

## Use of Radioactive Tracers in Water Analysis — Chloride Determination

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### INTRODUCTION

Radioactive tracers have been used for quite some time in the general area of analytical chemistry, and with good success. However, they are noticeably lacking from the applied area of water analysis. This is perhaps unfortunate, since radioactive tracers offer potentially at least the sensitivity of measurement so crucial to water analysis, where one is routinely analyzing at the parts per million or parts per billion level.

It would seem that one way in which the extreme sensitivity available with radioactive tracers could be realized would be to incorporate their use into more classical techniques. As an example, it is possible to achieve a greater sensitivity in a basically gravimetric method by forming a radioactive precipitate and counting it instead of weighing it. In favorable cases, it is possible to make measurements on as little as  $10^{-10}$  or  $10^{-11}$  g of material as contrasted to a practical limit of  $10^{-3}$  or  $10^{-4}$  g with weighing. A sensitivity in the range of  $10^{-4}$  g is usually adequate in water analysis and hopefully, at least, one could achieve this level easily with tracers.

A study was made of chloride analysis via precipitation and counting of radioactive silver chloride ( $^{110}\text{AgCl}$ ) to test the above approach and also because current methods of chloride analysis in water are open to question in concentration ranges below 25 mg/l.

### EXPERIMENTAL PROCEDURE

A. *Counting the precipitate*—Two techniques were investigated. In the first, the  $\text{AgCl}$  precipitate was filtered out and the filter paper was mounted and counted. Greater reproducibility was achieved in the second technique in which the precipitate was redissolved in  $\text{NH}_4\text{OH}$  and the resulting solution was counted. Of course both methods require previous calibration with known chloride solutions. After a brief investigation, counting the precipitate directly on the filter paper was abandoned in favor of the ammine method. Current work in sulfate analysis indicates that counting a solid precipitate directly will permit adequate precision if one is more careful about sample mounting techniques. The steps involved in each method were as follows:

1. Filter paper mount procedure
  - a. Twenty-five ml of sample was placed in a 50-ml beaker and 2 drops of 8 M  $\text{HNO}_3$  added.
  - b. Five ml of 0.003 M  $\text{Ag}^+\text{NO}_3$  solution was added. The mixture was stored in the dark for 10 minutes.
  - c. The mixture was filtered with a  $0.45 \mu$  membrane filter and the precipitate washed with dilute  $\text{HNO}_3$  and ethanol, then air dried.
  - d. The precipitate was mounted on a sample support and counted using a flat  $\text{NaI}$  scintillation assembly.
2. Ammine procedure
  - a. Twenty-five ml of sample was placed in a 50-ml beaker and 2 drops of 8 M  $\text{HNO}_3$  were added.

- b. Five ml of 0.01 to 0.003 M  $\text{Ag}^*\text{NO}_3$  were added. The mixture was stored in the dark for 10 minutes.
- c. the precipitate was filtered out with a 0.45  $\mu$  membrane filter and washed.
- d. The filter paper and precipitate were transferred to a counting tube containing 5.0 ml of 1:2  $\text{NH}_4\text{OH}$ .
- e. Five minutes were allocated for ammine formation, after which the solution was counted in a NaI well crystal assembly.

*B. Counting the filtrate*—In a series of chloride samples of constant volume, but varying amounts of chloride, a constant amount of  $\text{Ag}^*\text{NO}_3$  was added to each sample and the  $\text{Ag}^*\text{Cl}$  filtered out as before. The filtrate was counted and the counting rate related to residual  $\text{Ag}^*\text{NO}_3$ , which in turn was related to original chloride concentration. The procedure was as follows:

1. Twenty-five ml. of sample was placed in a 50-ml. beaker and two drops of 8 M  $\text{HNO}_3$  added.
2. Five ml. of 0.003 M  $\text{Ag}^*\text{NO}_3$  was added and the mixture stored in the dark for 10 minutes.
3. The precipitate was filtered out using 0.45-micron filter paper and washed with dilute  $\text{HNO}_3$ .
4. The filtrate was diluted to 100 ml., and a 10-ml. aliquot was counted in a NaI well crystal assembly.

#### CALIBRATION CURVES AND PRECISION

Calibration curves were determined using KCl solutions of known concentration. Typical curves obtained are given in Figs. 1, 2, and 3. A study of such calibration indicates an expected precision of  $\pm 0.4$  mg/l ( $2\sigma$ ) in the 0 - 20 mg/l range; and 3 mg/l ( $2\sigma$ ) in the 10-150 mg/l range using the ammine procedure. The overall precision of the method is affected by two factors; namely the errors in the procedure and the statistical nature of the decay process. The latter can be minimized by the use of higher specific activity  $^{110}\text{AgNO}_3$ . This latter effect is the major reason for the difference in precision between the 0-20 mg/l and the 10-150 mg/l range data.

#### COMPARISON OF TRACER METHOD WITH MOHR METHOD

The classic method of chloride analysis accepted by the water industry is the Mohr titration. A series of water samples taken in the Norman, Oklahoma area were analyzed by the Mohr titration method and by the tracer methods. Typical results are given in Table I.

TABLE I. COMPARISON OF MOHR TITRATION AND TRACER METHODS

Sample	Filtrate Method	Ammine Method	Mohr Method
A	10.2 mg/l	10.0	9.4
B	—	22.6	20.9
C	13.4	13.8	12.3
D	4.0	5.0	4.4
E	6.8	8.3	7.4
F	6.2	6.6	6.0
G	—	15.0	13.5
H	—	20.1	15.5

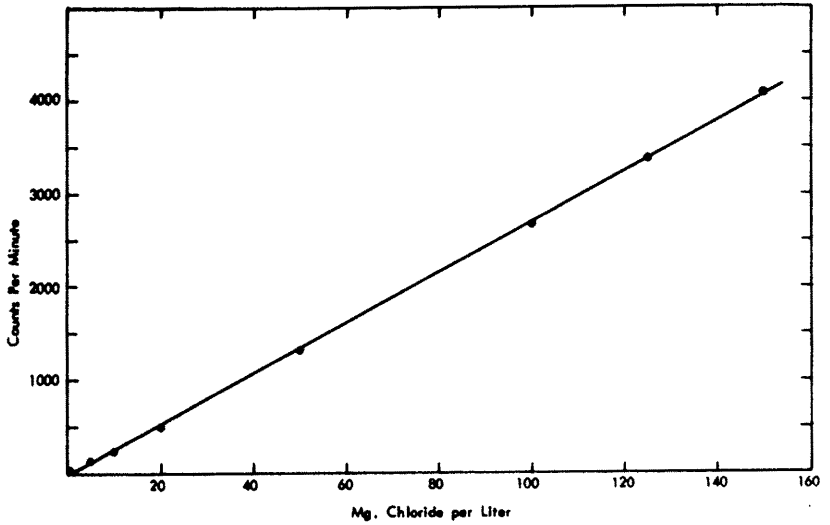


Figure 1. Calibration Curve for Ammine Method (High Range)

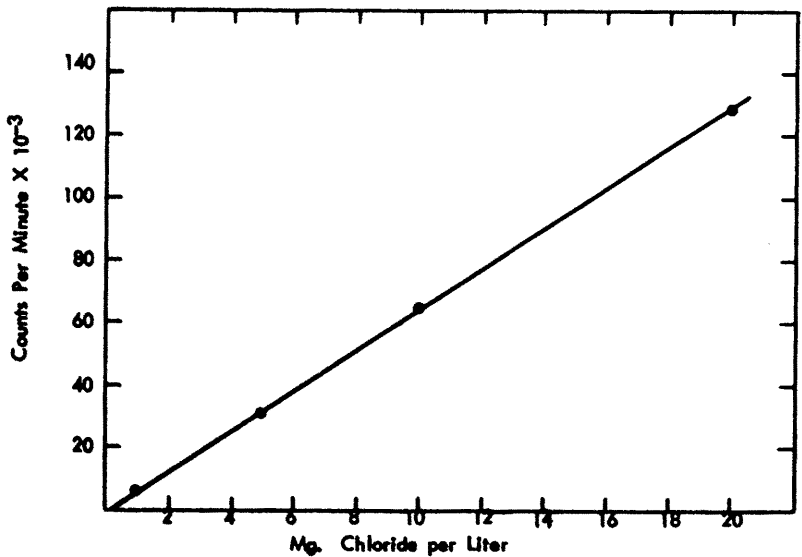


Figure 2. Calibration Curve for Ammine Method (Low Range)

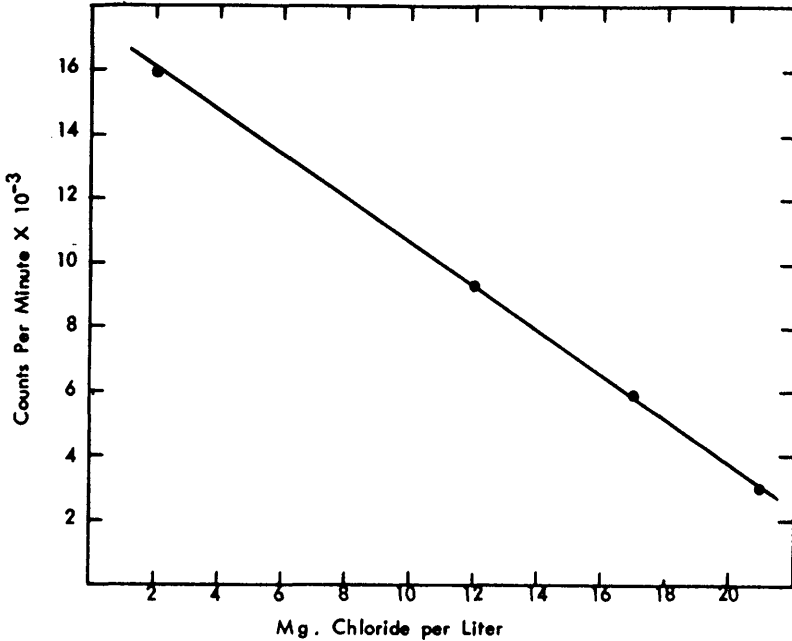


Figure 3. Calibration Curve for Filtrate Method (Low Range)

It is misleading to attempt a rigorous comparison of accuracy since the end point of the Mohr titration is somewhat difficult to determine in this concentration range.

The tracer method seems most useful in the 0-25 mg/l chloride range where current methods are unsatisfactory. Of the three modifications studied, the ammine method seems to offer the greatest precision in this range. Further the ammine method was found to be faster and far less demanding of technique than classical gravimetric procedures.

Investigation of this particular tracer application is continuing; current efforts involve comparison of the method with a mercuric chloride complex titration.

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