ture for a sufficient length of time. The lactic acid produced was isolated in the form of calcium lactate. This was not the case with some lactose crystallized in nodular masses of prismatic crystals which had been obtained originally from Kahlbaum, and had been standing for twenty-five years in a stoppered jar. It was sterile. With the exception of this specimen, all the others gave an abundant crop of bacteria when definite weights dissolved in sterilized water were submitted to ordinary gelatin-peptone culture. The maximum number obtained in this medium was 1400 colonies per gram of milk sugar. In studying these colonies I looked more particularly for the bacillus *acidi lactici* and the other ten or twelve species, which are at the present time classified as the specific milk bacteria, but without success. With a lactose-litmus gelatin solution a still larger number of colonies was obtained and possibly larger search in this medium, might have revealed the specific milk bacteria of lactic acid fermentation. But my immediate object had been attained, and the presence of bacteria as a common impurity in lactose, to be looked for and avoided by the chemist and the druggist, sufficiently demonstrated.

THE QUANTITATIVE DETERMINATION OF THE THREE HALOGENS, CHLORINE, BROMINE AND IODINE, IN MIXTURES OF THEIR BINARY COMPOUNDS.

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CHEMICAL literature contains many records of methods for the quantitative estimation of the halogen elements, and for any one of these elements in the absence of the others they are as satisfactory as may be required. There are also, it is true, many suggestions and several proposed methods for the separation and estimation of these elements when present together or when some two are found in the same mixture, although they are generally unsatisfactory for one reason or another. The methods for qualitative determinations as given by Hart and by Kebler, in the *Journal of Analytical Chemistry*, are thoroughly satisfactory. A very convenient qualitative method that is in use in this laboratory consists in first using chlorine water, or euchlor, (made from potassium chlorate and hydrochloric acid), which immediately determines the presence or absence of iodine and in its absence that of bromine. Carbon bisulphide is used as the final indicator. If iodine is present more chlorine water is added and the whole is heated until the iodine color is replaced by the light yellow color due to bromine. This point is easily discerned. If now one or more of these halogens are present a portion of the original solution is treated with concentrated nitric acid and boiled until both of these elements are removed. This solution is now tested for chlorine by the usual methods.

There are several methods for the quantitative estimation of the halogens by the formation of their silver salts, the further treatment depending on whether two or three of these elements are present. In all cases, however, much time is required for the analysis and great care in the manipulation of the precipitates. Sexton says, in his work on Quantitative Analysis, Third Edition, that there is no known method by which the two acids, hydrogen bromide and hydrogen chlorine can be completely separated. He recommends their precipitation as silver salts, the weighing of this product and the conversion of the bromide present into the chloride by passing chlorine gas over the fused mixtures. From the results the amount of each halogen is determined. Of course the general procedure could be used if an iodide were associated with the chloride but would not be applicable in case all three halogens were present.

Dr. Prescott, in the *Journal of Analytical Chemistry*, **3**, gives an acceptable method for the estimation of bromine in the presence of chlorine and calls attention to several others that have been employed. Fresenius gives, on pages 592 to 600 in the Second American edition of his work on Qualitative Analysis, elaborate methods for determining these elements in all possible mixtures of the binary compounds of these elements. They are generally difficult of application and employ rare reagents. It may be said, in general, that all methods of indirect estimation of the halogens in mixtures of their binary compounds are troublesome, although some of the recent modifications of these methods give fairly satisfactory results, especially in the separation of two of the elements like chlorine from bromine.

The authors, therefore, began the examinations of several of the recent methods for the direct estimations of these elements. The method of M. Dechan was tested and found to produce too low results for the chlorine since a portion of it was set free as hydrogen chloride by the action of the sulphuric acid added after the iodin was supposed to be set free. In the original contribution[1] the author directs that the volume of the liquid in the distilling flask must not be much reduced and never below two-thirds of the original amount. Even then the amount of the chlorine is low. Under the conditions required by M. Dechan the bromine is satisfactorily separated from the chlorine and the iodine from both.

In 1885, Dr. Hart published a method for the qualitative determination of these three elements in mixtures of their binary compounds. This method suggested the method developed by the authors for the quantitative estimation of these elements.

The alkali salts of these three elements were purified and dissolved in separate solutions. The salts were taken to be pure at the start and accordingly ten grams of each of the salts was dissolved each in a liter of water. The mixtures were made from these solutions by carefully measuring definite volumes and thoroughly mixing. In this way solutions containing varying amounts of any one of the salts were prepared. The salts were afterwards found to be somewhat impure and the proper correction for this impurity has been made in the tables.

Ferric ammonium alum was used to free the iodine. The solution was made from the crystallized alum, using 200 grams to the liter. The potassium permanganate solution was a saturated solution. This was used in a concentrated form, since considerable was required to oxidize the iron that had been reduced by the iodine. The solution for the absorption of the iodine and bromine contained 200 grams of potassium iodide to the liter and thirty-five cc. were used in the receiver.

The apparatus finally found to be the best for the distillation consisted of a 500 cc. Wurtz flask with the side tube inserted

[1] *J. Chem. Soc.*, 49.

quite near the bulb of the flask. The condenser was made with a long inner tube so that it could be bent at the lower end at the proper angle to fit into the receiver. A rubber stopper was slipped on the bent end so that when the tube was inserted in the receiver it would reach into the absorbing liquid. The best receiver was a three-bulbed U tube of about 250 cc. capacity. The upper end of the distilling tube was slightly smaller than the somewhat enlarged mouth of the inner tube of the receiver so that although the former did not enter the tube yet when they were brought together and covered by a piece of rubber tubing the latter was protected from any iodine or bromine vapors. The limb of the U tube into which the bent tube of the condenser passed was stopped by a rubber stopper. In a number of the estimations a second absorption tube was attached to the usually open limb of the U tube but in no case did any recognizable amount of iodine or bromine vapor escape.

The distillations were carried on as follows: To the distilling flask was added fifty cc. of the iron sulphate solution and to this water enough to make about 200 cc. The halogen salt solutions were carefully measured from burettes into the flasks. The proper connections were made and the distillation carried on for twenty-five minutes after the liquid had reached boiling temperature. Some fifteen or twenty glass beads were added to prevent bumping. The flasks were heated by a flat four and one-half inch burner. The flask and burner were carefully protected from currents of air to prevent the drawing back of the liquid in the receiver. It was found that the rubber stopper in the distilling flask of the form indicated was not noticeably attacked by the vapors in course of about 100 determinations.

When the distillation had been completed, as just described, the flask was detached from the condenser, the tube of which was washed with a warm solution of potassium iodide followed by hot water. Another receiver prepared exactly as for the absorption of the iodine was now attached to the condenser. Thirty-five cc. of potassium permanganate solution was now added, and with it water in sufficient quantity to make the volume about 200 cc., the connections made and the distillation carried on until the bromine was all set free. Twenty-five minutes time was used for each distillation, but less time was usually sufficient. In fact most of the halogens were driven over during the first few minutes of heating after boiling temperature was reached. In case very great accuracy is not required an estimation can be completed in a few minutes.

It is evident that in all cases there must be relatively large excess of reagents. When the distillations were complete the iodine set free in the receiver was titrated against decinormal sodium thiosulphate. The titration can be made in the receiver but it was found most convenient to pour the liquid into a six-inch evaporating dish before estimation.

The contents of the flask are now removed to a beaker and the excess of the permanganate reduced by ferrous sulphate, adding sulphuric acid enough to render the solution clear. The solution was slightly warmed to hasten the action. It was then cooled and made up to a definite volume and an aliquot part estimated by precipitation with silver nitrate. There was nothing to prevent the estimation of the chlorine by titration, but no determinations were made by that method.

The following tables give the results of the work :

	Potassium iodide taken.	Iodine in potassium iodide.	Iodine found.	Potassium bromide taken.	Bromine in potassium bromide.	Bromine found.	Potassium chloride taken.	Chlorine in potassium chloride.	Chlorine found.
1	0.986	0.0754	0.0745	0.198	0.1330	0.1329	0.994	0.4869	0.4829
2	0.493	0.0377	0.0374	0.198	0.1330	0.1299	0.994	0.4869	0.4859
3	0.493	0.0377	0.0377	0.099	0.0665	0.0658	1.988	0.9738	0.9699
4	0.493	0.0377	0.0376	0.099	0.0665	0.0662	0.994	0.4869	0.4870
5	0.493	0.0377	0.0378	0.099	0.0665	0.0659	0.994	0.4869	0.4858
6	0.493	0.0377	0.0375	0.0495	0.0332	0.0328	0.994	0.4869	0.4867
7	0.493	0.0377	0.0375	0.0495	0.0332	0.0331	0.994	0.4869	0.4857
8	1.972	0.1508	0.1499	0.099	0.0665	0.0664	1.988	0.9738	0.9679
9	1.972	0.1508	0.1484	0.099	0.0665	0.0659	0.497	0.243	0.241
10	0.493	0.0377	0.0375	0.0495	0.0332	0.0329	0.497	0.243	0.242

The tabular statement needs no particular explanation. The quantities represented are the amounts in grams in each case.

It may be well to note that this general method is applicable for rapid technical estimations of bromine or of iodine either by themselves or in case of mixtures of the same. Single analyses can be readily made in ten to fifteen minutes.

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