

## QUANTIZED QUALITATIVE ANALYSIS

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### DESCRIPTION OF THE COURSE

This paper is a description of a course in the systematic qualitative analysis of a solution for cations. The course was given by the author for several years at Valparaiso University and has been given at Roosevelt College since the college was founded in the fall of 1945.

The scheme of analysis is a modification of one of the many  $H_2S$  schemes. It was first derived from the procedures of Arthur and Smith. Its difference lies mainly in that it provides for a quantitative report for each cation present.

The idea of quantitative reports in connection with qualitative analysis is by no means a new one but our method of handling them does appear to be new.

All unknowns are one per cent cation solutions. That is to say the total weight of the cations present is one per cent of the weight of the solution. Each solution has the concentration that would result if one gram of an alloy were dissolved in an acid and diluted to 100 ml.

It is important to note here that the concentration of the solution is not proportional to the number of cations present, as is recommended by many text book writers. By the method we recommend if several cations are present the concentration of each is lowered.

The student is given a 5-10 ml. sample of the unknown solution. He is directed to take exactly 1.0 ml of this solution as the basis for his analysis. This is usually measured

with a pipet but a 10 ml. graduate is accurate enough if carefully used. The student is assured that this 1.0 ml. sample of the unknown contains just 10 mg. of total cations, certainly within the limits of 9.5 to 10.5 mg.

Furthermore, the student is assured that if more than one cation is present each will appear in even mg. units. For instance, one ml. of a solution containing Cu and Zn might contain 9 mg. of Cu and 1 mg. of Zn, or 8 mg. of Cu and 2 mg. of Zn, etc., but no quantities that would have to be expressed in fractions of mgs. per ml. This is the source of our title, "Quantized Qualitative Analysis." The different cations appear only in quanta without fractions just as radiant energy does.

Establishing this quanta rule is analogous to asking an analyst to find the major components in an alloy and determine the percentage present to within ten percent of the total. Any component making up less than about five percent of the total would be disregarded. It may also be considered as quantitative analysis to one significant figure.

The grade the student gets depends on how closely he comes in his report to the correct quantitative composition of the solution he analyzed. At first it might appear that this would involve too much concern on the part of the student and too great a burden in grading the reports. Actually neither of these things is true.

Consider a set of unknowns in the copper subgroup and some possible student reports on them:

Solutions	Cations					Grade
	Hg	Pb	Bi	Cu	Cd	
Unknown 1.....	0	50	0	50	0	
Report 1a.....	..	60	..	40	..	50+40=90
Report 1b.....	10	30	20	40	..	30+40=70
Report 1c.....	..	10	..	90	..	10+50=60
Unknown 2.....	20	30	30	10	10	
Report 2a.....	0	50	50	0	0	30+30=60
Report 2b.....	30	20	10	20	20	20+20+10+10+10=70
Report 2c.....	30	0	0	40	30	20+10+10=40

This system of grading has several characteristics.

(1) It is easy to use. The grade is obtained by comparing the composition and the report and adding together the smaller of the two figures appearing under each cation.

(2) Reporting ions not present or reporting them in excessive amounts is automatically penalized because then the student cannot report high enough percentages for the ions actually present. (See report 1b.)

(3) A student will get a fair mark if the qualitative part of his work is correct even though he misses the quantitative answer beyond all expectation. (See Reports 1c and 2b.)

(4) A student is not penalized so much for missing the minor components as for missing those present in large amounts. (See Reports 2a and 2c.)

The preparation of the unknown solution is a simple matter. Stock solutions of salts of the usual 24 cations are prepared. In each solution the concentration of the cation is one per cent (or 10 mg/ml). If the unknown is to contain only one cation, this stock solution also serves as the unknown. Other kinds of unknowns are made by mixing these

stock solutions in the proper proportions without otherwise diluting them. For instance, a solution containing 4 mg. of Cu and 6 mg. of Zn per ml. would be made by mixing 4 ml. of the Cu stock solution with 6 ml. of the Zn stock solution. If a large number of unknowns are to be issued, it may be desirable to prepare more concentrated stock solutions from which the above mentioned dilute stock solutions can be prepared. Most soluble salts are soluble to the extent of 100 mg. of the cation per ml., but a few become saturated at a much lower concentration.

#### SOME DETAILS OF THE ANALYSIS

To perform the analysis the student first makes the usual qualitative separations using standard semi-micro techniques. When a given cation has been isolated one of several different quantitative techniques is applied. Most of these involve comparison with standard solutions. These standard solutions are prepared by diluting the stock solutions referred to above by a ratio of 10 to 1. Thus the student always has access to a stock solution of each cation containing 1.0 mg. of the cation per ml., the minimum amount of that cation that could be present

in each unknown. If a large amount of the cation is present in the unknown, the amount will be a simple multiple of the amount in the standard.

The most common but most unsatisfactory method of estimating amounts is by comparison of precipitate volumes. Eleven of the 24 cations are handled in this fashion. They are Bi, Cd, As, Sb, Sn, Al, Zn, Ni, Mg, Na, K. For each of these that may be found present one mg. of the cation from one ml. of the stock is converted to the same precipitated compound as occurs in the course of analysis and the volumes of the two precipitates compared, usually after centrifuging. Some consideration has been given to the use of graduated centrifuge tubes but these have not been tried.

Amounts of Ag and Hg are estimated by nephelometry. For estimates to the first significant figure this does not require any special apparatus. The procedure is very simple. A 250 ml. beaker for the standard and a beaker of the same size for the unknown are placed over some reading matter. 200 ml. of distilled water is placed in each. The precipitating reagent is added to each beaker in equal amounts and a solution of the isolated cation is added to the unknown beaker. As soon as the fogginess produced by the precipitate has reached a maximum the standard solution is added to the standard beaker from a 10 ml. graduate, in 1 ml. units. The fogginess in the two beakers is compared by attempting to read the print through them. When enough standard has been added to match the fogginess of the unknown the volume of standard solution required is read from the graduate. This volume in ml. equals the number of mgs. of the cation in one ml. of the unknown solution.

Amounts of Cu, Cr, Mn, and Fe ions are estimated by measuring the intensity of the color produced by some form of the ion. Here again no special equipment is used. The volume of isolated cation solution which matches one ml. of the standard equals the number of mgs. of that cation in one ml. of the unknown.

The amount of Pb, Ba, or Sr is estimated by separating or precipitating it as a chromate, washing out the excess chromate reagent, dissolving the precipitate in HCl, and comparing the color formed with that produced in the same way from a one mg. standard.

Determining the amount of Co gives an opportunity to illustrate volumetric precipitation as a quantitative analysis technique. The Co is precipitated by alpha-nitroso-beta-naphthol and the number of drops of reagent required to complete the precipitation is determined. Three drops of the reagent precipitates 0.10 mg. of Co (not 1.0 mg.). This means 300 drops would be required to precipitate the maximum amount of cobalt that could be present. Therefore one-tenth of the isolated cation is tested. This requires from 3 to 30 drops. This illustrates the point that some tests are so sensitive that practical estimates in a reasonable time or reasonable volume can be made only by diluting the cation after it is isolated. Such dilutions are required in estimating Mn, Co, and Ni.

Ca is readily determined by an adaptation of the standard procedure in volumetric analysis where  $\text{CaC}_2\text{O}_4$  is oxidized with  $\text{KMnO}_4$ . Of course, a sufficiently accurate estimate may be obtained by counting the drops of  $\text{N}/3 \text{ KMnO}_4$  solution required. As before from 3 to 30 drops will be used.

The amount of ammonium ion is readily obtained by treating one ml.

of the original solution with NaOH and distilling the  $\text{NH}_3$  into cold water very much like the procedure in a semi-micro Kjeldahl determination. The number of drops of an HCl solution required to keep the distillate acidified is determined.

#### SOME REASONS FOR MAKING QUANTITATIVE REPORTS

Nothing has been said thus far about the reasons for requiring students to make quantitative estimations in conjunction with qualitative analysis.

In the first place, if a student does not estimate quantities he too easily gets the impression that concentration has nothing to do with qualitative analysis, that it is possible to list all conceivable components as being simply "present" or "absent" in a given mixture. To be sure, the teacher who makes up the unknowns knows that the concentrations have to be watched rather carefully, but too often this information is withheld from the student.

Furthermore, it is usually customary to emphasize the principles of chemical equilibrium in the theoretical part of a course in qualitative analysis. Numerical calculations involving solubilities, solubility products, and ionization constants take up much of the time of the course. Most of the value of these calculations is lost if an attempt is made to apply them to solutions of unknown concentration. Likewise the typical student of qualitative analysis will have had only one or two semesters to practice calculations based on balanced chemical equations. He cannot get too much practice in quantitative thinking.

#### REASONS FOR USING ONE PERCENT SOLUTIONS

Some textbook writers recommend that stock solutions be made to a specified normality. To be sure this makes it easy to calculate equivalent quantities of reagents but it is completely unrealistic since it is obviously impossible for a practicing analyst to prepare an unknown solution so it will have a specified normality. However, an analyst faced with the problem of studying an unknown metal or alloy can prepare a one percent solution of this substance and that would seem to be the intelligent way to attack the problem.

The concentration recommended here, one percent total cations, is somewhat more dilute than is commonly used in semi-micro qualitative analysis but it gives good results. In normalities it gives a range of about 0.01 normal to 0.1 normal. It has proved advantageous to conduct many of the separations by adding 1.0 ml. of a 1.0 N solution of the required reagent. It will be seen that this is from ten to a hundred times the equivalent amount, yet the reagent itself is so dilute that a large excess does no harm to the solution. Thus it is often possible to eliminate time consuming procedures that require the student to add a reagent drop by drop until a reaction is complete.

Adjusting the acidity before precipitating the first sulfide group is a simple matter in one percent solutions. One ml. of the solution is diluted to 3 ml. and made neutral to litmus. Adding 1.0 ml. of 1 ON HCl makes the solution about 0.25 N acid, a good condition for precipitating this group. The total concentration

of the cations to be precipitated is so small that any reaction involving them has no important effect on the hydrogen ion concentration.

SUMMARY

It is strongly recommended that students in qualitative analysis should be required to report the concentration of each cation found to

the nearest mg. per ml. and that each liquid unknown supplied to him should have a total cation concentration of one percent (or 10 mg. per ml.).

This gives the student a more realistic situation to deal with, makes it possible to grade his report more fairly, and provides for better application of the theory usually taught in conjunction with such a course.