



## Project Summary

# Improved Methods of Analysis for Chlorate, Chlorite, and Hypochlorite Ions at the Sub-mg/L Level

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A comparison is given of existing analytical methods for the oxyhalogen species, including chlorate ion, chlorite ion, and hypochlorous acid/chlorine. Known limitations of the methods and lower limits of analysis are discussed. New and improved precise methods of analysis for low level ( $<1$  mg/L) measurement of oxychlorine species including chlorate and chlorite ions are given. Advantages and disadvantages of speciation are noted.

A modified iodometric method is reported to measure chlorate ion concentration down to the sub-mg/L level with high precision and accuracy. Hexane and nitrogen are used as shielding agents to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. Chlorate ion is reduced by iodide ion in 6M hydrochloric acid. By the addition of saturated sodium phosphate, the hydrogen ion concentration is lowered to approximately 3M, and the liberated iodine is titrated with standard sodium thiosulfate solution. The endpoint is detected using Thyodene as the indicator or by the color of iodine in the hexane layer. A potentiometric endpoint is recommended for the determination of chlorate ion at concentrations less than  $1.0 \times 10^{-4}$  N (3.5 mg/L reported as chlorine). By this modified iodometric method, the chlorate ion down to the sub-mg/L level can be determined with a precision of better than  $\pm 1\%$  with a lower detection limit of 0.1 mg/L. The method is proposed as a standard baseline method of analysis.

An analytical method is reported to determine hypochlorite, chlorite, and chlorate ions in a mixture at the sub-mg/L level. Chlorate ion is determined directly by a modified iodometric method in which hexane, along with nitrogen gas, is used as a shielding agent to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. A saturated sodium phosphate solution is used to partially neutralize the acidic sample solution just before titrating. Chlorite ion is determined directly by the modified Suzuki-Gordon method where free residual chlorine (chlorine and hypochlorous acid) is converted to hypochlorite ion which in the mixture, is reduced to chloride ion by sulfite ion at pH 10.5. Following this oxidation, the chlorite ion followed by the oxidation of excess sulfite ion by iodine is reduced to chloride ion by iodide ion at pH 2. Hypochlorite ion is determined indirectly from the results of the modified iodometric method and the modified Suzuki-Gordon method. The titration endpoint is determined directly from the first derivative titration curve obtained by a potentiometric method. The overall precision is  $\pm 3\%$  for oxychlorine species at concentrations in the range of 0.3-100 mg/L with lower detection limits of 0.1 mg/L.

*This Project Summary was developed by EPA's Environmental Monitoring and Support Laboratory, Cincinnati, OH, to announce key findings of the*

research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

## Introduction

Methods for the chemical analysis of solutions of the chlorine-containing oxidizing agents above the 3 mg/L appear to be well defined in the chemical literature. In the 1979 update of "Drinking Water and Health," the National Academy of Science estimated acceptable exposure values of 0.38 mg/L for chlorine dioxide and 0.21 mg/L for chlorite ion. Later in 1979, the *Federal Register* published restrictions which should be placed on the level of residual oxidants such as chlorine dioxide and the chlorite and chlorate ions which result from the chlorine dioxide treatment of water to be used as drinking water.

In early 1980 none of the analytical techniques in the literature for the analysis of chlorine-containing oxidizing agents were capable of routinely determining chlorate ion concentrations down to the sub-mg/L level.

## Results

### Determination of Chlorate Ion at the Sub-mg/L Level

This is made possible by a modified iodometric method in which preferably hexane and nitrogen gas are used as shielding agents to prevent air oxidation of iodide ion. Chlorate ion is reduced by the iodide ion in 6M hydrochloric acid. In addition, saturated sodium phosphate solution is used to partially neutralize the acidic sample solution prior to the actual titration. The liberated iodine is titrated with standard thiosulfate solution. The endpoint is detected potentiometrically using the homemade combination Redox electrode as shown in Figure 1. The precision is better than  $\pm 5\%$  down to the sub-mg/L level.

The results are shown in Table 1 and indicate that the determination of chlorate ion in concentrations greater than  $1.0 \times 10^{-4}$  is possible by using this modified iodometric method—with appropriate blank corrections. In these experiments, time-dependent measurements show that chlorate ion is quantitatively reduced by iodide ion within 20 minutes. The reproducible blank volume correction is necessary since it corresponds to 0.0-5.0% of the sample titration volume. This result indicates that the air oxidation of iodide ion is effectively minimized by using hexane as a shielding agent and by

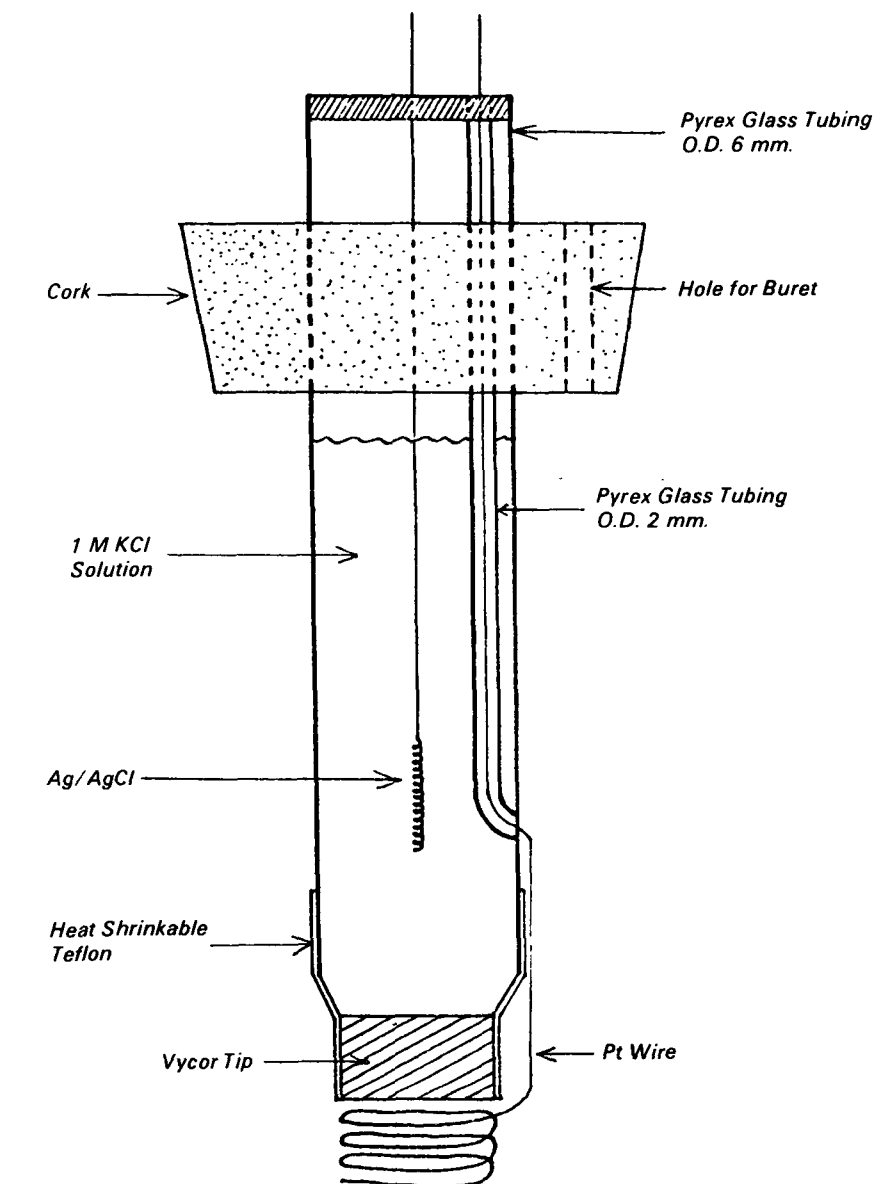


Figure 1. Combination redox electrode.

neutralization of the sample solution by the addition of a deaerated saturated solution of sodium phosphate.

On the basis of these results, the determination of chlorate ion at the level of  $1.0 \times 10^{-5}$  N (0.35 mg/L) was studied by using the same procedure. However, the color of iodine in the hexane layer is a very pale pink at this concentration level; hence the endpoint could not be detected correctly and reproducibly.

In order to improve the disadvantages inherent in the optical endpoint method described above for more concentrated solutions containing chlorate ion ( $< 1.0 \times$

$10^{-4}$  M  $\text{ClO}_3^-$ ), the potentiometric titration method was modified.

With lower chlorate ion concentrations, the reaction between chlorate ion and iodide ion requires 40 minutes for completion. The endpoint was detected from the first derivative titration curve. The results for solutions containing  $1.011 \times 10^{-5}$  equivalents per liter of chlorate ion were determined with a precision of  $\pm 1\%$ .

### Determination of Mixtures of Chlorate and Chlorite Ions

The concentrations of chlorite and chlorate ions are determined directly and

continuously on a single sample thus minimizing cumulative errors. Two successive titrations are followed potentiometrically with an internal precision and accuracy of better than  $\pm 2\%$ . Typical results are shown in Table 2.

### Determination of Hypochlorite, Chlorite, and Chlorate Ions in Mixtures at the Sub-mg/L Level

An analytical method is reported to determine hypochlorite, chlorite, and chlorate ions in a mixture at the sub-mg/L level. Chlorate ion is determined directly by a modified iodometric method in which hexane along with nitrogen gas is used as a shielding agent to isolate the sample solution from the air phase to prevent air oxidation of iodide ion. A saturated sodium phosphate solution is used to partially neutralize the acidic sample solution just before titrating. Chlorite ion is determined directly by the modified Suzuki-Gordon method where free residual chlorine (chlorine and hypochlorous acid) is converted to hypochlorite ion which in the mixture is reduced to chloride ion by sulfite ion at pH 10.5. Following this oxidation, the chlorite ion followed by the oxidation of excess sulfite ion by iodine is reduced to chloride ion by iodide ion at pH 2. Hypochlorite ion is determined indirectly from the results of the modified iodometric method and the modified Suzuki-Gordon method. The titration endpoint is determined directly from the first derivative titration curve obtained by a potentiometric method. A derivative endpoint curve is shown in Figure 2. The overall precision is  $\pm 3\%$  for oxychlorine species at concentrations in the range of 0.3-100 mg/L with lower detection limits of 0.1 mg/L. Typical results are shown in Table 3.

### Endpoint Determination

The potentiometric titration method is recommended for each of the determinations at low concentration levels (especially below 1 mg/L) because the blank is relatively small and no subjectivity by the investigator is involved.

**Table 1.** Determination of Chlorate Ion by the Modified Iodometric Method Using Hexane as a Shielding Agent

Sample	Equiv/L $\text{ClO}_3^-$ added	Equiv/L $\text{ClO}_3^-$ found <sup>a</sup>	% Error
1	$1.002 \times 10^{-1}$	$(1.007 \pm 0.001) \times 10^{-1}$	$0.5 \pm 0.1$
2	$1.031 \times 10^{-2}$	$(1.033 \pm 0.005) \times 10^{-2}$	$0.2 \pm 0.5$
3	$5.035 \times 10^{-3}$	$(5.03 \pm 0.08) \times 10^{-3}$	$0.1 \pm 0.6$
4	$2.609 \times 10^{-3}$	$(2.60 \pm 0.03) \times 10^{-4}$	$0.4 \pm 0.5$
5	$6.194 \times 10^{-4}$	$(6.21 \pm 0.07) \times 10^{-4}$	$0.2 \pm 0.8$
6	$1.011 \times 10^{-4}$	$(1.00 \pm 0.02) \times 10^{-4}$	$1.1 \pm 1.0$

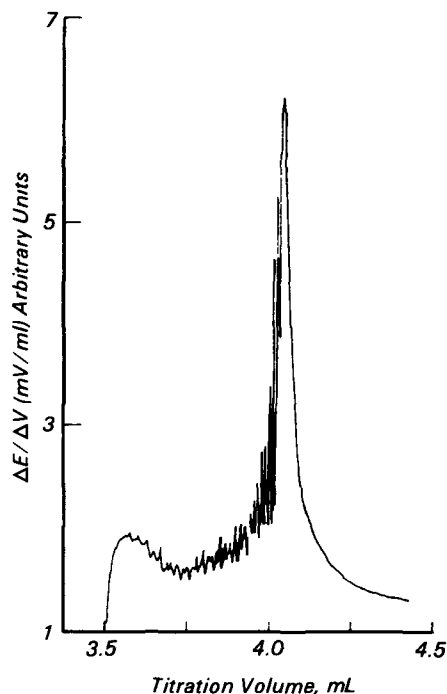
<sup>a</sup>The uncertainties represent the standard deviation from the mean for eight replicate samples except for samples 3 and 5 which consisted of nine replicates.

**Table 2.** Determination of Chlorite and Chlorate Ion Concentrations in Synthetic Mixtures

mg/L $\text{ClO}_2^-$ added $\times 10^{-5} \text{ N}$	mg/L $\text{ClO}_2^-$ found <sup>a</sup> $\times 10^{-5} \text{ N}$	mg/L $\text{ClO}_3^-$ added $\times 10^{-5} \text{ N}$	mg/L $\text{ClO}_3^-$ found <sup>†</sup> $\times 10^{-5} \text{ N}$
Single Sample Method			
0.9613	$0.955 \pm 0.024$	0.9957	$0.983 \pm 0.031$
3.384	$3.415 \pm 0.072$	0.9194	$0.911 \pm 0.028$
0.9025	$0.911 \pm 0.021$	3.948	$3.93_0 \pm 0.08_0$
1.763	$1.751 \pm 0.036$	1.873	$1.89_1 \pm 0.04_8$

<sup>a</sup>The uncertainties represent the standard deviation from the mean for eight replicate determinations.

<sup>†</sup>All numerals dropped below the line indicate less than total confidence in their absolute value, as determined.



**Figure 2.** Derivative endpoint curve.

**Table 3.** Determination of Various Oxychlorine Species in Synthetic Mixtures

	<i>Equiv/L HOCl x 10<sup>-6</sup> N</i>	<i>Equiv/L ClO<sub>2</sub><sup>-</sup> x 10<sup>-6</sup> N</i>	<i>Equiv/L ClO<sub>3</sub><sup>-</sup> x 10<sup>-6</sup> N</i>	<i>Aggregate Oxid. Power</i>
<i>added</i>	100.5	119.1	100.3	319.9
<i>found</i>	99.6	120.0	101.7	321.3
<i>% error</i>	0.9%	0.8%	0.4%	0.4%
<i>added</i>	8.741	9.613	9.957	28.311
<i>found</i>	8.60 <sub>1</sub>	9.81 <sub>4</sub>	9.78 <sub>6</sub>	28.20
<i>% error</i>	1.6%	2.1%	1.7%	0.4%

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*The complete report, entitled "Improved Methods of Analysis for Chlorate, Chlorite, and Hypochlorite Ions at the Sub-mg/L Level," (Order No. PB 86-118 684/AS; Cost: \$9.95, subject to change) will be available only from:*

*National Technical Information Service*

*5285 Port Royal Road*

*Springfield, VA 22161*

*Telephone: 703-487-4650*

*The EPA Project Officer can be contacted at:*

*Environmental Monitoring and Support Laboratory*

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