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PROGRESS REPORT NO. 13

CONTROL INDICES AND ANALYTICAL PROCEDURES

By

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SUMMARY

The colorimetric determination of nitrate based on the color resulting from its reaction with ferrous sulfate in sulfuric acid solution offers a rapid method for the determination of nitrate in a mixed inorganic salt solution. The method is capable of satisfactory accuracy, when applied without preliminary treatment to solutions of dissolved 347 stainless steel containing in addition magnesium and sulfate ions.

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SUMMARY OF RESULTS

ANALYTICAL PROCEDURE STUDIES

III. DETERMINATION OF ANALYTICAL PROCEDURES

FOR IRON, CHROMIUM, SULFATE AND NITRATE

IN A MIXED INORGANIC SALT SOLUTION

A. Objective and Implementation

The objective of the present investigation was to develop an accurate and rapid procedure for the determination of nitrate in a mixed inorganic salt solution of composition specified by the sponsoring agency. The composition of this solution is described in Progress Report No. 12 and is indicated in a subsequent section of this report.

A review of the existing methods for the determination of nitrate yielded several possibilities.

Polarographic methods, although rapid, proved to be too sensitive to the effect of foreign ions to give satisfactory accuracy. Titrimetric methods failed in that strictly stoichiometric relationships were generally lacking.

Colorimetric methods seemed most adaptable to this investigation. The method of English¹ seemed most feasible as it is claimed that iron, lead, copper, nickel, chloride and sulfate do not interfere in this procedure.

B. Experimental Procedure

Chemicals and Reagents. Reagent-grade products of the following were used in preparing standard, test, and reagent solutions: chromic sulfate, ferric sulfate, ferrous ammonium sulfate, potassium nitrate, and sulfuric acid.

Solutions. Several solutions were used in the investigation and they were prepared as follows:

Standard nitrate solution: 4.5951 grams of solid dry potassium nitrate was dissolved in water and diluted to 1 liter. This potassium nitrate standard and dilutions of 4/5, 3/5, 2/5, 1/5, and 0/5 were used in the calibration of the colorimeter.

Iron reagent solution: 40 grams of ferrous ammonium sulfate ($\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$) was dissolved in 100 ml of water, acidified with 20 ml of concentrated sulfuric acid, and filtered.

15M Sulfuric acid reagent solution: 500 ml of concentrated sulfuric acid was added to 100 ml of water.

Background solutions: 0.67 gram of $\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ was dissolved in water containing 2 ml of 6M sulfuric acid; the volume was then brought up to 50 ml. A solution consisting of 0.97 gram of $\text{Cr}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ dissolved in water and diluted to 50 ml was also prepared.

Mixed inorganic salt solution: This was the same solution as that described in Progress Report No. 12; it consisted of 22.5116 grams of 347 stainless steel dissolved in 350 ml of 6M sulfuric acid to which were added 3.9 grams of magnesium oxide, and 150 ml of 15M nitric acid, with final dilution to 500 ml. To prepare the sample solution for colorimetric analyses, this solution was diluted 1:100 with water.

Apparatus. A Bausch and Lomb colorimeter (filter photometer) equipped with round test-tube cells was used in conjunction with an interference filter which absorbed in the 430-m μ region. Standard volumetric apparatus and glassware were used for all work.

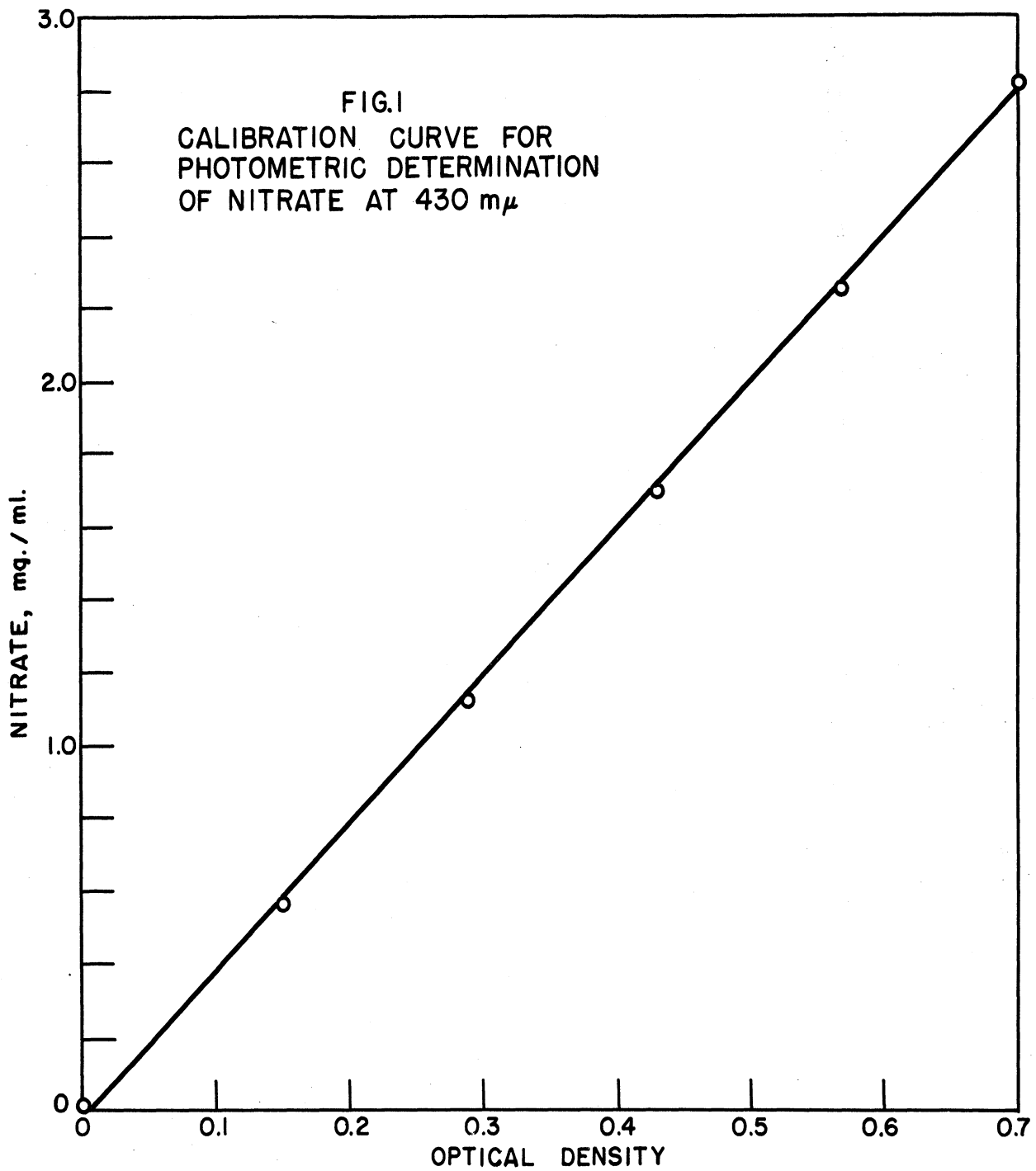
Analytical Procedure. A 1-ml portion of water was pipetted into a 50-ml beaker and 2.00 ml of nitrate-containing solution was added. The beaker and its contents were then cooled in an ice bath and 1 ml of iron reagent was added while the beaker was continuously swirled in the ice bath. Then 25 ml of the 15M sulfuric acid was very slowly added (total addition time was about 3 to 5 minutes), while the beaker was continuously swirled. The beaker was then removed from the ice bath, its contents stirred with a glass rod, and a portion of the solution transferred to the colorimeter cell for measurement. A blank containing all the reagents, but no test solution, was used for comparison, i.e., to determine the I_0 value.

C. Data Obtained and Interpretation

Determination of Optimum Conditions. It was observed in early experiments that constant readings could not be obtained. Tiny bubbles which were formed in the cell were first thought to be the cause of the drift in apparent absorption intensity; therefore, boiled 15M sulfuric acid was used. This did not entirely alleviate the situation; however, it was noticed that full color development was achieved much faster with the use of the boiled 15M sulfuric acid than with the unboiled 15M sulfuric acid. Therefore, the possibility of a time delay in the color development was considered. It was found that full color does not develop immediately, but requires about 10 to 15 minutes. A delay of beyond 30 minutes after the addition of the color-producing reagents causes the reading to increase, as the color is stable only for about that period of time.

Experimental Results. A calibration curve was prepared using the standard potassium nitrate solution. Dilutions of the latter were performed by adding an accurately measured amount to a volumetric flask and diluting to volume. The data (Table I) give a straight line when plotted (Fig. 1).

Solutions of ferric and chromic ions of concentrations equivalent to those expected in the mixed inorganic salt solution gave no perceptible radiant energy absorption when analyzed by the procedure outlined; e.g., a sample solution prepared by diluting 4 ml of the ferric background solution to 50 ml gave an optical density of about -0.003, while one similarly prepared from 1 ml of the chromic background had an optical density of + 0.003. A composite solution of the same ferric and chromic ion concentrations had an optical density of 0.000. To check further possible interference a known amount of nitrate, equivalent to that expected in the sample solution, was added to such a background



solution; i.e., 40 ml of standard nitrate solution, 4 ml of ferric sulfate solution, and 1 ml of chromic sulfate solution were diluted to 50 ml. The results of analyzing this solution are given in Table II; apparently no interference occurs.

The mixed inorganic salt solution was then analyzed; the data are given in Table II.

TABLE I

CALIBRATION OF COLORIMETER

Nitrate Content mg NO_3^- /ml	Optical Density
2.820	0.701
2.256	0.569
1.692	0.433
1.128	0.290
0.564	0.153
0.000	0.006

TABLE II

EFFECT OF CHROMIUM, IRON, AND OTHER IONS
ON THE PHOTOMETRIC DETERMINATION OF NITRATE

Sample	Calculated Nitrate Content g NO_3^- /ml	No. of De- terminations	Optical Density	Nitrate Found	Error, %
Background Solution	2.25×10^{-3}	3	0.571-0.574	2.28×10^{-3}	+ 1.3
Mixed Inorganic Salt Solution	$(2.4 \times 10^{-3})^*$	3	0.629-0.640	2.53×10^{-3}	(+ 4)

*Approximate value based on the label composition of the nitric acid used and assuming negligible loss of nitrate during preparation of the solution.

Discussion of Results. From the results in Tables I and II, it can be seen that the background solution's optical density agrees with that on the standard curve for an identical nitrate concentration to within the experimental accuracy of photometric measurement. Therefore it would seem that chromic and ferric ions do not present any serious interference.

The nitrate content of the mixed inorganic salt solution is somewhat higher than would be expected, but this is not too surprising since the nitrate content in the stainless-steel solution was not accurately known. The results are within the 5% limit of error specified in the Analytical Procedure Studies outline. It would probably be possible to improve the accuracy of the nitrate determination if more extensive manipulation of the sample solution were feasible, either by improving the present method or by changing to a more elaborate method.

E. Literature Cited

1. English, F. L., Anal. Chem., 19, 850 (1947).

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