test. Therefore, all jars not air-flushed should be weighed quickly after the test. Standing in desiccators will cause deviations, and to avoid this, the jars used call for inlet and outlet capacities of only 0.25 ml.

Barometric changes will affect ultimate results. For instance, a rise or fall of 10 mm. will give a change of 0.0015 gram in the sulfur dioxide capacity of the jar. This is 10 p. p. m., or 100 per cent error. By working in a 60-minute period, deviations from this source are avoided.

Large samples of 500 to 1500 grams of sulfur dioxide evaporated over periods of 5 to 24 hours checked the 60minute samples within 15 per cent, thus justifying the use of a quick method for control work.

Moisture tubes and other sampling flasks were flushed with dry sulfur dioxide, washed with liquid sulfur dioxide, and then used for the analytical sample. In these cases, the results checked standard analyses taken when the moisture tubes were merely wiped carefully with a warm cloth and kept in an oven between tests.

Blank Test

Variations in analyses made at different seasons of the year and by widely scattered laboratories led to a daily test of one 2000-pound (907-kg.) container called the barometer drum. The actual moisture content of this liquid sulfur dioxide could not alter, but the moisture content as reported by the laboratory varied from time to time. In warm weather, the apparent p. p. m. rose, but on cool, dry days, they decreased. This variation in moisture content was always accompanied by an atmospheric change—namely, the grains of moisture per cubic foot of air. The maximum average month at West Norfolk was June, with 7.5 grains, and the minimum average was December, with 2.5 grains. The daily maximum was 9, and the daily minimum was 0.6.

For 18 months, tests were made on this so-called barometer drum, or blank. The results figured in p. p. m. were plotted against the grains of moisture per cubic foot of air, and produced the curve shown in Figure 2. Several hundred subsequent tests have checked the correctness of this curve as applied to the analytical procedure just described.

The adjustment of all tests to standard conditions is made easy by the correction curve, Figure 3. This is based on a standard of 2.75 grains and 7 p. p. m. for the blank test. The moisture content of samples taken in groups with the blank reflect the variations shown by Figures 2 and 3. Therefore, any test with known humidity can be corrected to standard conditions. When the grains are above 2.75, a minus correction in p. p. m. is applied to the proximate analysis. Below 2.75, a plus correction is used.

ULTIMATE CALCULATION

P. p. m. in proximate analysis \pm p. p. m. correction = ultimate analysis

Example—Proximate result = 15 p. p. m.Grains per cu. ft. = 4.55Correction = -5Ultimate analysis = 10 p. p. m.

Conclusion

Elaborate equipment and methods of analysis with absolutely constant conditions the entire year should enable one to obtain check tests day by day. Small laboratories interested in the moisture content of sulfur dioxide do not have the facilities, the extensive technical control, and the equipment for this work. They can, however, follow the method just described and use the correction curve shown in Figure 3 to place their results on a standard basis for comparison.

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Quantitative Separation of Copper and Cadmium by Reduction of Their Salts with Potassium Formate^{1,2}

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THIS work grew from observations upon the effect of heat on the formates of several metals. Copper formate when heated gave off metallic copper in such a state of subdivision that the metal came from the mouth of the test tube in a heavy copper-colored vapor. Lead formate yielded metallic lead; zinc formate, the oxide; cadmium formate, the metal and some carbonate. It was very apparent that the temperatures required for these reductions varied greatly with the metal concerned. Hence experiments were instituted to apply this temperature differential to the separation of copper and cadmium.

The heating of the formates of these metals for $2^{1/2}$ hours at 150° C. effected a separation. However, this did not constitute a satisfactory quantitative method because of the

¹ Received February 7, 1931.

² This material is taken from a thesis submitted by the author for the degree of master of arts at the University of Nebraska in 1913. The author feels that the material here summarized is interesting not only for the separation involved but in calling special attention to potassium formate as a reagent of more general applicability. Permission has been given by F. W. Upson of the University of Nebraska for the publication of the material in its present form. The author wishes to thank Benton W. Dales for advice during the progress of the work. powdery nature of the copper and the presence of varying amounts of cuprous carbonate formed.

The next reagent studied was sodium formate. The solution of the sulfates of copper and cadmium was made acid with formic acid and about 15 grams of sodium formate were added to each sample and the solution evaporated to * dryness. The samples were placed in an oven at 130° C. for 1 hour. The residue, after cooling, was extracted with hot water. The undissolved material consisted of a mixture of metallic copper and an analysis showed all the cadmium to be present in the filtrate. The filtrate was evaporated to dryness and again placed in the oven. There was no reduction of cadmium salt until 145° C. had been reached.

Experiments with potassium formate showed several differences between this reagent and the sodium salt, which may be summarized as follows:

Reagent	MIXTURE	COPPER SALT	CADMIUM SALT
	FUSES	REDUCED	REDUCED
	°C.	° C.	° C.
Sodium formate	250	135 to 140	145 to 150
Potassium formate	150	100	200

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Moreover, the reduction of the copper salt with sodium formate gave a mixture of the metal and cuprous carbonate, whereas the reduction with potassium formate yielded the metal only in a spongy form. By means of this reagent, metallic copper was obtained from the sulfate, chloride, carbonate, nitrate, and fluoride. In the latter instance the beaker was etched by the hydrofluoric acid formed. The metals cadmium, cobalt, nickel, silver, and mercury were obtained by the same means.

For quantitative tests of potassium formate as reductant, the same procedure was used as above except that potassium formate was substituted, 15 grams of the reagent being added for each 2 grams of the sample. The solutions were evaporated on a hot plate until metallic copper began to separate out. The samples were then placed in the oven at 155° to 160° C.

for $1^{1}/_{2}$ hours. When cooled, the residues were extracted with hot water and filtered through weighed Gooch crucibles. The metallic copper was washed with hot water and then with alcohol and ether. The crucibles were dried for a short time at 75° C. and the residue weighed as metallic copper. Since the copper is in a spongy form, care must be taken to avoid oxidation. The cadmium in the filtrate was determined by the usual method of igniting the carbonate to the oxide. Results of typical analyses are given in Table I.

Table I—Results of Reducing with Potassium Formate					
WEIGHT OF CuSO4.5H2O	Copper by F	COPPER BY REDUCTION.			
Grams	Gram	%	%		
$\begin{array}{c} 1.0658 \\ 0.8750 \\ 1.1147 \\ 0.8474 \end{array}$	$\begin{array}{c} 0.2654 \\ 0.2180 \\ 0.2778 \\ 0.2112 \end{array}$	$24.90 \\ 24.92 \\ 24.92 \\ 24.92 \\ 24.92 \\ 24.92 \\ $	24.9324.9324.9324.9324.93		

Volumetric Determination of Chromium and Nickel in Same Solution¹

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\HE following procedure, which is nothing more than the combination of a comparatively new method for the determination of chromium with the well-known method of Moore as modified by Johnson (1) for the estimation of nickel, was made possible only by the discovery of Willard and Cake (3) that boiling concentrated perchloric acid would oxidize compounds of chromium. The facility with which these two methods can be combined so that both chromium and nickel can be determined in the same solution, compensates at least in part in both time and material for the additional expense involved in the use of perchloric acid for the routine analysis of chrome-nickel alloys. The method for nickel, however, cannot be used successfully if either copper or cobalt is present in appreciable quantities, as both metals interfere in the cyanide titration of nickel.

Silicon is precipitated by boiling perchloric acid and can be readily and accurately determined along with the chromium and nickel if the method as given for nickel-chromium iron is used. It is advisable, however, after first removing the filtrate obtained by washing with dilute perchloric acid, from the suction flask for the determination of chromium and nickel, to wash the silica on the filter again with hot dilute hydrochloric acid and water before finishing the determination in the usual manner. Otherwise it is ordinarily necessary to volatilize the ignited silica with hydrofluoric acid in order to obtain accurate results. The end point of the nickel titration is also more easily detected after boiling with perchloric acid, as the solution is both clearer and lighter colored than is the case if this determination is carried out in the usual manner.

The procedure described for nickel-chromium iron is objectionable, as the results obtained are low because the silica retains small quantities of chromium and nickel if washed only with perchloric acid. The tendency for this method to give low results may also be increased by the possibility that the chromium is not entirely oxidized unless the graphitic carbon is totally removed by boiling with an excess of perchloric acid, and even if completely oxidized it may be reduced by the paper pulp used as a filtering medium. The results obtained by this method are not sufficiently low, however, to effect its usefulness seriously as a routine procedure.

¹ Received February 12, 1931.

More accurate results can be obtained if the following method for nickel-chromium iron is so modified that the chromium is titrated before the silica is removed by filtration. The silica can then be filtered out and washed with hot dilute hydrochloric acid and water before titrating the nickel. If the method is modified in this manner it is necessary to boil off the chlorine in the presence of the insoluble silica, a condition under which the solution has a tendency to bump rather violently. This inclination to bump is avoided in the proposed method, as the silica which causes this trouble is removed before boiling off the chlorine, a procedure which is thought to be the most desirable for routine work even though the results obtained are not quite so accurate as can be obtained by removing the silicon after first titrating for chromium.

Method for Chrome-Nickel and Stainless Steel

CHROMIUM-Weigh 1 gram of chrome-nickel or 0.2 gram of stainless steel into a 500-cc. tall-form beaker and add 20 cc. of an acid mixture containing 250 cc. of nitric acid (sp. gr. 1.42), 750 cc. of hydrochloric acid (sp. gr. 1.19), and 1000 cc. of water. Heat until dissolved and add 20 cc. of perchloric acid (60 per cent). Boil until the perchloric acid fumes and the solution clears up and changes color. Continue to boil for 10 minutes after this change has taken place, cool, add 100 cc. of water, boil for 2 minutes, and cool. Add 25 cc. of sulfurie acid (sp. gr. 1.22) and an excess of 0.1 N ferrous sulfate. Titrate back with 0.1 N potassium permanganate to a permanent pink end point.

The chromium is calculated by means of the following formula which includes a titration correction of 0.2 cc. of 0.1 N potassium permanganate.

Des sent chromium -	$[(A \times B) - c + 0.2] \times 0.174 \times D$
Per cent chroninum -	Weight of sample

NICKEL-Add 50 ec. of citric acid solution and 110 cc. of ammonium hydroxide (sp. gr. 0.94) to the solution used for the determination of chromium. The citric acid solution is made by dissolving 500 grams of citric acid in 600 cc. of water and then diluting with 200 cc. of hydrochloric acid (sp. gr.