NOMOGRAM FOR CORRECTION OF LOW URINE CHLORIDE VALUES DETERMINED BY THE SILVER IODATE REACTION

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Sendroy (1–3) pointed out in his original papers on the determination of chloride by the reaction, $\text{AgIO}_3 + \text{Cl}^- \rightleftharpoons \text{AgCl} + \text{IO}_3^-$, that the $\text{IO}_3^-$ formed reduces the $\text{AgIO}_3$ solubility to a negligible value in analyses of plasma, and of urines except those with unusually little chloride. Sendroy ((1) Fig. 2) gave a curve of corrections for $\text{AgIO}_3$ solubility at 20–25°, for use in analyses of low chloride urines. The temperature solubility curves of Van Slyke and Hiller ((4) Fig. 1) afford a basis for estimating the corrections at temperatures varying over the maximal range of laboratory conditions. In accurate measurements of chloride balances of subjects with minimal excretions it has been found that, even when the 5-fold increased samples of urine recommended for such cases (4) are used, the corrections can become significant, especially with high summer temperatures.

The corrections are calculated by Equation 16 of Sendroy (1), viz

$$[\text{Cl}]_t = 1.0043[\text{IO}_3^-]_e - \frac{K_{\text{AgIO}_3}}{[\text{IO}_3^-]_e}$$

$[\text{Cl}]_t$ is the chloride concentration of the solution that is shaken with $\text{AgIO}_3$; $[\text{IO}_3^-]_e$ is the dissolved $\text{IO}_3^-$ concentration at the end of the reaction between $\text{AgIO}_3$ and $\text{Cl}^-$; and 0.0043 is the ratio $K_{\text{AgCl}} : K_{\text{AgIO}_3}$, where $K_{\text{AgCl}}$ and $K_{\text{AgIO}_3}$ are the millimolar solubility coefficients of $\text{AgCl}$ and $\text{AgIO}_3$ respectively. The ratio of the solubility coefficients remains near enough to 0.0043 over the range of room temperature to make the temperature effect negligible on the factor 1.0043. However, the effect of temperature on $K_{\text{AgIO}_3}$ is such that the solubility correction, represented by the term, $- K_{\text{AgIO}_3} / [\text{IO}_3^-]_e$ in Equation 1, can be affected significantly by temperature variations within the range of laboratory conditions.

The corrections indicated by Fig. 1 are calculated by Equation 1 from $[\text{IO}_3^-]$ values corresponding to the titration figures of the scale on the left side of the nomogram, and from the solubility values of $\text{AgIO}_3$ in 0.15 M $\text{H}_2\text{PO}_4$ found by Van Slyke and Hiller (4). Analyses of dilute chloride solutions have verified the accuracy of the theoretically calculated corrections.

The nomogram is designed for direct application to the titrimetric modi-
fication of the chloride method recently described by Van Slyke and Hiller (4), in which the $\text{IO}_3^{-}$ in the filtrate from the reaction mixture is titrated with 0.02303 N thiosulfate. A straight line connecting the observed titration value in the left-hand scale with the point on the temperature scale, that represents the temperature at which the $\text{AgIO}_3$ and chloride solution are shaken, cuts the inner scale at the point indicating the correction to subtract from the observed titration figure. The corrected titration value is used to calculate urine chloride by the usual formulae (4).

In the form given in Fig. 1, the nomogram is applicable independently of the number of times the urine or other analyzed chloride solution is diluted before it is shaken with $\text{AgIO}_3$.

If the line connecting the right and left scale points passes above the point for zero correction, the correction is zero. With temperatures below $35^\circ$, the connecting line cannot pass below the figure 0.9 on the inner scale because this figure represents a solution saturated with $\text{AgIO}_3$ at $35^\circ$. 

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**Fig. 1**

![Diagram showing the nomogram for iodometric chloride analysis](http://www.jbc.org/)

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from the observed titration figure. The corrected titration value is used to calculate urine chloride by the usual formulae (4).

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For general application to the iodometric chloride method, in which $[\text{IO}_3^-]$, is measured gasometrically (1), colorimetrically (3), or by titration other than with 0.02303 N thiosulfate, the figures on the left and inner scales of the nomogram can be converted into terms of millimoles of dissolved iodate per liter by multiplying the values on both scales by $100 \times 0.02303/6$, or 0.3838.

In applying the reaction between AgIO$_3$ and Cl$^-$ to chloride determination one cannot determine a "reagent correction" by performing a blank analysis with water in place of the chloride solution, and measuring the dissolved IO$_3^-$ as the correction. Under these conditions the solubility of the AgIO$_3$ would not be depressed by IO$_3^-$ formed by the reaction of AgIO$_3$ and Cl$^-$, and the filtrate would contain an amount of IO$_3^-$ which would correspond to the full AgIO$_3$ solubility, and would therefore be greater than the true correction for the depressed AgIO$_3$ solubility in analyses of chloride solutions. The reagents can be tested by analyses of standard chloride solutions, of which the one capable of most precise preparation appears to be standard hydrochloric acid made from constant boiling HCl by the method of Hulett and Bonner (5).

**SUMMARY**

In determining chloride by the measurement of the IO$_3^-$ that goes into solution as a result of the reaction, AgIO$_3$ + Cl$^-$ $\rightleftharpoons$ IO$_3^-$ + AgCl, correction for dissolved AgIO$_3$ becomes significant (>0.5 per cent) when Cl$^-$ concentration falls below 6 mM at 20$^\circ$ or 10 mM at 35$^\circ$. A nomogram is presented for calculating the correction from the temperature and the concentration of total dissolved IO$_3^-$. 

**BIBLIOGRAPHY**

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