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The Determination of Chlorate in Potassium Perchlorate Pyrotechnic Material by Specific Ion Electrode

William G. Yates

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Abstract

A method for the determination of chlorate ion in potassium perchlorate was developed. The analytical method utilized a reduction of the chlorate ion to the chloride ion with ferrous ammonium sulfate. The chloride ions produced by this reduction step were then determined with a specific ion electrode technique. The amount of chlorate ion was determined by calculating how much chlorate ion was represented by the analyzed chloride ion making an appropriate adjustment for the amount of free chloride ion found in the potassium perchlorate and deionized water.

Introduction

Potassium perchlorate has been used as a basic pyrotechnic material for many years by the military. Military use requires Mil Spec P217A certification before the material can be used in a pyrotechnic product. This specification requires a variety of chemical analyses to be performed on the material to determine if certain contaminants are below acceptable limits established by the specification. One such analysis is the determination of chlorate ion as potassium chlorate.

The military specification analysis for chlorate ion is time-consuming, somewhat antiquated, and limited because it has not been current with modern methods. Secondly, the procedure employed uses a gravimetric method. Gravimetric methods have a high degree of accuracy provided an adequate weight of the precipitate can be obtained. Previous experience with this procedure indicated minute amounts of chlorate to chloride precipitate. This affected the method's overall application for the determination of chlorate in terms of accuracy and precision. A need was felt to develop a new technique without sacrificing accuracy and precision and perhaps improving the lower detection limit for chlorate.

Specific ion electrodes have become acceptable in the analytical field as a powerful tool for determining a variety of trace contaminants. The solid state "Orion model 94-17A electrode" for the detection of the chloride ion is one such example. This specific ion electrode was used in the development of this analysis.

The essence of the military specification procedure is: (1) dissolution of the potassium perchlorate ($KClO_4$) with water, (2) a reduction of the potassium chlorate ($KClO_3$) to potassium chloride (KCl) with ferrous ammonium sulfate $(NH_4)Fe(NH_4)(SO_4)_2 \cdot 6H_2O$, and (3) precipitation of the KCl with silver nitrate $AgNO_3$.

The new method incorporates step (1) and (2) of the old method but then the ionized KCl is measured for chloride ion content with the specific ion electrode. Appropriate adjustment for free Cl^- content in the $KClO_4$ is made. This value is subtracted from the measured Cl^- produced in the reduction step. The difference obtained represents the chloride ion produced by the $KClO_3$ in the reduction step. Back calculations are made to determine how much chlorate ion is represented by this chloride ion value and how much $KClO_3$ is representative of the calculated ClO_3^- value. The value is then reported as weight percent $KClO_3$ as required by the military specification.

The new method provides these more desirable aspects:

1. Analysis time is cut one-third.
2. Very small quantities of ClO_3^- via reduction with $(NH_4)Fe(NH_4)(SO_4)_2 \cdot 6H_2O$ can be made. Detection limit of the method is 1 µg Cl/ml.
3. No accuracy or precision is lost with the new method.

Experimental

The first problem was to determine the amount of ferrous ammonium sulfate that would effectively reduce the chlorate ion present in the potassium perchlorate. Experiments were designed to evaluate the amount needed. Known standards of $KClO_3$ were made up. Theoretical calculations were computed to ascertain how much Cl^- would be produced by the reduction of $ClO_3^- \rightarrow Cl^-$ in the standards used. Different concentrations of ferrous ammonium sulfate solution were used to reduce the known $KClO_3$ standards. After reduction of the $KClO_3$, the known standards were analyzed for Cl^- with the specific ion electrode for Cl^-. Experimental data showed that a 0.4% ferrous ammonium sulfate solution did not adequately reduce the $KClO_3$. Solutions of 0.8%, 1.6%, 2.0%, and 2.5% produced sporadic and imprecise data generally on the low side of the calculated theoretical value of Cl^- (see Table 1).

At this point a different approach was taken. Observation of the different concentrations of the $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ solutions indicated that oxidation of the Fe^{+2} ions to Fe^{+3} ions was occurring immediately upon preparation of the aqueous solutions. The visual change in color is quite noticeable. Fe^{+2} ions in aqueous

Table 1

EXPERIMENTAL DATA FROM VARIOUS AMOUNTS OF FERROUS AMMONIUM SULFATE REDUCTIONS

Sample 10 µg/ml $KClO_3$	Theoretical Cl^- when reduced µg/ml	Amount Cl^- Analyzed µg/ml	$KClO_3$ Blank Cl^-
	0.4% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		
1	2.5	1.9	0.35
2	2.5	1.6	0.35
3	2.5	1.0	0.35
4	2.5	1.3	0.35
5	2.5	1.4	0.35
	0.8% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		
6	2.5	1.3	0.35
7	2.5	1.7	0.35
8	2.5	1.6	0.35
9	2.5	1.6	0.35
10	2.5	1.8	0.35
	1.6% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		
11	2.5	2.0	0.35
12	2.5	1.9	0.35
13	2.5	1.9	0.35
14	2.5	1.0	0.35
15	2.5	1.4	0.35
	2.0% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		
16	2.5	2.1	0.35
17	2.5	1.9	0.35
18	2.5	1.8	0.35
19	2.5	1.9	0.35
20	2.5	1.7	0.35
	2.5% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$		
21	2.5	2.2	0.35
22	2.5	1.8	0.35
23	2.5	1.9	0.35
24	2.5	1.9	0.35
25	2.5	2.0	0.35

media are pale green while Fe^{+3} ions are yellow-orange in color. Therefore, it was decided to add solid $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ directly to the aqueous solution containing ClO_3^- ions.

After much experimentation with different amounts of solid $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ (0.5, 0.7, 1.0, 1.5, 2.0, 2.5 g quantities), it was found that a 2.5 g quantity of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ in a 100 ml standard solution of 10 µg/ml $KClO_3$ effectively reduced the ClO_3^- to the theoretical value of Cl^- expected.

However, day to day reductions still indicated the presence of irregularities. Some experiments produced excellent recoveries of the reduced Cl^- while others produced precision and recovery problems. Since excellent results were produced in a majority of the experiments, the irregularity was not believed to be the reducing agent $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. Consideration was given to the range of the standard curve. Normally in a Cl^- determination by specific ion electrode, a calibration curve of the range of 10^{-5} M to 10^{-1} M (0.35 µg/ml - 3500 µg/ml Cl^-) is used, yet experiments thus far in the development of the analysis were utilizing approximately 10^{-5} M to 3 x 10^{-4} M (0.35 µg/ml to 10 µg/ml Cl^-) range. This is approximately 25% of 10^{-5} M to 10^{-1} M range. Secondly, observation of the portion of the curve (10^{-5} M to 3 x 10^{-4} M)

indicates that this part of the range represents the exponential part of the curve. Experiments have shown that results calculated from this portion of the curve are subject to less precision than from the linear part of the curve. Thus, it follows that Cl^- values produced by the reduction of ClO_3^- and calculated from this portion of the curve would be imprecise. This in turn would directly affect the recovery value of Cl^- when compared to the expected theoretical value of Cl^- produced by reduction of the ClO_3^- ion.

Two alternatives existed to resolve the problem. Either use a large enough sample of $KClO_4$ in the actual analysis to locate on the linear portion of the curve, or expand the 10^{-1} M to 3×10^{-4} M exponential portion to a full graph and attempt to eliminate as many factors contributing to the imprecision as possible. It appears that of the alternatives, the former would be the better approach. However, other problems are created with this choice: (1) $KClO_4$ has a low solubility in water 0.7 g/100 cc at room temperature, (2) previous analysis of ClO_3^- by Mil Spec P217A indicated very small amounts of ClO_3^- (0.05% to nondetectable), thus a very large sample of $KClO_4$ in a very large volume of water would be necessary to place the reduced Cl^- in the linear section of the calibration curve, (3) analyses of the chlorate ion are run in triplicate thus requiring more $KClO_4$, and (4) taking such a large sample for analysis is not in accord with production plans since only so much of the sample is allocated for analysis and the ClO_3^- analysis is one of many such analyses needed to certify the material.

It was decided to approach the problem from the standpoint of using an expanded portion of the calibration curve and optimize its feasibility as a working curve. One cycle semilog graph paper with standards of 1, 2, 4, 6, 8, 10 µg/ml Cl^- was chosen to draw the calibration curve. This differs from the normal curve which uses 4 cycle semilog graph paper with chloride standards of 0.35 - 3500 µg/ml. See examples of the graphs in Figures 1 and 2.

Because of the nonlinearity in this portion of the curve, potential readouts of the standards vary significantly from day to day and potential readouts take longer to stabilize. These two factors greatly influence the ability to draw a smooth curve through the standard solution potentials. It became imperative to control the operator and instrumental variables that would influence stability and precision. Stirring rates, temperature, depth and position of the electrodes in the solution and stirring bar position in the beaker were kept as constant as possible. At this point, the procedure became more of an art, than a mechanical operation.

After these variables were optimized, experiments were designed to evaluate the method for its application. The first experiment was designed to determine the amount of free Cl^- in the $KClO_4$ and $KClO_3$ to be used in the development of the analysis. Reagent grade $KClO_3$ was used. The $KClO_4$ was a special high purity material. Free chloride analyses of these materials were 0.35 PPM Cl^-.

The next series of experiments was designed to determine the optimum calibration curve to use in the experiment. Four curves were evaluated. They contained the following constituents:

1. known chloride standards (1 - 10 µg/ml) without ionic strength adjustment (ISA)

2. known chloride standards (1 - 10 µg/ml) with ISA

3. known chloride standards (1 - 10 µg/ml) with ferrous ammonium sulfate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$)]

4. known chloride standards with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and with ISA

A series of known chlorate ion standards and other standards were used as samples to be evaluated by each curve. All samples and standards were in 100 ml volumes.

The numerical value of the chloride ion in samples 1 to 6 represent the theoretical value of chloride ion produced when a ClO_3^- standard is reduced with 2.5 g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$. The samples are listed below and shown with data in Table 2.

Samples 1 and 2 - 1.5 µg Cl^-/ml

Samples 3 and 4 - 2.9 µg Cl^-/ml

Samples 5 and 6 - 5.8 µg Cl^-/ml

Sample 7 - Containing 10 µg ClO_3^-/ml but not reduced

Samples 8 and 9 - Containing 10 µg ClO_3^-/ml + 2.5 µg Cl/ml

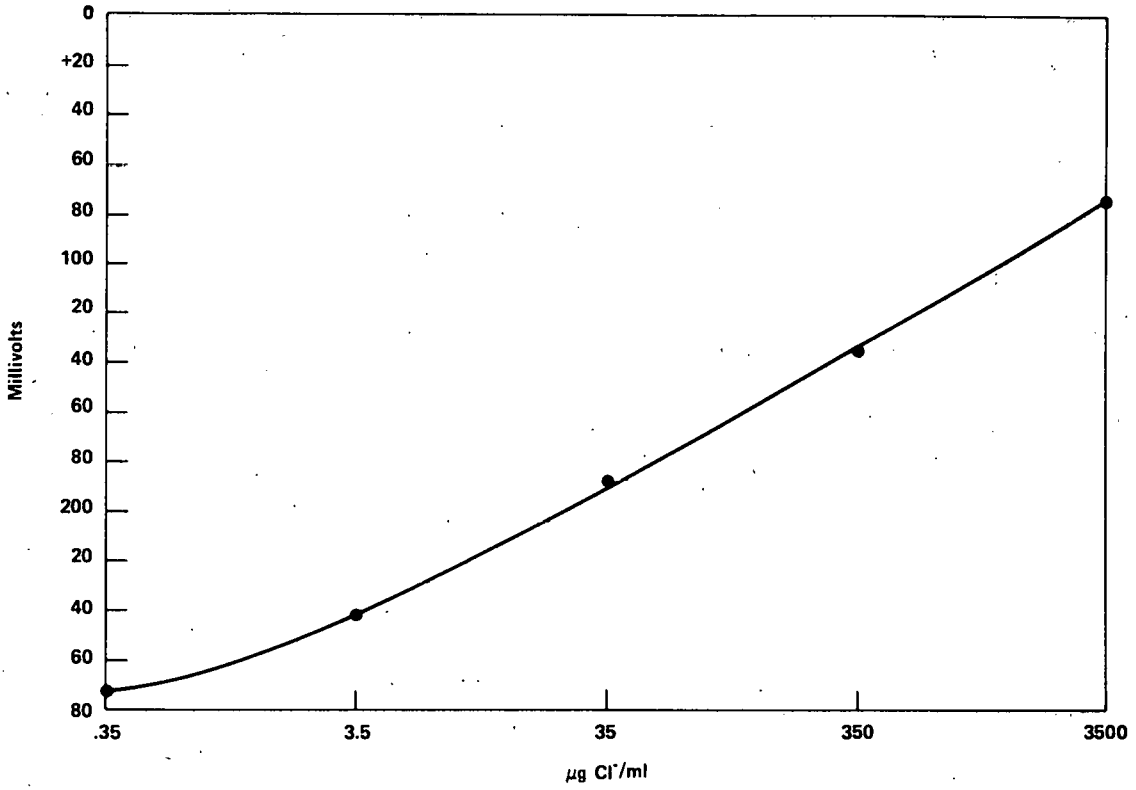

FIGURE 1 - Normal operating curve.

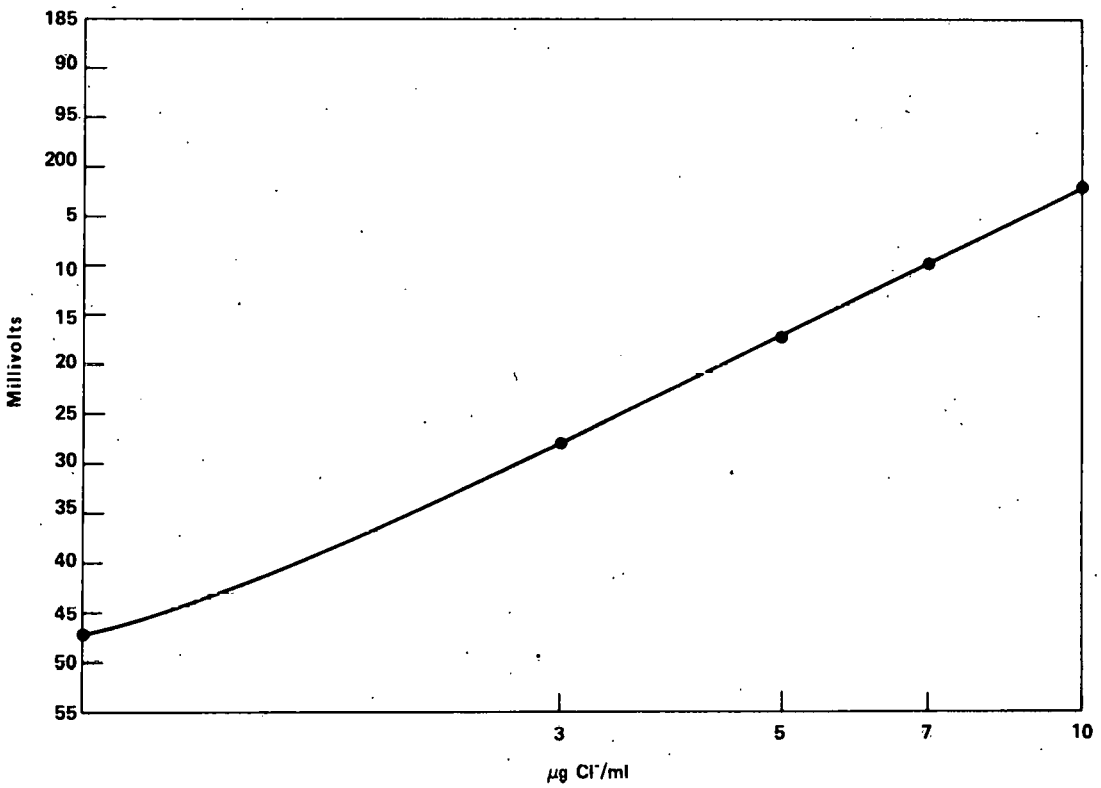

FIGURE 2 - Expanded calibration curve with $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ and ionic strength adjustment.

Table 2

OPTIMIZATION EXPERIMENT*

Sample Numbers	#1 Calibration Curve with no ISA Amount Added Cl^-	#1 Calibration Curve no Fe^{+2} Amount Found Cl^-	#2 Calibration Curve with ISA Amount Added Cl^-	#2 Calibration Curve no Fe^{+2} Amount Found Cl^-	#3 Calibration Curve with Fe^{+2} Amount Added Cl^-	#3 Calibration Curve No ISA Amount Found Cl^-	#4 Calibration Curve with Fe^{+2} Amount Added Cl^-	#4 Calibration Curve ISA Amount Found Cl^-
1	1.5	0	1.5	1.4	1.5	1.7	1.5	1.7
2	1.5	0	1.5	1.5	1.5	1.8	1.5	1.7
3	2.9	1.7	2.9	2.4	2.9	2.7	2.9	3.0
4	2.9	1.4	2.9	2.5	2.9	2.6	2.9	3.0
5	5.8	4.5	5.8	5.1	5.8	5.8	5.8	5.9
6	5.8	4.5	5.8	5.1	5.8	5.8	5.8	6.0
7	0	<1.0	0	<1.0	0	<1.0	0	<1.0
8	2.5	2.8	2.5	3.6	2.5	2.8	2.5	2.9
9	2.5	2.7	2.5	3.6	2.5	2.8	2.5	2.9
10	5.4	4.0	5.4	4.7	5.4	5.3	5.4	5.8
11	5.4	4.0	5.4	4.7	5.4	5.3	5.4	5.8

*Values shown are µg/ml

10 µg ClO_3^-/ml standard, when reduced gives 2.9 µg Cl^-/ml

Samples 10 and 11 - Containing 10 µg ClO_3^-/ml + 2.5 g Cl^-/ml spike and reduced.

The chloride ion values for all samples were calculated from each curve and the results compared. Sample 7 was a running check for free Cl^- in $KClO_3$. Samples 8 and 9 were run to check Cl^- recovery when spiked with a known chloride value and run through the procedure except for reduction. The purpose of 8 and 9 was to see if the electrode could accurately measure the chloride ion spike without the reduction step. Samples 10 and 11 were run to ascertain recovery of the Cl^- when reduced with ferrous ammonium sulfate plus with a known spike of Cl^- standard. The purpose of 10 and 11 was to determine if the electrode could sense accurately, the cumulative chloride ion values produced by the reduced $KClO_3$, and the known spike of chloride ion. Secondly, samples 10 and 11 would represent every possible source of chloride ion present in the samples. Samples 1, 2, 3, 4, 5, 6, 10, and 11 were reduced with 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$.

Under the amount-found column of Curve #1, the results indicated a general low on all samples analyzed. Note particularly the absence of Cl^- values in samples 1 and 2. In the amount-found column of Curve #2 with ISA present, there is somewhat of an improvement but the values in general are still low. Curve #3 is more representative of the theoretical values expected, but indicated a tendency to be low in Samples 3, 4, 10, and 11. In Curve #4, the optimum results achieved are shown. Generally all values are higher than the amount added to each sample, but this positive bias can reasonably be explained by the value of Sample 7 (ClO_3^- standard of free Cl^-). This value was lower than the lowest standard of 1 µg Cl^-/ml. The value could range from 0-1 µg Cl^-/ml being limited directly by the lowest standard used. Yet its Cl^- value, whatever its true value is, contributes positively to the overall Cl^- value in the samples. It is reasonably accurate to assume that curve #4 with the reducing agent and ISA presented the optimum curve for the analysis. This fact was further substantiated by the next series of experiments.

The next series of experiments contained the following species: (results and comparisons are listed in Table 3.)

Samples 1, 2, and 3 - 0.7 g $KClO_4$ + 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$

Samples 4, 5, and 6 - 0.7 g $KClO_4$ + 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ + 10 µg $KClO_3$/ml note, when 10 µg ClO_3^-/ml is reduced it = 2.9 µg Cl^-/ml theoretically

Samples 7, 8, and 9 - 0.7 g $KClO_4$ + 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ + 5 µg Cl^-/ml

Sample 10 - $KClO_3$ only

Sample 11 - 10 µg/ml $KClO_3$ + 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ free chloride analysis reagent grade $KClO_3$ ≤0.35 µg/ml Cl^-

Calibration curve - 2.5 g $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ + 2 ml of 1M KNO_3 ISA (ISA calculated on the basis 0.7 g $KClO_4$ sample)

Results of sample 1, 2, and 3 determinations show a Cl^- content of less than 1.0 µg/ml Cl^-. Previous free Cl^- analysis of this particular $KClO_4$ indicated a Cl^- content of <0.35 µg/ml Cl^-. Since this less-than number is totally dependent on the smallest standard used in the calibration curves it cannot be assumed that the difference between the <0.35 and <1.0 is due to reduction of $KClO_3$ to KCl, present in the reagent grade $KClO_4$. Rather, the better view is that if $KClO_3$ is present, it must be reported as a less-than value of the lowest standard used.

Samples 4, 5, and 6 indicated an average of 4 µg/ml Cl^-. Theoretical reduction of 10 µg $KClO_3$/ml gives 2.9 µg Cl^-. Add to this the $KClO_3$ free chloride of <1.0 µg Cl^-/ml plus the <1.0 figure found for $KClO_4$ reduction with Fe^{+2}, the 4.0 µg Cl^-/ml is a reasonably accurate number.

Table 3

FINAL COMPOSITE EXPERIMENT FOR CHLORIDE ($KClO_4$ and $KClO_3$)

Sample Number	µg Cl^-/ml Added	µg Cl^-/ml Found
1	0	<1.0
2	0	<1.0
3	0	<1.0
4	<1.0 + 2.9	4.0
5	<1.0 + 2.9	4.0
6	<1.0 + 2.9	3.9
7	5 + 1.0	5.5
8	5 + 1.0	5.5
9	5 + 1.0	5.3
10	0	<1.0
11		3.2

Samples 7, 8, and 9 contained 5 µg/ml Cl^- spiked plus Fe^{+2}. The resulting average of 5.4 µg/ml Cl^- when compared with the theoretical 5.0 + <1.0 indicates a reasonably accurate recovery. Sample 11 gave a chloride value of 3.2 µg. The theoretical chloride value of 3.3 compares favorably with the amount analyzed for chloride in sample 11.

Summary

$KClO_3$ contamination in $KClO_4$ can be analyzed accurately. The reduction of the $KClO_3$ to KCl via ferrous ammonium sulfate and subsequent determination of the ionized chloride ion by specific ion electrode is a quick and accurate method for the determination of ClO_3^-.

The development work for determining $KClO_3$ in $KClO_4$ is fully developed and a viable analysis for routine ClO_3^- determination in $KClO_4$ now exists. It is hoped that this procedure can be incorporated into the Mil Spec P217A for the following reasons:

1. Chloride and chlorate ion analyses can be determined consecutively, thus saving time in actual analyses.
2. The original chloride ion analysis required 5 g of $KClO_4$/sample and the original chlorate ion sample required 5 g $KClO_4$/sample. This method requires only 0.7 g $KClO_4$.
3. The specific electrode method is more sensitive and can work with much smaller values of Cl^- than the original gravimetric method.
4. Time required for analysis is reduced from 16 hr (2 work days) to 4 hr.
5. Detection limit of this method is 1 µg/ml Cl^-.

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