a method for the determination of the sensitiveness of the colorimeter devised by George Steiger, of the U. S. Geological Survey, and described by him in THIS JOURNAL, 30, 215 (1908). In order to determine the sensitiveness of the colorimetric estimation of titanium by means of the colorimeter described above, solutions similar to those employed by Wells were prepared. After the color produced by the action of hydrogen peroxide on each titanium solution had been developed, the tube *A* was filled to a depth of about 9 cm. with a portion of this solution. The remainder of the solution was placed in the tube *B* and reservoir *C*. The exact level of solution in tube *A* was then noted and ten readings, five on an ascending column and five on a descending column, were made. The results of these comparisons are given in the subjoined table:

				R. H. column B.				
Exp No.	Conc. $MgTiO_2$ in 100 cc.	Color seen through column 9 cm. deep.	Setting of L. H. Col'n. A.	Max. read.	Min. read.	Av. of 10 read.	Per cent. max. variation.	Per cent. error of avs.
1	0.30	Very slight	61.0	62.0	51.0	57.1	9.6	6.80
2	0.60	Light straw	60.0	64.0	57.0	60.05	5.8	0.08
3	1.00	Good straw	60.0	61.0	57.0	59.35	3.4	1.25
4	1.30	Pale lemon	60.3	61.0	59.0	59.90	1.7	0.66
5	1.6	Pale lemon	60.0	62.0	59.0	60.30	2.5	0.50
6	2.5	Lemon	60.5	62.0	58.0	60.30	3.3	0.33
7	4.0	Yellow	60.5	62.5	58.0	60.00	3.75	0.83
8	5.0	Yellow	61.0	63.0	58.5	60.90	3.7	0.16
9	8.4	Dark yellow	60.5	63.0	60.0	61.70	2.4	1.98
10	10.0	Dark yellow	60.0	61.0	58.0	60.00	2.5	0.00
11	11.2	Dark yellow	59.5	61.0	58.5	60.15	2.08	1.09
12	15.0	Good orange	60.0	62.5	59.0	60.30	2.9	0.50
13	20.0	Dark orange	60.0	62.0	58.0	60.15	3.3	0.25

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NOTES.

Analysis of Aboriginal Copper Objects from Mexico and Yucatan.—The following analyses were made at the request of Professor F. W. Putnam, of the Peabody Museum of American Archaeology and Ethnology of Harvard University.

The objects to be analyzed were four small copper bells, about 3.5 cm. long, and about 2 cm. in diameter, weighing in the neighborhood of 5 grams. Owing to their weathered condition and the thinness of the metal, it was impossible to obtain a fair sample of the metal without some oxide, but nevertheless the analyses show that the original metal must have been very pure. Any impurities in the original metal would have appeared in the analyses, because weathering would not have removed them to an appreciable extent. The bell designated as C was in the best condition, and it is probable that a clean sample of the metal was obtained for analysis. As a check on the procedure, an analysis was made of a piece of modern sheet copper.

The procedure in all cases was as follows: About 1 to 2 grams of metal were cut off, cleaned by scraping, weighed, and dissolved in strong nitric acid. The solution was then made up to 100 cc. and aliquot parts taken for the qualitative and quantitative analyses. The residue insoluble in nitric acid, which in every case but one weighed less than 0.001 gram and in that one case weighed a little less than 0.01 gram, was insoluble in yellow ammonic sulfide but was partially soluble in aqua regia, leaving a gritty residue. The residue weighing about 0.01 gram was from the metal of bell A, which was very friable and full of minute cracks impossible to clean out entirely. This residue left a much larger proportion insoluble in the acid, probably siliceous material. The aqua regia solution gave a test for gold with stannous and stannic chlorides, and also with ferrous sulfate.

In the course of the qualitative analysis, the sulfide precipitate, supposed to contain the arsenic and copper groups, was found to be insoluble in ammonic sulfide, showing absence of arsenic. Bismuth and cadmium were absent in every instance, and lead was found only in the bell from Mexico. After the precipitation of the sulfides of the copper group, the filtrate was evaporated to dryness, leaving a hardly appreciable residue which gave a test for iron.

In the quantitative work, the method described by Richards and Bisbee[1] was employed for depositing the copper electrolytically. The lead was determined as lead sulfate. The iron was not present in sufficient quantity to give a significant weight. There was no significant residue on evaporating the residual solution.

Bell.	Condition.	Cu. Per cent.	Fe.	Ag.	Au.	Pb. Per cent.	SiO_2.	O, CO_2, etc., by difference. Per cent.	Origin.
A	Deeply corroded......	80.2	trace	trace	trace	....	trace	19.8	Yucatan
B	Fair................	96.4	trace	....	trace	....	trace	3.6	Yucatan
C	Good................	99.7	trace	trace	trace	....	trace	0.3	Yucatan
D	Fair................	76.7	trace	trace	trace	19.3	trace	4.0	Mexico
	Modern sheet copper.	100.0	trace	....	....	....	....	...	

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The Analysis of Nitrous Oxide.—On attempting to analyze nitrous oxide as supplied in cylinders in the liquid state, we found ourselves confronted with certain difficulties. Consecutive samples of the gas, as drawn off from the cylinders, will vary somewhat in composition, apparently for the reason that the impurities (oxygen and nitrogen) are in

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[1] THIS JOURNAL, 24, 530 (1904).

solution in the liquid nitrous oxide and the sample of gas as drawn or may not have reached a state of equilibrium with the liquid. This evidently will depend on the rate at which the sample is drawn, the length of time elapsing between drawing samples, and various other factors. Duplicate results can easily be obtained from a sample large enough for several analyses but there is no certainty as to what such a sample represents. Again there is a regular progressive change in the composition of the samples as drawn from the cylinder. The impurities escape at a more rapid rate proportionally than the nitrous oxide in which they are dissolved and the nitrogen escapes faster than the oxygen. Below are three sets of figures obtained from the same cylinder of material.

	True content of cylinder.	Nearly full.	Nearly empty.
Per cent. O_2	1.4	2.9	0.7
Per cent. N_2	5.2	11.2	1.6
Per cent. N_2O	93.4	85.9	97.7

We find that all these difficulties can be avoided by the simple expedient of inverting the cylinder and drawing a sample from the bottom of the liquid. That this method gives a fair sample we have proved by drawing a sample in this manner and comparing the result obtained from this sample with that obtained by taking samples at regular intervals during the escape of a whole cylinder of the gas, plotting the results obtained from these samples on rectangular diagram paper and calculating percentages from the areas so obtained.

	From inverted cylinder.	From diagram.
Per cent. O_2	1.1	1.0
Per cent. N_2	3.1	3.3
Per cent. N_2O	95.8	95.7

Oxygen was determined by absorption with pyrogallate, nitrous oxide by explosion with hydrogen, and nitrogen by difference. No impurity other than oxygen and nitrogen was detected in the four cylinders examined except in one specimen, which contained a small amount of carbon dioxide.

The variation in composition in the gas as drawn from the cylinder must be of significance in the administration of the gas, and the method of getting a fair sample should be applicable to other liquefied gases such as carbon dioxide and ammonia.

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LEWIS INSTITUTE, CHICAGO,
May 8, 1911.

On the Qualitative Detection of Mercury by the Method of Klein.—In the work in qualitative analysis at Columbia University, the student is required to report not only what cations and anions are present, but also the approximate concentrations of nearly all the ions tested for. The concentrations may have one of several definit values. Twenty-five cc. of the "unknown" are taken for analysis, and a comparison test on 25 cc. of a standard solution of the ion tested for is carried out as each confirmatory test is made. This method of procedure, introduced at Columbia by Assistant Professor H. T. Beans, has, in general, yielded excellent results even in the hands of inexperienced students.

In confirming mercury, in either state of oxidation, however, difficulty has been experienced in getting the concentrations with sufficient accuracy. This was because the group precipitates of both mercurous and mercuric ions were dissolved in *aqua regia*; then after evaporation, a confirmatory test was made by reducing to metallic mercury by means of stannous chloride. This method, as is well known, yields colloïdal mercury, which is difficult to filter, and does not separate readily in a form suitable for making comparison tests.

It occurred to the author that this obstacle to the consistent application of the analytic procedure in use here might be overcome by a reversal of the process used in making the Nessler test for ammonia, *i. e.*, to test for mercury by means of a mixture containing potassium iodide, sodium hydroxide, and ammonium hydroxide.

After some experimental work on the method had been carried out, it was found that this method had already been proposed by Klein;[1] however, it does not seem to have been used at all in the qualitative detection of mercury, so it is here presented in order that attention may be called to the certain and positive results it yields in the hands of beginners in qualitative analysis.

Preliminary experiments showed that with a mixture containing 10 cc. tenth-normal potassium iodide, 10 cc. 2.5 normal sodium hydroxide and 10 cc. 3 normal ammonium hydroxide, a reagent was at hand, a few drops of which would yield a very decided reaction immediately with 5 cc. of a solution containing mercuric ion of ten-thousandth normal concentration, while 5 cc. of hundred-thousandth normal mercuric ion gave a slight turbidity on standing, when a few drops of this reagent were added.

As the unknowns assigned for analysis contain mercury in much greater concentration than these low concentrations, the amount and concentration of the potassium iodide was changed; a little experimentation showed that it was best to use 5 cc. of half-normal potassium iodide with 10 cc. of three-normal sodium hydroxide and 10 cc. of three-normal ammonium hydroxide; 25 cc. of this reagent give an immediate precipitate of red-brown "Nessler's precipitate," with 25 cc. of 0.001 N, 0.01 N, or 0.1 N mercuric chloride; and a mixture of the oxide and the above

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[1] Klein, *Arch. Pharm.*, [3] 27, 73 (1889); see also Denigès, *Chem.-Ztg.*, 20, 70 1896).

compound with 25.0 cc. of 0.5 *N* mercuric chloride. The precipitate settles rapidly, and there is no difficulty in making comparison tests.

To adapt the method for class use, the following directions were formulated:

"Dissolve the residue of mercury and amido mercuric chloride (Group I)[1] or the residue of mercuric sulfide, and double sulfide and nitrate ($Hg_3S_2(NO_3)_2$) (Group II)[1] in *aqua regia*, and evaporate nearly to dryness, *i. e.*, till only 0.5 to 1.0 cc. of liquid is left. Add 10 cc. water and filter. Wash the residue, if any, with two portions of water, each 2.5 cc. in volume, adding to the filtrate. Now add to this filtrate 10 cc. three-normal sodium hydroxide, and then 25 cc. of the following mixture: 10 cc. three-normal sodium hydroxide, 10 cc. three-normal ammonium hydroxide and 5 cc. half-normal potassium iodide. Red or brown-red precipitate indicates mercury. Make comparison tests by adding 25 cc. of the above test reagent to 25 cc. of a mercuric chloride solution of known concentration since a 25 cc. portion of the unknown was used for analysis."

In the hands of students having had absolutely no experience in the detection of mercury, this method has yielded excellent results where ordinary care and intelligence has been exercised. The main points to note are that the excess of *aqua regia* must be removed and that the mercuric chloride must not be volatilized by overheating the solid residue left on evaporation. In laboratories where concentrations are not reported by the students, the alkaline ammoniacal iodide solution should be added drop by drop, taking care, however, that the solution to be tested is neutral or alkaline before making the test.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.]

THE CONSTITUTION OF DEHYDROACETIC ACID.

BY WILLIAM J HALE.

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The construction of a satisfactory structural formula for dehydroacetic acid has occupied the attention of chemists ever since its discovery by Geuther[2] in 1866. He obtained this crystalline substance from the decomposition products of acetoacetic ester, but attempted nothing beyond its empirical formula, $C_8H_8O_4$. The determination of its correct structure has become highly important by reason of the great variety of well-known and important compounds that can readily be prepared from it, such, for

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[1] See Böttger's "Qualitative Analysis," Smeaton's translation, 1906 ed., pp. 9 and 24 for analysis on this point.

[2] *Jena'sche Zeitschrift*, II, 387 (1866).