ESTIMATION OF CHLORIDES IN 1 C.C. SEA WATER SAMPLES BY MEANS OF SYRINGE PIPETTES.

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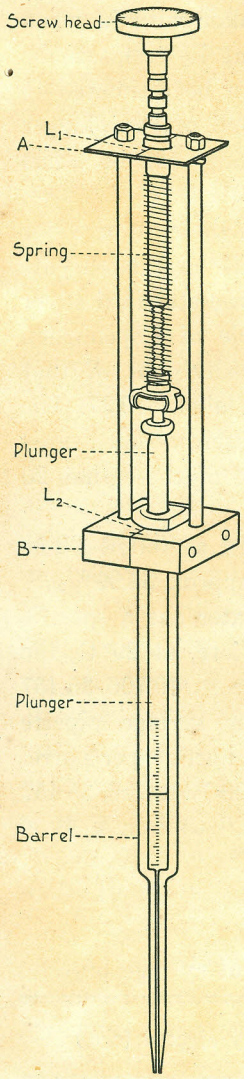

Fig. 1.
Syringe burette, × ½.

Rapid deliveries of small quantities of fluid can be made with a high degree of accuracy with syringe pipettes, as described by KROGH and KEYS (1931). In a somewhat modified form these pipettes are also in use now in the estimation of oxygen in about 1 c.c. of water (VAN DAM 1933, 1935, cf. also KROGH 1935 and FOX and WINGFIELD 1938), ensuring both the sampling and the addition of reagents to take place without coming into contact with air. TREVAN (1925) constructed a syringe pipette, the plunger of which was controlled by a micrometerhead, so that the syringe could also be used as a microburette. A similar microburette was employed by FOX and WINGFIELD (1938) in oxygen determination.

As far as is known syringe pipettes have not been used in chlorine titration [1]). Therefore, I carried out such titration, using a syringe pipette and a simple syringe burette.

The basis of the technique is the titration method of MOHR, which is generally used in Oceanography (cf. BEIN a.o. 1935).

The water sample (about 1 c.c.) is taken with a syringe pipette (VAN DAM 1935). The head of the plunger had been ground flat, making the surface of the head as near right angles to the axis of the plunger as possible. The lower end of the screw had been tapered, thus making the contact between the plunger and the screw small. As a result plunger rotations which may occur during manipulation have only little effect on the deliverance volume of the syringe.

The water sample is transferred into a small, white, porcelain dish (diam. 4 cm, height 1.5 cm) and is then titrated against silver nitrate solution. Since a TREVAN

[1]) At the Zoological Station, den Helder, Holland, chlorine titrations are carried out by taking samples with a syringe pipette and adding silver nitrate solution with an ordinary burette.

micrometer syringe (see above) was not available, the silver nitrate solution was added with the aid of a syringe pipette which was modified in a simple manner, in order to serve as a micro-burette.

This syringe burette is constructed as follows (fig. 1). The lower end of the barrel is calibrated. The distance between two adjacent graduations equals the speed of the screw. The screw is supplied with a fairly large head which has its circumference graduated into 50 divisions. To make readings at the head possible, the syringe is provided with a metal plate (A) on which a fine ink line is drawn (L_1). A white line (L_2), parallel with L_1, is painted on the vulcanite block B. Readings on the calibrated screw head are taken with L_1 when looking from the head downwards L_2 in such a position that L_2 seems to be covered by L_1 up to a fixed point (the cross line); they can be estimated to 0.002 of a barrel division. Thus the position of the lower end of the plunger can be roughly estimated on the barrel whereas precise readings can be taken at the head of the screw.

The capacity of the syringe burette was about 0.8 c.c. In the case of water with a chlorinity lower than 20 $^0/_{00}$, only the upper half of the graduated part of the barrel (about 20 divisions) was used in titration since the standard silver nitrate solution was made of such a strength that a sample of Copenhagen standard water required about the same number of barrel-divisions of that solution as its chlorine content in $^0/_{00}$ was stated to be, i.e. about 19.37. The weight of the amount of mercury ejected by turning the screw downwards from one position to another showed the deliverance volume of these first 20 barrel divisions to be practically constant (Table I).

The strength of the silver nitrate solution was calculated as follows. The Copenhagen standard water had a chlorinity of 19.368 $^0/_{00}$ = approx. 34.99 $^0/_{00}$ S. According to the graph of SCHUMACHER (1922, p. 305) this water has a specific gravity at 29° C (room temperature) of about 1.0221. Therefore, at 29° C, the water contains 1.0221 × 19.368 = 19.796 g. chlorine per litre ≡ 19.796/35.457 N sodium-chloride. Suppose the deliverance volume of the syringe pipette amounts to V c.c. and the deliverance volume of the syringe burette per barrel division to B c.c. Then the silver nitrate solution will be V/1000 × 19.796/35.457 × 1000/19.368 × 1/B N = V/B × 0.028826 N. Hence it will contain V/B × 0.028826 × 169.89 g. silver nitrate per litre.

Table I.

Determination of deliverance volume per 10 barrel divisions of syringe burette.

Plunger moved from graduation	Volume of mercury ejected (c.c.)	
	Exp. 1.	Exp. 2.
0 — 10	0.1857	0.1857
10 — 20	0.1858	0.1858

It proved to be of advantage to add the indicator (one drop of a 4 % K_2CrO_4 solution) before adding the silver nitrate solution, because if it was added before the precipitate of silver chloride would turn more or less black and so would obscure the endpoint of the titration.

Only carefully cleaned pipettes, porcelain dishes and glass rods should be used. The water to be analysed, together with the solution of Copenhagen standard water (or sodium chloride) and silver nitrate, should be placed in a large dish, filled with water, to avoid temperature differences. Since variations in room temperature cause variations in the deliverance volume of the pipettes, it is necessary to determine α (cf. the Knudsen Hydrographical Tables) at regular intervals, e.g. every hour.

The procedure during actual analysis is as follows:

1. The syringe pipette is rinsed three times with the water to be analysed. Then the sample is drawn in and ejected into a porcelain dish. If more samples are to be taken from the same water the pipette need not be rinsed again. During ejection of the sample care is taken that the pointed cannula of the syringe dips approximately as far below the water surface as during the sampling (two or three mm), uniformity of manipulation being necessary to keep the deliverance volume of the syringe constant. The cannula of the syringe must not be cleaned between sampling and ejection.

2. One drop K_2CrO_4 solution is added.

3. The syringe burette is rinsed with silver nitrate solution and then filled. Some excess of solution is drawn in. Then the burette is clamped with one of its metal rods, in such a way that between its axis and the table there is an angle of about 45^0. The screw is then turned so that both the lower end of the plunger and the head of the screw are adjusted to zero. Next the delivery end of the burette is cleaned by wiping with filter paper and then introduced one or two mm into the sample.

4. About ninety per cent. of the required amount of silver nitrate solution is added, after which the silver chloride precipitate is stirred for three minutes with a glass rod to release the chlorine that had been trapped in the precipitate into the solution (cf. BEIN a.o. 1935, p. 54). Then the titration is completed. I consider the endpoint to be reached when the titration fluid turns from yellowish green to yellowish brown and remains so if moderately stirred (cf. MEYER 1927, p. 41, footnote).

In routine work one analysis requires about 8 minutes.

A comparison between the above micromethod and the ordinary macromethod was made by analysing a series of samples of the same water (Table 2).

In the macromethod the sample was taken with an ordinary 15 c.c. Knudsen pipette, the silver nitrate solution was administered with a burette which had at its upper end a bulb with a capacity of about 16 units (1 unit = 2 c.c.) of the quantity of silver nitrate solution to be added. The stem of the burette was graduated, upwards from 16.00, into 0.05, so that 0.005 ‰ chlorine could be estimated. For this burette no volume correction table (cf. BEIN a.o. 1935,

Table 2.

Results obtained by micromethod and macromethod. The silver nitrate solution was standardized against a standard NaCl solution (sample no. 2) with a chlorinity of 19.368 ‰.

	No. of sample	Required amount of $AgNO_3$ solution	α	k	Cl ‰
Micromethod	1	19.224			
	1	19.224			
	1	19.224			
	1	19.226			
	2	19.370	-0.002		
	2	19.370			
	2	19.370			
	3	17.720		0.036	17.759
	3	17.726			
Macromethod	2	19.385	-0.017		
	2	19.385			
	2	19.385			
	3	17.750		0.023	17.775
	3	17.755			

p. 33) was available. In both methods α and k (cf. the Knudsen Hydrographical Tables) were obtained from graphical interpolation (cf. MÖLLER 1933, Fig. 2).

It will be seen that in the micromethod a relative accuracy of about 0.005 g. chlorine per litre was obtained.

If many titrations must be carried out the above method is relatively inexpensive since the required amount of silver nitrate is about one fifteenth of that used in the ordinary macromethod. Furthermore, it may be used with advantage in the field and on board ship since the apparatus is easily portable and no more liable to breakage than are ordinary pipettes and burettes.

Summary.

With the aid of syringe pipettes chlorine analyses are carried out on 1 c.c. samples of sea water, on basis of the MOHR procedure. With adequate lighting a relative accuracy of about 0.005 g. chlorine per litre is obtained.

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