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Identifying purity of the synthesized 1,1,1-trichloro-3-methyl-3-phospholene by four methods including the conductance titration, potentiometric titration, differential potentiometric and UV spectrophotometer

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Abstract: The purity of 1,1,1-trichloro-3-methyl-3-phospholene (TCMP) is considered important in its reaction with methanol for the preparation of 1-methoxy-3-methyl-2-phospholene oxide (MMPO) as an flame retardant. Additionally, in the kinetics studies of the reaction between TCMP and methanol it was highly necessary to identify the purity of the prepared TCMP for obtaining meaningful kinetic parameters. For this purpose, the experimental procedure, based upon the approach detailed in coleman's work, was used for the synthesis of TCMP. This work surveys the methods of analysis used for identifying purity of the synthesized TCMP. These procedures involve conductance titration, potentiometric titration, differential potentiometric and UV spectrophotometer methods. The conductance titration experiments for the measurement of HCl generated in the reaction between TCMP and water showed that the end point was overestimated due to interference. But, the results obtained from the UV spectrophotometer, potentiometric and differential titration experiments were much more reliable and also a good demonstration of the high purity of the prepared TCMP.

Keywords: Purity, Flame retardant, Conductance titration, Potentiometric titration, Differential potentiometric.

Introduction

In his patents of 1953, McCormack reported the synthesis and characterisation of seventeen products [1], based on a five-membered heterocycle containing one phosphorus atom, The products, properly referred to as phospholene oxides, represented a new class of heterocyclic system. Previously reported syntheses of the 1,1,1-trichloro-3-methyl-3-phospholene (TCMP) intermediate that is the compound necessary for preparation 1-methoxy-3-methyl-2-phospholene oxide (MMPO) took 20 days [2,3], or even longer [4,5].

Extensive work has been reported on the synthesis and properties of phospholene oxides [6-8], as flame retardant, formed from the reaction of methylphosphorous dichloride or phenylphosphorous dichloride with 1,3-butadiene and isoprene (2-methyl-1,3-butadiene). In Coleman's work it was decided to take a different synthetic approach [9]. A slight, but significant change to the starting materials mentioned above and also to the reaction temperature reduced the required reaction time from 20 days to 20 hours [2,3]. Replacing the expensive alkylphosphorous dihalide (RPX_2) with the more hazardous but cheaper phosphorous trihalide (PX_3) and then reacting the unstable 1,1,1-trichloro-3-methyl-3-phospholene (TCMP) intermediate with an alcohol produced the so called phospholene oxide esters. To identify the kinetic parameters of the rapid initial reaction of this intermediate (1,1,1-trichloro-3-methyl-3-phospholene) with CH_3OH using the stopped-flow apparatus, it was first necessary to synthesize sufficient quantities of 1,1,1-trichloro-3-methyl-3-phospholene [9]. For this purpose, the experimental procedure, based upon the approach detailed in Coleman's work, was used for the synthesis of TCMP [9]. As noted, the kinetic

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parameters were found to be strongly affected by small amounts of impurities, thus it was necessary to identify the purity of the prepared TCMP before it was employed in an experimental kinetics investigation. The methods of analysis used for this purpose involved conductance titration, potentiometric titration, differential potentiometric and UV spectrophotometer methods.

Experimental

Apparatus and Chemicals:

The UV spectrophotometer model used was a Hewlett Packard (vectra 286/12). The Conductance titration (Portland electronics conductivity meter model P310), Potentiometric titration (Digital potentiometer recorder with a Silver electrode as an indicator electrode and a calomel electrode as a reference electrode) and differential potentiometric (Digital potentiometer with two identical silver electrodes as indicator electrodes) apparatuses are schematically depicted in Figs. 2, 7. and 9, respectively.

All chemicals used were of analytical reagent grade and solutions were prepared using deionised water. 1,1,1-trichloro-3-methyl-3-phospholene (TCMP) was synthesized using the approach detailed in Coleman's work [9], HCl and NaOH (99.99%) were obtained from Merck and Aldrich, respectively. Standardization of HCl was performed using a secondary standard solution of 0.264 M NaOH. Standardization of the sodium hydroxide solution was performed against potassium hydrogen phthalate (PHP) as a primary standard according to the procedure described by Douglas [10]. After synthesis of TCMP, 0.1181 g of TCMP was weighted under inert condition for the making of a 5.75×10^{-3} M solution of TCMP. Saturated KNO_3 solution was used as a salt bridge and $Ag\ NO_3$ (0.100 M) was employed as a primary standard solution, in addition, 0.1847 g of KCl (Merck) was weighed accurately, dissolved in water and made up to 100 mL in a volumetric flask to obtain solution of KCl with a molarity of 2.477×10^{-2} M.

Conductance titration:

One of the most frequent uses of conductance is in quantitative titrations of systems in which the conductance of the solution varies in such a manner (prior to and after the end point) that two intersecting lines can be drawn to indicate the end point [11,12]. The actual shape of the curve depends on the sample, the titrant, and the reactions occurring. To maximize accuracy in all titration work, corrections to the measured conductance may have to be made for dilution by the titrant. Volume corrections for the added titrant are made according to the equation:

$1/R_s = (V + V_o/ V_o).1/R_o$

Where $1/R_o$ = the measured conductance

$1/R_s$ = the corrected solution conductance

V_o = the original volume of solution

V= the amount of titrant added at the time of reading $1/R_o$

As a measure of the purity of TCMP in the present work conductimetric titration is a useful technique for measuring the amount of hydrogen chloride which is generated during the reaction of TCMP and water (see Fig. 1) [9].

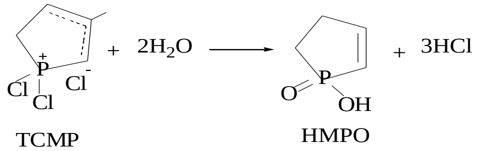

Figure 1: Reaction between 1,1,1-trichloro-3-methyl-3-phospholene (TCMP) and water.

2.2.1. Experimental procedure for the calibration of conductance apparatus

The equipment was set up as is shown in Fig. 2. The apparatus was calibrated by measuring the conductance changes during the neutralization of a standard solution of 0.03 M HCl with 0.264 M NaOH. Standardization of HCl was performed using a secondary standard solution of 0.264M NaOH. Standardization of the sodium hydroxide solution was performed against potassium hydrogen phthalate (PHP) as a primary standard according to the procedure described by Douglas [10]. The results are reported in Table 1. Using the apparatus set up as indicated in Fig. 2, at 25 ^{0}C, 100 mL of 0.03 M standard hydrogen chloride solution was gradually titrated with o.264 M standard NaOH solution and the conductance of the solution was monitored after each 2 mL of sodium hydroxide solution had been added during the process. After the addition of about 24 mL of NaOH solution, the graph of conductance was drawn against the volume of the added sodium hydroxide solution. Straight lines were plotted through the approximately linear portions of the graph which lie to either side of the end point. The end point could be taken as the titre (NaOH) at the point of intersection of these two straight lines. It should be noted that the conductance ordinates were corrected for volume change during titration by the ratio of $(V+V_o)/V_o$ and they are reported in Table 2 and the titration plot is shown in Fig. 3. From Fig. 3, the volume of sodium hydroxide at the point of intersection of two straight lines (blue and red) is about 11.40 mL which is in a good agreement with the theoretical volume of sodium hydroxide (11.36 mL) at equivalence point which is obtained as follow:

$V_{HCl} \times N_{HCl} = V_{NaOH} \times N_{NaOH}$

$100. \times 0.03 = V_{NaOH} \times 0.264$

$V_{NaOH} = 11.36$ mL

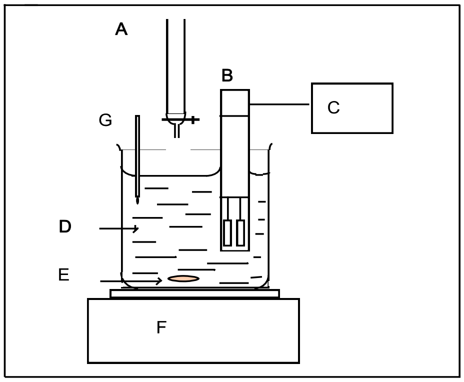

Figure 2: The apparatus for conductimetric titration. A, Burette containing the standard solution of NaOH. B, Conductance cell. C, Portland electronics conductivity meter model P310. D, Sample solution (100 mL). E, Teflon stirrer bar. F, Magnetic stirrer. G, Thermometer.

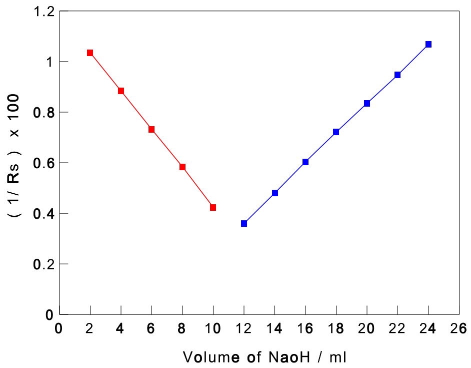

Figure 3: The conductance $[(1/R_s)/\Omega^{-1}]$ against volume of NaOH for the titration of neutralization of 100 mL of 0.03 M HCl with 0.264 M NaOH.

Table 1: Standardization of NaOH solution against potassium hydrogen phthalate (PHP).

Experiment. No.	Weight of PHP/g	V_{NaOH} /mL	M_{NaOH} /mol.L^{-1}
1	0.5749	10.65	0.264
2	0.5821	10.75	0.265

Table 2: The conductance ordinates during the titration of 100 mL (V_o) of 0.030 M HCl with 0.264 M NaOH at 25°C.

$(1/R_o)/\Omega^{-1}$	$1/R_s$=(V + V_o / V_o).1/R	$1/R_{H2O}$	Δ=1/ R_s - $1R_{H2O}$	V_{NaOH}/mL
1.020×10^{-2}	1.040×10^{-2}	5×10^{-5}	1.035×10^{-2}	2
0.855×10^{-2}	0.890×10^{-2}	5×10^{-5}	0.884×10^{-2}	4
0.695×10^{-2}	0.737×10^{-2}	5×10^{-5}	0.732×10^{-2}	6
0.545×10^{-2}	0.589×10^{-2}	5×10^{-5}	0.584×10^{-2}	8
0.390×10^{-2}	0.429×10^{-2}	5×10^{-5}	0.584×10^{-2}	10
0.325×10^{-2}	0.364×10^{-2}	5×10^{-5}	0.360×10^{-2}	12
0.425×10^{-2}	0.485×10^{-2}	5×10^{-5}	0.480×10^{-2}	14
0.525×10^{-2}	0.609×10^{-2}	5×10^{-5}	0.604×10^{-2}	16
0.615×10^{-2}	0.726×10^{-2}	5×10^{-5}	0.721×10^{-2}	18
0.700×10^{-2}	0.840×10^{-2}	5×10^{-5}	0.835×10^{-2}	20
0.780×10^{-2}	0.952×10^{-2}	5×10^{-5}	0.947×10^{-2}	22
0.865×10^{-2}	1.073×10^{-2}	5×10^{-5}	1.068×10^{-2}	24

2.2.2. Experimental procedure for the conductimetric titration in reaction between TCMP and water:

To determine the purity of TCMP by the conductance titration, it was necessary to design a special conical flask to trap the hydrogen chloride which is generated during the exothermic reaction of TCMP and Water. The design of the conical flask is shown in Fig. 4.

Before the beginning of the experiment 0.1181 gTCMP was weighted under inert condition. The molarity of TCMP in 100 mL deionised water is equal to 5.75×10^{-3} M. According to the stoichiometry of the reaction between TCMP and water (Fig. 1), each mole of TCMP generates 3 moles of HCl so that the theoretical concentration of hydrogen chloride in 100 mL deionised water is:

$M_{HCl} = 5.75 \times 10^{-3} \times 3.00 = 1.73 \times 10^{-2}$ M

To measure the concentration of HCl accurately by conductimetric titration, it was necessary that the TCMP be mixed with water when the conical flask was securely stoppered, otherwise some hydrogen chloride would escape from the flask. Thus, 30-40 mL of deionised water was placed into the conical flask from the side arm (Fig. 4) which was immediately stoppered. Then, the flask was placed in a cold water bath at 1°C for 30 minutes. The flask was shaken to bring the water in contact with the TCMP in the bowl. After allowing time for all the liberated HCL to dissolve in the cold water in the flask, the glass stopper was removed and the solution was transferred to a volumetric flask and diluted to exactly 100 mL. Using the apparatus set up as illustrated in Fig. 2, the HCl was slowly titrated with 0.203 M standard solution of NaOH using the same procedure that was employed to obtain the calibration plot. For this experiment, conductance values are reported in Table 3 and the titration plot is illustrated in Fig. 5. The end point was obtained as the point of intersection of the two straight lines (blue and red), unfortunately there was not a good agreement between the experimental (9.4 mL) and theoretical (8.5mL) end points. The volume of NaOH required to reach the end point was more than the predicted theoretical volume. This experiment was repeated three times with different quantities of TCMP. The enhancement of the volume of NaOH needed was observed to reach the end point in all the experiments. The results are reported in Table 4. It seems that 1-hydroxy-3-methyl-2-phospholene oxide (HMPO, Fig. 1) interferes near the end point when the hydrogen chloride is titrated with NaOH. To overcome this difficulty, it was decided to use the alternative approach of potentiometric titrations.

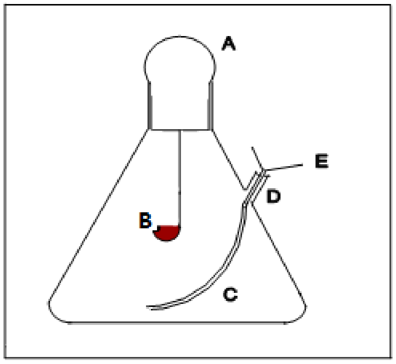

Figure 4: The specially designed conical flask for coductimetric titration of HCl following the reaction between TCMP and deionised H_2O. A, Glass stopper. B, TCMP in tiny bowl. C, PVC tubing connected to the small funnel to introduce the deionised water into the flask without splashing of the water. D, Sidearm of conical flask. E, small funnel which is replaced with small glass stopper when the water has been transferred into the flask.

2.3. Potentiometric titration:

The measurement of the potential of a suitable indicator electrode permits the establishment of the equivalence point for a titration (a potentiometric titration) [13]. The potentiometric end point is widely applicable and provides inherently more accurate data than the corresponding method that makes use of colour indicators. It is particularly useful for titration of coloured or turbid solutions and for detecting the presence of unsuspected species in a solution. Fig. 6, shows a typical apparatus for performing a potentiometric titration. Ordinarily, the titration involves measuring and recording a cell potential (in units of V) after each addition of reagent. The titrant is added in large increments at the outset; as the end point is approached (as indicated by larger potential changes per addition), the increments are made smaller.

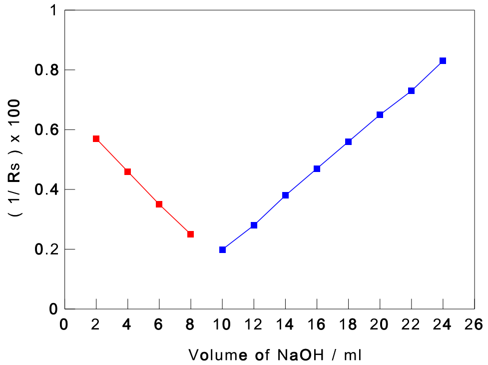

Figure 5: The conductance $[(1/R_s)/\Omega^{-1}]$ against volume of NaOH for titration curve of neutralization of 100 mL of the solution containing the HCl liberated from 0.1181 g TCMP with 0.203 M standard solution of NaOH.

Table 3: The conductance values during the titration of 100 mL (V_o) of HCl (liberated from the reaction between 0.1181g of TCMP and water) with 0.203 M NaOH at 25°C.

$(1/ R_o)/\Omega^{-1}$	$1/R_s=(V + V_o / V_o).1/R$	$1/R_{H2O}$	$\Delta=1/ R_s - 1R_{H2O}$	V_{NaOH}/mL
0.565×10^{-2}	0.576×10^{-2}	5×10^{-5}	0.571×10^{-2}	2
0.445×10^{-2}	0.463×10^{-2}	5×10^{-5}	0.458×10^{-2}	4
0.330×10^{-2}	0.350×10^{-2}	5×10^{-5}	0.345×10^{-2}	6
0.240×10^{-2}	0.259×10^{-2}	5×10^{-5}	0.254×10^{-2}	8
0.185×10^{-2}	0.204×10^{-2}	5×10^{-5}	0.199×10^{-2}	10
0.255×10^{-2}	0.286×10^{-2}	5×10^{-5}	0.281×10^{-2}	12
0.340×10^{-2}	0.388×10^{-2}	5×10^{-5}	0.383×10^{-2}	14
0.405×10^{-2}	0.470×10^{-2}	5×10^{-5}	0.465×10^{-2}	16
0.475×10^{-2}	0.560×10^{-2}	5×10^{-5}	0.555×10^{-2}	18
0.545×10^{-2}	0.654×10^{-2}	5×10^{-5}	0.650×10^{-2}	20
0.605×10^{-2}	0.738×10^{-2}	5×10^{-5}	0.733×10^{-2}	22
0.670×10^{-2}	0.830×10^{-2}	5×10^{-5}	0.825×10^{-2}	24

Table 4: Relationship between the experimental volumes of NaOH at the end point with the theoretical amount for the neutralization of 100 mL (V_o) of HCL liberated from the reaction between 0.1181 g TCMP and water using conductance titration.

No	W^a_{TCMP} /g	M_{TCMP}	M_{HCl}	V_0 /ml	M_{NaOH}	V^b /ml	V^c /ml
1[d]	0.1181	5.75	1.73	100	0.203	9.4	8.5
2	0.234	1.14	3.4	100	0.203	17.7	16.8
3	0.2137	1.04	3.12	100	0.196	16.4	15.9
4	0.1563	7.6	2.28	100	0.196	12.5	11.6

[a] Weight of solid TCMP.

[b] Experimental volume of NaOH at end point.

[c] Volume of NaOH required to neutralise HCl predicted on the basis of reaction stoichiometry at equivalent point (Fig 1): $V_{HCl} \times M_{HCl} = V_{NaOH} \times M_{NaOH}$

$100 \text{ mL} \times 1.73\times10^{-2} \text{ M} = V_{NaOH} \times 0.203 \text{ M}$ and $V_{NaOH} = 8.50$ mL.

[d] As a typical example, the molarity of TCMP and HCl are calculated for the calibration experiment as follows; 0.1181 g of TCMP was weighted under inert condition for the making of a 5.75×10^{-3} M solution of TCMP. Each mole of TCMP (see Fig. 1) generates 3 mole of HCl so that the theoretical concentration of hydrogen chloride is

$M_{HCl} = 3M_{TCMP} = 5.75\times10^{-3} \text{ M} = 1.73\times10^{-2} \text{ M}$.

Sufficient time must be allowed for the attainment of equilibrium after each addition of reagent. Precipitation reactions may require several minutes for equilibration, particularly in the vicinity of the equivalence point. Several methods can be used to determine the end point for a potentiometric titration. The most straightforward involves a direct plot of potential versus reagent volume. A second approach is to calculate the change in potential per unit change in volume of reagent (that is, $\Delta E/\Delta V$), as has been done in column 3 of Tables 5 and 7 for present work. A plot of this parameter as a function of the average volume leads to a sharp maximum at end point.

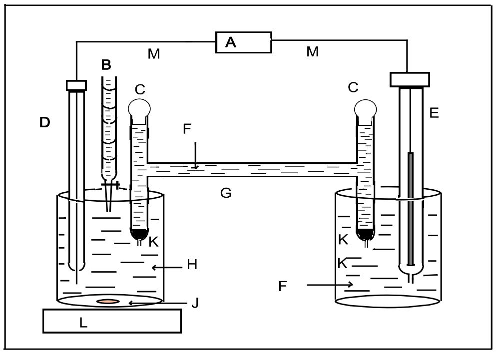

Figure 6: Apparatus for potentiometric titration. A, Digital potentiometer recorder. B, Burette containing reagent, in these experiments 0.100 M standard silver nitrate. C, Glass stopper. D, Silver electrode as an indicator electrode. E, saturated calomel electrode as a reference electrode. F, Saturated KNO_3. G, Salt bridge. H, Sample solution. J, Teflon stirrer bar. K, Wad of cotton wood. L, Magnetic stirrer. M, connecting leads.

2.3.1. Experimental procedure for calibration of apparatus for a potentiometric titration:

To calibrate the system, the apparatus set up as shown in Fig. 6. About 0.2 g of KCL was weighed accurately, dissolved in water and made up to 100 mL in a volumetric flask. For example 0.1847 g generates a molarity of 2.477×10^{-2} mol L^{-1}. A measured volume (35 mL) of this 2.477×10^{-2} M KCl solution was placed in the beaker containing the silver electrode (Fig. 6). To prepare a 0.100 M standard solution of $AgNO_3$, 1.699 g silver nitrate was dissolved in water and made up to volume in a 100 mL volumetric flask. To perform the experiment, burette was filled with $AgNO_3$ solution, and saturated KNO_3 solution was placed in the salt bridge which linked the titration vessel to the beaker containing the calomel electrode. The solution of KCl was titrated with the 0.100 M silver nitrate solution. After each addition of a known volume of Ag NO_3, the cell potential was measured by the digital potentiometer. The potentiometric data are reported in Table 5. To determine the end point for this experiment, the change in potential per unit change in the volume of $AgNO_3$ solution ($\Delta E/\Delta V$) was calculated and is shown in column 3 of Table 5. A plot of this parameter as a function of the volume of $AgNO_3$ added leads to a sharp maximum at the end point. This plot is shown in Fig. 7, from which, it can be seen that the maximum is located between 8.60 and 8.70 mL; an average value of 8.65 mL would be adequate for most purposes. The experimental volumes of silver nitrate required to reach the end point and predicted theoretical volume of silver nitrate at equivalence point, on the basis of reaction stoichiometry, for this and a subsequent experiment are reported in Table 6. There is a good agreement between both the end and equivalence points. As a typical example, the theoretical volume of $AgNO_3$ at the equivalence point that can be predicted is as follows:

$V_{AgNO3} \times M_{AgNO3} = V_{KCl} \times M_{KCl}$

$V_{AgNO3} \times 0.1 \text{ M} = 35\text{mL} \times 2.477 \times10^{-2} \text{ M}$

and $V_{AgNO3} = 8.67$ mL

2.3.2. Experimental procedure for potentiometric titration in reaction between TCMP and water:

To perform a potentiometric titration experiment for the reaction between TCMP and water, about 0.2 g of TCMP was weighed and dissolved in 100 mL deionised water using the specially designed conical flask described for conductance titration (Fig. 4). Using the apparatus shown in Fig. 6, 35 mL of the HCl solution obtained from the reaction of a known quantity of TCMP (0.1894 g) with water (each mole TCMP generates 3 mole of HCl) was titrated with 0.100 M $AgNO_3$ solution. After each addition of a known volume of $AgNO_3$ solution, the cell potential was measured using the digital potentiometer. Potentimetric titration data are reported in Table 7 and a titration curve is illustrated in Fig. 8.

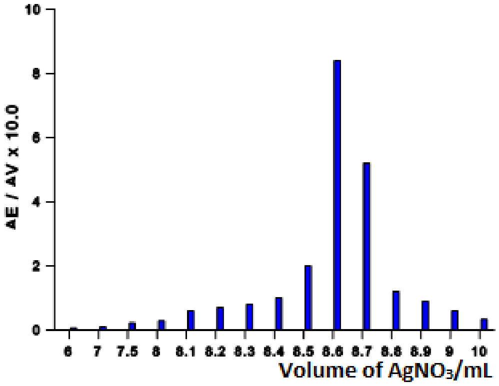

Figure 7: Potentiometric titration curve of 35 mL of 2.477 $\times 10^{-2}$ M KCl (equivalent to a 0.867 mmol Cl^-) with 0.100 M $AgNO_3$.

Table 5: Potentiometric titration data for 0.867 mmol of chloride with 0.100 M Ag NO_3.

V^{a}_{AgNO3}/ml	E/Volt	$\Delta E^{b}/\Delta V$	V^{c}_{AgNO3}/ml
5	0.184	-	5
1	0.19	6×10^{-3}	6
1	0.2	1×10^{-2}	7
0.5	0.211	2.2×10^{-2}	7.5
0.5	0.225	2.8×10^{-2}	8
0.1	0.231	6×10^{-2}	8.1
0.1	0.238	7×10^{-2}	8.2
0.1	0.246	8×10^{-2}	8.3
0.1	0.256	1×10^{-1}	8.4
0.1	0.276	2×10^{-1}	8.5
0.1	0.36	8.4×10^{-1}	8.6
0.1	0.412	5.2×10^{-1}	8.7
0.1	0.424	1.2×10^{-1}	8.8
0.1	0.433	9×10^{-2}	8.9
0.1	0.439	6×10^{-2}	9
1	0.472	3.3×10^{-2}	10

[a] Volume of $AgNO_3$ which is added in each step.
[b] As a typical example, ΔE/ΔV is calculated for the first two step of Table 5: $\Delta E/\Delta V = 0.190 - 0.184/(6\text{-}5) = 6\times10^{-3}$.
[c] Total volume of Ag NO_3 in each step.

Table 6: Relationship between the volume of silver nitrate at the end point and equivalence point for potentiometric titration of 0.867 and 1.12 mmol of chloride with 0.100 M $AgNO_3$.

Test No.	M_{KCl}/mol.L^{-1}	V_{KCl}/ml	$V_{AgNO3}{}^{a}$/ml	$V_{AgNO3}{}^{b}$/ml
1	2.477×10^{-2}	35	8.65	8.67
2	3.19×10^{-2}	35	11.15	11.2

[a] Experimental volume of $AgNO_3$ at end point.
[b] Volume of $AgNO_3$ at equivalence point; predicted on the basis of reaction stoichiometry.

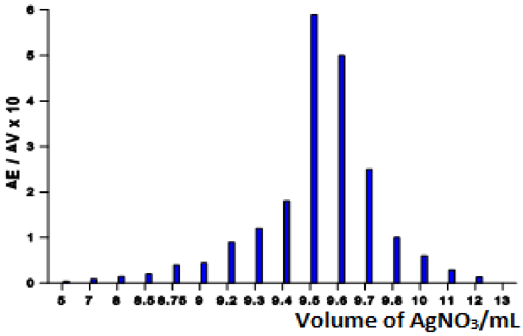

Figure 8: Potentiometric titration curve of chloride generated ion in the reaction between TCMP (0.1894 g) and deionised water with 0.100 M $AgNO_3$.

In Fig. 8, it seen that the maximum is located between 9.5 and 9.6 mL; an average value of 9.55 mL as a volume of $AgNO_3$ at end point would be adequate for most purposes, particularly for comparison with the predicted volume of $AgNO_3$ at the equivalence point:

$V_{AgNO3} \times M_{AgNO3} = V_{Cl\_} \times M_{Cl\_}$

$V_{AgNO3} \times 0.1\ M = 35mL \times 2.76 \times 10^{-2}\ M$ and

$V_{AgNO3} = 9.66\ mL$

The results of this experiment and two repeat subsequent works are also recorded in Table 8. As can be seen, there is a good agreement between the volume of silver nitrate at the end point and equivalence point. These results confirm the generation of HCl solution, in practical, from the reaction of a known quantity of TCMP and water (each mole of TCMP generate 3 moles of HCL, Fig. 1) in comparison with theoretically predicted HCL solution, they are nearly same; this agreement shows that the purity of synthesized TCMP is extremely high.

Table 7: Potentiometric titration data for the titration of Cl^- (arising from the reaction between 0.1894 g of TCMP and water) with 0.100 M $AgNO_3$.

V^a_{AgNO3}/ml	E/Volt	$\Delta E^b/\Delta V$	V^c_{AgNO3}/ml
0	0.155	-	5
5	0.175	4×10^{-3}	6
2	0.193	9.0×10^{-3}	7
1	0.207	1.4×10^{-2}	7.5
0.5	0.217	2.8×10^{-2}	8
0.25	0.227	9.0×10^{-3}	8.1
0.25	0.238	1.4×10^{-2}	8.2
0.1	0.242	4.0×10^{-2}	8.3
0.1	0.251	9.0×10^{-1}	8.4
0.1	0.263	1.2×10^{-1}	8.5
0.1	0.281	1.8×10^{-1}	8.6
0.1	0.340	5.9×10^{-1}	8.7
0.1	0.390	5.0×10^{-1}	8.8
0.1	0.415	2.5×10^{-1}	8.9
0.1	0.442	2.8×10^{-2}	9
1	0.483	1.3×10^{-2}	10

[a] Volume of silver nitrate which is added in each step.
[b] As a typical example, $\Delta E/\Delta V$ is calculated for the first two step of Table 7: $\Delta E/\Delta V = 0.175 - 0.155/(5 - 0.0) = 4\times10^{-3}$.
[c] Total volume of silver nitrate in each step.

Table 8: Relationship between the volume of silver nitrate at end point and equivalence point for the potentiometric titration with 0.100 M $AgNO_3$ of the chloride ion formed in the reaction between TCMP and water.

Experimental No.	W_{TCMP}/g	V_{Cl^-}/ml	$V_{AgNO3}{}^a$/ml	$V_{AgNO3}{}^b$/ml
1	0.1894	35	9.55	9.66
2	0.2089	35	10.55	10.68
3	0.1894	50	13.65	13.8

[a] Experimental volume of $AgNO_3$ at end point.
[b] Volume of $AgNO_3$ at equivalence point; predicted on the basis of reaction stoichiometry.

2.4. Differential titration method:

In the previous section, it was observed that a derivative curve generated from the data of a conventional potentiometric titration curve (e.g. Figs. 7. and 8.) reaches a distinct maximum in the vicinity of the end point. It is also possible to acquire titration data directly in the derivative form by means of a relatively simple apparatus. A differential titration requires the use of two identical indicator electrodes, one of which is well shielded from the bulk of the solution [14-16]. Fig. 9 illustrates the arrangement, with two identical silver electrodes as the indicator electrodes, used in the current work. As can be seen, one of the silver electrodes is contained in a small sidearm test tube. Contact with the bulk of the solution, in this case hydrogen chloride solution generated from the reaction between TCMP and water, is made through a small (~1mm) hole in the bottom of the tube. Because of this restricted access, the composition of the solution surrounding the shielded silver electrode will not be immediately affected by an addition of titrant to the bulk of the solution. The resulting difference in solution composition gives rise to a difference in potential, ΔE, between the electrodes. After each potential measurement, the solution is homogenized by squeezing the syringe, whereupon ΔE again became zero. The main advantage of a differential method is the elimination of the need for the reference electrode and salt bridge. Furthermore, measurement of a difference in potential (ΔE) is done automatically.

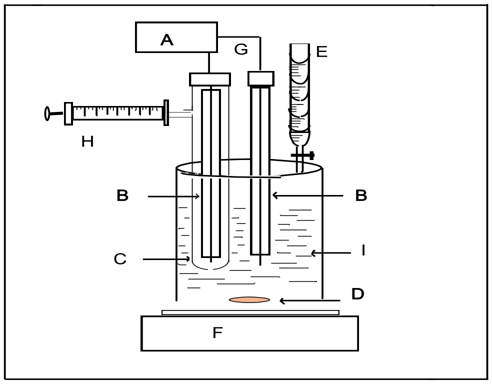

Figure 9: Apparatus for differential potentiometric titration. A, Digital potentiometer. B, Two identical silver electrodes as a indicator electrodes. C, Test tube with a small sidearm. D, Teflon stirrer bar. E, Burette. F, Magnetic stirrer. G, Connection lead. H, 20 mL syringe. I, Sample solution.

2.4.1. Experimental Procedure for the Calibration of the Differential Titration Apparatus:

To calibrate the apparatus a measured volume (35 mL) of 2.50×10^{-2} M KCl solution was placed in the beaker and was titrated with 0.100 M $AgNO_3$ solution. Before any addition of silver nitrate to the KCl solution, the difference in potential (ΔE) was zero due to the homogenized solution. After the first addition of $AgNO_3$, the difference in potential was changed because of the difference in solution composition surrounding the shielded electrode and the bulk of the solution. This difference ΔE was measured by the potentiometer. The procedure was repeated for second, third and subsequent additions of titrant. After each ΔE measurement, the solution was homogenised by the squeezing the syringe, whereupon ΔE again become zero. The differential titration data are reported in Table 9 and a plot of ΔE/ΔV against the volume of silver nitrate is shown in Fig. 10. The end point for this titration was determined to be the same as that for the conventional potentiometric titration method. The results for this work and repeat experiment are recorded in Table 10. There was a good agreement between the end point and theoretical equivalence point. In Fig. 10, it is seen that the maximum is located between 8.70 and 8.80 mL. The mean value of 8.75 mL for the volume of $AgNO_3$ at the end point, in practical, is identical with the predicted volume of silver nitrate at the equivalence point (Table 10).

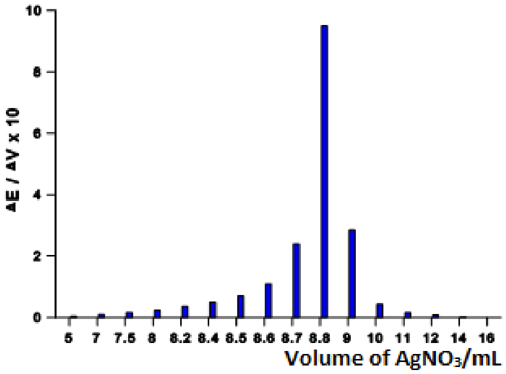

Figure 10: Differential titration curve of 0.875 mmol of Cl^- with 0.1 M $AgNO_3$.

2.4.2. Experimental procedure for the differential titration in reaction between TCMP and water:

Using the apparatus shown in Fig. 9, 35 mL of HCl solution obtained from the reaction between 0.7873 g of TCMP and water, and making up to 250 mL, was titrated with 0.100 M $AgNO_3$ solution. Differential titration data are reported in Table 11 and the titration curve shown in Fig. 11. In Fig. 11, it is seen that maximum is located between 15.60 and 15.70; selection of 15.65 mL as a volume of silver nitrate at end point is in a good agreement with the theoretically predicted volume of $AgNO_3$ (15.75 mL) at the equivalence point. The result for this experiment and that of a subsequent repeat experiment are reported in Table 12.

Table 9: Differential titration data for 0.875[a] mmol of chloride with 0.100 M Ag NO_3.

V^b_{AgNO3}/ml	E/Volt	$\Delta E^b/\Delta V$	V^c_{AgNO3}/ml
0	0.000	-	0
5	0.023	4.6×10^{-3}	5
2	0.019	9.0×10^{-3}	7
0.5	0.008	1.4×10^{-2}	7.5
0.5	0.012	2.8×10^{-2}	8
0.2	0.007	9.5×10^{-3}	8.2
0.2	0.011	1.6×10^{-2}	8.4
0.1	0.010	2.4×10^{-2}	8.5
0.1	0.007	7.0×10^{-2}	8.6
0.1	0.011	1.1×10^{-1}	8.7
0.1	0.010	5.0×10^{-2}	8.8
0.2	0.007	7.0×10^{-2}	9
1	0.011	1.1×10^{-1}	10
1	0.024	2.4×10^{-1}	11
1	0.008	8.0×10^{-3}	12
2	0.004	2.0×10^{-3}	14

[a] mmol Cl^- = 35 m L × 2.50 ×10^{-2} mol.L^{-1} =0.875 mmol.
[b] Volume of silver nitrate which is added in each step.
[c] As an example, ΔE /ΔV is calculated for the first two steps of Table 9: $\Delta E/\Delta V = 0.023/(5 - 0.0) = 4.6 \times 10^{-3}$.
[d] Total volume of silver nitrate in each step.

Table 10: Relationship between the volume of $AgNO_3$ at end point and equivalence point for differential titration of 0.875 mL of Cl^- with 0.100 M $AgNO_3$.

Test No.	M_{KCl}/mol.L^{-1}	V_{KCl}/ml	$V_{AgNO3}{}^a$/ml	$V_{AgNO3}{}^b$/ml
1	2.5×10^{-2}	35	8.75	8.75
2	2.5×10^{-2}	35	8.75	8.75

[a] Experimental volume of $AgNO_3$ at end point.
[b]Volume of $AgNO_3$ at equivalence point; predicted on the basis of reaction stoichiometry (Fig. 1).

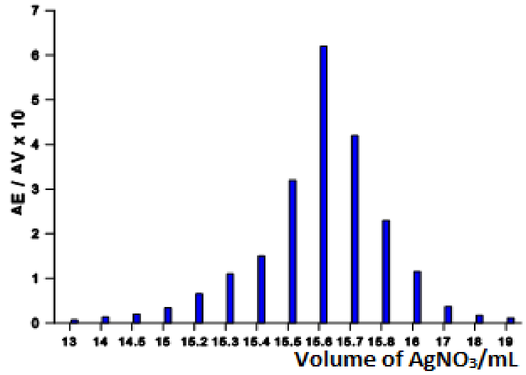

Figure 11: Differential titration curve of chloride ion generated in the reaction between TCMP (0.7873 g) and deionised water with 0.100 M$AgNO_3$.

Table 11: Differential titration data with 0.100 M $AgNO_3$ for the titration of Cl^- (arising from the reaction between 0.7873 g of TCMP and water).

V^a_{AgNO3}/ml	E/Volt	ΔE/ΔV	V^b_{AgNO3}/ml
0	0	-	0
5	0.017	3.4×10^{-3}	5
5	0.021	4.2×10^{-3}	10
3	0.021	7.0×10^{-3}	13
1	0.013	6.5×10^{-2}	14
0. 5	0.010	2.0×10^{-2}	14.5
0. 5	0.017	3.4×10^{-2}	15
0.2	0.013	6.5×10^{-2}	15.2
0.1	0.011	1.1×10^{-1}	15.3
0.1	0.015	1.5×10^{-1}	15.4
0.1	0.032	3.2×10^{-1}	15.5
0.1	0.062	6.2×10^{-1}	15.6
0.1	0.042	4.2×10^{-1}	15.7
0.1	0.023	1.15×10^{-1}	17
1	0.017	1.7×10^{-2}	18
1	0.010	1.0×10^{-2}	19

[a] Volume of $AgNO_3$ which is added in each step.
[b] Total volume of $AgNO_3$ in each step.

Table 12: Relationship between the volume of silver nitrate needed to reach the end point and that predicted to reach the equivalence point for the differential titration with 0.100 M $AgNO_3$ of the chloride ion formed in the reaction between 0.7873 g of TCMP with water.

Experimental No.	W_{TCMP}/g	V_{Cl^-}/ml	$V_{AgNO3}{}^a$/ml	$V_{AgNO3}{}^b$/ml
1	0.7873	35	15.65	15.70
2	0.7873	35	15.65	15.75

[a] Volume of $AgNO_3$ at end point.
[b] Volume of $AgNO_3$ at equivalence point calculated on the basis of the reaction stoichiometry (Fig. 1):
[c] $M_{Cl^-} = 3\times M_{TCMP} = 3\times1.5\times10^{-2}$ mol.L^{-1} = 4.5×10^{-2} M
$V_{AgNO3}\times M_{AgNO3} = V_{Cl^-}\times M_{Cl^-}$
$V_{AgNO3}\times 0.100$ M = 35 mL $\times 4.5\times10^{-2}$ M and V_{AgNO3} =15.75 mL.

2.5. Investigation of the UV spectral properties of the prepared TCMP:

TCMP reacts rapidly and quantitatively with water to produce 1-Hydroxy-3-Methyl-2-Phospholene Oxide (HMPO) as shown in Fig. 1.

This reaction was therefore applied as a method of determining the purity of the TCMP samples used for the kinetic studies. A known quantity of the TCMP could hydrolysed and the (1-Hydroxy-3-Methyl-2-Phospholene Oxide) HMPO thus produced was measured via calibration plots of HMPO absorption versus HMPO concentration. The quantity of HMPO thus determined is equivalent to the quantity of pure TCMP in the original weighted sample. Fig. 12 shows the UV spectra of 8×10^{-3} M HMPO for 2 and 10 mm path length cells. As a simpler check on the purity of the TCMP, Table 13 tabulates ratios of the two different initial concentrations (C_1/C_2) of TCMP and compares these with the experimental ratios of absorptions values (A_1/A_2) for HMPO. The ratios are in a good agreement with each other. This good agreement can be taken as a demonstration of the high purity of the TCMP used.

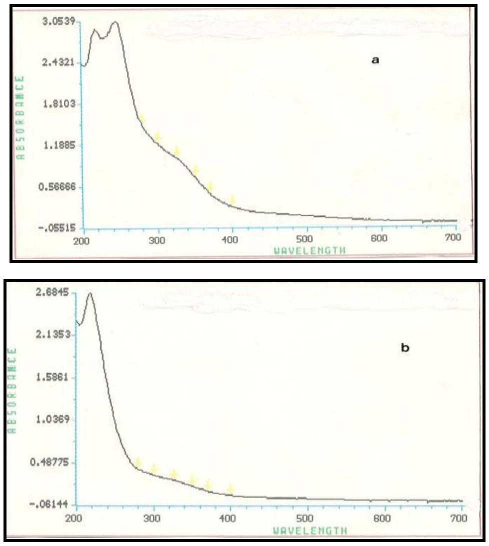

Figure 12: The UV spectrums of 8×10^{-3} M TCMP in deionised water in both 10 (a) and 2 mm (b) light path cells, respectively.

Table 13: The relationship between the ratios of absorptions (A_1/A_2) of HPMO and ratios of concentrations values (C_1/C_2) of TCMP in 10 mm light path cell.

λ/nm	C_1/M	C_2/M	A_1	A_2	C_1/C_2	A_1/A_2
280	8×10^{-3}	6×10^{-3}	2	1.5	1.33	1.32
300	8×10^{-3}	6×10^{-3}	1.6	1.21	1.33	1.33
326	8×10^{-3}	6×10^{-3}	1.34	1	1.33	1.34
350	8×10^{-3}	6×10^{-3}	0.96	0.7	1.33	1.35
370	8×10^{-3}	6×10^{-3}	0.62	0.46	1.33	1.35
400	8×10^{-3}	6×10^{-3}	0.35	0.26	1.33	1.35
280	6×10^{-3}	4×10^{-3}	1.5	1	1.5	1.5
300	6×10^{-3}	4×10^{-3}	1.21	0.82	1.5	1.48
326	6×10^{-3}	4×10^{-3}	1	0.67	1.5	1.49
350	6×10^{-3}	4×10^{-3}	0.71	0.47	1.5	1.49
370	6×10^{-3}	4×10^{-3}	0.46	0.31	1.5	1.48
400	6×10^{-3}	4×10^{-3}	0.26	0.18	1.5	1.48

The absorptions of measured for HMPO in the 10 mm light path cell were very high (>1) over the concentrations used (see Table 13). To double check the validity of the conclusions drawn from this data, The UV spectra of HMPO were obtained under the same condition in a 2 mm light path cell. The absorption values were then five times less than previous experiments, but could be measured more accurately. Addition to the theoretical ratios $(A_{10}/A_2)^b$, the experimental ratios $(A_{10}/A_2)^a$ of absorption values of HMPO in 2 and 10 mm light path cell are also reported in Table 14. As can be seen from this Table, these values $(A_{10}/A_2)^a$ are acceptably consistent with the theoretical ratios of absorption values $(A_{10}/A_2=5.00)^b$. According to the Beer-Lambert law (A= ξbc) under the same conditions of concentration, temperature and wavelength, absorption in 10 mm light path cell (A_{10}) is five time more than the absorption in 2 mm light path cell (A_2). These results are good confirmation for the results obtained with 10 mm light path cell as a demonstration of the high purity of the synthesized TCMP.

Table 14: The experimental ratios of absorption values of HPMO in both10 and 2 mm light path cells.

λ/nm	C/M	A_{10}	A_2	$(A_{10}/A_2)^a$	$(A_{10}/A_2)^b$
280	8×10^{-3}	2.00	041	4.90	5.0
326	8×10^{-3}	1.34	0.27	5.00	5.0
350	8×10^{-3}	0.96	0.19	5.00	5.0
280	6×10^{-3}	1.50	0.31	4.90	5.0
300	6×10^{-3}	1.21	0.25	4.90	5.0
326	6×10^{-3}	1.00	0.21	4.90	5.0
280	4×10^{-3}	1.00	0.22	4.60	5.0
350	4×10^{-3}	0.47	0.10	4.90	5.0
370	4×10^{-3}	0.31	0.06	4.98	5.0

[a] Experimental ratio of absorption in both10 and 2mm light path cells.
[b] Theoretical ratio of absorption in both 10 and 2mm light path cells.

Conclusion

The purity of the prepared TCMP according to the synthesized approach detailed in Coleman's work was identified on the basis of four methods involving UV spectrophotometer, conductance titration, potentiometric titration and differential potentiometric methods. Investigation of the UV spectral of the prepared TCMP indicated a demonstration of the high purity of the TCMP used. The conductance titration experiments for the measurement of HCl generated in the reaction between TCMP and water showed that the end point was overestimated due to interference. The results obtained from the potentiometric and differential titration experiments were much more reliable. These data showed that the volume of silver nitrate needed to reach the end point was exactly equivalent to the chlorine content predicted on the assumption that the TCMP sample was pure. Thus, the data are consistent with the synthesized TCMP being of high purity.

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