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MEASUREMENT OF THE VAPOR PRESSURE OF TBP

A. Faure
W. Davis, Jr.

OAK RIDGE NATIONAL LABORATORY
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Chemical Development Section B

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ABSTRACT

Two methods, the transpiration and direct P-32 counting methods, were tested for use in measuring the vapor pressure of TBP. With the transpiration technique, measured TBP vapor pressures were sufficiently reproducible, and probably of sufficient accuracy, to warrant improvement of the apparatus and its use in measuring the vapor pressure of TBP over various TBP-diluent-HNO_3-H_2O-$UO_2(NO_3)_2$ solutions. With this method the vapor pressure of TBP containing 0.2 wt % H_2O was determined to be $\sim 0.8\ \mu$ while that of TBP saturated with H_2O, ~ 6.5 wt % H_2O, was $\sim 0.51\ \mu$. The direct P-32 counting technique was abandoned because of experimental difficulties.

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INTRODUCTION

This report summarizes brief studies of the potential utility of two methods, the transpiration and direct P-32 beta counting methods, of measuring the vapor pressure of tributyl phosphate, TBP, over solutions such as TBP-diluent-HNO_3-H_2O-$UO_2(NO_3)_2$. These vapor pressures are needed to provide values of the activity coefficients of TBP species, which, in turn, are needed for accurate mathematical representation of the extraction of various materials by solutions of TBP in kerosene diluents. The scope of the work included vapor pressure measurements with nearly anhydrous TBP and with TBP saturated with water, which corresponds to ~50 mole % or ~6.5 wt % H_2O.

TRANSPIRATION METHOD

In this method a known volume of inert gas is saturated with vapor, which is then condensed in a cold trap. Normally the amount of condensed vapor is determined by weighing; in this study it was determined by using P-32-labeled TBP and determining the beta activity.

Apparatus

The most important part of the apparatus is the saturator, in which air is saturated with vapor. The one used here (Fig. 1) is similar to that used by Bent and Francel (1). In action, the air passes up the inner spiral, carrying slugs of liquid with it by an air-lift effect. Both air and liquid pass down the outer spiral, after which the saturated air passes out of the apparatus while the liquid recirculates.

The saturator differs from that of Bent and Francel in the following respects: (a) The liquid reservoir was modified to hold a magnetic stirrer, since it was intended to make measurements on two-phase liquid systems. At the same time, the volume of the reservoir was kept as small as possible to conserve material in measurements on pure TBP. (b) Since measurements were to be made at room temperature only, the heating coil on the outlet tube was not essential. An infrared heating lamp was used instead. (c) To minimize adsorption effects, the outlet tube was made of capillary tubing.

The air for the saturator was obtained by displacement with water from a 10-liter bottle, which had been accurately calibrated. The flow of water into this bottle was controlled by a Teflon stopcock with a needle valve adjustment. Before going to the saturator, the air was dried by passage through two U tubes in series, the first filled with Drierite and the second with P_2O_5.

The vapor was condensed from the saturated air in a spiral cooled in dry ice-trichloroethylene mixture. For runs with pure TBP, a spiral of 2 mm bore proved quite satisfactory, but with water present the narrow bore was soon blocked with ice. A 5-mm-bore spiral was then used successfully, and this is recommended for general use.

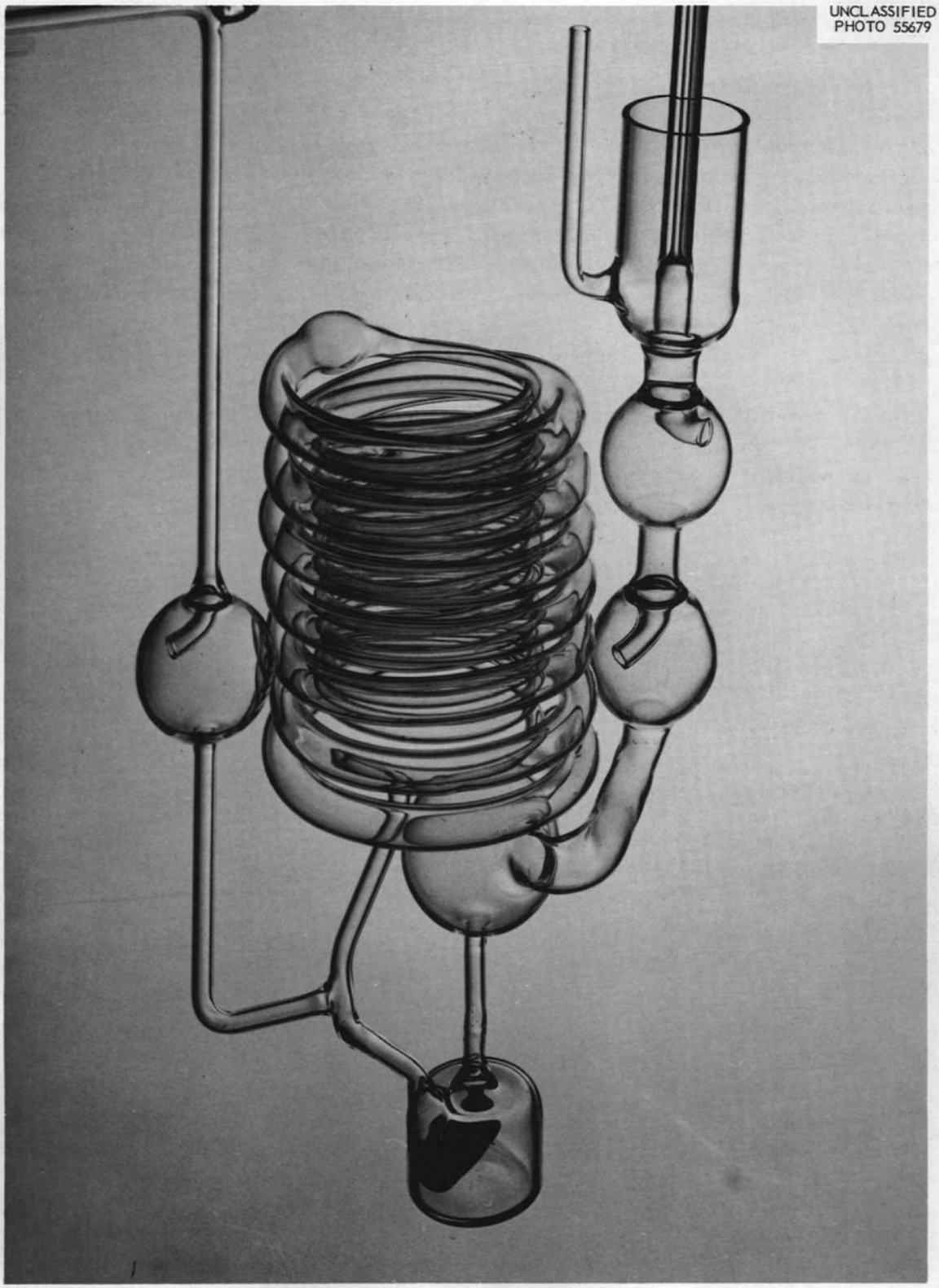

Fig. 1. Saturator with Suggested Modifications.

During use, the saturator was completely submerged in water in a 3-liter beaker. The large volume of water served to keep the temperature sensibly constant during a run, and was a satisfactory substitute for a thermostat in these experiments.

Preparation of P-32-labeled TBP

TBP was labeled by an ester exchange reaction between normal TBP and P-32-labeled phosphoric acid (2). 20 mc of P-32 was obtained from the Isotopes Division in the form of a dilute aqueous solution of H_3PO_4, total volume 0.9 ml. To this was added 0.1 ml of H_3PO_4 to act as carrier. (It is important to add this carrier before dehydration; otherwise the exchange is very inefficient.) Water was then removed by evaporation under reduced pressure (100 μ) for about 2.5 hr. To prevent bumping, the solution was initially frozen in dry ice and allowed to warm up to room temperature slowly. The vacuum system in this and subsequent operations was protected by a dry ice-trichloroethylene trap.

10 ml of redistilled TBP was added to the anhydrous H_3PO_4, and a reflux condenser was fitted. The mixture was warmed in a bath of Silicone 550 to 205-207°C for 1 hr to allow the exchange to take place. It was then allowed to cool slowly in the bath to room temperature.

The labeled TBP was transferred to a 250-ml erlenmeyer flask, the test tube being washed twice with CCl_4 and twice with water. The mixture was titrated to the phenolphthalein endpoint with 6.3 ml of normal NaOH. The phases were separated, and the aqueous phase was washed once with CCl_4, this washing being added to the organic phase. The latter was then washed once with water, and left to stand overnight to get rid of entrained water. All aqueous washings were combined, made up to 100 ml, and sent for analysis. The results showed the waste contained only 15% of the total activity, indicating that 85% of the activity was in the TBP.

The TBP solution was transferred to a falling film molecular still and the CCl_4 removed by evaporation under reduced pressure at room temperature. During this stage the still was mounted in a vertical position, instead of the normal horizontal position, to prevent losses by splashing and bumping. A further 5 ml of redistilled normal TBP was added, and the still was changed over to the horizontal, or normal, position for distillation.

On distillation, the first drop came over at 65°C at 100 μ pressure. The first 6 drops were discarded. Collection started at 67°C and was continued until the still was almost dry. At this point the thermometer indicated 80°C and the pressure was 50 μ. The temperature at this point was probably not a true indication of liquid temperature since the thermometer was no longer immersed. The product was water white.

Before use in the transpiration experiments the labeled TBP was diluted with redistilled TBP until its activity was ~70 μc/ml. At the end of these experiments the activity had decayed to ~30 μc/ml.

Experimental

Some preliminary tests were carried out with the saturator to be sure that it worked as anticipated. It soon became clear that, for proper operation, the quantity of liquid was fairly critical, especially with TBP. With water, any quantity between 10 and 17 g was satisfactory, while with TBP, 16 g appeared to be the optimum amount. With the mixture, 15 g of water plus 1.5 g of TBP worked well, with both phases circulating through the spirals.

In preparation for a run, grease from the previous run was removed from the female ground glass joint of the saturator, by a pipe cleaner moistened with acetone while a constant stream of air was flowing through the saturator. The apparatus was then left to equilibrate for 0.25 to 0.5 hr under an infrared lamp and with air flowing. The spiral collector was washed out with acetone, and dried with a stream of air. Inactive TBP was then added to the spiral so as to wet the walls thoroughly. The object of this was to facilitate washing out the small amount of active TBP, 100 μg or less, which would be collected during the run. In the 2-mm-bore spiral this was done by pipetting 25 λ of TBP into the spiral. In the 5-mm-bore spiral, approximately 3/4 ml of TBP was added, and run completely through the spiral so as to wet the walls thoroughly; the excess was drained out, leaving less than 100 mg of TBP behind. The weight of TBP was obtained by weighing the spiral before and after treatment. The Dewar flask was filled with the dry ice-trichloroethylene mush used to cool the spiral. Air and water temperatures were noted, and, occasionally, barometric pressure. When all other preparations were complete, the 10-liter bottle was emptied. Before the last 50 to 100 ml was emptied out, the bottle was shaken thoroughly to saturate the air with water vapor. The run was then started and the flow rate adjusted.

In general, the average flow rate during a run could be determined accurately by noting the volume change during a measured time. For overnight runs the flow rate was estimated by noting the rate at which the water was running in at the start of the run.

At the end of the run, the spiral was removed and allowed to warm up to room temperature. TBP was washed out of the 2-mm spiral into a 10-ml beaker by flowing about 5 ml of acetone slowly through the spiral in a reverse direction. This technique did not work with the 5-mm spiral, which was washed out four times with roughly 1.5 ml portions of acetone, the spiral being rotated about its axis in such a way as to ensure complete coverage of the walls. Sufficient inactive TBP was then added to bring the total weight of TBP to 90-100 mg. After evaporation of the acetone at room temperature, the TBP was transferred to a counting dish, the beaker being washed twice with small amounts of acetone. The acetone was again allowed to evaporate at room temperature, after which the dish was mounted on a plate, covered with Mylar film, and inserted in the lead shield for counting.

The counter used was a halogen-quenched end-window G. M. tube with a conventional decade scaler. A standard uranium source was used to check it periodically, but there was never any variation in counting efficiency greater than normal statistical fluctuations.

In evolving a suitable counting technique, flat-bottomed porcelain dishes were used initially, but the results were rather variable, probably because the TBP was not distributed evenly over the bottom of the dish. A change was then made to small watch glasses, in which the TBP would largely accumulate in a pool at the bottom. The watch glasses seemed to work better, and were used in all experiments reported here.

The counter was standardized against a 500-fold dilution by weight, with normal TBP as the diluent, of the labeled TBP used in these experiments. 100-λ aliquots were pipetted into the counting dishes, but since measurement of small volumes is inaccurate, the amount of TBP, 90-100 mg, was determined by weight. Variations in self-absorption due to weight variations within these limits are insignificant. In order to simulate experimental conditions as closely as possible, acetone was added to the TBP in the counting dish and allowed to evaporate before the sample was counted.

In all cases the background count was first determined with the empty dish mounted in the lead shield. Background was 40 c/m. Samples from the runs had counting rates in the range 600 to 1100 c/m. The counting rate for a 100-λ aliquot of the 500-fold dilution was about 2600 c/m. In all cases the sample was counted for 20 min.

After determinations on pure TBP had been completed, a sample of the labeled TBP from the saturator was sent for analysis. It was found to contain 0.2% water.

In some runs with TBP plus water, the collector was weighed before and after the run. Since the condensate was almost entirely water, the difference in weight could be used to calculate the vapor pressure of water.

Results

All activity measurements were corrected for background and for decay of P-32 in the usual manner, assuming a half-life of 14.3 days for P-32. No correction was applied for counter dead time. Measurements on the 500-fold dilution gave the specific counting rate of the labeled TBP, which was then used to calculate the weight of TBP collected in the runs.

For runs with pure TBP, the volume of air was calculated from the equation

$$V = V_o \times \frac{T_{air}}{T_{TBP}} \times \frac{P - p}{P}$$

where V_o = volume of bottle;

T_{air} = air temperature at start of run, °K;

T_{TBP} = temperature of water bath in which saturator was immersed, °K;

P = barometric pressure (assumed to be 740 mm Hg for runs in which it was not measured);

p = vapor pressure of water at T_{TBP}, mm Hg.

For runs with TBP plus water

$$V = V_o \times \frac{T_{air}}{T_{TBP}}$$

The vapor pressure of TBP was calculated from the equation

$$p_{TBP} = \frac{W}{266} \times \frac{62.36}{V} \times T_{TBP}$$

where

p_{TBP} = vapor pressure, mm Hg;

W = weight of TBP collected;

molec. wt of TBP = 266 g/mole;

gas constant = 62.36 liter mm Hg/mole °K.

The vapor pressure of water was calculated from

$$p_{H_2O} = \frac{W_{H_2O}}{18} \times \frac{62.36}{V} \times T_{TBP}$$

where

p_{H_2O} = water vapor pressure, mm Hg;

W_{H_2O} = weight of water.

The results obtained with TBP containing 0.2% water and with a mixture of water and TBP are given in Tables 1 and 2, respectively.

The vapor pressure of TBP over the two-phase system (Table 2) seems to be much more reproducible than the results with nearly dry TBP (Table 1). In part this may be due to improvement in technique with practice. Agreement with accepted values for water (Table 2) is considered satisfactory since the saturator was not thermostatted and the thermometer used for temperature measurement had not been calibrated.

The vapor pressure of dry TBP does not agree with the value derived from an equation given in the literature (4), viz. 6.7 μ at 25°C. However, the equation is based on data obtained at 150°C and above; hence a considerable extrapolation is involved.

Table 1. Vapor Pressure of TBP over TBP Containing 0.2 wt % H_2O

Temp, °C	Approximate Air Flow Rate, liters/hr	TBP Vapor Pressure, μ Hg
25.5	0.4	0.802
25.1	0.75	0.774
25	1.75	0.817
25.8	2.25	0.566

Table 2. Vapor Pressures of TBP and H_2O over Two-phase TBP-H_2O Solutions

Temp, °C	Approximate Air Flow Rate, liters/hr	TBP Vapor Pressure, μ Hg	Vapor Pressure of H_2O, mm Hg	
			Experimental	From Lit. (3)
26.2	0.75	0.509	---	---
26.0	1	0.512	24.9	25.2
26.1	1	0.513	24.8	25.4
26.0	2	0.515	---	---
26.0	2.25	0.467	24.0	25.2

At flow rates of 2 liters/hr and above, the results tend to be low, probably owing to incomplete saturation of the air.

Recommendations for Future Work

1. In order to take advantage of the potential accuracy of the method, the saturator should be immersed in a thermostat controlled to better than ±0.1°C.

2. A presaturator, run 10 to 20°C above thermostat temperature, as recommended by Redemann et al. (5), would make higher flow rates practicable.

3. The use of TBP of slightly higher activity would improve the statistical accuracy of counting.

4. A rotameter would be of assistance in adjusting flow rates. A constant-head device would make a constant flow rate throughout a run feasible. The Teflon stopcock used to adjust the flow of water is not very satisfactory, as the setting of the needle valve is erratic.

5. Various modifications to the saturator are indicated: (a) A bulb on the inlet tube would eliminate any possibility of sucking active TBP back into the drying train. This can happen when the 10-liter bottle is opened at the end of a run unless precautions are taken. (b) The bulb at the bottom of the outer spiral is too low, so that it fills up when liquid from the spirals drains down when the air flow stops. In starting up, air has to bubble through the liquid to escape, and this may cause spray to be carried over to the spiral collector. A larger bulb, slightly higher, would prevent this. (c) For working with unsaturated solutions (say, TBP in water), the reservoir should be much larger to minimize changes in composition during a run. Provided the geometry of the upper part of the apparatus is not altered, there does not seem to be any limit on the size of the reservoir. (d) Heating the outlet tube with a resistance wire would probably be more satisfactory than the infrared lamp. (e) The ground glass joint used to connect the saturator and condenser was rather awkward in use. A small spherical ground glass joint might prove more convenient.

6. The counting technique could probably be improved. The chief defect of the present system is the limited volume of the counting dish, which easily leads to loss of TBP.

GAS-PHASE ACTIVITY METHOD

Attempts have previously been made by Davis and Hill (6) and by Hill, Jenkins, and Whitmarsh (7) to measure the vapor pressure of TBP by determining the beta activity of the P-32-labeled TBP gas phase. In their apparatus, air was first displaced with a stream of nitrogen; the apparatus was then sealed and allowed to reach equilibrium. However, in use a series of steadily increasing readings was obtained, which never reached an equilibrium value.

In order to speed up the attainment of equilibrium, the apparatus was redesigned to work under reduced pressure. In the modified version, air was pumped out with a vacuum system instead of being displaced with nitrogen. Work with this apparatus is described below.

Experimental

The electronic equipment was the same as in previous work here (6,7). The hot box was also the same, but had been modified by the addition of a temperature control unit.

In this section activities are given in counts per minute. Corrections have been applied: (a) for background, by subtracting 230 c/m from the reading obtained; (this background is rather higher than would be expected because of stray radiation from active TBP stored in the hood, etc.); (b) for decay of P-32.

When the first readings were taken after labeled TBP had been added to the apparatus, a surprisingly high count was obtained at room temperature (where the activity of TBP vapor should be negligibly low). At first this was thought to be due to condensation of TBP around the G. M. tube well. When the lower part of the apparatus was cooled in dry ice, in order to condense all TBP into this section, the residual activity was still 2700 c/m. For convenience, this is called the "dry ice" count. In later readings the back-scattering and bremsstrahlung from the liquid phase gave a count of only 130; hence it appears that the "dry ice" activity must be due mainly to TBP adsorbed on the well in which the G.M. tube was located and on the inner wall of the gas phase chamber.

The amount of TBP adsorbed depends on the temperature difference between the liquid TBP and the adsorbing surface. This was shown experimentally by immersing the lower half of the apparatus in a water bath, in which the temperature was varied, the upper part of the apparatus containing the G.M. tube being at room temperature. The results are shown in Table 3.

Although no satisfactory method of correcting for adsorption was worked out, it is clear that it would be necessary to know accurately the temperature differential between the G.M. tube and the liquid phase. In the present apparatus, the upper thermocouple well is so placed that it does not indicate the mean temperature of the well containing the G.M. tube. The lower thermocouple well would presumably give the temperature of the liquid phase accurately if it were immersed, but in order to conserve labeled TBP, only a few milliliters was used in each experiment. Under these conditions serious errors in temperature measurement could arise, as shown in Table 4. These readings were taken by immersing the lower part of the apparatus in a water bath of known temperature and reading the thermocouple.

Table 3. Activity of Adsorbed TBP at Different Liquid TBP Temperatures

Temp of TBP, °C	Temp of G.M. Tube, °C	Activity, c/m
-78 (dry ice)	~25	1950
0	~25	2900
20	26	3700
23	26	5500

Table 4. Errors in Readings of Bottom Thermocouple

Water Bath Temp, °C	Thermocouple Reading, °C
23.2	24.5
20.8	22.8
11	16.5
0.5	15

These results showed that modifications to the apparatus were necessary before any attempt to correct for adsorption could be made, and also in order to know the temperature at which the vapor pressure was being measured. Correction for adsorption would be difficult, since even under nominally identical conditions with pure TBP, the "dry ice" count varied from 1000 to 2700 c/m. It was therefore decided not to continue work on this method.

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