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**CORRECTION FOR BROMIDE DURING CHLORIDE
TITRATION OF SEA-ICE BRINE**

by

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PREFACE

This report deals with a technical refinement in the interpretation of chemical tests on brine samples from sea ice. The work was prepared by Dr. Assur, physicist, for the Applied Research Branch, Mr. W. K. Boyd, Chief, under USA SIPRE Project 022.02.007, Properties of sea ice.

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The concentration of chloride ion in sea water or brine is determined by means of titration with a silver nitrate solution. Other halides, in particular bromides and iodides, also precipitate, of course, during this operation. This has always been a matter of international concern in the study of sea water, but in relation to sea-ice brine the question has barely been touched.

According to the latest definition:

"The number giving the chlorinity in grams per kilogram of a sea-water sample is identical with the number giving the mass in grams of atomic weight silver just necessary to precipitate the halogens in 0.3285233 kilogram of the sea-water sample" (Sverdrup et al., 1942).

Using the 1956 atomic weights, the Cl/Ag ratio is 0.3286707. Therefore the value $\frac{0.3286707 - 0.3285233}{0.3285233} = 0.000449$, multiplied by the chlorinity, must be added to the chlorinity to obtain the chloride equivalent, if international "normal water" is used for titration. For instance, if Cl = 19.0000‰, the chlorine equivalent is 19.00842‰.

The normal content of Br⁻ in sea water of chlorinity Cl = 19.000 is 0.0646‰ (Sverdrup et al., 1942) with a chlorine equivalent of $0.0646 \times 0.44368 = 0.0286617$ ‰. The iodide content is very small (= 0.00005‰) with a chlorine equivalent of $0.00005 \times 0.27939 = 0.0000014$ ‰. Adding the chlorine equivalent of Br and I to the chloride content 18.9799‰ of sea water with Cl = 19.000 (Sverdrup et al., 1942, p. 173) we obtain the total chlorine equivalent of 19.00856 in satisfactory agreement with the value obtained above.

If a usual chemical analysis of sea water is made (not adhering to special oceanographic methods), the chlorine equivalent Cl_e obtained by titration with silver nitrate has to be multiplied by

$$\frac{\Delta Cl_e}{Cl_e} = \frac{19.00856 - 18.9799}{19.00856} = 0.001508$$

and the resulting value subtracted from Cl_e in order to obtain the true chloride content.

It would be a mistake to assume that the same correction also applies in general to brine obtained from sea ice upon freezing and further cooling. The correction changes as soon as Cl⁻ or Br⁻ precipitates. We suspect that Cl⁻ begins to precipitate below -18°C in MgCl₂ · 8H₂O (Assur, 1958) and we know that it precipitates below -22.9°C. The concentration of Cl⁻ staying in solution within the brine was recently computed up to -54°C (Assur, 1958).

Nelson and Thompson (1954) did not consider Br^- in their analysis of brine remaining at various temperatures. They did, of course, precipitate Br^- together with Cl^- using silver nitrate, but no correction was applied. This leads to small inconsistencies in the computation of phase relations, which are considered only indirectly in our Research Report 44.

The presence of bromide was a matter of considerable concern to Ringer (1906). He made a number of calometric tests but did not get much further than to ascertain that all bromide is still in solution at -30, -40 and -53C and possibly even below this temperature. We assume here that it is in solution at least up to -54C. Evidence to the contrary is not available.

In such a case the correction factor is

$$r = \frac{\Delta \text{Cl}_e}{\text{Cl}^- + \Delta \text{Cl}_e}$$

with $\Delta \text{Cl}_e = -0.02866\text{‰}$ in the case of normal sea-water (chlorinity 19.00‰ salinity 34.325‰ - see Table II in Research Report 44) and Cl^- taken from Table III of the same paper.

The values are given here in Table I and are graphically shown in Figure 1. With these corrections applied by graphical interpolation to the values reported by Nelson and Thompson (1954), the chloride concentration of brines obtained from sea ice at different temperatures is given in Table II.

It should be kept in mind that the correction has to be applied for the titration of brine separated upon freezing up to a certain temperature θ . The correction for the analysis of melt water from sea-ice samples is constant.

In many cases the correction for Br^- will not be important. This should not deter us, however, from obtaining all feasible accuracy. In some cases it is the only way to explain certain discrepancies.

References

- Assur, A. (1958) Composition of sea ice and its tensile strength, US National Academy of Sciences, National Research Council Pub. No. 598; (also USA SIPRE Research Report 44, in preparation.)
- Nelson, K. H. and Thompson, T. G. (1954) Deposition of salt from sea water by frigid concentration, University of Washington, Dept. of Oceanography. Technical Report 29.
- Ringer, W. E. (1906) Changes in the composition of sea-water salts upon freezing, Verhandelingen, Rijks Instituut voor het Onderzoek der Zee, Netherlands, I^{III}, p. 3-55 (original title not available; text seen in German).
- Sverdrup, H. W. et al. (1952) The Oceans, New York.

Table I: Correction for Br during Cl-titration of sea ice brine.

Freezing point of brine θ	Correction r	Freezing point of brine (C)	Correction r
-2	-0.001508	-38	-0.00622
-4		-40	-0.00654
-6		-42	-0.00683
-8			
-10		-44	-0.00886
-12		-46	-0.01413
-18		-48	-0.02059
-20	-0.00151	-50	-0.02767
-22	-0.00151	-52	-0.03501
-24	-0.00201	-54	-0.04155
-26	-0.00302		
-28	-0.00391		
-30	-0.00462		
-32	-0.00513		
-34	-0.00558		
-36	-0.00592		

Explanation: The true chloride concentration is $Cl^- = Cl_e - rCl_e$ with Cl_e as the measured chlorine equivalent.

Table II: Corrected chloride concentration for various temperatures.

Temp (C)	Corrected Cl^- (g/kg)	Temp (C)	Corrected Cl^- (g/kg)
-2.2	22.766	-19.2	126.419
-4.4	42.646	-20.6	131.521
-5.5	51.103	-22.2	139.700
-6.1	56.405	-23.25	142.155
-6.9	62.316	-23.75	143.803
-8.3	72.782	-24.7	145.889
-8.6	74.358	-25.6	147.557
-9.6	80.888	-26.4	148.895
-10.6	87.178	-27.9	152.100
-10.75	87.847	-29.95	155.725
-13.1	99.580	-32.9	160.767
-14.7	106.919	-34.9	165.580
-15.2	109.634	-36.25	166.528
-16.25	144.128	-36.55	167.237
-18.5	123.084	-40.2	173.228
		-43.15	174.336

Values correspond to an initial chlorinity $Cl = 18.01\%$ of the sea water. The third decimal is given as a computational convenience. The original data of Nelson and Thompson (1954) have two decimals.

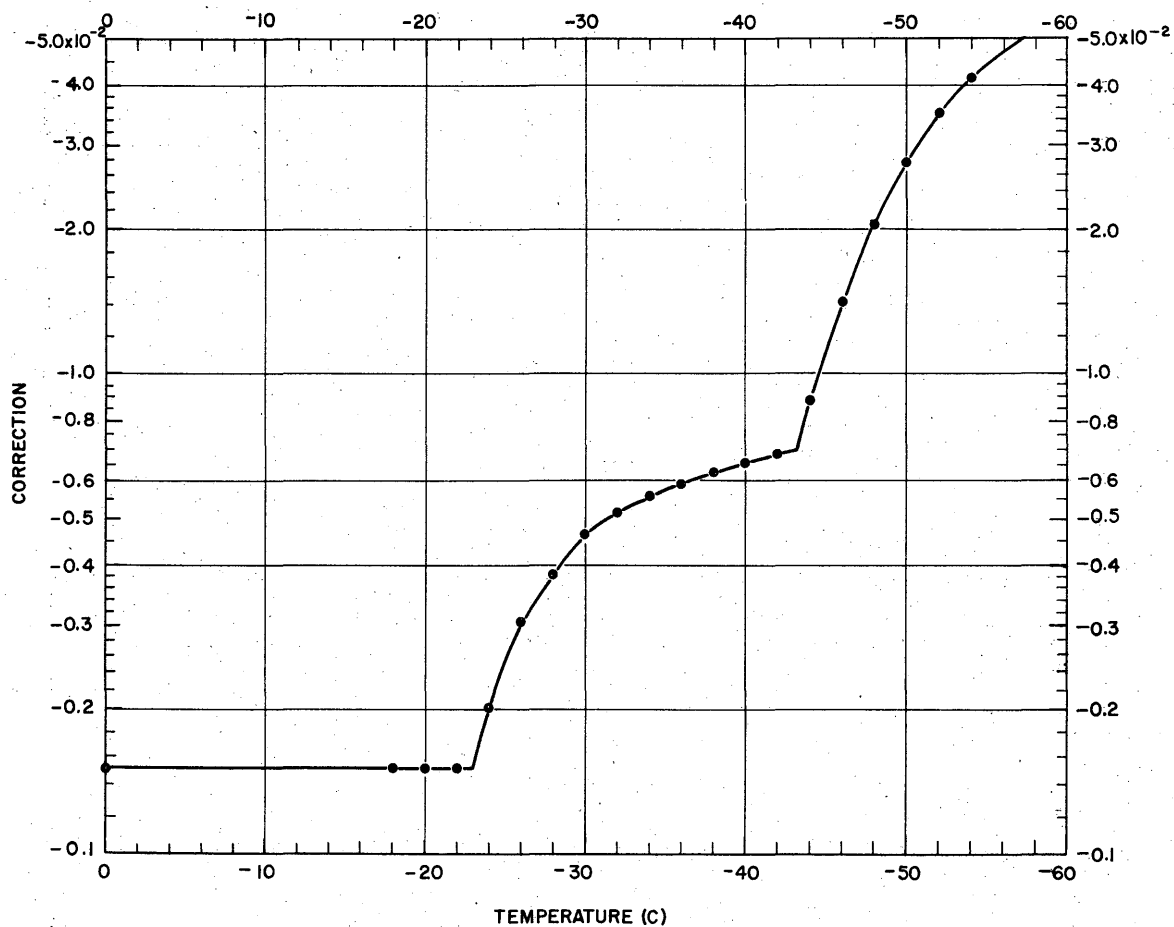


Figure 1. Correction r for Br during Cl-titration of sea-ice brine, depending upon temperature.

The sharp changes are due to precipitation of $\text{NaCl} \cdot 2\text{H}_2\text{O}$ at -22.9°C and of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ at -43.2°C . Note that $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ precipitates at approx. -36.0°C (Ringer, 1906) if seeded, otherwise it easily stays in solution even at much lower temperatures. The temperature -43.2°C (Assur, 1958) is a compromise which might later be changed in favor of -36.0°C .