are never oxidized by permanganate but require a stronger oxidant. Ungar (29) noted the effect, on oxygen consumption, of varying the time and temperature of reaction (see Table 3). In addition, the results of varying times of exposure as reported by Wilson (30) are reproduced in Table 4.

TABLE 3

Comparison of Tests of Oxygen Consumed  
from Permanganate (29)

Sample (200 ml)	Oxygen consumed (mg/l) after			
	4 hr at 27°C	5 min boiling	10 min boiling	60 min at 100°C
Distilled water	0.04		0.28	0.46
A	0.54		1.07	1.15
B	0.08		0.28	0.52
C	0.02		0.26	0.48
D	0.04		0.42	0.48
E	1.0	1.3		



TABLE 4

Effect of Time on Oxygen Consumed from Permanganate (30)

Sample	Permanganate (Ml/N/ 80) consumed at boiling after		
	15 min	30 min	45 min
1	1.02	1.25	1.43
2	2.26	2.54	2.73
3	4.51	5.07	5.34
4	5.29	5.71	5.86
5	1.33	1.49	1.58

Wilson reported that fulvic acid obtained from natural water averaged an oxygen consumption, in the cold, of 0.52 mg per gram of acid, while those obtained from peat gave a comparable average of 0.65 mg per gram. He also showed that the acid used in the test is important. High chloride concentrations interfere when  $H_2SO_4$  is used; Wilson considered more than 300 ppm chloride detrimental. Roberts (31) recommended the use of phosphoric acid to overcome chloride interference when  $H_2SO_4$  is used. Also, if inorganic reducing agents are present, compensation for these must be made. The oxygen demand of fulvic and humic acids in natural waters increases with increasing molecular complexity. The interference of the reductant nitrite is eliminated, according to Subrahmanyam et al. (32), by the addition of sulphamic acid. Urea may also be used to overcome nitrite interference, but is said to be not as efficient as sulfamic acid, especially when phosphoric acid is used.

Experimental

A number of natural waters varying from 0 to 30 Hazen colour units were measured by the oxygen consumption test as well as by other means. The results are shown in Table 5. Many other oxygen consumption tests on natural waters of varying colour have been carried out over a period of several years.

Discussion

Table 5 shows--and this is confirmed by other studies--that there is little correlation between the visible colour and the oxygen consumption. As a measurement of colour the permanganate test is not completely reliable; this is expected, since its use is based on the premises that colour is caused by organic matter of the same reducing power and that no other reducing or oxidizing matter, such as colourless organic or inorganic matter, is present.

TABLE 5  
Comparison of Various Measurements on Coloured Waters

Sample No.	Transmittance at 265 mμ (ultra-violet)		Oxygen Consumed from Permanganate (30 min. at boiling), (ppm)		Hazen Colour Units		% Fluorescence (1 ppm quinine sulphate = 100%)		pH		Total Hardness, ppm CaCO <sub>3</sub>		Turbidity (units)	
	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.	Unfilt.	Filt.
5313	97.9		8.0		0		1.4		8.3		117.3			
5434*	96.7	94.7	2.2	2.5	0	0	4.0	3.9	8.1	8.1	119	119	0	
5435*	95.0	93.6	3.1	3.2	0	0	4.3	5.0	8.1	8.1	118.8	118.8	0	
5299	90.2		3.4		10		3.7		8.0		103.6			
5330	87.1		5.4		0		3.5		8.1		62.9			
5293	84.3		5.1		10		7.1		7.8		107.6			
5295	84.0		4.8		10		5.0		7.4		153.0			
5432	83.6	84.3	3.3	3.6	0	0	5.5	6.2			109.4	109.4	0	
5297	75.0		7.0		15		5.9		6.0		10.7			
5437*	74.1	73.3	5.4	5.9	5	5	11.6	12.4	7.8	7.8	81.4	81.4		0.4
5433*	73.0	75.4	6.6	6.6	15	10	11.3	11.9	7.6	7.6	71.9	71.9	21	
5331	73.1		2.8		10		6.0		8.2		70.2			
5329	60.9		4.0		25		9.0		7.7		51.2			
5431*		59.5		8.8		20		22.1	7.8		65.8		1.5	
5436*	53.0	92.0	11.5	11.8	30	40	27.5	27.8	7.5	7.5	48.1	48.1	1.2	

\*Waters studied both before and after filtration.

The test conditions must be rigidly maintained, for a lack of uniformity in test conditions detracts from the general usefulness of the test. However, experience has shown that the test can serve a useful purpose in water analysis, because in some areas where water character is generally similar a relationship is found between colour and permanganate oxygen consumption. Also, with the same water a sudden change in the oxygen consumption indicates organic contamination. Differences in oxygen consumption in waters of similar Hazen colour may be due to differences in the nature of the colouring matter and the test may still have some usefulness in classifying waters.

In England, tests with permanganate on the same water for 3 minutes and for 60 minutes are used to differentiate between oxidizing inorganic and oxidizing organic matter. The usefulness of this modification to show pollution of Canadian waters has not yet been studied.

## MEASUREMENT OF COLOUR BY FLUORESCENCE

Measurement of the fluorescence of organic matter has been used by several workers for identification, especially of oils in water. A number of materials other than organic matter may fluoresce to varying degrees, depending on test conditions.

For some time all surface waters entering the laboratory were examined for fluorescence. All showed some fluorescence, but those of high colour fluoresced the most.

A few additional tests have since been carried out on waters from several northern lakes and elsewhere, partly to show whether there is a direct relationship between fluorescence and other methods used for determining colour or organic matter.

The tests were made with a Fisher Nefluorometer, using 1 ppm quinine sulphate as the fluorescing standard. This solution is considered to give 100% fluorescence when a mercury light source having a wavelength of 425 mμ is used; all other fluorescence units reported are related to this as per cent fluorescence.

Table 5 showed the fluorescence of some northern lake waters and Table 6, below, tabulates the fluorescence and oxygen consumption for thirteen other waters. There appears to be no definite relationship between the two methods of measurement, although generally oxygen consumption increases with the fluorescence.

TABLE 6

Fluorescence of Some Natural Waters

Water	Fluorescence, %	Oxygen Consumed from $\text{KMnO}_4$ (1 hr at boiling temp.), ppm
A	3.1	9.2
B	3.9	8.3
C	3.9	13.8
D	4.3	5.6
E	4.4	4.3
F	4.5	5.8
G	4.8	6.2
H	5.1	11.9
I	5.5	9.8
J	5.5	16.8
K	5.8	19.4
L	5.8	16.5
M	6.1	19.3

As with the ultra-violet measurement, once the relationship between fluorescence and colour, or organic matter, is known, this test may be of value to show a change in the quality of a river water. However, because different materials may fluoresce at different wavelengths, the final value at any one wavelength may mean very little.

Further work is planned on this test at other wavelengths, possibly using other fluorescing standards.

COMPARISON OF METHODS FOR MEASURING THE ORGANIC  
COLOURING MATTER IN WATER

It has been reported that the theoretical density of a coagulated surface-water was often generally proportional to the oxygen demand value and thus, in some degree, was a measure of the amount of organic colouring matter removed by coagulation. Wilson (15) reported a linear relationship between the amount of organic acids determined by ultra-violet absorption and the oxygen consumed from permanganate. Hoather and Rackham (16) found that in many waters the absorption at 275 m $\mu$  (40-mm cell) multiplied by 7 was approximately equal to the ppm oxygen consumed from permanganate.

## Experimental

Some 30 samples of surface waters from various parts of Canada were examined for absorption at 300 m $\mu$ , in a 100-mm cell, using a Beckman DU spectrophotometer. The oxygen consumed from permanganate in a boiling-water bath at 100°C for 30 minutes was also determined on all these waters.

The possible use of absorption at near ultra-violet wavelengths as a routine test was also investigated. A Lumetron filter photometer was employed, using a filter with a peak wavelength of 365 m $\mu$ , and a 15-mm cell. Several of the waters studied in the DU spectrophotometer were re-examined; these waters were first hydrogen ion-exchanged to eliminate heavy metal interference, turbidity, and possible pH effects.

Waters from several small lakes, under study with regard to different in-situ colours, were also examined by the oxygen-consumption, ultra-violet absorption and fluorescence methods.

## Discussion

Figure 8 shows the relationship between the absorbance at 300 m $\mu$  and the oxygen consumption for the 30 waters. Despite the relatively poor reproducibility of the permanganate test, these points are reasonably close to a straight line up to 10-11 ppm oxygen consumption. Above this point the oxygen consumption test appears to become less reliable. No allowance was made in this curve for interference by nitrate, because most of these samples contained very little or no nitrate. The apparent oxygen-consumption figure shown for distilled water (average zero absorbance for three tests) should be noted.

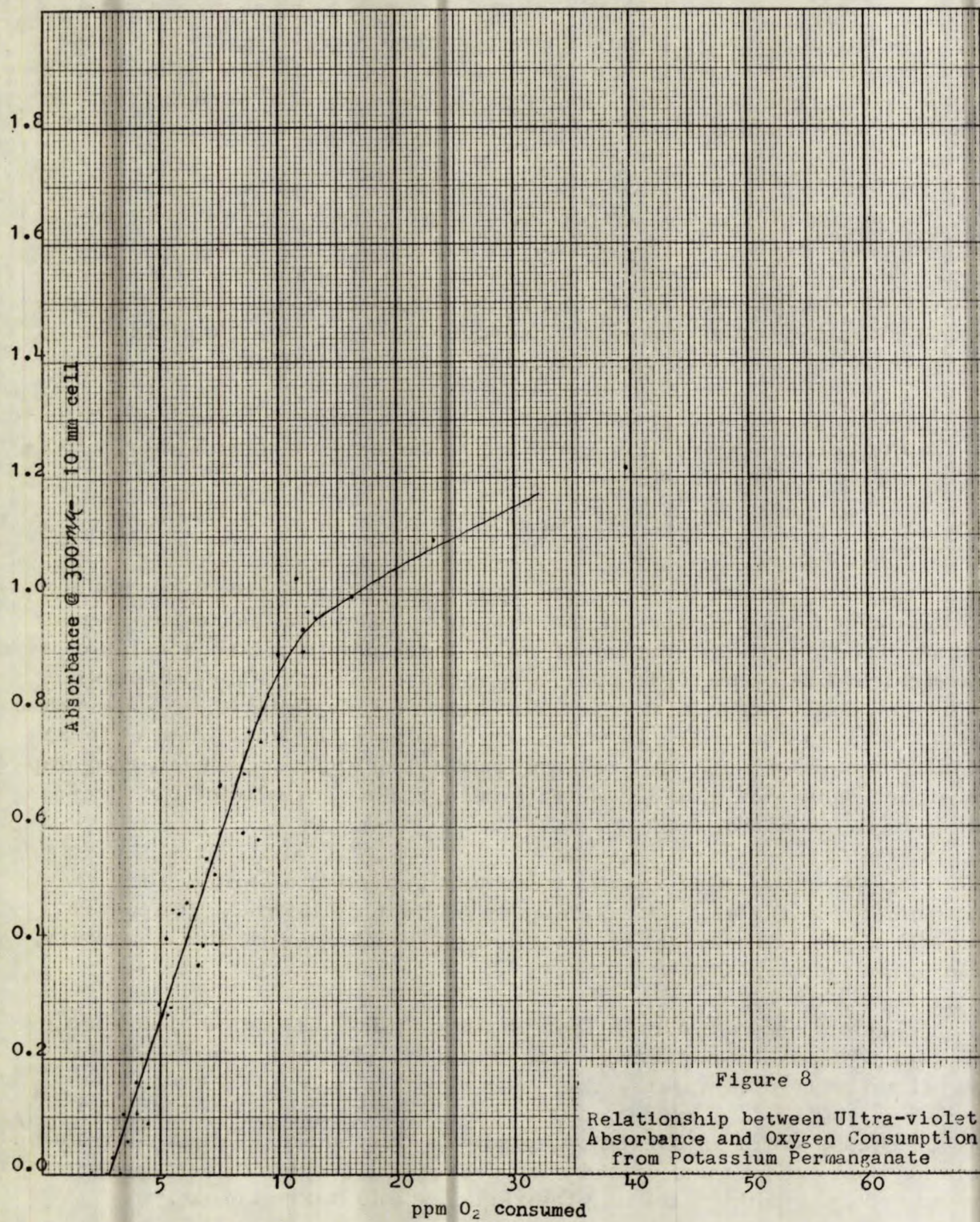
Somewhat similar results were obtained using a simple filter spectrophotometer at the near ultra-violet wavelength of 365 m $\mu$ . It appears that such a procedure might be feasible as a routine test in the laboratory, for organic matter.

Table 5 shows a comparison of ultra-violet absorption at 265 m $\mu$ , fluorescence, oxygen consumed, Hazen colour, pH and hardness for the several northern lake waters.

When a set of unfiltered samples was first studied, little correlation could be seen except that, at 265 m $\mu$ , decreasing transmittance appears to coincide roughly with increasing fluorescence and Hazen colour.

Filtered and unfiltered lake waters (Table 5, marked with asterisk) bear a definite relationship to each other, although exceptions are noted.







Fluorescence, Hazen colour, and oxygen consumption decrease with increasing transmission at 265 m $\mu$ ; however, the differences are not proportional. On the basis of these results, the ultra-violet absorption test is probably simpler and more satisfactory, for measuring organic colouring matter, than the oxygen consumption test, because it is less influenced by such factors as time and temperature.

## SUMMARY

The rather extensive preliminary studies and the brief literature review presented in this report confirm that the common methods of measuring colour and organic matter--i.e., by fluorescence, oxygen consumption from permanganate, and adsorption of visible or ultra-violet light--all have their limitations.

Measurement of the transmission or absorption of a buffered water at a definite wavelength of 425 m $\mu$  is preferable to using the Hazen colour scale.

Oxygen consumption from permanganate, and ultra-violet absorption, can be used to measure colour only when it is assumed that all colour is caused by organic matter of the same type and that other reductants are not present. As a means of measuring organic matter (colour), ultra-violet absorption is better than the oxygen consumption test, because it is not affected by testing conditions such as time and temperature.

The usefulness of fluorescence as means of measuring organic colouring matter in water needs further study.

It is evident that once the significance of any of these tests is known, any of the procedures can be used to indicate changing conditions in a river. Any direct comparison between rivers must be made with caution, however, because of the presence of interfering substances, differences in nature of organic matter, and other factors.

Additional studies are required to support the theory that differences in measurements in different waters are due entirely to differences in the nature of the colouring matter.

## ACKNOWLEDGEMENT

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## REFERENCES

1. "International Standards for Drinking Water", published by World Health Organization (W.H.O.), Geneva, 1958.
2. Joseph Shapiro, "Chemical and Biological Studies on the Yellow Organic Acids of Lake Water", *Limnology and Oceanography* 2:161 (1957).
3. John Ungar, "Organic Matter in Water. I: Some Preliminary Tests", Internal Report MPI 60-38, Mineral Processing Division, Mines Branch, Dept. of Mines and Technical Surveys, Ottawa, Canada, Sept. 1960, p. 5.
4. G. Thiessen and C.J. Engelder, "Isolation of the Humic Acids", *Ind. Eng. Chem.* 22, 1131 (1930).
5. F.E. Hale, "The relation between aluminum sulfate and colour in mechanical filtration", *Ind. Eng. Chem.* 6 (No. 8), 632 (1914).
6. G. van Beneden, "Sur le comportement des matières humiques dans les eaux - Étude de flocculation des acides humiques dans les eaux de Fagnes (Study of flocculation of humic acids in Fagnes water), Part I"; *Bull. Trim. CEBEDEAU*, No. 28, p. 118 (1955).
7. *Ibid.*, Part II; *Bull. Trim. CEBEDEAU*, No. 33, p. 173 (1956).
8. A. Berg, "Analyse des conditions impropres au développement de la jacinthe d'eau dans certaines rivières de la cuvette congolaise" (Analysis of conditions unfavourable for the development of the water hyacinth in certain rivers in the Congo basin), *Bull. Trim. CEBEDEAU*, No. 47, p. 28 (1960).
9. H.E. Freytag, "Absorptionsphotometrische Änderungen der Huminstoffe in Verlaufe des Wurzelabbaues" (Absorptiometric changes of humic matter in the course of root degeneration), *Z. Pflanzenern. Dung. Bodenkunde* 71 (No. 1), 67 (1955).
10. American Public Health Assn. and American Water Works Assn., "Standard Methods for the Examination of Water, Sewage and Industrial Wastes" 10th edn. (1955), Am. Public Health Assn. Inc., New York.
11. A.T. Palin, "Photometric determination of color and turbidity in water", *Water and Sewage Works*, 104 (No. 11), 492 (1957).
12. A.M. Buswell and E.C. Dunlop, "Present status of tests for organic pollution loads", *J. Am. Water Works Assn.* 34, 1063 (1942).

13. W. Fuchs and E. Kohler, "Über die quantitative Bestimmung der wasserlöslichen Huminsäuren und ihre Entfernung aus Kesselspeisewasser" (The quantitative estimation of water-soluble humic acids and their removal from boiler feedwaters), Mitt. VGB 47, 107 (1957).
14. A.L. Wilson, "Determination of fulvic acids in water", J. Appl. Chem. 9, 501 (1959).
15. A.L. Wilson, "Organic fouling of strongly basic anion exchange resins", J. App. Chem. 9, 352 (1959).
16. R.C. Hoather and R.F. Rackham, "Oxidised nitrogen in waters and sewage effluents observed by ultra-violet spectrophotometry", Analyst 84, 548 (1959).
17. J.F.J. Thomas, "Studies on the Colouration and Chemical Quality of Some Lake Waters in the Shabuskwia-Badesdawa-Miminiska Lake Areas of Northern Ontario in 1960-61", Mines Branch Investigation Report IR 62-44, Dept. of Mines and Technical Surveys, Ottawa, Canada, 1962.
18. B.A. Southgate, "Treatment and disposal of industrial waste water" (1st edn., 1948), H.M. Stationery Office, London.
19. The Institution of Water Engineers, "Approved methods for the physical and chemical examination of water" (revised edn., 1953), The Inst. of Water Engrs., London.
20. G. Gad and M. Knetsch, "The chemical analysis of water, using minimum quantities", Ges. Ing. 70, 259 (1949).
21. H. Lecoq, "La c rim trie appliqu e   l'analyse des eaux" (Cerimetry applied to water analysis), Chim. Anal. 39, 232 (1957).
22. Am. Society for Testing and Materials, "Manual on industrial water" (2nd printing - 1954), ASTM Special Technical Publication No. 148-A, ASTM, Philadelphia.
23. H.A. Faber, "Chlorine consumed tests for pollution", J. Am. Water Works Assn. 34, 746 (1942).
24. E. Windle-Taylor, "The Examination of waters and water supplies" (Thresh, Beale and Suckling), 7th Edn. (1958), J. and A. Churchill Ltd., London.
25. Industriele Naatschappij Activit N.V., "Humic acid removal with new Asmit 259", Amsterdam, Netherlands, 1958.

26. A. Käss and H. Keukircher, "Neues zur Methodik der Wasseruntersuchung" (New methods in water analysis), Vom. Wasser 24, 134 (1957).
27. J. Hissel, "Relations entre fer et matières humiques dans les eaux des Hautes Fagnes" (Relation between iron and humic matter in Hautes Fagnes water), Bull. Trim. CEBEDEAU, No. 28, p. 127 (1955).
28. Permutit A.-G., "Permutit Taschenbuch" (Permutit Handbook), 6th Edn. (1953), Berlin.
29. J. Ungar, private notes (unpublished).
30. A.L. Wilson, "Determination of organic matter in water by oxidation with potassium permanganate", J. Appl. Chem. 9, 510 (1959).
31. R.F. Roberts, "Oxygen absorbed from acid permanganate in the presence of chloride", Analyst 80, 517 (1955).
32. P.V.R. Subrahmanyam, C.A. Sastry, and S.C. Pillai, "Determination of permanganate value for waters and sewage effluent containing nitrite", Analyst 84, 731 (1959).

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