RECORDS ADMINISTRATION
R0138644

UNCLASSIFIED

DP - 75
Copy 36 A

Chemistry-General

TIS FILE
RECORD COPY

DIELECTRIC DETERMINATION OF TRIBUTYL PHOSPHATE IN KEROSENE

by

H. M. HUBBARD
ANALYTICAL CHEMISTRY DIVISION

August 1954

~~RESTRICTED DATA~~

This ~~document contains Restricted Data as defined in the Atomic Energy Act of 1946~~. Its ~~transmittal~~ or the disclosure of its ~~contents in any manner to an unauthorized person is prohibited.~~

RECORD COPY
DO NOT RELEASE FROM FILE

RECORD COPY
DO NOT RELEASE FROM FILE

E. I. du Pont de Nemours & Co.
Explosives Department — Atomic Energy Division
Technical Division — Savannah River Laboratory

DECLASSIFIED

UNCLASSIFIED

~~CONFIDENTIAL~~

DEC[redacted]IED

UNCLASSIFIED

DP-75

CHEMISTRY-GENERAL

This document consists of 19 Pages, Number 36 of 147 Copies, Series A.

DIELECTRIC DETERMINATION OF TRIBUTYL PHOSPHATE IN KEROSENE

by

H. M. Hubbard
Analytical Chemistry Division

August 1954

Classification Cancelled or Changed
TO Declassified
By Authority of

T.D.1112 V.R. 12 no. 5, 3-15-56
Name Title Date
6-7-56

HSH 8/6/79

RESTRICTED DATA

This document contains Restricted Data as defined in the Atomic Energy Act of 1946. Its transmittal or the disclosure of its contents in any manner to an unauthorized person is prohibited.

E. I. du Pont de Nemours & Co.
Explosives Department - Atomic Energy Division
Technical Division - Savannah River Laboratory

Contract AT(07-2)-1 with the
United States Atomic Energy Commission

UNCLASSIFIED DEC[redacted]IFIED

UNCLASSIFIED DE[redacted]ED

CHEMISTRY-GENERAL

ABSTRACT

The Sargent Model V Chemical Oscillometer was applied to the dielectric constant determination of tri-n-butyl phosphate (TBP) in mixtures of TBP and kerosene over the range of 0 to 10 per cent TBP. Under the most favorable conditions, the precision approached 0.02 per cent absolute.

UNCLASSIFIED
DE[redacted]IED

UNCLASSIFIED
DECLASSIFIED

TABLE OF CONTENTS

	Page
INTRODUCTION	6
SUMMARY AND CONCLUSIONS	6
DISCUSSION	7
Equipment	7
Reagents	7
Experimental Methods	8
Investigation of Variables	9
Water Content	9
Temperature	11
Kerosene	12
Impurities	13
Application of the Method	13
BIBLIOGRAPHY	16

LIST OF FIGURES AND TABLES

Figure 1	Effect of Temperature on Oscillometer Readings	17
Figure 2	Reference Curve	18
Table I	The Effects of Impurities	19

UNCLASSIFIED
DECLASSIFIED

UNCLASSIFIED
D[redacted]ED

DIELECTRIC DETERMINATION OF TRIBUTYL PHOSPHATE IN KEROSENE

INTRODUCTION

In the course of the laboratory investigation of process conditions and for control purposes, it is necessary to determine the amount of tri-n-butyl phosphate (TBP) present in kerosene. The study reported here was undertaken to develop a method applicable to the determination of TBP in 0 to 10 per cent solutions in "Ultrasene" with a precision of ±0.1 absolute per cent. "Ultrasene" is an especially purified high-boiling kerosene produced by the Atlantic Refining Company.

The measurement of dielectric constant has been the most reliable of several physical methods which have been applied to the determination of TBP in hydrocarbon solvents. An instrument for this purpose was designed by M. T. Kelley, et al. (1). A similar dielectric constant meter, manufactured by the Paul Morrow Company of Wilmington, Delaware, was used for TBP analysis at the Savannah River Plant; however, the Morrow instrument is difficult to operate and in the range of interest it cannot be used without modification. Therefore, a readily available commercial instrument, the Sargent Model V Chemical Oscillometer, was applied to the problem.

SUMMARY AND CONCLUSIONS

The Sargent Oscillometer was used in the analysis of TBP in "Ultrasene" over the range of 0 to 10 per cent TBP. Under the most favorable conditions, the precision of the method approached 0.02 per cent absolute. The precision of the method as applied to routine samples is limited by the presence of trace impurities and by variations in the properties of the solvent. In practice the precision is expected to be 0.1 per cent absolute or better. The method can be extended to 50 per cent and perhaps to 100 per cent TBP solutions. However, difficulty in water-saturating the solutions may seriously limit the precision at the higher concentrations.

The principal variables which must be controlled are temperature, water content, and variations in the solvent. The method is satisfactory for control analyses and is in routine use at the Savannah River Laboratory.

UNCLASSIFIED
[redacted]ED

DISCUSSION

EQUIPMENT

The instrument used throughout this investigation was a Sargent Model V. Chemical Oscillometer. This instrument incorporates a cathode-coupled oscillator operating at five megacycles. Resonance methods of measuring dielectric constant are thoroughly discussed elsewhere (2) and this particular instrument is reported in the manufacturer's literature (3). The general procedure is as follows: the instrument is tuned to resonance by adjusting a series of precision condensers, when the condenser-type cell in the resonance circuit is filled with air or some other reference substance. The cell is then emptied, refilled with the material to be analyzed and the circuit is returned to resonance by adjusting the capacitance. The amount of capacitance added or subtracted to re-establish resonance is a direct measure of the change in capacitance of the cell.

The Sargent Oscillometer has an arbitrary scale covering from 0 to 32,000 units. Ordinarily, it is adjusted to read zero with air in the sample cell. Materials with higher dielectric constants give higher readings, but the scale is not exactly linear. A compensator is furnished as an attachment to provide a more nearly linear response and to expand the scale. The compensator is an inductance which, when placed in series with the cell, effectively increases the scale reading of any sample placed in the cell.

The small cells supplied with the instrument were used throughout this study. Approximately 8 ml of solution is required for a single measurement. There are considerable differences in capacitance between various cells of the same size, and measurements made with different cells cannot be compared quantitatively unless a cell correction is made.

REAGENTS

Eastman tri-n-butyl phosphate (TBP) was used throughout this investigation without additional purification. "Ultrasene", a high-boiling kerosene produced by the Atlantic Refining Company, was used as the solvent. The crude mono-n-butyl (MBP) and di-n-butyl (DBP) phosphates were synthesized in these Laboratories and were partially resolved mixtures of acid butyl phosphates. The impure MBP contained approximately 80 per cent MBP with most of the remainder DBP, and the impure DBP was approximately 70 per cent DBP with most of the remainder MBP. All other chemicals used were analytical grade reagents.

Analyses of the TBP and Kerosene follow:

ANALYSES OF COMMERCIAL TBP AND KEROSENE

	Butanol, Volume %	Water, Volume %	Acidity, Meq/l
Eastman TBP	0.10	0.48	0.3
"Ultrasene" kerosene		0.01	0.1

EXPERIMENTAL METHODS

The Oscillometer was allowed to warm up for at least one hour before use. Even after this warm-up period, considerable drift was observed in the instrument. The practical effect of this drift was eliminated by zeroing the Oscillometer before each reading, using a particular empty cell as an arbitrary reference. When the compensator was used, the standard of highest dielectric constant was placed in the cell first and the instrument was adjusted to give a maximum scale reading. All other scale readings were determined relative to this reference point.

Preliminary readings were taken on TBP-"Ultrasene" solutions both with and without the compensator. These data follow; values reported are expressed in scale units.

OSCILLOMETER SCALE READINGS ON TBP-"ULTRASENE" SOLUTIONS

TBP %	Without Compensator	Compensator	Compensator
0	1130	2950	21400
5	1300	-	24300
10	1470	4020	29900
100	6300	31800	-

Use of the compensator greatly expanded the scale, but considerably reduced the reproducibility of the scale readings. Since preliminary tests indicated that the sensitivity and reproducibility were satisfactory without the compensator, it was not used in the remainder of the investigation.

The procedure for making measurements was as follows: The sample cell was washed with acetone and allowed to dry at room temperature. Next, the sample cell was rinsed once

with a portion of the test solution and was filled with the solution. An empty cell, used as an arbitrary reference cell, was placed in the cell holder and the instrument was adjusted to resonance at zero scale reading. The reference cell was replaced with a second cell containing the sample, and the scale reading at resonance was determined and recorded. Care was taken to seat the cells firmly in the cell holder, and the level of the solution in the cell was at least 1 cm above the electrodes.

All of the known TBP-"Ultrasene" solutions were made up on a volumetric basis. The TBP was dispensed from a buret and diluted with "Ultrasene" in a volumetric flask. Changes in partial molal volume introduce no significant error. Johnson and Dillon (4) found that the partial molal volume of TBP, from 0 to 0.75 volume fraction in benzene, hexane, and several other solvents, was constant and differed only slightly from the molal volume of TBP. The molal volume of TBP at 25°C was reported by these authors to be 273.7 ml/gram mole, which compares with partial molal volumes of 273.3 in benzene and 272.6 in hexane.

Water determinations were made by Karl Fischer titration with a dead-stop end point. A dichromate oxidation procedure was used for the determination of butanol. The acidity was determined by titration to a phenolphthalein end point using a standard solution of potassium hydroxide in isopropanol.

INVESTIGATION OF VARIABLES

Water Content Since the dielectric constant of water is approximately 81 as compared to eight and two for TBP and kerosene respectively, small variations in the water content of the solution drastically affect the method. Two approaches to this problem were considered: either to dry the samples completely or to saturate them reproducibly. The saturation approach appeared to be more simple.

To verify the adequacy of the saturation approach, a series of TBP-"Ultrasene" solutions were made up covering the range of 0 to 100 per cent TBP. Measurements were made on the original untreated solutions and on additional aliquots after washing with water. The data are given in the following table. The samples were washed by shaking them for several minutes in separatory funnels with approximately equal volumes of distilled water. The phases were allowed to separate and the organic phases, which were usually cloudy with water droplets, were centrifuged before the measurements were made.

EFFECT OF WATER WASHING ON
THE DIELECTRIC CONSTANT OF TBP-"ULTRASENE" SOLUTIONS

TBP %	Oscillometer Scale Readings					
	untreated	one wash	two washes	one wash	two washes	three washes
0	1325			1323		
20	2169	2223	2223	2224	2226	
30	2660	2793	2792	2793	2793	
40	3186	3420	3419	3420	3418	
50	3758	4110	4112	4119	4120	
60	4346	4831	4860	4840	4864	4868
70	4978	5659		5653	5657	
80	5624	6486		6512	6511	6509
90	6278	7323		7377	7415	7409
100	6961	8332				

These data indicate that one water-wash will satisfactorily saturate the samples containing up to about 50 per cent TBP. Above this point. additional washes will be necessary.

Since the range of 0 to 10 per cent TBP was of particular interest, a second series of runs was made at concentrations in this range. Each solution was divided into two portions. Oscillometer readings were made on the first portion directly while the second portion was equilibrated with water for 48 hours prior to the tests. These data follow:

EFFECT OF WATER ON THE DIELECTRIC CONSTANT OF 0 TO 10 PER CENT TBP-"ULTRASENE" SOLUTIONS

TBP, %	Untreated Samples		Water Equilibrated	
	Scale Reading	H_2O, Vol. %	Scale Reading	H_2O, Vol. %
0	1325 ± 1	0.007	1325 ± 1	0.010
2	1408 ± 2	0.026	1405 ± 0	0.026
4	1487 ± 0	0.028	1486 ± 1	0.027
5	1528 ± 1	0.034	1527 ± 1	0.034
6	1571 ± 1	0.033	1571 ± 1	0.057
8	1650 ± 0	0.040	1656 ± 0	0.064
10	1737 ± 1	0.051	1745 ± 1	0.113

The scale readings are based on two measurements in the case of the untreated samples, and three in the case of the water-equilibrated samples.

The temperature of water equilibration might affect the scale reading obtained on a given sample, since the solubility of water in kerosene-TBP solutions varies with temperature. This effect was eliminated by equilibrating both sample and standard at the same temperature. The use of a comparison standard is an important part of the overall technique described in this report.

Temperature Temperature effects were determined at concentrations of 0, 5, and 10 per cent TBP. Water-washed samples were placed in a constant temperature bath and allowed to reach equilibrium. The sample cell was filled with solution at the desired temperature and allowed to stand a minute or two in order to bring the cell to the approximate temperature of the solution. The cell was refilled with solution and the measurement was made as rapidly as possible. The data follow. Temperature values are reliable to ± 0.2°C.

UNCLASSIFIED

[redacted]

THE EFFECT OF TEMPERATURE
ON
OSCILLOMETER SCALE READINGS

Temp. °C	0% TBP	5% TBP	10% TBP
19.2	-	-	1749
20.0	1328	1528	-
22.0	1322	-	-
25.0	1320	1521	1740
27.0	1318	1518	1738
30.4	1312	1509	1726

At a given concentration of TBP, the scale readings decreased with increasing temperature. These results are shown graphically in Figure 1. All three curves are essentially linear over the range 20 to 27°C with a slope of -1.5 scale units/°C which is equivalent to -0.038 per cent TBP/°C. These results were expected for two reasons. As the temperature increases, the density of the solution decreases and this effectively lowers the dielectric constant. Also, as the temperature increases, the thermal energy of the molecules increases and it becomes more difficult to align the molecular dipoles in the applied electrical field.

Kerosene One of the principal objections to the dielectric constant method and many other physical methods is that they are not specific. Variations in the properties of the solvent from lot to lot may introduce an error into this particular method. To estimate the magnitude of this error, samples of five different lots of "Ultrasene" were obtained and measurements were made on each. These data are shown in the table following. Measurements were made on the kerosene directly at 22°C and after one water wash at 25°C. The difference between the values obtained for a given sample in the two runs was due primarily to this difference in temperature. The standard deviation between lots was not changed significantly by washing and was equivalent to 0.05 per cent TBP.

UNCLASSIFIED

[redacted]

VARIATIONS IN OSCILLOMETER READINGS
WITH
DIFFERENT "ULTRASENE" LOTS

Lot #		Scale Reading 22°C (unwashed)		Scale Reading 25°C (one water wash)
A		1322		1321
B		1325		1323
C		1320		1318
D		1321		1320
E		1322		1320
	Ave.	1322	Ave.	1320.4
	Std. Dev.	1.9	Std. Dev.	2.1

The dielectric constant method might yield a different precision if applied to TBP in hydrocarbons other than "Ultrasene". The variation should be small, but would have to be determined for the specific system used.

Impurities The impurities most likely to be present in process samples are, MBP, DBP, butanol, uranyl nitrate, phosphoric acid, and nitric acid. These impurities are normally present in trace amounts and their effects were investigated at low concentration levels. The effect of phosphoric acid was not determined, but should be similar to that of nitric acid. The results are summarized in Table I. All samples were made up to contain 5 per cent TBP plus the added impurity. Four control samples which were run with the spiked samples gave a value of 5.00 ± 0.02 per cent TBP.

Traces of nitric acid, uranyl nitrate and up to about 0.2 per cent MBP were removed by a single wash with distilled water. Butanol and DBP were not completely removed by this procedure and increased the apparent concentration of TBP. One-tenth per cent of either of these impurities was approximately equivalent to 0.1 per cent TBP. If necessary, the DBP could be removed with a sodium carbonate wash.(5)

APPLICATION OF THE METHOD

Eleven standard solutions were made up and were used to determine the reference curve. Three series of determinations were run to confirm the fact that a single water-wash was

sufficient to saturate the solutions. The first series of measurements was made on the untreated solutions, and a second and third series were made after one and two water-washes respectively. The second and third series gave essentially duplicate values, and substantiated the conclusion that one wash is sufficient. These data are tabulated below, and the reference curve (solution with one wash) is shown in Figure 2. The curve is essentially linear up to 5 per cent TBP with a slope of 39 scale units/% TBP.

REFERENCE CURVE 0 TO 10% TBP-"ULTRASENE" SOLUTIONS

TBP %	Scale Reading		
	untreated	one wash	two washes
0	1323	1321	1321
1	1360	1359	1359
2	1401	1401	1398
3	1438	1439	1438
4	1478	1478	1477
5	1517	1517	1518
6	1557	1561	1561
7	1599	1604	1605
8	1642	1647	1647
9	1681	1688	1689
10	1726	1737	1737

Since the temperature coefficient is -0.038 per cent TBP per °C, day to day variations in laboratory temperature can seriously affect the results. This temperature effect can be eliminated either by thermostating the samples at a given temperature or by running a standard with the samples and correcting each measurement accordingly. The second alternative was adopted.

In summary, the routine procedure used was as follows:

1. A standard, or set of standards, was selected to be carried through the procedure for reference purposes.

2. The samples and standards were washed and centrifuged (under the same conditions to minimize differences in water content).
3. Readings were obtained by the Oscillometer. The technique used is described on page 8 (Experimental Methods).
4. A correction factor, or a set of factors, was obtained by subtracting the experimental readings for each standard from the "reference value" for the concentration of the standard, as obtained from a "reference curve". The "reference curve" used in this work is Figure 2 of this report; a similar curve should be made for a different Oscillometer, with a different kerosene solvent, or with any other special differences from so-called standard conditions.
5. The correction factor was added algebraically to the Oscillometer readings obtained on the samples, and the TBP concentrations were read from the reference curve.

This procedure was applied to a series of synthetic samples and determinations were made on two different days at appreciably different laboratory temperatures. The data are shown below:

ANALYSIS OF SYNTHETIC TBP-"ULTRASENE" SAMPLES

TBP found, per cent				
Series #1	Series #2	Average	TBP added, per cent	Deviation
1.32	1.34	1.33	1.40	-0.07
2.65	2.70	2.68	2.70	-0.02
3.78	3.74	3.76	3.75	+0.01
4.51	4.55	4.53	4.48	+0.05
5.10	5.10	5.10	5.06	+0.04
5.70	5.65	5.68	5.64	+0.04
6.51	6.51	6.51	6.46	+0.05
9.06	9.02	9.04	9.04	0.00

These results show that the method met the required precision of ±0.1 absolute per cent.

H. M. Hubbard
Analytical Chemistry Division

BIBLIOGRAPHY

1. Kelley, M. T., Thomason, P. F., Horton, A. D., and Horton, J. L. ORNL-599, Feb. 21, 1950 (Secret).

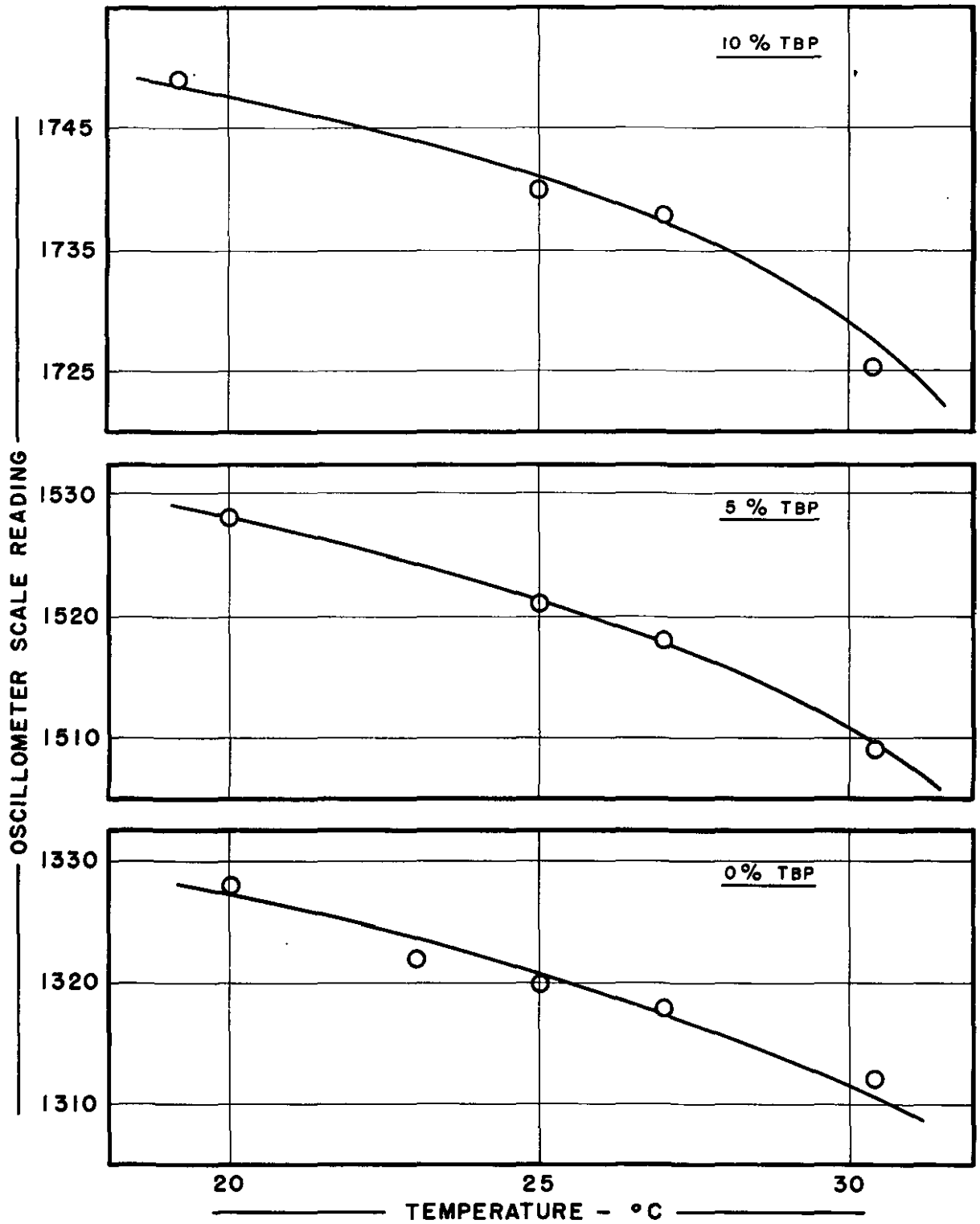
2. Weissberger, A. Physical Methods of Organic Chemistry, Part II, pp. 1630-33 (1949).

3. E. H. Sargent & Co., Scientific Methods and Apparatus. Spring Edition (1951).

4. Johnson, W. F., and Dillon, R. L. HW-29086, Sept. 7, 1953 (Secret).

5. Wagner, R. M. HW-19959, p. 29. April 15, 1951 (Secret).

UNCLASSIFIED

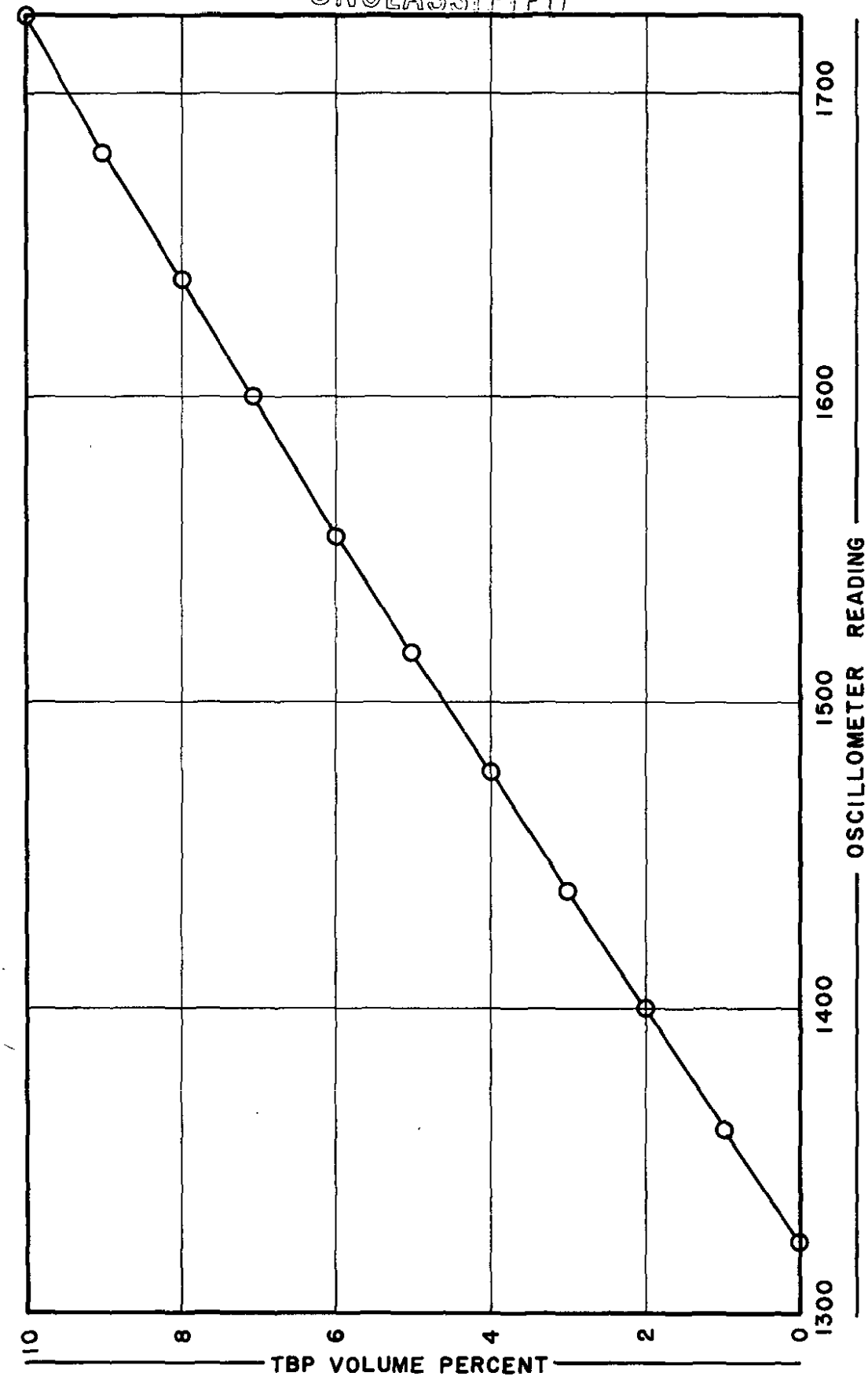


EFFECT OF TEMPERATURE ON OSCILLOMETER READINGS

UNCLASSIFIED

Figure 2

UNCLASSIFIED



REFERENCE CURVE

UNCLASSIFIED

D[redacted]
UNCLASSIFIED

TABLE I

THE EFFECTS OF IMPURITIES

Impurity	Concentration	Apparent % TBP Untreated	Apparent % TBP Washed
None	-	-	4.98
	-	-	5.04
	-	-	4.98
	-	-	5.00
Mono-n-butyl Phosphate	0.1 vol. %	5.10	5.00
	0.2	-	5.04
	0.4	-	5.11
Di-n-butyl Phosphate	0.1 vol. %	5.08	5.08
	0.2	-	5.10
	0.4	-	5.20
n-Butanol	0.1 vol. %	5.10	5.12
	0.2	-	5.19
	0.4	-	5.35
Nitric Acid	3×10^{-3}M	5.19	5.00
	6×10^{-3}	-	5.01
Uranyl Nitrate	0.017 mg U/ml	4.96	5.00
	0.034	-	5.00

UNCLASSIFIED
[redacted]