KANSAS GEOLOGICAL SURVEY
OPEN-FILE REPORT 91-15

Correction of Technicon Autoanalyzer II Chloride Analyses for the Presence of Bromide

by

L.R. Hathaway

Kansas Geological Survey
1930 Constant Avenue
University of Kansas
Lawrence, KS 66047-3726

KANSAS GEOLOGICAL SURVEY
Analytical Services Section

L. R. Hathaway

CORRECTION OF TECHNICON AUTOANALYZER II CHLORIDE ANALYSES FOR THE PRESENCE OF BROMIDE

General Comments:

Bromide (Br) ion has been found to be useful as a conservative tracer in hydrogeologic investigations of the mass transport of dissolved solids in ground water[1] and as a diagnostic tool in the identification of brine sources which contribute to the pollution of natural water systems[2]. In the analysis of major constituents of water samples taken during the course of such studies it might be expected that Br present in a water sample would have a simple additive effect in the chloride (Cl) ion measurement for a solution. This relationship can be expressed as:

$$Cl_{eff} = Cl_{bkg} + Cl_{app}$$

where Cl_{eff} is the measured halide response which is expressed as an effective mg Cl/L concentration, Cl_{bkg} is the true background concentration of the solution analyzed, and Cl_{app} is the apparent Cl concentration which is the increase in the measured Cl concentration due to the presence of Br in the solution analyzed. To a first approximation, the magnitude of Cl_{app} should be given by the product of the Br concentration and the Cl/Br molar ratio (0.4437), hereafter referred to as the theoretical Cl_{app} concentration. Thus, the presence of 50.0 mg Br/L in a sample with a 27.4 mg/L Cl_{bkg} value should yield a measured Cl_{eff} concentration of 49.6 mg/L.

Measurements made on water samples from field-tracer tests in accordance with the ferric thiocyanate procedure outlined for Cl analyses by the Technicon AutoAnalyzer II system[3] suggest the above approximation is reasonably valid if the Br level in the solution as analyzed is less than about 2 mg/L; however, marked discrepancies appear to exist when higher Br levels are present in the solution analyzed. Determined Cl_{bkg} concentrations appear to increase with concurrent increases in the amount of Br tracer in the solutions analyzed, even though no addition of Cl had been made to the system during the course of the tests. These preliminary observatrions suggest that a detailed experimental evaluation of the influence of Br levels upon the determination of Cl by the Technicon AutoAnalyzer II system is warranted.

Experimental:

A 40-60 mg Cl/L range is desirable in solutions to be analyzed by the Technicon system. With this in mind, three series of test solutions were prepared which had fixed Cl_{bkg} levels (0, 30, and 60mg/L) and variable Br levels (0.0, 0.5, 1.0, 2.0, 4.0, 8.0, 16, 30, 45, 60, and 75 mg/L). These three series of solutions serve to blanket the 40-60mg Cl_{eff}/L range which typically would be maintained in the analysis of unknown samples. A UV-VIS spectrophotometer was employed as the detector in the Technicon AutoAnalyzer II system.

Results and Discussion:

Table 1 lists the Cl_{eff} concentrations measured for the test solutions, as well as the theoretical Cl_{app} values for the Br concentrations employed. Figure 1 displays a curve for the theoretical Cl_{app} concentration as a function of the Br concentration used in the three series of test solutions, as well as curves of the experimentally determined Cl_{app} concentration versus Br concentration for each of the three Cl_{bkg} levels used in the present study. There are several things worthy of note in this figure. First, up to about 2 mg Br/L in the solution being analyzed, the measured Cl_{app} values for all three series agree fairly well with the theoretical curve; but above this point the curves based upon Cl_{eff} measurements exhibit a marked positive deviation from the theoretical curve. Second, the higher the Cl_{bkg} concentration the greater the deviation from the theoretical curve; however, the rate of change appears to decrease with increasing Cl_{bkg} levels. Both observations may be related to the lower solubility product constant for $HgBr_2$ (1.1×10^{-19}) as compared to that of $HgCl_2$ (6.1×10^{-15}). Thus, elevated Br values may produce more suspended particles in the analytical flowstream than their equivalent Cl concentrations which result in additional light scattering that is not compensated for in the Cl calibration curve. The $HgBr_2$ particles may also serve as seed crystals which promote more effective precipitation of $HgCl_2$, again resulting in light scattering not compensated for by the simple Cl calibration curve.

It is evident from the curves of Figure 1 and the data of Table 1 that substantial errors may exist in calculated Cl_{bkg} levels when theoretical Cl_{app} values are used to compensate for the presence of Br in the solutions being analyzed. A solution which contains 30.0 mg Br/L in the presence of a 30.0 mg/L Cl_{bkg} level exhibits a measured Cl_{eff} concentration of 47.1 mg/L. The theoretical Cl_{app} for this solution is 13.3 mg/L, but that determined by actual measurement is 17.1 mg/L. The 3.8 mg Cl/L underestimation by the theoretical correction factor translates into a +12.7% error in the Cl_{bkg} calculated for this solution.

Corrections for the presence of Br which are applied to the Cl_{eff} data for solutions are of two types and must be made before analytical dilution factors are applied. The theoretical Cl_{app} value is used to correct the measured Cl_{eff} value if the Br level is less than 2 mg/L in the solution subjected to analysis. This case prevails for almost all natural waters, from fresh waters to oil brines. In the cases where Br tracer has been added to a hydrogeologic system, the Br level may will exceed a value of 2 mg/L in the solution being subjected to Cl analysis. For samples of this type it is important that experimentally derived Cl_{app} values be used in making corrections to the measured Cl_{eff} data.

The data used to construct the experimentally derived curves of Figure 1 are presented in Figure 2 as a series of Br concentration curves for the 2-75 mg Br/L range on a plot of $\log(Cl_{app})$ vs Cl_{bkg}. A correction is shown as a dashed line for the 4 mg Br/L curve because the measurement of the Cl_{eff} value for the 4 mg Br/L-60 mg Cl/L test solution appears to be somewhat low. This figure makes it possible through an iterative process to correct measured Cl_{eff} data for the presence of known amounts of Br in solutions which have been analyzed. The first step in the correction process begins at the 0 mg Cl/L level with an estimation of the Cl_{app} value for the Br concentration of the solution. The Cl_{app} value is then subtracted from the measured Cl_{eff} value to yield an approximate Cl_{bkg} concentration. The second step entails the determination of Cl_{app} at the approximate Cl_{bkg} concentration and subtracting this new value from Cl_{eff} to obtain an improved estimate for Cl_{bkg}. This second step is repeated until Cl_{bkg}

values reaches an acceptable level of constancy, normally 2-3 iterations will suffice. Since the curves of Figure 2 are reasonably parallel, it is possible to calculate the Cl_{app} values through interpolation for Br levels which fall in between the experimental curves shown.

Consider the case of a water sample for which a 1/5 dilution produces a solution which contains 20 mg Br/L and has a measured Cl_{eff} of 46.5 mg/L. A Cl_{app} of 10.3 mg/L is estimated for the 0 mg Cl/L level, which yields a first approximation of 36.2 mg/L for Cl_{bkg}. A second estimate of Clapp now becomes 11.4 mg/L, and a value of 35.1 mg/L is calculated for Cl_{bkg}. A repeat of the process produces a Cl_{app} estimate of 11.3 mg/L and a value of 35.2 mg/L for Cl_{bkg}. At this point the iteration process probably can be stopped. The Cl concentration of the original water sample is then calculated to be 176 mg/L.

Conclusion:

Cl analyses made by the ferric thiocyanate method on the Technicon AutoAnalyzer II system are subject to interference by Br ions present in the solutions analyzed. The product of the Cl/Br molar ratio and the Br concentration, theoretical Cl_{app}, adequately corrects for the interference at Br levels below 2 mg/L, a range which encompasses almost all natural hydrogeologic systems. Correction for higher Br levels, which might be encountered in tracer studies, requires the use of experimental Cl_{eff} data in an iterative process in order to obtain reasonable Cl_{bkg} values.

References:

1. Sophocleous, M., Townsend, M.A., Orountitotis, C., Evenson, R.A., Whittemore, D.O., Watts, C.E., and Marks, E.T., 1990, Movement and Aquifer Contamination Potential of Atrizine and Inorganic Chemicals in Central Kansas Croplands,: Kansas Geological Survey Ground Water Series No. 12, 64p.

2. Whittemore, D.O., 1988, Bromide as a Tracer in Ground-Water Studies: Geochemistry and Analytical Determination: In Proceedings of the Ground Water Geochemistry Conference, Water Well Journal Publishing Co., Dublin, Ohio, pp.339-359.

3. Technicon Industrial Systems, 1976, Chloride in Water and Wastewater: Industrial Method No. 99-70W/B, Technicon Instrument Corporation, Terrytown, N.Y.

Table 1. Effect of Br on Cl analyses run on the Technicon AutoAnalyzer II system

mg Br/L	Measured Cl_{eff}			Theoretical Cl_{app}
	0 mg Cl/L	30 mg Cl/L	60 mg Cl/L	
0.0	0.0	30.0	60.0	0.0
0.5	0.3	30.3	60.4	0.2
1.0	0.4	30.5	60.2	0.4
2.0	0.9	31.1	61.2	0.9
4.0	2.0	32.3	62.2	1.8
8.0	3.9	34.4	64.9	3.5
16.0	8.2	38.9	69.6	7.1
30.0	15.6	47.1	78.6	13.3
45.0	24.1	56.8	88.5	20.0
60.0	33.4	66.4	99.0	26.6
75.0	42.9	77.4	---	33.3

Figure 1. Cl_{app} as a function of Br concentration.

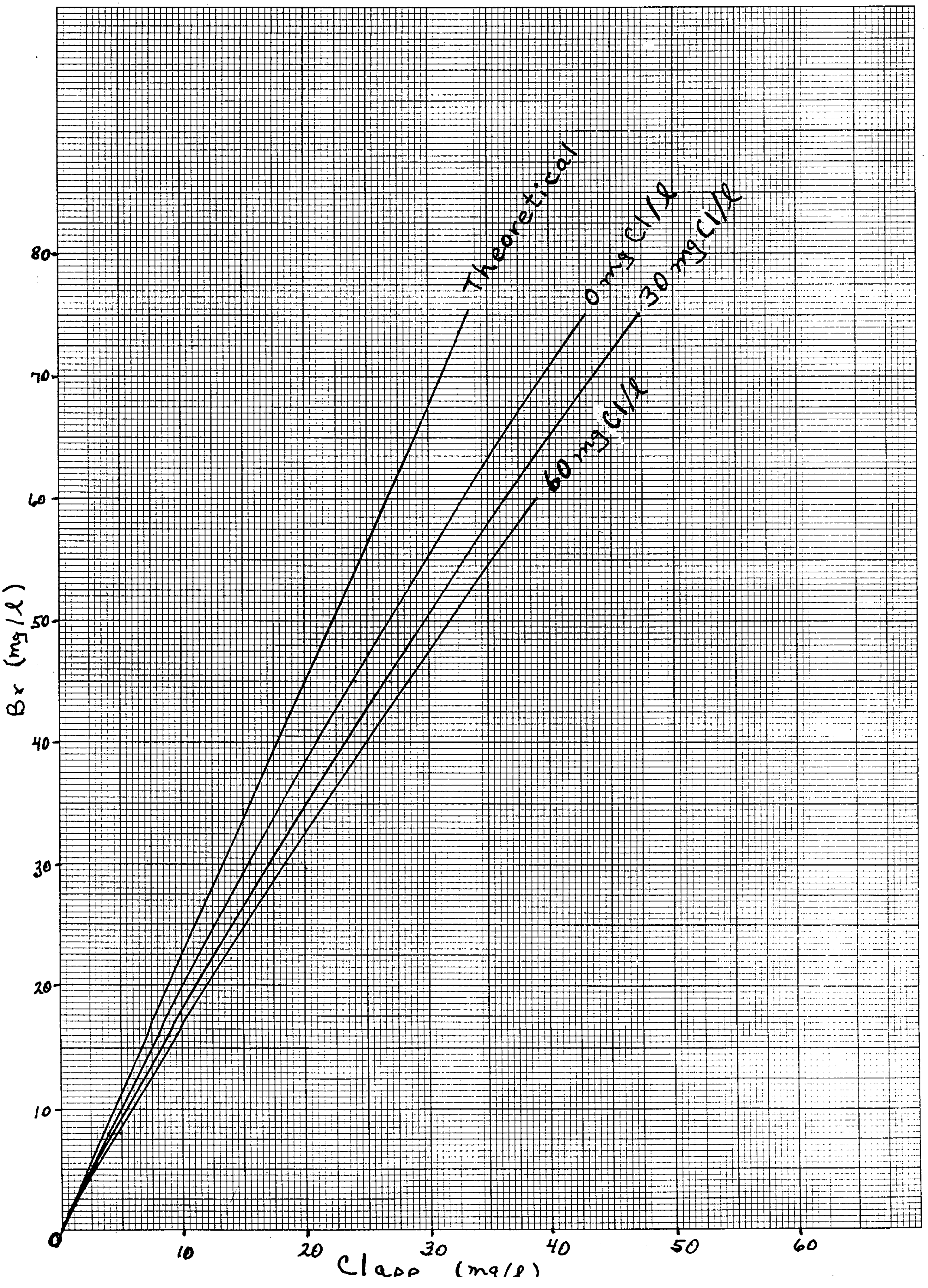

Figure 2. Br curves for a plot of $\log(Cl_{app})$ vs Cl_{bkg}