

vanometer deflection is noted. Five standards suffice to plot a calibration curve, as shown in Figure 2, which automatically eliminates any error due to traces of impurities in a given set of reagents.

Analysis is accomplished by taking 5 cc. of a solution in which the amount of phosphorus lies within the range of 0.001 to 0.010 mg. The color is developed and the galvanometer deflection obtained as in the case of the standards. From the position of the galvanometer reading on the calibration curve the quantity of phosphorus present may be read off.

TABLE III. PHOSPHORUS IN BONE ASH

Experiment No.	Age of Rat Days	Weight of Ash Mg.	Dilution Factor	Scale Reading ^a Mm.	Phosphorus Mg.	%	Variation of Duplicate Readings ^b %
61	10	2.4	100	32.9	0.00115	4.79	2.61
				33.3	0.00112	4.67	2.68
62	6	1.4	50	24.1	0.00205	7.32	8.29
				25.7	0.00188	6.71	9.06
64	20	15.6	1000	32.4	0.00120	7.69	1.67
				32.2	0.00122	7.82	1.65
66	11	5.1	200	15.2	0.00395	15.49	1.26
				15.4	0.00390	15.29	1.28

^a Photronic cell No. 1, Nessler tube No. 1.

^b Difference in mg. $\times 100$, mg.

The character of the calibration curve is conditioned by the particular photronic cell, Nessler tube, and set of reagents employed. With these three factors constant, the reproducibility of the calibration curve for photronic cell No. 9, tube No. 3, was determined by noting the galvanometer reading of five sets of standards. Table I lists the mean and individual galvanometer readings for the blank and four solutions containing known concentrations of phosphorus.

The results of a number of typical analyses for phosphorus in bone ash are given in Tables II and III. The data in

Table II were obtained with photronic cell No. 9 and Nessler tube No. 2 and fit the calibration curve shown in Figure 2. The data in Table III, using a different photronic cell and Nessler tube, furnish additional evidence of the applicability of the method.

The variation in phosphorus content of bone ash in different experiments is due to the fact that bones from rats of different ages, as well as poisoned and unpoisoned rats, were used. These variations are of no significance for this paper and will be discussed in a subsequent publication.

Summary

A simple photoelectric colorimeter employing a Weston photronic cell is described, and its application to the determination of phosphorus between the limits 0.001 and 0.01 mg. is demonstrated.

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Sodium Chlorite as a Volumetric Oxidizing Agent

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Sodium chlorite of high purity is now available in quantities which permit it to be considered as a laboratory reagent, particularly as an oxidant in volumetric analysis. A sodium chlorite solution is easily prepared and standardized, and is stable over a period of several months if kept in a dark bottle. Standard sodium chlorite solutions have been successfully used in the determination of sulfur dioxide, sulfites, and bisulfites, and preliminary work indicates that their use can be extended to the quantitative oxidation of other reducing substances.

SODIUM chlorite of high purity has recently been made available (The Mathieson Alkali Works, Inc., 62 East 42nd St., New York, N. Y.) in quantities which permit it to be considered as a laboratory reagent. The stability of sodium chlorite solution and its smooth and easily controlled oxidation reactions suggested that it might prove of use as an oxidizing reagent in volumetric analysis. The authors' investigations have shown that dissolved sulfur dioxide, sulfurous

acid, and sulfites can be satisfactorily determined by oxidation with sodium chlorite. Preliminary work indicates that it can probably be applied to the volumetric determination of certain other reducing substances.

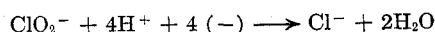
There are but few references in the literature to the use of chlorites (1, 3, 4, 5) and only one to their use as a quantitative analytical reagent. Levi and Ghiron (4) made use of the reaction between calcium chlorite and a permanganate in a neutral solution to determine the permanganate.

The sodium chlorite as obtained is a white, finely crystalline material. Being slightly hygroscopic, it takes up some moisture when exposed to air. The salt dissolves readily in water, its solubility being 91.3 parts in 100 parts of water at 30° C. (6). The freshly prepared solutions are entirely clear and colorless. The more concentrated solutions gradually turn yellow and yellow-green if allowed to stand exposed to light.

An analysis (8) of a sample of sodium chlorite showed the following percentages: NaClO₂, 97.6; NaCl, 0.7; NaOH, 1.5; NaClO₃, 0.0; and H₂O (by difference), 0.2.

Preparation and Standardization of Solutions

The equivalent weight of sodium chlorite (as an oxidizing agent in an acid solution) is one-fourth of its molecular weight:



In this investigation, standard solutions of two different strengths, approximately 0.1 *N* and 0.3 *N*, were prepared by dissolving the calculated amount of salt in freshly boiled distilled water and diluting to the desired volume.

The sodium chlorite solutions were standardized by comparing them against a standard sodium thiosulfate solution whose strength had been determined by the use of potassium iodate according to the modified method of Than (9). An accurately measured volume of the sodium chlorite solution was run into an Erlenmeyer flask containing 75 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, and 15 ml. of 30 per cent acetic acid. The liberated iodine was titrated with sodium thiosulfate, 5 ml. of a 1 per cent starch solution being added near the end of the titration.

Stability of Sodium Chlorite Solutions

Levi and Natta (5) working with solutions of 0.2 *N* and 0.02 *N* sodium chlorite found that the chlorite was stable in the presence of 0.5 per cent sodium hydroxide. The stability of the authors' solutions was tested as follows:

The sodium chlorite solution was carefully standardized and divided into two parts. One portion was placed in a clear, glass-stoppered Pyrex bottle; the second portion was placed in a similar bottle which had been heavily coated on the outside with black paint and wrapped in heavy black paper. The two bottles were then stored in the laboratory (at room temperature) so that they were protected from direct sunlight but exposed to ordinary light. Tests were made on the chlorite solutions (as in the standardization) from time to time. The results are shown in Table I.

TABLE I. THIOSULFATE EQUIVALENT TO 1 ML. OF SODIUM CHLORITE SOLUTION

Elapsed Time Days	Solution Protected from Light Ml.	Solution Exposed to Light Ml.
0	1.00	1.00
1	1.00	1.00
2	1.00	0.94
5	1.00	0.92
8	1.00	0.92
21	1.00	0.88
30	1.00	0.83
90	1.00	..
210	1.00	..

The sodium chlorite solution is entirely stable over a period of several months when stored so that light is excluded.

Determination of Sulfites

A standard solution of sodium chlorite has been used to determine the sulfites in calcium bisulfite, sodium sulfite, sulfurous acid solutions, and the cooking acid used in the sulfite pulping process. The latter solution contains lignin derivatives, sugars, and other organic matter. The sodium chlorite solution has been found satisfactory in each case.

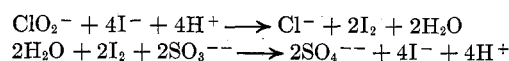
Hendrixson (2) has shown that the oxidation of sulfite by iodate is quantitative. Palmrose (7) has shown that the iodate oxidation is not affected by the presence of organic matter in the solution being tested. In this investigation, the results obtained by the iodate titration were taken as the standard and the results of the sodium chlorite titrations compared with them.

Procedure

A measured amount of the solution being tested (or an aliquot part of the diluted solution) was transferred, with the usual precaution to avoid loss of gas, to an Erlenmeyer flask containing 100 ml. of distilled water, 15 ml. of 10 per cent potassium iodide solution, 15 ml. of 30 per cent acetic acid, and 5 ml. of 1 per cent starch solution. The standard chlorite solution was then run in rapidly until near the end point and then drop by drop until the blue starch-iodine color persisted. It is best to avoid shaking the solution until most of the chlorite has been added.

The reaction $\text{ClO}_2^- + 2\text{SO}_3^{--} \rightarrow \text{Cl}^- + 2\text{SO}_4^{--}$ probably takes place if chlorite is allowed to react with sulfite alone. It appears, however, to be a time reaction and seems to go

fairly slowly. In the presence of potassium iodide the reactions probably are:



When all the sulfite has reacted, the free iodine gives the deep blue color to the starch, indicating the end of the reaction.

Results

Most of the authors' work has been done on solutions of calcium bisulfite containing from 0.3 to 6.0 per cent of total sulfur dioxide (free and combined). Some of the results obtained are given in Table II. The agreement among different operators was good, the results usually checking within 4 parts per thousand.

TABLE II. DETERMINATION OF TOTAL SULFUR DIOXIDE IN SOLUTIONS OF CALCIUM BISULFITE

Sample No.	Sulfur Dioxide	
	Iodate method %	Chlorite method %
1	0.537	0.539
2	0.497	0.492
3 ^a	4.18	4.18
4	5.66	5.65
5	5.71	5.71
6	5.21	5.19
7	5.25	5.27
8 ^a	3.14	3.14
9 ^a	3.07	3.07
10	5.07	5.06
11	5.52	5.51
12	5.32	5.33
13	4.88	4.90
14	5.68	5.68
15	5.03	5.02

^a Solutions did not contain organic matter.

Conclusions

Sodium chlorite gives an easily prepared, easily standardized volumetric oxidizing solution which is stable when properly protected from the light. The analytical procedure is simple and rapid.

Sodium chlorite solutions have been found satisfactory for the determination of sulfur dioxide, sulfites, and bisulfites in various solutions and especially in the calcium bisulfite solutions used in the sulfite pulping process. The chlorite oxidation is not affected by the presence of small quantities of organic substances such as are present in the cooking acid used for the sulfite process.

Preliminary work indicates that sodium chlorite probably can be used for the quantitative oxidation of other reducing substances.

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