

THE DEAD SEA:
A
STOREHOUSE OF CHEMICALS

- BY

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S. Baranki

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INTRODUCTION

"The Lord rained upon Sodom and Gomorrah, brimstone and fire from the Lord out of heaven; and He overthrew those cities and all the plain, and all the inhabitants of the cities and that which grew upon the ground!"¹

In the region of Sodom and Gomorrah lies a most remarkable salt lake, known among many other names by the Sea of Lot and the "Dead Sea."

The Dead Sea forms part of a long fault trench known by the name of "Ghor", the Arabic for hollow, which so far as the boundaries of Palestine are concerned, extends from the Gulf of Akaba in the south to the Lake of Huleh in the north. The length of this trough from the Gulf of Akaba to the source of the river Jordan is 416 kilometers, whilst its width varies from 8 to 26 kilometers. It is one of the most striking phenomena on the globe, being the deepest and lowest point on the earth's land surface. The water surface of the Dead Sea is exposed to considerable changes annually, but the average level can be taken as 396 meters below the Mediterranean Sea level, and its maximum^{depth} is also about 396 meters. It has a length of over 75 kilometers and an average breadth of 14.5 kilometers. The surface of the water has an area of around 360 square miles (932 square kilometers).

The Dead Sea represents a great reservoir of water without outlet, and while it receives daily over 8,500,000 cubic meters of water 75% of which come from the river Jordan, its only method

1. Genesis, XIX

of discharge is by the vapors rising from its surface due to rapid evaporation of the water under the action of the glowing oppressive heat and the almost continual winds, blowing mostly from the north and south, which disperse the vapors during the eight totally rainless months of the year.¹

The chemical composition of the Dead Sea water, which represents a brine almost saturated with salts in which the human body is unsinkable, changes from the surface downwards with the increase of specific gravity. The specific gravity reaches its highest point in Autumn² which, according to Novomeysky³ is 1.1770 on the surface at 23 C. The lowest specific gravity on the surface is reported⁴ as 1.1475 at 20 C. The nauseous taste of the water is due to $MgBr_2$ and the $Ca Cl_2$ present gives the brine its smooth oily feeling.

The object of this treatise is to study the possibility of extracting potassium chloride from the Dead Sea and to develop the technique for the separation of potassium chloride from the other salts present in the brine. Methods and techniques for the determination of potassium in the brine will also be studied, since it is essential to know the potassium content in the brine and to determine the purity of the potassium chloride produced.

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1. Estimate of evaporation is 13.5 mm. per day, and rainfall rarely exceeds 12.7 cms. per year.
 2. A sample collected early in October 1952 from the surface of the Dead Sea, away from the mouth of the river, had a sp. gr. of 1.1940 at 20 C.
 3. M.A. Novomeysky, "The Dead Sea: A Storehouse of Chemicals" Trans. Inst. Chem. Eng. (1936)
 4. B. Panteleymonoff, "L'Exploitation des Eaux de la Mer Morte". La Revue de Chemie Industrielle, 118 (1934).

Chapter I

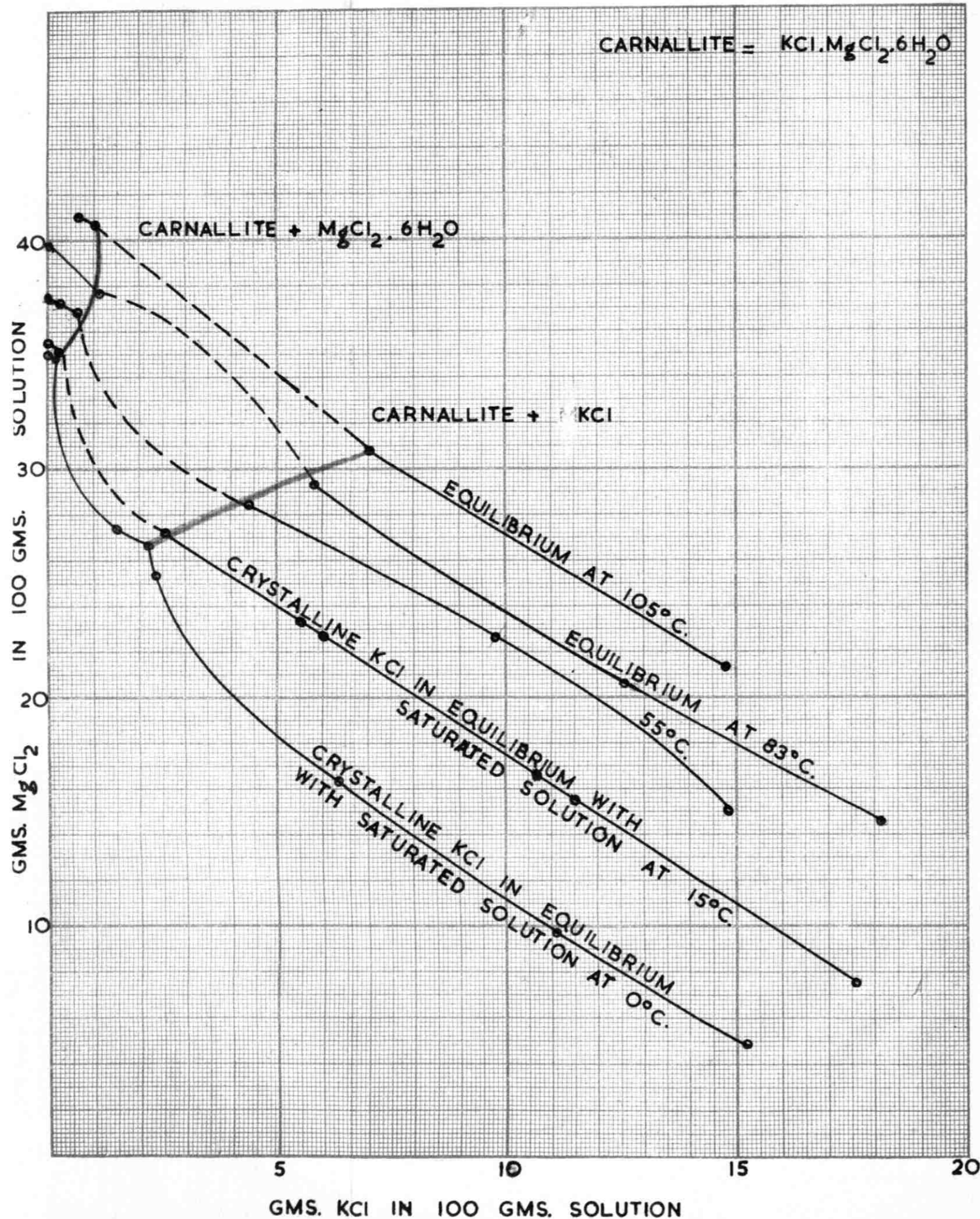
a) Extraction of Potassium Chloride:

Theoretical Discussion:- If we take the average composition of the Dead Sea water at sp.gr. of 1.1725¹ at 23 C. as:

NaCl	82.4 gms./L.
KCl	11.8 gms./L.
MgCl ₂	142.4 gms./L.
CaCl ₂	33.0 gms./L.
MgBr ₂	3.9 gms./L.
CaSO ₄	1.3 gms./L.

and if we evaporate the brine gradually, then eventually we shall reach a point (sp.gr. 1.20 - 1.22) of saturation with respect to one of these salts. Examination of the solubilities of these salts will reveal that NaCl will be the first salt to reach saturation and hence will precipitate first. NaCl will continue to crystallize as evaporation goes on until we reach a sp.gr. of 1.29 where Carnallite (KCl.MgCl₂.6H₂O) starts to separate from the solution together with NaCl. The field of crystallization of Carnallite is between sp.gr. 1.29 - 1.32 after which we come to the stage where MgCl₂ starts to crystallize instead of Carnallite.

Now if we plot a graph for the equilibrium existing in saturated solutions of KCl and MgCl₂ we can see clearly why Carnallite and not KCl or MgCl₂ crystallized at sp.gr. 1.29. The graph clearly shows that solutions with low KCl content



1. Analysis reported by the Laboratories of Palestine Potash Ltd.

2. Values taken from "The Solubilities of Inorganic Compounds" by A. Seidell - pages 764-5.

and high $MgCl_2$ content would tend to form Carnallite at saturation, and that this condition is essential for the formation of Carnallite. It is evident, therefore, that solutions containing equal amounts of KCl and $MgCl_2$ will not yield Carnallite at saturation, but would give crystals of KCl until the amount of KCl in the solution becomes low enough to allow precipitation of Carnallite, and that when Carnallite is dissolved in a small amount of water will leave KCl to crystallize if evaporation is started to get a saturated solution. That means that Carnallite can be decomposed with a calculated amount of water to yield KCl crystals and a solution containing mostly $MgCl_2$.

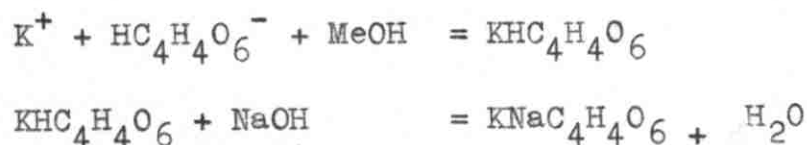
Since NaCl is more soluble than KCl at lower temperatures, then any NaCl that crystallizes with Carnallite would dissolve on decomposing Carnallite with cold water. In practice more than one washing is essential to bring the purity of KCl up to 99% .

b) Methods for Determination of Potassium in Dead Sea Water:

Theoretical Discussion:- From the various methods of determination of Potassium, I have selected four methods, each dealing with the problem from a different angle . In the following paragraphs I shall discuss briefly the principle involved in each method, together with the data used in that method of quantitative analysis:

i) Precipitation of Potassium as Potassium Bitartrate from an aqueous Solution of Methyl Alcohol ¹.

In this method sodium hydrogen tartarate is added to the potassium salt solution, and then methyl alcohol is added to form a 50% solution. The precipitate of KH tartarate is left for one hour at 12° C, then it is filtered, washed with methyl alcohol, and then the precipitate is dissolved in 1N NaOH solution, the excess NaOH is then back titrated with an acid; and from the amount of base used up we calculate the weight of potassium salt.



A modification of this method has also been used. In this modification, the ppt. of $\text{KHC}_4\text{H}_4\text{O}_6$ was washed and dried, then it was weighed as such, and from the weight the amount of potassium was calculated.

This method (both modifications) can be worked out in half a day. As many as four samples can be handled simultaneously without using much more time than that used for one sample.

1. Organic Analytical Reagents, Vol. 2, Page 178.

ii) Precipitation of Potassium as the Perchlorate from a solution of equal parts of n-Butyl alcohol and Ethyl acetate.^{1.}

In this well known method for the determination of potassium, ions other than the alkali metals are removed. Here Mg is removed as the $MgNH_4PO_4$; the phosphate is then removed as Barium phosphate and the excess Barium removed by means of ammonium carbonate, and lastly the ammonium ions are changed to ammonium chloride and volatilized by ignition. Perchloric acid is then added to the solution of the mixed alkali chlorides, the water removed by evaporation and the mixture of solvents - n-Butyl alcohol and Ethyl acetate - is then added. Filtration takes place in an ignited and previously weighed Gouch crucible and the potassium perchlorate is then dried and weighed as such.

This method - though accurate - is long and tedious, the part of removing the other ions before adding the $HClO_4$ is specially tiresome and definitely takes more than half the time for the whole determination.

The removal of Mg and Ca salts seems unnecessary due to the relatively great solubility of their perchlorates in the mixed solvents:

Solubility² of the perchlorates of Ca, Mg, K, Na & NH_3
in gms/100 ml. at 25°C.

	<u>Water</u>	<u>n-Butyl Alc.</u>	<u>Ethyl Acetate</u>
$NaClO_4$	113.880	1.4950	8.425
$KClO_4$	2.0394	0.0036	0.0013
NH_4ClO_4	21.910	0.0137	0.0286
$Mg(ClO_4)_2$	73.453	44.6380	54.173
$Ca(ClO_4)_2$	112.340	68.4190	57.377

1. Methods of Analysis of the A.O.A.C. Page 643.

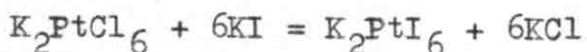
2. Table taken from H.H. Willard & G.F. Smith, J. Am. Chem. Soc. 45, 293 (1923); found also in Hillebrand & Lundel, "Applied Inorganic Analysis".

It is quite evident from the above table that, not only is the removal of the calcium and magnesium perchlorates useless, but that by removing them we introduce eventually NH_4^+ which may greatly interfere with the result if NH_4Cl is not carefully and completely removed.

The two procedures shall be followed experimentally, and as we shall see later, each method has its cons and pros.

iii) A Micro Method for Determination of Potassium as the Iodoplatinate.¹

This method depends upon the formation of K_2PtCl_6 then converting it to K_2PtI_6 by the addition of KI. Because of the deep wine colour of the K_2PtI_6 in solution, amounts as small as 0.1 mg. of potassium can be estimated in this form by colorimetric comparison with known amounts of K_2PtCl_6 also treated in this way.



The colour varies in proportion to the amount of K_2PtCl_6 present when KI is added to solutions of this salt. This proportion is maintained from 0.2 mg% to 10 mg%. The colour so formed is stable for 24 hours or longer. The only interfering substances are iron, which forms a coloured iodide, copper which precipitates out as the cuprous iodide in acid solution, ferricyanide which gives a green colour, and alcohol which reduces K_2PtI_6 .

1. A.T. Shohl & H.B. Bennett, J.Biol. Chem.78, 643.

The K_2PtI_6 can also be determined volumetrically by reducing it with a standard $Na_2S_2O_3$ solution. The end point is a lemon yellow colour free from red.



A combination of these two procedures can also be followed. After the volumetric method (titration with $Na_2S_2O_3$) the solution can be oxidized by means of H_2O_2 .



The K_2PtI_6 can then be compared to a standard.

Three or four samples can be handled simultaneously and the whole determination (the combination of volumetric and colorimetric procedures) will take between three and four hours.

iv) Determination of Potassium by means of the Flame Photometer.^{1.}

The flame photometer is an instrument for the rapid determination of sodium, potassium and other metals in solution. It is designed to measure quantitatively the light emitted by various metals when they^{are} atomized from solution, led to a burner and excited to emission by a flame. Since the intensity of the light emitted by each element depends primarily on the concentration of its atoms in the flame at any given instant, a measurement of the light intensity produced by a given element makes possible the quantitative determination of that element.

1. Ind. Eng. Chem. Anal. Edition 23, 137-42 (1951).

The method by which the intensity of light emitted by a certain metal when solutions of a compound of that metal are atomized and blown into a flame, is by focussing that light on a photo-electric cell. The light is passed first through a filter which allows the optimum wave length of the light emitted by the metal to pass. The photo-electric cell is usually a quartz cell covered with a photo sensitive metal, such as one of the alkali metals, which is made the cathode, while a platinum wire forms the anode. When the light hits the metallic cathode some electrons are emitted from the surface of that photo sensitive metal and hence a small current, detected by a sensitive galvano-meter, passes through the cell. The current passing through the cell depends upon the intensity of the light hitting the cathode, and hence a graph drawn by plotting galvanometric readings against concentration would serve to determine unknown concentrations which give certain readings on the galvanometer attached to the instrument. This "direct intensity" method assumes that the atomizer delivery is constant, the portion nebulized remains the same, and the flame characteristics do not vary. The assumptions cannot be strictly valid and their failure can result in some error of reading.

An alternative procedure to the "direct intensity" method is the "internal standard" method. Here a known amount of an element not present in the unknown "(Lithium is used) is added to the sample preparation and the same concentration of the element is used in each standard. The amount of light emitted by the unknown element is measured on one photo-tube while that emitted by the constant amount of internal standard element is measured by another.

Analysis is made by adjusting the internal standard signal with a potentiometer until it just balances the signal due to unknown - in effect, determining the ratio of unknown concentration to known internal standard concentration. Since many of the invariables, such as sample viscosity, rate of atomization, flame temperature, foreign materials, gas and air pressure, tend to effect both the internal standard and the unknown in the same way, the ratio tends to be invariant.

Chapter II

Experiments:

In this chapter I shall describe the experiments performed on the Dead Sea water with a view of extracting the KCl found in it. As it is necessary to know the amount and purity of the KCl produced at every stage of the process of extraction, technique and skill in the quantitative determination of potassium are found to be extremely important. The four methods for the determination of potassium described in the previous chapter will be performed here, and the results of each method will be studied. On the basis of these results, the method to be adapted for the determination of potassium in the brine and in the various products produced by the gradual evaporation of the brine will be decided.

a) Determination of potassium:

i) Potassium Hydrogen Tartarate Method:- 10.2193 gms. of KCl (analytical reagent) were dissolved in water and the volume made up to 100 ml. 10 ccs. of the above solution were placed in a 150 ml. beaker, and then 39 ccs. of $\text{NaHC}_4\text{H}_4\text{O}_6$ (sodium bitartarate) solution - 14.2 gms./250 ml. - were added, and to the mixture was added 50 ccs. of methyl alcohol. A white ppt. formed directly. The beaker was placed in a water bath kept at 12°C . by adding ice every now and then. After an hour the beaker was removed and left aside for some time to bring it to room temperature. Filtration was followed and the ppt. was washed with methyl alcohol diluted with an equal amount of water, and then transferred to a filter paper. This residue together with

the filter paper were placed later in a clean beaker and 12 ccs. of 1N. NaOH were run in, and phenolphthalien was added to insure that the base was in excess. The solution was then back titrated with 1N. HCl. This procedure was followed three times with the same result every time viz. 0.6 gms. KCl/10ccs.

In order to avoid possible sources of error, two modifications were adapted:

1st:- It was thought that a possible source of error was in the evaporation of methyl alcohol during filtration, the aqueous ^{solution} thus left contained more water and hence a better chance for the $\text{KHC}_4\text{H}_4\text{O}_6$ to go into solution. To prevent this a Gouch crucible with an asbestos bed was used for filtration, and instead of a 50 - 50 alcohol water mixture, 70% methyl alcohol was used for washing. The ppt. together with the Gouch crucible were placed in a beaker, the ppt. was washed out of the Gouch crucible with the aid of a wash bottle containing distilled water. Using this modification I got a result of 0.85 gms. KCl per 10 ccs.

2nd:- Here filtration was carried out in an ignited and previously weighed Gouch crucible. Washing was made with 90% methyl alcohol. The precipitate in the crucible was then dried at 80°C . for 20 hours and it was weighed in that form. I got a result of 0.845 grms.KCl in 10 ccs. of solution.

Another solution of KCl was then prepared. It contained 10.2025 gms.KCl/100 ml. solution. Both modifications were carried out simultaneously. The results were as follows:-

Volumetric method 8.28 gms./100 ml. solution

Gravimetric method 8.23 gms./100ml. solution

That shows that in order to use this method for the quantitative determination of potassium a factor has to be used.

To determine the potassium chloride content in Dead Sea water by this method, 10 ccs. of a solution containing 20.5150 gms. KCl/500 ml. solution were used along with 10 ccs. of Dead Sea water (sp. gr. 1.1940). Using the volumetric method the results were as follows:

Standard: Mg.eq. of base used = 3.8937

$$3.8937 \times 74.5 = 290 \text{ mgs. KCl/10 ccs.}$$

Actual KCl content in 10 ccs. = 410 mgms.

$$\text{Factor} = 410/290$$

Dead Sea water: Mg.eq. of base used = 0.005

$$\frac{0.005}{1000} \times 74.5 \times \frac{410}{290} = \frac{0.0527}{100} \text{ gms. KCl/10 ml.}$$

Or 0.00527 gms. KCl/100ml. of Dead Sea water.

In the gravimetric method 5ccs. of the standard solution were used together with 10 ccs. of Dead Sea water, and the result was as follows:

Standard: Wt. of $\text{KHC}_4\text{H}_4\text{O}_6 = 0.3905 \text{ gms.}$

$$0.3905 \times \frac{74.5}{189} = 0.154 \text{ gms. KCl}$$

Actual KCl content in 15 ml. = 0.2052 gms.

$$\text{Factor} = 2052/1540$$

Dead Sea water: Wt. of $\text{KHC}_4\text{H}_4\text{O}_6 = 0.0078 \text{ gms.}$

$$0.0078 \times \frac{74.5}{189} \times \frac{2052}{1540} = \frac{0.0409}{100} \text{ gms. KCl}$$

Or 0.00409 gms. KCl/100 ml. of Dead Sea water.

ii) Potassium Perchlorate Method:- As was already mentioned, two procedures would be followed here. In one procedure all metals other than the alkali metals were to be removed, while in the other no such removal seemed necessary.

Method 1. In a 150 ml. pyrex dish, 10 ccs. of a KCl solution (10.2025 gms/100 ml.) were placed, and then excess $(\text{NH}_4)_2\text{CO}_3$ made alkaline with NH_4OH was added. After filtration the solution was heated on a steam bath almost to dryness, then 3 ccs. of concentrated HCl were added slowly to convert the salts to the chloride form. A fairly hot flame was applied to remove the ammonium chloride; that was done until no white fumes evolved from the salts. The chlorides were then dissolved in water, and about 12 ccs. of HClO_4 (70% solution) were added, and the resulting mixture was heated on a hot flame to dryness. The residue was again dissolved in a few ml. of water and heated to fumes and finally to dryness. After cooling, 20 ml. of a mixture of equal parts of n-butyl alcohol and ethyl acetate were added, and the mixture was heated for a few minutes at near boiling point. The mixture was cooled and the supernatant liquid was decanted through an ignited and previously weighed Gouch crucible. The precipitate was washed thrice by decantation with the same solvent. The residue was then dissolved in a few ml. of water and again evaporated to dryness. 10 ml. of the mixed solvents were added and the mixture was again digested for a few minutes. The ppt. was then transferred to the Gouch crucible by means of the solvents and a policeman. After washing the ppt. in the Gouch crucible with the same solvents for many times, the Gouch was placed in an oven at 110°C . for one hour.

Result:- Wt. of $\text{KClO}_4 = 1.855$ gms.

$$1.855 \times 0.5381 = 0.996 \text{ gms. KCl/10 ml.}$$

(A small portion of the KClO_4 was lost during weighing)

The determination of the potassium chloride content in Dead Sea water was done by this method, save that magnesium was removed as MgNH_4PO_4 and was determined gravimetrically this way. This was done by adding to 10 ccs. of Dead Sea water (Sp.gr. 1.1940) 10 ccs. of 10% Na_2HPO_4 and then with stirring 2 ccs. conc. NH_3 . Allowing the ppt. to settle for some time, I filtered through a quantitative filter paper, and the filtrate was received in a clean 150 ml. beaker. The filter paper containing the magnesium ammonium phosphate was placed in a previously weighed and ignited crucible, and they were ignited on a torch.

Results:- Wt. of $\text{MgNH}_4\text{PO}_4 = 2.1163$ gms.

$$2.1163 \times 0.3623 \times \frac{95}{40} \times \frac{100}{10} = 18.33 \text{ gms. MgCl}_2/100 \text{ ml.}$$

(Actually MgNH_4PO_4 changes to $\text{Mg}_2\text{P}_2\text{O}_7$ on heating and it is weighed as such).

To the filtrate, a slight excess of Ba(OH)_2 solution was added to remove the phosphates. The mixture was concentrated on a water bath and then sufficient $(\text{NH}_4)_2\text{CO}_3$ was added to ppt. excess Ba(OH)_2 . This also would ppt. calcium ions. The mixture was filtered and the clear filtrate was evaporated on a water bath. 3 ml. of conc. HCl were added and the ammonium chloride was removed by heating on a flame as before. Following the procedure mentioned above I got a weight of 0.2100 gms. KClO_4

$$0.2100 \times 0.5381 \times \frac{100}{10} = 1.13 \text{ gms. KCl/100 ml. solution.}$$

Method 2. For determining the potassium content of Dead Sea water by this method without removing the calcium and magnesium salts, 10 ccs. of Dead Sea water (Sp.gr. 1.1940) were placed in a 150 ml. beaker and 2.5 ccs. 70% perchloric acid were added. The mixture was evaporated on a hot plate to fumes and then to dryness. 20 ccs. of the mixed solvents (n-butyl alcohol and ethyl acetate mixture) were added to the cooled beaker and the contents were then brought to a boil and digested for 2 minutes. The solvent was then filtered (after cooling) through a weighed Gouch crucible with asbestos bed (dried in an oven at 110°C for 2 hours). The residue was dissolved then in a few ml. of hot water, and again dried on a hot plate. The beaker and contents were cooled and 10 ml. of the mixed solvents were added, and the mixture was transferred to the Gouch crucible by means of a rubber policeman. It is worth mentioning that the KClO_4 formed a solid mass in the beaker and it was well ground in a semi-powder form by means of a glass rod before it was digested with the mixed solvents.

Result:- Wt. of KClO_4 after drying = 0.2499 gms.

$$0.2499 \times 0.5381 \times \frac{100}{10} = 1.345 \text{ gms. KCl/100 ml.}$$

The difference in the results of the two methods is most probably due to the incomplete removal of the calcium and magnesium perchlorates by the mixed solvents. This is definitely not due to their lack of solubility but must be due to their being occluded in the potassium perchlorate ppt.

Though the ppt. was reduced to fine particles and though it was dissolved in water and reprecipitated, yet some of the Calcium and magnesium perchlorates must have stayed there in spite of the frequent washings with the mixed solvents.

Nevertheless, the time consumed in the first method (removal of the magnesium and calcium salts) is more than double the time used in the latter method. The many steps involved in the former, each step necessitating the utmost care, are responsible for the long time this method needs.

iii) The Micro-method for the determination of Potassium as the Iodoplatinate:- The solutions needed for this determination are:

- a) 1N HCl solution (prepared with a factor of 1.082)
- b) Chloroplatinic acid solution containing 10% platinum.
- c) Absolute alcohol C_2H_5OH .
- d) Ethyl alcohol saturated with K_2PtCl_6 (prepared by using a small amount of K_2PtCl_6 adding to it alcohol and centrifuging to remove the ppt).
- e) KCl solution 10% saturated with K_2PtCl_6 (prepared as above).
- f) 2N KI solution (33.5 gms. of KI dissolved in 100 ml. solution).
- g) 0.01 N $Na_2S_2O_3$ solution (Prepared with a factor of 1.04).
- h) 0.2% H_2O_2 solution - must be prepared freshly by diluting 0.66 ccs. of 30% solution up to 100 ml.

A solution ~~is~~ prepared to contain 0.4103 mgms. KCl/cc.

was used to prepare standards.

Procedure: From the standard KCl solution, 3 and 4 ccs. were taken and put in two centrifuge tubes. In a third tube 0.1 cc. of Dead Sea water was placed. The tubes were brushed on a small flame to remove the water. One drop of 1N HCl was added to each of the tubes and then 0.3 ccs. of platinic acid solution (10% platinum) were added to each of them, followed by 5 ccs. of alcohol. After allowing them to stand for about 20 minutes, the mixture was centrifuged for 5 minutes. The excess platinic acid with the alcohol were poured in a beaker which is kept for the recovery of the platinum. The residue in the tubes was washed four times with alcohol saturated with K_2PtCl_6 . Then the residue was washed 5 times with 10% KCl solution saturated with K_2PtCl_6 . The yellow ppt. of K_2PtCl_6 was then dissolved in hot water (around 4 ccs. were used in all, for each tube) and the solution was placed in a 25 ml. volumetric flask. To this solution, 5 ccs. of 2 N KI were added to each flask, and then one cc. of N HCl. The solution was made up to volume, and the wine red color resulting was measured by means of a Dubosce colorimeter.

Results:- On putting the 4 ccs. solution in the left hand side, and in the right side were put the two other solutions the readings were as follows:

<u>Left side reading</u>	<u>Right side reading</u>
20° (4 ccs.)	7.35° (3 ccs.)
20° (4 ccs.)	8.40° (Dead Sea water)

Ratio of the standard to Dead Sea water = $\frac{7.35}{8.40} = \frac{x}{3 \times 0.4103}$
x = 1.077 mg. KCl/0.1 cc. or 1.077 gms.KCl/100 ml. solution.

The 4 ccs. solution was spoilt and gave erroneous results.

The combination of the volumetric and the colorimetric procedures was followed later. The procedure was as before, but after washing with hot water, the solution was placed in a small pyrex dish and 1cc. of 2N KI was placed in each solution. This solution was then let to boil only for a few minutes on a small flame and was titrated while hot with a 0.01N $\text{Na}_2\text{S}_2\text{O}_3$ solution through a micro burette. The end point is a lemon-yellow color free from red. This solution was then mixed with 0.1cc. of a 0.2% H_2O_2 solution prepared freshly and 1cc. of 1N HCl. After leaving for one hour the solutions were compared colorimetrically.

Results:- Volume of 0.01N ($F = 1.04$) $\text{Na}_2\text{S}_2\text{O}_3$ used for 0.1cc. of Dead Sea water = 1.5ccs.

$$0.01 \times 1.5 \times 1.04 \times 74.5 = 1.162 \text{ mgms. KCl}/0.1\text{cc.}$$

Or 1.162 gms. KCl/100 ml. of Dead Sea water

Compared colorimetrically with the 3ccs. solution in a Dubosce colorimeter, the readings were:

$$12^\circ \text{ (3ccs. solution) : } 13.7 \text{ (0.1cc. Dead Sea water)}$$

$$\frac{12}{13.7} = \frac{x}{3 \times 0.4103}, \quad x = 1.075 \text{ mgms. KCl}/0.1\text{cc.}$$

Or 1.075 gms. KCl/100 ml. of Dead Sea water.

The standard solution (3ccs. taken) used up 1.47ccs. of $\text{Na}_2\text{S}_2\text{O}_3$ solution, and hence a result of 1.14 mg. KCl instead of 1.2309 mg.

Using two and three ml. of the standard KCl solution and following the volumetric method, I obtained the following result:

2ccs. solution used 0.968ccs. $\text{Na}_2\text{S}_2\text{O}_3$

3ccs. " " " 1.495ccs. $\text{Na}_2\text{S}_2\text{O}_3$

$$0.986 \times 0.01 \times 1.04 \times 74.5 = 0.7275 \text{ mg. KCl}$$

$$\text{Actual content} = 0.8206 \text{ mg. KCl}$$

$$1.495 \times 0.01 \times 1.04 \times 74.5 = 1.12 \text{ mg. KCl}$$

$$\text{Actual content} = 1.23 \text{ Mg. KCl}$$

It is evident from the above results that with a desk-type centrifuge (500 r.p.m.) such as was used in those experiments, the complete separation of a fine ppt. from the solution is not possible and hence results lower than those expected were obtained. Using a large centrifuge and working at about 2500 r.p.m. I got the following results:

$$\begin{aligned} \text{Volume of Na}_2\text{S}_2\text{O}_3 \text{ used} &= 1.63 \text{ ml. (3 ml. of standard)} \\ &= 2.00 \text{ ml. (0.1 ml. of Dead Sea water)} \end{aligned}$$

$$1.63 \times 1.04 \times 0.01 \times 74.5 = 1.263 \text{ mg. KCl}$$

$$\text{actual content} = 1.2309 \text{ mg. KCl}$$

$$2 \times 0.01 \times 1.04 \times 74.5 = 1.55 \text{ mg. KCl/0.1 ml.}$$

Or 1.55 gms. KCl/100 ml. of Dead Sea water.

Due to the high content of other salts in Dead Sea water, washing the ppt. of K_2PtCl_6 to remove the other salts becomes a very important step in this method. Unfortunately, when working at 2500 r.p.m., washing a well packed ppt. in a small centrifuge tube is not quite possible, and therefore an optimal operating speed, which will separate the ppt. from solution as completely as possible and which will still keep the ppt. in a condition that allows efficient washing, must be worked out.

iv) Determination of Potassium by the use of the Flame Photometer:- Turn instrument on. Adjust air pressure to 10 lb. per sq.in., and propane gas to 5 lb./sq.in.. Light flame and wait for 30 minutes. Turn on the wave-length selector to the optimal wave-length of potassium. Adjust the galvanometer to 50 and pour the lithium standard into the funnel, and adjust to 50 again. Pour the highest standard, dial internal standard knob to 100 and adjust by means of the coarse and fine adjustment to get the null point (50° on galvanometer scale) again. Pour again the lithium and adjust by the potentiometer knob to the null point. The process is repeated until two consecutive readings of the fine and coarse adjustments coincide. The fine and coarse adjustments are then left during the whole experiment. The next lower standard is then added and the null point adjusted by means of the internal standard dial. Two readings are made after each reading the highest standard is poured. The average is made and the point recorded. The standards were prepared as follows:

A stock solution of LiNO_3 was prepared to contain 25.0151 gms/500 ml. A stock solution of KCl was prepared to contain 20.5150 gms/500 ml.

To minimize the effect of the comparatively large amounts of Mg^{++} , Ca^{++} and Na^+ in solutions of the unknown the standard KCl solutions were mixed with a solution containing: 6.1 gms. CaCl_2 14.4 gms NaCl and 59.8 gms $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, all dissolved in water and the volume made up to 250 ml.

The standards were made as follows:-

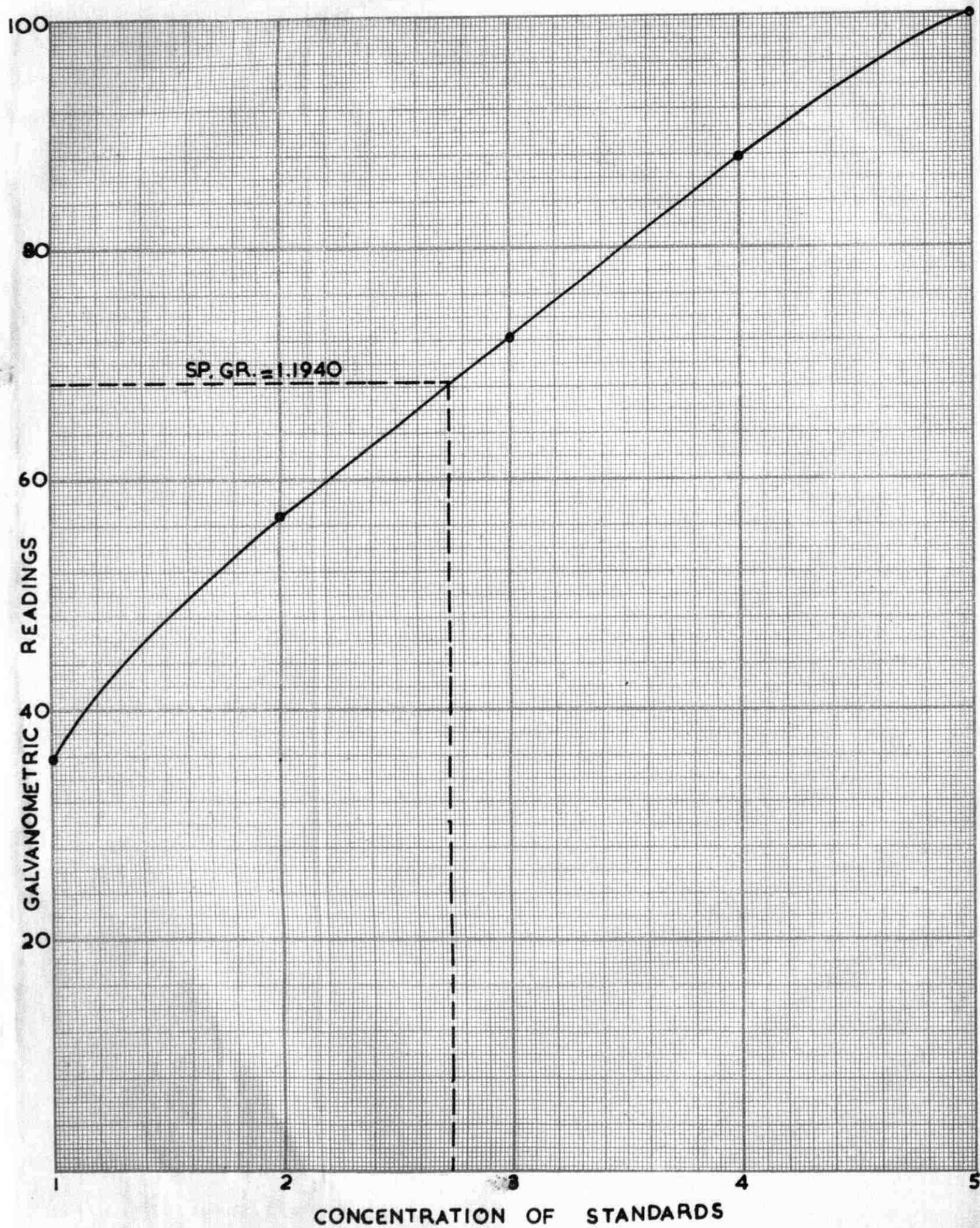
No.1:	10 ml. LiNO_3 solution)						
	5 ml. KCl)						
	25 ml. from the mixture))						diluted to make 100 ml.
No.2:	10 ml. LiNO_3 solution)						
	4 ml. KCl)	"	"	"	"	"	
	20 ml. mixture)						
No.3:	10 ml. LiNO_3 solution)						
	3 ml. KCl)	"	"	"	"	"	
	15 ml. mixture)						
No.4:	10 ml. LiNO_3 solution)						
	2 ml. KCl)	"	"	"	"	"	
	10 ml. mixture)						
No.5:	10 ml. LiNO_3 solution)						
	1 ml. KCl)	"	"	"	"	"	
	5 ml. mixture)						

The internal standard was prepared to contain 10 ml. of the LiNO_3 solution diluted to 100 ml.

The solution of the mixed salts was so made that in the standard solutions the ratio of the salts to KCl is more or less the same as found in Dead Sea water. The readings were as follows:

<u>Sample No.</u>	<u>Int. Standard Reading</u>	<u>Gain Settling</u>	<u>Average Difference</u>	<u>Average Calibration curves</u>
1	100	4:46		
1	100	4:41		
1	100	4:41		

Since the coarse and fine adjustments gave on consecutive trials the same readings they are set aside during the rest of the experiment while the null point will be adjusted - on adding the standards - by means of the internal standard knob.



Sample No.	Int. Standard Reading	Difference	Average Difference	Average Calibration Curves
1	99.2			
2	87.9	11.3		
1	100.2	12.3	12.15	87.78
2	87.8	12.4		
1	100.4	12.6		

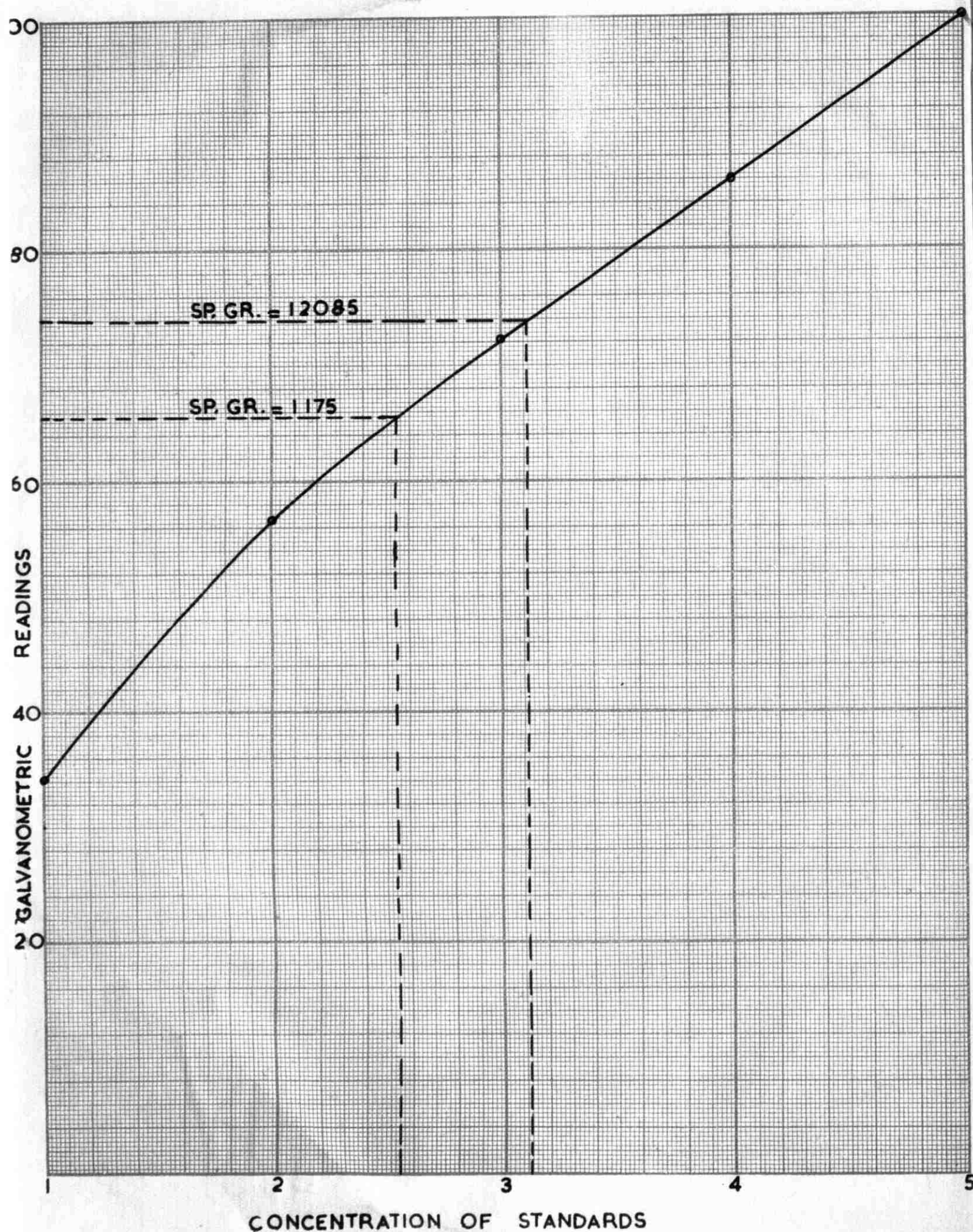
1	99.3			
3	72.3	27.0		
1	99.1	26.8	26.8	72.3
3	72.3	26.8		
1	98.9	26.6		

1	99.4			
4	57.1	42.3		
1	99.8	42.7	42.7	56.8
4	56.7	43.1		
1	99.4	42.7		

1	99.4			
5	35.3	64.1		
1	99.5	64.2	63.7	35.7
5	35.7	63.8		
1	99.3	62.6		

1	99.1			
D.S.*	68.2	30.9		
1	98.2	30.0	30.4	68.3
D.S.	68.1	30.1		
1	98.8	30.7		

* Solution made from 10 ccs. of Dead Sea water (Sp.gr. 1.194 at 20°C) and 10 ccs. of LiNO₃ solution diluted to 100 ml.



Results:- On plotting galvanometric readings (average calibration) against concentration, we got almost a straight line from which the concentration of the unknown with an average reading of 68.3 was found to be 1.0828 gms.KCl per 100 ml.

Another calibration was made with a view of finding the KCl content in two samples of Dead Sea water. One sample was taken from the surface (specific gravity 1.175) and another was taken from a depth of 40 metres (sp.gr. 1.2085). The calibrations were made as before. After adjusting the coarse and fine adjustments to 4:36.5 the readings were as follows:

<u>Solution</u>	<u>Average Calibration Curve</u>
2	85.9
3	72.4
4	56.6
5	34.2
(sp.gr.1.175)	65.5
(sp.gr.1.208)	74.1

On plotting galvanometric readings against concentration as before, the KCl content of the brine (sp, gr. 1.175) was found to be 1.0742 gms KCl/100 ml. and in the brine (sp.gr. 1.2085) was found to be 1.2792 gms.KCl/100 ml.

Once the standards and the unknown solutions are prepared, the whole experiment will not take more than one and a half hours; this includes the time of heating the instrument which is half an hour.

The instrument is a Perkin-Elmer model, and is adapted for the determination of Mg^{++} and Ca^{++} as well provided a hot flame such as an acetylene flame is used.

b) Evaporation Experiments:

In a two-liters beaker, 1800 ml. of Dead Sea water (sp. gr. 1.1940) were placed and then were boiled until the specific gravity of the cooled brine came up to 1.305. The volume of the water evaporated during this stage was about 850 ml.. The salt which separated was filtered by suction and the filtrate was again boiled until the specific gravity became 1.32. The volume of water evaporated during this period was about 260 ml. The weight of the carnallite which crystallized during this period was 49.5 gms. and this was decomposed with 28 gms. of water and then filtered by suction. The weight of crude KCl thus produced was 6.2 gms. The residual brine was evaporated to a specific gravity of 1.337 and during this period $MgCl_2 \cdot 6H_2O$ in characteristic crystals separated out. The volume of the brine left after removing the $MgCl_2 \cdot 6H_2O$ was 260 ml. Analysis of the carnallite and KCl produced during this experiment:

Analysis of Carnallite: Using the perchlorate method for potassium, and removing the magnesium as $MgNH_4PO_4$ and determining it in this form, the result of the analysis was as follows:-

Weight of sample taken = 1.0586 gms.

This amount was dissolved in water and the volume made up to 50 ml. 10 ml. were used for analysis.

Wt. of $Mg_2P_4O_7$ = 0.0843 gms.

Percentage of $MgCl_2$ in sample =

$$0.0843 \times 0.3623 \times \frac{95}{40} \times \frac{50}{10} \times \frac{100}{1.0586} = 34.2\%$$

The filtrate containing the KCl was then analysed.

Weight of $KClO_4 = 0.0900 \text{ gms.}$

$$\begin{aligned} \text{Percentage of KCl in sample} &= 0.0900 \times 0.5381 \times 5 \times \frac{100}{1.0586} = \\ &= 22.93\% \text{ KCl} \end{aligned}$$

Analysis of crude KCl:- The KCl produced by the decomposition of carnallite gave the following result:

Weight of sample taken for analysis = 0.2145gms.

Weight of $KClO_4 = 0.3142 \text{ gms.}$

$$\begin{aligned} \text{Percentage of KCl in sample} &= 0.3142 \times 0.5381 \times \frac{100}{0.2145} = \\ &= 79\% \text{ KCl} \end{aligned}$$

Note:: The KCl sample was directly treated with perchloric acid after dissolving in water, since only traces of $MgCl_2$ are expected to be present, the only other impurity being NaCl.

Discussion: From the results of the analysis made above, we can calculate the purity of the carnallite produced. Since the KCl found must all have precipitated with an equimolecular quantity of $MgCl_2$ in the form of carnallite, then 29.3 gms. of $MgCl_2$ must be combined with the 22.93 gms. of KCl together with 32.97 gms. of water of crystallization, a combination corresponding to a carnallite which is 85.2% pure:

	KCl	22.93%)		
	H ₂ O (cryst.)	32.97%)		
	(MgCl ₂	29.3%)		Carnallite 85.2% pure
Total = 34.3% MgCl ₂	(MgCl ₂	5.0%)		
	NaCl+H ₂ O ...	9.8%)		Adherent liquor

The recovery of the KCl from the brine is about 25% of the original amount found. This was calculated from the amount and purity of the KCl produced from carnallite:

KCl content in Dead Sea water (sp.gr. 1.194) = 1.13%

Total amount of KCl in 1800 ml. = $\frac{1.13 \times 1800}{100} = 20.34$ gms.

Amount of pure KCl recovered from carnallite =

$\frac{6.2 \times 79}{100} = 4.96$ gms.

Recovery = $\frac{4.96 \times 100}{20.34} = 25\%$

c) Extraction of Bromine:-

The bromine content of Dead Sea water, sp.gr. 1.194, calculated as $MgBr_2$ was found to be 3.4 gms. $MgBr_2/l.$ The method used here to determine the bromide in the presence of chloride is based on the fact that acidified $K_2S_2O_8$ oxidizes the Br^- to Br_2 but does not oxidize the Cl^- . The Br_2 can then be extracted three or four times with CCl_4 . The extract is then treated with KI and the I_2 liberated is determined volumetrically by means of $Na_2S_2O_3$.

Due to the complete absence of iodine in the Dead Sea water, the extraction of Br_2 becomes fairly simple. The bromine is set free by means of chlorine gas, the free bromine can then be removed by bubbling air through the solution and warming the mixture; the bromine is then collected in cooled containers.

The maximum concentration of $MgBr_2$ is reached when the specific gravity of the brine reaches 1.33 i.e. in the liquor/after the carnallite has been separated. At this stage the solution becomes saturated with $MgCl_2$ and on further evaporation $MgCl_2 \cdot 6H_2O$ would start to separate. In this third stage where $MgCl_2 \cdot 6H_2O$ separates till sp.gr. 1.37, most of the $MgCl_2$ is removed but only a small amount of $MgBr_2$ is removed out with it (only 0.483 gms. $MgBr_2/l.$). The concentration of $MgBr_2$ at sp.gr. 1.37 is 26 gms./l. It is, therefore, much more economical to separate the $MgCl_2 \cdot 6H_2O$ in the pans first, and then transfer the mother liquor for the extraction of bromine, rather than do the opposite since energy would be saved both in the reansfer of the brine and later, where fuel could be saved in heating the reduced volume of the brine for the liberation of bromine.

Procedure:- After the removal of the $MgCl_2 \cdot 6H_2O$ (third stage in the evaporation of the brine), the liquor - sp.gr. 1.37 - was placed in a distilling flask. Chlorine in another container was liberated by the oxidation of conc. HCl by MnO_2 . This chlorine gas was passed into an empty bottle which served as a safety valve and as a pressure regulator, and then was bubbled through the brine in the distilling flask. Through the condenser, which was connected to the distilling flask, cold water at around $10^{\circ}C$. was circulated. The receiver - a weighed erlenmeyer flask - was also surrounded by ice and water. If the Cl_2 gas were allowed to bubble quickly through the solution a considerable amount of bromine would be lost with the outcoming chlorine inspite of the precautions taken, due to the high vapor pressure of bromine even at low temperatures*. Soon after the bubbling of the Cl_2 started, the solution acquired a brown-red colour which darkened as the bubbling of Cl_2 went on. After allowing ample time for the replacement of Br_2 , the current of Cl_2 was stopped and was replaced by a current of air. Blowing air was started after heating the mixture till about $50^{\circ}C$. The bromine - dark brown in colour - started to pass through the condenser moving slowly downwards. Since the receiver was immersed in an ice - salt mixture, the bromine was collected in a semi-solid brown mass.

* Vapor pressure of bromine at various temperatures in mm. Hg:-

-7.3	(F.P.)	=	44.4	mm.
0	(L.)	=	65.9	mm.
10	(L.)	=	109	mm.
20	(")	=	173	mm.
30	(")	=	264	mm.
40	(")	=	392	mm.
58.78	(B.P.)	=	760	mm.

Table taken from the Handbook of Chemistry and Physics.

Driving out the bromine in earlier experiments was done by boiling the mixture and no air was bubbled through, in which case some water was collected together with the bromine. Later on, however, when air was bubbled through, boiling was unnecessary and no water was collected with the bromine. However, a small amount of bromine was left after the heating and treatment with air (about 7% of the total bromine liberated) and this needed a higher temperature for its liberation and hence some water was collected together with it. The bromine left in solution after this treatment was found to be 0.612 gms./l. (using the method mentioned above).

Calculations: Br⁻ content in Dead Sea water, sp.gr. 1.194 using 25 ml. of the brine; volume of Na₂S₂O₃ (N = 0.957) = 1 cc.

$$1 \times 0.957 \times \frac{1}{25} \times 80 = 3.06 \text{ gms. Br}_2/\text{l. or } 3.06 \times \frac{180}{160} = 3.4 \text{ gms. MgBr}_2/\text{l.}$$

Starting with 3300 ml. brine sp.gr. 1.194 and evaporating to 640 ml. solution sp.gr. 1.37 and using 470 ml. for the experiment, the

$$\text{bromine content in solution used} = \frac{3300}{1000} \times 3.06 \times \frac{470}{640} = 7.42 \text{ gms. Br}_2$$

Weight of bromine liberated in the first stage = 4.6 gms.

" " " " " " second " = 6.5 gms. Total = 5.1 gms.

$$\text{Percentage recovery of bromine} = \frac{5.1}{7.42} \times 100 = \underline{68.7\%}$$

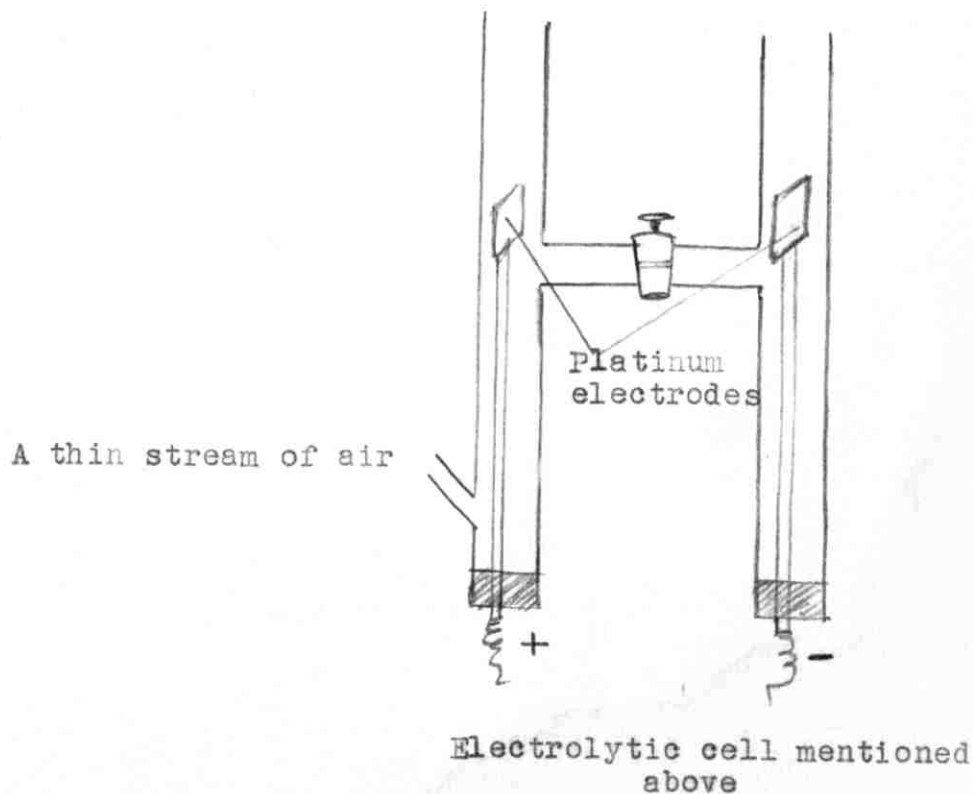
Electrolysis of Dead Sea brine was contemplated as a means for extracting Br₂ from it. This method was found to be impractical industrially for two main reasons:-

1st. The resistance of the brine (sp.gr. 1.36) turned out to be very high. A cell, designed as shown in figure next page, was used, with platinum electrodes. The voltage across the cell was adjusted to 3.7 volts, and the current passing through it did not exceed 2.4 milliamperes.

According to the data given above, between 6.9 and 14 mgms. of Br_2 will deposit in an hour in such a cell - figures that make the method economically impossible.

2nd. Using the same power and assuming the same current efficiency, one ton of Br_2 and 363 kgms. of $\text{Mg}(\text{OH})_2$ can be prepared on electrolysing aq. MgBr_2 , while one ton of Br_2 and 500 kgms. of NaOH are produced on electrolysing aq. NaCl (pure NaCl is produced in huge quantities in the first stage of evaporation of the brine). In this case the Br_2 is produced by liberating it by means of Cl_2 gas in the electrolytic cell.

It is clear from what was mentioned above, that a by-product of 500 kgms. of NaOH is much more valuable than a by-product of 363 kgms. of $\text{Mg}(\text{OH})_2$ specially now that Mg metal is prepared mostly from the fused MgCl_2 and only a small amount of the metal is prepared from the fused MgO (by electrolysis in both cases).



Appendix

Table A

Results of KCl determination of Dead Sea water by different methods. (Sp.gr. of sample = 1.1940)

	<u>Gms.KCl/100 ml.</u>
1. Bitartarate method:	
a) Volumetric	# 00527
b) Gravimetric	# 00409
2. Perchlorate method	
a) Removal of Mg ⁺⁺ & Ca ⁺⁺ ...	1.13
b) Without removal	1.345
1.108
3. Micro method	
a) Colorimetric	1.076*
b) Volumetric	1.162
4. Flame Photometer	1.0828
* Average taken.	

Table C

Specific gravity* of Dead Sea water at various depths. (Samples taken 30th. April, 1953.)

Surface	1.175
1 meter	1.178
2 "	1.180
3 "	1.180
5 "	1.183
10 "	1.185
25 "	1.185
35 "	1.183
40 "	1.185
40 [@] "	1.2085
60 "	1.190

* Taken at 23°C.

@ Sample taken from a southward part

Table B

KCl content in Dead Sea water as reported by different workers.

<u>Worker</u>	<u>Gms.KCl/100 ml.</u>	<u>Sp.Gr.</u>	<u>Temperature</u>
Novomeysky ¹	1.18	1.1725	23°C
	1.47	1.224	23
Panteleymonoff ²	0.9841	1.1475	20
Lieut. Lynch ³	0.8081	1.2274	20
The Writer (G.B.)	1.151	1.1940	20
	1.0742	1.175	23
	1.2792	1.2085	23

1. Trans. Inst. Chem. Eng. 14, 60 (1936)

2. La Revue de Chemie Industrielle, 118, (1934)

3. Official Report of the U.S. Expedition to explore the Dead Sea and the River Jordan, 1852.