

Gran Method of Endpoint Determination in Chloride Analysis by Potentiometric Titration

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The Gran method of endpoint determination can replace the currently used first-derivative method in the potentiometric titration procedure for the analysis of chloride in hardened concrete. This modification improves the procedure by (a) circumventing the frequently encountered difficulty in endpoint determination that arises from unstable electrode potentials, (b) eliminating the need to spike solutions of low-chloride concrete samples with a known amount of chloride before titration, (c) enabling the titration to be performed more quickly, and (d) improving the overall precision and accuracy.

To repair the damage to bridge decks that results from corrosion of the reinforcing steel, it is necessary to locate the concrete showing the potential for inducing further corrosion as well as the material already exhibiting damage. The location of the potentially corrosive material requires analysis of the chloride (Cl^-) content of concrete samples from the bridge deck. The chemical procedure widely used for these analyses is based on the potentiometric titration technique developed by Berman (1). Briefly, the procedure has three parts:

1. Extraction of the soluble Cl^- from a powdered concrete sample by using 1:16 nitric acid and separation of the extract from the undissolved residue by filtration;
2. Potentiometric titration of the Cl^- with a standard silver nitrate (AgNO_3) solution in the presence of a Cl^- or a silver ion-specific electrode; and
3. Determination of the endpoint of the titration by using the first-derivative ($\Delta E/\Delta V$) method, followed by calculation of the Cl^- content.

A frequently encountered difficulty in this procedure involves the determination of the endpoint, particularly for samples that have relatively low Cl^- contents. Because the method is based on the occurrence of a maximum $\Delta E/\Delta V$ at the endpoint, its accuracy and precision are susceptible to the instability in the electrode potential that occurs in the vicinity of the endpoint.

This difficulty can be circumvented by using the Gran method for endpoint determination, which uses the comparatively more stable potential readings beyond the endpoint (2).

GRAN METHOD OF ENDPOINT DETERMINATION

In a dilute solution, the electrode potential is related to the Cl^- concentration by the simplified Nernst equation

$$E = E_0 - (2.3RT/F) \log C_a \quad (1)$$

where

- E = electrode potential,
- E_0 = constant determined by the normal and junction potentials,
- R = universal gas constant,
- T = temperature ($^\circ\text{K}$),
- F = Faraday constant, and

$C_a = \text{Cl}^-$ concentration.

Before the endpoint in a titration is reached, the Cl^- concentration in the sample solution is related to the amount of silver ion (Ag^+) added by

$$C_a = (C_a' V_a - C_t V_t) / (V_a + V_t) \quad (2)$$

where

- C_a' = initial concentration of Cl^- in the sample solution,
- C_t = concentration of Ag^+ in the titrant,
- V_a = initial volume of the sample solution, and
- V_t = volume of titrant added.

Substituting Equation 2 into Equation 1 gives

$$E = E_0 - (2.3RT/F) \log [(C_a' V_a - C_t V_t) / (V_a + V_t)] \quad (3)$$

which relates the electrode potential to the volume of titrant added and can be rearranged to give

$$(V_a + V_t) \times 10^{(E_0 - E) \times (F/2.3RT)} = C_a' V_a - C_t V_t \quad (4)$$

This indicates that a plot of $[(V_a + V_t) \times 10^{(E_0 - E) \times (F/2.3RT)}]$ versus V_t should give a straight line whose point of interception with the V_t -axis corresponds to the endpoint. This is so because at the endpoint $C_a = 0$, and therefore, from Equation 2, the left side of Equation 4 becomes zero. A similar analysis can be made after the endpoint is passed, when the continued addition of titrant increases the concentration of Ag^+ in the solution.

Although such linear plots have many advantages, some of which are illustrated later, the method has not become popular because the time required to calculate the complex term on the left side of Equation 4, which is needed for plotting, usually offsets the advantages. Recently, however, the need for this calculation has been obviated because volume-corrected graph paper for obtaining linear plots directly from the potential readings has become commercially available.

In applying the Gran method for determining the endpoint in the titration of concrete-sample solutions with AgNO_3 , we have chosen to use the potentials beyond the endpoint ($E > 300$ mV for our titration system) rather than the potentials before the endpoint, because the latter are complicated by the formation of Cl^- complexes that make a linear Gran plot nondefinitive.

ADVANTAGES OF USING GRAN METHOD

The unstable potential readings in the vicinity of the endpoint do not present any difficulty when the Gran method is used. Consider the actual potential readings observed during the titration of a concrete-sample solution (Table 1): The fluctuation in each potential reading becomes larger as the titration approaches the endpoint, which was at approximately 3.5 ml 0.01N AgNO_3 . With those

large fluctuations, it would be difficult to accurately determine the endpoint by the $\Delta E/\Delta V$ method. However, with the Gran method, the determination of the endpoint is relatively easy because it requires plotting only the few potential readings that are greater than 300 mV on Gran-plot paper and extrapolating the straight portion

Table 1. Electrode potentials observed in actual titration.

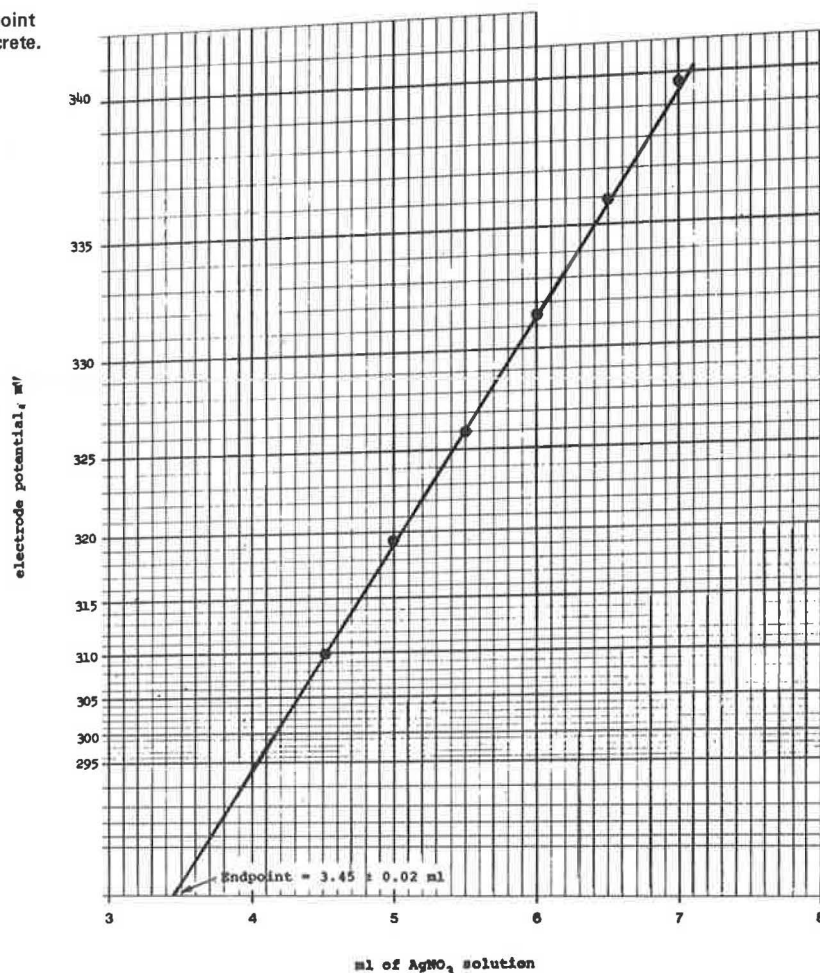
0.009 93N AgNO_3 (ml)	Potential (mV)	Range (mV)
0.00 \pm 0.01	219.1 to 219.2	0.1
0.50	222.2 to 222.3	0.1
1.00	225.7 to 225.8	0.1
1.50	229.8 to 229.9	0.1
2.00	235.2 to 235.4	0.2
2.50	242.4 to 242.6	0.2
3.00	253.8 to 254.4	0.6
3.10	257.1 to 257.7	0.6
3.20	260.9 to 261.5	0.6
3.30	265.1 to 265.5	0.4
3.40	269.8 to 270.6	0.8
3.50	273.5 to 274.3	0.8
3.60	278.3 to 279.2	0.9
3.70	283.2 to 283.8	0.6
3.80	287.5 to 288.1	0.6
3.90	291.5 to 292.1	0.6
4.00	295.5 to 296.1	0.6
4.10	299.0 to 299.4	0.4
4.20	302.1 to 302.5	0.4
4.50	309.9 to 310.1	0.2
5.00	319.2 to 319.3	0.1
5.50	325.9 to 326.0	0.1
6.00	331.4 to 331.5	0.1
6.50	335.8 to 335.9	0.1
7.00	339.5 to 339.6	0.1

until it intersects the V_t -axis as shown in Figure 1. In this titration, the endpoint was at 3.45 ± 0.02 ml.

Because the analyst needs only 3 or 4 points at most to obtain a definitive linear plot, the titration can be done more quickly, as shown by the improved procedure outlined in Figure 2, than when using the $\Delta E/\Delta V$ method. In using the latter method, for the region from approximately 0.5 ml before the endpoint to 0.5 ml beyond the endpoint, the analyst must observe the rate of change in the potential with every 0.1-ml increment of AgNO_3 .

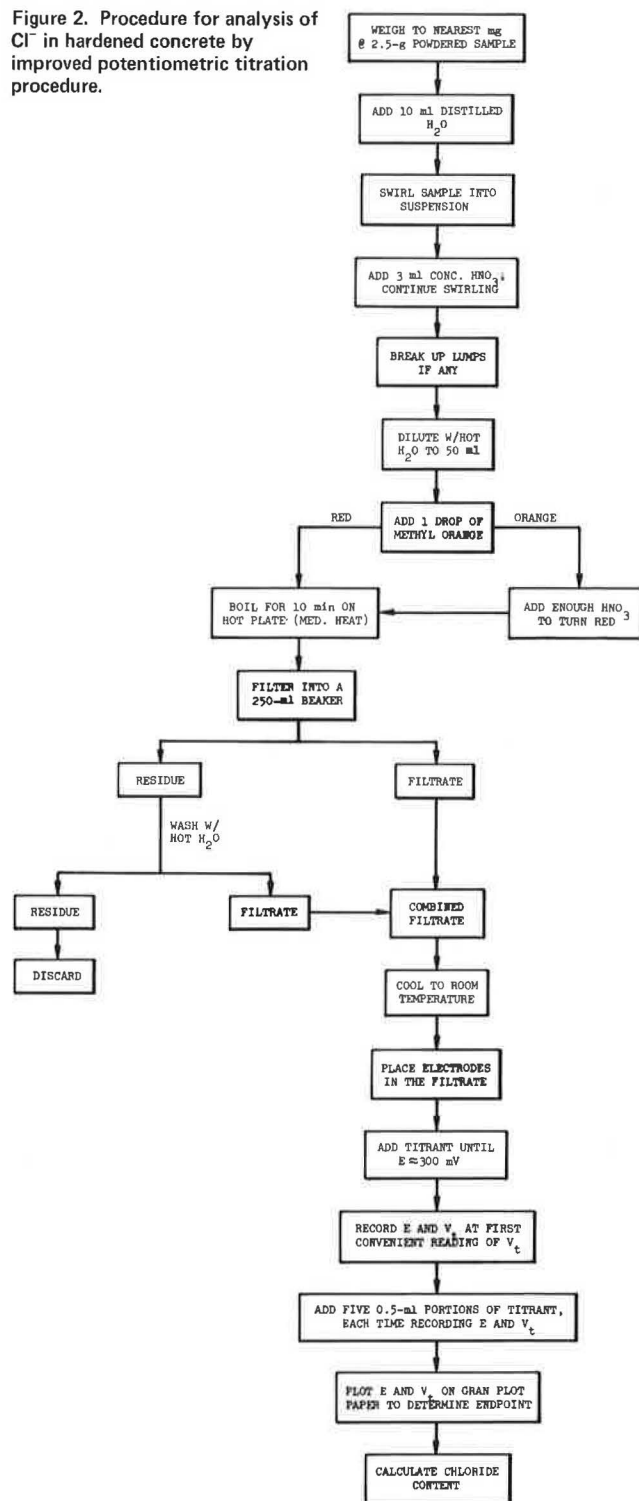
In Berman's original potentiometric titration procedure, ambiguities in determining the endpoint in the titration of samples with Cl^- contents lower than 0.01 percent were another problem. Figure 3 shows an example of an ambiguity that involved titration of a 100-ml aliquot containing 2.4090 g of a concrete sample whose Cl^- content was approximately 0.01 percent. As the figure shows, it is not clear where the endpoint is when the $\Delta E/\Delta V$ method is used. To eliminate such ambiguities, Berman has suggested that voltage readings of less than 65 mV below the endpoint when the electrodes are first immersed in a sample solution be taken as an indication that the sample has a low Cl^- content and that the analyst spike the solution with 1 or 2 ml 0.01N NaCl solution before proceeding with the titration (3). This spiking is supposed to shift the endpoint by 1 or 2 ml so that it is easier to determine. As shown in Figure 4, spiking another aliquot of the same sample with 2.00 ml 0.010 08N NaCl did provide improvement; however, the ambiguity in locating the endpoint was still not completely eliminated.

Figure 1. Use of Gran method to determine endpoint in potentiometric titration of acid extract of concrete.



In using the Gran method, the endpoint can be clearly determined with or without spiking, regardless of the Cl^- content of the sample. To illustrate this, the potentials from the titrations shown in Figures 3 and 4 were plotted on Gran-plot paper as shown in Figure 5. The resulting endpoints were 2.58 and 0.63 ml for the spiked and nonspiked solutions respectively. And subtraction of 1.95 ml 0.010 31 N AgNO_3 (the equivalence of the 2.00 ml 0.010 08N NaCl added) also gives 0.63 ml as the endpoint for the nonspiked solution.

Figure 2. Procedure for analysis of Cl^- in hardened concrete by improved potentiometric titration procedure.



The experiment was repeated with several concrete samples whose Cl^- contents ranged from 0.001 to 0.019 percent. The overall results are shown in Table 2 and indicate that the average absolute difference in the endpoints of the spiked and nonspiked solutions was approximately 0.02 ml. This is about the precision with which one can read the Gran-plot paper, which means that the differences are insignificant.

Figure 3. Titration of low- Cl^- concrete sample (without NaCl spike).

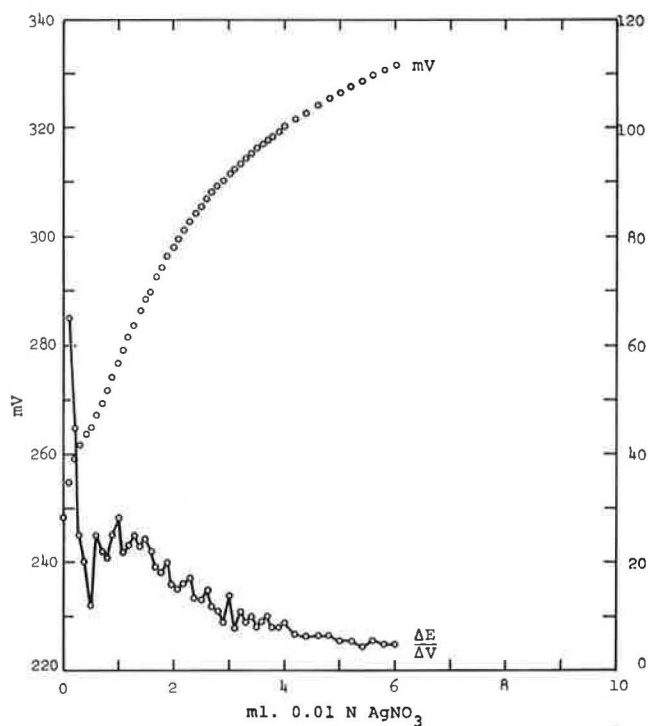


Figure 4. Titration of low- Cl^- concrete sample (spiked with 2.00 ml 0.1N NaCl).

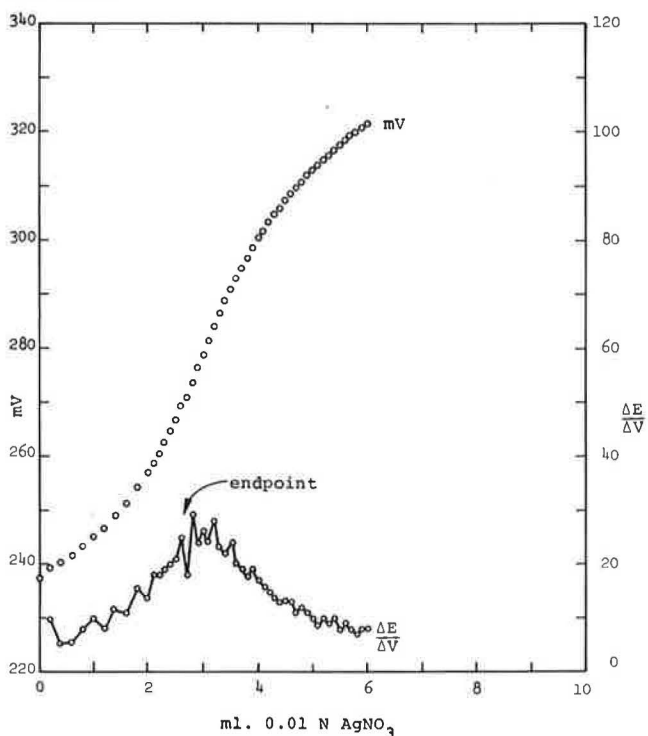


Figure 5. Gran plots of titrations shown in Figures 3 and 4.

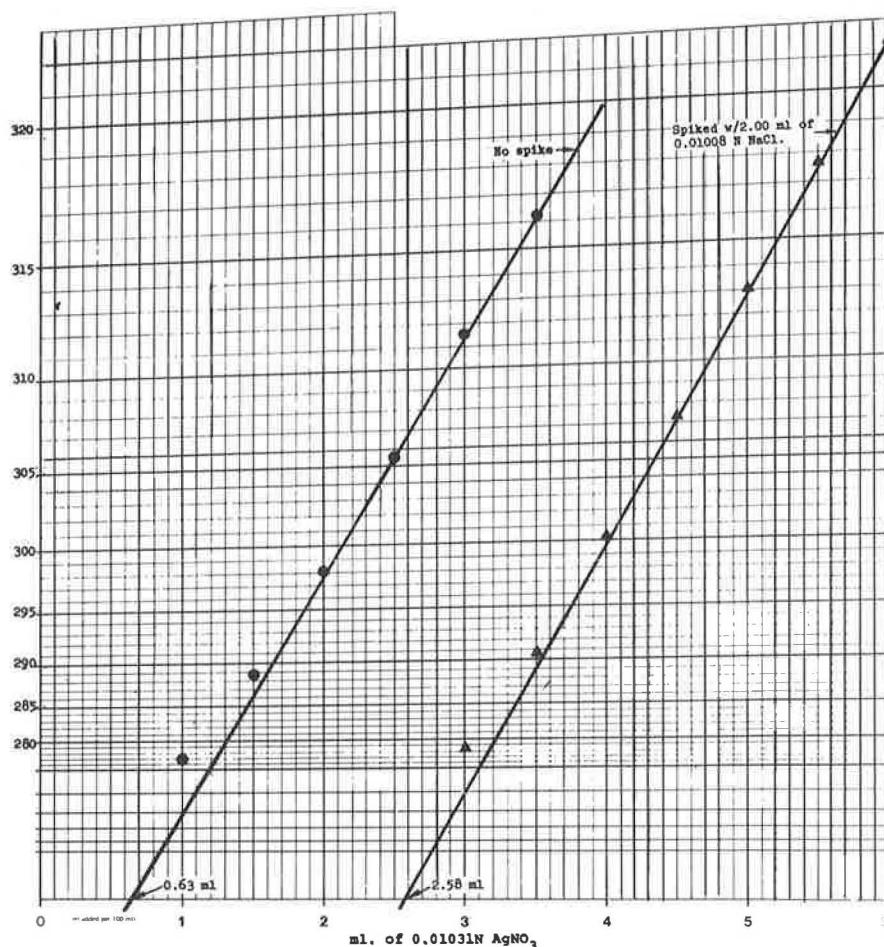


Table 2. Analysis of low-Cl⁻ concrete samples by using Gran method of potentiometric endpoint determination (with and without added NaCl).

Sample	Mass (g)	NaCl ^a Added (ml)	Total AgNO ₃ ^b Added (ml)	Net AgNO ₃ ^c Needed (ml)	Cl ⁻ (%)
L-1	2.4018	2.00	2.05	0.10	0.0015
		0	0.07	0.07	0.0011
L-3	2.4028	2.00	2.40	0.45	0.0068
		0	0.45	0.45	0.0068
W-3	2.4090	2.00	2.58	0.63	0.0095
		0	0.63	0.63	0.0095
W-4	2.3999	2.00	2.87	0.92	0.0140
		0	0.96	0.96	0.0146
W-5	2.4005	2.00	3.18	1.23	0.0187
		0	1.22	1.22	0.0186

^a 0.010 08 N.

^b 0.010 31 N.

^c Including adjustment for equivalency between NaCl and AgNO₃ solutions.

PRECISION AND ACCURACY

The replacement of the $\Delta E/\Delta V$ method by the Gran method should also improve the overall precision and accuracy of the potentiometric titration procedure. This agrees with the results of a theoretical study [Anfalt and Jagner (4)] that compared the various methods of endpoint determination.

Precision

As a test of the overall precision of the improved pro-

cedure using the Gran method, two concrete samples were divided into five portions each, and each portion was analyzed for Cl⁻. The results shown below showed an average standard deviation of 0.0005 percent Cl⁻, which is a large improvement over the value of 0.0026 percent given by Lankard and others (5).

Concrete Sample	Cl ⁻ Content	Concrete Sample	Cl ⁻ Content
1	Portion 1 0.0236	2	Portion 1 0.0439
	Portion 2 0.0244		Portion 2 0.0432
	Portion 3 0.0237		Portion 3 0.0439
	Portion 4 0.0232		Portion 4 0.0431
	Portion 5 0.0239		Portion 5 0.0444
Range	0.0012	Range	0.0013
Standard deviation	0.0004	Standard deviation	0.0005

This precision includes variations in the Cl⁻ contents of the individual portions, in the extraction and titration, and in the determination of the endpoint. The variation in the determination of the endpoint had a standard deviation of approximately 0.0003 percent Cl⁻, as determined by multiplicate titrations of aliquots from each of several extracts prepared from the same concrete samples.

Accuracy

Because of difficulty in preparing test specimens without any material loss during their mixing and curing, the accuracy of the original potentiometric titration pro-

Table 3. Cl^- analysis of prepared concrete specimens by potentiometric titration, atomic-absorption spectroscopy, and neutron-activation analysis.

Concrete Specimen	Cl^- Added (%)	Measured Cl^- Content (%)			Difference (% Cl^-)		
		PT ^a	AA ^b	NAA ^c	PT ^a	AA ^b	NAA ^c
S1	0.0100	0.0107	0.0078	0.0127	+0.0007	-0.0022	+0.0027
S2	0.0200	0.0206	0.0185	0.0216	+0.0006	-0.0015	+0.0016
S3	0.0300	0.0310	0.0278	0.0297	+0.0010	-0.0022	-0.0003
S4	0.0400	0.0393	0.0379	0.0368	-0.0007	-0.0021	-0.0032
C1	0.0061	0.0066	0.0058	0.0068	+0.0005	-0.0003	+0.0007
C2	0.0121	0.0118	0.0110	0.0117	-0.0003	-0.0011	-0.0004
C3	0.0182	0.0179	0.0159	0.0160	-0.0003	-0.0023	-0.0022
C4	0.0243	0.0243	0.0203	0.0202	0.0000	-0.0040	-0.0041
Avg absolute difference	—	—	—	—	0.0005	0.0020	0.0019

^aPT = potentiometric titration.

^bAA = atomic absorption spectroscopy.

^cNAA = neutron activation analysis.

Figure 6. Analysis of Cl^- in prepared concrete specimens by potentiometric titration procedure.

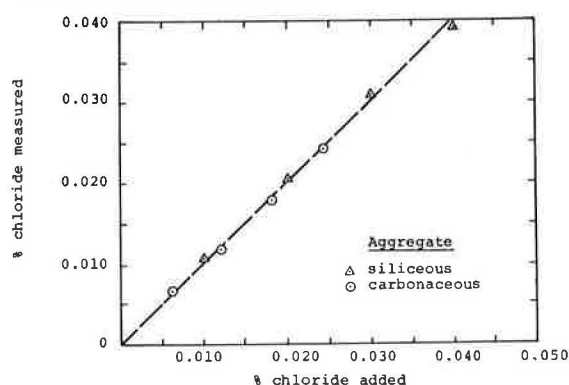
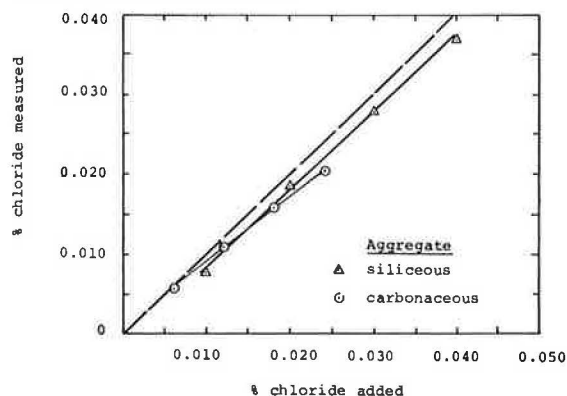
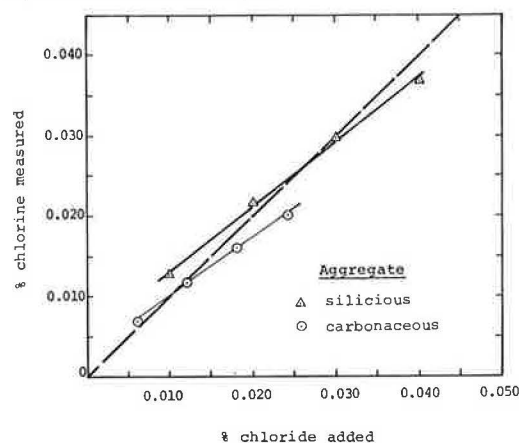


Figure 7. Analysis of Cl^- in prepared concrete specimens by atomic-absorption spectroscopy.



cedure was estimated by using samples having Cl^- contents considerably higher than the corrosion threshold value of 0.030 percent Cl^- suggested by Clear (6). However, because decisions about expensive repairs are made on the basis of Cl^- contents found to exceed the corrosion threshold, it is important to know the reliability of the analytical procedure used, particularly near the threshold level. To estimate the accuracy of the improved procedure at the threshold level, we compared its results to those of two procedures adapted from well-established analytical techniques (7)—atomic-absorption spectrometry and neutron-activation analysis. For the comparison, two series of test specimens—one using a siliceous aggregate and one using a carbonaceous aggregate—were prepared by adding Cl^- in increments. Then,

Figure 8. Analysis of Cl^- in prepared concrete specimens by neutron-activation analysis.



each of the specimens was analyzed by all three procedures.

The results, shown in Table 3, indicated that the smallest average absolute difference in Cl^- content was obtained by using the potentiometric titration procedure. These values are probably fairly good indications of the accuracy of each of the procedures.

In Figures 6, 7, and 8, the Cl^- contents measured by the three procedures and corrected for a blank determination are plotted separately against the Cl^- added to the specimens. Figure 6 shows that the results obtained by the potentiometric titration procedure clustered around the 45° dashed line, which indicates excellent agreement and no discernible aggregate effect.

The Cl^- content measured by the atomic-absorption procedure (Figure 7) averaged about 11 percent lower than the known Cl^- added. In addition, this procedure apparently was affected by the nature of the aggregate in the test specimens, as indicated by the existence of two lines. In the neutron-activation procedure (Figure 8), the aggregate effect appeared to be more pronounced than in the atomic absorption procedure, and this procedure showed positive differences with samples having relatively low known- Cl^- contents and negative differences with those having relatively high Cl^- contents.

CONCLUSIONS

1. The use of the Gran method of endpoint determination eliminates the difficulty that unstable potential readings cause in the $\Delta E/\Delta V$ method.
2. The use of the Gran method eliminates the need

to spike solutions of concrete samples having low Cl^- contents with a known amount of Cl^- before titration to facilitate endpoint determination.

3. The use of the Gran method improved the precision of the potentiometric titration procedure.

4. The average absolute difference of 0.0005 percent Cl^- between measured Cl^- and known added Cl^- contents, as determined by analyzing several test specimens, is probably a good indication of the accuracy of this improved potentiometric titration procedure.

5. Among the procedures tested, the improved potentiometric titration procedure showed the best agreement among the test specimens. In addition, this procedure showed no discernible effects of the particular siliceous and carbonaceous aggregates used to prepare the specimens.

ACKNOWLEDGMENTS

The work described in this paper was supported by Highway Planning and Research funds administered through the Federal Highway Administration. All opinions and conclusions expressed are ours and do not necessarily reflect the view or policy of the Federal Highway Administration or the Virginia Highway and Transportation Research Council.

REFERENCES

1. H. A. Berman. Determination of Chloride in Hardened Portland-Cement Paste, Mortar, and

Concrete. *Journal of Materials*, Vol. 7, 1972, p. 330.

2. G. Gran. Determination of the Equivalence Point in Potentiometric Titration, Part 2. *The Analyst*, Vol. 77, No. 11, 1952, p. 661.
3. H. A. Berman. Determination of Low Levels of Chloride in Hardened Portland-Cement Paste, Mortar, and Concrete. *Journal of Testing and Evaluation*, Vol. 3, No. 3, 1975, p. 208.
4. T. Anfalt and D. Jagner. The Precision and Accuracy of Some Current Methods for Potentiometric Endpoint Determination With Reference to a Computer-Calculated Titration Curve. *Analytica Chimica Acta*, Vol. 57, 1971, pp. 165-176.
5. D. R. Lankard and others. Neutralization of Chlorides in Concrete. Battelle Memorial Institute; Federal Highway Administration, First Quarterly Rept., Nov. 1973.
6. K. C. Clear. Evaluation of Portland-Cement Concrete for Permanent Bridge-Deck Repair. Federal Highway Administration, Interim Rept. FHWA-RD-74-5, Feb. 1974.
7. G. G. Clemencia, J. W. Reynolds, and R. McCormick. Comparative Study of Procedures for the Analysis of Chloride in Hardened Concrete. Virginia Highway and Transportation Research Council, Rept. VHTRC 77-R7, July 1976.

Publication of this paper sponsored by Committee on Performance of Concrete—Physical Aspects.

Comparison of Performance of Concrete Bridge Decks in British Columbia

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The bridges of the freeways south and east of Vancouver, British Columbia, were chosen as a sample of concrete bridge decks in the area. They are of similar ages and quality of supply of ready-mixed concrete and subject to the same weather, salting, and traffic conditions. They have the following types of decks: monolithic, monolithic recapped, two layer on precast box beams, and two layer on cast-in-place concrete; the two-layer decks used either cement grout or two-part epoxy as bonding agents. The use of site-mixed versus plant-mixed concrete is related to the performance of the bridge decks. Six observations are made why two-layer decks are more satisfactory than monolithic decks, and 16 recommendations for construction of two-layer decks are given. It is concluded that (a) two-layer decks are more durable than monolithic concrete decks and guarantee a minimum coverage of the steel, (b) the placement of the overlay requires rigid quality control of the site-mixed concrete, and (c) application of the two-part epoxy bonding agent requires constant technical attention.

There are more than 2600 bridge and overpass decks in British Columbia, of which 650 are exposed concrete. Of the latter, 570 are monolithic and 80 are of two-layer deck construction. Of the monolithic concrete decks, 140 have concrete resurfacing, 30 are in immediate

need of resurfacing, and a further 100 will need resurfacing in the next 3 or 4 years. Some of the older bridges that are still in use were built before 1920, and some of the newer bridges have been resurfaced with concrete just a few years after being opened to traffic.

The weather conditions cover a freezing-index range of from 100 to 500 degree days (1), and the traffic volumes vary from very light to 20 000 vehicles/lane/d. The concrete aggregate used in British Columbia varies from a granular material taken from a river bank to a high-quality aggregate produced to size and standard in modern plants. The concrete quality is variable and depends on the location of the bridge site and the plant and expertise available. The types of concrete deck used are (a) 20 700-kPa (3000-lbf/in²) monolithic, (b) resurfaced monolithic, (c) two layer with precast box beams as the structural deck, and (d) two layer with 20 700-kPa concrete as the structural deck, both with a concrete running surface. Either cement grout or two-part epoxy is used to bond the overlays to the structural decks.