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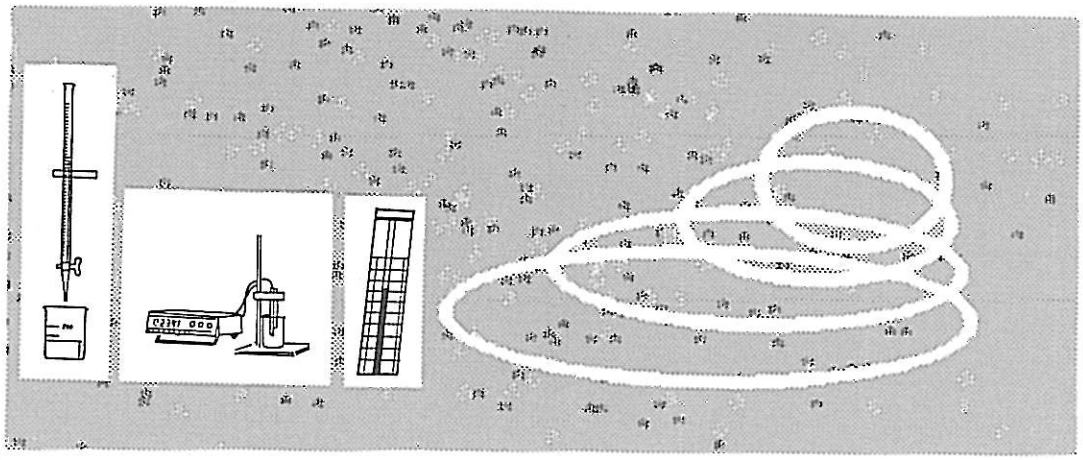
Norwegian Building Research Institute (NBI)

Hans Chr. Gran

Measurement of chlorides in concrete

An evaluation of three different analysis techniques



10 NBI Project Report 1992

NORDTEST Technical Report 188

BYGGFORSK
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CONTENT

SUMMARY

A round robin test has been done to evaluate three different chloride analysis techniques regarding accuracy, precision and reproducibility between laboratories. Five Nordic laboratories participated in the test. The measurements were performed on laboratory produced reference concrete containing three different concentrations of chloride, 0.025 %, 0.1 % and 0.5 % by weight of concrete.

The three analysis techniques were Quantab test (extraction with H_2O), chloride selective electrode against reference curve (extraction with HNO_3) and Volhard titration (extraction with HNO_3). A short description of each technique is given in the report.

Results from four additional techniques, Quantab test (extraction with HNO_3), Ion chromatography, RCT and Mohr titration are included, though these are not part of the round robin test evaluation as only two laboratories participated.

Satisfactory results were obtained by all techniques at 0.5 % chloride concentration, by Volhard and ion selective electrode at 0.1 % concentration, and only by ion selective electrode at 0.025 % concentration. Both Volhard titration and Quantab tests failed seriously at the lowest concentration, which is a reason for concern as the concentration lies between the chloride levels specified in the standard for ordinary reinforced and stressed concrete.

The effect of the experience of each laboratory on accuracy and precision was seen only for Volhard titration and the Quantab test.

MEASUREMENT OF CHLORIDES IN CONCRETE - AN EVALUATION OF THREE DIFFERENT ANALYSIS TECHNIQUES

1. INTRODUCTION

On a number of occasions, we have received reports that measurements of chloride content show considerable variations between different techniques as well as between laboratories. Variations of up to 100 % are not uncommon. This is in agreement with the experience that we have at the Norwegian Building Research Institute. Techniques where variations have been observed cover all the more frequently used tests such as titrations (Volhard, potentiometric), Quantab test, rapid chloride test (RCT) and analysis with chloride selective electrodes.

On this background, we have chosen to carry out a round robin test with the participation of five Nordic laboratories. The aim has been to do a more systematic investigation of the variations in measured chloride concentrations using laboratory made reference concrete samples with known chloride content.

The participating laboratories have been Forskningsinstituttet for Cement og Betong (SINTEF - FCB), Norway, Swedish National Testing Institute (SP), Sweden, Danish Technological Institute (TI), Denmark, Technical Research Center of Finland (VTT), Finland and Norwegian Building Research Institute (NBI), Norway, (project coordinator).

Each laboratory has been instructed to perform parallel analyses with three different measuring techniques. These techniques were: i) Quantab test (extraction with boiling destilled water), ii) measurement of electrode potential using chloride selective electrodes (extraction with HNO_3) and iii) Volhard titration (extraction with HNO_3).

2. THE SAMPLES

The concrete that was used in this project was supplied by the firm of Norwegian Concrete Technologies, Oslo. The concrete was available in the form of finely ground dust samples packed in 10 g sachets and was produced under continuous and strict control to serve as a reference material for chloride analysis.

The concretes were produced [1] as 25 l batches at NBI at the turn of the year 1989/90. The batches were sent to the Research Laboratories of Taywood Engineering, Southall, Middlesex, UK, where they were ground to dust. The dust was subsequently packed in 10 g sachets made from laminated foil of aluminium, plastic and paper. The packing process [2] was done automatically in a packing machine at Maskinpakking A/S, Slemmestad, Norway, under the control of representatives from NBI. Chloride concentrations used here were 0.025 %, 0.1 % and 0.5 % (all in % by weight related to the weight of the concrete). The water cement ratio was 0.45. As a cheque on the chloride content of the concrete samples, a statistically random selection of the sachets were sent back to Taywood Engineering for chloride analysis by means of potentiometric titration (auto titration apparatus). Taywood Engineering is accredited for chloride analysis on concrete. With this

technique, a check was done on 40 parallel samples from each concentration.The mean values and variations for each chloride concentration are given in table 1 below.

Table 1.

Chloride content in reference samples. Mean value and standard deviation. Measured at Taywood [3].

Mix concentration of chloride (% by weight of concrete)	Mean value X	Standard deviation S	Standard deviation in percent, S %
0.025	0.028	$1.6 \cdot 10^{-3}$	5.7
0.10	0.094	$1.7 \cdot 10^{-3}$	1.8
0.50	0.451	$3.9 \cdot 10^{-3}$	0.9

3. EXPERIMENTS

Each participating laboratory received 36 sachet samples for analysis. A set of 12 samples was used for each analysis technique. Each set of 12 samples then containing three chloride concentrations with four samples from each. The sachets were marked only with numbers from 1 to 36. No one but the project coordinators at NBI therefore had any knowledge of the exact chloride concentrations in each individual sample.

In the following a short description of each of the analysis techniques is given.

Determination of chloride content with chloride selective electrode

Test principle

The technique is based on the principle of comparing the measured potential between two electrodes in a solution of unknown Cl^- concentration to potentials measured in solutions of known concentrations plotted as a calibration curve [4]. For an example, see figure 1. To measure the Cl^- concentration, a chloride selective electrode is used in combination with a reference electrode. The chloride selective electrode is an all solid state electrode with a single crystal AgCl membrane. The electrode is equally sensitive to Ag^+ and Cl^- ions, but is unaffected by most other common ion species. The reference could be a mercurous sulfate electrode or a calomel electrode with a double salt bridge.

The electrodes are connected to a millivolt meter having an accuracy of at least 10^{-1} mV.

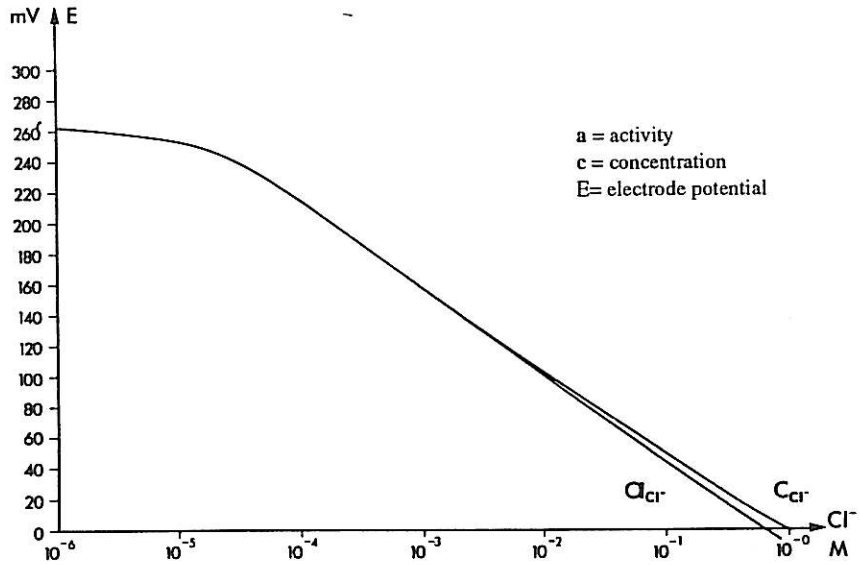


Fig. 1. An example of a calibration curve obtained using a chloride selective electrode [4].

Extraction procedure

The extraction procedure used is described in Norwegian Standard NS 3671, "Chloride content in Hardened Concrete".

However, there are two slight modifications.The first is using boiling water instead of merely hot, and second, specifying the time for the duration of each step in the procedure.

The exact procedure for extraction of chlorides is thus:

1. A beaker is weighed to an accuracy of $1 \cdot 10^{-4}$ g. About 5 grams of concrete dust is poured into the beaker and dried at 105 °C until a constant weight is reached. The sample is then cooled in a desiccator at amibient temperature and exact weight determined to an accuracy of $1 \cdot 10^{-4}$ g.

2. Deionized water (20 ml) is added and the mix is stirred for 2 minutes to separate the particles.

3. 10 ml of concentrated HNO_3 (65 % by weight) is added, followed by stirring for 15 minutes.

4. 50 ml boiling deionized water is then added, and the sample is cooled while stirring, until ambient temperature is reached (1 hour).

5. The sample is filtered and the filter washed with 10 % HNO_3. The filtrate is used for the chloride analysis.

Determination of chloride content with Volhard technique

Test principle

The Volhard technique is used for the indirect determination of chloride. A measured excess of standard silver nitrate solution is added to the chloride sample, and the excess silver ion is determined by back titration with a standard potassium thiocyanate solution (KSCN). The reaction is [5]:

$$Ag^{+} + SCN^{-} \Leftrightarrow Ag\,SCN(s)$$

Iron (III) ion serves as an indicator, imparting a red coloration to the solution at the first slight excess of thiocyanate (after Ag^{+} from $Ag\,NO_3$ is consumed):

$$Fe^{3+} + SCN^{-} \Leftrightarrow Fe\,(SCN)^{2+}$$

When the red coloration occurs, the chloride content can be determined from the amount of thiocyanate consumed. Acid solution prevents precipitation of iron (III) as the hydrated oxide. After addition of $Ag\,NO_3$, benzylalcohol is added to prevent the AgCl from going into solution as it is more soluble than Ag SCN.

Extraction procedure

The extraction procedure is the same as that used for analysis with a chloride selective electrode.

Determination of chloride content using the Quantab test

The Quantab product identification was Titrator No. 1175 with titration range 0.005 % to 0.1 % NaCl.

Test principle

QUANTAB Chloride Titrators consist of a thin, chemically inert plastic sheath. Laminated within the sheath is a strip impregnated with silver dichromate. When QUANTAB is placed in aqueous solutions, fluid will rise up the strip by capillary action. The reaction of silver dichromate with chloride ion produces a white column of silver chloride in the strip. When the strip is completely saturated, a moisture-sensitive signal string across the top of the titrator turns dark blue.

The length of the white column in the strip is proportional to the chloride ion concentration.

Extraction Procedure

In the round robin test the extraction procedure specified in the information summary by the manufacturer and supplied with the test strips was used. This procedure is as follows:

1. Weigh 10 grams of finely divided product and place into a suitable container. Add 90 ml. boiling water.

2. Stir mixture vigorously for 30 seconds, then wait one minute and stir another 30 seconds. Allow to cool to room temperature.

3. Fold filter paper circle in half twice, and open up into a cone-shaped cup. Place cup into sample to allow several ml of filtrate to enter the bottom of the cone.

4. Inset QUANTAB Chloride Titrator into the filtrate in the cone and follow the test procedure.

4. RESULTS

Tables showing results of all the individual measurements are given in appendix 1 at the end of the report.

Results from the different laboratories and techniques are shown in figures 2, 3 and 4. The chloride contents are plotted as histograms and are given as average values of the four parallels for each concentration (0.025 %, 0.10 % and 0.5 %). Standard deviations are indicated on top of each bar. The histograms give an illustration of the precision and accuracy obtained in the measurements. A dotted line across each figure indicates the nominal concentration. The real concentration as measured by Taywood Engineering is given in Table 1 on page 2.

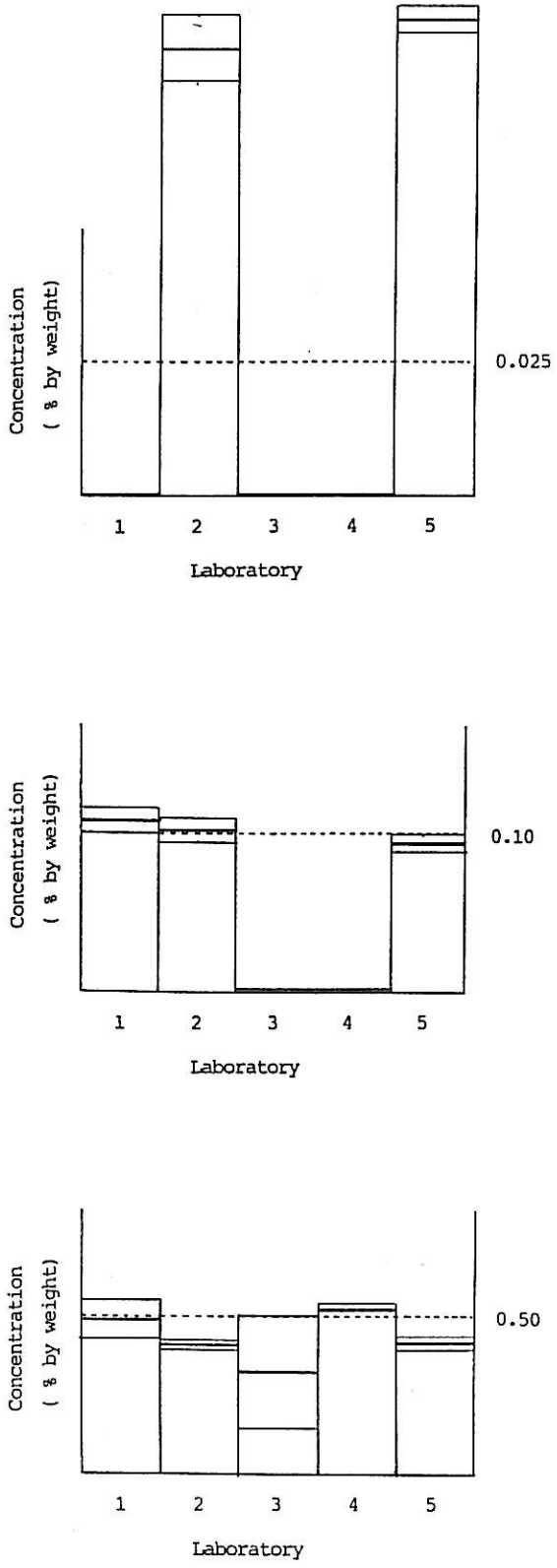
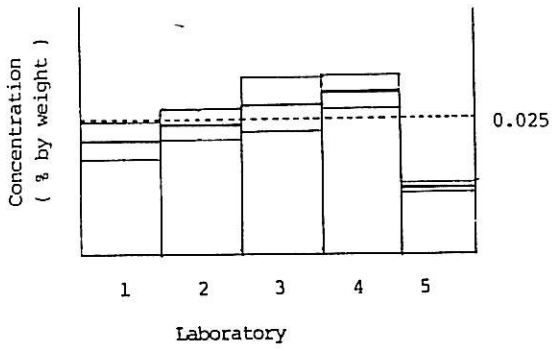
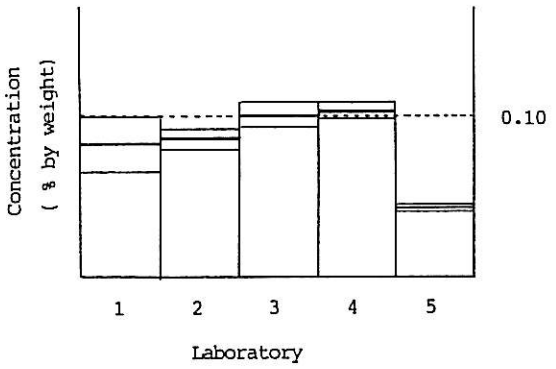


Fig. 2 Chloride content determined by Quantab test. The diagrams show the chloride concentrations and standard deviations measured at the different laboratories. The upper, middle and lower diagram represent chloride concentrations of 0.025 %, 0.10 % and 0.50 % (by weight of concrete) respectively.





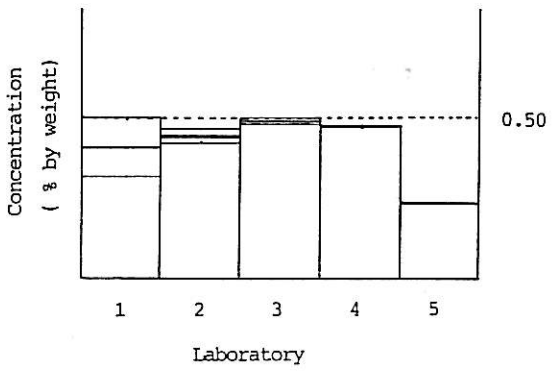
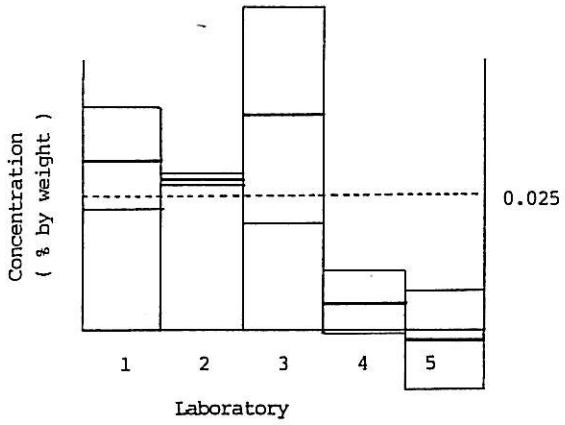
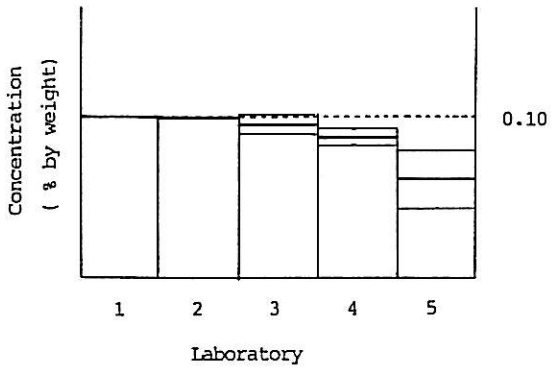


Fig. 3 Chloride content of concrete samples determined by chloride ion selective electrode and calibration curve. For explanation of histogram, see figure 2.





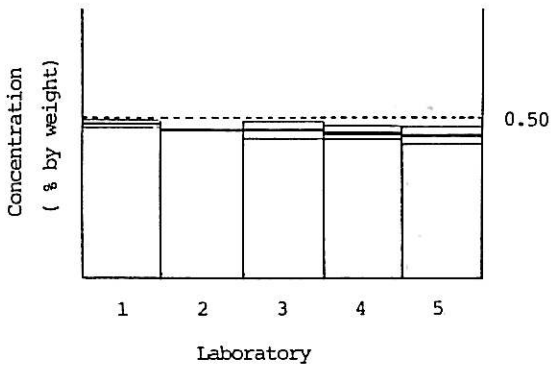


Fig. 4 Chloride content concrete samples determined by Volhard titration. For explanation of histogram, see figure 2.

Tables 2 to 4 show the variation of measured chloride content between laboratories. The presentation is meant to give a measure of the reproducibility, and thus the applicability, of each technique when used in different laboratories. For each technique and concentration, the mean value and standard deviation is calculated combining the measurements from all of the five participating laboratories.

Table 2

Quantab test. Mean value, x, standard deviation, s, and standard deviation in percent of mean value (s %) calculated taking the measurements from all five laboratories into account.

Concentration (% by weight)	x	s_d	s %
0.025	0.035	0.044	126.2
0.10	0.061	0.051	84.5
0.50	0.429	0.105	24.5

Table 3

Chloride selective electrode and reference curve. Parameters are as explained in table 2.

Concentration (% by weight)	x	s_d	s %
0.025	0.0230	0.00679	29.5
0.10	0.0825	0.0238	28.8
0.50	0.411	0.102	24.8

Table 4

Volhard technique. Parameters are as explained in table 2.

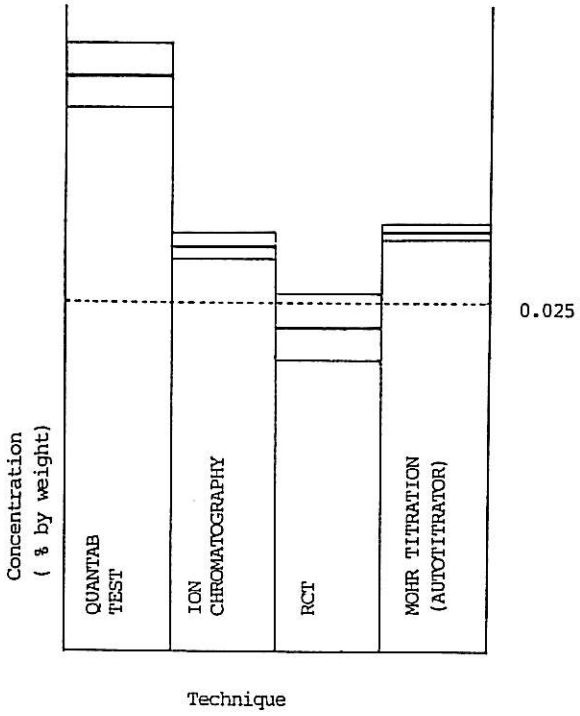
Concentration (% by weight)	x	s_d	s %
0.025	0.0206	0.0192	93.2
0.10	0.0886	0.0163	18.4
0.50	0.457	0.0192	4.2

5. ADDITIONAL TECHNIQUES

Two of the laboratories have for different reasons supplemented their analysis by including a few other techniques. Although lacking the additional information obtained through a round robin test, the results definitely are of interest to the subject dealt with in this report.

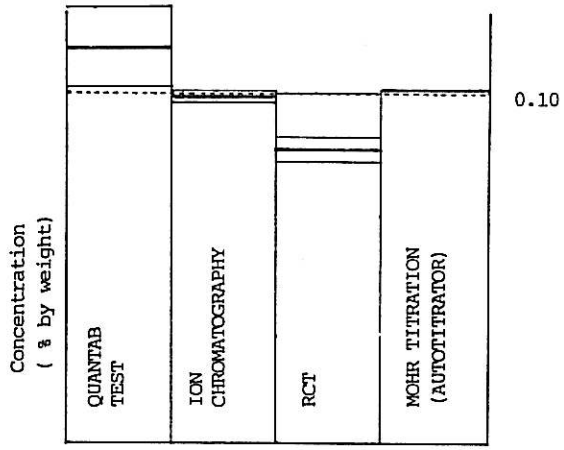
With the permission from the two laboratories, we therefore present the results from these separate experiments as well.

The mean values and standard deviations are illustrated as histograms in fig. 5 below. For detailed results the reader is referred to appendix 2 at the end of the report. The presentation of mean values and standard deviations is based on four parallels at each chloride concentration. An exception is laboratory 5 (RCT) which received 5 parallels of concentration 0.1 % (0.8 %) and 3 parallels of concentration 0.025 (0.2 %).

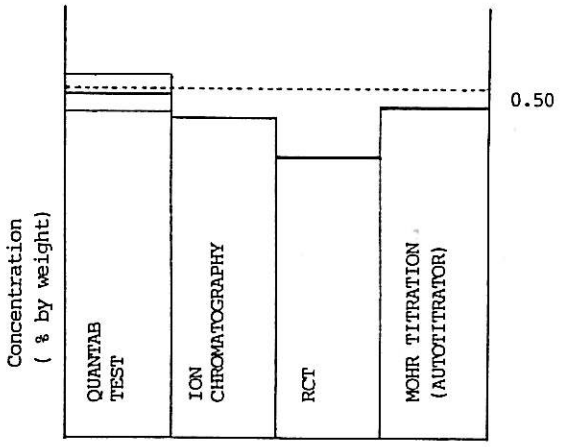


Concentration 0.025 %

Fig. 5 The histograms show the mean values and standard deviations of chloride measurements obtained using Quantab test extraction with HNO_3 (lab. 2), ionchromatography (lab 2), rapid chloride test (RCT) (lab 5), and Mohr titration using automatic titration equipment (lab. 5). Chloride concentrations are 0.025 % (above), 0.1 % and 0.5 % (overleaf).



Concentration 0.10 %



Concentration 0.50 %

6. DISCUSSION

Chloride contents - requirements in standard and probability of corrosion

The chloride concentrations used in this project are chosen to cover the range of relevant chloride contents in concrete. That is, it covers the range from negligible to certain danger of reinforcement corrosion. Chloride concentration in concrete is often given in percent by weight of the cement content. Using this unit, the correlation between chloride content and danger of steel corrosion illustrated in table 5 below is often referred to [6].

Table 5

The following is a much quoted table showing the relation between chloride content and corrosion risk to the reinforcement steel. Taken from Ø. Vennesland [6].

Chloride content % by weight of cement	Probability of steel corrosion
< 0.4	negligible
0.4 - 1.0	possible
1.0 - 2.0	likely
> 2.0	inevitable

The correlation is also reflected in the Norwegian Standard NS 3420 (1986) [7] by the requirement that chloride content in ordinary steel reinforced concrete may not exceed 0.4 % by weight of the amount of clinker, and in stressed concrete produced with sulphate resistant cement and/or exposed to particularly chloride rich environment, the chloride content may not exceed 0.1 % by weight of clinker. The cement content in the concrete samples used in this project was 300 kg/m^3. Conversion of the chloride concentrations to % by weight of cement thus gives:

Chloride content in:	
% w/w concrete	% w/w of cement
0.025	0.2
0.10	0.8
0.50	4.0

In the following, all concentrations are given in % by weight of concrete followed in parentheses by % by weight of clinker.

Experience of the laboratories

The amount of experience with the different techniques of analysis varies for each laboratory. As this supposedly is important when interpreting the results, this experience is taken into account. A survey of the amount of experience based on wether the technique is in use at the laboratory or not is given in table 6.

Table 6

The table shows a survey relating analysis technique and experience in each laboratory. Criterium for saying no in the survey is that the technique is not in use. Yes means that the laboratory has experience with the technique.

Laboratory	Technique		
	Quantab	Ion selective electrode	Volhard
1	Yes	No	Yes
2	Yes	Yes	Yes
3	No	No	Yes
4	No	No	Yes
5	No	No	No

Discussion of results of analysis techniques

The Quantab test

This technique shows by far the most varying results. It suffers from rather poor accuracy although precision is good. It should, however, be noted that in two of the laboratories, the Quantab test give zero results for chloride contents which were known to be 0.1 %. The relatively good precision obtained in each of the laboratories indicates that there is nothing wrong with the technique itself, as long as the same experimental procedure is maintained. The strips give reproducible results when put into the same pure chloride solution.The poor accuracy could mean, however, that the technique is sensitive to deviations in the extraction procedure. It should be remembered that the extraction procedure differs from the other techniques in using boiling water instead of HNO_3. Some laboratories use the Quantab test with HNO_3 extraction, according to BRE (Building Research Establishment) [8]. This reportedly gives better results. We decided to run this test according to the manufacturers instructions and as it is intended to be done in the field and not with the more complicated HNO_3 extraction procedure which preferably should be kept in laboratory.

Laboratory 4 also indicated difficulties in interpreting the colour change in the strips. Problems in making a correct reading of the strips may be an additional reason for the variation between laboratories.

A standard deviation between laboratories of 126.4 % and 84.5 % for concentrations 0.025 % (0.2 %) and 0.01 % (0.8 %) respectively is unacceptably high. The technique is thus unable to distinguish between the concentrations of 0 % and 0.085 % (0.7 %). As mentioned earlier, the Norwegian standard puts 0.1 % and 0.4 % by weight of clinker as the requirement for stressed reinforced concrete and ordinary reinforced concrete respectively. This turns out to be beyond the reach of the Quantab technique in the present work. The situation looks somewhat brighter at a concentration of 0.1 % by weight of concrete (0.8 % by weight of clinker), where three laboratories give correct results. However, that two out of five laboratories still measure zero concentration when the real concentration is 0.1 % (0.8 %) is a reason for concern.

The manufacturer specifies a range from 0.005 % to 0.1 % NaCl corresponding to 0.030 % (0.24 %) and 0.6 % (4.7 %) by weight of concrete. A concentration of 0.1 % w/w of cement as specified in the standard is thus in fact well below the lower limit of the system.

A correlation between experience and results can only be seen at 0.1 % (0.8 %) concentration, where two of the three unexperienced laboratories measured wrongly. The results at the lowest concentration varied too much to furnish information. Using extraction with boiling water, the Quantab test is the fastest of the three techniques.

The ion selective electrode

The ion selective electrode technique comes out best as regards reproducibility and accuracy between laboratories, although beaten in reproducibility by the Volhard technique at the highest concentration. The standard deviation within each laboratory is fairly good although the values of about 20 % measured in laboratory 1 pull the overall impression down.

Laboratory 5 measured only about half the correct concentration at all concentrations. This reflects the nature of this type of test, and thus the great care that must be taken when producing a calibration curve. Variations in both temperature and pH have an influence on the results. A displaced calibration curve normally reveals itself by a systematic error.

Results of the ion selective electrode technique do not show any significant correlation to the amount of experience of the laboratories.

The Volhard technique

Of the three techniques, the Volhard back titration is the only one covered by the standard Nordtest build NT 208, (also NS 3671, DS 423.28 and BS 1881, Part 6, Clause 9.1). At higher concentrations, the Volhard titration is the best in all aspects. At the lowest concentration of 0.025 % (0.2 %), the Volhard technique exhibits somewhat unexpectedly both rather poor accuracy and poor precision within each laboratory. This is also demonstrated by the high standard deviation of 93.2 % when all five laboratories are taken into account.

The results show the problems that can occur when working with back titration and small concentrations, as are fully demonstrated by the results from laboratories 4 and 5, the latter even producing a negative value for the chloride content.

The explanation is straightforward: According to the standard, 20 ml 0.1 N $AgNO_3$ is to be added to the chloride solution. All the Cl- will react with a part of the $AgNO_3$ to produce a precipitate of AgCl.

The chloride concentration is then determined indirectly by measuring the amount of unreacted $AgNO_3$. This is done by reacting it volume for volume with 0.1 NH_4SCN until a permanent red colour indicates that all $AgNO_3$ is consumed.

The difference between the added 20 ml of $AgNO_3$ and the required volume of NH_4SCN then gives the volume of $AgNO_3$ which reacted to precipitate the Cl^-, and consequently the Cl^- concentration in the sample.

This difference, which we may call D, is at the three different actual chloride concentrations which are used in this work as follows (the requirement of the standard, 0.1 % by weight of clinker is also included for comparison):

Chloride concentration, %	D (ml)
0.013 (0.1)	0.18
0.025 (0.2)	0.35
0.1 (0.8)	1.4
0.5 (4.0)	7.0

A 25 ml burette is specified in the standard both for addition of $AgNO_3$ and NH_4SCN. Normally a 25 ml burette gives a reading accuracy of 0.05 ml. This, combined with a colour change that is not quite discrete may result in the mentioned situation when the chloride concentration is 0.025 % (0.2 %), consequently making it difficult to distinguish between the 0.1 % and 0.4 % requirements in the standard. The solution to this is to change to more dilute solutions of $AgNO_3$ and NH_4SCN, for instance 0.01 N. This will have the effect of increasing the accuracy of reading the burette. The laboratory is of course then left with having to do two titrations to cover the whole range of possible concentrations.

The results indicate a correspondence between experience and both accuracy and precision. The correspondence is evident at concentrations of 0.025 % and 0.1 %, where laboratories 1 to 4 report experience.

The Volhard titration is the most tedious of the three techniques evaluated in this work.

Additional techniques

Quantab test, extraction with HNO_3

Compared to the extraction with boiling destilled water done at the same laboratory, the Quantab test using a HNO_3 extraction procedure does not result in a significant change in precision.

Accuracy is improved at chloride concentrations 0.5 % (4.0 %) and 0.025 % (0.2 %), although the latter still gives a result that is larger than the minimal concentration by a factor of 1.6. At chloride concentration 0.1 % (0.8 %), the accuracy is satisfactory, and does not differ much from that obtained using extraction with boiling H_2O.

Extraction with HNO_3 does not alter the fact, however, that the lowest concentration is close to the lower limit of the recommended concentration range.

Ion chromotography

This technique gives good accuracy and precision at all chloride concentrations. The results are also very close to the measurements obtained at the laboratory of Taywood Engineering.

RCT

The techniques gives good presision at all three concentrations. The accuracy, however, shows somewhat low values. This tendency becomes more evident with increasing chloride concentration.

Mohr titration (automatic titration apparatus)

The technique gives good accuracy and precision at all concentrations and may be compared to the measurements from ion chromotography done by laboratory 2.

7. CONCLUSION

All evaluated techniques show satisfactory results at the highest concentration of chloride, 0.5 % (4.0 %). At chloride concentration 0.1 % (0.8 %), the Volhard technique and analysis with ion selective electrode came out with acceptable results, while the Quantab test failed due to measured chloride concentrations of zero in two of the laboratories. At concentration 0.025 % (0.2 %), the Volhard analysis, done as specified in the standard, and the Quantab test failed seriously as regards both accuracy and precision. This is definitely a reason for concern since the lowest concentration is located between the values set as requirements in the standard.

As regards the Quantab test, the requirements stated in the standard are at the extreme lower limit of what one could expect to achieve with the test. This should be kept in mind when the test is used.

The problems found concerning the Volhard titration can partly be solved by using more dilute solutions of $AgNO_3$ and NH_4SCN. It should be considered to include this information in the standard.

Although the analysis using chloride selective electrodes showed the best all round results, measurements at one of the laboratories demonstrate that care should be taken when determining the calibration curve. At the same time one should take into consideration the importance of pH, temperature and interfering ions.

The importance of a clearly worded experimental procedure should be stressed. This is probably one of the causes where poor reproducibility between laboratories is observed.

Although only qualitative evaluation of the effect of experience on the results has been done, a correlation may be seen for both the Volhard titration and the Quantab test. The analysis using chloride selective electrodes did not show a similar correlation.

Finally, one should consider including reference samples of known concentration at certain intervals during analysis. This would have the effect of assisting laboratories to detect errors in procedure and faulty apparatus, as well as being of great help to laboratories that are unfamiliar with chloride analysis.

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