

**A STUDY OF CHLORINE DETERMINATION IN FERTILIZERS**

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**by**

**Patrick Henry Butler, Jr.**

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## Table of Contents

|                                    | Page |
|------------------------------------|------|
| Purpose of Investigation . . . . . | 1    |
| Historical . . . . .               | 2    |
| Theoretical . . . . .              | 7    |
| Experimental Details . . . . .     | 8    |
| Discussion . . . . .               | 10   |
| Summary . . . . .                  | 12   |
| References . . . . .               | 13   |

### Purpose of Investigation

The purpose of this investigation was to determine chlorides in fertilizers with special interest on the following points:

1. Whether or not the same sample on which potash is determined can be used in running chlorides.
2. Effect of N. U. Tankage on the determination.
3. Effect of leaching with room temperature water instead of hot water which is used in the A.O.A.C. method.

### Historical

Although the most accurate method of determining the amount of chlorine present in a soluble chloride is the gravimetric, the majority of the analysts use the volumetric because of the time saved. Besides the gravimetric and volumetric methods, electro-metric method and methods using optical instruments have come into use for soluble chloride determinations. It is desired to review the methods most used. The first to be taken up will be the gravimetric methods.

The gravimetric methods (1) are very long and much time is required for analytical work done by this method. E. Marmann (2) has found that by adding to the precipitate a small amount of paper from ashless pulp, the residue after burning will be pure, spongy metallic silver, free from  $\text{AgCl}$ . The chlorine is determined from the amount of silver present. After removing the organic compounds present Muelen (3) used gravimetric methods to determine the chlorine present.

The gravimetric analyses are very accurate, but the time saved by use of the volumetric determinations have made this type of chlorine analysis to be more used than the older gravimetric type. Of the volumetric methods, the Mohr's method is the most accurate. This method was first worked out by Mohr (4) in 1856. It consists of the halide being titrated with silver nitrate using potassium

chromate as indicator. Several modifications of this method are used. F. N. van Eck (5) points out the error in the Mohr' method caused by increase in solubility of the silver chromate to temperature change. The presence of nitrates also increases the solubility of the silver chromate. The amount freed during the titration is not enough to affect the accuracy of the determination. H. W. Bolam (6) points out that if a chromate is less soluble than silver chromate is formed, the end point is very hard to see. This is remedied by adding a little more potassium chromate than is necessary to precipitate the metallic ion and then titrate with silver nitrate as usual. A faint brown tinge, permanent on shaking, shows the reaction to be complete. Another very good modification is by E. B. Meldrum and J. C. Forbes (7). They dried the substance to be analyzed and then dissolved it in water (75 cc). Next, they made it acid to methyl orange with nitric acid and added enough one percent sodium bicarbonate to turn the indicator. Following this by titrating the silver ion with potassium chromate slowly to a faint end point, boiling the solution, freezing it in ice water and then finish the titration. H. W. Van Urk (8) points out that the solution must be between the Eh values of 7 and 11. J. V. D. Bos (9) suggests titrating to excess with N/10 silver nitrate and then back titrate with N/10 salt solution.

The Mohr' method has a superior (10) in the Volhard method when applied to acid solutions. The Volhard method (11), however, is

accurate only when small amounts of chlorine are in small volume. The Mohr's method also requires a shorter length of time (12) than the Volhard, but is less accurate.

In using the Volhard method Kolthoff (13) suggests a modification in the Volhard method after adding the  $\text{AgNO}_3$ , fill to a known volume, shake, allow to settle and pipette from aliquot part for titration. By doing this he gets a sharp end point. E. Schylek (14) makes use of the Volhard method when cyanides are present by changing the cyanide into a glycolate and hexamethylenetetramine by use of formaldehyde ( $\text{HCHO}$ ). A method very similar to Volhard's has been worked out by Emil Votocsek (15). He replaces silver nitrate with mercuric nitrate ( $\text{Hg}(\text{NO}_3)_2$ ), in presence of small quantities of nitric acid. He uses sodium nitroprusside as an indicator.

A volumetric method which is regarded as giving more accurate results than either the Volhard or the Mohr's method is that of Iodometric titration. This process consist of the titration of iodine against sodium thiosulphate, with starch as an indicator. The end point in this method can be determined more accurately (16) by waiting until the end point is nearly reached. Then add about ten cc of ten percent starch solution and titrate to the end point. This test is not sufficiently delicate for use with water containing less than 0.05 p.p.m. of chlorine. By freezing the water

(that is, part of it), the chlorine may then be determined. (17)

When free chlorine is to be determined that are gravimetric methods as well as volumetric processes that can be used. C. C. Perkins (18) gives quite an interesting article on his gravimetric method. The starch iodide test as described by LeRoy (19) gives a very good volumetric method for determining free chlorine in water supplies. For determining the active chlorine in bleaching liquors a colorimetric titration by Hauser (20) gives very good results.

The use of an optical instrument to determine the chlorine present has been shown to give good results as shown by Hauser in my last paragraph. The colorimeter, refractometer, and the nephelometer are some of the instruments used in chlorine determinations that give good results.

Strauss (21) gives a colorimeter method with results that compare favorably with those obtained by the Volhard method. J. Becke (22) makes use of a refractometer. Its use is based on the reaction which occurs on mixing two solutions. The observed angle will be different from those of the two solutions before mixing. This principle leads to the deriving of a formula giving percent of chlorine from the angles observed. The nephelometer has great use when delicate tests are needed. A. B. Lamb (23) makes use of the nephelometer in testing for small amounts of poison chlorine gases. The effect of acids and

salts on the nephelometer determination have been investigated.

(24)

The methods that make use of optical instruments do not give a high degree of accuracy.

A general process which does give high degree of accuracy, higher than the volumetric methods, is the electrometric determination of halogens as silver halides. Aten (25) bases the theory of this method on Nernst's diffusion theory. The accuracy of this method depends on the dilution. (26) Konoysa (27) makes use of the electrometric titration of chlorine in the presence of ferrocyanides. Satisfactory results were obtained.

Most of the fertilizers contain organic compounds and consequently the previously stated methods can not be used on this general type of substances unless modified. In the "Report on the Analysis of Fertilizers" by Frapes (28) describes the method of getting the chlorine free from the organic matter. Another method (29) used in the removal of organic matter on the formation of ammonium salts. After removing the interfering material the chlorine may be determined gravimetrically or by using the Volhard reaction.

### Theoretical

It is known (30) that the solubility of silver chromate and silver oxalate is approximately the same ( $\text{Ag}_2\text{CrO}_4$  is .0025 parts per one hundred and  $\text{Ag}_2\text{C}_2\text{O}_4$  is .00359 parts per one hundred). So when ammonium oxalate is added to the solution and the solution titrated with silver nitrate, silver chromate and silver oxalate will precipitate together. There is a fugitive end point that makes the determination very inaccurate.

Leaching fertilizers that have soluble organic compounds present will tend to color the filtrate. This color will make titrating to accurate end points very hard. If a yellow light is used, all of this color will be absorbed by the light and make titrating much easier.

The solubility of chlorides in hot water is a great deal more than in cold water. The quantity of water used (250 cc) in leaching soluble chlorides is enough to dissolve all chlorides present even if cold water is used.

Using smaller amounts of sample will mean more accurate results because the same leaching (250 cc) will bring down all the chlorides and same leaching will hold smaller quantities of chlorides per cubic centimeter of aliquot part. This will also mean less color to interfere with obtaining accurate end points.

## Experimental Details

### 1. Materials

(1) Fertilizer 8-4-4. Furnished by F. S. Royster Guano Company of Norfolk, Virginia.

(2) Silver nitrate solution. Five grams of recrystallized silver nitrate dissolved in one liter of water. It was standardized against sodium chloride.

(3) Indicator. Five grams of potassium chromate dissolved in one hundred cc of water.

(4) Yellow light. The determinations were carried on in a dark room with a yellow light.

(5) Burettes, crucibles, pipettes and volumetric flasks.

### 2. Methods

#### Standardization of silver nitrate solution.

Dissolve five grams of pure recrystallized silver nitrate in freshly distilled water and dilute to one liter. Standardized against pure dry sodium chloride and adjust so that one cubic centimeter of the solution is equivalent to .001 grams of chlorine.

#### A.O.A.C. Method

Place twenty-five grams of the sample on a 11 cm. filter paper and wash with successive portions of boiling water until the wash-

ings amount to 250 cc, collecting the filtrate in a 250 cc volumetric flask. Cool and mix well. Pipette 50 cc into a 150 cc beaker and add one cubic centimeter of the potassium chromate indicator, and titrate with the standard silver nitrate solution until the color produced by the silver chromate appears as a permanent red.

Recommended Method

Place 2.5 grams of the sample on a filter paper and wash with successive portions of room temperature water until the washings amount to 250 cc, collecting the filtrate in a 250 cc volumetric flask. Dilute to the mark and mix well. Pipette an aliquot proportion into 100 cc white crucible and add one cubic centimeter of potassium chromate indicator, and titrate (using yellow light instead of daylight) with the standard silver nitrate solution until the color produced by the silver chromate appears as a permanent red.

### Discussion

When I had leached a sample of fertilizer and had added ammonium hydroxide and saturated ammonium oxalate I took an aliquot part and started titrating with silver nitrate. The yellow of the indicator gradually turned orange and then finally the pink color appeared. This change took place over a range from one to three cubic centimeters, which is very inaccurate for quantitative work.

N. U. Tankage was added to a few of the samples. The leachings from these samples showed a deeper color. When the yellow light was used the color was absorbed. The color was less after taking aliquot parts and after diluting the aliquot part before titrating. The results were very near the same as other samples in which no tankage was present. The figures in Table 1 show some of the results. Incidentally, only about 2.5 grams of sample was used and cold water was the leaching agent.

Table No. 1

| Amount of sample | Temp. of water      | Amount of water | % Chlorine |
|------------------|---------------------|-----------------|------------|
| 1.1615           | Boiling             | 250             | 8.2        |
| 1.9383           | Cold                | 250             | 8.4        |
| .7052            | Cold                | 250             | 8.2        |
| 2.0545           | Cold (N.U. Tankage) | 250             | 8.2        |

I ran samples using the required 25 grams of the A.O.A.C. method and others using only 2.5 grams and got the same results. Also,

I used room temperature water on a number of samples and the results compared very well with those of boiling water leachings, as Table No. 2 shows.

Table No. 2

| Amount of sample | Temperature of water | Amount of water | % chlorine |
|------------------|----------------------|-----------------|------------|
| 22.1000          | Cold                 | 250             | 8.4        |
| 22.7703          | Cold                 | 250             | 8.4        |
| 21.1613          | Boiling              | 250             | 8.2        |
| .7022            | Cold                 | 250             | 8.2        |
| 4.2210           | Boiling              | 250             | 8.3        |
| 1.9293           | Cold                 | 250             | 8.4        |

### Summary

The determination of chlorides in fertilizers has been studied.

The same sample may be used to run chlorine and potash, if after leaching, aliquot parts are taken. Chlorine is run on one part and potash on another.

N.U. Tackage has no effect except to color the filtrate a deeper yellow.

Room temperature water can be used instead of boiling water in leaching the sample.

Yellow light gives a more prominent end point than white light.

A smaller sample than 25 grams can be used satisfactorily.

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