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MEMORANDUM REPORT

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SUMMARY

Experimental data were obtained on the distribution coefficients of technical xylidines for the system gasoline-water. The distribution coefficient is defined as the ratio of the concentration of xylidines in the gasoline layer to that in the water layer. The data may be used to estimate the maximum loss of xylidines from the fuel layer in water-displacement storage systems. The gasoline-water distribution coefficients for xylidines in three different fuels (grade 65 aromatic free, grade 65 as received plus 15 percent of an aromatic mixture, and grade 130) were determined. The effects of concentration of xylidines in the fuel, aromaticity of the fuel, sea water instead of fresh water, and temperature were investigated. The variation in the loss of xylidines from gasoline stored over water is discussed in terms of the distribution coefficients.

The results are summarized in the following table:

Temperature (°F)	Xylidines (percent)	Fresh-water extraction			
		Grade 65, aromatic-free		Grade 130	
		K_{wt}	K_{vol}	K_{wt}	K_{vol}
40	1.0	12	8.5	19	13
	3.0	15	10.5	22	15
100	1.0	24	17.0	36	25
	3.0	26	18.0	37	26

The distribution coefficient K increased with the addition of about 18 percent aromatics to the aromatic-free fuel to values comparable with these for grade 130 fuel. The use of sea water instead of fresh water also increased the distribution coefficient.

INTRODUCTION

When gasoline containing xylidines is stored over water, a certain amount of xylidines is extracted from the fuel by the water. A mathematical expression has been derived (reference 1) from which the minimum quantity of xylidines present in the gasoline can be determined for any amount of fuel remaining in the storage tank. The solution of this equation requires a value for the distribution coefficient of the additive. The distribution coefficient is defined as the ratio of concentration of additive in the gasoline to the concentration of additive in the water.

It is the purpose of this report to present values of the distribution coefficients for technical xylidines as an additive and to investigate the variation of this coefficient with concentration of xylidines in the fuel, with temperature, with aromatic hydrocarbon content of the fuel, and with sea water instead of fresh water. The investigation was conducted at the request of the Army Air Forces at the Aircraft Engine Research Laboratory of the NACA at Cleveland, Ohio, during May and June 1943.

PREPARATION OF SAMPLES AND APPARATUS

Samples containing 1, 3, and 6 percent by weight of xylidines in gasoline were prepared and a quantity of water equal in weight to the gasoline was added. The total sample weight was approximately 50 grams. The samples were placed in a stoppered bottle and rotated on a wheel in a constant-temperature bath to attain equilibrium conditions. After adequate mixing, specimens of the water layer were taken by separating the gasoline and water phases in a separatory funnel. The water layer was analyzed spectrographically for content of xylidines.

Three different fuels were used for the determination of the coefficients:

1. Grade 65, specification AN-VV-F-756, amendment 2, from which the aromatic hydrocarbons had been removed by extraction with concentrated sulfuric acid and adsorption by silica gel.

2. Grade 65 as delivered to which was added 15 percent by volume of an aromatic mixture consisting of 5 parts xylene, 1 part toluene, and 2 parts cumene.

3. Grade 130, specification AN-F-28, amendment 1.

Grade 65 fuel as delivered contained about 3 percent of aromatic hydrocarbons, approximately 60 percent of which was toluene and 40 percent benzene. Grade 130 fuel contained about 17 percent aromatic hydrocarbons, 4 ml of tetraethyl lead per gallon, as well as inhibitor and dyes. Identical aromatic contents were found in each case by refractive-index measurements and the spectrometric method.

ANALYTICAL PROCEDURE

The water extracts of the fuels containing xylidines were analyzed by spectrophotometric methods. Two different instruments were used. The data for the grade 65 gasoline were obtained with a grating spectrograph. The data for the grade 130 fuel were obtained by the use of a Beckman quartz spectrophotometer. Data obtained with the spectrograph were checked with the spectrophotometer and were reproducible to within 5 percent of the value of the distribution coefficient given. The use of the spectrophotometer greatly enhanced the speed with which the analyses could be performed. By use of these instruments it was possible to measure quantitatively concentrations of 0.001 percent xylidines in water.

The analytical methods were fundamentally the same with both instruments. Technical xylidines, a mixture of five of the six possible xylidines, have an absorption band at about 285 millimicrons wave length (ultraviolet). The extinction of the sample contained in a quartz cell placed in the light path was compared with the extinction of a prepared standard of known concentration of xylidines and the concentration of xylidines in the sample calculated. The extinction (absorption) of light is related to the concentration of the absorbing group by the Beer-Lambert law.

It was necessary to dilute the samples to a concentration measurable with the instruments. The concentration of xylidines in the sample was then obtained by multiplying the observed result by the correct dilution factor. It was necessary to correct the observed extinction for absorption by substances other than the xylidines, which were also extracted from the fuel. This correction was measured by extracting with water a sample of the fuel containing no xylidines and applying the same correction to the other samples. Since the correction was not larger than 5 percent of the calculated extinction, the error introduced by the assumption that the correction is a constant factor was not appreciable.

CALCULATION OF THE DISTRIBUTION COEFFICIENTS

The reported distribution coefficients were calculated on a weight basis. The weight of xylidines extracted by the water was subtracted from the original weight of xylidines in the gasoline. Then the concentration of xylidines remaining in the gasoline was divided by the concentration of xylidines in the water phase to get the weight basis coefficient K_{wt}. The distribution coefficient on a volume basis K_{vol} was calculated by multiplying the weight coefficient by the relative density of the fuel and water at the same temperature.

Sample calculation. -

Original weight of xylidines in gasoline (gram)	Weight of gasoline (gram)	Weight of water (gram)	Amount of xylidines in water (percent)
0.2663	26.4	26.4	0.0326

$$\frac{26.4\ (0.0326)}{100} = 0.00861 \text{ gram xylidines extracted by water}$$

$$0.2663 - 0.00861 = 0.2577 \text{ gram xylidines remaining in gasoline}$$

$$K_{wt} = \frac{\frac{0.2577}{26.4}}{\frac{0.00861}{26.4}} = 29.9$$

$$K_{vol} = K_{wt}\left(\frac{\text{density of gasoline}}{\text{density of water}}\right)$$

$$K_{vol} = 29.9 \times 0.7$$

$$K_{vol} = 20.9$$

RESULTS

Experimental data for the distribution coefficients of xylidines in the three fuels at three temperatures are given in table I.

TABLE I

Temperature ($^{\circ}F$)	Percentage xylidines	Grade 65, aromatic free		Grade 65 as delivered plus 15 percent aromatics[1]		Grade 130	
		K_{wt}	K_{vol}	K_{wt}	K_{vol}	K_{wt}	K_{vol}
Fresh-water extractions							
40	1.0	12	8.5	20	14	19	15
	3.0	15	10.5	23	16	22	15
	6.0	20	14.0	28	20	27	19
77	1.0	20	14.0	28	20	30	21
	3.0	21	15.0	31	22	31	22
	6.0	27	19.0	37	26	37	26
100	1.0	24	17.0	33	23	36	25
	3.0	26	18.0	37	26	37	26
	6.0	31	22.0	43	30	41	29
Sea-water extractions							
40	1.0	----	----	-----	-----	21	14
	3.0	----	----	-----	-----	26	18
	6.0	----	----	-----	-----	31	21
77	1.0	27	18.0	32	22	31	21
	3.0	29	20.0	36	25	36	25
	6.0	35	24.0	40	28	42	29
100	1.0	----	----	-----	-----	37	25
	3.0	----	----	-----	-----	41	28
	6.0	----	----	-----	-----	47	32

[1] Added aromatics consisted of 5 parts xylene, 1 part toluene, 2 parts cumene.

DISCUSSION

Effect of concentration of xylidines. - The values of the distribution coefficients of xylidines increased as the concentration of xylidines in the fuel was increased. This effect is illustrated in figure 1. The distribution coefficient increased approximately 1 for each increase of 1 percent by weight of xylidines originally contained in the fuel in the range 1 to 3 percent xylidines. From 3 to 6 percent xylidines the distribution coefficient increased even more rapidly. This increase was largely independent of temperature, whether or not the fuel contained aromatic hydrocarbons and whether extracted with fresh or sea water. The curves of distribution coefficient against percentage xylidines in the gasoline can be extended as approximate straight lines at least through one-half percent by weight of xylidines.

Effect of aromatic content of fuel. - Aromatic hydrocarbons in the gasoline increased the distribution coefficients of xylidines. This effect is illustrated by the data for grade 65 fuel with no aromatics and with added aromatics (fig. 1). The addition of 18 percent by volume of aromatics to a fuel containing no aromatics increased the distribution coefficient about 7. The data for the fuel containing 18 percent aromatics were similar to the data for grade 130 fuel, which was found to contain about 17 percent by volume of aromatic hydrocarbons. The effect of aromatic constituents on the distribution coefficient was largely independent of temperature and of concentration of xylidines in the fuel.

Effect of sea water. - The use of sea water instead of fresh water as a displacing fluid increased the values of the distribution coefficients (fig. 1). The distribution coefficients were raised about 8 for a gasoline containing no aromatics and about 5 for gasolines containing 17 or 18 percent aromatics. An exception was noted in the case of 1 percent xylidines in grade 130 fuel, where the distribution coefficient was raised only 1. The effect of sea water was essentially independent of temperature.

Effect of temperature. - Figure 2 shows that the values of the distribution coefficients of xylidines increased with increase in temperature. The effect of temperature was probably the most important single effect investigated. An average temperature coefficient of the distribution coefficient was approximately 0.25 per degree F. The distribution coefficient-temperature relationship was largely independent of concentration of xylidines, aromaticity of the gasoline, or the substitution of sea water for fresh water.

Aircraft Engine Research Laboratory,
National Advisory Committee for Aeronautics,
Cleveland, Ohio, June 29, 1943.

APPENDIX - pH OF SEA WATER USED IN DETERMINATION OF GASOLINE-WATER DISTRIBUTION COEFFICIENTS

The determination of the pH value for the sample of sea water used in the tests on the solubility of xylidines presented in the present report has been made by Dr. W. T. Olson of the Fuels and Lubricants Division.

The pH of the sample of sea water was measured with both a Coleman and a Beckman pH meter. The value obtained was 8.9.

pH is defined as the negative logarithm (to the base 10) of the hydrogen-ion concentration. The pH of water is 7. Lower values of pH than 7 indicate acidity; higher values, basicity. Low pH would be expected to increase solubility of xylidines in the aqueous solution; high pH would be expected to decrease solubility of xylidines in the aqueous solution.

The grade 130 fuel described in the subject report was the same as that used in the knock tests at AERL.

Sea water contains organic material, a good portion of which is undoubtedly protein in character. If it is largely protein, the subsequent decay of such material will result in an increased basicity. Chemists at AERL agree that, if it is low in protein, the solution will tend to become more acidic. All are agreed that the determination of pH of samples of Back River water is not necessarily indicative of its original pH value. For this reason, too much importance should not be attached to the value of 8.9.

The average value of the pH of sea water as given in reference 2 was 8.13.

It will be noted that these samples were less basic than the old sample inspected, although one would normally expect less organic material in ocean water than in the Back River sample.

The pH of the sea water used in the AERL tests, 8.9, is higher than the values of pH given in the literature. This higher pH value means that the distribution coefficients with sea water are on the high side.

For general information, Back River, from which the AERL sample was taken, is a tributary of Chesapeake Bay and borders on Langley Field, Va.

REFERENCES

1. Olson, Walter T., and Tischler, Adelbert O.: Loss of Xylidines in Overwater Storage of Xylidine-Blended Fuel. NACA Memo. rep., March 18, 1944.

2. Miller, Robert C.: Observations on Hydrogen Ion Concentration and Temperature of Surface Waters of Several Seas. Proc. of the Fifth Pacific Science Congress, Canada 1933, vol. III, sec. A5, no. 24, Univ. Toronto Press, 1934, pp. 2111-2113.

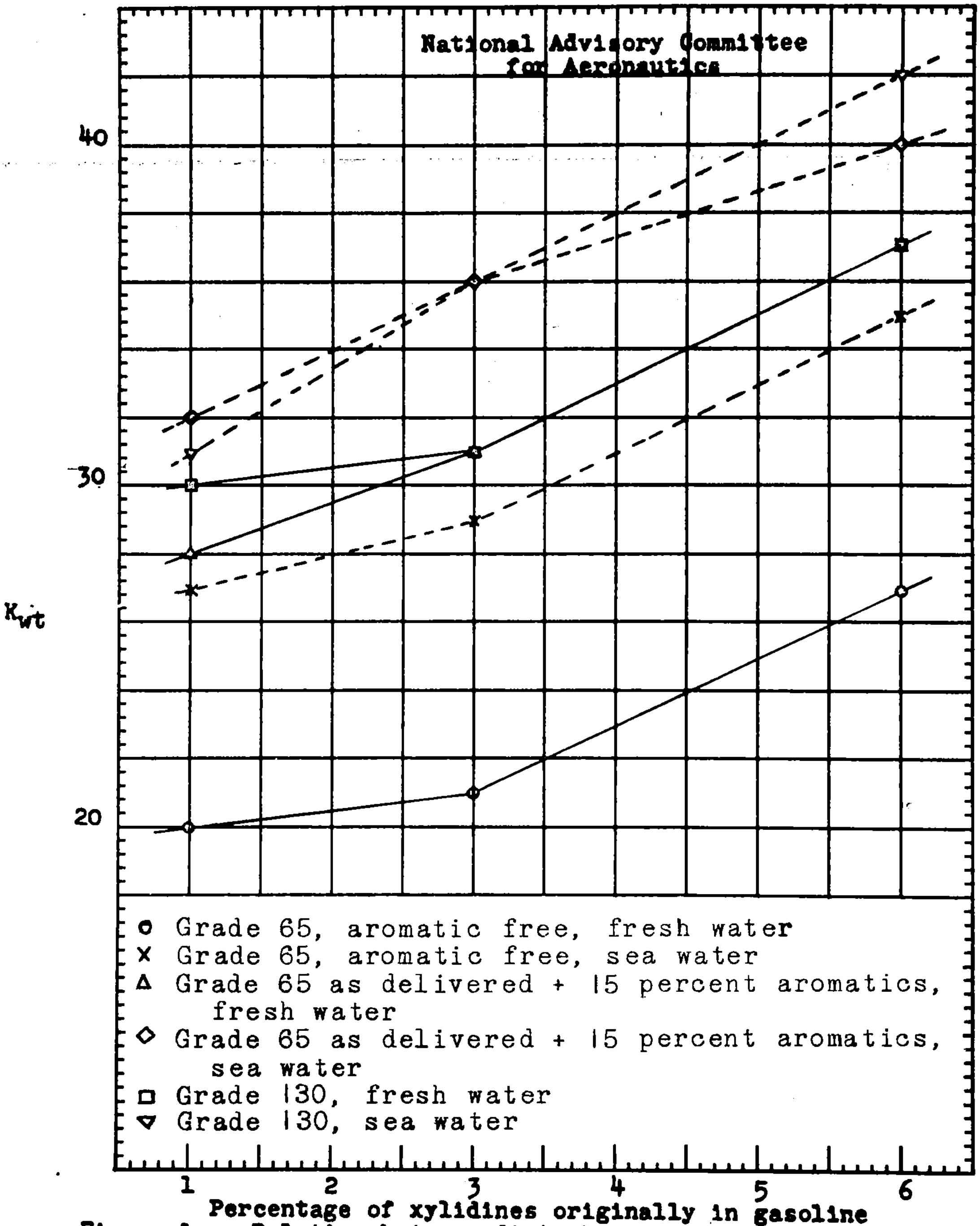

Figure 1. - Relation between distribution coefficients of xylidines and percentage of xylidines originally in gasoline for three fuels extracted with fresh water and with sea water.

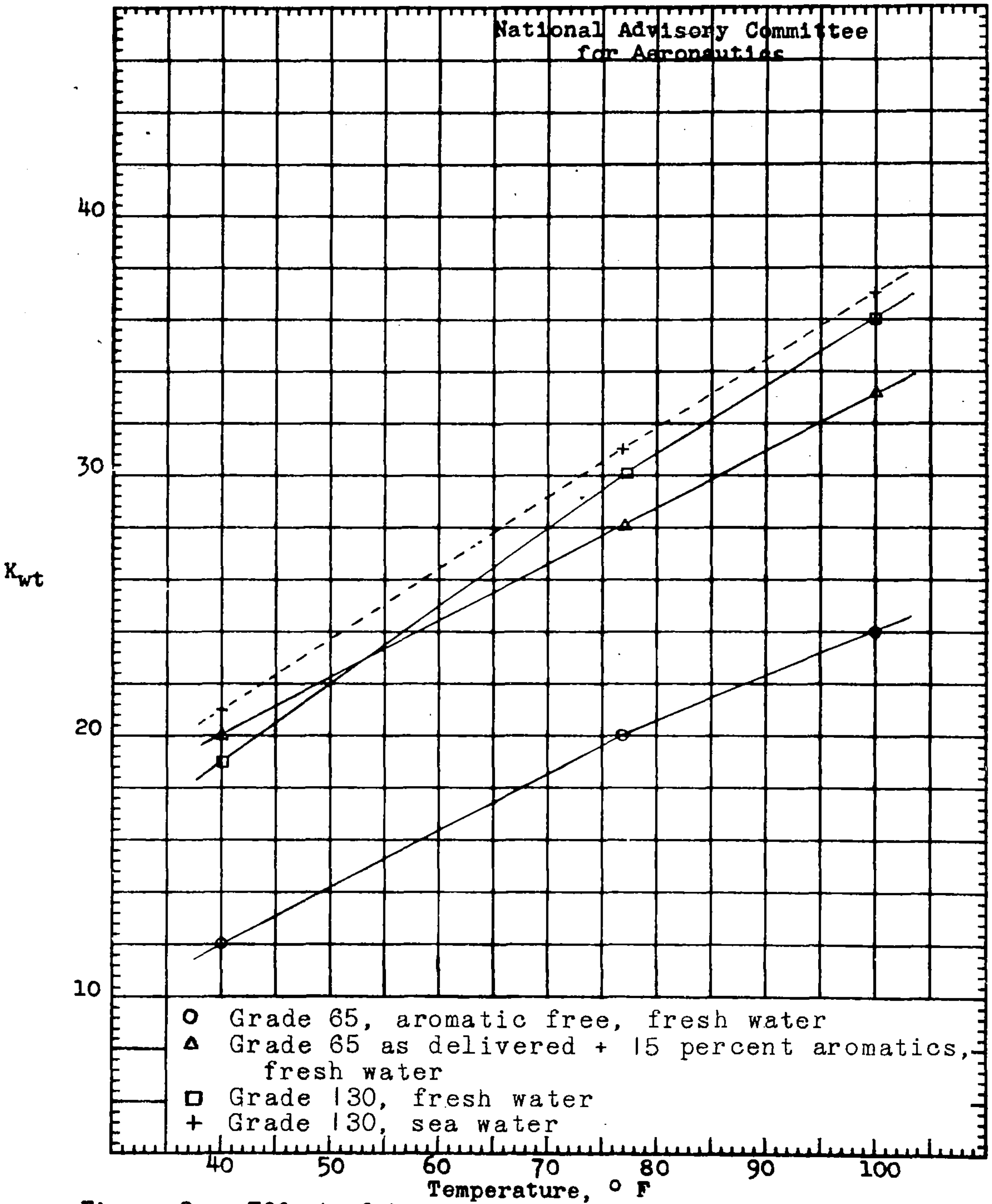

Figure 2. - Effect of temperature on distribution coefficient of xylidines for 1-percent xylidines originally in fuel.