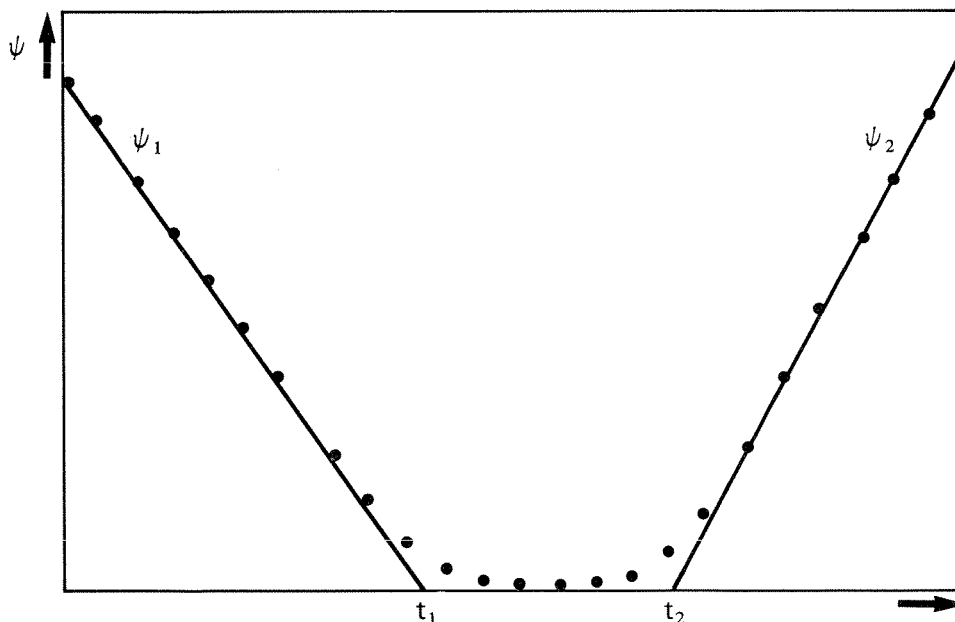# Acid Rain Research

REPORT 12/1987

A coulometric Gran titration method for the determination of strong and weak acids in freshwater

Norwegian Institute for Water Research 〇 NIVA

NIVA – REPORT

Norwegian Institute for Water Research NIVA

Report Title:	Date:
A coulometric Gran titration method for the determination of strong and weak acids in freshwater	24 August 1987
	Project No: 0-85244

Author(s):	Topic group: Acid precipitation
Eirin J.S. Røgeberg	Geographical area: Norway
	Number of pages (incl. app.) 28
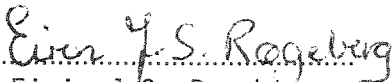
Contractor: Surface Water Acidification Programme	Contractors ref. (or NTNF - No)

Abstract:

A modified Gran titration procedure for the determination of strong and weak acids in freshwater is described. The titrations are carried out by coulometric generation of hydroxide ions in the pH range 3.6-10.3. The method measures the amount of non-volatile strong and weak acids with a precision of $\pm$ 5 μmoles/l. Application to natural water samples is demonstrated.
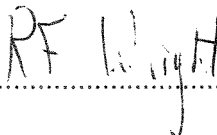
4 keywords, Norwegian	4 keywords, English
1. Sterke syrer	1. Strong acids
2. Svake syrer	2. Weak acids
3. Granstitrering	3. Gran titration
4. Coulometrisk metode	4. Coulometric method

Project leader

Eirin J.S. Røgeberg

For the Administration

Norwegian Institute for Water Research NIVA

0-85244

A COULOMETRIC GRAN TITRATION METHOD FOR THE DETERMINATION

OF STRONG AND WEAK ACIDS IN FRESHWATER

Oslo, 24 August 1987

Project leader : Eirin J.S. Røgeberg

SUMMARY

The Gran procedure described by Molværsmyr and Lund (1) was modified for the routine analysis of strong and weak acids in freshwater. The titrations are carried out by coulometric generation of hydroxide ions in the pH range 3.6-10.3. The method measures the amount of non-volatile strong and weak acids in freshwater with a precision of $\pm$ 5 μmoles/l. An automated version of this method has been developed later and will be published elsewhere.

The contribution to weak acid acidity, including aluminum, was 11.8 $\pm$ 2.0 μeq/mg C for 17 lake water samples from the Langtjern area in southern Norway. The contribution from weak organic acids was 8.4 $\pm$ 1.9 μeq/mg C, assuming an aluminum contribution of 4 eq/mole total aluminum. This value probably overestimates the aluminum weak acidity due to undissociated aluminum-organic complexes. Further work is needed to obtain more exact values of the aluminum contribution to weak acidity.

Organic anion concentrations calculated by the method of Oliver et al. (26) compared favourably with excess cations in the Langtjern samples.

CONTENTS

1. ESTABLISHMENT OF A CHEMICAL METHOD FOR THE DETERMINATION OF STRONG AND WEAK ACIDS IN FRESHWATER

A modified Gran procedure described by Molværsmyr and Lund (1) was adapted for routine analysis of strong and weak acids. The titrations are carried out by coulometric generation of hydroxide ions in the pH range 3.6-10.3. The amount of non-volatile strong and weak acids in freshwater is determined with a precision of ± 5 µmoles/l.

1.1 Choice of method

Normally, the determinations of strong and weak acids are based on Gran's method (2). The method includes potentiometric pH titration and transformation of titration data to straight lines, so called "Gran plots". Several variations of the Gran procedure have been reported (3-15, 1).

Potential errors associated with the method have been widely discussed in the literature (16-22, 14). For example, Barnard and Bisogni (22) claimed that the two most serious errors were

1) an overestimate of total acidity due to CO_2 contamination of the titrant and

2) an overestimate of strong acid acidity at the expense of an underestimate of weak acid acidity due to dissociated weak acids present in the low pH region of the titration curve. Also, the weak acid acidity may be underestimated if they are not fully dissociated at the end of the titration.

The problem of CO_2 in the titrant is not easily eliminated unless a procedure such as coulometric titration is used (23, 1). The second error can be reduced, though not totally eliminated, by adding strong acid to the sample. The amount added must be subtracted from the final result. In practice, the amount of acid added is restricted, since increasing the acid addition leads to reduced accuracy of the strong acid determination, which is calculated as the difference between two relatively large numbers.

The titration should be continued until all weak acids have been fully titrated.

From a critical survey of the literature the modified Gran procedure

described by Molværsmyr and Lund (1) seemed to be the best choice of method in order to avoid the most serious errors.

The titrations are carried out by coulometric generation of hydroxide ions, thus avoiding carbonate contamination of the titrant. A pH titration range from 3.6 to 10.3 was assumed adequate for a majority of freshwaters. With minor modifications this method was adapted for routine analysis of strong and weak acids.

1.2 A short description of the method

The modified Gran procedure described by Molværsmyr and Lund (1) was adapted for routine analysis with minor modifications.

The content of non-volatile strong and weak acids in natural water is determined with a precision of ± 5 μmoles/l. Volatile acids will disappear during the argon bubbling prior to the analysis, and are not included in the results. The samples are titrated by a coulometric procedure in the pH range 3.6-10.3, and the strong and weak acid content calculated from Gran plots.

The procedure is described in detail in Appendix 1.

Our routine method deviates from Molværsmyr and Lund's method in the following respects:

1. Instead of the stepwise coulometric titration allowing time for steady potentiometer readings between each hydroxide generation, a continuous titration procedure at low current strength was preferred. This procedure was faster and more convenient than the discontinuous one, and results obtained with the two methods were in good agreement. The same precision was obtained with both methods.

    The continuous procedure will also be more suitable for automation. An automatic version of the method has been developed later.

2. A sample volume of 50 instead of 100 ml was chosen due to the volume of the titration cell.

3. The amount of KBr added to the sample was increased from 2.38 to 4.00 g/l. Kortelainen and Mannio (24) had found that the linear part of the Gran plot at high pH values could be extended by increasing the amount of KBr.

   The KBr was dissolved in the HCl and added as a HCl-KBr solution instead of adding it in a solid form.

4. The precision reported by Molværsmyr and Lund was ± 0,5 μmoles/l for strong acids and ± 3 μmoles/l for weak acids. In our method the precision was ± 5μmoles/l for both strong and weak acids.

2. DETERMINING THE CONTRIBUTION OF NATURAL WEAK ACIDS TO FRESHWATER ACIDIFICATION

The contribution to acidity from weak acids was 11.8 ± 2.0 μeq/mg C for water samples from the Langtjern area.

The contribution from weak organic acids was 8.4 ± 1.9 μeq/mg C, assuming aluminum is the most important contributor to weak acidity besides organic carbon. An aluminum contribution of 4 eq/mole used in the calculations probably overestimates the aluminum weak acidity. Organic anion concentrations calculated by the method of Oliver et al. (26) were in good agreement with charge balance calculations.

2.1 Analysis of water samples from the Langtjern area

16 localities in the Langtjern area sampled and analyzed by Arne Henriksen in 1977 were resampled in March 1986 and analyzed for strong and weak acids by our routine method. The chemical composition of the samples is listed in table 1, appendix 2. Lower results were now obtained for strong acids and higher results for weak acids, as would be expected from the different analytical techniques. The mean difference for strong acids was - 14 μeq/l, and for weak acids 38 μeq/l (table 1). The method used by Henriksen (25) involved a preacidification to pH 4.0-4.1. Findings of Molværsmyr and Lund (1) indicated that weak acids are not totally undissociated at this pH. This will result in an overestimation of strong acids and an underestimation of weak acids. Our routine method involved a preacidification to pH about 3.6, as suggested by Molværsmyr and Lund. Molværsmyr and Lund also suggested that the titrations should be continued until a pH of 10.3 was reached to ensure complete dissociation of all weak acids. Incomplete dissociation will result in an underestimation of weak acids. In Henriksen's result this may have contributed to the low weak acidity values, which were obtained by titrating to pH about 10.0.

Analysis of a water sample from Langtjern with our routine method gave values of - 18.6 and 168.8 μeq/l for strong and weak acids, respectively. This is in good agreement with the results of - 16.6 and 163.8 μeq/l reported by Molværsmyr and Lund.

Table 1. Comparison of strong (SA) and weak acids (WA) in water samples
from the Langtjern area calculated by Henriksen (1977) and
by NIVA's present routine method.

Locality	Present results		Henriksen's results (1977)	
	SA (μeq/l)	WA (μeq/l)	SA (μeq/l)	WA (μeq/l)
St. Y	17.9	141.7	41.0	90.0
St. X	− 0.8	164.3	− 6.5	90.0
Lille Pipan	− 114.1	107.1	− 63.0	67.0
Store Pipan	− 18.0	171.4	28.3	116.0
Store Røytjern	− 6.5	61.9	− 1.8	37.0
Lille Røytjern	0.1	65.6	3.2	52.0
Vestre Holmetjern	21.1	128.0	28.0	86.0
Holmetjern	0.7	109.0	5.1	66.0
Veiputt	8.4	67.8	2.5	53.0
Lauvskartjern	9.4	106.9	7.0	74.0
LAVN 1 m	− 8.0	133.7	3.8	95.4
2 m	− 6.8	122.6	0.3	84.5
4 m	− 7.6	129.2	0.3	93.4
6 m	− 8.9	135.6	2.0	95.5
LAE 01	− 8.6	125.1	1.8	89.7
LAE 03	− 18.6	168.8	31.6	150.2
Mean value	− 8.8	121.2	5.2	83.7
Std.dev.	± 29.3	± 33.1	± 22.3	± 25.9

Mean difference SA : − 14 μeq/l
  "   "   WA   37.5 μeq/l

2.2 Contribution to weak acid acidity from weak organic acids and aluminum

Findings of Henriksen and Seip (25) indicated that the variance in weak acid concentrations in lakes in Southern Norway and Southwestern Scotland was largely explained by the concentrations of organic carbon and aluminum. Other weak acids as silica and ammonia play minor roles, except at very low aluminum and organic carbon concentrations.

They calculated the following empirical relationship between weak acids (WA), and aluminum and total organic carbon (TOC):

(1)   WA (μeq/l) = 3.7 + 0.114 . Al (μg/l) + 5.46 TOC (mg/l)

This relationship which is based on results from 200 Norwegian and Scottish lakes, indicated an average contribution of 5.5 μeq per mg organic carbon to the weak acid acidity. The aluminum contribution is about 3 eq per mole.

The corresponding relationship for 100 small Norwegian lakes including the Langtjern area was:

(2)   WA (μeq/l) = - 12.6 + 0.145 . Al (μg/l) + 6.38 TOC (mg/l)

indicating an average contribution of 6.4 μeq/mg C and about 4 eq/mole Al.

Our results from the Langtjern area indicated an average contribution of 11.8 μeq/mg C to the total weak acidity. By subtracting an aluminum contribution of 4 eq/mole Al from the total weak acidity, a mean contribution of 8.4 μeq/mg C from weak organic acids was calculated (table 2). However, great individual variations excist, ranging from 4.8 to 13.4 μeq/mg C.

Obviously, the carboxyl content of humic substances varies, depending on the character of the organic material. The measured values also depend on the analytical techniques applied. Oliver et al. (26) reported a mean carboxyl content of 10.0 μeq/mg C, ranging from 5.1 to 13.4 μeq/mg C, for water samples from various locations in the United States and Canada. The carboxyl content of humic acids ranged from 5.1 to 9.1 μeq/mg C with a mean of 7.7 μeq/mg C, while fulvic acids contained an average of 10.7 μeq/mg C, ranging from 9.9 to 13.4 μeq/mg C. The carboxyl content was measured on isolated, proton saturated material.

Weber and Wilson (27) reported carboxyl contents of 8.4 and 8.2 μeq/mg C for two aquatic humic acids and 13.3 μeq/mg C for an aquatic fulvic acid.

Beck et al. (28) reported values from 14-22 μeq/mg C with an average of 18 μeq/mg C for nine humic water samples from the Satilla river in Georgia, while Perdue et al. (29) showed a range of 8.8 - 12.6 μeq/mg C for a humic water sample from the same river, using a different method.

Visser (30) reported carboxyl contents in the range 11.4 to 14.6 and 13.2 to 17.4 μeq/mg C for aquatic humic and fulvic acids, respectively.

Generally, fulvic acids have a higher carboxyl content than humic acids.

Direct comparison of results from different studies is difficult because of the different isolation and titration procedures used. Some of the organic material will be lost during the isolation procedures. For instance, a recovery of 40-75 percent is reported after resin extraction (26). The loss of organic material will probably influence the results.

Compared to other studies, our results tend to be a little lower. One reason for the discrepancy may be that we studied actual water samples, whereas most of the other experiments were performed on isolated humic materials.

In spite of the different methods used our results compare favourably with the results of Oliver et al., who reported weak organic acid values from 5.1 to 13.4 μeq/mg C, while results from our study ranged from 4.8 to 13.4 μeq/mg C. The low results reported by Henriksen and Seip (25) are probably due to an underestimation of weak acids by the titration method used.

Table 2.   Measured values of weak acids, aluminum and total organic carbon in Langtjern samples. Contribution of organic carbon to total weak acidity and weak organic acidity is calculated.

Locality	WA μeq/l	Al μeq/l	TOC mg/l	WA/TOC μeq/mg C	(WA-Al)/TOC μeq/mg C
St. Y	141.7	33.9	14.2	10.0	7.6
St. X	164.3	36.9	13.4	12.3	9.5
Lille Pipan	107.1	22.8	10.2	10.5	8.3
Store Pipan	171.4	44.0	11.9	14.4	10.7
Store Røytjern	61.9	15.4	6.57	9.4	7.1
Lille Røytjern	65.6	14.4	8.03	8.2	6.4
Vestre Holmetjern	128.0	32.1	11.9	10.8	8.1
Holmetjern	109.0	32.6	9.40	11.7	8.1
Veiputt	67.8	36.6	5.91	11.5	4.8
Lauvskartjern	106.9	39.3	9.83	10.9	6.9
Bekaren	135.8	35.3	9.37	14.5	10.7
LAVN 1 m	133.7	42.7	10.7	12.5	8.5
2 m	122.6	42.1	11.8	10.1	6.8
4 m	129.2	42.4	10.5	12.3	8.3
6 m	135.6	42.4	10.2	13.3	9.1
LAE 01	125.1	41.0	10.7	11.7	7.9
LAE 03	168.8	32.1	10.2	16.5	13.4
Mean value				11.8	8.4
Std. dev.				± 2.0	± 1.9

2.3   Estimating organic anion concentrations in Langtjern samples by Oliver's method

Charge balance calculations of humic waters will give excess of cations if organic anions are not included. The cation excess is a rough estimate of the organic anion concentration.

By the method of Oliver et al. (26) the organic anion concentration (A^-) can be estimated from pH and organic carbon concentration.

(A^-) is given by the equation:

1) $$(A^-) = \frac{K \, [C_t]}{K + [H^+]} \quad (eq/l)$$

where K is calculated from the following empirical equation:

2) $$pK = 0.96 + 0.90 \, pH - 0.039 \, (pH)^2$$

$[C_t]$ is the weak organic acid concentration. Instead of measuring $[C_t]$ it can be estimated from the organic carbon concentration if the average carboxyl content of the organic material is known. For instance, Oliver et al. reported an average carboxyl content of 10 $\mu eq/mg$ C.

Rearrangement of equation (1) yields

3) $$\alpha = \frac{[A^-]}{[C_t]} = \frac{K}{K + [H^+]}$$

where α is the dissosiation degree of the humic material.

The organic anion concentrations of the Langtjern samples were calculated by equation (1) from pH and the measured values of weak organic acids. The results were compared to excess cation values from charge balance calculations (table 3). Generally, there was good agreement between the two sets of data. Values obtained from TOC values, using an average carboxyl content of 8.4 $\mu eq/mg$ C, also showed good agreement with charge balance results.

Table 3. Concentrations of organic anions in some coloured Norwegian
lakes calculated from charge balance and by Oliver et al.'s
method.

Locality	Charge balance [1] Σcations-Σanions μeq/l	$[A^-]$ [2] μeq/l	$[A^-]$ [3] μeq/l
St. Y	74.4	73.2	81.0
St. X	101.9	96.6	85.3
Lille Pipan	69.4	78.6	79.9
Store Pipan	99.3	102.3	80.3
Store Røytjern	34.6	36.4	43.2
Lille Røytjern	42.8	39.4	51.9
Vestre Holmetjern	65.4	66.5	69.3
Holmetjern	56.3	56.8	58.7
Veiputt	39.1	24.2	38.5
Lauvskartjern	55.8	51.2	62.6
Bekaren	71.1	90.6	70.9
LAVN 1 m	72.2	69.7	68.8
2 m	70.4	61.7	75.9
4 m	73.3	66.1	67.2
6 m	76.6	71.2	65.5
LAE 01	77.0	64.4	68.8
LAE 03	75.8	110.0	69.0

1) Cations included : H^+, Ca^{2+}, Mg^{2+}, Na^+, K^+ Al^{3+}
   Anions included : Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-
2) Organic anion concentration calculated by Oliver et al.'s
   method (26), from measured values of weak organic acids.
3) Organic anion concentration calculated by Oliver et al.'s method
   from TOC values and an average carboxyl content of 8,4 μeq/mg C.

.2.4 Discussion of the aluminum contribution to weak acid acidity

The contribution from aluminum to weak acid acidity depends on the aluminum speciation.

Analysis of synthetic samples containing 250 µg/l Al showed that aluminum contributed with 4 eq per mole to the total weak acidity, consistent with the formation of $Al(OH)_4^-$. The same value was reported by Barnard and Bisogni (22).

In natural water samples strong aluminum-organic complexes may not be completely dissociated at pH 3,6. Consequently, the contribution to total weak acidity will be less than 4 eq per mole of total aluminum. Henriksen and Seip (25) reported a contribution of 3-4 eq per mole, based on empirical calculations.

In addition to total aluminum, the following operationally defined aluminum fractions were measured in the present study:

    Reactive Al ("total monomeric Al", RAL)
    Non-labile Al ("organic monomeric Al",ILAL)
    Labile Al ("inorganic monomeric Al", LAL)

Aluminum fractions are separated by ion exchange and measured by a spectrophotometric method. The labile fraction, which is the fraction retained by the ion exchange resin, is measured as the difference between reactive and non-labile aluminum. This fraction is thought to give a good estimate of the inorganic aluminum species.

The labile aluminum fraction measured in samples that were acidified to pH 3,6 and bubbled with argon was thought to be a good estimate of the aluminum fraction that is dissociated at the beginning of the titration. This fraction will probably give a better estimate of the weak acid contribution than total aluminum.

Analysis of eight acidified and argon-bubbled Langtjern samples indicated that about 50 % (39-67 %) of the aluminum-organic complexes still remained undissociated at the beginning of the titration.

In the untreated samples about 30 % (21-44 %) of total aluminum was in the labile form, while about 80 % (77-84 %) was reactive aluminum. None of these fractions could therefore be used directly in calculating the weak acid contribution of aluminum in these humic water samples. The labile aluminum fraction would result in an

underestimation, while the reactive fraction would result in an overestimation of the aluminum weak acidity.

The total aluminum concentration of the samples was about 250 µg/l, or about 40 µeq/l. Roughly, the aluminum weak acidity would be overestimated by about 20 µeq/l from total aluminum, about 12 µeq/l from reactive aluminum and underestimated by about 8 µeq/l from labile aluminum.

The data from this study are too scarce to draw any general conclusions regarding the aluminum contribution to weak acidity. Further work is needed to obtain empirical and experimental data on the relationships between the aluminum weak acidity and other parameters as aluminum fractions, pH, total organic carbon and weak acids.

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APPENDIX 1

A coulometric procedure for the determination
of strong and weak acids according to Gran's
theory.

A COULOMETRIC PROCEDURE FOR THE DETERMINATION OF STRONG AND WEAK ACIDS ACCORDING TO GRAN'S THEORY.

1. PRINCIPLE

By this method the content of non-volatile strong and weak acids in natural water is determined. Volatile acids are not determined, as they disappear during the argon bubbling before the titration.

The method is based on Gran's theory (1). The samples are acidified to pH about 3.6 and titrated to pH 10.2 - 10.3 with OH- generated electrolytically by a coulometric procedure.

By transforming the titration curves to straight lines it is possible to determine accurately the endpoints of the titration and calulate the content of strong and weak acids in the sample.

The precision of the method is $\pm$ 5 µmoles/l.

The method is a modified version of the Molværsmyr and Lund's method (2). The manual procedure described below has later been automated.

Litterature:

1) G. Gran, Analyst, 77 (1952) 661.
2) K. Molværsmyr and W. Lund, Water Res., 17 (1983) 303.

2. REAGENTS

HCL-KBr solution

Stock solution, approx. 0.12 M HCl
10 ml conc. HCl (p.a.) is diluted to 1 liter.

Working solution, approx. 1.8 mM HCl - 20 g KBr/l.
Dilute 15 ml of the stock solution to 1 liter.

Add 5.0 g KBr pr. 250 ml of the 1.8 mM solution. This HCl-KBr solution should be renewed every third day.

3. STANDARDIZATION OF HYDROCHLORIC ACID

The HCl-KBr working solution should be renewed and standardized every third day.

Transfer with a pipet 50 ml distilled water to the titration cell, add 10.0 ml (accurately!) of the HCl-KBr solution and perform the titration as described for samples in chapter 4. However, it is not necessary to continue the titration beyond the first end point (where the potential shifts from positive to negative).

Titrate three parallels and calculate the strong acid content by formula 3A in chapter 5. Calculate the mean value and standard deviation. The standard deviation should not exceed $\pm$ 3 μmoles/l.

4. PROCEDURE

Transfer 50 ml sample by pipet to the titration cell. Acidify the sample with 10.0 ml (accurately!) HCl-KBr solution. The pH should be approx. 3.6.

Bubble the solution with argon for 10 min. to remove carbon dioxide and other volatile components. Then turn the valve to lead the argon above the solution during the titration.

Stir the solution continuously by a magnetic stirrer during the whole procedure.

Titrate the sample coulometrically by a constant current of 3 mA. The titration should be performed continuously, and the potential read to the nearest 0.1 mV every 30 sec.

The titration is interrupted when the sample reaches a pH of approx. 10.3 (The potential corresponding to pH 10.3 should be determined in advance).

Start and stop of the titration is controlled by the push button EA 858 (fig. 7.1).

Between each titration the silver electrode should be purified in 57 % hydrogen iodide solution. Remaining coating on the electrode can be removed by rubbing with fine emery paper. Every day before use the silver electrode should be rubbed with fine emery paper.

The platinum electrode should be purified in 57 % hydrogen iodide solution after each titration. When not in use the electrode should be stored in a weak hydrochloric acid solution (e.g. 1.8 mM HCl solution).

5. CALCULATION OF RESULTS

Calculate the functions φ_1 and φ_2.

$$1) \quad \varphi_1 = 10^{\frac{E. F}{RT\ln 10}} = 10^{E. \, 0.016904}$$

where E is the potential in mV for E > 0 mV

$$2) \quad \varphi_2 = 10^{\frac{-E . F}{RT\ln 10}} = 10^{-E . \, 0.016904}$$

for E < 0 mV

Plot φ_1 and φ_2 against the electrolysis time t. The graphs of the functions φ_1 and φ_2 will form straight lines that deviate near the equivalence points if the sample contains weak acids.

By extrapolation the straight parts of the graphs will intersect the t-axis in t_1 and t_2 (fig. 5.1). An accurate determination of t_1 and t_2 should be done by linear regression analysis (chapter 6).

The total amounts of strong (SA) and weak (WA) acids are calculated by the formulas:

$$3) \quad SA = \frac{i . t}{F . V}$$

where   i=current (mA)
V=sample volume (ml)

$$4) \quad WA = \frac{i.(t_2 -t_1)}{F . V}$$

F=Faraday's constant

At a constant current of 3mA and 50 ml sample volume the formulas above can be written:

3A) $SA = 0.621 \cdot t$ (μmoles/l)

4A) $WA = 0.621 (t_2 - t_1)$ (---"----)

The HCl added must be subtracted from the total strong acid:

5) $SAo = 0.621 (t_1 - t_1 HCl)$ where $t_1 HCl$ is the endpoint of the strong acid titration of the HCl

    SAo denotes the original content of strong acid in the sample before HCl addition.

    A negative value of SAo indicates that the sample contained free base.
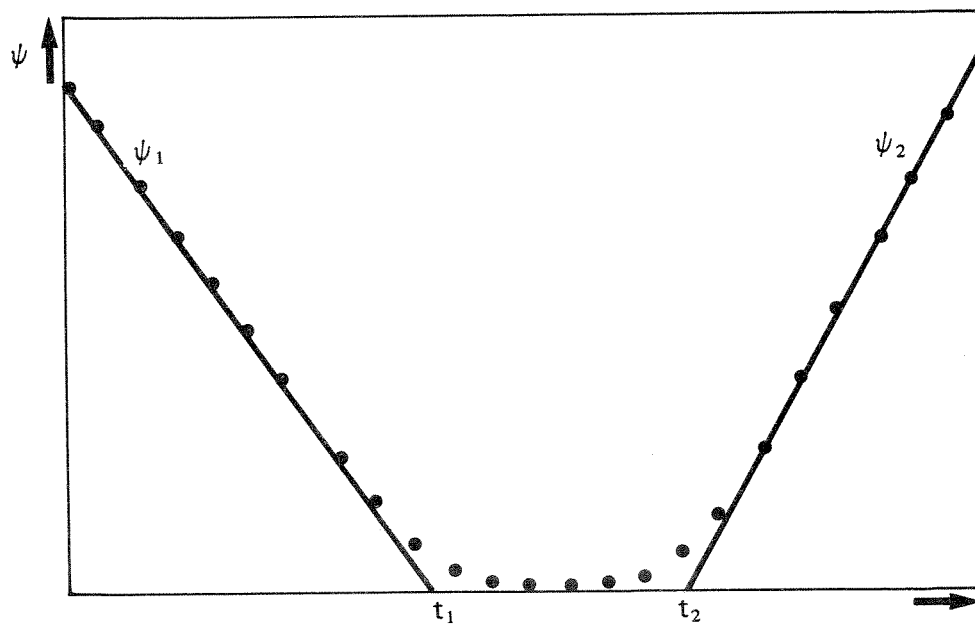
Electrolysis time, t (s)

Fig. 5.1 Gran's plot for coulometric titration
of strong and weak acids

S U M M A R Y

Calculate

$$\varphi_1 = 10^{E. \, 0.016904} \quad \text{for } E > 0$$

and

$$\varphi_2 = 10^{-E \, . \, 0.016904} \quad \text{for } E < 0$$

Plot φ_1 and φ_2 against electrolysis time (t).

Determine t_1 and t_2 by linear regression analysis, using points from the straight lines of the φ_1 and φ_2 graphs.

The strong acid content is calculated by:

5) $SAo = 0.621 \, (t_1 - t_1 HCl)$ (μmoles/l)
   The weak acid content is calculated by:

4A) $WA = 0.621 \, (t_2 - t_1)$ (μmoles/l)

6. DETERMINATION OF T_1 AND T_2 BY LINEAR REGRESSION ANALYSIS

Plot φ_1 and φ_2 against t and determine the straight parts of the graphs. The first few points of the φ_1 graph may deviate from the straight line, and in this case these points should be discarded.

Choose approx. 10 points from the straight parts of each graph and determine t_1 and t_2 by linear regression.

The linear regression analysis can be performed e.g. by the data programme (PROG) MINITAB in the following way:

ENTER
PASSWORD
PROJ. PASSWORD

CXϱ (PROG) MINITAB

-- READ ^C1, C2
>t(1)   ^φ(1)   t(2) and φ(1) etc. are corresponding
>t(2)   ^φ(2)   values of t and φ.
   .
   .
   .
>t(n)   ^φ(n)
>END
--REGR^C1^1^C2

The following will be shown on the screen:

	COLUMN	COEFFICIENT	ST.DEV. OF COEF.
	--	t	--
X1	C2	--	--

R - SQUARED = %
R -   "   = %, ADJUSTED FOR DF

-- STOP   or repeat the procedure from -- READ ^C1, C2
              for another set of data.

@LOG

The coefficient t is the intersection point between the straight
line and the t-axis.

R - SQUARED should be close to 100 % (99,8=100 %).

7. INSTRUMENTAL

The following equipment is used:

- Coulometer
- pH meter with potential readings to nearest 0.1 mV.
- Titration cell
- pH electrode (Ross-electrode from Orion)
- Silver electrode (anode)
- Platinum net electrode (cathode)
- Argon gas
- Magnetic stirrer

Titration cell

The titration cell consists of a glass cell closed with a plastic lid provided with holes for electrodes and for introduction and efflux of argon. The cell also contains a magnetic stirrer to keep constant stirring during the titrations.

The cathode is a circular net electrode, consisting of a platinum net (approx. 2x4 cm) mounted on a platinum rod of 1 mm diameter.

The anode is a Metrohm silver electrode consisting of an 8 cm silver rod of 2 mm diameter.

The pH electrode is a Ross combined pH electrode, model 81-02, from Orion.

Coulometer

The coulometer is of the type Metrohm Herisau - E211 A.

There can be chosen between constant currents of 0.03, 0.1, 0.3, 1, 3, 10 and 20 mA.

The electrolysis current and the stop watch that indicates the electrolysis time can be started and stopped by push button EA 858.

Fig. 7.1
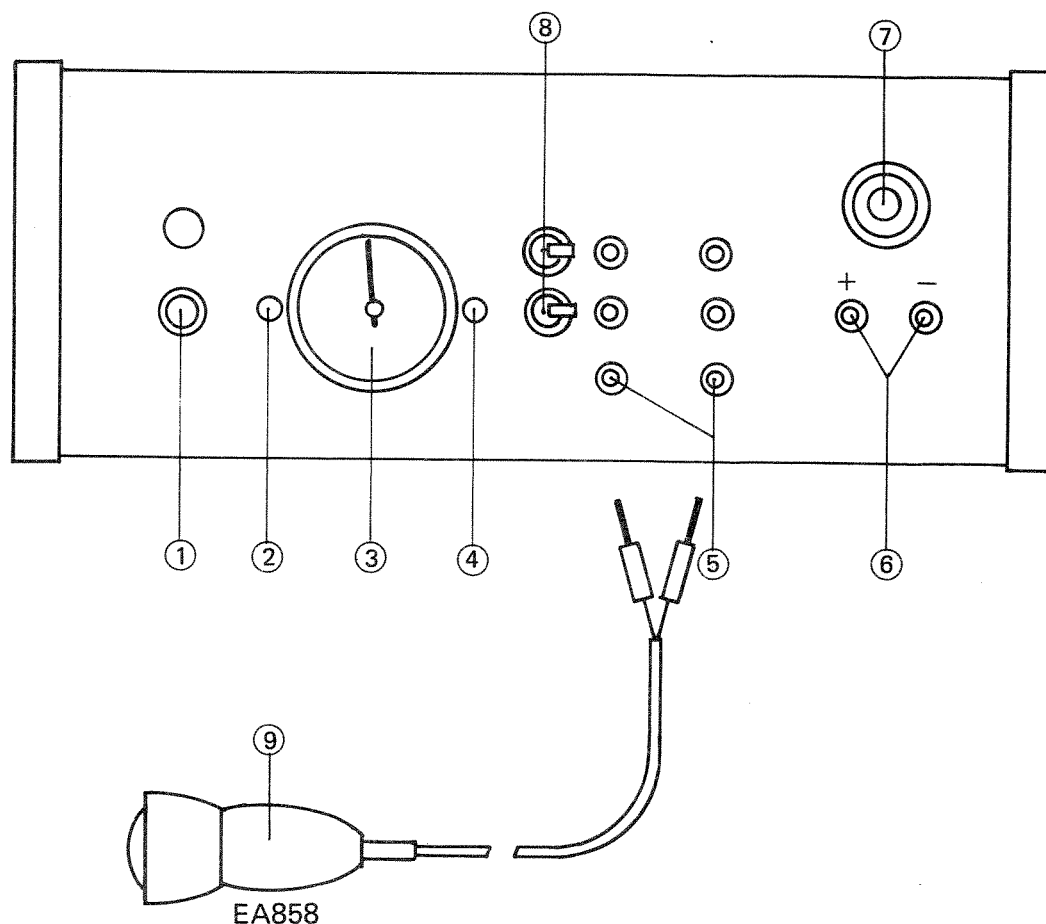
1. On/off switch.
2. Button for resetting the stop watch.
3. Stop watch, start and stop is controlled by push button EA 858.
4. Button for winding up the stop watch.
5. Connections for push button EA 858.
6. Electrode connections, silver electrode is conected to +, platinum electrode to -.
7. Current selector.
8. External standard switches. Both shall be in 0-position.
9. Push putton EA 858.

Appendix 2

Table 4   Chemical composition of small lakes in the Langtjern area 1986.

Locality	pH	Cond. mS/m	Ca mg/l	Mg mg/l	Na mg/l	K mg/l	Cl mg/l	SO$_4$ mg/l	NO$_3$ µg/l	Alk mmoles /l	TOC mg/l	Al µg/l	RAL µg/l	ILAL µg/l	LAL µg/l	Σcations µeq/l	Σanions µeq/l	Σcations -Σanions µeq/l
St. Y	4.60	1.96	0.86	0.21	0.50	0.18	0.4	2.4	19	-	14.2	229	192	156	36	137.1	62.7	74.4
St. X	4.96	1.86	1.55	0.28	0.52	0.12	0.5	2.8	40	-0.018	13.4	249	188	158	30	164.9	75.3	101.9
Lille Pipan	6.16	2.53	3.73	0.24	0.58	0.15	0.4	3.1	39	0.105	10.2	154	109	105	4	253.1	183.7	69.4
Store Pipan	5.19	1.76	1.82	0.18	0.58	0.11	0.5	2.8	26	-0.001	11.9	297	215	188	27	173.3	74.0	99.3
Store Røytjern	5.08	1.44	0.98	0.18	0.38	0.18	0.4	2.6	66	-0.005	6.57	104	75	52	23	104.8	70.2	34.6
Lille Røytjern	5.02	1.36	0.98	0.16	0.35	0.15	0.3	2.3	34	-0.012	8.03	97	77	55	22	101.6	58.8	42.8
Vestre Holmetjern	4.66	1.78	0.98	0.17	0.40	0.08	0.4	2.4	24	-	11.9	217	160	133	27	128.4	63.0	65.4
Holmetjern	4.89	1.63	1.05	0.20	0.46	0.09	0.4	2.8	38	-	9.40	220	166	120	46	128.6	72.3	56.3
Veiputt	5.05	1.53	0.97	0.19	0.52	0.14	0.4	3.6	17	-	5.91	247	189	92	97	126.6	87.5	39.1
Lauvskartjern	4.96	1.54	1.03	0.19	0.42	0.07	0.4	2.8	31	-	9.83	265	197	140	57	127.6	71.8	55.8
Bekaren	5.85	2.20	2.35	0.46	0.79	0.12	0.6	3.6	37	0.055	9.37	238	167	151	16	220.6	149.5	71.1
LAVN 1 m	5.00	1.55	1.23	0.18	0.49	0.05	0.4	2.7	15	-0.005	10,7	288	238	152	86	140.9	68.7	72.2
2 m	5.00	1.63	1.20	0.18	0.53	0.11	0.5	2.7	19	-	11.8	284	232	151	81	142.2	71.8	70.4
4 m	4.98	1.58	1.21	0.18	0.49	0.05	0.4	2.6	19	-	10.5	286	225	162	63	140.2	66.9	73.3
6 m	4.99	1.62	1.24	0.19	0.51	0.07	0.4	2.6	21	-	10.2	286	225	158	67	143.6	67.0	76.6
LAE 01	5.00	1.60	1.28	0.19	0.51	0.05	0.4	2.6	20	-	10.7	277	221	162	59	143.9	66.9	77.0
LAE 03	5.20	1.64	1.27	0.21	0.73	0.08	0.4	2.6	51	-	10.2	217	173	151	22	144.9	69.1	75.8

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