

COMPARATIVE STUDY OF PROCEDURES FOR THE ANALYSIS
OF CHLORIDE IN HARDENED CONCRETE

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Virginia Highway & Transportation Research Council
(A Cooperative Organization Sponsored Jointly by the Virginia
Department of Highways & Transportation and
the University of Virginia)

In Cooperation with the U. S. Department of Transportation
Federal Highway Administration

Charlottesville, Virginia

July 1976
VHTRC 77-R7

1212

ABSTRACT

In the widely used potentiometric titration procedure for the analysis of chloride in powdered hardened concrete samples, difficulties have often been encountered when determining the endpoint. These difficulties have been eliminated through the use of the Gran method of endpoint determination, which also simplifies the titrations and improves the overall precision of the procedure.

Using test specimens, the accuracy of this improved potentiometric titration procedure was evaluated by comparison with the atomic absorption and neutron activation procedures developed for the same analysis. The comparison indicated that the improved potentiometric titration procedure is the simplest and most economical of the three, and possibly is the most accurate.

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INTRODUCTION

Bridge deck concrete contaminated with sufficient amounts of chloride to induce corrosion of the reinforcing steel does not always exhibit symptoms of active corrosion, because ingredients such as moisture and oxygen that are also prerequisite to the corrosion process are not present. However, such contaminated concrete is potentially corrosive as indicated by the common occurrence of previously passive but contaminated concrete deteriorating around a patched area. Therefore, for the permanent repair of bridge decks, it is necessary to locate and remove all potentially corrosive concrete, in addition to the concrete exhibiting active corrosion, to replace these materials with new concrete, and to prevent future applications of deicing salts from reaching the reinforcing steel.⁽¹⁾

The location of potentially corrosive concrete requires a chloride analysis of concrete samples taken from the bridge deck being considered for permanent repair. The chemical procedure widely used for the chloride analysis of concrete was developed by Berman⁽²⁾ and is an adaptation of the potentiometric titration technique. The chloride is extracted from a concrete sample using nitric acid and then titrated with a standardized silver nitrate solution, using a chloride ion-specific electrode to aid the equivalence point detection.

The precision of this potentiometric titration procedure had been evaluated mainly with concrete samples containing chloride contents considerably higher than the corrosion threshold value of approximately 0.030% Cl^- suggested by Clear⁽¹⁾, and its accuracy had only been estimated. Since decisions on expensive

repairs are made on the basis of determined chloride contents exceeding the corrosion threshold level, it is important to know the reliability of the analytical procedure used, particularly near the corrosion threshold. Beside this question on accuracy, the authors as well as others have at times experienced difficulty in pinpointing the equivalence point of the titration, especially for samples with low chloride levels or levels near the corrosion threshold. The authors also believe that a silver ion-specific electrode can be used in the titration to provide better results than are obtainable with a chloride ion electrode.

The well established techniques of atomic absorption spectrometry and neutron activation analysis can be similarly adapted for chloride analysis of concrete samples. The authors believed that methods based on these techniques could be developed to provide, if not a better procedure for the chloride analysis of concrete, at least some means for estimating the accuracy of the potentiometric titration procedure.

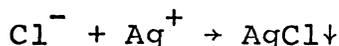
In view of the above, an investigation at relatively low chloride levels ($<0.05\%$) was conducted by the authors. This report describes: (1) the use of the Gran method of endpoint determination in treating titration data to successfully avoid the aforementioned difficulty of pinpointing the equivalence point of a titration; (2) the comparison between silver ion-specific and chloride ion-specific electrodes in the titration of digested concrete samples; (3) the development of two other procedures for chloride analysis of concrete samples that involved adaptations of atomic absorption spectrometry and neutron activation analysis; and (4) evaluation of the potentiometric titration procedure, as improved by the authors, and the authors' procedures with prepared concrete samples containing chloride contents lower than 0.05% .

The term "chloride" is used in this report to identify the acid-soluble chemical form of chlorine atoms which contributes to corrosion of reinforcing steels in concrete, while the term "chlorine" identifies all the chlorine atoms that may be present in various chemical forms, soluble or insoluble, in concrete.

POTENTIOMETRIC TITRATION PROCEDURE

As mentioned earlier, the potentiometric titration procedure is widely used to determine the chloride content of concrete samples. In this procedure, a powdered concrete sample is digested

with a 1:16 HNO₃ solution to extract the chloride. The chloride is then titrated with a standardized AgNO₃ solution to form precipitate of AgCl. This chemical reaction is represented simply as



By measuring the electrical potential between a chloride ion-specific electrode and a reference electrode as the titration progresses, the equivalence point can be determined and, subsequently, the chloride content can be calculated.

In the following sections, some results obtained from investigation of different aspects of this procedure of chloride analysis are presented.

Advantages of Using the Gran Method in Endpoint Determination

The equivalence point in a titration, commonly referred to as the endpoint, is the point of inflection of a curve (Figure 1) obtained by plotting the electrode potential, E , against the volume, V , of AgNO₃ solution added. Berman suggested that this point may usually be estimated accurately without plotting the curve, but only by finding the midpoint of the increment which produces the largest change in potential per unit volume of AgNO₃ solution added. This approach for the potentiometric endpoint determination, called the first derivative, or $\Delta E/\Delta V$ method, is based on the fact that when the sigmoid curve is differentiated with respect to volume, the endpoint corresponds to the volume of AgNO₃ added that yields the maximum value of $\Delta E/\Delta V$.

In the titration of digested concrete samples, particularly those with low chloride contents, the electrode potentials are often unstable (a range of 1 mV is not uncommon for a reading) around the endpoint. Since the successful use of the $\Delta E/\Delta V$ method relies on accurate potential readings in the vicinity of the endpoint, these unstable potential readings cause difficulty in the endpoint determination, which in turn leads to uncertainty in the determined chloride content.

It is suspected by the authors that the fluctuating potentials in the vicinity of the endpoint arise because the level of Cl⁻ being sensed has been lowered, and the solubility of the AgCl precipitate formed becomes significant enough to slow the equilibrium between Cl⁻ from the sample and Ag⁺ from the titrant. In addition, a simple calculation would indicate that even at

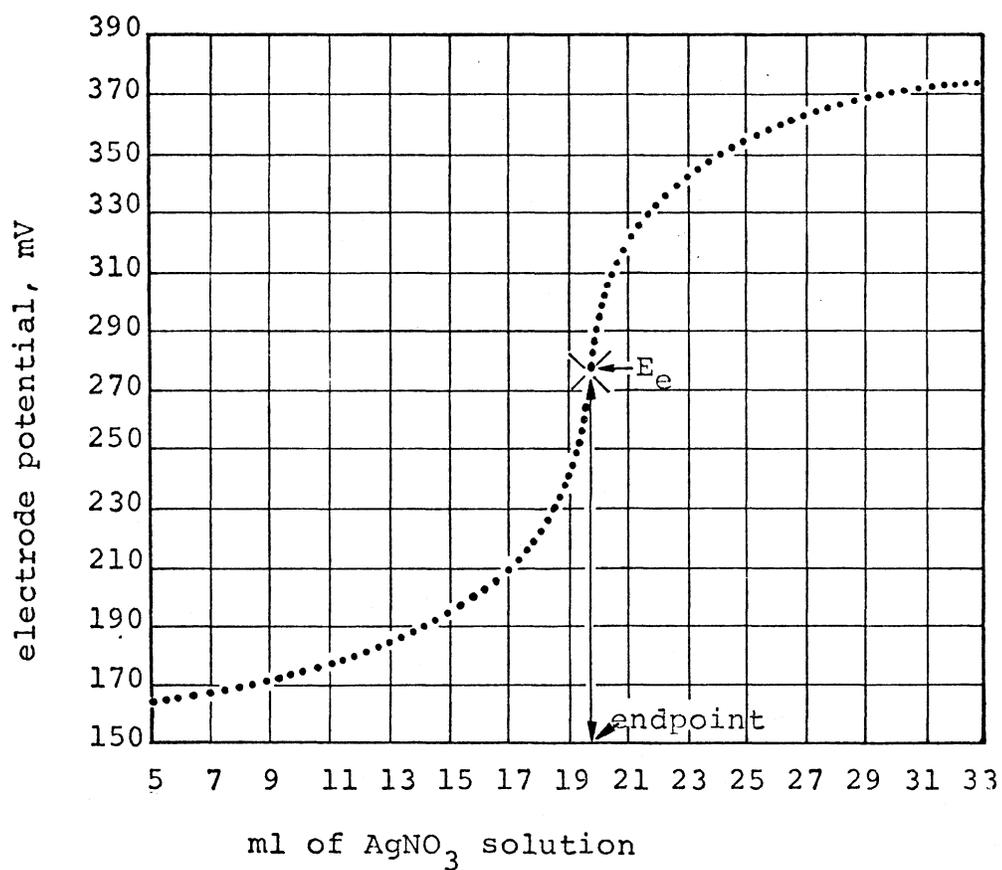


Figure 1. A potentiometric titration curve plotted as potential versus volume of AgNO₃ solution added.

approximately 0.70 ml of 0.01N AgNO₃ solution before the endpoint, the Cl⁻ left in the sample solution is already below the recommended lower working limit of commercial chloride ion-specific electrodes.

The authors believe that this difficulty in endpoint determination can be avoided if the Gran method, which uses the comparatively more stable potential readings past the endpoint, is used.⁽³⁾ (A brief discussion of the Gran method for endpoint determination is given in Appendix A). To illustrate this point, consider the potential readings observed in an actual titration of a digested concrete sample shown in Table 1. Notice that the fluctuation in potential for each reading became larger as the titration approached the endpoint, which was approximately 3.5 ml titrant. With these large fluctuations, not to mention drift, in potential, it would be extremely difficult to determine the endpoint by the $\Delta E/\Delta V$ method. However, with the Gran method, which uses the relatively more stable potential readings (>300 mV) considerably past the endpoint, it is relatively easy to determine the endpoint as shown in Figure 2. In this titration, the endpoint was 3.45 ± 0.02 ml.

Beside making the endpoint determination easier, the use of the Gran method has the additional advantage explained in the following discussion.

Berman suggested that if the voltage read when the electrodes are first immersed in a digested concrete solution is less than 65 mV below the equivalence point (this criterion may vary with individual titration systems), the indication is that the sample is of low chloride content. He indicated that in such a case the analyst should spike the solution with 1 or 2 ml of 0.01N NaCl solution before proceeding with titration to avoid extreme difficulty in determining the endpoint.⁽⁴⁾ Since the Gran method uses potential readings past the endpoint, with this method it is not necessary to spike the sample solution as suggested by Berman, regardless of its chloride level.

An experiment was performed to illustrate this additional benefit provided by the Gran method. A sufficient amount of a low chloride concrete was digested, then separate aliquots of the sample solution were titrated with and without the addition of a known amount of NaCl. After each titration, the endpoint was determined by the Gran method. This experiment was repeated with several concrete samples whose chloride contents ranged from 0.001% to 0.019%. The results, shown in Table 2, indicate that the largest observed difference between titrations with and without the addition of the NaCl solution was 0.0006% Cl⁻. As is shown later, this difference is approximately the precision attainable

Table 1
Electrode Potentials Observed in an Actual Titration

ml of titrant*	potential (mV)	range (mV)
0.00 ± 0.01	219.1 - 219.2	.1
0.50	222.2 - 222.3	.1
1.00	225.7 - 225.8	.1
1.50	229.8 - 229.9	.1
2.00	235.2 - 235.4	.2
2.50	242.4 - 242.6	.2
3.00	253.8 - 254.4	.6
3.10	257.1 - 257.7	.6
3.20	260.9 - 261.5	.6
3.30	265.1 - 265.5	.4
3.40	269.8 - 270.6	.8
3.50	273.5 - 274.3	.8
3.60	278.3 - 279.2	.9
3.70	283.2 - 283.8	.6
3.80	287.5 - 288.1	.6
3.90	291.5 - 292.1	.6
4.00	295.5 - 296.1	.6
4.10	299.0 - 299.4	.4
4.20	302.1 - 302.5	.4
4.50	309.9 - 310.1	.2
5.00	319.2 - 319.3	.1
5.50	325.9 - 326.0	.1
6.00	331.4 - 331.5	.1
6.50	335.8 - 335.9	.1
7.00	339.5 - 339.6	.1

*0.00993N AgNO₃ solution.

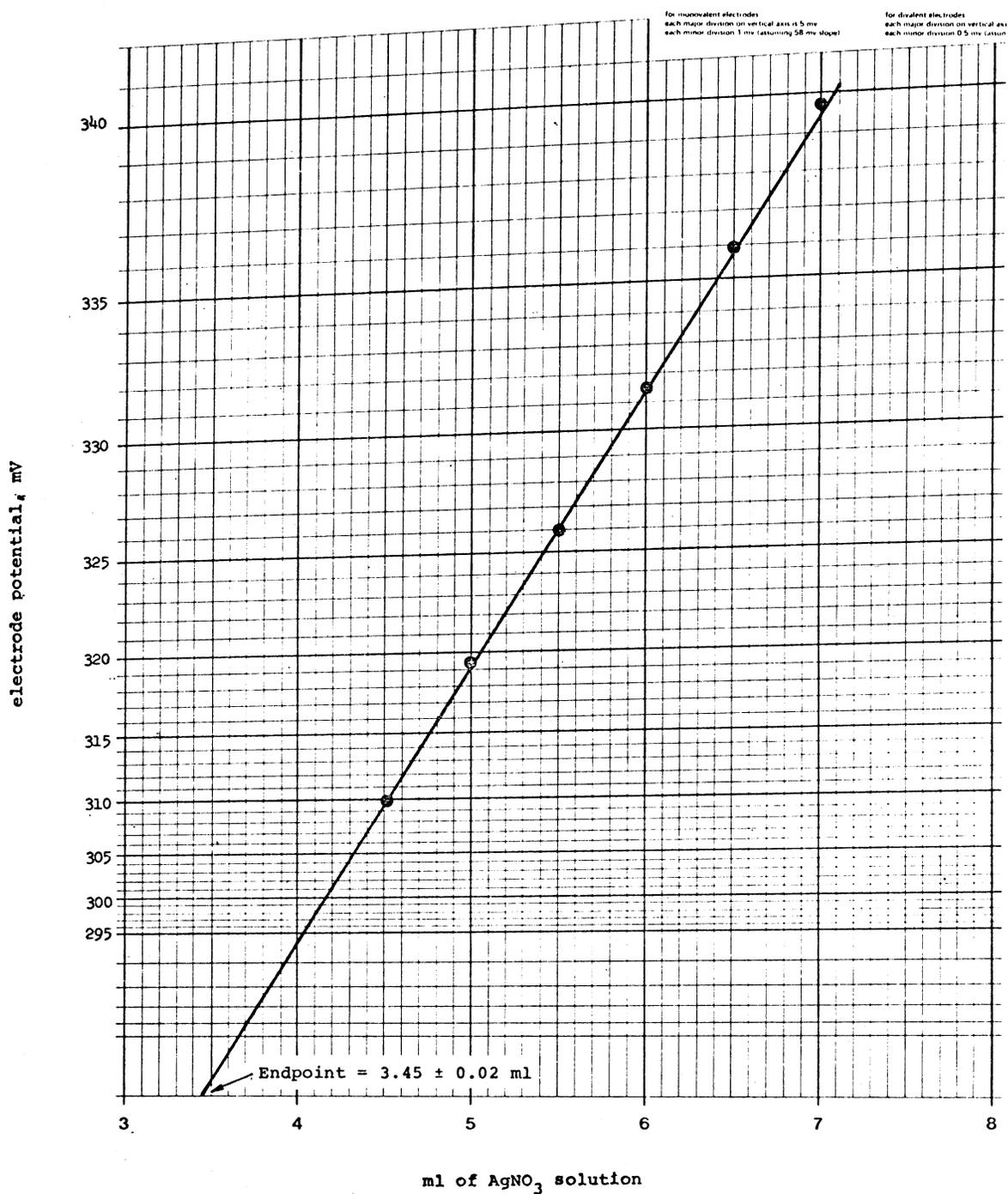


Figure 2. Use of Gran method to determine endpoint in the potentiometric titration of an acid extract of concrete.

Table 2

Analyses of Low Chloride Concrete Samples Employing Gran Method of Potentiometric
Endpoint Determination, With and Without Addition of NaCl Solution

Sample	ml NaCl* added	Total ml of AgNO ₃ ** added	Net ml of AgNO ₃ *** needed	% Cl ⁻	Difference, % Cl ⁻
L-1 (2.4018 gm)	2.00	2.05	0.10	0.0015	0.0004
	0	0.07	0.07	0.0011	
L-3 (2.4028 gm)	2.00	2.40	0.45	0.0068	0.0000
	0	0.45	0.45	0.0068	
W-3 (2.4090 gm)	2.00	2.58	0.63	0.0095	0.0000
	0	0.63	0.63	0.0095	
W-4 (2.3999 gm)	2.00	2.87	0.92	0.0140	-0.0006
	0	0.96	0.96	0.0146	
W-5 (2.4005 gm)	2.00	3.18	1.23	0.0187	0.0001
	0	1.22	1.22	0.0186	

* 0.01008 N NaCl.

** 0.01031 N AgNO₃*** Including adjustment for equivalency between the NaCl and AgNO₃ solutions

by incorporating the Gran method in the potentiometric titration of concrete for chloride analysis, and is therefore insignificant. In terms of the net milliliters of AgNO_3 needed, (Column 4 in Table 2) the average difference is 0.02 ml, which is the precision with which one can read the volumetric scale in the Gran plot paper.

Finally, it is worthwhile to mention that with the Gran method the titration can be performed faster than when using the $\Delta E/\Delta V$ method. With the latter method, the analyst has to observe the rate of change in potential reading with every 0.1 - ml increment of AgNO_3 added at the vicinity of the endpoint, while with the Gran method it is necessary to obtain only a few potential readings, in 0.5-ml increments, past the endpoint to define the straight line needed for extrapolation to the endpoint (see Figure 2).

Comparison Between Chloride and Silver Ion-Specific Electrodes

Until now the chloride analysis of concrete samples by potentiometric titration reported in the literature has involved the use of only the chloride-ion specific electrode. The silver ion-specific electrode is an alternative electrode that can be used for the same purpose. The sensing membranes in silver and chloride ion-specific electrodes are different. In the former, the membrane is pressed from crystalline Ag_2S , while in the latter, it is pressed from a mixture of crystalline Ag_2S and AgCl . This difference in the membrane materials provides some differences in the working ranges of the electrodes and the types of ionic species that can interfere in the electrode's performance, with the silver ion-specific electrode being susceptible to fewer interferences.⁽⁵⁾ In view of the differences cited, a comparison of the performances of the electrodes was attempted as an adjunctive study.

Several concrete samples were made from different combinations of cements and aggregates, and sufficient amounts of the samples were extracted with HNO_3 and filtered by the procedure described by Berman. To compare the electrodes, aliquots from each sample solution were then titrated using the two electrodes separately.

The chloride contents determined by using each type of electrode are given in Table 3 for comparison. It should be mentioned that each of the chloride content values listed is the average of 4 to 5 multiplicate titrations. The observed absolute differences between the two electrodes range from 0.0000 to

Table 3
Comparison Between Chloride and Silver Ion-Specific Electrodes

Cement - Aggregate	Sample	% Cl ⁻ as determined by		Difference, % Cl ⁻
		Cl ⁻ specific electrode	Ag ⁺ specific electrode	
II - carbonaceous	1	0.0087	0.0084	0.0003
	2	0.0133	0.0136	-0.0003
	3	0.0200	0.0197	0.0003
	4	0.0266	0.0261	0.0005
II - siliceous	5	0.0134	0.0139	-0.0005
	6	0.0220	0.0238	-0.0018
	7	0.0342	0.0342	0.0000
	8	0.0418	0.0425	-0.0007
I - carbonaceous	9	0.0221	0.0221	0.0000
	10	0.0332	0.0337	-0.0005
	11	0.0421	0.0428	-0.0007
III - carbonaceous	12	0.0132	0.0122	0.0010
	13	0.0211	0.0212	-0.0001
	14	0.0314	0.0312	0.0002
	15	0.0410	0.0410	0.0000

$$1/15 \sum d = 0.0001\%$$

$$1/15 \sum |d| = 0.0005\%$$

0.0018% Cl^- , with an average of 0.0005% Cl^- , which is approximately the precision attainable with potentiometric titration using the Gran method for endpoint determination, as shown in a later section. Except for the maximum difference of 0.0018% Cl^- , the others were all insignificant at the 95% confidence level when analyzed with the student's t test.⁽⁶⁾ These findings indirectly indicate that the two electrodes probably provide comparable accuracies. To compare their precisions, the standard deviations (not shown in Table 3) for all sets of multiplicate analyses were calculated and averaged for each type of electrode. The silver ion-specific electrode yielded an average standard deviation of 0.0003% against 0.0005% for the chloride ion-specific electrode, which indicates no significant difference between their precisions.

The above comparison indicates that the two electrodes are probably not significantly different with regard to their accuracy and precision. Nevertheless, it must be mentioned that during this study there was an instance in which the chloride electrode showed no indication of malfunction when used to check the normality of a titrant (0.01N AgNO_3 solution) against a standard 0.01N NaCl solution, but when this electrode was immediately thereafter used in the titration of a concrete sample of known chloride content, an erroneous endpoint was obtained. Repeated titrations yielded the same endpoint, which was 0.50 ml from the true endpoint and, in terms of percent chloride, represents a large error of 0.007% Cl^- based on a 2.5-g sample. To be certain that the sample was what it was supposed to be, a silver ion-specific electrode was used in titrating the same concrete sample; this test yielded the correct endpoint, as shown in Figure 3. It can only be assumed that such a performance by the chloride ion-specific electrode in a concrete acid extract and not in a standard NaCl solution was due to eventual poisoning of the electrode's sensing membrane by yet unsuspected interfering ionic species in the extracts after accumulated use. Whatever the interference mechanism may have been, the authors suggest that the analyst should check an electrode with a concrete sample of known chloride content, instead of with only a standard NaCl solution, prior to titration of unknown concrete samples to avoid such an error. The possibility of such erroneous readings being obtained with a silver ion-specific electrode cannot be ruled out. However, since the silver ion-specific electrode has less known interferences than the chloride ion-specific electrode, the authors would recommend using the former.

Reproducibility of the Analysis Employing Gran Method

A reproducibility test was performed to endpoint detection by the Gran method in the titrations of ten different concrete samples. In the test, a sufficient amount of each sample was

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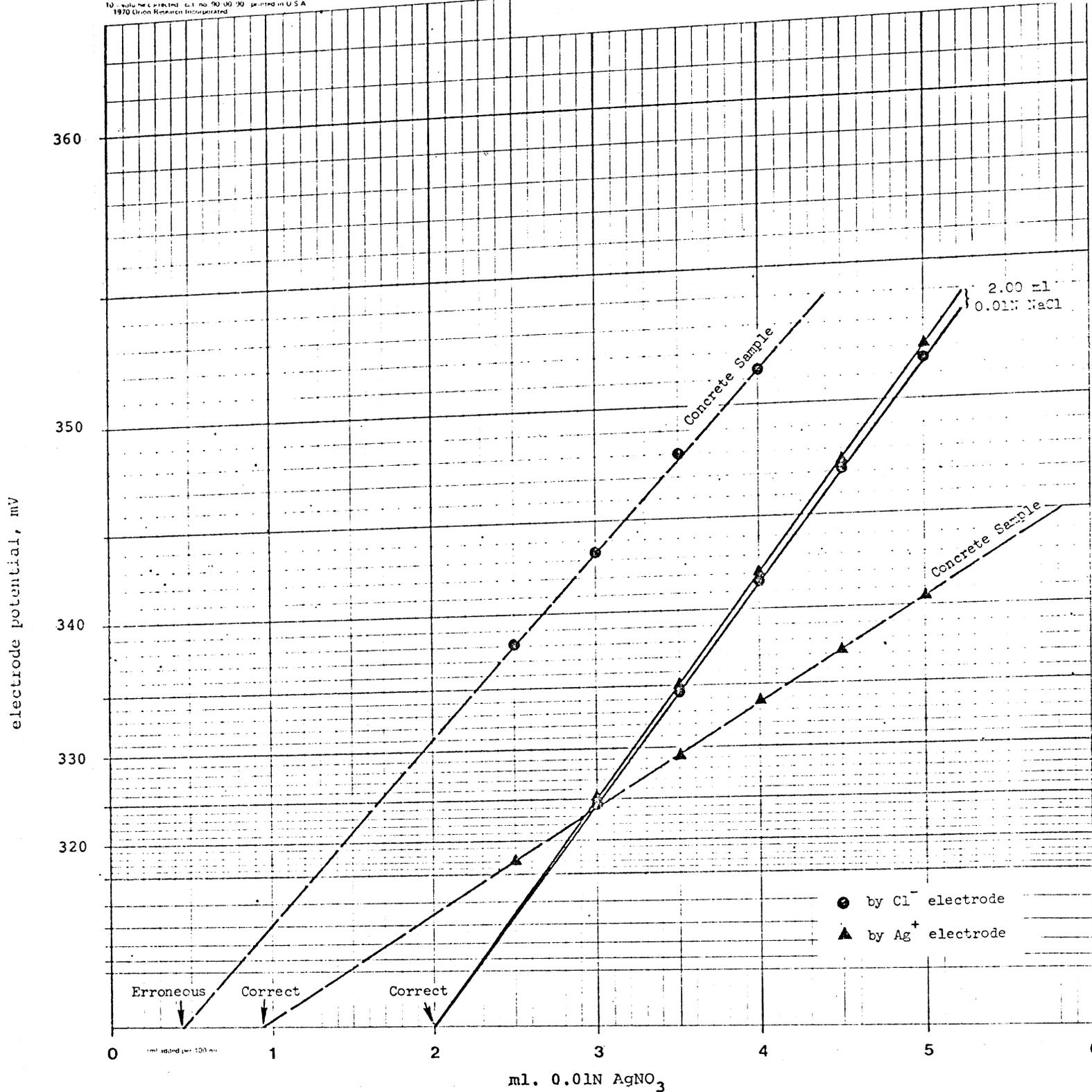


Figure 3. Malfunction in chloride ion-specific electrode detected only in titration of concrete sample with known chloride content.

extracted and filtered in accordance with the procedure described by Berman. Then five aliquots, each containing an approximate 2.5g-sample, from each sample solution were titrated in the presence of a silver ion-specific electrode and the Gran method was used to determine the endpoints. The results (Table 4) showed that the maximum standard deviation was only 0.0004% Cl^- , while the average was 0.0003% Cl^- . A similar reproducibility test performed with the identical sample solutions on the titration procedure described by Berman, which employed the $\Delta E/\Delta V$ method of endpoint determination, gave a maximum standard deviation of 0.0013% Cl^- , while the average standard deviation was 0.0006% Cl^- . This comparison obviously indicates that the Gran method is two to three times more precise than the $\Delta E/\Delta V$ method, a finding that is in agreement with reported results of a critical survey of the various methods most frequently used to evaluate the endpoint from potentiometric titration data. (7)

The overall reproducibility of the entire improved chloride analysis procedure (described in detail in Appendix B), which included the extraction process, potentiometric titration, and endpoint determination by the Gran method, was also determined. Each of two concrete test samples was divided into five portions and a chloride analysis was performed on each portion. The average overall standard deviation obtained was 0.0005% Cl^- (Table 5), which represents considerable improvement over the 0.005% Cl^- reported by Berman.

ATOMIC ABSORPTION PROCEDURE

In this section a procedure which the authors developed for the analysis of chloride in concrete by atomic absorption spectrometry is discussed.

The orbital electrons in the atoms of an element can exist at different discrete energy states which are characteristic of its atomic structure. A transition from the ground electronic state to an excited energy state can be induced with the absorption by the atoms of light whose wavelength corresponds to the energy difference between the two energy states. Atomic absorption spectrometry is, therefore, based on the measurement of the amount of light absorbed, at a wavelength characteristic of a particular element, to provide a quantitative measure of the concentration of that element.

The most common light source used is the hollow-cathode lamp, whose cathode contains the element of interest. Because a light source is not available for chlorine, the determination of chlorine in a material must be done indirectly. This can be

Table 4

Reproducibility of the Gran Method of Endpoint Determination
in Chloride Titration

Concrete sample	Chloride content, %					Range, %	Std. D %
	Aliquot 1	Aliquot 2	Aliquot 3	Aliquot 4	Aliquot 5		
2-L-3	0.0081	0.0081	0.0083	0.0087	0.0089	0.0008	0.000
2-L-4	0.0133	0.0140	0.0133	0.0136	0.0136	0.0007	0.000
2-L-5	0.0197	0.0196	0.0198	0.0194	0.0201	0.0007	0.000
2-L-6	0.0268	0.0259	0.0261	0.0261	0.0259	0.0009	0.000
2-W-3	0.0137	0.0139	0.0141	0.0137	0.0139	0.0004	0.000
2-W-4	0.0242	0.0239	0.0234	0.0239	0.0238	0.0008	0.000
2-W-5	0.0343	0.0343	0.0347	0.0339	0.0340	0.0008	0.000
2-W-6	0.0426	0.0422	0.0422	0.0432	0.0425	0.0010	0.000
2-P-4	0.0288	0.0295	0.0288	0.0290	0.0295	0.0007	0.000
2-R-4	0.0219	0.0222	0.0219	0.0217	0.0217	0.0005	0.000
Average						0.0007	0.000

Table 5

Reproducibility of the Entire Potentiometric Titration Procedure for
Chloride Analysis of Concrete

Concrete sample	Chloride content, %					Range, % Cl ⁻	Std. dev., % Cl ⁻
	portion 1	portion 2	portion 3	portion 4	portion 5		
1	0.0236	0.0244	0.0237	0.0232	0.0239	0.0012	0.0004
2	0.0439	0.0432	0.0439	0.0431	0.0444	0.0013	0.0005
Average						0.0013	0.0005

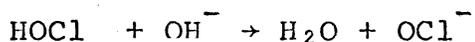
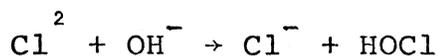
done by precipitating the chloride in a sample solution by the addition of a known and excess amount of silver ion. Then, the amount of either the unreacted silver ion or the precipitated silver ion is measured by atomic absorption spectrometry. From either quantity, the amount of chloride in the sample can be stoichiometrically calculated.

Development of Procedure

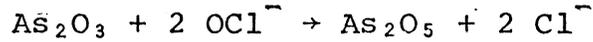
In using the measurement of the amount of unreacted silver ion for the indirect determination of the chloride content in a concrete sample solution, it is necessary to match the matrix of standard solutions of silver ion to that of the sample solution in order to eliminate error due to a matrix effect. Because of the difficulty in matching the matrices, the authors opted instead to use the amount of reacted silver in the AgCl precipitate formed for the indirect measurement of chloride in their initial attempt. In this approach, the precipitate has to be separated from the acid extract of a concrete sample and be redissolved with an NH₄OH solution before the reacted silver can be measured. However, problems caused by the dissolved concrete matrix were encountered in achieving quantitative filtration of the precipitate. Because of the problems, a distillation procedure adapted from the literature was developed for separating chloride from the concrete matrix. (8,9)

In the procedure, the chloride is transformed and vaporized from the ground concrete as HCl and Cl₂ by boiling in concentrated nitric acid. These gases are then collected by passage through a scrubbing solution composed of 10% NaOH and 2% As₂O₃, after which the solution is acidified and the chloride is precipitated by the addition of excess AgNO₃. The AgCl precipitate is then filtered and redissolved in an ammoniacal solution, which is followed by the determination of the reacted silver by atomic absorption. (Appendix C describes the procedure in detail.)

Initially the scrubbing solution used was AgNO₃. However, it was found that the efficiency of this scrubber was 50% at best; presumably, because the Cl₂ was not being absorbed. Consequently, the scrubber composed of 10% NaOH and 2% As₂O₃ and described by Thompson and Oakdale⁽⁹⁾ was tried and found to be quite efficient. The chlorine is probably absorbed in the following manner⁽¹⁰⁾



Then, the arsenic trioxide reduces the hypochlorite ion by⁽¹¹⁾



while the hydrogen chloride reacts with the sodium hydroxide to form sodium chloride, which dissociates in the aqueous scrubber and thereby provides efficient collection of the chloride volatilized from the concrete sample heated in concentrated nitric acid.

To determine the reproducibility of the procedure, several powdered concrete samples were analyzed in triplicate for chloride. Table 6 shows that the averaged standard deviation was 0.0006% Cl^- , which is comparable to that reported in the previous section for the potentiometric titration procedure. However, the atomic absorption procedure is slightly less consistent between samples, as indicated by the variation in the standard deviations. Nevertheless, even the poorest reproducibility observed for the procedure compares favorably with that reported by Berman for the original potentiometric titration procedure.

Table 6

Repeatability of the Atomic Absorption Procedure
for Chloride Analysis of Concrete

Concrete sample	Chloride content, %			Range, % Cl^-	Std. Dev., % Cl^-
	portion 1	portion 2	portion 3		
1	0.0077	0.0076	0.0074	0.0003	0.0002
2	0.0128	0.0130	0.0125	0.0005	0.0003
3	0.0170	0.0184	0.0176	0.0014	0.0007
4	0.0104	0.0120	0.0106	0.0016	0.0009
5	0.0219	0.0212	0.0213	0.0007	0.0004
6	0.0305	0.0310	0.0316	0.0011	0.0005
7	0.0422	0.0400	0.0412	0.0022	0.0011
Average				0.0011	0.0006

NEUTRON ACTIVATION ANALYSIS PROCEDURE

Neutron activation analysis (NAA) is another well established technique that can be adapted for chloride analysis of concrete. It is a nuclear method of elemental analysis wherein a sample is bombarded with neutrons to transform the element(s) being analyzed into radioisotopes, which are then identified and measured quantitatively. For the analysis of chlorine, the natural isotope of ^{37}Cl is transformed by neutron bombardment to ^{38}Cl , which emits 1.64-MeV and 2.16-MeV gamma rays and has a half-life of 37.3 min. This radioisotope of chlorine is related to the amount of its precursor isotope by

$$D_i = N_i \sigma_i \phi (1 - e^{-\lambda_i t}) \quad (1)$$

where

- D_i — the radioactivity of ^{38}Cl present at the end of bombardment,
- N_i — the number of ^{37}Cl target nuclei in the sample matrix,
- σ_i — the cross section of $^{37}\text{Cl} (n,r) ^{38}\text{Cl}$ reaction,
- ϕ — the neutron flux to which the sample matrix was exposed,
- λ_i — the decay constant of the radioactive ^{38}Cl produced, and
- t — the bombardment time.

All other parameters being equal, the amount of ^{38}Cl produced in a sample during the bombardment is directly proportional to the amount of its precursor isotope ^{37}Cl . Therefore, by comparing the radioactivities of the ^{38}Cl from a sample and a standard, both being irradiated under identical conditions, the chlorine content in the sample can be determined. Neutron activation analysis is the most sensitive means for the detection of the majority of the elements of the periodic table, and its approximate interference-free limit of detection for chlorine has been calculated by Buchanan⁽¹²⁾ to be 0.1 ug with irradiation of 1-hour or less in a thermal neutron flux of 1.8×10^{12} n/cm²-sec.

Preliminary work on the application of NAA in the analysis of chlorine in concrete has been reported by Clear, who indicated

that their results, although not conclusive, showed that NAA has a potential as a means of rapidly determining the chlorine content of concrete. In view of its potential, the authors included the investigation of NAA as a means for chlorine analysis of concrete in this study, with the main objective of using the technique to evaluate the accuracy of the potentiometric titration and the atomic absorption procedures.

Development of Procedure

The authors' initial experiment involved determining whether a purely instrumental NAA procedure, based upon multichannel gamma ray spectrometry, which is rapid and nondestructive, can be used satisfactorily to analyze chlorine in concrete samples. In the experiment, several portions (0.3 to 0.4g) of each of 5 concrete test samples were transferred to small snap-cap polyethylene vials that were closed by heat sealing with a soldering iron. The vials were then irradiated for 1 minute in a constant geometry by a thermal neutron flux of 10^{14} n/cm²-sec in the 2-megawatt research reactor at the University of Virginia. The irradiated materials were not counted until approximately 30 minutes after irradiation in order to allow background radioactivity, due to some short-lived radioisotopes, to decay. Each vial was counted for 20 minutes at a distance of 50 cm away from a Ge(Li) detector connected to a kicksort 4096-channel pulse height analyzer.

Table 7 shows the averaged chlorine contents and the averaged uncertainty in the results obtained from multiplicate analyses of each of five test samples. The presence of such radioisotopes as ²⁴Na, ²⁷Mg, ²⁸Al, ⁴²K, ⁵¹Ti and ⁵⁶Mn contributed toward high backgrounds that made chlorine determination difficult. This difficulty is evident in the high uncertainties, shown in Table 7, which ranged from $\pm 119\%$ to $\pm 22\%$ and generally decreased with higher chlorine contents. These uncertainties are higher than those reported earlier by Clear, whose preliminary analyses were conducted under slightly different irradiation and counting conditions.

Another series of test samples, which were made of aggregate different from that used in the above series, was also irradiated. However, the background radioactivity was extremely high and it was virtually impossible to determine the chlorine content.

These difficulties indicate that if satisfactory results are to be obtained with the NAA procedure, post-irradiation radiochemical separation of chlorine must be incorporated. Consequently, a modified NAA procedure employing post-irradiation separation was developed. (This procedure is discussed in detail in Appendix D.)

Briefly, it involved irradiating 5 ml of a nitric acid extracted solution of a concrete sample with thermal neutrons, followed by separation of the radioactive ^{38}Cl through precipitation with an AgNO_3 solution. Prior to the addition of a slight excess of AgNO_3 solution, a small amount of NaCl solution was added into the radioactive sample solution to provide bulk to the would-be formed AgCl precipitate for easy filtration. The precipitate formed was then filtered from the solution and its radioactivity measured.

This procedure provided effective separation of the sought for ^{38}Cl from other interfering radioisotopes and resulted in a tremendous improvement in the analysis. The improvement is evident in the results presented in Table 8, where the observed average weighted uncertainty of $\pm 3.04\%$ is better than the best value of $\pm 22\%$ reported above for the instrumental procedure and the values of $\pm 5\%$ to $\pm 15\%$ reported by Clear. The various ranges of chloride contents observed, which provide a measure of the procedure's reproducibility, averaged $0.0004\% \text{Cl}^-$. This value is comparable to those reported previously for the potentiometric titration and atomic absorption procedures. It is worthwhile to mention that the first three samples in Table 8 were a few of the samples for which the researchers previously had failed even to estimate chloride contents by the instrumental procedure because of interference from other radioisotopes.

It must be emphasized that since it uses an acid-extract of a concrete sample, the procedure determines the acid-soluble chloride content of the sample.

Table 7

Summarized Results for Chlorine Analysis
of Concrete by Instrumental Neutron Activation Analysis

Concrete sample	Number of analysis	Avg. chlorine content % by wt.	Avg. uncertainty, %
1	4	0.0031	± 96
2	9	0.0071	± 119
3	5	0.0160	± 37
4	8	0.0204	± 25
5	5	0.0275	± 22

Table 8

Chloride Analysis of Concrete by Neutron Activation Analysis
Employing Post-Irradiation Radiochemical Separation

Concrete sample	Analysis number	Chloride content % by wt.	Weighted uncertainty, %	Range of chloride contents, %
W-3	1	0.0160	±1.76	
	2	0.0162	±2.24	
	3	0.0156	±5.33	0.0006
W-5	1	0.0327	1.94	
	2	0.0330	2.59	
	3	0.0330	3.52	0.0003
W-6	1	0.0397	2.01	
	2	0.0402	1.85	0.0005
L-5	1	0.0177	5.84	
	2	0.0179	3.31	0.0002
Average ±3.04%				0.0004%

COMPARISON ON THE ACCURACY OF THE THREE
PROCEDURES FOR CHLORIDE ANALYSIS

Two series of concrete specimens were prepared — one using a siliceous aggregate and one a carbonaceous aggregate. In each series there was a blank wherein no chloride was added, and the

rest contained chloride in increments. The specimens were analyzed for chloride in duplicate, using the three procedures discussed previously. The results, shown in Table 9, indicated that potentiometric titration provided the smallest average absolute difference, or error, of 0.0005% Cl^- , compared to 0.0020% Cl^- and 0.0019% Cl^- , respectively, for atomic absorption and neutron activation.

In Figures 4, 5, and 6, the corrected chloride contents as measured by the three procedures are plotted separately against the chloride added in the specimens. It is shown by Figure 4 that the results from potentiometric titration clustered around the 45° dashed line, which indicates excellent agreement and no discernible aggregate effect.

For atomic absorption, the measured chlorides were consistently lower than the chloride added. This discrepancy, which averaged approximately an 11% loss in chloride (Table 9 and Figure 5), is probably due to a combination of less than 100% efficiency in the distillation process which separates the chloride from the concrete matrix and a chloride loss in the filtration of the AgCl precipitate. In addition to yielding lower results, the atomic absorption is apparently affected by the nature of the aggregate present in the concrete samples, as indicated by the existence of two separate lines in Figure 5. It appears that the effect of the particular siliceous aggregate used was more consistent, in terms of differences from the four chloride values, than that exhibited by the carbonaceous aggregate used.

Some aggregate effect was also observed in the results obtained by the neutron activation procedure. However, the effect appeared to be more pronounced with this procedure than with the other procedures. Figure 6 shows that neutron activation yielded positive errors at relatively low chloride contents and negative errors at relatively high chloride contents. Possibly, this finding indicates the combined effects of two contributing factors: (1) the background contributions from previously mentioned interfering radioisotopes, which would cause positive error in the measured chloride contents, and (2) the absorption of radioactive ^{38}Cl by the wall of the vials in which the sample solutions were irradiated, which would cause negative error. Although the incorporation of post-irradiation chemical separation in the procedure significantly reduced the first type of interference, apparently it still caused errors ranging from 0.0007% to 0.0027% Cl^- for the low chloride concrete specimens tested. It should be noted that the first type of error is more pronounced with specimens containing the siliceous aggregate, which has more of the elements that produce the interfering radioisotopes in its composition, than the carbonaceous aggregate. The second type

Table 9

Analysis of Prepared Concrete Specimens for Chloride by Potentiometric Titration, Atomic Absorption, and Neutron Activation Analysis

Concrete specimen	Chloride added %	Corrected Chloride Content measured by			Difference, % Cl^-		
		PT	AA	NAA	PT	AA	NAA
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. Abs. Diff., % Cl^-			0.0005	0.0020	0.0019

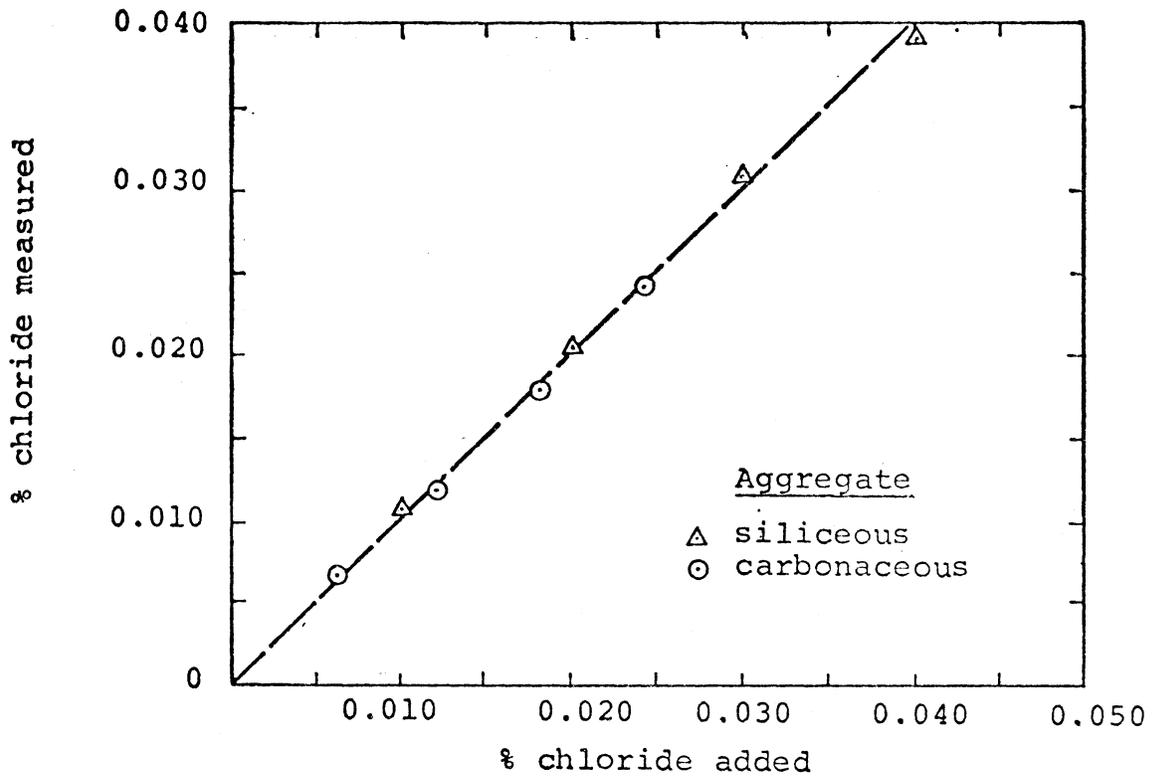


Figure 4. Analysis of chloride in prepared concrete specimens by potentiometric titration procedure.

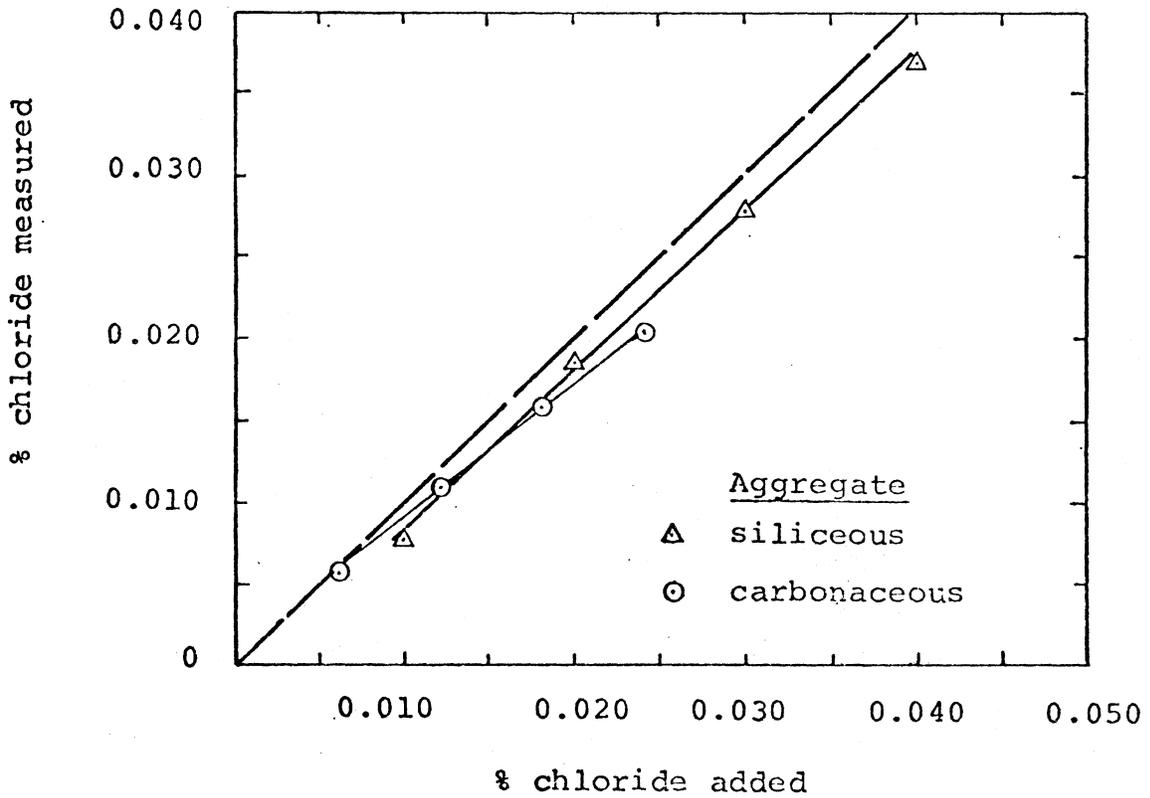


Figure 5. Analysis of chloride in prepared concrete specimens by atomic absorption procedure.

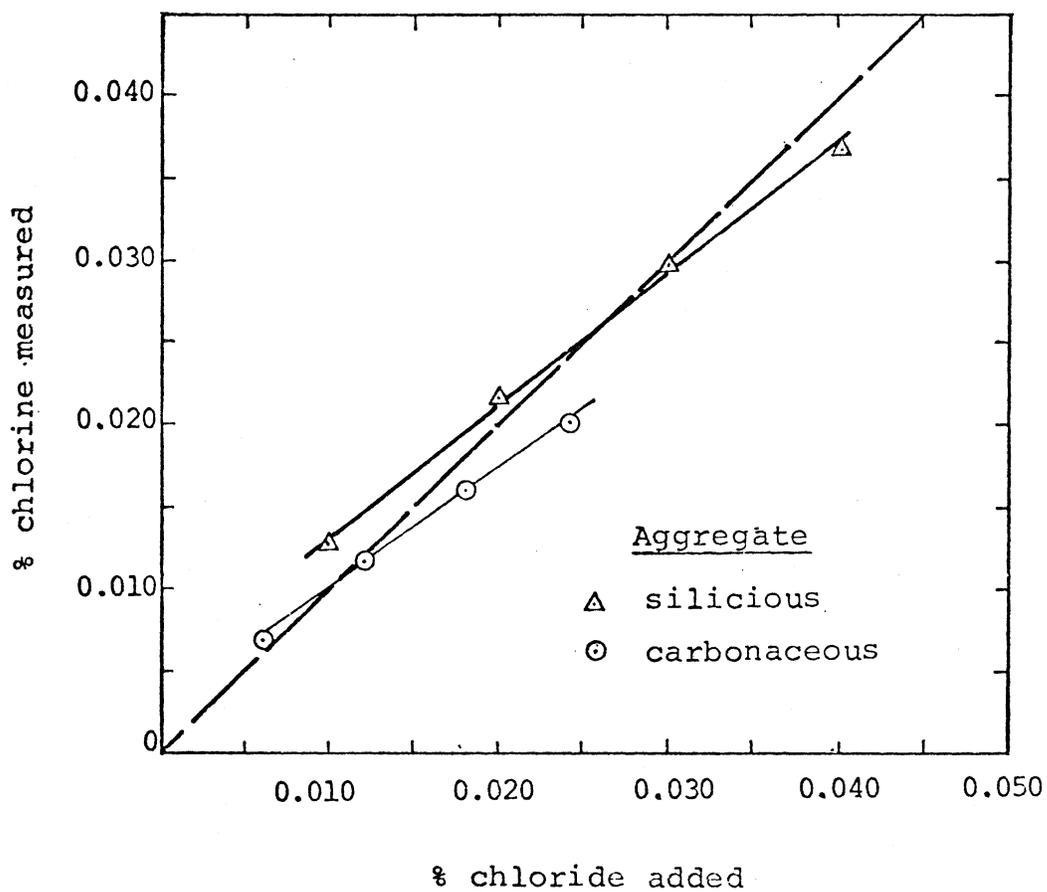


Figure 6. Analysis of chloride in prepared concrete specimens by neutron activation procedure.

of interference, which increases with increased chloride content, can possibly be reduced by the use of relatively expensive quartz containers that may provide less permeation for the ^{36}Cl . The use of a quartz container was not attempted, because it is thought that the neutron activation procedure is already relatively expensive to a point that precludes its popular use and the potentiometric titration procedure appears to be ideal.

CONCLUSIONS

From the preceding presentation, the following conclusions can be drawn.

1. In the improved potentiometric titration procedure for the analysis of chloride in concrete, the use of the Gran method of endpoint determination eliminates the difficulty in determining the endpoint as caused by unstable potential readings in the vicinity of the endpoint.
2. The Gran method also eliminated the need to spike solutions of low chloride concrete samples with a known amount of chloride before titration.
3. The use of the Gran method of endpoint determination improved the reproducibility, or precision, of the potentiometric titration procedure.
4. There was no significant difference in the results of titrations using silver and chloride ion-specific electrodes, when both electrodes functioned properly.
5. A malfunction of a chloride ion-specific electrode was observed. It was detected only by checking the electrode with a titration of a known concrete's acid solution.
6. The improved potentiometric titration procedure provided the best agreement with the concrete test specimens, and the most economical and simple means for chloride analysis as compared with the atomic absorption and neutron activation procedures. It also exhibited no discernible effects by the two different types of aggregates, siliceous and carbonaceous, used in the test specimens.

7. The atomic absorption procedure provided satisfactory precision. However, it exhibited an aggregate effect and yielded measured chloride contents consistently lower than the known chloride contents, with the observed differences ranging from 0.0003% to 0.0040% Cl^- . If such errors are tolerable, the atomic absorption procedure may be used for chloride analysis when a potentiometric titration apparatus is not available.
8. The neutron activation procedure exhibited pronounced aggregate effects. It yielded measured chloride contents differing from the known contents by -0.0041% to +0.0027% Cl^- . It is also the most time-consuming and expensive of the three procedures tested.

RECOMMENDATION

In view of the above conclusions, it is recommended that the Gran method of endpoint determination be incorporated in the potentiometric titration procedure. Its use will improve the procedure and provide possibly the most accurate means for the analysis of chloride in hardened concrete.

ACKNOWLEDGEMENT

This investigation was financed by HPR funds administered through the Federal Highway Administration.

The authors extend their gratitude to Dr. R. Allen of the Chemistry Department, University of Virginia, for his assistance, and to M. C. Anday for his administrative guidance.

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APPENDIX A

GRAN METHOD OF ENDPOINT DETERMINATION

In the discussion below, the Gran method is applied to the potentiometric titration of Cl^- with Ag^+ , in which AgCl precipitate is formed.

Before the equivalence point is reached, the concentration of Cl^- in the solution is related to the amount of Ag^+ added by the simple expression

$$C_a = \frac{C'_a V_a - C_t V_t}{V_a + V_t} \quad (3)$$

where

C_a = concentration of Cl^- in solution,

C'_a = initial concentration of Cl^- in solution,

C_t = concentration of Ag^+ in the titrant,

V_a = initial volume of analyte solution, and

V_t = volume of titrant added.

The electrode potential is related to the molar activity of chloride, A_{Cl^-} , by the Nernst equation

$$E = K - \frac{RT}{F} \ln A_{\text{Cl}^-} \quad (4)$$

where

E = electrode potential,

K = constant determined by formal potential and junction potential,

R = the universal gas constant,

T = temperature in Kelvin, and

F = the Faraday constant.

In dilute solution the activity approaches the concentration, so that

$$E = K - \frac{RT}{F} \ln C_a \quad (5)$$

Substituting Equation 3 into Equation 5, we get

$$E = K - \frac{RT}{F} \ln \left[\frac{C'_a V_a - C_t V_t}{V_a + V_t} \right] \quad (6)$$

which relates the electrode potential, E, to the volume of titrant added, V_t . This can be rearranged to yield

$$(V_a + V_t) \cdot 10^{\frac{F}{2.3RT}(K-E)} = C'_a V_a - C_t V_t \quad (7)$$

which indicates that a plot of $(V_a + V_t) \cdot 10^{\frac{F}{2.3RT}(K-E)}$ versus V_t should give a straight line. Since at the equivalence point all the chloride ions have been precipitated so that $C_a = 0$, then

$$C'_a V_a - C_t V_e = 0$$

This corresponds to the intercept of the straight line with the horizontal axis and the value of V_t , at this point, is the endpoint of the titration. A similar analysis can be made after the endpoint is passed, in which case

$$(V_a + V_t) \cdot 10^{\frac{F}{2.3RT}(E-K)}$$

plotted against V_t .

Orion Research Incorporated of Cambridge, Mass., has developed a "Gran's Plot Paper", shown in Figure A-1, which eliminates the

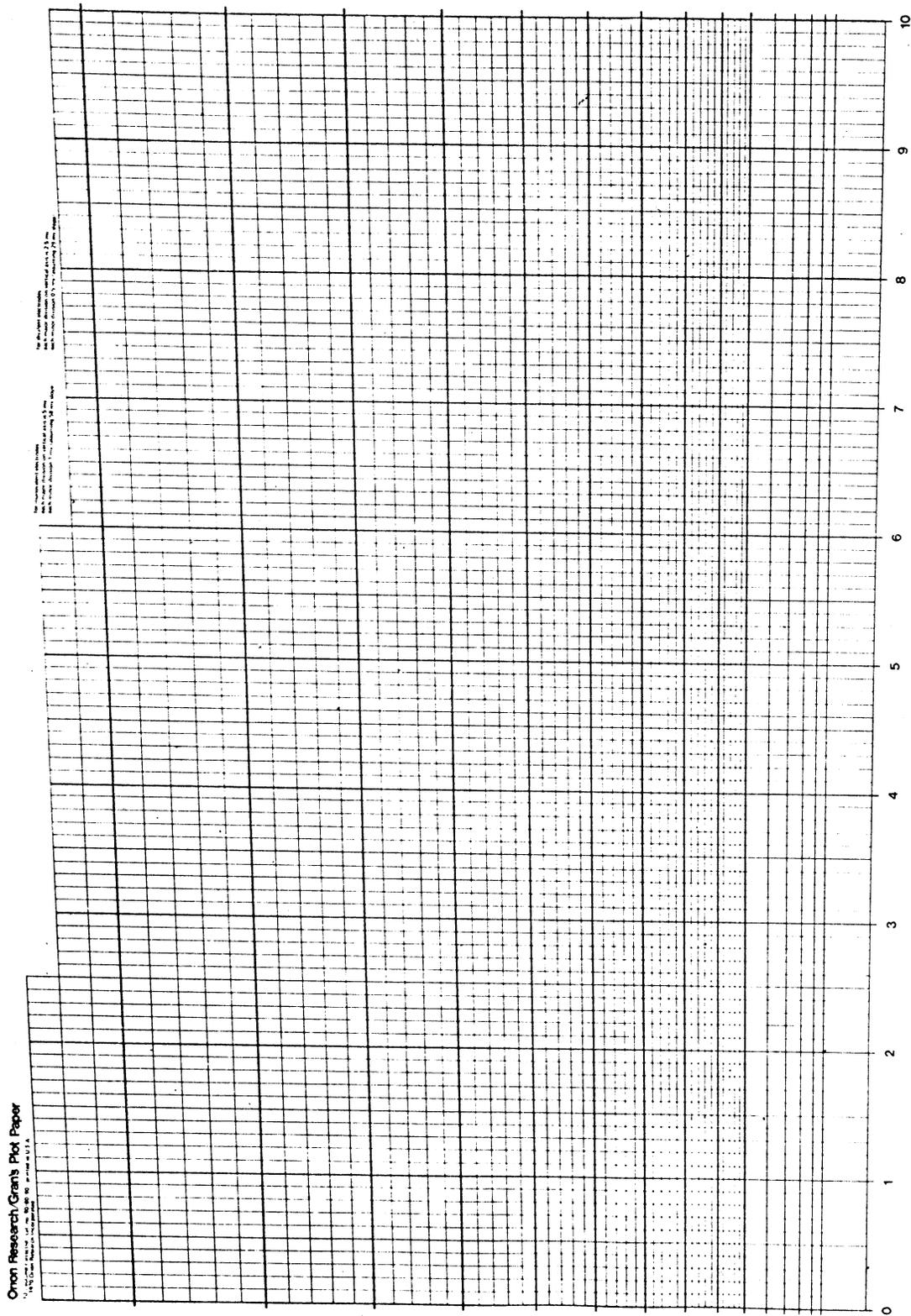


Figure A-1. Gran's plot paper. (Reproduced with permission from Orion Research, Inc.)

need for calculating the complicated

$$(V_a + V_t) \cdot 10^{\frac{F}{2.3RT} (K-E)}$$

term and enables the analyst to plot the measured electrode potential against the volume of titrant directly.

In the titration of the acid-soluble chloride from concrete, the potential readings after the endpoint, i.e., >300mV for the authors' titration system, are plotted against the titrant volume to determine the endpoint. A plot of a potentiometric titration using a Gran's plot paper is shown in Figure 2. Since these readings are more stable than those in the vicinity of endpoint, this method of endpoint determination has a better precision and accuracy than the $\Delta E/\Delta V$ method.

APPENDIX B

IMPROVED POTENTIOMETRIC TITRATION PROCEDURE

Reagents

1. Concentrated HNO_3
2. Sodium chloride, NaCl , reagent grade (primary standard).
3. Silver nitrate, AgNO_3 , reagent grade.
4. Standard 0.01N NaCl solution. Used as a primary standard against which the titrant, a 0.01 AgNO_3 solution, is standardized. Dry NaCl in an oven at 105°C . Cool, weigh out 0.5844 gram, dissolve in distilled H_2O , and transfer quantitatively to a 1-liter volumetric flask. Make up to the mark with distilled H_2O and mix.
5. Standard 0.01N AgNO_3 solution. Weigh 1.7 grams of reagent grade AgNO_3 , dissolve in one liter distilled H_2O and mix thoroughly. Standardize with the standard 0.01N NaCl solution.

Apparatus

1. Silver ion-specific electrode and manufacturer recommended accessories. The authors prefer this electrode over the chloride ion-specific electrode.
2. An Accumet 520 pH/ion meter manufactured by Fisher Scientific Company.
3. Magnetic stirrer and teflon-coated stirring bars.
4. Burette with 0.1 ml graduations.
5. Gran's plot papers, manufactured by Orion Research, Inc.

Procedure

The improved potentiometric titration procedure is briefly described by the flow chart shown in Figure B-1. The only significant difference from the original procedure developed by Berman is in the titration part. Because the Gran method of endpoint determination is used in this improved procedure, only several readings of potential and titrant volume are necessary; therefore the titration is simple and fast.

Weigh to the nearest milligram a 2.5-gram powdered sample representative of the material under analysis. Add 10 ml of distilled H_2O , swirl to bring the powder into suspension. Add 3 ml of concentrated HNO_3 with continued swirling for a few minutes. Break up any lumps with a stirring rod and dilute with hot H_2O to 50 ml.

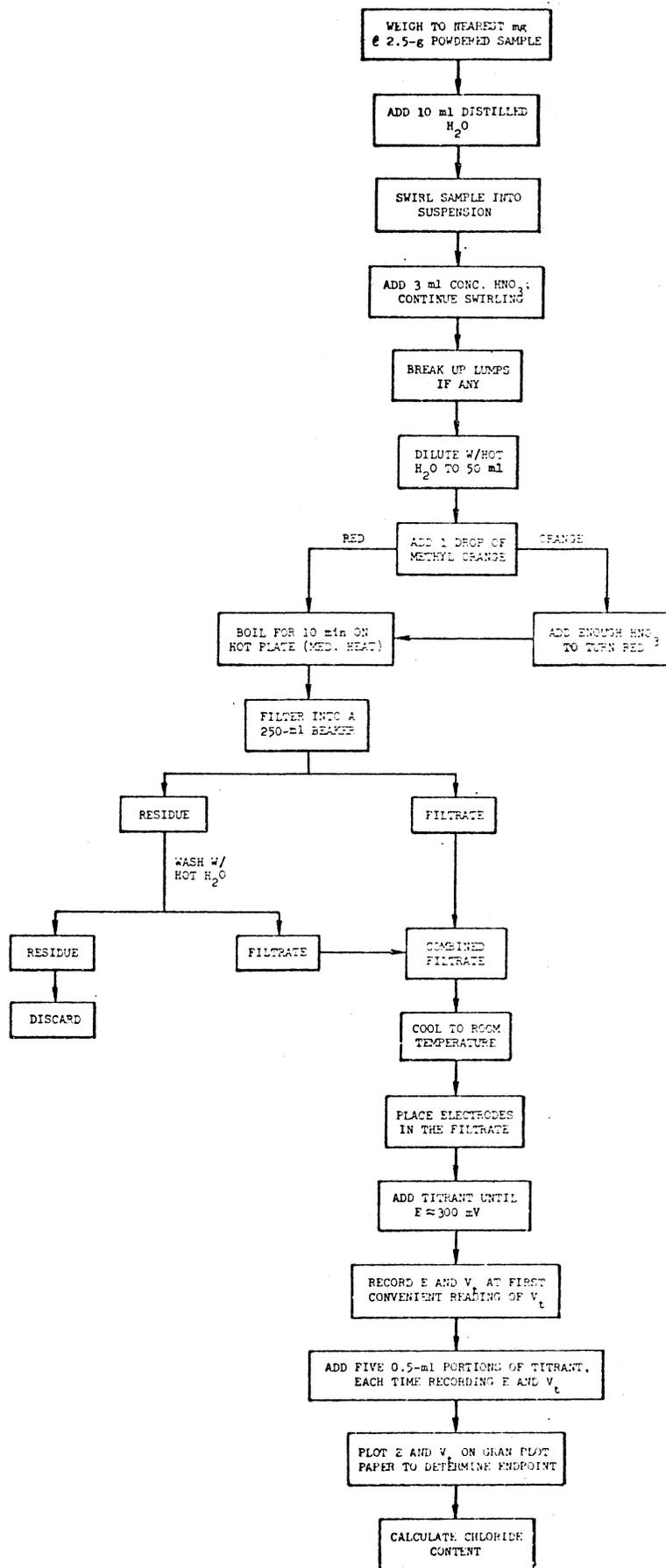


Figure B-1. Analysis of chloride in hardened concrete with the improved potentiometric titration procedure.

If the solution is not acidic at this point, add only enough HNO_3 to produce a red color with methyl orange.

Heat the mixture to boiling on a hot plate at medium heat and gently boil for about 10 minutes, covering the mixture with a watch glass. Meanwhile, prepare the filter papers to be used. The filter papers recommended are the Whatman 50 series, which are washed with HNO_3 , since the other papers have been found to contribute chloride in the analysis. A combination of a medium porosity paper under one of high porosity is most suitable.

Decant the clear solution into the filter paper and collect the filtrate in a beaker with a stirring bar. Wash the residue in the beaker twice with distilled water from a wash bottle. Transfer the residue into the filter paper. Wash the residue on the filter paper thoroughly several times with hot water. Allow the filtrate to cool to room temperature. Place the beaker on a magnetic stirrer, then submerge the ends of the silver ion-specific electrode and a reference electrode in the solution. Start stirring.

Add titrant from a burette until the potential reading is approximately 300 mV (This potential corresponds to that region at which a straight line starts to form in a Gran's plot, as shown in Figure 2, for the titration system used by the authors.) Then, at the very first convenient titrant volume (V_t) reading, record the potential (E) and V_t . Add five 0.5-ml increments of titrant, each time recording E and V_t . Plot these six pairs of E and V_t in a Gran's plot paper (shown in Figure A-1) to determine the endpoint, then calculate the chloride content of the sample by the simple expression

$$\% \text{Cl}^- = \frac{3.5453 \text{ NV}}{W}$$

where

N = the normality of the standard solution,

V = the volume of AgNO_3 solution, in ml, added up to the endpoint, and

W = the weight of the sample in grams.

The authors recommend running a blank determination as a correction for the determined endpoints.

APPENDIX C

ATOMIC ABSORPTION PROCEDURE

Reagents

All chemicals used are of reagent grade.

1. Scrubber Solution: To 100 mls of distilled water add 2 grams Arsenic Trioxide (As_2O_3) and 10 grams NaOH. The arsenic trioxide is not readily soluble and requires stirring for 15 minutes to effect dissolution. The scrubber is not stable against oxidation by molecular oxygen and should be prepared fresh daily.
2. Distilling Medium: Reagent grade concentrated nitric acid is used.
3. Standards: A 100 ppm Ag^+ stock solution is prepared from 1000 ppm Fisher "certified" silver standard. Appropriate dilutions of the stock solution are made to give 1.0, 2.0, and 3.0 ppm Ag^+ working standards. These standards are matched in ammonia concentration to that of the samples.
4. 1500 ppm Ag^+ solution: Dissolved 2.3621 gm of $AgNO_3$ in liter of distilled water.
5. 3N NH_4OH : Dilute 200 ml of concentrated NH_4OH (14.8 molar) to 1 liter.
6. 2% HNO_3 : Dilute 20 ml of concentrated HNO_3 (16.4 molar) to 1 liter.

Apparatus

1. Distillation: A diagram of the distillation apparatus shown in Figure C-1. The addition of concentrated nitric acid to the concrete samples was done through an addition funnel. This prevented any losses due to the effervescence created by the reaction of the acid with the carbonates present in the sample. A gentle flow of nitrogen through the apparatus provided an efficient transfer of the distillates to the scrubber solution.
2. Filtration: Filtration of the precipitate was done under vacuum through a fritted glass filter with a pore size of 4 to 5.5 microns. Figure C-2 is a diagram of the filtration apparatus used.

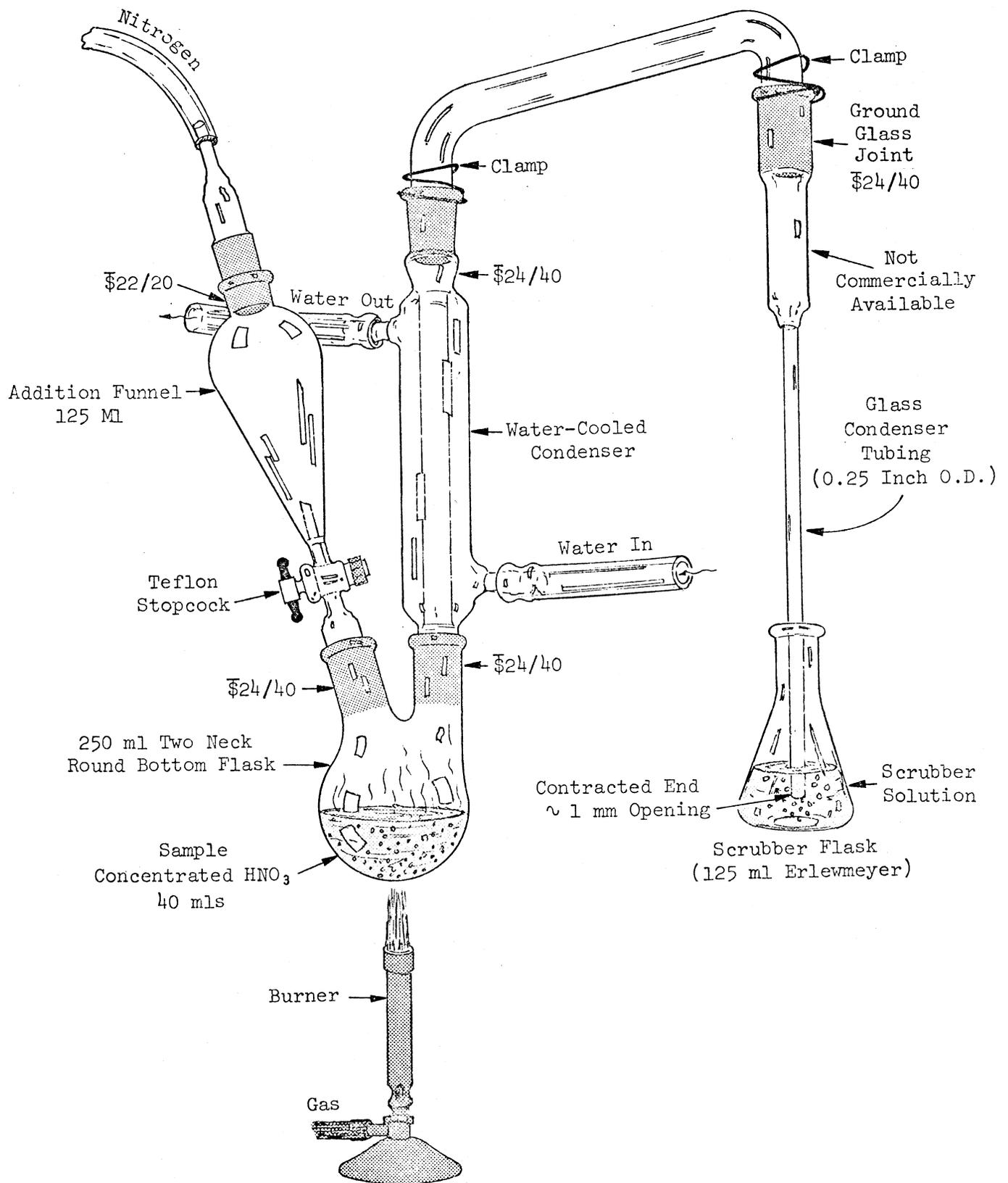


Figure C-1. A distillation apparatus

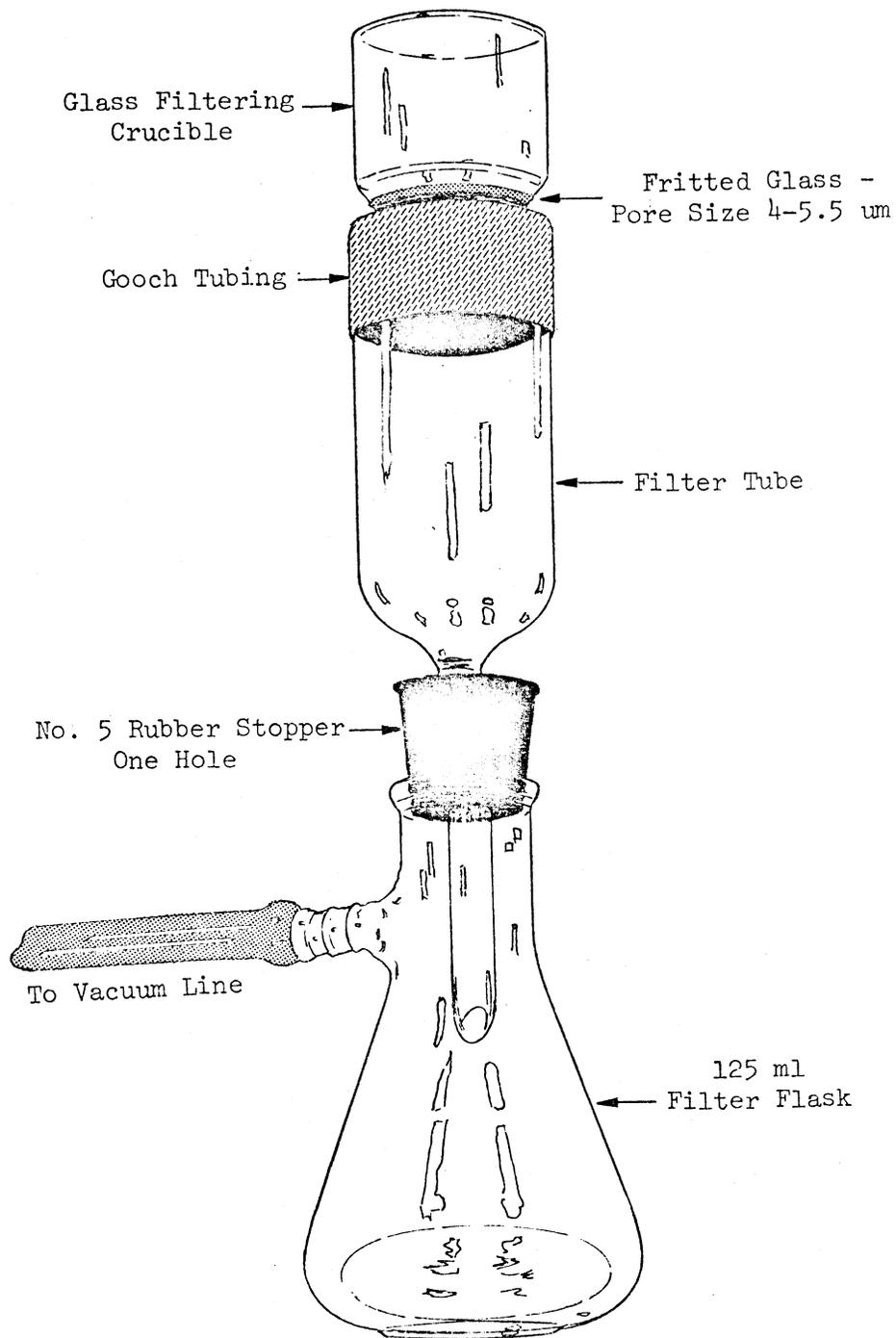


Figure C-2. Filtration apparatus.

Procedure

The procedure is briefly described by the flow diagram in Figure C-3. Approximately 5 grams of sample are weighed to the nearest milligram and transferred into the distillation flask. The distillation apparatus is then assembled. A 40-ml solution of concentrated HNO_3 is transferred to the addition funnel from a graduated cylinder. The acid is then slowly added to the distillation flask. (The rate of addition depends on the type of aggregate in the concrete sample. For carbonaceous aggregate, the addition of acid should be slow enough to avoid too rapid evolution of CO_2 , which would sometimes cause the acid to flow up into the condenser. For siliceous aggregate, the acid could be added relatively faster.)

Nitrogen flow is started at a flow rate of approximately 100 ml/min. Then the mixture in the distillation flask is heated to gentle boiling, and continued for 45 minutes. (A violent boiling will cause some nitric acid to distill over into the scrubber solution and render it ineffective.) After the distillation, the scrubber flask and the condenser are removed in that order, then the inside wall of the condenser is rinsed several times with small portions of deionized water; the rinsings are collected in the scrubber flask.

The scrubber solution is then neutralized slowly with 50% nitric acid solution using pH paper to test acidity. The inside wall of the scrubber flask is washed with deionized water and an excess of the 1500-ppm Ag^+ is added into the flask. (For a 5-g sample with less than 0.05% Cl^- , 6 ml of 1500 ppm Ag^+ will provide an excess.) The flask is swirled gently to ensure mixing and then heated to just under boiling for 45 minutes in a dark place to coagulate the AgCl precipitate. The flask is then covered with a watch glass and allowed to sit in the dark overnight.

The filtration described below should be performed under subdued light since the precipitate undergoes decomposition in the presence of ultraviolet light. The filtration apparatus is assembled, after which the content of the scrubber flask is slowly and quantitatively transferred into the filter crucible. When all the liquid has passed through the filter, any small amount of precipitate that may have adhered to the wall of the filter crucible is washed down to the filter with a few milliliters of 2% HNO_3 . Then, the precipitate collected in the filter is washed repeatedly with three 4-ml portions of 2% HNO_3 . (The 2% HNO_3 is used to prevent peptization of the precipitate that would result if distilled water was used.)

The crucible is removed from the holder, the undersize of which is washed with a few milliliters of deionized water from a

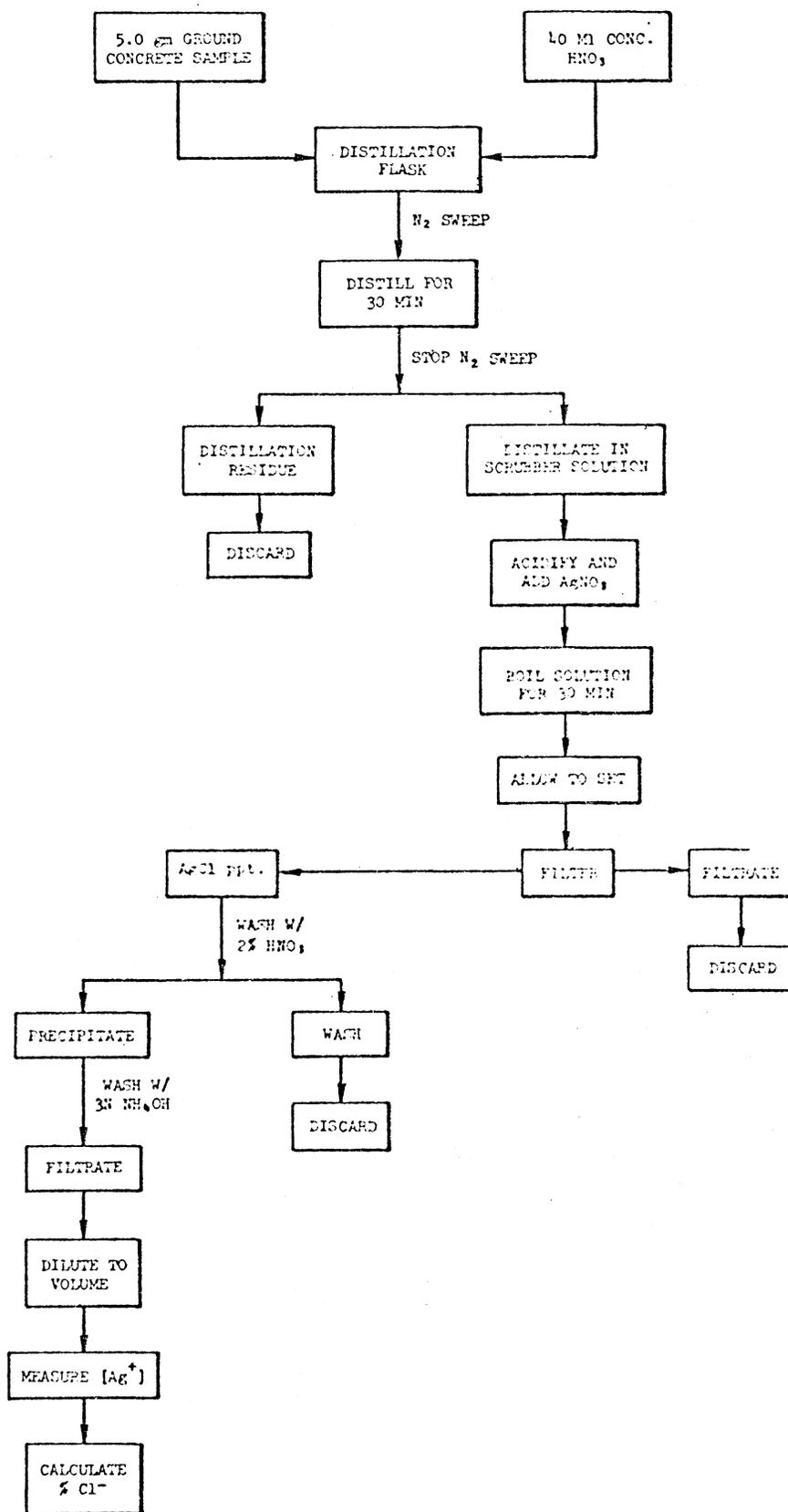


Figure C-3. The atomic absorption procedure for analysis of chloride in concrete.

wash bottle, and the crucible is placed on a clean holder and filter flask. Fifty milliliters of 3N NH_4OH are then added in two portions to the filter crucible to dissolve the precipitate, with the washings being collected in the filter flask. The crucible is removed from the filter tube and its underside rinsed with deionized water. The filter tube is similarly rinsed. All washings are collected in the filter flask.

The collected ammoniacal solution is then transferred quantitatively to a volumetric flask and appropriate dilutions are made such that the silver concentration lies within the linear working range of the atomic absorption spectrometer. In those cases where different dilutions are made, the ammonia contents of those diluted solutions are adjusted to correspond to that of the least diluted solution by addition of appropriate volumes of 3N NH_4OH .

The spectrometer is then calibrated with the standard silver solutions. This is followed by the sample solutions in order to determine their silver concentrations. The chloride content of the concrete sample is then calculated by

$$\% \text{Cl}^- = 3.287 \times 10^{-5} \left[\frac{C_{\text{ag}} \times V}{W} \right] \quad (8)$$

where

C_{Ag} = concentration of Ag in the ammoniacal solution in $\mu\text{g/ml}$,

V = total volume of the ammoniacal solution in ml, and

W = weight of concrete sample in grams.

APPENDIX D

NEUTRON ACTIVATION ANALYSIS PROCEDURE

The acid extract of a ground concrete sample is analyzed for chloride by neutron activation analysis. The discussion below includes a radiochemical separation procedure which was used to improve the precision and accuracy of the technique. Figure D-1 is a flow diagram of the procedure used.

Reagents

1. Cl^- standard: 100 ppm Cl^- prepared from primary standard KCl dissolved in H_2O .
2. Cl^- carrier: 10 mg/ml Cl^- solution prepared from reagent grade KCl dissolved in H_2O .
3. Al, Mn, Na, K carrier: 1000 ppm in Al, Mn, Na, K. The Al and Mn prepared from reagent grade metal dissolved in H_2SO_4 . The Na and K prepared from reagent grade salts (nitrates).
4. Ag^+ solution: 50 mg/ml Ag^+ , prepared from reagent grade AgNO_3 dissolved in H_2O .
5. Flux wires: Reagent grade iron wire was used.

Apparatus

1. Sample container: The samples were heat sealed in .5-inch I. D. polyethylene tubing that had been leached for 24 hours with 25% HNO_3 to remove any residual chlorine.
2. Irradiation facility: The samples were irradiated in the 2-megawatt University of Virginia Research Reactor. The flux of this facility is approximately 10^{14} neutrons/cm²-sec.
3. Filtration apparatus: The filtration device used is illustrated in Figure D-2. The filter paper was a fine porosity paper, 2.3 cm in diameter.
4. Counting system: The samples were counted 4 inches above a lithium-drifted germanium detector. The detector was coupled to a kicksort 4096-channel pulse height analyzer, with .5-kev. resolution.

Procedure

The flow diagram in Figure D-1 briefly describes the procedure. Five milliliters of an acid extract containing 2.5 g sample/100 ml were heat sealed in 0.5-inch I. D. polyethylene tubing. A 5-ml aliquot of the 100-ppm Cl^- standard solution was similarly encapsulated. Each of the sealed capsules was then wrapped with a

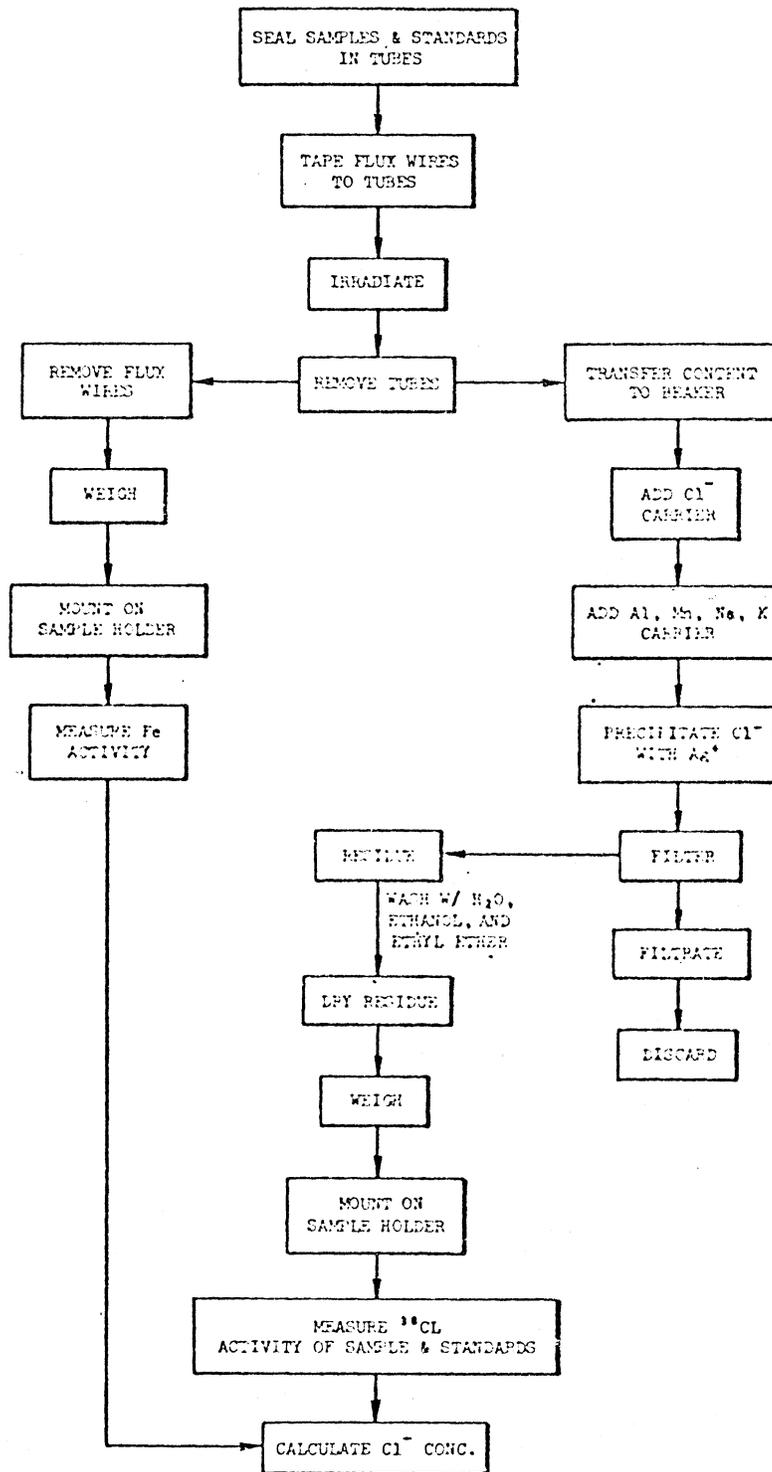


Figure D-1. The neutron activation procedure for analysis of chloride in concrete.

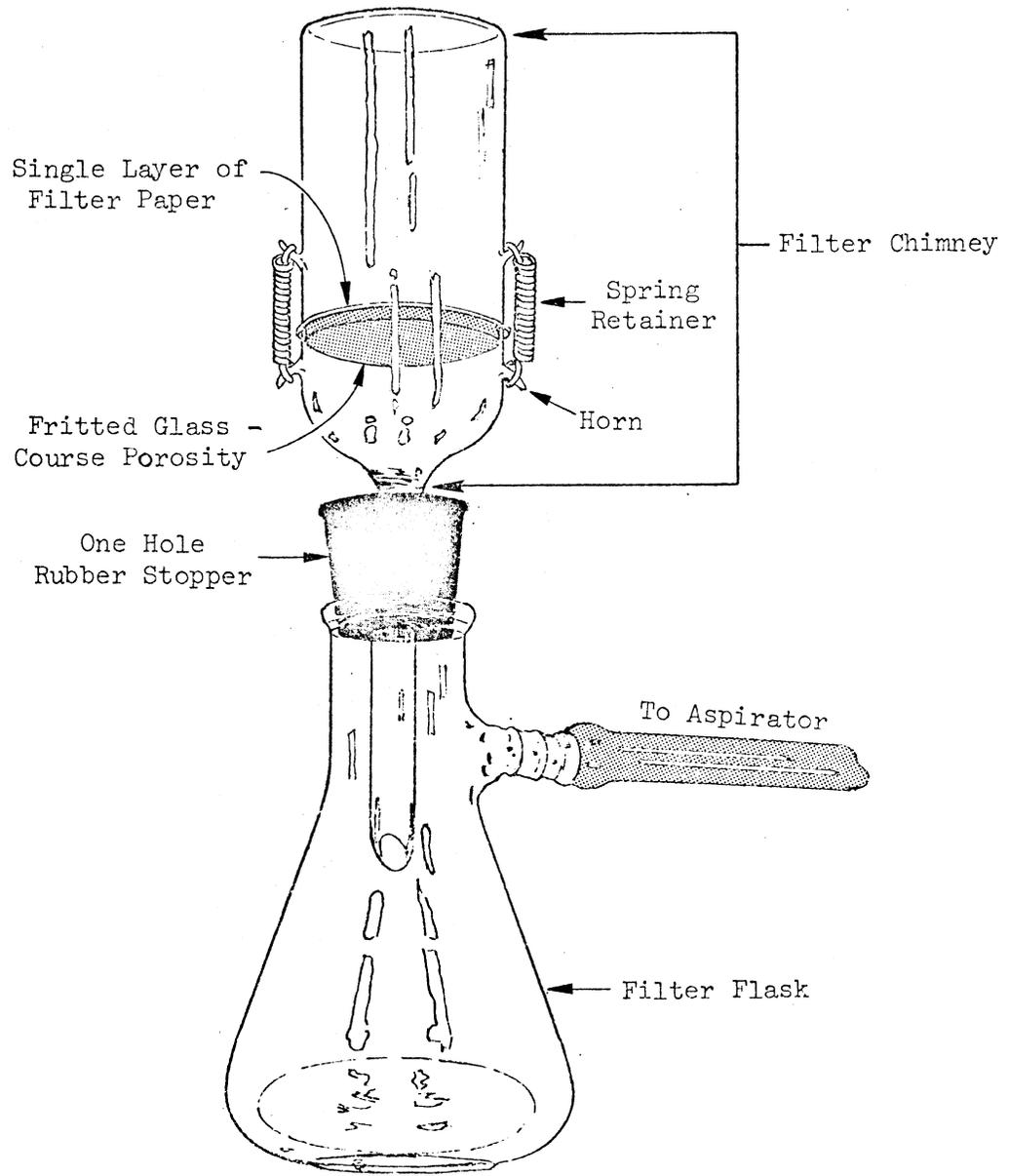


Figure D-2. Filtration apparatus used for radioactive precipitate.

6-inch length of iron wire (the wires were used for flux correction). Then the capsules were taped into a bundle and placed in an aluminum irradiation container and lowered into a flux trap of the research reactor of the University of Virginia for a 30-minute irradiation at a flux of 10^{14} neutrons/cm²-sec. After the irradiation, the container was taken out of the flux trap and allowed to cool in the reactor pool for 1 hour.

The capsules were taken out of the container and each flux wire removed and marked for later use. Each capsule was cut open and the content transferred to a beaker, then washed with 3 mls of the 10 mg/ml Cl⁻ solution and 6 mls of 6N HNO₃, with each wash being collected in the beaker. An additional 2 mls of the chloride solution was added. (The 50 mg of chloride added served as a carrier for the radioactive ³⁸Cl and also provided bulk to the AgCl precipitate formed later.) Then 3 mls of the Al, Mn, Na, K carrier solution were added, followed by the slow addition of 4 mls of the 50 mg/ml silver solution to precipitate the chloride. (The carrier solution added reduced through isotopic exchange the amount of radioisotopes of Al, Mn, Na, and K that may become occluded in the precipitate.) The solution was allowed to sit for 10 minutes in a dark place, to enable the precipitate to coagulate.

Meanwhile, the filtration apparatus was assembled. The filter paper was washed with 6N HNO₃ followed by distilled water, ethanol, and ethyl ether. It was then dried at 70°C for 20 minutes, allowed to cool in a dessicator and then weighed. The washed paper was placed on the filtration apparatus into which the precipitate was quantitatively transferred and collected. The precipitate was then washed with deionized water, ethanol, and ethyl ether; dried at 70°C for 10 minutes, cooled, and weighed.

The filter paper and the precipitate were mounted on a cardboard holder and counted for 20 minutes at a distance of 4 inches from a Ge(Li) detector. For ³⁸Cl, the two gamma radiations of interest were of 1.64 MeV and 2.17 MeV, and the radioactivities for both radiations were recorded and used separately for calculation of the chloride concentration in the acid extract, which is given by

$$C_{Cl} = C_b \cdot \frac{S_s}{S_b} \cdot \frac{F_b}{F_s} \quad (9)$$

where

C_{Cl} = concentration of chloride in sample acid extract.
in $\mu\text{g/ml}$,

C_b = standard solution's chloride concentration, in
 $\mu\text{g/ml}$,

S_s = specific activity of sample precipitate, in
Counts/min-gm,

S_b = specific activity of standard precipitate, in
Counts/min-gm,

F_b = specific activity of standard flux wire, in
Counts/min-gm, and

F_s = specific activity of sample flux wire, in
Counts/min-gm.

The chloride content of the ground concrete sample is calculated by

$$\% \text{Cl}^- = \frac{C_{Cl}}{C_s} \times 100 \quad (10)$$

where C_s = concentration of the sample in the acid extract, in $\mu\text{g/ml}$. The two chloride contents calculated from using the radioactivities from the two gamma radiations were averaged to yield the chloride content of the sample.

