

Development of Analytical Methods for Commercial Sodium Chloride

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ABSTRACT

A vision is given of the methods of analysis of salt at present, based on the personal experience of the author and also of the project of norms of European Committee for the Study of Salt; such study has been divided in four subjects:

Chlorides: the mercurimetric method is recommended for its determination, which procedure is explained in detail.

Macroimpurities: in it is explained the system of determination of moisture, insoluble matter in water, calcium and magnesium, sulfates, and also the eventual one of potassium and bromides, explaining in detail in one side the technique for the complexometric determination of calcium and magnesium, and on the other side the volumetric one of potassium with STFB.

Microimpurities: commenting their determination and giving special reference to the analysis of copper with APDC by atomic absorption spectrophotometry.

Additives: also commenting the determination of iodides, flourides and ferrocyanides specially.

All the procedures of the determinations are not included but much literature is cited which includes the most important themes concerning this question.

INTRODUCTION

In every analytical technique there is an obligation to develop procedures that are concrete and exact. They must also be easily applicable with respect to the characteristics of the product and the possibilities for its use. Further, it should be noted

that there are various needs for quality control, which may be extraordinarily diverse.

This is typical for commercial sodium chloride employed for industrial purposes, whether derived from mined rock salt, solar evaporation, or vacuum pans. Its analytical methods require both chemometric and instrumental techniques. The procedures described in this paper are based upon our experience concerning these problems, the conclusions of the Standardization Commission of the European Committee for the Study of Salt (E.C.S.S.), and the directives of the International Standards Organization (I.S.O.).

We have systemized the analytical techniques for the following determinations: (1) chlorides (2) macro-impurities (3) micro-impurities, and (4) additives.

DETERMINATION OF CHLORIDES

The direct determination of chlorides is favored over another viewpoint that it is merely necessary to calculate them by subtracting the content of macro-impurities.

The general method which has been in use is Mohrs' argentometric one—well known for its exactness and rapidity. At present, there is a new tendency to substitute the mercurimetric method which is equally precise but requires less costly reagents.

The basis of the mercurimetric method is the determination of the halide ions with mercuric nitrate, using diphenylcarbazone as an indicator.

We recommend the following working technique (Ref. 1):

1.1 Reagents:

- 1.1.1 Nitric acid: Sp. Gr. about 1.4, solution at 63% (m/m) or about 14N.
- 1.1.2 Nitric acid: solution about 2 N, obtained through dissolution of solution 1.1.1.
- 1.1.3 Hydrochloric acid: solution about 2 N, obtained through dissolution of a 37% acid solution—about 12 N or a Sp. Gr. of 1.19.
- 1.1.4 Silver nitrate: solution at 5.0 g/liter (dissolve 5.0 gr. of silver nitrate in water and dilute to 1.000 ml.)
- 1.1.5 Barium chloride: solution about 1 N (dissolve 122 gr. of barium chloride ($\text{BaCl}_2 - 2\text{H}_2\text{O}$) in water and dilute to 1 liter).
- 1.1.6 Sodium chloride: standard solution 0.1 N; dissolve in water 5.8443 g of sodium chloride previously dried during 2 hours at 500°C , and afterwards please cool and complete the concerned volume at 1.000 ml.
- 1.1.7 Indicator blank: This blank should be prepared just before it is used. Introduce then, into a 500 ml Erlenmeyer flask, 200 ml of water, 3 drops of bromophenol blue (1.1.9) and some nitric acid (1.1.2) added dropwise until obtaining the change of color from blue to yellow. Add then an excess of 3 drops of that acid, 1.0 ml of diphenylcarbazone (1.1.10) and the volume of solution of mercuric nitrate (1.1.8) contained into a buret, necessary for making the solution to change from yellow to blue violet (say 1 drop).
- 1.1.8 Mercuric nitrate—Strengthened solution 0.1 N: Dissolve 10.85 g of mercuric oxide (HgO) in 10 ml of nitric acid (1.1.1) and dilute the acidified $\text{Hg}(\text{NO}_3)_2$ solution with water to 1.000 ml. Standardize the solution by the method described in paragraph 1.2.4.
- 1.1.9 Bromophenol blue: solution at 1 g per liter in ethanol at 95% in volume.
- 1.1.10 Diphenylcarbazone: solution at 5 g per liter in ethanol at 95% in volume.

*1.2 Procedure**1.2.1 Test taking*

E = about 50 g weight at about 0.01 g being sure, of course, that the sample represents the whole.

1.2.2 Solution

Begin the test by taking a 600 ml beaker and add 350 ml of water. Heat for 10 minutes keeping the temperature just below boiling, stirring it well; put it into a water bath for 30 minutes and keep the beaker covered with a watch glass.

Filter using a glass or porcelain crucible with porous bottom and with such a porosity that the filtrate is limpid; collect the filtrate into a 500 ml flask. Wash with cold water up to the moment that 20 ml of water of washing does not muddy when adding either 10 ml of solution of silver nitrate (1.1.4) (absence of chlorides) or 10 ml of solution of barium chloride (1.1.5) and 0.5 ml of solution of hydrochloric acid (1.1.3) (absence of sulphates).

Complete at volume with water at 20°C and homogenize.

1.2.3 Preparation of test solution

Take 50 ml of previous solution, at the pipet and dilute them at 500 ml.

1.2.4 Calibration of the solution of mercuric nitrate (1.1.8)

Introduce, into a 500 ml Erlenmeyer flask 40 ml of standard solution of sodium chloride (1.1.6), 160 ml of water and 3 drops of bromophenol blue (1.1.9), add the solution of nitric acid (1.1.2) dropwise until the color changes from blue to yellow, add an excess of 3 drops of this acid and after 1.0 ml of diphenyl carbazone (1.1.10). The chloride with help of the solution of mercuric nitrate to be calibrated, up to some color as the indicator blank (1.1.7) introduced at the time of preparation of this blank (about 1 drop):

The correct titration is 40.00 ml. Calculate the normality factor.

1.2.5 Dosage

Introduce 25 ml of the test solution, previously taken at the pipet, into a 500 ml Erlenmeyer flask. Dilute at 200 ml after adding 3 drops of bromophenol blue (1.1.9) and a solution of nitric acid dropwise (1.1.2), up until the indicator changes from blue to yellow, add an excess of 3 drops of this acid followed by 1.0 ml of diphenylcarbazone (1.1.10).

Titrate with a solution of mercuric nitrate (1.1.8) up to the same color as the indicator blank (1.1.7).

1.3 Expression of the results

1.3.1 Calculation

The halogens contents, expressed in chlorine, is computed in percentage of mass by the following formula:

$$(V-V') \times \frac{0.1}{1000} \times f \times 35.453 \times \frac{500}{25} \times \frac{500}{50} \times \frac{100}{E} = \frac{(V-V') f}{E} \times 70.906$$

where:

V = the volume, in milliliters, of standard solution of mercuric nitrate (1.1.8) required for titration of the test solution

V' = the volume, in milliliters, of standard solution of mercuric nitrate (1.1.8) required for titration of the blank

f = the normality factor of the solution of mercuric nitrate (1.2.4)

E = the mass, in grams, of the test taking

1.3.2 Note

Make at least two determinations and take the average one; show the result with 3 significant figures.

DETERMINATION OF MACROIMPURITIES

The macroimpurities include moisture, the insoluble matter in water, the sulphate, calcium and magnesium ions of which determination is usually made, and also the bromide and potassium ions, which are not commonly determined.

We will consider each of these techniques in this way:

- 2.A — Determination of moisture
- 2.B — Determination of insoluble matter in water
- 2.C — Determination of calcium and magnesium
- 2.D — Determination of sulphates
- 2.E — Determination of potassium
- 2.F — Determination of bromides

DETERMINATION OF MOISTURE

The exact determination of moisture has several difficulties because it requires the differentiation of the moisture itself from crystallization water which normally is found with the impurities which are in the salt. The risks of the reaction of the impurities (magnesium chloride, for example) and the water in accordance with the temperature must be considered.

In order to avoid these difficulties, it is necessary to normalize a conventional method of determination of "loss of mass" at $110^{\circ}\text{C} \pm 2^{\circ}\text{C}$ instead of its determination through chemical methods (Ref. 2).

DETERMINATION OF INSOLUBLE MATTER IN WATER

These are determined in the following manner (Ref. 3):

2.B Procedure

2.B.1 Taking of test

E = about 50 gr weight at 0.01 gr near, being sure, of course, that the sample represents all of the whole.

2.B.2 Dosage

Introduce the test sample into a 600 ml beaker and add 350 ml of water. Heat for 10 minutes to the limit of ebullition keeping the temperature just below boiling, stirring it well; place in a water bath for 30 minutes and keep the beaker covered with a watch glass.

Filter through a crucible with a porous bottom previously dried at 110°C and tared. Wash with cold water. Ensure that at the end of the washing there will be no trace of chloride, through a test with silver nitrate. In case the quantity of calcium and/or sulphates should be very high, it should be ensured that at the end of the washing of the beaker there is no trace of sulphates through a test by barium chloride in the presence of hydrochloric acid.

Dry the crucible and its contents in an oven at $110^{\circ}\text{C} \pm 2^{\circ}\text{C}$ until reaching a constant mass. Perform several weighings regularly spaced taking precaution, before every weighing, to let the crucible cool in a dessicator (two weighing performed within one hour intervals should not differ in more than 0.2 milligrams.)

DETERMINATION OF CALCIUM AND MAGNESIUM

After having definitively disregarded the determinations of calcium and magnesium in the gravimetric method, they have been determined by the volumetric method with EDTA and several other indicators.

Several years ago (Ref. 4) we determined that the process with EDTA was good whatever the rel-

ative proportions of calcium and magnesium in salt. We employed ammonium purpurate (murexide) and eriochrome black T, color index 14645, respectively, as the end point indicators of the determination of calcium and the sum of the calcium and magnesium.

In the determination of calcium two new indicators, calconcarboxylic acid and GBHA, have been used. Both one and the other afford a precise end point and a perfect reproducibility, for which reasons both can be adopted with all safety. The E.C.S.S. has elected GBHA simply because it is an indicator recommended by ISO for analogous determinations (Ref. 5). The usefulness of calconcarboxylic acid is well known. We were interested in studying it as in our previously mentioned work (Ref. 4) we obtained satisfactory results with Patton & Reeder indicator (calconcarboxylic acid) in certain conditions. By always employing blank titration we have been able to show that it was attributable to the purity of the dye.

As far as the determination of magnesium, the indicator most generally accepted continues to be the eriochrome black T.

The operating technique recommended in this report and which coincides with that of the E.C.S.S. for both determinations is as follows (Ref. 6):

2.C.1 Reagents

2.C.1.1 Hydrochloric acid, solution 1:1.

Dilute 50 ml of hydrochloric acid sp. gr. about 1.18, solution at 37% (m/m) with water and complete up to 100 ml.

2.C.1.2 Sodium Hydroxide sp. gr. 1.08, solution at 7.5% (m/m) or 2 N, approximately. Dissolve 80 grams of sodium hydroxide in water and complete the volume up to 1,000 ml.

2.C.1.3 Silver nitrate: solution at 5.0 g per liter. Dissolve 5.0 g of silver nitrate in water and dilute to 1,000 ml.

2.C.1.4 Barium chloride: solution about N. Dissolve 122 g of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in water and dilute to 1 liter.

2.C.1.5 Ethanol at 95% (v/v).

Alcohol denaturalized with acetone can be eventually used, but not in a colored state.

2.C.1.6 Disodium Ethylenediamine Tetracetate Dihydrate (E.D.T.A.) standard solution at 0.02 M.

Dissolve about 7.7 gr of EDTA into water.

Transfer into a 1,000 ml flask, complete up to the volume and homogenize. Adjust the strength of this concentrated solution to 0.02 M in comparison with the standard solution of calcium chloride (2.C.1.8) by operating as follows:

Take off 25.0 ml of the solution of calcium chloride (2.C.1.8) and introduce them into a 250 ml Erlenmeyer flask. Add successively about 25 ml of water, and afterwards, with the help of graduated pipets, 4 ml of the solution of sodium hydroxide (2.C.1.2), 15 ml of ethanol (2.C.1.5) and 1.0 ml of the solution of GBHA (2.C.1.11). Wait for about one minute and afterwards strengthen with help of the solution to be verified until attaining a color change from red to straight yellow. In order to facilitate the correct color change, the eventual help of a basic witness solution is employed as a comparative reference, prepared by introducing successively into a second 250 ml Erlenmeyer flask about 75 ml of water, 4 ml of the sodium hydroxide solution (2.C.1.2), 15 ml of ethanol (2.C.1.5) and 1.0 ml of the GBHA solution (2.C.1.11). The correct titration is 25.0 ml. Calculate the molarity factor.

2.C.1.7 Disodium Ethylenediamine Tetracetate Dihydrate (E.D.T.A.); standard solution 0.002 M.

Take off 100.0 ml of the EDTA solution 0.02 M (2.C.1.6) and introduce them into a 1,000 ml flask. Fill until reaching the capacity level line, and then homogenize. Calculate the molarity factor.

2.C.1.8 Calcium chloride, standard solution 0.02 M.

Weigh 2.0000 g of pure calcium carbonate which has been previously dried in an oven for a minimum of two hours at 130-140°C, and pour them into a 400 ml beaker. Mix 75 ml of water with 25 ml of hydrochloric solution (2.C.1.1), and pour such solution into the beaker. Boil it and keep such ebullition for about five minutes in order to eliminate the carbon dioxide. Cool at about 20°C, transfer quan-

tatively into a 1.000 ml flask, fill up to the volume and homogenize.

2.C.1.9 Buffer solution.

Dissolve 54 g of ammonium chloride in water. Add 350 ml of ammonia (sp. gr. 0.920) and make up to 1 liter with water.

2.C.1.10 Methylorange, solution at 0.5 g per liter.

Dissolve 0.05 g of methylorange in water and bring the volume up to 100 ml.

2.C.1.11 Glyoxal bis (2-hydroxy-anil) (GBHA) alcoholic solution at about 2.5 g per liter.

Pour about 0.25 g of GBHA into a 100 ml glass bottle tightly stoppered, dark colored. Add 100 ml of ethanol (2.C.1.5) and shake until reaching the dissolution.

2.C.1.12 Eriochrome Black T, powder at about 0.4 (m/m).

Mix intimately 0.4 g of Eriochrome Black T, color index 14645, with 100 g of powdered sodium chloride, taking care that such mixing results in a perfectly homogeneous solution.

2.C.2 Procedure

2.C.2.1 Test

E = about 50 g weighed at about 0.01 g, being sure, of course, that the sample represents the whole.

2.C.2.2 Solution

2.C.2.2.1 Put in solution of calcium and magnesium soluble in water.

Introduce the "test" into a beaker of 600 ml and then add 350 ml of water. Heat for ten minutes keeping the temperature just below boiling and stirring it well. Leave it in a water bath for 30 minutes and the beaker covered with a watch glass.

Filter in glass or porcelain crucible with porous bottom and with such a porosity that the filtrate is limpid, and then collect the filtrate into a 500 ml flask. Wash with cold water up to the moment that 20 ml of water of washing does not cause mudding, when adding either 10 ml of solution of silver nitrate (2.C.1.3) (absence of chlorides) or 10 ml of solution of barium chloride (2.C.1.4) and 0.5 ml of solution of hydrochloric acid (2.C.1.1) (absence of sulphates).

Bring up to the original volume with water at 20°C and homogenize.

2.C.2.2.2 Putting total calcium and magnesium in solution:

Introduce the "test solution" into a 600 ml beaker, add 350 ml of water, 3 drops of the methylorange solution (2.C.1.10) and hydrochloric acid solution (2.C.1.1) drop by drop, until reaching the color changes from yellow to red. Heat for 10 minutes keeping the temperature just below boiling while stirring it well. Leave it in the water bath for 30 minutes and keep the beaker covered with a watch glass.

Filter following the instructions of (2.C.2.2.1) and bring up to the original volume with water at 20°C and homogenize.

2.C.2.3 Dosage

2.C.2.3.1 Dosage of calcium:

Take 50.0 ml of the filtrate and pour them into a 250 ml Erlenmeyer flask. Add successively, by means of graduated pipets, 10 ml of the sodium hydroxide solution (2.C.1.2), 15 ml of ethanol (2.C.1.5) and 1.0 ml of the GBHA solution (2.C.1.11) pH of the solution should be higher than 12; if it is not so, add a quantity of the sodium hydroxide solution (2.C.1.2) being sufficient to exceed such pH. Wait about two minutes and afterwards titrate with standard EDTA solution (2.C.1.6) the color changes from red to pure yellow. The titration must be performed in less than three minutes.

2.C.2.3.2 Dosage of magnesium:

Take 100.0 ml of the filtrate and pour it into a 400 ml Erlenmeyer flask and dilute to about 200 ml. Add 5 ml of buffer solution (2.C.1.9) and a little less than double the quantity of ml of standard EDTA solution (2.C.1.6) employed for the dosage of calcium.

Then heat at 50°C, add about 0.1 of Eriochrome Black T (2.C.1.10): this causes a winy red coloring.

Continue adding EDTA (2.C.1.6), which should be done slowly especially when coming close to the end point until obtaining a dark blue color (without any violet reflection).

2.C.3. Expression of the results

2.C.3.1 Calculation

Let it be

E = the mass, in grams, of the test

V = the volume, in milliliters, of standard solution of EDTA required for the titration of calcium

V' = the volume, in milliliters, of standard solution of EDTA required for the titration of calcium and magnesium

t = the molarity of the standard solution of EDTA

f = the molarity factor of the standard solution of EDTA

2.C.3.1.1 Calcium contents

The calcium contents is computed in percentage of mass by the following formula:

$$V \cdot \frac{t \cdot f}{1000} \cdot 40.08 \cdot \frac{500}{50} \cdot \frac{100}{E} =$$

$$\frac{V \cdot t \cdot f}{E} \cdot 40.08$$

2.C.3.1.2 Magnesium contents

The magnesium contents is computed in percentage of mass by the following formula:

$$(V' - 2V) \cdot \frac{t \cdot f}{1000} \cdot 24.32 \cdot \frac{500}{100} \cdot \frac{100}{E} =$$

$$\frac{(V' - 2V) \cdot t \cdot f}{E} \cdot 12.16$$

2.C.3.2 Note

Make at least two determinations and take the average one; show the results with 3 significant figures and with a maximum of 3 decimals.

These methods have been normalized, foreseeing the possibility of employing EDTA 0.02 M or EDTA 0.002 M, in accordance with the quantity of calcium and/or magnesium being present. One should always employ the same standard EDTA for both determinations. It is necessary that the difference in consumption of EDTA solution between that of calcium titration and that of calcium and magnesium titration is of a minimum of 0.5 mL.

The change from winy red to blue of the determination of the addition of calcium and magnesium with Eriochrome Black T is difficult to fix in certain cases. It presents some difficulties of a subjective character. With a view to improve observing, it is necessary to revert to a blank titration which

can be performed either by employing a "synthetic witness" or making the determination in duplicate. One employs the first change—slightly exceeded—as a witness to the second definitive change. Generally speaking, one prefers the second way since, among other reasons, the "synthetic witness" might not contain certain elements which are present in industrial salt and which might affect the tonality of the change. All of it, apart from that the preparation of the "synthetic witness," constitutes a supplementary operation which makes the determination difficult without any apparent advantage over the second method.

In the magnesium determination one can substitute the Eriochrome Black T for the Eriochrome Blue Black B (C.I. 201, C.I. 14640 or F 239), with the advantage that the titration is made at an ambient temperature. This product, which differs from the Eriochrome Black T in that it does not contain in it the "nitro" group, is the sodium salt of the 1-(1-hydroxy-2-naphthylazo)-2-naphthol-4-sulfonic acid. This reagent can be found on the market as a zinc salt. Both the sodium salt and the zinc salt afford concordant and reproducible results as well as a definite and clear change. The use of this dye can be recommended without reservation.

SULFATE DETERMINATION

This is done gravimetrically. They are determined as barium sulfate. It is unnecessary to reproduce the operating technique for such a determination (Ref. 7).

The quelometric procedure for the sulfates determination have been attempted. But the methods of B. Riva (Ref. 8) and JMC (Ref. 9) have not given convincing results.

POTASSIUM DETERMINATION

Although the determination of this element is not usually made, some consumers perform it systematically by sodium tetraphenylborate or by flame photometry. They have abandoned the classical methods which required chloro-platinate, perchlorate or cobaltinitrite which were employed until a few years ago.

At present we determine it by precipitating it as potassium tetraphenylborate with an ulterior dissolution of this precipitate in acetone and mercuric chloride. We finish with a titration of hydrochloric acid which has been formed, according to the following technique:

*2.E.1 Reagents**2.E.1.1 Sodium carbonate, about 3 N.*

Dissolve 80.0 gr of dried sodium carbonate in about 450 ml of water and transfer into a 500 ml flask. Complete at this volume.

2.E.1.2 Saturated solution of aluminum chloride.

Add 25 ml of water containing 25 gr of aluminum chloride ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$) into an 100 ml Erlenmeyer flask. Stir well from time to time, let it decant and use the overflowing solution, which can be muddy without causing any difficulty.

2.E.1.3 Sodium tetraphenylborate, (STPB), solution of 30 gr/l.

Dissolve 15.0 grams of STPB in 500 ml of water. Verify that the pH of the solution is 6-7 and, if necessary, make sure that it maintains such level by addition of sodium hydroxide or hydrochloric acid.

To the muddy solution add 1 drop of a saturated aluminum chloride solution and 5 mgr of lithium chloride. After the precipitate is flocculated, filter it and keep the clear solution in a plastic flask.

2.E.1.4 Washing solution saturated in potassium tetraphenylborate (PTPB).

Dissolve about 100 mgr of potassium chloride in 100 ml of water, and after adding about 20 ml of solution of STPB, filter and wash five times with water. Transfer the precipitate to a 1,000 ml flask. Complete up to the volume. Leave it for one hour, stirring frequently. Filter the solution and keep it in a polythene bottle.

2.E.1.5 Methyl Red Indicator (1 g per liter).

Dissolve 0.1 g of methyl red in ethanol (95 percent) and dilute to 100 ml.

*2.E.1.6 Mercuric chloride solution: saturated.**2.E.1.7 Neutral acetone: its neutrality should be checked as follows:*

By pouring 15 ml of acetone into 50 ml of distilled water containing 3 drops of methyl red indicator (2.E.1.5). The addition of 1 to 2 drops of sodium hydroxide 0.1 N (2.E.1.9) on one side and hydrochloric acid 0.1 N (2.E.1.10) on the

other side should be sufficient to cause the color to change.

2.E.1.8 Potassium iodide solution.

Dissolve 50.0 grams of potassium iodide in water, dilute to 500 ml, and keep the solution in dark bottle.

*2.E.1.9 Sodium Hydroxide, Standard solution 0.1 N**2.E.1.10 Hydrochloric Acid, Standard solution 0.1 N**2.E.1.11 Lithium Chloride Reagent**2.E.2.1 Procedure:*

Introduce into a beaker 100 ml of the solution prepared analogously as for the chlorides determination (1.2.1 and 1.2.2), add about 5 ml of sodium carbonate solution (2.E.1.1) and boil during one minute. Let it cool slightly (to about 70°C). Add dropwise and stirring 10 ml of the STPB solution (2.E.1.3).

Wash the sides of the beaker with 5 ml of acetone (2.E.1.7) passing them through the filter-stick stirring the precipitate with a glass rod. Collect the PTPB solution in a flask containing 5 ml of saturated mercuric chloride solution (2.E.1.6). Blow twice 5 ml of acetone (2.E.1.7) each time through the filter-stick to ensure that it is perfectly clean. Wash the filter-stick three times with 10 ml water each time.

Add to the "kitasato" 5 drops of methyl red indicator (2.E.1.5) and 0.1 N sodium hydroxide solution (2.E.1.9) until the color changes from red to yellow. Add an excess of 0.1 N sodium hydroxide solution (2.E.1.9) of about 10 ml.

Boil and add 10 ml of the potassium iodide solution (2.E.1.8) and 5 drops of methyl red indicator (2.E.1.5). Titrate with 0.1 N hydrochloric acid solution (2.E.1.10) until the color changes to intense red.

Submerge the beaker in a cool water bath until it reaches room temperature. Filter through a grade B² porcelain filter-stick. Wash the precipitate three times with a washing solution saturated in PTPB (2.E.1.4), (5 ml each time) and after-

wards wash the filter-stick twice with 2 ml of water each time.

2.E.3.1 Calculation

Let it be:

E = the mass, in grams, of the test taking

V = the volume of 0.1 N sodium hydroxide solution added

V' = the volume of 0.1 N hydrochloric acid solution required for the titration of the excess of 0.1 N sodium hydroxide solution.

The potassium contents in grams per 100 grams of salt is computed by the formula:

$$(V-V') \cdot \frac{0.1}{1000} \cdot \frac{1}{3} \cdot 39.096 \cdot \frac{500}{100} \cdot \frac{100}{E} = \frac{V-V'}{E} \cdot 0.65$$

Such a method is efficient. It has been employed by us as another method for the determination of potassium other than by atomic absorption spectrophotometry, or by the procedure mentioned in a recent article (Ref. 10).

BROMIDES DETERMINATION

We employ the classic technique of oxidation from bromide up to bromate with sodium hypochlorite. The excess is eliminated with sodium formate, enabling us to determine iodometrically the bromate which has been formed. The details of the procedure are presented in a recent paper (Ref. 11).

This is a determination which usually is not made.

DETERMINATION OF MICROIMPURITIES

It is difficult to standardize the analysis of what we have called the "microimpurities," because it includes or may include so great a range of determinations. For these reasons it is practically impossible to study them in detail within the limits of this article. The Japan Monopoly Corporation, for example, in its book (Ref. 9) includes the methods for determination of 13 trace components, and Bloomberg & Ladenburg's study presents the spectrophotographic detection of 35 elements in salt (Ref. 12).

We have been obliged to consider the microimpurities in a sporadic way, with the exception of

copper due to the fact that the codfish curing industry has requested a meticulous control of its contents which must not exceed 0.1 ppm. We usually determine it spectrophotometrically. Previously, we extracted it with sodium diethyldithiocarbamate (Ref. 13). The latter method is generally accepted in the codfish curing industry. But, we will present a method based on the technique of atomic absorption spectrophotometry (Ref. 10).

Ten g of salt are dissolved in 50 ml of water. One ml of 5% aqueous solution of ammonium pyrrolidine dithiocarbamate is added and the pH is adjusted to 2.8 with hydrochloric acid. The analyte is extracted by shaking with 10 ml of methyl isobutyl ketone. This extract is atomised in a flame and the absorption of the atomic cloud at the copper band is measured at 3247 Å. The value obtained is compared in front of a series of aqueous standards in the same procedure as for the extraction with APDC and MIBK.

We think that some of the determinations which are recommended for the salt—or brines—are in reality impurities not imputable to the salt itself. Some contamination is due to the reaction of the solutions with the electrodes.

DETERMINATION OF ADDITIVES

Several substances are added to the salt which give it some peculiar properties.

For example, in the salt used for curing, several countries authorize the addition of nitrite; vitamins are added to the salt used for making bread (thiamine, riboflavin, niacin); in order to avoid the caking of salt, several anti-caking agents are used (ferrocyanides, magnesium carbonate, calcium aluminosilicate, etc) and to the salt used for alimentary purposes is added iodine and fluorine compounds for the prophylaxis of the goiter and tooth caries.

CONCLUSION

The aim of this article is to review several methods of analysis of commercial sodium chloride, and this has been done. The article does not pretend to be exhaustive, because certain determinations in some fields can be important (i.e., pH, alkalinity or nitrates). My only intention is that norms are established for the analysis of such a vital raw material. This study coincided with the intentions and labor of the European Committee for the Study of Salt.

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