THE PREPARATION OF QUALITATIVE "KNOWN" SOLUTIONS.

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In a recent article,¹ the advantages of the use of qualitative "unknown" solutions prepared on a quantitative basis were pointed out; a table was also supplied by means of which these solutions could be rapidly and accurately prepared. Gratifying as the results of this system have been at the college where it has been in use for two years, the full benefits of this method can only be obtained when the "unknowns" are preceded by "known" solutions made up on a similar quantitative basis.

To the conservative teacher in qualitative analysis, this departure from strictly qualitative lines may seem uncalled for; but a consideration of a few reports of qualitative analyses carried out on the old system will, it is believed, thoroughly convince him of the absolute necessity of introducing the quantitative factor in qualitative analysis. Indeed, without it a complete qualitative analysis on the old lines is almost worthless, as the following examples will make evident:

Report 1. Metals found: Fe, Al, Ca.

Acid radicals: PO_4 , SO_4 , SiO_2 .

Report 2. Alloy contains Fe and Mn.

Report 3. Alloy consists of Fe and C.

Report 4. Metals: Mn, Fe, Ca, Mg.

Acid radicals: SiO_2 .

Report 5. Metals: Ba, Sr, Ca.

The substance of Report 1 was an iron oxide ore containing as much as 60% of iron, yet the student from his analysis judged it to be a complex silicate of iron and aluminum mixed with CaSO_4 and $\text{Ca}_3(\text{PO}_4)_2$. The substance of Report 2 was a steel containing a little manganese. From the results of his analysis the student considered it an alloy of Fe and Mn. The material of Report 3 was a sample of cast iron, which was regarded by the student to be essentially a carbide of iron. The sample of Report 4 was a zinc ore; zinc was not reported, and the substance was considered a complex silicate of manganese, iron, calcium, and magnesium. The material of Report 5 was a solution of commercial BaCl_2 , containing relatively small amounts of strontium and calcium. The presence of the latter elements

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was determined solely by their flame reactions. These false conclusions may seem slightly exaggerated, but the fact remains that they are daily made in qualitative work in which the quantitative feature is not emphasized. No such erroneous conclusions could have been reached concerning the nature of the substance submitted for analysis if, in the course of his work, the student gave attention to the proportions in which the components were present. These and similar cases demonstrate the necessity of a good qualitative analysis establishing not only the presence of certain ingredients, but also, though roughly, their quantitative relations; for it must be evident that without this quantitative information a correct idea of the composition of the unknown can not be formed.

It is the purpose of this article to give the method of preparing and using solutions of known strength which in our laboratories have given uniformly satisfactory results. As with the "unknowns" the exact strength will depend upon the scheme of analysis employed. In our work on the metals we prefer schemes of analyses in which precipitation reactions are almost exclusively used because of the indications they strikingly supply concerning the quantities of the metals precipitated. The figures supplied below are for stock solutions of one liter quantity. It is a good plan to prepare 5 or 10 liters of these solutions at one time and thus provide oneself with sufficient to last for several terms. In order to prevent the possible loss of such large quantities of solutions through accidental breakage of the bottle and to preclude the possible contamination of the entire stock in consequence of carelessness of students, we find it a good plan to place in the laboratory, on a shelf of convenient height, one liter of the solution contained in a bottle provided with a siphon and pinch-cock. Each bottle bears a label supplying the following data:

1. The volume of the solution to be drawn off for analysis.
2. The number of milligrams of each metal contained in this specified volume.

The advantages of the use of known solutions prepared to contain definite quantities of metals are: first, the size of the precipitates may be controlled by the instructor and those of unwieldy bulk avoided; second, and this is the chief advantage, that in addition to familiarizing himself with reactions and separations of a particular group of metals, the student also learns the *relation between the quantities of metals present and*

the size of the precipitates which they yield. The quantitative information thus acquired in the analysis of "known" solutions is subsequently applied to the analysis of "unknowns," with the inevitable result that the student is able to report not only the components present but also, though roughly, the quantitative composition of his "unknown." In consequence of this training, the student finds little difficulty in distinguishing between a trace and a significant amount, and is able, at the conclusion of his analysis, to make an intelligent statement as to the identity of the substance submitted for analysis.

In deciding on the strength of these known solutions, it is believed that the two extremes have been avoided. They are neither of such high concentration that satisfactory results can readily be obtained by the careless worker, nor are they prepared of such low strength that only the most careful and painstaking can obtain good results. Allowance has also been duly made for the inexperience of the beginner; and it has been our experience that unless the student exercises a moderate amount of care, he will find it necessary to repeat his analysis to get satisfactory results.

With solids such as salts, ores, and alloys, the same quantitative principle may be followed by requiring the student to weigh out a definite quantity for analysis. In general, 1 to 1.5 grams of an ore and from 0.5 to 1 gram of an alloy will be a convenient amount.

PREPARATION OF "KNOWN" SOLUTIONS.

Group 1. To prepare 1 liter of solution of strength such that 25 c.c., the volume the student takes for analysis, shall contain—

50 mg. Ag,
25 mg. Hg,
125 mg. Pb,

dissolve the following salts, in amounts given in Column 2 of the table below, in water, and then make the volume up to 1 liter:

SALT	Quantity to be dissolved in water
AgNO ₃	3.2 g.
HgNO ₃ ·H ₂ O	1.4
Pb (NO ₃) ₂	8
Conc. HNO ₃	10 cc.

Group II. Division A. The Copper Group.

25 c.c. of solution to contain—

50 mg. Hg^{''},
 100 mg. Pb,
 50 mg. Bi,
 50 mg. Cu,
 100 mg. Cd.

SALT	Quantity to be dissolved in water to make up to 1 liter
Hg (NO ₃) ₂ · ½H ₂ O	3.3
Pb (NO ₃) ₂	6.4
Bi (NO ₃) ₃ · 5H ₂ O	4.6
Cu (NO ₃) ₂ · 6H ₂ O	9.3
Cd (NO ₃) ₂ · 4H ₂ O	11.1
Conc. HNO ₃	In sufficient quantity to keep the solution clear.

Group II. Division B. The Tin Group.

25 c.c. of solution to contain—

50 mg. As^{'''}
 50 mg. Sb^{'''}
 100 mg. Sn^{iv}

SALT	Quantity to be dissolved in water to make up to 1 liter
As ₂ O ₃	2.6
SbCl ₃	3.8
SnCl ₄	8.7
Conc. HCl	In sufficient quantity to keep the solution clear.

Group II. Divisions A and B.

25 c.c. of solution to contain—

50 mg. Hg^{''},
 100 mg. Cu,
 100 mg. Sn,
 50 mg. Sb.

SALT	Quantity to be dissolved in water to make up to 1 liter
HgCl ₂	2.7
Cu (NO ₃) ₂ · 6H ₂ O	18.6
SnCl ₄	8.7
SbCl ₃	3.8

Group III.

25 c.c. of solution to contain—

100 mg. Al,
 100 mg. Cr,
 50 mg. Fe^{'''},
 100 mg. Ni,
 50 mg. Co,
 50 mg. Mn,
 100 mg. Zn.

SALT	Quantity to be dissolved in water to make up to 1 liter
AlCl ₃ .6H ₂ O	35.9
Cr(NO ₃) ₃ .9H ₂ O	30.8
FeCl ₃ .6H ₂ O	9.6
Ni(NO ₃) ₂ .6H ₂ O	20
Co(NO ₃) ₂ .6H ₂ O	10
MnCl ₂ .4H ₂ O	7.2
Zn(NO ₃) ₂ .6H ₂ O	18.2

Group IV.

25 c.c. of solution to contain—

100 mg. Ba,
 100 mg. Sr,
 50 mg. Ca.

SALT	Quantity to be dissolved in water to make up to 1 liter
BaCl ₂ .2H ₂ O	7.2
SrCl ₂ .6H ₂ O	12.2
CaCl ₂	5.5

Group V.

25 c.c. of solution to contain—

50 mg. K,
 100 mg. Na,
 50 mg. NH₄,
 50 mg. Mg.

SALT	Quantity to be dissolved in water to make up to 1 liter
KNO ₃	5.1
NaCl	10
NH ₄ Cl	5.9
MgCl ₂ .6H ₂ O	16.8

Known solution for all groups.

25 c.c. of solution to contain 100 mgs. of each of the following: Ag, Cu, Al, Co, Mg, K, and NH_4 .

SALT	Quantity to be dissolved in water to make up to 1 liter
AgNO_3	6.3
$\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	18.6
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	20
$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	23.6
$\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	42.5
KNO_3	10.3
NH_4NO_3	17.8

PHOSPHATE MINING BREAKS RECORD.

United States Geological Survey Figures Show Production for 1910 over Two and a Half Million Tons.

The mining of phosphate rock for fertilizer showed increased activity in 1910, with the greatest production in the history of the industry. The output was 2,654,988 long tons, against 2,330,152 tons in 1909. Prices, however, were lower, the value of the 1910 output being \$10,917,000, or \$4.11 per ton, against \$10,772,120, or \$4.62 per ton, for 1909. Nearly half of the phosphate rock produced in 1910 was exported, the shipments being 1,083,037 long tons. In 1909 the exports were 1,020,556 long tons. These and other statistics of production, exports, imports, etc., are given by F. B. Van Horn, of the United States Geological Survey, in an advance chapter from "Mineral Resources" for 1910. A copy of the phosphate report may be obtained by request from the Director of the Geological Survey, Washington, D. C.

According to Mr. Van Horn, there are at present five producing phosphate fields in the United States. In the order of quantity of production they are (1) Florida, (2) Tennessee, (3) South Carolina, (4) Arkansas, (5) Idaho, Wyoming, and Utah.

By far the largest of these fields is the Idaho-Wyoming-Utah field, where enormous deposits of high-grade phosphate rock, recently discovered, are available for mining. The field next in available unmined rock is probably Tennessee, where large areas are underlain by deposits of high-grade rock. Florida has a large reserve tonnage, but at the present rapid rate of mining it will not be many years before the rock will be exhausted.

South Carolina has been mining phosphate rock since 1868, and the production has steadily declined since 1889, with the exception of two or three years, when a slight increase in production was noted.

Arkansas has never been much of a factor, and, so far as known, the deposits of this state are not of great extent.