Determining Precision of ASTM's Rapid Test Method for Sodium Chloride

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The American Society for Testing and Materials is the preeminent standards setting organization in the United States. ASTM D 632-94 (now ASTM D 632-99) *Standard Specification for Sodium Chloride* is widely used in the U.S. for purchasing highway-deicing salt. Along with chemical purity and grading requirements, D 632-94 includes a non-mandatory, rapid test procedure to determine the purity of the salt. The Rapid Test Method for Sodium Chloride, which measures total chlorides rather than sodium chloride, is used to quickly determine if the salt complies with the chemical requirements of ASTM D 632-94. The test is simple, low cost, and serves the needs of users and producers of deicing salt, particularly for continuing shipments from the same source. ASTM E 534-98 *Standard Test Methods for Chemical Analysis of Sodium Chloride*, which measures NaCl, may be used as the referee test method in cases of disagreement.

By 1996, evolving ASTM Form and Style requirements mandated that all test methods contain a precision and bias statement. In 1997, The Salt Institute initiated an interlaboratory study to provide analytical data from which to prepare a precision statement for ASTM D 632-94.

Twelve laboratories participated in the study without regard to their experience in testing salt purity. Four salt locations, each of which produced or distributed salt of slightly different purity, provided material samples meeting the grading requirements of ASTM D 632-94. The samples ranged from an estimated 92% to 99% NaCl to assure collection of data over the entire expected purity range of ASTM grade salt. Experienced laboratory technicians split, blended and ground to 300 µm (minus 50 mesh) four 27-kg (60-lb) bagged samples of rock salt. The sources of the samples were three U.S. salt mines and one U.S. salt distributor. Lab technicians packaged the split and blended samples into 0.45-kg (1-lb) containers for shipment to the twelve participating laboratories. Each laboratory received three identical samples of each of the four sample materials. This allowed three replicate tests on each sample material. Test protocol followed the requirements of ASTM C 802-96 *Standard Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials*. A combined, randomized test schedule minimized potential variations in test results due to increased operator proficiency as lab technicians conducted successive tests. Data were recorded and statistically analyzed to determine both single-operator and multilaboratory precision.

Single-operator precision for NaCl composition >95.0% indicates that two properly conducted tests by the same operator should not vary by more than 0.70%. Same operator tests conducted on NaCl of composition <94.9% and >90.0% should not vary by more than 1.21%. Multilaboratory precision for NaCl composition >95% shows that two properly conducted tests in different laboratories should not vary by more than 1.79%. Multilaboratory tests conducted on NaCl of composition <94.9% and >90.0% should not vary by more than 2.00%.

The test data provided the necessary information to write a precision statement for the test method. Variances were higher than anticipated, most likely because endpoint determination is difficult and subject to operator interpretation. The test method will be reviewed and revised to reduce variance. Particularly, significant digits in recording data must be specified, and the visual endpoint definition strengthened. However, ASTM's Rapid Test for Sodium Chloride remains a suitable procedure for routine determination of salt purity.

1. INTRODUCTION

The American Society for Testing and Materials is the preeminent standards setting organization in the United States. ASTM D 632-94 (now ASTM D 632-99) Standard Specification for Sodium Chloride, is widely used in the United States by federal, state and local government agencies to purchase deicing salt. ASTM D 632 requires minimum chemical purity of 95% NaCl. The specification covers sodium chloride from natural deposits or produced by solar or mechanical evaporation of sodium chloride brines. This paper describes a 1997 interlaboratory study based on the then-current standard specification ASTM D 632-94 (94 is the year of reapproval).

During 1999, the designated committee, ASTM Subcommittee D04.31 on Calcium and Sodium Chloride and Other Deicing Materials, revised and reapproved D 632-94. The new version, D 632-99, contains the precision statement described in this paper and the revised Rapid Test Method for Sodium Chloride. Chemical and grading requirements remain unchanged. However, the 1999 reapproved version contains editorial changes required by ASTM's Form and Style for ASTM Standards. ASTM D 632 without the reapproval date reference is used throughout this paper except where the year of reapproval is necessary for clarity.

2. ASTM D 632

ASTM D 632 recognizes two types and grades of sodium chloride. Type I must meet one of two specified sieve analyses: Grade 1 and a slightly finer Grade 2. Type II must conform to the grading requirements set by the purchaser for the intended use. For salt sampled after delivery to the buyer, each sieve size may vary by 5 percentage points (except the 12.5 mm and 9.5 mm for Grade 1, and 19.0 mm for Grade 2). The minimum chemical composition may vary by 0.5% (to 94.5%). ASTM D 632 does not contain a limit on moisture. However, it specifies that shipments must arrive at the buyer's delivery point in a "free flowing and usable condition."

2.1 Rapid Test Method

D 632's Annex A.1, Rapid Method of Analysis for Sodium Chloride is a fast, easy and low-cost test. It is used for routine control and approval to ensure that purchased salt meets ASTM D 632 chemical requirements. ASTM E 534-98 Standard Test Methods for Chemical Analysis of Sodium Chloride is a more complex test. E 532-98 is the referee method used in case of disagreement between buyer and seller.

The Rapid Method of Analysis for Sodium Chloride measures total chlorides rather than sodium chloride. Results of the test are reported as NaCl. Rock salt and solar salt sold in the United States, and elsewhere, vary in chemical purity depending on the producing location. However, salt from a particular production source is usually consistent in composition. Thus, measurement of total chlorides reliably indicates whether the material meets ASTM D 632 purity requirements.

2.2 Precision Statement

Evolving ASTM form and style requirements mandate that all ASTM test methods contain a precision and bias statement. The precision statement advises purchasers that variations in test results can occur between different laboratories and between different tests by the same operator within the same laboratory. The precision statement in ASTM D 632-94 stated that "Duplicate samples should check within 0.25% NaCl." The statement was inadequate and was not based on actual test data. Without an adequate precision statement, ASTM regulations required deletion of the Rapid Test Method from the next revision, ASTM D 632-99. A more complex and higher cost test procedure, ASTM E 534-98, would have become mandatory for determining salt purity. The loss of the Rapid Test Method would have increased analytical costs and complexity for salt users and producers, without a corresponding benefit.

3. INTERLABORATORY STUDY

To avoid the loss of the Rapid Test Method, the Salt Institute decided to conduct an interlaboratory study to obtain data with which to develop a precision statement for inclusion in the next revision of ASTM D 632-94. Twelve laboratories were selected to participate in the interlaboratory study or "round-robin." They were selected without regard to their experience in testing for sodium chloride, and were provided with detailed instructions showing how to conduct the tests in a way that would not bias the results.

3.1 Sources of the Samples

Four geographically separate sources of rock salt were chosen to assure representative data from the entire range of salt purity expected with ASTM grade salt. Three U.S. salt mines were selected based on estimated salt purity to provide samples with estimated NaCl content of 95%, 96-98%, and 99% respectively. A U.S. salt distributor provided a fourth rock salt sample with an estimated NaCl content of 92%. Solar salt was not included in the test series. The minimum purity for ASTM D 632 grade salt is 95% NaCl. A 92% NaCl grade was included in the study to ensure that enough data were gathered to determine precision over the entire range of expected salt purity (equal to or greater than 95% NaCl).

3.2 Sample Preparation

Each of the four sources providing rock salt samples was asked to prepare a single 27-kg (60-lb) bagged sample typical of ASTM grade deicing salt produced at the location. Each of the four samples was sent to one of three laboratories where the samples were prepared for shipment to the 12 laboratories participating in the study. Laboratory technicians ground each 27-kg (60-lb) sample to 300-μm (minus 50 mesh), and split and mixed the sample according to standard laboratory procedures. A technician then prepared sixty individually packaged 0.45-kg (1-lb) samples. Technicians were instructed not to dry the samples unless the salt appeared wet (as required in E 534-98).

The salt samples from each of the four different sources were identified and labeled as materials A, B, C and D. Each 0.45-kg (1-lb) sample container was individually labeled with the material identification letter (A, B, C and D), notation of the ASTM interlaboratory study, and a contact name, e-mail address, telephone and fax number. The Salt Institute provided preprinted, self-adhesive sample identification labels and mailing labels to each of the laboratories responsible for sample preparation.

Three 0.45-kg (1-lb) samples of each of the four materials (A, B, C and D) were sent to each of the twelve laboratories participating in the study. Each laboratory was instructed to perform three replicate analyses (a, b and c) on each of the four materials using the Rapid Test Method for Sodium Chloride specified in ASTM D 632-94. The production sources of the samples were identified only as A, B, C and D.

3.3 Methodology

The methodology used for the interlaboratory study is contained in ASTM C 802-96 Standard Practice for Conducting an Interlaboratory Test Program to Determine the Precision of Test Methods for Construction Materials. ASTM C 802-96 requires participating laboratories to have proper facilities and testing equipment. Laboratory technicians must have adequate experience and must be competent to run the test. However, they should not be so expert compared to typical laboratories that the results of the study are biased. The intent of ASTM C 802-96 is that laboratories and personnel are representative of conditions in which the test method will be used in actual practice.

To avoid another form of bias, a statistician prepared a written, randomized testing sequence. This test sequence assured that bias was not built into the test results due to increased operator proficiency gained as the tests were conducted in successive order.

Laboratories were instructed to conduct the test series during a few days time and to report the data exactly as specified in the Rapid Test Method. Laboratory technicians were cautioned against running a number of tests and selecting the best results or reporting the average of several determinations or discarding test data because it looked faulty. Reporting the test results exactly as they appeared was crucial to the interlaboratory study because the validity of the statistical analyses was dependent on data accurately determined by the test series. A statistician determined the validity of outliers and questionable results after the data were reported. ASTM C 802-96 requires the reporting of all individual test results, even those that appear to differ from the others by suspiciously large amounts.

Data obtained from the measurements were reported without rounding, even if it resulted in recording more digits than is customary, or more than the test method calls for. These steps were necessary because the variation in the precision of the test method is contained in the least significant digits, which are often discarded in reporting the results of routine testing. If test data were the result of calculations based on two or more measured quantities, the basic measurements were to be used in the calculations without rounding. All parameters specified in the test method were recorded on the data reporting sheet provided.

4. TREATMENT OF THE DATA

Analysis of data showed that the arithmetic means for material A, (A = 94.90%) and material B (B = 94.83%) were nearly identical. In order to keep the data balanced between the two purity ranges selected for the study, one material (A) was randomly removed and material B was selected for inclusion in the analysis (see Table 2).

Table 2
Mean NaCl Values of the Materials

Material	No. of Samples	Mean %	Std Error
A	36	94.9000	0.33797
B	36	94.8278	0.33797
C	36	98.2564	0.33797
D	36	92.0447	0.33797

Stand. Error uses a pooled estimate of error variance

ASTM D 632 requires a minimum chemical composition of 95.0% NaCl. Therefore, the two value ranges selected for comparisons were: (1) NaCl greater than 95.0%, and (2) NaCl less than 94.9% but greater than 90.0%. Initial statistical analyses of the effects of laboratories suggested that laboratory number 3 was an outlier for materials B and C, and laboratory number 2 an outlier for material D. ASTM C 670-96 requires that outliers remain in the analysis unless a valid reason exists for exclusion. Further analyses (ratio of variances, analysis of variance, etc.) confirmed both laboratories 2 and 3 as outliers. First analysis with all laboratories showed that critical ratio of high variance to sum of variance was exceeded by laboratory 3 for materials B and C, and laboratory 2 for material D (see Table 3).

Interactions were analyzed with conventional analysis of variance using materials B, C, and D and all twelve laboratories. The data confirmed that an interaction existed between laboratories and materials. These analyses provided adequate information to remove laboratory 3 from materials B and C, and laboratory 2 from material D. Low variances were not considered at this point in the analysis.

Between and within analyses (laboratory 3 removed from materials C and D and laboratory 2 removed from material D) were performed. Material B in particular appeared to be troubled with the ratio of high to sum of variances as a measure of homogeneity of variance. Calculations were made using procedures included in JMP as furnished by the SAS Institute. A similar test, but with laboratories 2 and 3 included in all analyses, confirms that variances were not homogeneous. However, in order to conduct an analysis of variance for interactions between material and laboratory, laboratories 2 and 3 were removed from all materials, leaving 10 laboratories for development of the precision statement. Removal of laboratories 2 and 3 from all materials shows variances are equal according to the JMP analysis and the same analysis shows that interactions between materials and laboratories exist.

Standard deviation appeared constant and coefficient of variation decreased with average composition of the three materials. The data (see Table 4) suggests a different coefficient of variation for composition >95% (materials B and C) versus compositions <95% and >90% (material D), at least for within-lab standard deviation. Therefore, precision statements for each case of material purity (≥95.0%, and <94.9% but >90.0%) were developed based on a relatively constant standard deviation.

5. PRECISION STATEMENT

A precision statement for ASTM D 632-99 was developed from the data. Tests conducted in

Table 3
Ratios of Variances (All Laboratories Included)

Mat'l	Sum of Variance	High Var	Lab	Ratio High:Sum	Critical	Low Var	Lab	Ratio High:Low	Critical
B	13.5616	9.3884	3	0.6923	0.5410	2.15E-04	8	43570.397	704
C	20.8527	19.8636	3	0.9526	0.5410	1.82E-12	4	1.092E+13	704
D	16.4898	12.5622	2	0.7618	0.5410	1.82E-12	7	6.906E+12	704

Table 4
Averages, Standard Deviations, and Coefficients of Variation for All Materials Included in the Analyses

Material	Average %	Standard Deviations		Coefficient of Variation	
		Within-Lab	Between-Lab	Within-Lab	Between-Lab
D	91.71	0.1823	0.8289	0.2	0.9
B	95.14	0.0840	0.6257	0.1	0.7
C	98.74	0.0421	0.7395	0.0	0.7

different laboratories, and by the same operator in the same laboratory can vary between 0.70% and 2.00%.

5.1 Single-Operator Precision – NaCl > 95.0%

(NaCl composition greater than 95.0%) – The single-operator standard deviation of a single test result for average NaCl composition above 95.0% was found to be 0.248%[1]. Therefore, results of two properly conducted tests on the same material by the same operator with the same equipment and under the same conditions should not differ by more than 0.70%[1].

5.2 Multilaboratory Precision – NaCl >95.0%

(NaCl composition greater than 95.0%) – Thje multilaboratory standard deviation of a single test result for average NaCl composition greater than 95.0% was found to be 0.633%[1]. Therefore, results of two properly conducted tests of the same material in different laboratories should not differ by more than 1.79%[1].

5.3 Single-Operator Precision – NaCl <94.9%

(NaCl composition less than 94.9% and greater than 90.0%) – The single-operator standard deviation of a single test result for average NaCl composition below 94.9% and greater than 90.0% was found to 0.427%[1]. Therefore, results of two properly conducted tests on the same material by the same operator with the same equipment and under the same conditions should not differ by more than 1.21%[1].

5.4 Multilaboratory Precision – NaCl <94.9%

(NaCl composition less than 94.9% and greater than 90.0%) – The multilaboratory standard deviation of a single test result for average NaCl composition below 94.9% and greater than 90.0% was found to be 0.711%[1]. Therefore, results of two properly conducted tests of the same materials in different laboratories should not differ by more than 2.00%[1].

Table 5
Precision of the Test Method (1s% and d2s%)

	Purity >95.0%		Purity <94.9%	
	Std. Dev.	2.83 (1s%)	Std. Dev.	2.83 (1s%)
Within	0.248	0.701	0.427	1.208
Between	0.633	1.790	0.711	2.011

6. Discussion and Recommendations

Based on the statistical analysis of data gathered from the interlaboratory study, the Rapid Test Method for Sodium Chloride has some problems in clarity or process. The titration endpoint determination is difficult and highly subjective. A single drop of silver nitrate titrant can result in a significant difference in the reported NaCl value. The buret reading must be estimated to two decimal places to assure precision. Recording of decimal places when weighing the original 10-gram samples varied between different laboratories. These variations may have affected the results of the study.

As a result of the interlaboratory study, ASTM Subcommittee D04.31 made several revisions to the test method. These revisions appear in ASTM D 632-99 and should reduce multilaboratory and single-operator variance in test results. The revisions include (1) the addition of Note A4 to the Rapid Test Method describing titration endpoint color development and the proper time to stop the titration, and (2) a requirement to estimate the titrant from the buret to the second decimal place.

[1] These numbers represent, respectively, the (1s%) and (d2s%) limits as described in ASTM Practice C 670

The Rapid Test Method should be reviewed further to determine if other changes are appropriate to reduce variations in multilaboratory and single-operator results.

However, the test, based on the results of the interlaboratory study, is completely satisfactory for determining NaCl content of continuing salt shipments from a known source. It is fast, easy to perform, and low in cost. Properly used, it can provide the salt user with the means to ensure that purchased highway salt meets the ASTM standard specification.

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