

Eastern Deciduous Forest Biome  
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PROCEDURES FOR CHEMICAL ANALYSIS OF STREAMFLOW AND PRECIPITATION  
AT THE COWEETA HYDROLOGIC LABORATORY

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Procedures for Chemical Analysis of Streamflow and Precipitation at  
the Coweeta Hydrologic Laboratory

Elemental determinations for both precipitation and streamflow at Coweeta basically follow the procedures outlined by Technicon Industrial Systems and The Perkin-Elmer Company.

Five anions are determined; nitrogen as ammonia, nitrogen as nitrates and nitrites, total inorganic phosphate, chloride and sulfate. Using the Technicon Auto Analyzer II Configuration, ammonia-nitrate and chloride-phosphate are determined simultaneously. These same anion pairs are combined in common 1000 mg/l stock standard solutions. Sulfate is determined independently.

The model 305 Perkin-Elmer Atomic Absorption Spectrophotometer is used with an air-acetylene flame for four cation determinations: calcium, magnesium, sodium, and potassium.

Collection and Storage of Samples

Streamflow and precipitation samples are collected on Tuesday of each week.

All collection bottles are washed with Micro cleaning solution (an ammonia base cleaner), rinsed for one minute in tap water, rinsed three times in distilled, deionized water, and dried in a hot air oven before they are taken to the field. One ml of preservative stock, phenyl mercuric acetate, is added to sample bottles that remain in the field 24 hours or longer.

The formulation for the stock PMA preservative is:

0.1 g phenyl mercuric acetate

15 ml dioxane

Dilute to 100 ml with distilled water.

Grab samples are collected from the streams above the ponding basins. Care is taken that the samples remain downstream of the actual collection point so that hands or clothing do not contaminate the sample. The mouth of the bottle is submerged beneath the stream surface taking care not to pick up silt and debris. In warm weather, samples are cooled with ice as they are collected. Phenyl mercuric acetate is added to the weekly composite streamflow samples collected with proportional samples.

When collecting rainfall samples, full bottles (containing at least 0.5 inches of rain) are replaced by clean, empty bottles.

Dry precipitation is collected by washing down the sides and bottom of the dry precipitation collector with a clean paint brush and exactly 500 ml distilled water.

Samples are immediately refrigerated on return to the laboratory and remain refrigerated until at least all anions are determined. Clean glassware and collection bottles are spot checked monthly as a check for possible contamination. All such tests to date have revealed no readable contamination when 10 ml or more distilled water is added to the container.

The 1/4 ml sample cups used with the Technicon Sampler IV do reveal small amounts of chloride and phosphate contamination. For this reason, sample cups are rinsed with distilled water before samples are added.

## Anions

Modifications of some of Technicon's anion procedures have been made to better fit the needs of analysis at Coweeta. Following are method briefs for each anion determination with comments on any modifications:

### A. Nitrogen as low level ammonia

1. Basic procedure: Technicon Industrial Method 108-71W
2. Performance:
  - a. Accuracy (against EPA Standard) - less than 0.2% error
  - b. Reproducibility at .100 ppm -  $\pm$  .001 mg/l
  - c. Resolution - .001 mg/l
3. Modifications: These pump tube changes have been made -

<u>Material</u>	<u>Flow Rate Changed To</u>
Tartrate	0.60 ml/min
Sample	1.06
Phenol	0.32
Hypochlorite	0.23
Nitroprusside	0.23
From F/C	1.37

The 15 mm flow cell has been replaced with a 50 mm cell.

### B. Nitrogen as nitrates and nitrites

1. Basic procedure: Technicon Industrial Method 100-70W
2. Performance:
  - a. Accuracy (against EPA standard) - 0.0% error
  - b. Reproducibility at .100 mg/l -  $\pm$  0.0 mg/l
  - c. Resolution - better than .001 mg/l

3. Modifications: Sample flow rate has been increased to 0.60 ml/min. Repumping of the sample as it flows from the cadmium column has been eliminated due to the "noise" it produces.

#### C. Chloride

1. Basic procedure: Methods of Chemical Analysis of Water and Waste, Environmental Protection Agency, 1971.
2. Performance:
  - a. Accuracy at 17.4 mg/l - 3.45% maximum error
  - b. Reproducibility at 1.0 mg/l -  $\pm$  .010 mg/l
  - c. Resolution - 0.0025 mg/l
3. Modifications:
  - a. Color reagent - 180 ml ferric ammonia sulfate stock is combined with 80 ml mercuric thiocyanate stock. This volume is brought up to 500 ml with the addition of 1.0 ml BRIJ wetting agent and distilled water. A 50 mm flow cell is used in the sample portion of the colorimeter. Addition of phenyl mercuric acetate as a preservative produces interferences with this determination. PMA appears to reduce the inherent (baseline) color of the Ferric Ammonium Sulfate reagent. In addition to this baseline shift, an additional error appears to the actual chloride concentration of the sample. The addition of Dowex 50-X8 as a cation exchange column in the manifold sample line reduces this error to a negligible amount.

The relationship between PMA concentration (dependent on the PMA dilution by rainfall) vs. the negative deviation from several known standards and the effect of the cation exchange column on these interferences is shown in Figures 1 and 2.

D. Total Inorganic Phosphate

1. Basic procedure: Technicon Method 93-70W
2. Performance:
  - a. Accuracy against EPA Standard - less than .001% error at 0.200 mg/l
  - b. Reproducibility at 0.100 mg/l -  $\pm$  .001 mg/l
  - c. Resolution - better than .001 mg/l
3. Modifications: None except the addition of a 50 mm flow cell.

E. Sulfate

1. Basic procedure: Technicon Method 226-72W
2. Performance:
  - a. Accuracy - .006% error at .500 mg/l
  - b. Reproducibility at 0.500 mg/l -  $\pm$  .003 mg/l
  - c. Resolution - .002 mg/l
3. Modifications: The working methylthymol blue solution is further diluted by 50% with 95% ethanol. Other modifications are more easily demonstrated by Figure 3.

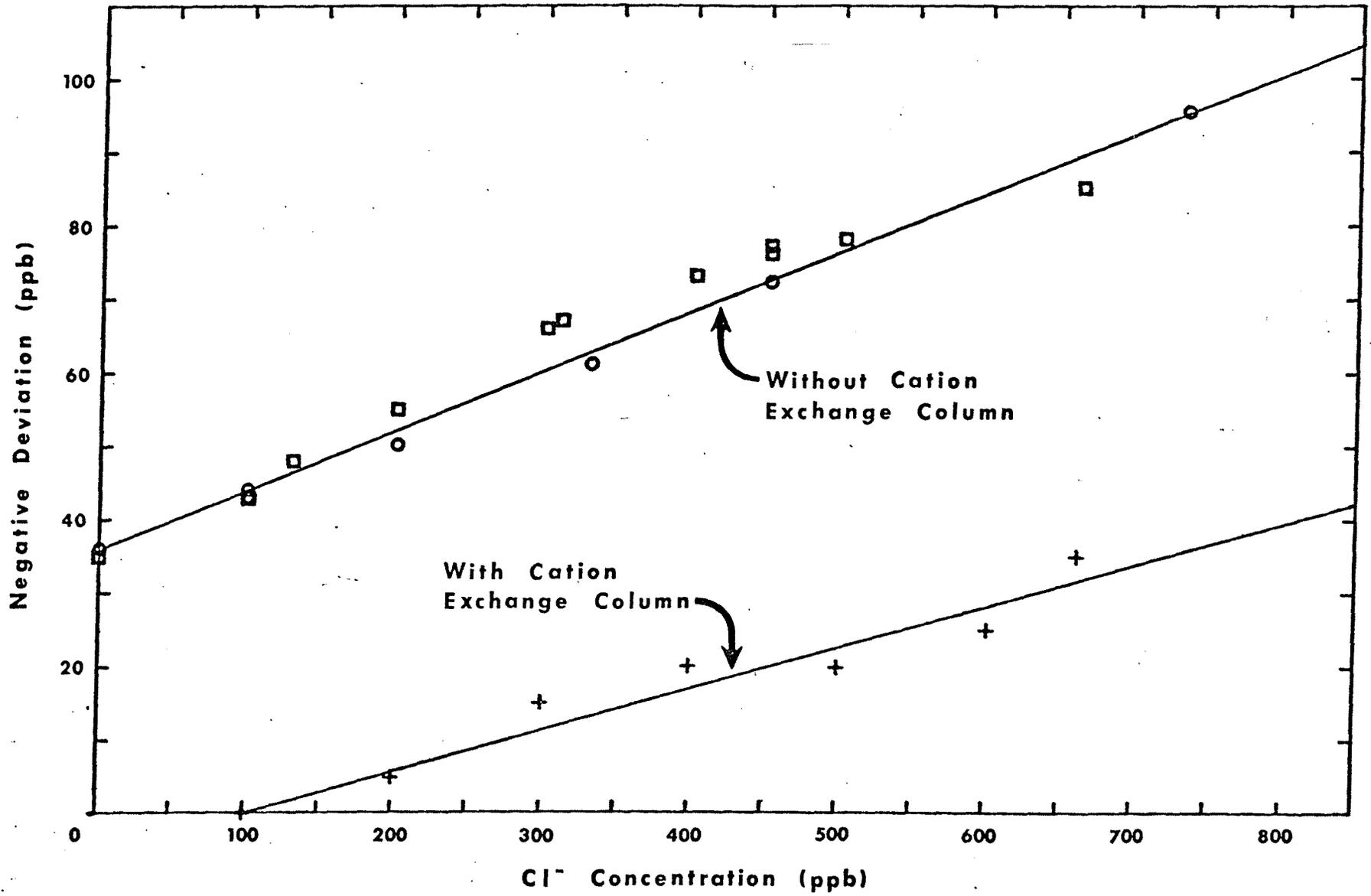


FIGURE 1. Negative deviation of chloride readings from known standards due to phenyl mercuric acetate addition (1ml/L stock)

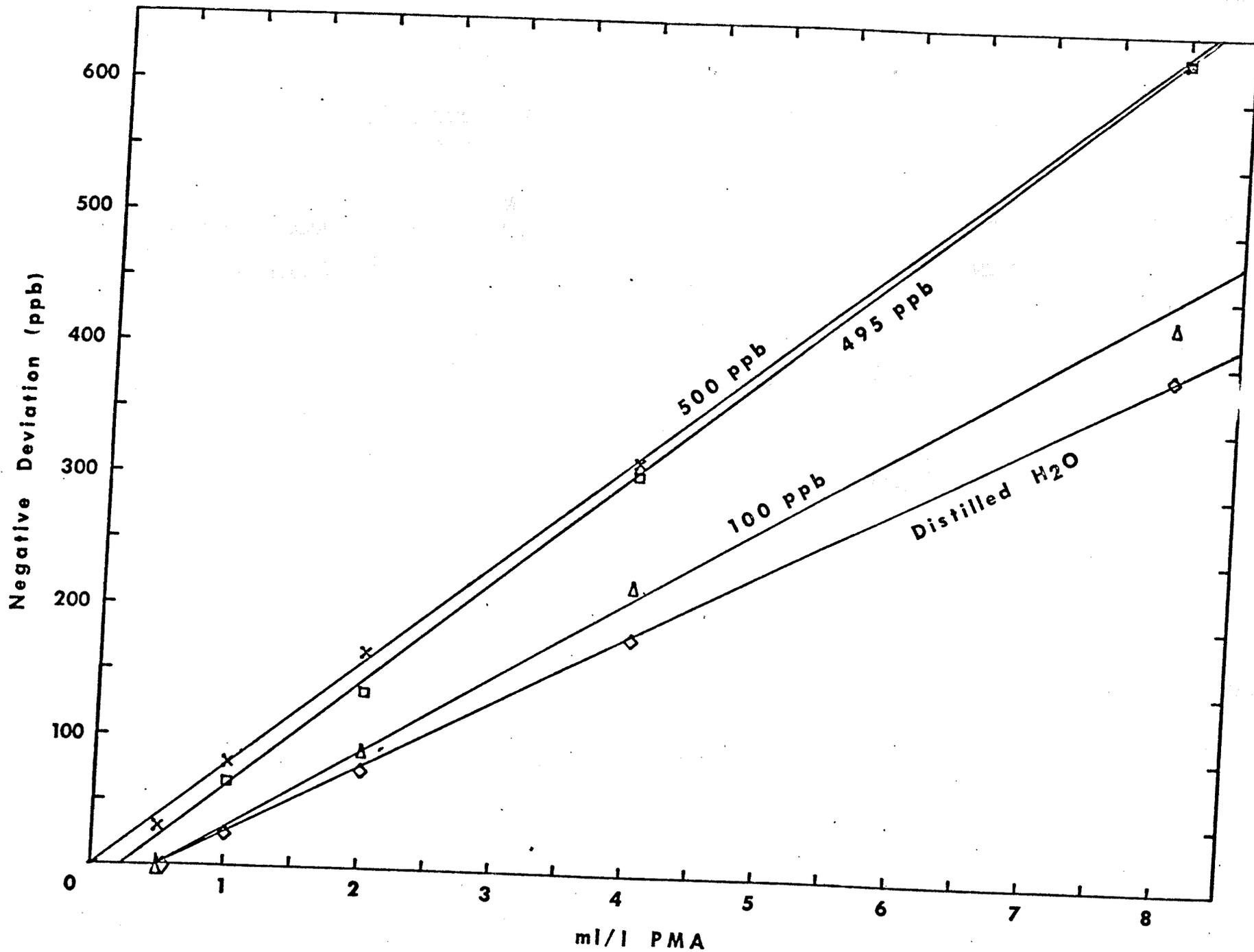


FIGURE. 2. Concentration of phenyl mercuric acetate in ml/L vs. negative deviation from known standards .

### Cation Determinations

Cations are determined using a Perkin-Elmer Model 305 double beam Atomic Absorption Spectrophotometer. Basic analytical procedures do not vary significantly from those recommended by Perkin-Elmer for an air-acetylene flame.

#### Potassium

A/ Standards: 0.049 ppm at 5 units to greater than 80 units at 0.978 ppm

B/ Performance:

1. Accuracy (Against EPA Standards) = 1.38% error at .400 mg/l
2. Reproducibility:  $\pm$  .010 ppm at 0.500 ppm
3. Resolution: App. .003 ppm
4. Modifications: Lamp energy level is maintained slightly less than 8.0 volts to improve stability.

#### Sodium

1. Accuracy (Against EPA): 0.146% error at .800 mg/l
2. Reproducibility:  $\pm$  .005 ppm
3. Resolution: .003 ppm
4. Modifications: None

#### Magnesium

1. Accuracy: (EPA): 1.43% error at 2.1 mg/l
2. Reproducibility: Better than  $\pm$  .003 mg/l
3. Resolution: .001 ppm
4. Modification: Lanthanum oxide is added to each sample as recommended. Determination of the amount to be added to each

sample was accomplished by peaking a sample taken as an "average" magnesium value. That  $\text{La}_2\text{O}_3$  amount added is 2 ml  $\text{La}_2\text{O}_3$  stock/50 ml sample. The Lanthanum Stock solution is 1.4% La.

#### Calcium

1. Accuracy (EPA) 0.022% error at 0.900 ppm
2. Reproducibility:  $\pm .005$  ppm
3. Resolution: .001 ppm
4. Modification: Lanthanum oxide is added to suppress sulfate-phosphate interference. A sample representing an "average" calcium value was peaked to determine the proper amount of lanthanum.

## Literature Cited

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