cautions than is ordinarily possible by the direct titration by the customary process.

This work seems to open up a rather promising field for further investigation. The use of other oxidizing agents than potassium bichromate and potassium permanganate; the reaction of these substances with a variety of reducing agents; the possible determination of two or more oxidizable substances in the same solution (as can be readily accomplished in the case of two acids in the same solution), and the practical application of the method to cases in which the procedure of ordinary volumetric analysis in unavailable or uncertain, are problems which present themselves at once. Work will be continued along these lines in this laboratory.

Summary.

(1) Measurements have been made of the change of conductivity of solutions of ferrous salts during their oxidation by potassium bichromate and potassium permanganate.

(2) It has been shown that the conductivity measurements may serve to determine the end point of the reaction with a degree of accuracy equal to or greater than that obtainable by the usual volumetric procedure.

(3) The experimental technique, the general nature of the "conductivity-reaction" curves, and the influence of various factors upon these curves, have been discussed.

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[CONTRIBUTION FROM THE BUREAU OF STANDARDS.]

REDUCING MATTER EXTRACTABLE FROM FILTER PAPER.

BY R. S. McBRIDE AND J. A. SCHERRER.[1]

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In the determination of iron with potassium permanganate, it is sometimes necessary to precede the titration by a filtration, *e. g.*, to remove free sulfur formed during reduction with H_2S. Recently there were described by Boller[2] some experiments which were designed to show that such filtration through filter paper previous to titration with potassium permanganate was without effect. Since the results appear to be at variance with earlier conclusions of Hillebrand,[3] it was desired to conduct some additional experiments which might throw light on the subject, which is of importance in connection with an extensive investigation of methods for the determination of iron now in progress at the Bureau of Standards.

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[1] Published with permission of the Director, Bureau of Standards.

[2] "Beiträge zur titrimetrischen Bestimmung des Antimons. Zinns, Titans, Eisens, und Urans." Dissertation, Zürich (1915).

[3] "Analysis of Silicate and Carbonate Rocks," U. S. Geol. Survey, *Bull.* **422**, 15 (1910).

The results of Rosa, Vinal, and McDaniel[1] are also of interest in this connection as showing from the character of the action of filter paper extracts on silver nitrate solutions that reducing substances were to be expected in appreciable quantities. We desired to determine, first, if reducing matter was extracted; second, the magnitude of the error, if great enough to be considered in either technical or exact analysis; and third, if any evidence of the extraction of reducing material was found, what reagent and what conditions would be best for the elimination of the error.

Samples of seven of the most widely used filter papers, six quantitative and one qualitative, were taken from the original packages in order to avoid any effects due to exposure to laboratory fumes, but other tests on older paper were also made. The procedure for each test was as follows: The filter papers were folded and placed in funnels in the usual way, and the reagent was poured through, 250 cc. being used in each case except where otherwise noted. A blank was run with each group of the tests in order to make evident any irregularity due to differences of the temperature of the solutions tested, and to detect any accidental impurities which might have found their way into the reagents. To the solution which had passed through the filter sufficient permanganate was at once added to produce a distinct pink (equivalent to that of 0.03 cc. of 0.1 *N* $KMnO_4$ in an equal bulk of pure water). Distilled water and alkaline solutions were acidified before testing. By this procedure any reducing material extracted from the filter paper could be detected at once by comparing the time before disappearance of the pink color with that for the blank. Temperature is, of course, a very important factor in the speed of the reaction. When the term "hot" is used a temperature of 70–80° is meant.

Blanks.—In the case of cold water, cold sulfuric acid, both $2^1/_2$ and 5% by volume, and cold solution of ammonia, a drop (0.03 cc.) of the 0.1 *N* potassium permanganate gave a pink color which persisted for over three hours. If the test with these reagents was carried out hot the color disappeared in about one hour. With cold sodium hydroxide and sodium carbonate solutions the pink color produced with one drop of the potassium permanganate lasted about one hour, but with hot solutions the pink faded in 10 to 15 minutes.

Single Filtrations.—The results of the first series of tests are shown in the tabulation. It is to be noted that cold water, cold acid of either strength, and cold ammonia solution gave the same results; and moreover, a filtration with these reagents hot followed by a quick cooling before the permanganate was added gave the same result as a filtration made cold. On the other hand, if the whole test was made while the reagent was hot, or if the reagent passed through the paper cold but was heated before the

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[1] *Bull. Bur. Standards*, 9, 209–82.

permanganate was added, much more rapid fading of the color was observed. Indeed, the temperature at which the reagent passed through the paper seemed to be a negligible factor, whereas the temperature at the time of testing is of considerable importance.

In the case of sodium hydroxide or carbonate solutions, there is evidence of a somewhat greater amount of reducing matter in the filtrates;[1] but with the cold reagent on any of the quantitative filter papers the influence is small or perhaps even negligible.

Successive Filtrations.—In order to determine whether or not all extractable reducing matter was removed by the first 250 cc. of reagent, tests were made with another equal portion. It was found that the second portion gave a much more permanent color with permanganate, in most cases being almost as free from reducing matter as the reagent itself as judged by the "blanks." Furthermore, it was found that the papers, after being washed with one portion, could be left for as long as several hours moist and exposed to the air without re-formation of any reducing matter that would be found by another extraction with 250 cc. of the same reagent after this interval.

Since these results indicated that almost all of the extractable matter was removed rapidly, further tests on some of the papers were made by filtering first a 25 cc. portion and then a 250 cc. portion. The 250 cc. portion gave a much more permanent color, which was, however, less permanent than that of the "blanks" on the reagent. This showed a measurable rate of extraction of the reducing material, but the first 25 cc. portion certainly removed all of the reducing matter except a small amount that would ordinarily be negligible.

Digestion of Papers with Reagents.—In some cases macerated filter paper is used with precipitates, for instance, calcium oxalate or the whole of a filter paper is thrown into the titration vessel before addition of permanganate. It was desired to determine the probable magnitude of the influence of these practices on the titration and also to test the result of longer action of the reagent on the filters. To do this, 2 sheets of each of five kinds of paper were macerated and then digested for an hour with 500 cc. of each reagent; tests were made, both hot and cold. After this digestion, half the liquid was decanted from the pulp and tested with permanganate. The other half was tested in the presence of the filter-paper pulp. The permanganate was decolorized somewhat faster in the

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[1] It is worth while to note here that the first few cubic centimeters of the sodium hydroxide solutions which pass through the S. & S. 590 papers were colored slightly yellow. This fact, which had previously been noted by Hillebrand (U. S. Geol. Survey, *Bull.* 422, 147), but which was not definitely ascribed to the action of the alkali on the paper, is of considerable importance in rock analyses, where the presence of chromium is often determined by observation of the yellow color of the filtrates after fusion with alkaline carbonates.

TABLE OF RESULTS.[1]

Reagents filtered.	S. & S. 590.		S. & S. 589 blue band.		S. & S. 589 white band.		S. & S. 589 black band.		S. & S. 595.		Whatman No. 40.		Baker & Adamson.	
	Cc.	Min.	Cc.	Min.	Cc.	Min.	Cc.	Min.	Cc.	Min.	Cc.	Min.	Cc.	Min.
Cold water. Hot water, cooled before testing. Cold H_2SO_4 ($2^1/_2\%$ by volume). Hot H_2SO_4 ($2^1/_2\%$), cooled before testing. Cold H_2SO_4 (5%). Cold NH_4OH ($2^1/_2\%$ by volume of conc. 0.90 sp. gr.), neutralized before testing.	0.03	10	0.03	30	0.03	15	0.03	30	0.03	10	0.03[3]	15	0.03[3]	2[0]
Hot water. Hot H_2SO_4 ($2^1/_2\%$). Hot NH_4OH ($2^1/_2\%$), neutralized before testing. Same 3 reagents cold, but heated before testing..	0.03	0.5	0.03	15	0.03	5	0.03	15	0.03 0.06 0.09	[2] 1 10	0.03[3]	2	0.03[3]	2
Cold NaOH (1%), neutralized before testing..	0.03	0.5	0.03	3–5	0.03	2	0.03	3–5	0.09	0.5	0.03	3	0.03	4
Hot NaOH (1%), neutralized before testing.	0.12	2–3	0.06	3–5	0.12	2	0.09	3–5	0.24	2	0.09	2	0.09	3
Cold Na_2CO_3 (2%), neutralized before testing	0.03	3–5	0.03	10	0.03	5	0.03	10	0.06	5				
Hot Na_2CO_3 (2%), neutralized before testing	0.06	2	0.06	3	0.06	2	0.06	3–4	0.09	2				

[1] In the table of results the columns headed "cc." represent the number of cc. of 0.1 N $KMnO_4$ required to color. The columns headed "min." give the approximate duration of the color in minutes.

[2] Lasted only a few seconds.

[3] Not all the tests were made on these papers.

presence of the pulp, but in all cases the results were not very different from those obtained by the rapid passage of a single portion of the reagent through a similar paper. It appears, therefore, that no material increase in the reducing matter results from such digesting of the paper with the reagent.

Action of Old Papers.—In order to determine whether filter papers kept in the laboratories would yield extracts with any greater consumption of permanganate than those from the original packages, about twenty samples of filters were gathered from different laboratories, and tested in the same way as those from the new stock. These papers showed no marked difference in action. It is concluded, therefore, that the exposure to ordinary laboratory atmosphere conditions is not serious in its effect.

Comparison with Other Results.—Hillebrand,[1] in his method for reduction of vanadium with hydrogen sulfide, filters off sulfides through S & S. 590 filter paper, and titrates at 70–80° with very dilute permanganate. He advocates, however, making one or two checks by reducing with sulfur dioxide, boiling this out, and repeating the titration. He says that these results are apt to be very slightly lower than the first and are to be taken as the correct ones. In a private communication he attributes the high results to oxidizable material removed from the filter paper. Our work corroborates this view; but the results of varying acidity of the solution at the time of reduction with hydrogen sulfide may also be a factor.[2]

Boller[1] made some tests to determine the influence of a filtration before titrating with permanganate. He treated 500 cc. of water containing 25 cc. 2 N sulfuric acid with carbon dioxide while boiling for 10 minutes, allowed to cool, and titrated with 0.01 N permanganate. He then repeated the above, but before titrating passed the liquid through a S. & S. 590 filter. He repeated these experiments with 200 cc. of 2 N sulfuric acid. In both cases he found no greater blank when the liquid was poured through the filter than when the filtration was omitted.

It will be noticed that in our work we found that the action upon permanganate was much more rapid when the reagent was hot than when cold; the difference is probably sufficiently great to account for the difference of opinion of the authors quoted.

General Conclusions.—There is undoubtedly some substance extracted from the kind of filter papers ordinarily used which reduces permanganate. Identification of this material was undertaken by McDaniel[1] and he concluded that it was furfural or a closely related substance produced by oxidation and hydrolysis of the cellulose. When an end point permanent for 30 seconds is satisfactory, it does not appear to make much difference

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[1] *Loc. cit.*

[2] See footnote *c* on page 108 of *Bull.* 422, referred to in footnote on p. 930.

what the reagent is, nor whether it is hot or cold. Apparently the more liquid used in the first washing, the greater the amount of reducing substance removed; but only a small amount of reagent is needed to remove most of the material.

When the titration is made in the cold and 0.1 *N* permanganate is used, there is practically no significant effect on the titration as ordinarily carried out, but when 0.02 or 0.01 *N* permanganate is used, and especially when the titration is carried out hot, the error may become relatively great.

Washing the filter paper previous to use is a great aid in avoiding excessive consumption of permanganate. In fact, our work indicates that if the filter is given a preparatory washing with 25 cc. of the reagent, filtration and titration can be carried out, even at 70–80°, without error on this account. Even comparatively long exposure of paper, or titration in the presence of the paper, is not ordinarily objectionable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW HAMPSHIRE COLLEGE.]

A STUDY OF SOME RARE EARTH COMPOUNDS.

BY A. J. GRANT AND C. JAMES.

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von Welsbach has shown that the double oxalates of the rare earths and ammonia may be used for the separation of the rare earths, and that these compounds are better suited for the purpose than the similar potassium salts. These facts brought to the minds of the authors the possibility of using the derivatives of some of the amines with perhaps even better results. This paper describes the work carried out by the authors along this line together with the examination of a few new salts.

It was decided to study roughly the solubilities of several suitable rare earth oxalates in solutions of oxalates of methylamine, ethylamine and triethylamine. Methylamine was prepared from acetamide in the usual manner. However, the preparation of the latter upon a large scale did not appear to be a simple matter at first, for the use of sealed glass tubes was too slow and expensive. A trial with an iron mercury bottle soon showed that this type of apparatus could not be employed since the iron was badly attacked. The method recommended by Schulze in which one molecule of ammonium thiocyanate was heated with two and one-half molecules of glacial acetic acid at the boiling point for four days gave a good yield. In this case the crude product appeared to contain impurities which were hard to remove, and, in addition, unpleasant gases and vapors were evolved during the process.

The authors found that the best method for the production of acetamide was to pass a large amount of dry ammonia into glacial acetic acid until