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A SYSTEM OF QUALITATIVE ANALYSIS FOR THE COMMON ELEMENTS[1]

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INTRODUCTION: OUTLINE OF THE INVESTIGATION

THIS investigation was undertaken for the purpose of studying the processes of qualitative analysis in general use, with reference to their effectiveness in enabling small quantities of each of the more common elements or element-groups to be detected in the presence of any of the other elements, and for the purpose of selecting the methods best adapted to this end and of improving them wherever desirable and practicable. In spite of the vast number of text-books on qualitative analysis in which more or less different processes are recommended, there seems to have been made in recent years no exact systematic study of the relative effectiveness of the separations or of the delicacy of the final tests. It has seemed to us, therefore, worth while to make a detailed investigation of this kind; and as a result of it to develop, if possible, a system of analysis which will enable a quantity of any element as small as one or two milligrams to be detected in any mixture. Effort will also be made to employ only such processes as enable a rough estimate to be made of the quantity of the various elements present; for this is usually a more important function of a good qualitative analysis than the mere determination of their presence or absence. To this end tests of excessive delicacy, like certain color reactions, will be avoided, and each element will be obtained in the solid form as a precipitate or residue, as far as possible.

Especial attention will also be devoted to the chemical reactions involved in the process and to the explanations of them furnished by the Mass-Action Law and Ionic Theory. Since the first systematic application of modern theories to analytical chemistry was made by Ostwald, many physico-chemical researches have been published which make it possible to give such explanations with certainty in a greater number of cases. References to the more important articles relating to the chemistry of the processes and to their theoretical interpretation will be given.

The elements and element-groups included in this system of analysis are primarily those which, with remarkable unanimity, are treated of in the ordinary schemes of qualitative analysis; but we have also introduced

the more important of the so-called rare elements, in so far as this has seemed practicable without seriously complicating or modifying the process best adapted to the more common elements. An independent "System of Qualitative Analysis Including Nearly All the Metallic Elements" is also being worked out in this laboratory; and parts of it have already been published under this title.[1] The latter scheme differs from the one here presented in that the detection of the rare elements forms the essential feature, instead of a merely incidental one.

The results will be presented in the form that seems best adapted to the purposes of the analyst. The "System of Analysis" is for convenience in publication primarily divided into a series of parts, each of which treats of one of the large divisions of the subject. Under each part is first presented a "General Discussion," in which are given the reasons for the adoption of the process employed. This is followed by a "Tabular Outline," which gives a survey of the important steps and the chemical reactions involved in the process of analysis. Then comes the chapter entitled, "Procedures and Notes," in which the details of the process are presented and discussed. Next are given the "Test Analyses," which were made with known mixtures in order to test the efficiency of the process. Finally are presented "Confirmatory Experiments and References," which serve to substantiate the statements made in the notes and to justify the details of the procedures.

In the procedures the operations are described in much detail; it is, however, assumed that the analyst is familiar wtih the manipulative processes of exact qualitative analysis and with the ordinary precautions for assuring completeness of precipitation, washing, etc. In the notes are explained the purposes of the operations and the specific chemical reactions involved from the point of view of the Mass-Action Law and the Ionic Theory, with the general principles of which the reader is assumed to be acquainted. The directions are almost always given in the form applicable to the case where all elements that might be present are present, the modifications admissible when certain operations lead to negative results being usually sufficiently evident. The scheme consists of a series of numbered "Procedures," a new one being begun whenever the substance has been resolved into two parts (such as a precipitate and filtrate) which are to be submitted to different operations. Procedures which are devoted to the detection or separation of the rarer elements are preceded by an asterisk, and are further designated by a letter attached to the procedure number: they may be omitted if such elements are not to be tested for. Notes under other procedures, when they relate to such elements, are also distinguished by an asterisk. At the beginning of each procedure the one by which the substance was last treated, and at the end of

[1] Noyes, *Tech. Quart.*, 16, 93 (1903); 17, 214 (1904).

each procedure those by which the two separated portions of it are next to be treated, are referred to by number.

Most of the experiments described under "Confirmatory Experiments and References" are undoubtedly merely confirmations of previously known chemical facts. The application of these facts to the specific conditions of the procedures it was, however, constantly necessary to test; and it has seemed worth while to make the results a matter of record.

Of the abbreviations employed only a few need be explained: G. D. is used for General Discussion; P. for Procedure; N. for Note; C. E. for Confirmatory Experiments; T. A. for Test Analyses. A number within parentheses expresses the specific gravity at 15°. When it is directed to add a variable quantity of a reagent (for example, 5-15 cc.), the amount used should be adjusted to the size of the precipitate or residue.

The metallic elements have been classified in "Groups" on the basis of their behavior toward the general ("group") reagents, and these groups are designated and defined as follows, the rarer elements here considered being indicated by an asterisk: *silver group,* elements precipitated wholly or in part by hydrochloric acid (Ag, Pb, Hg [mercurous], *Tl); *copper group,* elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides remain undissolved in large quantity by yellow ammonium sulphide (Hg [mercuric], Pb, Bi, Cd, Cu, *Au, *Pt); *tin group,* elements precipitated by hydrogen sulphide from weakly acid solution whose sulphides dissolve readily or in considerable quantity in yellow ammonium sulphide (As, Sb, Sn, *Au, *Pt, *Se, *Te, *Mo); *iron group,* elements not precipitated by hydrogen sulphide from acid solution, but precipitated by ammonium hydroxide and sulphide (Co, Ni, Fe, Mn, Cr, Al, Zn, *Ti, *Zr, *U, *V, *Be); the *alkaline-earth group,* elements not precipitated by any of these reagents, but precipitated by ammonium carbonate (Ba, Sr, Ca); the *alkali group,* elements not precipitated by any of the preceding reagents (Mg, Na, K, *Li).