

HIGH-PRECISION DETERMINATION OF CALCIUM IN THE PRESENCE OF HIGHER CONCENTRATIONS OF MAGNESIUM BY MEANS OF A COMPUTERIZED PHOTOMETRIC TITRATION

APPLICATION TO SEA WATER

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(Received 22nd May 1973)

The determination of calcium in the presence of magnesium is a classical problem in compleximetry. In sea water, where the calcium and magnesium concentrations are approximately 0.01 *M* and 0.05 *M*, respectively, at 35‰ salinity, the determination of calcium involves a particular aspect of this problem, namely the precision determination of calcium in the presence of higher concentrations of magnesium. In order to be able to establish significantly the small variations in the calcium/chlorinity ratio occurring in the oceans, a method yielding a relative standard deviation less than 0.001 is required. Moreover, it is an advantage if the method is automatic, thus facilitating the analysis of a large number of samples. At the present time, only titration methods can meet these requirements, because flame absorption and emission methods do not yet yield precisions of this order, while gravimetric methods are unsuitable for automation.

Of the titration methods hitherto used for the determination of calcium in sea water, that of Riley and Tongudai¹ yields by far the highest precision. The method requires, however, ion-exchange separation of the alkaline earth metals before titration and is, consequently, time-consuming and difficult to automate.

Potentiometric titration methods based on the Orion ion-exchanger calcium-sensitive electrode have been found to yield poor results in sea water^{2,3}, mainly because of interference with the electrode from sodium and magnesium. A new calcium-sensitive electrode, developed by Růžička *et al.*⁴, is, however, being tested at this laboratory and the preliminary results would seem to be promising. The advantage of using a calcium-sensitive electrode is, of course, that it is not necessary to separate calcium from the other alkaline earths before titration.

Another procedure for the determination of calcium in sea water which does not require previous separation of calcium is that proposed by Culkin and Cox⁵. This is a photometric titration method, with zinc-zincon as an indirect calcium indicator, based on principles originally suggested by Ringbom *et al.*⁶. The theory is analogous to that first outlined by Reilley and Schmid⁷. Ringbom *et al.*⁶ did not, however, cover the case where the magnesium to calcium ratio was as unfavourable as five to one. Such a high ratio ought to give rise to systematic errors and decreasing precision, as is also shown in the present paper by means of computer-simulated titration curves.

A new approach to the determination of calcium in sea water by photometric titration based on the zinc-zincon indicator system is described in this paper. The evaluation procedure used has similarities with those outlined by Higuchi *et al.*⁸, Dyrssen *et al.*⁹ and Johansson¹⁰.

THEORY

In order to be able to estimate the magnitudes of the accuracy and precision associated with different methods of evaluating the titration of calcium in sea water with zinc-zincon as an indirect indicator, theoretical titration curves were calculated by means of the computer program HALTAFALL^{11,12}. The total concentrations used in the calculations were: calcium 0.00128 *M*, magnesium 0.0066 *M*, strontium 0.00004 *M*, zinc-EGTA 0.000128 *M*, zincon $6 \cdot 10^{-6}$ *M*, EGTA 0.016 *M*, the latter being the obvious choice as complexing agent for the titration of calcium in the presence of magnesium. The calculations were performed at pH values between 8 and 10, an initial volume of 200 ml being assumed. The total concentrations chosen correspond to 25 g of sea water (of 35‰ salinity) diluted to 200 ml. The equilibrium constants, relevant at 0.1 *M* ionic strength, have been taken from Ringbom^{6,13} and are specified in Table I. In order to avoid confusion, the notation for the indicator species used in this paper is the same as that used by Ringbom *et al.*, namely ZnOHI (blue) for the zinc-zincon complex and HI (yellow) and I (yellow-red) for the proton-indicator complexes. According to preliminary experiments carried out at this laboratory, these complexes would, however, appear to be better represented by ZnI, H₂I and HI, respectively.

TABLE I

STABILITY CONSTANTS USED IN THE HALTAFALL CALCULATION OF THE TITRATION OF CALCIUM IN DILUTED SEA WATER WITH EGTA

(H₄Y denotes EGTA and H₃I denotes zincon)

Equilibrium	Log. of constant
H + Y ⇌ HY	9.46
2 H + Y ⇌ H ₂ Y	18.31
Ca + Y ⇌ CaY	10.70
Mg + Y ⇌ MgY	5.40
Sr + Y ⇌ SrY	8.10
Zn + Y ⇌ ZnY	12.80
H + I ⇌ HI	8.25
Zn + H ₂ O + I ⇌ ZnOHI + H	-1.00
Zn + H ₂ O ⇌ ZnOH + H	-9.60
Zn + 3 H ₂ O ⇌ Zn(OH) ₃ + 3 H	-27.60

The results of the calculations are illustrated in Fig. 1, in which the concentration of the zinc-indicator complex has been plotted against *v* ml of EGTA added for different pH values.

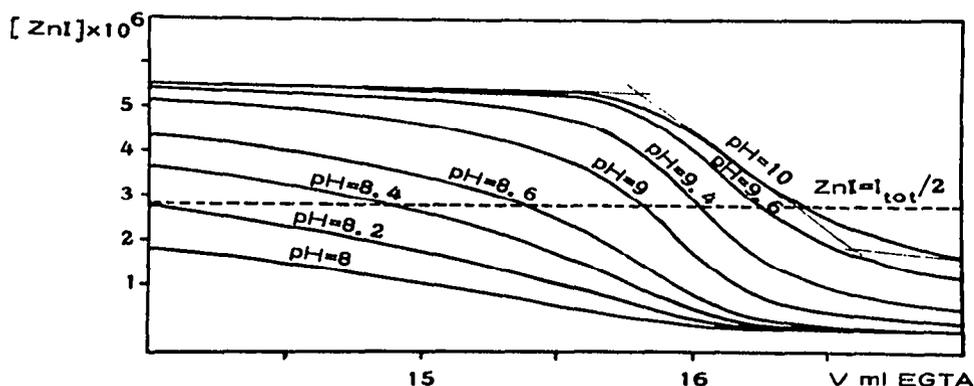


Fig. 1. Computer-simulated titration curves for the determination of calcium in sea water.

Visual evaluation

If the visual end-point, v_{end} , is defined as the v value corresponding to

$$[\text{ZnOHI}] = [\text{HI}] + [\text{I}] \quad (1)$$

then the percentage systematic error is given by

$$\% \text{ error} = 100(v_{\text{end}} - v_{\text{eq}})/v_{\text{eq}} \quad (2)$$

The v_{end} value for a specific pH value is obtained from Fig. 1 as the value corresponding to the intersection of the dashed horizontal line $[\text{I}]_{\text{tot}}/2$ and the relevant $[\text{ZnOHI}]$ plot. The results are summarized in Table II. From Fig. 1 it can also be concluded that, apart from giving rise to systematic errors, visual evaluation is also associated with a poor precision.

Maximum slope

The v value corresponding to the maximum slope of the absorbance curve is often taken to be v_{end} . The systematic errors thus obtained for the system under consideration are given in Table II. In spite of the fact that these errors are con-

TABLE II

PERCENTAGE SYSTEMATIC ERROR OBTAINED BY DIFFERENT EVALUATION METHODS FOR THE TITRATION OF CALCIUM IN DILUTED SEA WATER AT DIFFERENT pH VALUES (cf. Fig. 1)

pH	Evaluation method				
	Visual	Linear extrapolation	Maximum slope	F_1	F'_1
8.0	< -20	0.2	—	0.5	0.1
8.2	-13.0	0.4	—	0.4	0.1
8.4	-7.4	0.7	-1.4	0.3	0.1
8.6	-3.9	1.0	-0.9	0.3	0.1
9.0	-1.2	1.2	-0.3	—	—
9.4	0.2	-2.0	0.3	—	—
9.8	1.5	-1.5	0.6	—	—
10.0	2.6	-1.3	0.9	—	—

siderably smaller than those obtained in the visual evaluation, it can be concluded from Fig. 1 that the precision of this method is not sufficiently high.

Linear extrapolation

Break-point curves^{14,15}, *i.e.* curves yielding large systematic errors in visual evaluation, can be evaluated by linear extrapolation. Straight lines are approximated through the almost linear parts of the absorbance curve before and after the equivalence point. These lines are allowed to intersect the best line drawn through the steepest part of the absorbance curve and one of the two points of intersection thus obtained is taken as v_{end} . Which of the two intersection points should be used in order to obtain the best accuracy can normally be seen directly from the shape of the plot. This procedure is illustrated by means of the fine lines in Fig. 1 for the plot at pH 10, and the systematic errors are specified in Table II.

Visual, maximum slope and linear extrapolation methods have all been tested in practice and the orders of magnitude of all errors given in Table II have been verified experimentally.

Linear regression

The methods discussed above exploit only a small part of the titration curve in the evaluation of the equivalence point. From the aspect of precision it would, of course, be advantageous if as many titration points as possible could be used in this evaluation *e.g.* by a linear regression method analogous to the Gran¹⁶ method used in potentiometric titrations. In the derivation of Gran plots it is, however, assumed that there is a dominating main reaction. This requirement is, of course, never fulfilled in an indicator titration since in the part of the titration curve where measurable colour changes occur there must always be interfering side-reactions between the metal to be titrated and the indicator. These side-reactions can be neglected only if the total indicator concentration is very low in comparison with the total metal ion concentration. The importance of indicator side-reactions can easily be ascertained from theoretical titration curves calculated with *e.g.* HALTAFALL.

Supposing that, in the titration under consideration, the only reaction before the equivalence point, v_{eq} , is the formation of calcium-EGTA, then

$$(v_0 + v)[\text{Ca}] \propto v_{\text{eq}} - v \quad (v_0 \text{ here } 200) \quad (3)$$

$$(v_0 + v)[\text{CaY}] \propto v \quad (4)$$

and, consequently,

$$[\text{Y}] \propto v / (v_{\text{eq}} - v) \quad (5)$$

Assuming, moreover, that only a minor part of the Zn-EGTA added dissociates, then

$$(v_0 + v)[\text{ZnY}] = \text{constant} \quad (6)$$

and, after combination with eqn. (5),

$$v(v_0 + v)[\text{Zn}] \propto v_{\text{eq}} - v \quad (7)$$

In the photometric titration, absorbance values proportional to either $[\text{ZnOHI}]$ or

$[I'] = [HI] + [I]$ are the only measurable parameters. These are related to the free zinc concentration by

$$[Zn] \propto [ZnOHI]/[I'] \quad (8)$$

provided that pH is constant.

Thus, as seen from eqns. (7) and (8), F_1 , where

$$F_1 = v(v_0 + v)[ZnOHI]/[I']$$

is a linear function of v ml of titrant added, provided that all the assumptions made above are valid. Moreover, this line when extrapolated to $F_1 = 0$ will intersect the v -axis at $v = v_{eq}$.

Plots of F_1 applied to the HALTAFALL simulated titration data at different pH values are shown in Fig. 2, and the dependence of the systematic error on the pH is evident from Table II. As is seen from the figure, the F_1 plots are very nearly linear in the pH range under consideration.

The main reason for the systematic errors and the slight non-linearity of F_1 is the formation of the calcium-EGTA complex from the EGTA liberated from the zinc-EGTA complex during the formation of the zinc-indicator complex. Also, of course, very close to the equivalence point, magnesium- and strontium-EGTA complexes are present. Interference from the latter complexes is best overcome by choosing a pH value such that the measurable colour changes occur before their formation commences.

Interference from zinc-EGTA is partly compensated for by introducing v_1

$$v_1 = v + v_0[ZnOHI]/t_{EGTA} \quad (9)$$

and plotting F'_1

$$F'_1 = v_1(v_0 + v)[ZnOHI]/[I'] \quad (10)$$

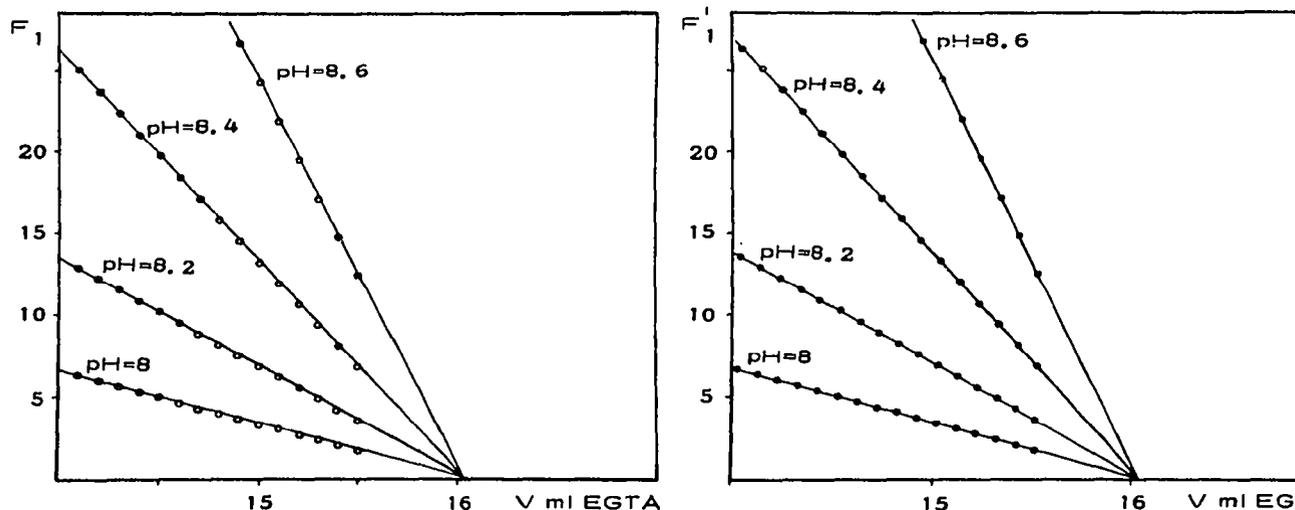


Fig. 2. Straight-line regression evaluation of the equivalence point by means of the plot F_1 (arbitrary scale).

Fig. 3. Straight-line regression evaluation of the equivalence point by means of the plot F'_1 (arbitrary scale).

against v_1 . As is seen from Fig. 3, the theoretical plots thus obtained are linear and on extrapolation to $F'_1 = 0$, they intersect the v -axis very close to the theoretical endpoint. The systematic error is small and independent of pH, as is seen from Table II.

As pointed out above, the concentrations of the indicator species cannot be measured directly. The relationship between these values and the experimentally measurable absorbance, A , at constant pH, is

$$A = \varepsilon_1[\text{ZnOHI}] + \varepsilon_2[\text{I}'] \quad (11)$$

Furthermore, if the wavelength is such that $\varepsilon_1 > \varepsilon_2$, then

$$A_{\max} = f\varepsilon_1[\text{I}]_{\text{tot}} \quad (12)$$

$$A_{\min} = f\varepsilon_2[\text{I}]_{\text{tot}} \quad (13)$$

where

$$f = v_0/(v_0 + v) \quad (14)$$

and

$$f[\text{I}]_{\text{tot}} = [\text{ZnOHI}] + [\text{I}'] \quad (15)$$

By combining eqns. (12) and (15)

$$A_{\max} - A = (\varepsilon_1 - \varepsilon_2)[\text{I}'] \quad (16)$$

and by combining eqns. (13) and (15)

$$A - A_{\min} = (\varepsilon_1 - \varepsilon_2)[\text{ZnOHI}] \quad (17)$$

Thus,

$$[\text{ZnOHI}]/[\text{I}'] = (A - A_{\min})/(A_{\max} - A) \quad (18)$$

which is used to calculate F_1 and F'_1 .

Moreover, by combining eqns. (16), (17) and (18)

$$[\text{ZnOHI}] = (A - A_{\min})f[\text{I}]_{\text{tot}}/(A_{\max} - A_{\min}) \quad (19)$$

which can be used to calculate F'_1 , provided that a value for $[\text{I}]_{\text{tot}}$ is known.

EXPERIMENTAL

Apparatus

The photometer used was an EEL filter photometer with a selenium photocell. Since it is not necessary to protect the titration vessel from external light, the instrument has many advantages, *e.g.*, samples can be changed rapidly. The main drawback of the instrument, the non-linearity between the illumination and the output current, due to the external load resistance, was overcome by means of an operational amplifier (Fairchild μA 725 C) used as a current amplifier, as shown in Fig. 4. Calibration of the photocell response against zincon concentration yielded linear plots in the range 0–1.0 absorbance units. The computer-processed titrator used was that described previously¹⁷ and the automatic burets were of type Metrohm Dosimat E 412.

Reagents

All reagents were of analytical grade and were analysed for calcium im-

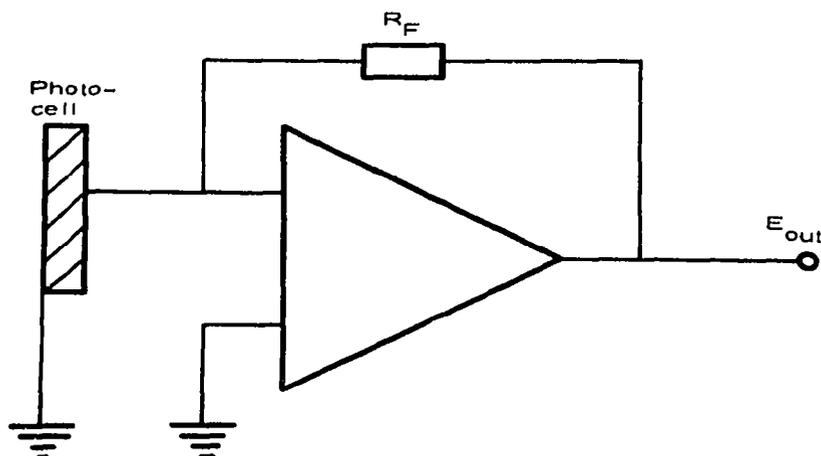


Fig. 4. Current amplification of photocell signal.

purities by means of atomic absorption spectrometry. A *ca.* 0.15 M solution of tetrasodium-EGTA was prepared by dissolving the acid in sodium hydroxide. Calcium standards corresponding to "sea water" of 35‰ salinity were prepared by dissolving calcium carbonate in hydrochloric acid. After neutralization, sodium, potassium, magnesium, strontium, chloride, sulphate and hydrogencarbonate were added in the same proportions as in sea water. Standard Sea Water was obtained from Charlottenlund Slot, Denmark. Buffer solutions (pH 8.6) were prepared from boric acid and the indicator solution was prepared by dissolving the monosodium salt in ethanol.

Computerized titration procedure

A portion (25 g) of a 35‰ salinity sea water sample was accurately weighed into the titration vessel and diluted with calcium-free doubly distilled water and buffer solution. For water samples of lower salinity, a proportionately greater amount was weighed in, the ionic strength and composition thus always being approximately the same. The procedure commenced with the titrator asking for the weight of the sample and the temperature in the EGTA storage vessel. The latter information was used by the processing computer program to correct for variations in the EGTA concentration caused by fluctuations in temperature. Such a correction is necessary in high-precision analysis unless the temperature can be kept constant to within 0.2°. Density variation corrections were calculated by the processing computer program according to experimental data relevant for 0.5 M sodium chloride. Information concerning the concentration of EGTA, at a given temperature, and the total indicator concentration were specified in the processing program and not as input data for each separate titration, since these parameters were changed only when new stock solutions were prepared.

The reference intensity, I_0 , for the solution without indicator was measured for 10 s, after which the titrator added one-half the amount of indicator from an automatic syringe buret and measured the absorbance. The amount of indicator was chosen so that the absorbance value obtained, $A_{max}/2$, was between 0.4 and

0.5 units, *i.e.* within the optimal range for accurate photometric measurement. From the measured value of A_{\max} , the relevant A_{\min} value was calculated, using the value of the ratio A_{\max}/A_{\min} specified in the processing program. This ratio was determined separately and is, of course, relevant for the specific photometric equipment only at a given pH value. It would be possible to determine A_{\min} in each separate titration by programming the computer to add a large excess of titrant at the end of each titration. In this region the absorbance value is, however, so small that the photometric precision is poor. In the separate determination of the ratio A_{\max}/A_{\min} , the value of A_{\min} was determined for a total indicator concentration approximately ten times higher than that used in the titrations.

The remainder of the indicator was then added, followed by EGTA titrant, until the value of $(A - A_{\min})/(A_{\max} - A)$ approached 2, after which increments of 0.1 ml of titrant were added, the values being stored in the core memory. Addition of titrant was continued until $(A - A_{\min})/(A_{\max} - A) \approx 0.3$. The criterion for a stable absorbance reading after an addition of titrant was that two consecutive sets of mean values differed by less than 0.1%, each mean value being calculated from twenty readings, which took a little longer than 1 s. Stable readings were normally achieved in less than 10 s after the addition of a new increment of titrant.

In the evaluation of the equivalence point by means of F'_1 , only titration points for which $(A - A_{\min})/(A_{\max} - A)$ lay between 2 and 0.3 were included. This was because even small errors in A cause large errors in this ratio if the absorbance value is close to either A_{\max} or A_{\min} . Moreover, interference from magnesium-EGTA can be neglected if data for which $(A - A_{\min})/(A_{\max} - A) < 0.3$ are excluded.

Tests were made to establish whether or not improved precision was obtained if a weighting scheme was applied to the experimental points included in F'_1 , those values with high F'_1 values being, of course, assigned the lowest weights. Since the computerized titrator permits the titration of a larger number of samples, the weighting function was derived empirically rather than theoretically, that finally adopted being

$$\text{Weight of point No. } Q = \text{Integer } (1.5 Q)^{\dagger} \quad (20)$$

point No. 1 being the first experimental point with $(A - A_{\min})/(A_{\max} - A)$ less than 2. It should be emphasized that the weighting function improves the analytical precision only by *ca.* 20%. The time required for a single titration is about 10 min, including the time needed for evaluation and printing out of the edited results.

RESULTS AND DISCUSSION

Precision

Ten sets of measurements, each set consisting of twenty titrations of 20–25 g sea-water samples, yielded a mean value with a relative standard deviation of 0.00028. This is considerably better than the relative standard deviations obtained previously from linear regression photometric titrations, *e.g.* reference 18. The main reasons for this were found experimentally to be:

- (i) the method does not require pretreatment of the samples;
- (ii) the current amplifier coupled to the photocell results in a linear absorbance *vs.* concentration relationship;

(iii) the plot F'_i takes interfering indicator side-reactions into account and permits exploitation of a part of the titration curve where the formation of magnesium-EGTA complex is negligible;

(iv) both A_{\max} and A_{\min} are measured within the optimal region for absorbance measurement;

(v) the titration procedure is automatic, permitting the collection of a large number of titration data in a reasonable space of time; it is, of course, possible to perform the titration manually but this will increase the time needed for one titration considerably;

(vi) temperature variations in the titrant storage vessel are compensated for;

(vii) evaporation from the titrant storage vessel is kept at a minimum by using a syringe-shaped vessel, thus reducing the volume of air above the titrant solution.

Accuracy

The accuracy of the titration procedure depends on the accuracy of the calcium concentration in the standard solution and on how closely the ionic composition of the standard resembles that of sea water. Calcium carbonate is an accurate calcium standard, and since the relative compositions of the main sea water constituents differ only very slightly from one sample to another it is possible to prepare a representative "sea water" standard. The great sensitivity obtainable in the atomic absorption analysis for calcium ensures, moreover, that calcium impurities are not introduced with chemicals used in preparing the standards. The suggested method ought to be sufficiently accurate for sea-water samples with salinities greater than 5‰. Nevertheless, it is the author's opinion that, in order to be able to compare results obtained by different methods, it is imperative to agree on an international standard to be used, as emphasised by Culkin and Cox⁵, for example.

Calcium concentration in sea water

The calcium concentration of Copenhagen Standard Sea Water of 19.3745‰ chlorinity was determined to be 10.28 mmol kg⁻¹. This value is in good agreement with the mean values of 10.26 and 10.29 obtained for North Atlantic samples by Riley and Tongudai¹⁹ and Culkin and Cox⁵, respectively.

Field experiments

The suggested method has been used by Dyrssen *et al.* to determine the calcium concentration in samples of Pacific sea water taken by Eng. Dmitry Mendeleev. The preliminary results²⁰ show that the method is well suited to analysis on board ship.

Financial support from Knut och Alice Wallenbergs Stiftelse and the Swedish Natural Research Council (NFR) is gratefully acknowledged.

SUMMARY

A computerized photometric titration procedure for the determination of

calcium in the presence of magnesium with zinc-zincon as indicator is described. The evaluation method is based on straight-line regression, the method yielding a relative precision of 0.00028 when applied to sea water samples in the salinity range 5–35‰.

RÉSUMÉ

On décrit une méthode de titrage photométrique avec ordinateur pour le dosage du calcium en présence de magnésium, en utilisant le zinc-zincon comme indicateur. Cette méthode est basée sur une régression en ligne droite permettant une précision relative de 0.00025 pour des échantillons d'eau de mer de salinité comprise entre 5 et 35‰.

ZUSAMMENFASSUNG

Es wird ein photometrisches Titrationsverfahren unter Verwendung eines Computers für die Bestimmung von Calcium in Gegenwart von Magnesium mit Zink-Zincon als Indikator beschrieben. Die Auswertmethode beruht auf einer geradlinigen Regression und ergibt eine relative Reproduzierbarkeit von 0.00025, wenn sie auf Meerwasser-Proben mit einem Salzgehalt von 5–35‰ angewendet wird.

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