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Aus dem Institut für Meereskunde an der Universität Kiel

## The Chemical Composition of Sea Water from the Suez Canal Region

Part II: Major Cations<sup>1)</sup>

By

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**Die chemische Zusammensetzung von Meerwasser aus dem Gebiet des Suez Kanals (Zusammenfassung):**

Teil II: Die Hauptkationen

Nach einer modifizierten Methode von Greenhalgh et. al. (1966) werden Kalium, Natrium und Magnesium durch Trennung mittels eines Ionenaustauschers bestimmt. Die Veränderungen der Methode enthalten die Anwendung kleinerer Mengen Elutionslösung, leichtere Trennung und Titration des Kalziums mit EDTA.

Es werden Veränderungen in der chemischen Zusammensetzung des Meerwassers aus dem Suez Kanal beobachtet. Die Auswirkungen der Verdünnung durch das Nilwasser bestehen aus einem geringfügig erhöhten  $\text{Ca}^{++}/\text{Cl}^-$ -Verhältnis im Mittelmeer auf der Höhe von Port Said und im Lake Timsah. Das Salzbett ist sehr arm an Magnesium und Kalium, Kalzium ist geringfügig vermindert, jedoch ist das  $\text{Na}^+/\text{Cl}^-$ -Verhältnis gegenüber Meerwasser erhöht. Das salzreiche Wasser aus den Bitterseen zeigten kleinere  $\text{K}^+/\text{Cl}^-$ - und  $\text{Mg}^{++}/\text{Cl}^-$ -Verhältnisse als normal. Die Beziehungen zwischen dem Chloridgehalt und den Kationen (berechnet nach der Methode der kleinsten Fehlerquadrate) sind nicht konstant, sondern nehmen mit steigendem Chloridgehalt ab oder zu. In einer Tabelle (10) wird eine Formel für die relative Zusammensetzung von Meerwasser aus den Bitterseen angegeben, die ein höheres  $\text{Na}^+/\text{Cl}^-$ -Verhältnis anzeigt als normal.

**(Summary):** Potassium, sodium, calcium and magnesium were determined after separation on an ion-exchanger according to a modified method of Greenhalgh et al (1966). The modifications include smaller amounts of eluting agents, easier separation and titration of calcium with EDTA.

Variations in the chemical composition of sea water from the Suez Canal were detected. The effect of dilution by the Nile water is evident in the slightly higher chlorinity ratios of calcium in the Mediterranean off Port-Said and in Lake Timsah. The salt bed was found to be very poor in magnesium and potassium, calcium is slightly reduced, while sodium has higher chlorinity ratio than in sea water. The highly saline waters of the Bitter Lakes show lower values of chlorinity ratios for potassium and magnesium, higher values for sodium, while calcium is slightly reduced. Relationships between the chlorinity and the cations calculated by the least square method show that the chlorinity ratios of the cations are not constant but decrease or increase with increasing chlorinity. A suggested formula for the relative composition of sea water from the Bitter Lakes is given in Table (10) which indicates a higher sodium/chlorinity ratio than normal, and supports the experimental findings.

The present work deals with the concentration of sodium, potassium, magnesium and calcium of the same samples of sea water and salt bed which has been reported in Part I.

<sup>1)</sup> For Part I, see S. A. MORCOS (1967), Kieler Meeresforsch. Band 23, S. 80.

## Experimental

The four major cations reported in the present work were determined by a modified procedure of Greenhalgh, Riley and Tongudai (1966). The main cations in sea water are adsorbed on a column of Amberlite C G 120. Sodium and potassium are eluted together using 0.15 M ammonium chloride and determined gravimetrically as sulphates; potassium is then determined gravimetrically as potassium tetraphenylboron and sodium is determined by difference. Magnesium and calcium are eluted by means of 0.35 M ammonium chloride and 1 M ammonium acetylacetonate (pH 9.6) respectively, and titrated with E D T A. Finally strontium is eluted with 2 M nitric acid and determined by flame photometry.

When the present work was conducted, the above procedure was not yet published in its final form, and only a concise account of the method was available. Because of this, and because of the special nature of the samples investigated, the author has introduced some modifications which are described below. The modifications are mainly in the separating columns, in the eluting curves and in the separation of calcium.

### Ion Exchanger:

A column of Amberlite C G 120, 18.5 cm in length and 6 mm internal diameter (instead of 7 mm) was found to retain the cations from 20 ml of sea water of chlorinity 21‰ and allow for the separation of cations during elution. For sample should be decreased or increased proportionately.

### Eluting Curves:

#### Sodium and Potassium:

An eluting curve of sodium was made by using 80 ml of 0.15 M ammonium chloride followed by six 20 ml. aliquots. The sodium is determined spectrophotometrically in the solutions after diluting to known volumes. Half of the aliquots making the first 160 ml of eluant were combined together and determined gravimetrically. The eluting curve (Fig. 1) shows that the first 80 ml elutes 98.9% of the sodium, while all the sodium is almost completely eluted by 140 ml of the eluant. Potassium was not detected spectrophotometrically in the next 20 ml aliquots of 0.15 M ammonium chloride, i. e. completely eluted with the sodium.

#### Magnesium:

Magnesium was determined by photometric titration in the 20 ml aliquots of 0.15 M  $\text{NH}_4\text{Cl}$ . It was found that in 64% of the cases, the elution of Mg starts after passing 120 ml of 0.15 M ammonium chloride, while in the rest of cases after passing 140 ml. The eluting curve in Fig. 2, shows that the elution of Mg is completed by 180 ml of 0.35M ammonium chloride. The following 20ml are tested either for magnesium or calcium.

#### Calcium:

Carpenter (1957) used ammonium acetylacetonate reagent to elute calcium, Greenhalgh et al. (1966) used the same reagent. They attempted to elute calcium with 0.35—1.0 M ammonium chloride solutions; even after 250 ml of the 1.0 M eluant had been passed through the column, the elution was not complete and strontium had begun to appear. Fig. (2) shows that calcium and strontium are completely eluted by 480—500 ml 0.35 M ammonium chloride. This eluant has the advantage that calcium (+ strontium) can be titrated in it directly using E D T A, unlike the ammonium acetylacetonate reagent,

which interferes in the titration. It was found that much time is consumed in destroying this reagent and in washing the column free from it. Moreover, there is also the risk of loss of calcium during treating and transferring the solution. Strontium is determined directly in sea water by the method of Culkin and Cox (1966), and calcium can be estimated by difference.

#### Procedure :

The procedures and the reagents used in the present work are that of Greenhalgh et al (1966), except for the following points :

1 — A weighing pipette or burette is used to transfer a known weight of the sample to the top of the ion exchange column. This technique reduces the error in transferring the sample if it is weighed in a conical flask.

2 — A 250 ml glass flask (Fig. 3) is used to transfer the eluants continuously to the upper chamber of the ion exchange column. It is possible in this way to use larger amounts of eluants, and to operate the columns almost continuously. Twelve columns were employed simultaneously in the present investigation.

#### 3 — Eluting Scheme :

a — The percolate from the sample is received in a 100 ml measuring flask and diluted to the mark (Solution A).

b — Elute sodium and potassium from the column with 120 ml of 0.15 M ammonium chloride solution (Solution B).

c — Pass a further 20 ml of this eluant through the column. Dilute the eluate to 50 ml in a measuring flask (solution C) and retain for determination of both sodium and magnesium.

d — Elute magnesium with 180 ml 0.35 M ammonium chloride solution and collect the eluate in a 250 ml measuring flask. Dilute to the mark (Solution D).

e — Pass a further 20 ml of this eluant through the column. Receive the eluate and dilute in a 50 ml measuring flask (Solution E). Retain for determination of either magnesium or calcium.

f — Elute calcium and strontium with 480 ml 0.35 M ammonium chloride. Dilute to 500 ml. — (Solution F).

#### Determination of Sodium :

Sodium is determined by a flame spectrophotometric technique in solution A and solution C and the values obtained are added to the value of sodium determined gravimetrically in solution B. However, the values obtained from solution A and solution C contribute only to the fifth decimal of the weight of sodium in solution B. A Carl Zeiss flame spectrophotometer P M Q II was employed, and a wave length of 590.2 nm was used for the determination of sodium.

#### Determination of Magnesium and Calcium :

##### Reagents :

Buffer Solution: 70 g ammonium chloride + 600 ml ammonia solution (sp. gr. 0.880), and make up to 1 L.

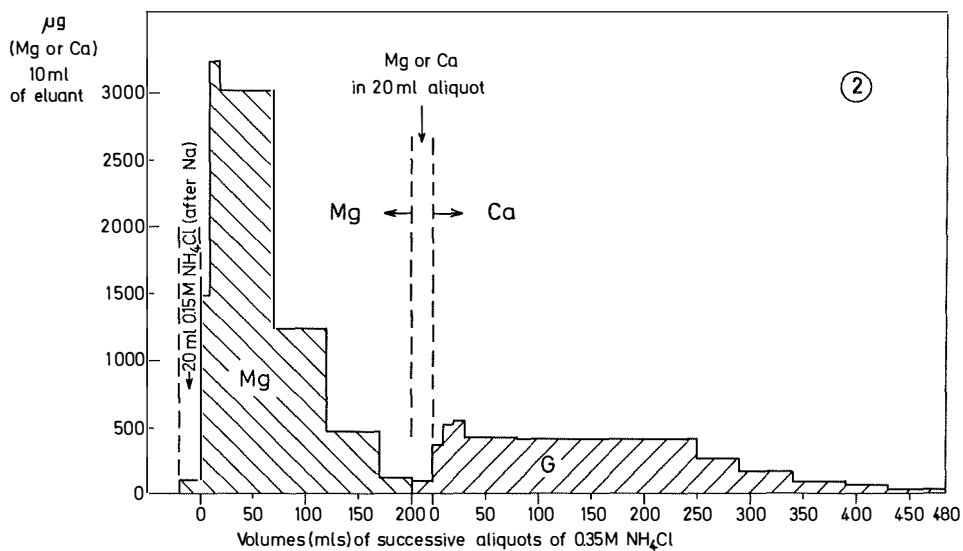
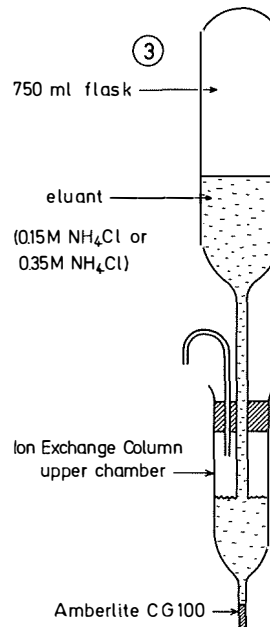
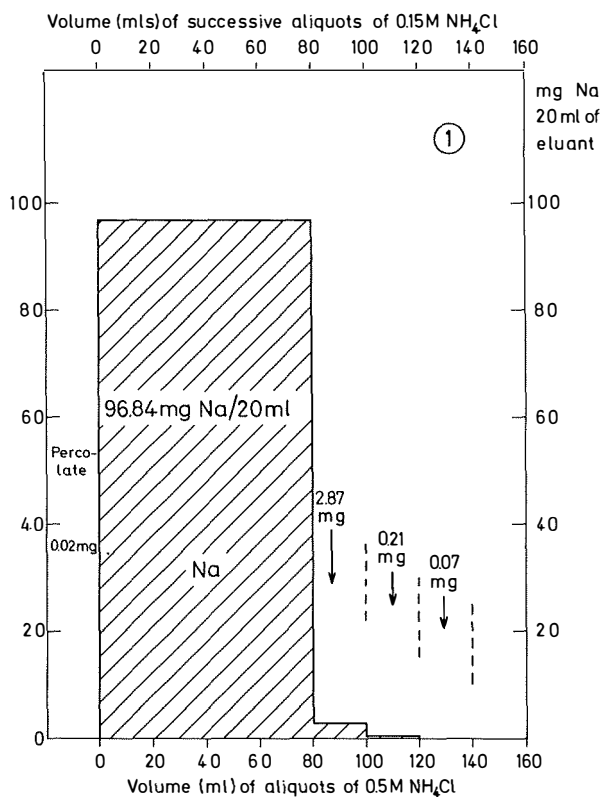
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#### Plate (1)

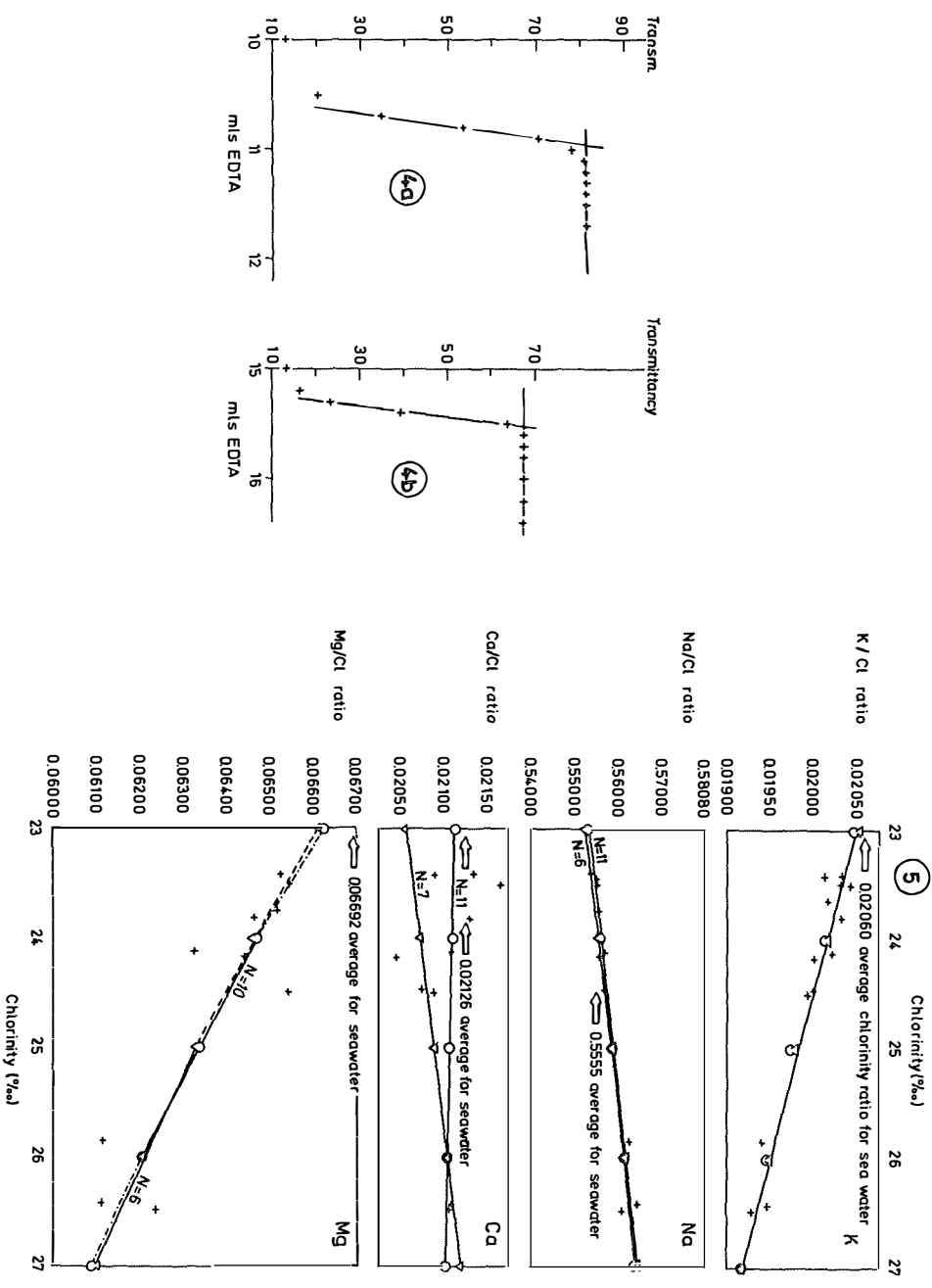
Fig. 1: Elution of sodium.

Fig. 2: Elution of Magnesium and calcium.

Fig. 3: Upper part of the ion exchange column.



Tafel 1 (zu S. A. Morcos)



Tafel 2 (zu S. A. Morcos)

E D T A Solution: Dissolve 2.5 g of disodium salt of the ethylenediamine tetracetic acid in 800 ml of distilled water. Add 2—3 drops of toluene and make up to 1 L. This solution does not contain a known volume of standard magnesium solution as described by Greenhalgh et al (1966).

Eriochrome Black T indicator: 0.1 g/50 ml of ethyl alcohol.  
Triethanolamine: (T E A).

Standard magnesium solution: Weigh out 0.15 g of pure magnesium, dissolve in minimum dil. hydrochloric acid, evaporate to near dryness, make up to 1 L. This solution contains 150  $\mu\text{g}$  Mg/ml.

Standard calcium solution: 0.49945 g of pure calcium carbonate/500 ml. This solution contains 400  $\mu\text{g}$  Ca/ml.

Magnesium is determined directly in solutions C, D and E by photometric titration, with E D T A using Eriochrome black T as indicator. The solutions should be brought to pH 10 with ammonia solution.

A Carl Zeiss Electrophotometer "Elko II" was used after some modifications for photometric titration. A titration vessel was constructed from a plexiglass sheet. It was 6.5 cm deep, 2.5 cm wide, and 6.5 cm long. The vessel was placed in the cell compartment, and covered with a light-proof lid which was provided with two holes, one for a glass rod attached to a stirrer and the other for the tip of an automatic mechanical microburette. The filter used was I 66 which has its maximum transmission at 665 nm. After stirring the solution, the photometer slit was adjusted so that the measuring cylinder reads 10 transmittance degrees. The end point should be reached before the instrument reads 100 transmittance degrees. For this reason an appropriate dilution of the solutions should be used. It was found that the titration is completed successfully by adding 15 ml of the eluate (C, D or E) or the standard + 45 ml distilled water + 2 ml of the buffer solution + 0.5 T E A + 1 ml E B T indicator.

Calcium is titrated in the same way as magnesium except that in this case 0.5 ml of standard magnesium solution is added to each calcium titration to give a stable end point. E B T forms a less stable complex with calcium than with magnesium. If magnesium is present in solution, the red magnesium E B T complex is formed, and will be decomposed only after all the calcium in solution disappears, since it is preferentially complexed by the E D T A. When the last trace of magnesium is complexed by the E D T A, the red colour is replaced by the pure blue colour of the free indicator.

This is applied in the titration of solution E, which marks the end of magnesium or the beginning of calcium. If it gives red a colour, then titrate for magnesium. If it gives a blue colour with E B T, then magnesium is not present. Add 0.5 ml of standard magnesium solution and titrate for calcium. The titre obtained thus includes that of 0.5 ml of standard magnesium solution which is subtracted.

The recommended dilutions for the calcium titration is; 40 ml of solution F + 20 ml of distilled water or 10 ml of the standard calcium solution + 50 ml of distilled water.

The magnesium is calculated as the sum of that present in solution C + solution D + eventually solution E.

The calcium is calculated as that in solution F + eventually solution E.

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#### Plate (2)

Fig. 4: Typical titration curves with a Zeiss Elko II photometer, filter I 66. a) magnesium, b) calcium.  
Fig. 5: Chlorinity ratio for potassium, sodium, calcium, and magnesium.

Table 1a Potassium and

Sample No.	Station	Position	Month (1964)	Depth (m)	S <sup>0</sup> / <sub>00</sub> computed from Cl <sup>0</sup> / <sub>00</sub>	Cl <sup>0</sup> / <sub>00</sub>
1	1 A'	N. of Port Said	Sept.	0	27.085	14.989
2	1 l	Lake Timsah	Sept.	0	32.646	18.070
3	1 A' }	N. of Port Said	Sept.	13	38.910	21.540
4	1 A' }		April	6	39.244	21.725
5	25'a		April	0	42.274	23.404
6	25'a		April	0	42.325	23.432
7	25'b	Suez Bay	April	0	42.419	23.484
8	25'b		April	0	42.472	23.514
9	25'		Sept.	0	42.896	23.749
10	25		Sept.	0	43.020	23.817
11	K a		April	12	43.576	24.125
12	K b	Great Bitter	April	12	43.836	24.169
13	13 a	Lake and	April	12	44.192	24.466
14	i b	Southern	April	12	44.256	24.502
15	K	Canal	Sept.	13	46.697	25.854
16	19		Sept.	13	47.727	26.425
17	22		Sept.	14	47.834	26.484
A		Salt Bed of the	Octob.	16	38.155	21.121
B		Great Bitter Lake	1955	16	38.730	21.440
C				16	40.050	22.171

The calcium values are corrected for the strontium content in sea water assuming a strontium/chlorinity ratio of 0.00043 for all the samples. Variations in the Sr/Cl ratio will never affect the calcium/chlorinity ratio by more than  $1 \times 10^{-5}$ . It appears that the previously accepted value for the strontium content is too high and therefore the corrected calcium content was too low. Due to the increasing number of calcium analysis of sea water, and the difficulty in separating small amounts of strontium from relatively large amounts of calcium one recalls WEBB's (1938) suggestion to adopt a convention to use a calcium to chloride ratio meaning "calcium after the strontium and barium have been replaced by calcium".

Typical titration curves of magnesium and calcium are shown in Fig. (4).

#### 1 — Potassium

Potassium was determined in sea water and salt bed samples by the method of sodium tetraphenylboron as described by Greenhalgh et al. (1966). Determinations were made in quadruplicates or triplicates and they gave a coefficient of variation of 0.57% i. e. 0.00011 potassium/chlorinity ratio. The results for the 17 sea water samples and the 3 samples from the salt bed are shown in (Table 1a).

The estimate of the potassium/chlorinity ratio calculated by THOMPSON and ROBINSON (1932) from the analysis of sea water published since 1880 showed considerable variation, in spite of the fact that all earlier workers used the chloroplatinate method. A potassium/chlorinity ratio = 0.02000 was obtained by them as an average of all the analysis published up to their time. This value was accepted by LYMAN and FLEMING (1940), who considered it in good agreement with the result of WEBB (1939) of 0.02009. When the



Sodium in the Suez Canal

K (g./kg.)	Potassium		Scatter	Sodium		Na/Cl Average	Na/Cl Scatter
	K/Cl	K/Cl Average		Na (g./kg.)	Na/Cl		
0.3055	0.02038			8.311	0.5545		
0.3639	0.02024			9.977	0.5521		
0.4385	0.02036	0.020,37	0.00046	11.924	0.5536	0.5534	0.0024
0.4475	0.02060						
0.4755	0.02032			12.965	0.5540		
0.4717	0.02013			13.010	0.5552		
0.4796	0.02031	0.020,28	0.00031	—	—	0.5553	0.0019
0.4805	0.02044			13.606	0.5554		
0.4788	0.02016			13.202	0.5559		
0.4843	0.02033			13.240	0.5559		
0.4874	0.02021	0.020,03	0.00028	13.441	0.5571	0.5567	0.0012
0.4859	0.02002			13.490	0.5559		
0.4888	0.01998	0.019,76	0.00092	13.629	0.5570	0.5598	0.0088
0.4883	0.01993			—	—		
0.5018	0.01941	0.019,39	0.00019	14.548	0.5627	0.5628	0.0036
0.5147	0.01948			15.283	0.5647		
0.5110	0.01929	0.019,76	0.00092	14.861	0.5571	0.5598	0.0088
0.0002	0.00001			13.677	0.6475		
0.0003	0.00002	0.000,32	0.000,92	13.846	0.6458	0.6417	0.0156
0.0206	0.00093			14.010	0.6319		

extreme values of potassium/chlorinity ratio in all the determinations up to 1956 are ignored, the figures range from 0.0195 to 0.0213 (CULKIN, 1955). CULKIN and COX (1966) established a potassium/chlorinity ratio of 0.0206 as a mean of 54 samples between 0.0203 and 0.0209 show much less scatter than the older data, and suggest that no significant variation exists with depth or geographical position.

Comparison with the published data (Table 2) shows that the potassium/chlorinity ratios of Port Said and Suez Bay regions are slightly higher than those of WEBB (1939) and JENTOFF and ROBINSON (1956) who used the cobaltinitrite method, but they are slightly lower than those of SPOREK (1956) and CULKIN and COX (1966) who determined potassium directly in sea water as potassium tetraphenylboron. The present figures are obtained by the tetraphenylboron method, but after eluting sodium and potassium from the other cations. The difference between these figures and those obtained by direct precipitation from sea water may be attributed to regional differences. It points out, however, the need for a comparison between the methods of direct precipitation from sea water as potassium tetraphenylboron, and that involving precipitation after separation of the potassium and sodium from the rest of the ions. SPOREK (1956), who used the direct method, admitted that other metal ions present in sea water caused a positive error of about 1%. CULKIN and COX (1966) found that this method gives satisfactory results for synthetic sea water of known potassium content if the precipitation were carried out at lower acidity than that used by SPOREK.

The potassium/chlorinity ratio in river waters amounts to 0.37 (Calculated from CLARKE, 1924 and KALLE, 1945), i. e. as much as 20 times that of sea water. However, no effect of the Nile water is detected when comparing the potassium/chlorinity ratio in Port Said region (0.0204) with that of the Suez Bay (0.0203). The scatter in the two

Table 1b. Calcium and Magnesium in the Suez Canal

Sample No.	Region	Month (1964)	Calcium		Mg (g/kg)	Magnesium		Mg/Cl Scatter
			Ca (g/kg)	Ca/Cl Average		Mg/Cl Average	Mg/Cl Scatter	
1	N. of Port Said	Sept.	0.3305	0.02205	0.0066	0.066,49	0.00048	
2	Lake Timsah	Sept.	0.3972	0.02198	1.207	0.066,79		
3	N. of Port Said	Sept.	0.4550	0.02112	1.429	0.066,35		
4	N. of Port Said	April	0.4638	0.02135	1.441	0.066,31		
5		April	0.5002	0.02137	—	—		
6		April	0.4901	0.02092	1.541	0.06578		
7	Suez Bay	April	—	—	—	—		
8		April	0.5096	0.02167	1.540	0.06549		
9		Sept.	—	—	1.549	0.06524		
10		Sept.	0.5075	0.02131	1.541	0.06470		
11		April	0.5089	0.02110	1.526	0.06327		
12	Great Bitter	April	0.4969	0.02047	1.565	0.06449		
13	Lake	April	0.5079	0.02076	—	—		
14	and	April	0.5121	0.02090	1.604	0.06548		
15	Southern	Sept.	0.5500	0.02127	1.583	0.06122		
16	Canal	Sept.	0.5579	0.02111	1.617	0.06119		
17		Sept.	0.5582	0.02108	1.654	0.06243		
A	Salt Bed	Oct. 1955	0.2851	0.01350	0.000	0.00000		
B			0.3496	0.01631	0.000	0.00000		
C	G. B. L.		0.4095	0.01847	0.0890	0.00401		
				0.02115		0.06161		
				0.02081		0.06441		
				0.02096		0.06301		
				0.00019		0.00124		
				0.00063		0.00221		
				0.00080		0.00429		

regions is 0.0005 and 0.0003 respectively, compared with 0.0005 for the surface samples of CULKIN and COX (1966). It seems that the Nile water has no influence on the potassium concentration in the diluted sea water in the Mediterranean off Port Said, and in Lake Timsah. Potassium has a great tendency to be adsorbed on the suspended and colloidal matter in the rivers and much of this material is coagulated upon reaching the sea. THOMPSON and ROBINSON (1932) pointed out that potassium is only 3.6% of that of sodium in sea water, 25% in river waters, while in igneous rocks both occur in about

Table 2 Recent determinations of potassium in sea water

Author	K/Cl	Region
WEBB (1939) . . . . .	0.02009	Atlantic
JENTOFT and ROBINSON (1956) . . . . .	0.02023	Atlantic and Pacific
SPOREK (1956) . . . . .	0.0207	English Channel
CULKIN and COX (1966) . . . . .	0.0206	54 Samples
	0.0206	Mediterranean Sea
	0.0206	Red Sea
MORCOS (1968) . . . . .	0.0204	Mediterranean, Off Port-Said
	0.0203	Red Sea, Suez Bay

equal proportions. More sodium than potassium goes into solution and finds its way into rivers, while more of the potassium is adsorbed and precipitated on reaching the sea. Their theory is supported by the fact that many oceanic sediments and deposits show a greater proportion of potassium to sodium.

As seen from Table (1a), the salt bed is very poor in potassium. Samples A and B contain negligible quantities, while the potassium in sample C is less than 5% of its concentration in sea water. The effect of the salt bed on the potassium content of the Great Bitter Lake is clearly observed. The potassium/chlorinity ratios of the samples 11 to 17 shows a reciprocal relationship with the salinity. The minimum potassium/chlorinity ratio of 0.01929 is determined in the most saline sample No. 17 collected at the southern end of the Canal in September. At that time of the year the water mass of the Great Bitter Lake attains its maximum salinity, expands in volume, and is shifted towards the south. The average for September (0.0194) is less than that of April (0.0200), and both of them are less than those determined for the Suez Bay and Port Said region. The scatter in the data is relatively small indicating that the low values of the Bitter Lake are significant.

## 2 — Sodium

Sodium is the most abundant cation in sea water, and it is of prime importance to establish its chlorinity ratio. However, no direct method is available for the determination of sodium. The total sulphate method which has been used by earlier investigators, consisted of determining the total cations as sulphates, followed by separate determinations as sulphates, followed by separate determinations of potassium, magnesium and calcium (+ strontium). The earlier figures for sodium depend therefore on the accuracy of the determinations of the other cations.

The older methods were not sufficiently precise to reveal the existence of small variations in the sodium chlorinity ratio in sea water. The figures calculated by THOMPSON and ROBINSON (1932) from the determinations of different investigators, range from

0.5476 to 0.5567 with an average of 0.5509. WEBB (1939) proved experimentally and theoretically that the true value of the sodium/chlorinity ratio lies closer to the upper limit of this range than to the mean. Only recently CULKIN and COX (1966) were able to conclude, from the analysis of 49 samples, that there are no significant differences between waters from different depths or different regions.

The following table (3) compares some of the recent results with those from the Mediterranean off Port Said, and from the Suez Bay. The determinations of sodium gave a coefficient of variation 0.10% i. e. 0.00055 sodium/chlorinity ratio. The average

Table 3 Recent determinations of Sodium in Sea Water

Author	Na/Cl	Region
WEBB (1939)	0.5549 0.5554	Firth of Clyde (by calculation)
LYMAN and FLEMING (1940)	0.5556	(by calculation)
ROBINSON and KNAPMAN (1941)	0.5562 0.5549	Puget Sound Pacific
CULKIN and COX (1966)	0.5555 0.5557 0.5563	49 samples Mediterranean Sea Red Sea
MORCOS (1968)	0.5534 0.5553	Mediterranean Off Port Said Red Sea, Suez Bay

value of Port Said is slightly less than the average (Table 3) values in the table. However, this value agrees well with the lower values of CULKIN and COX who got a mean of 0.5554 for 29 surface samples ranging from 0.5572 to 0.5535. The river waters have a sodium/chlorinity ratio of 1.02 which is about twice that of sea water (calculated from CLARKE, 1928 and KALLE, 1945). This is a relatively small difference, compared with the occurrence of other ions like sulphate and calcium in both kinds of water. It is supposed therefore, that no significant variation in the sodium/chlorinity ratio would occur in regions where mixing with river water takes place.

Table (1a) shows that the salt bed has a sodium/chlorinity ratio much higher than that of sea water. If a pure sodium chloride solution is analysed for Cl ‰ and sodium, the sodium/chlorinity ratio will be = 0.6487 on a theoretical basis. The difference between this figure and that obtained for the salt bed can be taken as a measure of the presence of other cations (as chlorides) in the salt bed. Thus:

$$\text{Sample A } 0.6487 - 0.6475 = 0.0012$$

$$\text{Sample B } 0.6487 - 0.6458 = 0.0019$$

$$\text{Sample C } 0.6487 - 0.6319 = 0.0168$$

A preliminary study of the values of the other ions shows that sample A and sample B are mostly sodium chloride with few calcium sulphate. The other ions bromine, potassium, and magnesium are absent or present in negligible quantities. Even sample C has a much higher sodium/chlorinity ratio than that established for sea water, indicating the wide change in the percentage composition of the salt bed from that of sea water.

The higher concentration of the sodium in the salt bed manifests itself in the sodium/chlorinity ratio in the waters of the Bitter Lakes. The average value for April (0.5567) is higher than the value of the Suez Bay, and compares well with the higher values obtained

by Culkin and Cox. The average for September, when the salinity in the southern part of the Canal is markedly high, is 0.5628. This ratio is higher than any value published for sea water, thus giving an outstanding evidence that the increase in salinity in the Bitter Lakes is due, at least in summer, to dissolution from the salt bed, in addition to the evaporation, and not due to evaporation only.

### 3 — Calcium

The methods for determining calcium in sea water which have been reported in the literature, can be classified as follows:

- a — By precipitation as oxalate, and the precipitate either ignited to the oxide and weighed or dissolved in sulphuric acid and the oxalic acid titrated with potassium permanganate.
- b — By flame photometry either directly or after precipitation as oxalate.
- c — By E D T A titration either directly or after ion exchange separation.

The figures obtained by flame photometry are either high or low. In spite of the great difficulties and sources of error encountered in the method of oxalate precipitation, the earlier figures which were obtained by this method compare well with the most recent methods involving the use of E D T A titration. However, the earlier figures should be subjected to two corrections (a) for changes in atomic weights (LYMAN & FLEMING, 1940) and (b) for the strontium content of the precipitate (CULKIN, 1965).

The recent figures obtained by E D T A titrations are compared with those from Port Said region and the Suez Bay in Table (4). The determinations of calcium gave a coefficient of variation 0.12% i.e. 0.00003 calcium/chlorinity ratio (Table 4). The Port Said and Lake Timsah waters show a higher calcium/chlorinity ratio than that of the Suez Bay, and that of the Mediterranean samples of CULKIN and COX (1966). The increase in calcium content of these waters is presumably due to the Rish calcium content of fresh water.

Table 4 Recent determinations of Calcium in Sea Water

Author	Ca/Cl	Region
PAT and ROBINSON (1958) . . . . .	0.02134	Pacific
CARPENTER (1957) . . . . .	0.02122	Atlantic
VOIPIO (1959) . . . . .	0.02085	Barents
CULKIN and COX (1966) . . . . .	0.02126	66 Samples
	0.02131	Mediterranean
	0.02115	Red Sea
MORCOS (1968) . . . . .	0.02162	Mediterranean Off Port Said
	0.02132	Red Sea, Suez Bay

GRIPENBERG (1937) has demonstrated the influence of dilution by river water, by distinguishing four water masses in the Baltic Sea on the basis of the relationship between their calcium content and chlorinity.

It is interesting to note that among the averages given by Culkin and Cox for the different oceanic areas, the Mediterranean attains the maximum, while the Red Sea attains the minimum (the Baltic was represented by one sample). The relatively low calcium

content in the Red Sea may find its explanation in the absence of calcium supply by river water inflow and its removal from water by the coral organisms. However, the results are too scanty to draw conclusions, and suggest further studies on the calcium content in the Red Sea.

The calcium/chlorinity ratio of the salt bed is lower than that of sea water, but it is not too low as observed with potassium and magnesium. However, the calcium/chlorinity ratio of the Bitter Lakes and southern part of the Canal show lower values than the waters of the Suez Bay.

The general trend observed with the distribution of potassium, sodium, and magnesium is that the salt bed has a greater influence on the composition of the waters of the Great Bitter Lake during the month of September when the waters has a maximum salinity. The calcium distribution shows, however, an opposite trend. The September values of the calcium/chlorinity ratio are higher and not lower than those of April. An explanation may be found in the seasonal change of the regime of currents in the Canal. In April the current is northward and the Great Bitter Lake is supplied with water from the Suez Bay. In September, the lake is supplied with Mediterranean water from the north, which is diluted by Nile water, and irrigation water from Port Said to Lake Timsah. The relatively high calcium/chlorinity ratio of this water will be reduced by the salt bed but its value remains higher than that of April. This inflowing water from the north is also rich in the sulphates, but opposite to the calcium, the September value in the lake is lower than the April value. Here, the salt bed plays a greater role, while the chlorinity ratio of the sulphate in the salt bed is only 21.5% of that of sea water, the calcium is 76%, of that of sea water.

#### 4 — Magnesium

Up to 1955 the magnesium/chlorinity data are obtained by the gravimetric determination of magnesium as magnesium pyrophosphate. The following table (5) contains the recent determinations made by EDTA titration either directly or after separation with an ion exchanger.

Table 5 Recent determinations of magnesium in Sea Water

Author	Mg/Cl	Region
CARPENTER (1957)	0.0667	Atlantic
VOIPIO (1957)	0.06693	Baltic
VOIPIO (1959)	0.06742	Barents
PATE and ROBINSON (1961)	0.06689	Pacific
CULKIN and COX (1966)	0.06692	66 samples
	0.06685	Mediterranean
	0.06685	Red Sea
MORCOS (1968)	0.06648	Mediterranean Off Port Said
	0.06530	Red Sea, Suez Bay

The present determinations show a coefficient of variation of 0.10% i.e. 0.00007 magnesium/chlorinity ratio.

The average magnesium/chlorinity ratio of Port Said and Lake Timsah regions are lower than the published values. However, considerable scatter is observed in present data, as well as in the data of CULKIN and COX, e.g. a scatter of 0.00058 for Port Said

region, compared with 0.00044 for surface water from all oceans. CULKIN and COX were of the idea that the variations are certainly larger than would be expected from analytical errors alone but they are not surprising in view of the known geological and biological activity of magnesium.

THOMPSON and ROBINSON (1932) calculated the magnesium/chlorinity ratios from U. S. rivers (from Data by CLARKE, 1928), and found them to range between 0.7295 and 3.265. Appreciable variations in the magnesium/chlorinity ratio can be expected in areas affected by land drainage. Comparison between the Suez Bay and Port Said regions shows that the latter is higher in its chlorinity ratio.

Magnesium is completely absent in samples A and B of the salt bed; sample C is very poor. Its chlorinity ratio is only 6% of that of sea water. A decrease in the magnesium/chlorinity ratio must therefore be expected in Bitter Lake waters. This can be amply demonstrated by the following figures:

		Mg/Cl
September	Great Bitter Lake	0.06161
	Suez Bay	0.06497
April	Great Bitter Lake	0.06441
	Suez Bay	0.06564

The salt bed has its greater influence on the water mass of the great Bitter Lake in September, the time of maximum salinity. As a result the magnesium chlorinity ratio reaches a minimum value. This water mass is transported southward where it mixes with the Suez Bay waters, thus lowering its magnesium/chlorinity ratio. In April the salinity drops in the lake to a minimum and the magnesium/chlorinity ratios increase in September but remain less than in the source water in the Suez Bay.

#### Comparison with other data

As has been shown before (Part 1, Morcos 1967) the sulphate/chlorinity ratio calculated from the published data on the waters of the Suez Canal gave support to conclusions based on the present data. The analyses of DURAND-CLAY (1874) and Cambridge Expedition (Fox, 1926) have demonstrated that the minimum sulphate/chlorinity ratio was calculated in the sample showing maximum salinity along the canal (in the Great Bitter Lakes), while the maximum chlorinity ratio was obtained with the minimum salinity at Port Said. The data for potassium, sodium, calcium and magnesium which have been published by earlier investigators show much scatter and some abnormal value. The average chlorinity ratios of potassium, calcium, magnesium were calculated for the three natural regions of the Canal from DURAND-CLAY (1874), and FOX (1926) and are shown in Table (6). With the exception of two cases, all the minimum values of the chlorinity ratios occur in the Great Bitter Lake, while the maximum values occur at Port Said. The exceptions are probably due to the fact that the Suez Bay is represented by only one sample. In spite of the limitations inherent in such old data, they support to a great extent the conclusions based on the present results.

Opposite to our findings, the sodium/chlorinity ratios calculated from earlier workers show lower and not higher values in the Great Bitter Lakes. Only SCHMIDT (1878) gave 0.5615 sodium/chlorinity ratio for Timsah waters of chlorinity 38.37‰, compared with 0.5540 for the Red Sea. KALLE (1945) gave a table containing 23 complete analysis by different authors for different sea areas. It is always more reliable to compare the results of one author on different regions, then the results of different authors from one particular region. Of the 23 complete analysis given by Kalle, 6 were made by SCHMIDT. The percentage of sodium in the total salts in the 6 analyses are given in comparison

Table 6 Chlorinity Ratios calculated from older data

Region	DURAND-CLAYE (1874)				FOX (1926)				
	No. of Samples	SO <sub>4</sub> /Cl	Mg/Cl	No. of Samples	SO <sub>4</sub> /Cl	K/Cl	Na/Cl	Ca/Cl	Mg/Cl
Port Said . . . . .	2	0.1482	0.0787	2	0.1373	0.0258	0.5274	0.0195	0.0763
Great Bitter Lake . . . . .	10	0.1372*	0.0602*	8	0.1349*	0.0203*	0.5219	0.0174	0.0691*
Suez Bay . . . . .	1	0.1447	0.0783	1	0.1371	0.0210	0.5060*	0.0161*	0.0837

Table 7 Sodium in the determinations of Schmidt (1878)

	Na % in Sea Water	% Na $\times \frac{100}{(D)}$
Dittmar (D) . . . . .	50.593	100.0
Baltic Sea . . . . .	30.47	99.6*
White Sea . . . . .	30.65	100.2
North Sea . . . . .	30.85	100.9
Suez Canal . . . . .	31.21	102.1
Red Sea . . . . .	30.81	100.8
Indian Ocean . . . . .	30.89	101.0



with that of DITTMAR in Table (7) which shows that the sodium/chlorinity ratio in the Suez Canal is higher than the rest of SCHMIDT analysis. It is actually higher than any value in the 23 analyses compiled by KALLE.

### Discussion and Conclusions

#### Sources of Variations in the Suez Canal

The results from the Suez Canal show that slight but significant variation in the chemical composition do occur between sea water from the canal and the average composition of oceanic water. In addition, significant variations are present between one region and another in the canal itself. The magnitude of variation is larger than can be accounted for by analytical error. The scatter in the sodium/chlorinity ratio and potassium/chlorinity ratio for the different regions is low and can be compared with CULKIN's and Cox' (1966) data, while the scatter in the calcium/chlorinity and magnesium/chlorinity ratios are higher. Differences in the relative composition of sea water must be expected in coastal waters where disturbing influences exist. Such agencies bring about changes so small compared with the bulk of the substances present in sea water that the relative amounts are slightly affected. It is due to the accurate analytical methods which have been developed recently that such small variations are detected and estimated.

When considering the influences capable of bringing about changes in the chemical composition of sea water in the Suez Canal, two main factors must be considered:

Table 8 Comparison between chlorinity ratios of sea water, river water and salt bed

Ion	Percentage Composition <sup>1</sup>		Chlorinity Ratio			Percentage to Sea Water	
	Sea Water	River Water	Sea Water <sup>2</sup> (S.W.)	River Water <sup>3</sup> (R.W.)	Salt Bed (S.B.)	$\frac{R.W.}{S.W.} \times 100$	$\frac{S.B.}{S.W.} \times 100$
Cl	55.038	5.68	—	—	—	—	—
Br	0.188	—	0.00348	—	0.00016	—	4.6*
SO <sub>4</sub>	7.685	12.14	0.1400	2.1373	0.0293	<b>1526.6</b>	20.9
CO <sub>3</sub>	0.413	35.15	0.0073 <sup>3</sup>	6.1884	—	825.1	—
Na	30.584	5.79	0.5555	1.0194	0.6417	183.5	<b>115.5</b>
K	1.110	2.12	0.0206	0.3732	0.00032	<b>1811.6</b>	1.5*
Ca	1.184	20.39	0.02126	3.5898	0.01609	<b>16885.2</b>	75.7*
Mg	3.684	3.41	0.06692	0.6004	0.00134	897.2	2.0*
Sr	0.037	—	0.00040	0.00040	—	—	—
B (OH) <sub>3</sub>	0.077	—	—	—	—	—	—
NO <sub>3</sub>	—	0.90	—	—	—	—	—
(Fe.Al) <sub>2</sub> O <sub>3</sub>	—	2.75	—	—	—	—	—
SiO <sub>2</sub>	—	11.67	—	—	—	—	—
	100.000	100.00					

<sup>1</sup>) After KALLE (1945).

<sup>2</sup>) After MORRIS and RILEY (1966) and CULKIN and COX (1966).

<sup>3</sup>) Calculated from Kalle (1945).

- a — the Nile flood influencing the Mediterranean Water off Port Said coast, and Lake Timsah region in summer,
- b — the salt bed in the Great Bitter Lake, which influences the Lake and the southern part of the Canal, and may extend its influence to the Suez Bay in summer.

In order to evaluate the magnitude of variations caused by these two factors, Table (8) was calculated to compare between the chlorinity ratios in sea water and those in river waters and in the salt bed. The table shows that the greatest variations in Port Said region influenced by Nile waters must be expected in the potassium, calcium, and the sulphate ratios. The role of calcium in the mixed water appears from the fact, that among the three cations — calcium, magnesium and sodium — calcium is the most abundant in river waters while it is the least abundant in sea water. Potassium plays a smaller role due to its more readily adsorption on particles of detritus and its consequent concentration in bottom deposits. There are very few analysis published of the waters of the Nile. TULLING (1957) determinations gave a calcium/chlorinity ratio ranging from 0.5 to 4.35, and a sulphate/chlorinity ratio of about 0.75, which is relatively low for river waters. MORCOS (1967) found a sulphate/chlorinity ratio of 1.69 which still belongs to the lower values. Several investigators (BEAUCHAMP, 1953, BISHAI, 1962, and DROVER & BISHAI, 1962) have emphasized the relatively low concentrations of sulphates in the Nile waters.

Table (8) indicates also that the most serious changes in the great Bitter Lake must take place in bromine, potassium and magnesium which are very low in the salt bed. Sulphate is also markedly reduced in the salt bed, but the calcium/chlorinity ratio is not much below that of the sea water. While sodium is only higher by a fraction in the salt bed, its ratio in the sea water in the Great Bitter Lake must be seriously affected because sodium is the most dominant cation in the salt bed and in sea water.

“In natural salt deposits, the less soluble compounds, especially calcium sulphate and even sodium chloride — are usually overrepresented since during evaporation in epicontinental basins, the more soluble potassium and magnesium salts flowed over constraining bars back to the ocean. Nowhere in an evaporation basin could the water be expected to retain the normal marine ionic ratios. Consequently the sum of precipitated salts cannot correspond to the original composition of sea water“. (BORCHERT, 1965)

The high salinity of the Great Bitter Lake is presumably due to two factors; the excessive evaporation and solution of salts from the salt bed. If evaporation only is responsible these will be no change in the chemical composition of the waters. The role played by every one of the two factors can be evaluated by a thorough investigation of the relative composition of the salt bed and the overlying waters. Since there is a marked seasonal change in the salinity and in the relative composition of the waters of the Bitter Lakes it is safe to say that the role played by every one of the two factors contributing to the high salinity of these waters shows also a marked seasonal change.

#### Relationship between Chlorinity and Cations

It is an accepted fact in oceanography that, with few limited exceptions, there is a constant chlorinity ratio for every major cation or anion in sea water far away from land drainage. GRIPENBERG (1937) was the first to compute four empirical equations between the calcium and the chlorinity in the Baltic Sea. The equations imply that the calcium/chlorinity ratio changes with the change in the chlorinity.

The preliminary study of the chlorinity ratios in the Suez Canal shows that they change with the changing chlorinity. In order to evaluate this change, empirical formulae were computed by the method of least squares from the observed values of the four

Table 9 Relation of Cations to Chlorinity

Cation	Bitter Lakes and Suez Bay		Great Bitter Lake		Relation to Cl ‰
	N	Relation to Cl ‰	N	Relation to Cl ‰	
Potassium	13	$K = 0.0117 \text{ Cl } \text{‰} + 0.2018$	7	$K = 0.0114 \text{ Cl } \text{‰} + 0.2097$	—
Sodium	11	$Na = 0.6287 \text{ Cl } \text{‰} - 1.7368$	6	$Na = 0.6348 \text{ Cl } \text{‰} - 1.8950$	—
Calcium	11	$Ca = 0.0204 \text{ Cl } \text{‰} + 0.0171$	7	$Ca = 0.0249 \text{ Cl } \text{‰} - 0.0998$	$Ca = 0.02025 \text{ Cl } \text{‰} + 0.0154$
Magnesium	10	$Mg = 0.0303 \text{ Cl } \text{‰} + 0.8269$	6	$Mg = 0.315 \text{ Cl } \text{‰} + 0.7963$	$Mg = 0.06684 \text{ Cl } \text{‰} + 0.0020$

Table 10 Balance Sheet of Cations and Anions in the Great Bitter Lake in September (1961 Atomic Weights)

Cations	Cl-Ratio	g/kg	Millimoles	Milli equivalents	Anions	Cl-Ratio	g/kg	Millimoles	Milli equivalents
Na*	0.5643	14.6725	638.2193	638.2193	Cl'	0.99888	25.9707	732.5439	732.5439
K*	0.01939	0.5041	12.8929	12.8929	Br'	0.00333	0.0866	1.0835	1.0835
Mg**	0.06161	1.6019	65.8876	131.7753	F'	0.00006	0.0015	0.0766	0.766
Ca**	0.2115	5.5499	13.7201	27.4401	SO''	0.1366	3.5516	36.9721	73.9442
Sr**	0.00040	0.0104	0.1187	0.2374	Excess Base	$0.112 \times 10^{-3}$	—	—	2.9168
Total				810.5650	Total				810.5650

cations and the corresponding chlorinities. Two equations were calculated for every cation, one for the Bitter Lakes only, and the other from the samples representing both the Bitter Lakes and the Suez Canal. The equations are given in Table (9). For the purpose of comparison, two equations from the Baltic Sea are included; one for calcium and the other for magnesium (LYMAN and FLEMING, 1940) Figure (4) contains plots relating the chlorinity ratios of the four cations to the change in chlorinity. In addition to the strait lines computed from the equations in Table (9), the actual observations are plotted to show the scatter around the two strait lines of every cation. The ratios of potassium and magnesium decrease with increasing chlorinity. The line representing calcium in the Bitter Lakes (No. 7) shows an increase in the chlorinity ratio with increasing chlorinity, while the line representing the two regions shows very slight decrease with increasing salinity. The lines are very close to each other on potassium, while they intersect at some high chlorinity value in the other three cations.

#### The relative composition of the Bitter Lake Waters

Sodium is the major cation occurring in sea water, and any error in its determination would bring about a serious error in the relative composition of sea water. In order to examine the validity of the high sodium/chlorinity ratio in the Bitter Lakes, and in order to establish a proposed formula for the relative composition of these waters, a balance sheet (Table 10) was drawn up for sea water of chlorinity 26‰, taking the average chlorinity ratios for September in the Bitter Lakes as basis of calculation.

The chlorine/chlorinity ratio is calculated as 0.99888, taking bromine/chlorinity ratio as 0.00348 (after MORIS and RILEY, 1966) and using 1961 atomic weights. This figure is used in Table (10) instead of 0.99894; the figure of LYMAN and FLEMING (1940) based on 1939 atomic weights and a bromine/chlorinity ratio = 0.00340. The strontium/chlorinity ratio is considered to be 0.00040. Preliminary examination of the Bitter Lake water suggests a lower limit for specific alkalinity as 0.116, which was used for calculating Table (10).

Since the sum of cations must be equivalent to the sum of anions plus excess base, sodium can be evaluated if the chlorinity ratios of the other constituents are known. In this way sodium is calculated as 14.6725 g/kg of sea water of  $\text{Cl } \text{‰} = 26$ , which gives a sodium/chlorinity ratio = 0.5643, i.e. slightly higher than the average of September of 0.5628 which is calculated from the directly determined sodium in sea water. This emphasises the higher sodium/chlorinity ratio and ascertains the relative composition of these waters.

Sodium may also be calculated, but with less certainty as the difference between the salinity calculated from chlorinity, and the sum of all anions and "cations except sodium" after converting the bromides to chlorides and the bicarbonates and carbonates to oxides. The bromides are converted to chlorides by multiplying the bromine content in g/kg by chlorine/bromine =  $35.453 / 79.909 = 0.443,667$ . Assuming all the carbonate alkalinity as bicarbonates and using a mean density of 1.034, the 26‰ chlorinity sea water contains 0.173443 g/kg bicarbonate equivalent to 0.022,736 oxides obtained by multiplying the bicarbonates by  $0/2 (\text{H CO}_3) = 0.1311$ .

Although boron is assumed to exist in sea water as boric acid ( $\text{H}_3 \text{BO}_3$ ) it decomposes on heating to boron trioxide  $\text{B}_2 \text{O}_3$ . It is therefore more correct to consider it as the oxide and not as boric acid, as it often appears in oceanographic literature, when it is added to the constituents of the residur obtained by evaporating sea water to 480°C according to the definition of salinity. Taking the recently established Boron/chlorinity ratio of 0.00023 (CULKIN, 1965), and using the factor  $\text{B}_2 \text{O}_3/\text{B}_2 = 3.21988$ , boron was calculated in sea water of 26‰ chlorinity as 0.019,240.

The salinity was calculated from the chlorinity = 26‰ using the MORCOS and RILEY (1966) equation and the Knudsen (1901) equation. The sodium is evaluated in the following way: —

	MORCOS and RILEY (1966)	KNUDSEN (1901)
	$S \text{ ‰} = 1.802 \text{ Cl ‰}$	$S \text{ ‰} = 0.03 + 1.805 \text{ Cl ‰}$
	= 46.852	= 46.960
Ions-Na	= 32.2706	= 32.2706
Na	14.5814	14.6894
Cl-ratio	0.5608	0.5650

Table 11 Sodium/chlorinity ratios by different methods

	Method of Estimation	September	April	Average of all
a.	Difference from $S \text{ ‰} = 1.802 \text{ Cl ‰}$ . . . . .	0.5608	0.5563	0.5584
b.	Experimental . . . . .	<b>0.5628</b>	<b>0.5567</b>	<b>0.5598</b>
c.	Balance Cations vs Anions . . . . .	0.5643	0.5597	0.5621
d.	Difference from $S \text{ ‰} = 0.03 + 1.805 \text{ Cl ‰}$ . . .	0.5650	0.5605	0.5626
e.	$\frac{a + c}{2}$ . . . . .	0.56255	0.55800	0.56025
f.	$b - e$ . . . . .	0.00025	—0.0013	—0.00045

Table (11) gives the average of determined sodium/chlorinity ratios, the calculated ratio from the balancing of anions and cations, and the two ratios obtained from the salinity as a function of chlorinity. The table which contains the average values for September, April and the average of all samples, indicates that the determined values lie between that obtained from the balance sheet, and that from MORCOS and RILEY equation  $S \text{ ‰} = 1.802 \text{ Cl ‰}$ . The average of the two values is very close to the observed value. Although the figures obtained by applying KNUDSEN's equation are closer to those obtained from the balance sheet they are, however, far from the determined figures which indicate an additional evidence that KNUDSEN's equation gives slightly higher values than the real salinities of the Bitter Lakes waters.

Table (10) and table (11) provide a confirmatory evidence of the relatively high sodium/chlorinity ratio and the relatively low chlorinity ratios of most of the major ions in the Great Bitter Lake water.

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