

## Thermo. Titr. Application Note No. H-033

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| <b>Title:</b> | <b>Determination of Low Levels of Chloride in Water</b> |
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| <b>Scope:</b> | Determination of low levels of chloride (to approximately 5 mg/L Cl <sup>-</sup> ) by thermometric titration. |
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| <b>Principle:</b> | Chloride in acidified solution is precipitated by reaction with standard silver nitrate solution. A direct titration down to at least 20 mg/L Cl <sup>-</sup> is possible with samples of natural water. With care, the lower limit can be extended to 15mg/L. For samples where the chloride content is in the range 5 – 20mg/L automated addition of a chloride „spike“ solution is used. |
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| <b>Reagents:</b> | 0.1 mol/L silver nitrate solution<br>5 mol/L nitric acid solution<br>~1000mg/L chloride “spike” solution. Weigh ~1.649g NaCl, and make to 1000mL with DI water in a volumetric flask. |
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**Method:**

## Basic Experimental Parameters:

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| Titrant delivery rate (mL/min.)           | 2   |
| No. of exothermic endpoints               | 1   |
| Data smoothing factor                     | 30  |
| Stirring speed (802 stirrer)              | 6   |
| Delay before start (secs.)                | 120 |
| *Pre-dose chloride spike solution (mL)    | 5*  |
| <i>*for samples &lt;20 mg/L chloride*</i> |     |

*For chloride levels >20 mg/L:* Pipette 50mL water into a titration vessel freshly rinsed with chloride-free DI water. Add 1mL 5 mol/L nitric acid solution. Titrate to a single thermometric endpoint.

*For chloride levels 5 – 20 mg/L:* Pipette 50mL water into a titration vessel freshly rinsed with chloride-free DI water. Add 1mL 5 mol/L nitric acid solution. Titrate to a single thermometric endpoint. Utilize a titration program which adds 5mL of chloride “spike” solution from a slave Dosino prior to commencement of titrant addition.

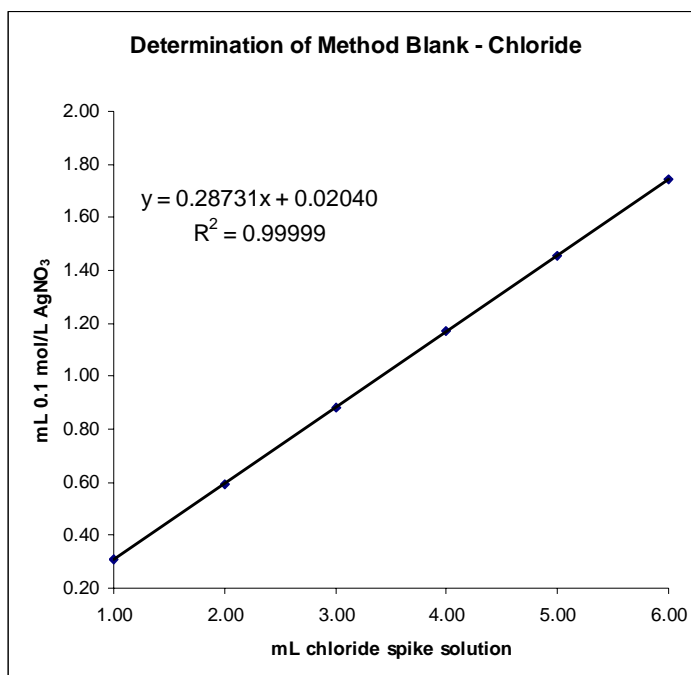
*A delay of 120 seconds is programmed to permit vessel contents to thoroughly equilibrate with respect to temperature prior to commencement of the titration. This time may be reduced with further experience with the method.*

| <b>Example:</b>   |                    |                                     |                         |                      |
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| <p><i>Different samples of waters were obtained from a supermarket, and compared to a sample of tap water</i></p> <p><i>*Published data from Brisbane Water for February 2006</i></p> | Brand              | mg/L chloride                       |                         |                      |
|   |                    | Typical analysis claimed (on label) | Titration without spike | Titration with spike |
|   | Brisbane tap water | *32 -36                             | 37.1±0.1 (n=6)          |                      |
|   | Home Brand         | 20.0                                | 19.6±0.2 (n=5)          |                      |
|   | Dancing            | 16.0                                | 17.4±0.3 (n=5)          |                      |
|   | Nuqua              | 90.0                                | 96.9±0.3 (n=5)          |                      |
|   | Mount Franklin     | 12.8                                | 20.7±0.2 (n=5)          |                      |
|   | Grandoz            | 14                                  | 15.0±0.5 (n=5)          | 14.9 (n=3)           |
|   | Crystal Waters     | 7                                   | 30.5±0.3 (n=5)          | 30.6±0.4 (n=5)       |
|   | Aqua 1             | 4                                   |                         | 5.6±0.3 (n=5)        |

| <b>Calculation:</b>   |
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| $\text{mg/L Cl}^- = ((\text{titre-blank}) * \text{mol/L AgNO}_3) * 35.4527 * 1000 / 50$ |

| <b>Determination of method blank:</b>   |
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| <p><i>For titrations without spike:</i> Using a Dosino, dispense aliquots of 6, 5, 4, 3, 2 and 1 mL ~1000 mg/L chloride solution into a titration vessel containing 50 mL DI water and 1 mL 5 mol/L nitric acid solution prior to titrating with standard silver nitrate solution. Plot mL of chloride solution (x-axis) against mL 0.1 mol/L silver nitrate solution (y-axis). Determine the y-intercept by regression analysis, and use this as the method blank.</p> <p><i>For titrations with spike:</i> Using a Dosino, dispense an aliquot of 5 mL of ~1000 mg/L chloride solution into a titration vessel containing 50 mL DI water and 1 mL 5 mol/L nitric acid solution prior to titrating with standard silver nitrate solution. Perform this determination 5 times. Take the mean titre as the method blank.</p> |

**Determination of method blank (titrations without chloride spike):**



**Thermometric Titration Plot:**

**Titration of „Grandoz“ brand water, 15.0 mg/L, analyzed without addition of chloride spike**

**Legend:**  
 Red = solution temperature curve  
 Black = second derivative curve

