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Some contributions to the anomaly of the anion relationships in Baltic waters

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There is a growing interest in the relations between salinity, density and conductivity of the Baltic waters, and also in the deviations from the relations established for ocean water. The magnitude of these differences can be explained by a knowledge of the chemical composition.

Therefore, the determination of the anomalies of the cation and the anion relationships in Baltic waters are of great significance. This report is restricted to the investigation of the sulphate and the fluoride content in Baltic waters. The samples shave been taken in April/May 1966 at 16 hydrographic stations as described in Fig. 1. The detailed results of these investigations will be published elsewhere (Kremling, 1968).

Sulphate

Morris and Riley (1966) determined the SO_4/Cl factor of ocean water from a large number of samples to be 0.1400. The sulphate content in Baltic waters has been investigated only very Seldom. Thompson, Johnson and Wirth (1931) found from 5 samples (only one of deep water) a SO_4/Cl ratio of 0.1414. Zarins and Ozolins (1935) obtained from the Gulf of Riga and for the Latvian coast a mean factor of 0.1410. Kwiezinski (1965) studied 28 samples from 4 hydrographic stations and found an average value of 0.1413 (coefficient of variation = 1.3%). Recently Trzoinska (1967) published a mean value of 0.1436 with a very wide scatter (coefficient of variation = 2.9%) for samples from the Bornholm Deep, the Arkona Deep, and the Gdansk Deep.

The determination of sulphate reported here, was made gravimetrically as barium sulphate after the method of Bather and Riley (1954). This methoed, with a coefficient of variation of 0.16%, is the most accurate available. The chlorinity was determined by potentiometric titration according to the method of Hermann (1951). The accuracy was 0.003 ‰. Therefore, the accuracy of the SO_4/Cl ratio resulting from the experimental procedure was 0.0003. The determined SO_4/Cl factors are plotted in Fig. 2 as a function of chlorinity. The surface, the intermediate, and the deep waters are characterized by dots (.), open circles (o) and crosses (+), respectively. Depending on the chlorinity two types of water can be distinguished:

1) with Cl $>$ 5‰ 2) with Cl $<$ 5 ‰

The SO_4/Cl factor from the high chlorinity range which includes most of the intermediate and the deep water samples have an average value of 0.1403 with only a small variation. The standard deviation of 0.0004 in the So_4/Cl ratio is almost the same as the analytical error.

On the contrary the SO_4/Cl ratios from the low chlorinity range show a relatively wide scatter, which is caused by the different SO_4/Cl factors of run-off and river water, and is also due to mixing with the surface layers of the Baltic. These samples show a mean value of 0.1410, which is significantly higher than that from the high chlorinity range. The standard deviation of 0.0007 is almost two times as large as that from the deep waters.

The surface water from the Bothnian Bay (Station 15, Fig. 1) and from the Gulf of Finland (Station 16, Fig. 1) are excluded from these calculations because of their special hydrographic situations. These SO_4/Cl ratios are strongly influenced by river water. The water from the Bothnian Bay (Cl = 1.213‰) has a factor of 0.1437 and the sample from the Neva estuary (Cl=0.434 ‰) shows a SO_4/Cl ratio of 0.1463. (The latter is not described in Fig. 2).

A vertical stratification can be observed at all stations with the exception of the Arkona Deep, the Bornholmgàttet, and the Farö Deep (Stations 3, 4, and 10).

The extreme values in the Baltic proper have been found in the surface waters at the Bornholm Deep (0.1421) and the Farö Deep (0.1394). In general there is an excess of sulphate in the Baltic waters. Only 4 of the determined SO_4/Cl factors have a negative deviation from the ocean ratio.

Fluoride

The determination of the fluoride content in the oceans has led to some very interesting results. Greenhalgh and Riley (1963) and Riley (1965) investigated the F /Cl factor of the main oceans and found a value of $6.7 \pm 0.1 \times 10^{-5}$. However, in certain regions, especially the North Atlantic, the authors observed a significant increase of this ratio with depth, sometimes to 9×10^{-5}. Morcos (1967) recently reported upon a negative deviation of the fluoride content from the Suez Canal region.

The cause of these anomalies are hitherto unknown. It seems, therefore, that the fluoride may not be considered furthermore as a conservative component of sea. Perhaps it can serve as an indicator for currents and water masses. Investigations of the fluoride content of Baltic waters have - by the knowledge of the author - never been carried out.

The fluoride was determined by the lanthanum alizerin complexon method of Greenhalgh and Riley (1961). Duplicate determinations were made. They gave a coefficient of variation of 1.1%, i.e. about 0.07×10^{-5} F/Cl ratio.

The results presented in Table 1 show a strong vertical stratification of the F/Cl factor at most stations. Except in the Bornholmgattet (St. 4) and in the Stolpe Rinne (St. 6) the F/Cl ratio decreases significantly with depth. The differences are sometimes as high as 2.0×10^{-5} (see Table 1). The high values of the surface samples are due to the large discharge of river water the F/Cl ratio of which is a multiple of that established for the surface ocean water. This may be seen from the surface samples of the Bothnian Bay (St. 15) and the Neva estuary (St. 16) where the F/Cl ratios reach 10.02×10^{-5}, and 38.71×10^{-5}, respectively. The ratio of surface ocean water is found in the deep waters of Fehmarn Belt (St. 1), the Kadetrinne (St. 2), and the Bornholm Deep (St. 5).

However, the F/Cl factor in the Baltic is no function of chlorinity. On the contrary, there seems to be a characteristic stratification at each hydrographic station. In Fig. 3 (a - c) the very interesting results from the Gotland Deep, the Landsort Deep and the Farö Deep (Station 9, 11 and 10) are plotted. The surprising fact here is the observation of an evident fluoride deficiency. At the Gotland Deep, and the Landsort Deep the negative deviation of the F/Cl factor only occurs below the halocline. At the Farö Deep, however, the fluoride deficiency is already found in the surface water. The F/Cl ratio here is 5.97×10^{-5}. The difference between this value and that established for the surface ocean water is more than tenfold the anaytical error. Contrary to the Gotland Deep, and the Landsort Deep, the vertical stratification is only small in the Farö Deep. The F/Cl factor of its deep water (150 m) is the lowest determined in the Baltic (5.51×10^{-5}, see Fig. 3 c). The phenomenon of fluoride deficiency in these basins is difficult to explain. If there is a sedimentation of fluor apatite and fluorspar then the fluoride content calculated from the apparent equilibrium constant of Roberson (1965), of Pytkowicz and Kester (1967), and of Sillén (1959) would be significantly higher than the determined one. Probably some of the F^- is deposited in silicate phases substituting O^{2-} and OH^- groups as predicted by Sillén (1959).

But much more samples are needed to answer the question whether there is a relationship between fluoride content and chemical conditions.
Therefore the determination of fluoride will be the subject of further investigations in Baltic waters.

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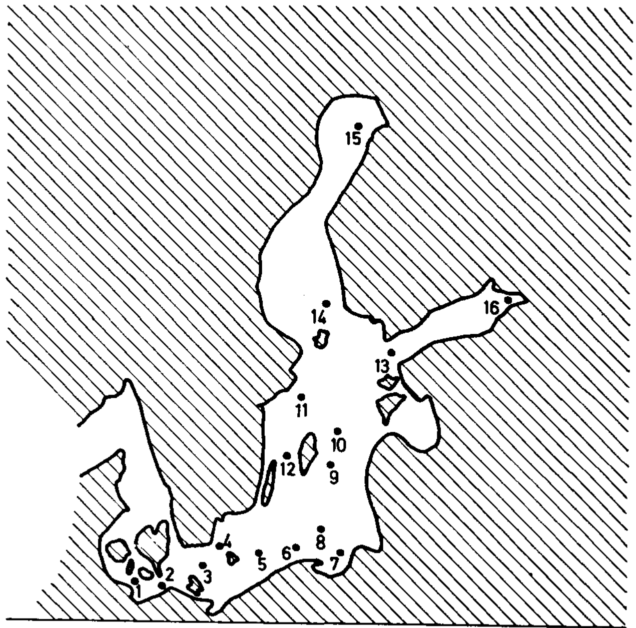

Fig. 1 Chart of the hydrographic stations

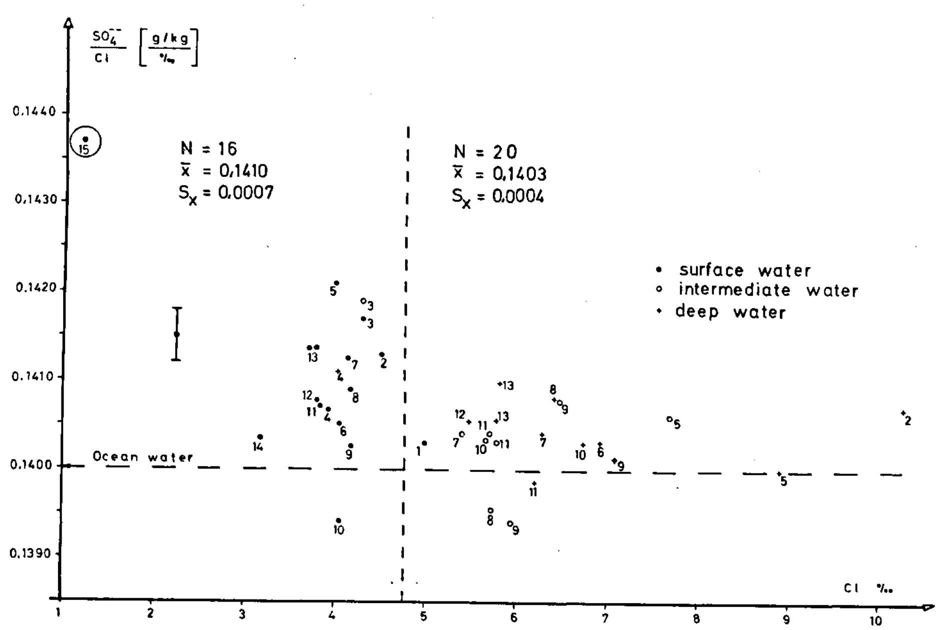

Fig. 2 Distribution of the ratio SO_4^{--}/Cl as a function of chlorinity

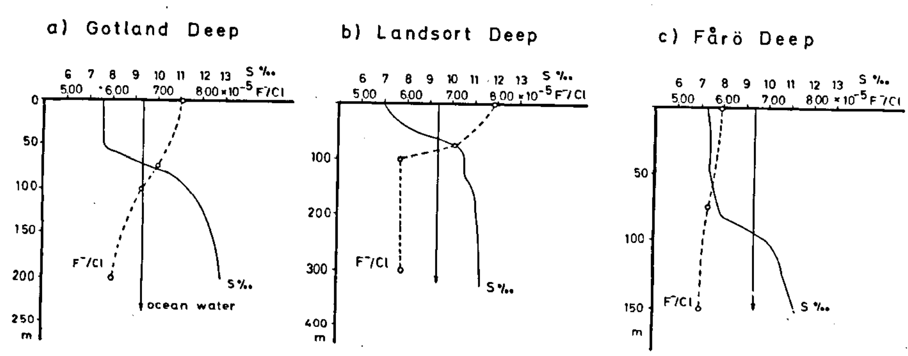

Fig. 3 Distribution of the ratio F^-/Cl and S ‰

Table 1

Stat.	m	Cl ‰	F^-/Cl [g/kg / ‰] x 10^5
1	0	4,984	8,73
	25	10,981	6,82
2	0	4,517	7,41
	20	10,252	6,72
3	0	4,307	8,82
	20	4,306	7,81
4	0	3,932	8,05
	50	4,036	8,46
5	0	4,002	8,09
	75	7,675	6,60
	90	8,906	6,74
6	0	4,043	7,70
	90	6,915	7,61
7	0	4,129	7,62
	75	5,403	7,21
	100	6,261	7,02
8	0	4,162	8,87
	75	5,727	7,91
	100	6,390	7,08
9	0	4,170	7,55
	75	5,949	7,03
	100	6,450	6,67
	200	7,072	6,03
10	0	4,058	5,97
	75	5,654	5,69
	150	6,731	5,51
11	0	3,847	7,93
	75	5,693	7,07
	100	5,781	5,85
	300	6,196	5,93
12	0	3,813	7,96
	90	5,483	7,32
13	0	3,743	8,18
	90	5,803	7,03
14	0	3,196	8,06
	120	3,895	7,26
15	0	1,213	10,02
16	0	0,434	38,71