

## Phthalic Acid as a Reagent in Inorganic Qualitative Analysis of Metal Ions. Part I. A New System for Qualitative Analysis

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A new scheme for the qualitative chemical analysis of metal ions that is based on the use of phthalate ion as a precipitating reagent is outlined. Sulphide ion is not employed as a precipitating reagent. Evaporations of solutions are minimized and mineral acid and hydrogen sulphide vapours in the laboratory atmosphere are avoided. The analysis scheme has worked well during twelve semesters (from June, 1968) when several hundreds of students have used it in our laboratory.

The value of classical qualitative analysis in the teaching of chemistry has been discussed in, for example, the columns of the Swedish journal *Svensk Kemisk Tidskrift* in recent years.<sup>1</sup> Opinions that stress the importance of the subject have been expressed but also derogatory ones. The fact remains that at least at present inorganic qualitative analysis offers the cheapest and most effective method for teaching and learning laboratory procedures and reactions of inorganic chemistry.<sup>2</sup>

The greatest changes and improvements in qualitative analysis have resulted from the introduction of semimicro and micro methods and the replacement of precipitation with hydrogen sulphide by homogeneous precipitation with thioacetamide.<sup>3</sup> A further step towards a more systematic analytical scheme was the introduction by West and Vick<sup>4</sup> of precipitation with hydroxide and benzoate ions to replace precipitation with sulphide ions.

We have here in the Department of Chemistry at the University of Jyväskylä investigated this last-mentioned analytical scheme and its application as a method of instruction in inorganic qualitative analyses to freshmen and sophomore students and have come to the conclusion that phthalate ion (*e.g.*, potassium biphthalate) is a better reagent than benzoate ion in combination with hydroxide ion as a precipitant.<sup>5-6</sup> The alkaline earth metals calcium, magnesium, strontium, and barium are precipitated as their fluorides and certain divalent metal ions as their hydroxides with sodium hydroxide as in the scheme of West and Vick.<sup>4</sup> In other respects the analytical scheme follows

the classical scheme and the reactions of individual ions are the generally known customary ones.<sup>4,7</sup>

The analytical scheme that is briefly outlined below has been devised primarily for practical laboratory work and instruction and hence only the most essential aspects of the nature and reactions of the elements and their ions are presented.<sup>5,6</sup> The most noteworthy advantage of the presented analytical scheme in addition to its more systematic nature is the almost complete elimination of the evil-smelling, poisonous and corrosive hydrogen sulphide and the suppression of the evaporation of ammoniacal solutions and solutions containing mineral acids to a minimum. Also the costs of chemicals consumed are lower in the new scheme than in the earlier analytical schemes. The scheme does, however, require that the student exercises care in the handling of reagents and the adjustment of the pH values of the solutions.

### THE ANALYTICAL SCHEME

The various ions that can be identified by following the analytical scheme and the reagents that divide them into groups are presented in Table 1. The ions in parentheses are not included in the samples to be analysed in the early stages of instruction. The underlined ions are only rarely identified in the groups in question or they are transferred to the groups under exceptional conditions.

The sample of unknowns is examined by semimicro methods. Anions are analysed first. Preliminary tests that are extensively employed in many other analytical schemes have been omitted almost completely because the information they provide is of relatively minor significance from the point of view of systematic analysis.<sup>5,6</sup>

Table 1. The ions identified by the presented analytical scheme and their division into groups.<sup>5,6</sup>

Group	Group reagent	Ions identified
Anion group I	None	$\text{NO}_3^-$ , $\text{HS}^-$ , $\text{S}^{2-}$ , $\text{HCO}_3^-$ , $\text{CO}_3^{2-}$ , $(\text{BO}_2^-)$
Anion group II	None	$\text{Cl}^-$ , $\text{Br}^-$ , $\text{I}^-$ , $\text{HSO}_4^-$ , $\text{SO}_4^{2-}$ , $\text{H}_2\text{PO}_4^-$ , $\text{HPO}_4^{2-}$ , $\text{PO}_4^{3-}$ , $\text{Ac}^-$ , $\text{AsO}_2^-$ , $\text{AsO}_4^{3-}$
Cation group I	HCl	$\text{Ag}^+$ , $\text{Hg}_2^{2+}$ , $\text{Pb}^{2+}$
Cation group II	Potassium bi-phthalate and sodium hydroxide	$(\text{Sn}^{2+})$ , $(\text{Sn}^{4+})$ , $(\text{Sb}^{3+})$ , $(\text{Bi}^{3+})$ , $\text{Fe}^{2+}$ , $\text{Fe}^{3+}$ , $\text{Al}^{3+}$ , $(\text{Cr}^{3+})$
Cation group III	NaF	$\text{Mg}^{2+}$ , $\text{Ca}^{2+}$ , $(\text{Sr}^{2+})$ , $\text{Ba}^{2+}$ , $\text{Pb}^{2+}$
Cation group IV	NaOH	$\text{Mn}^{2+}$ , $\text{Hg}^{2+}$ , $\text{Cu}^{2+}$ , $(\text{Co}^{2+})$ , $(\text{Ni}^{2+})$ , $(\text{Cd}^{2+})$
Cation group V	$\text{NH}_4\text{OH}$	$\text{AsO}_2^-$ , $\text{AsO}_4^{3-}$ , $\text{Zn}^{2+}$ , <u><math>\text{Sn}^{2+}</math></u>
Cation group VI	None	<u><math>\text{Na}^+</math></u> , <u><math>\text{K}^+</math></u> , <u><math>\text{NH}_4^+</math></u>

### Identification of anions

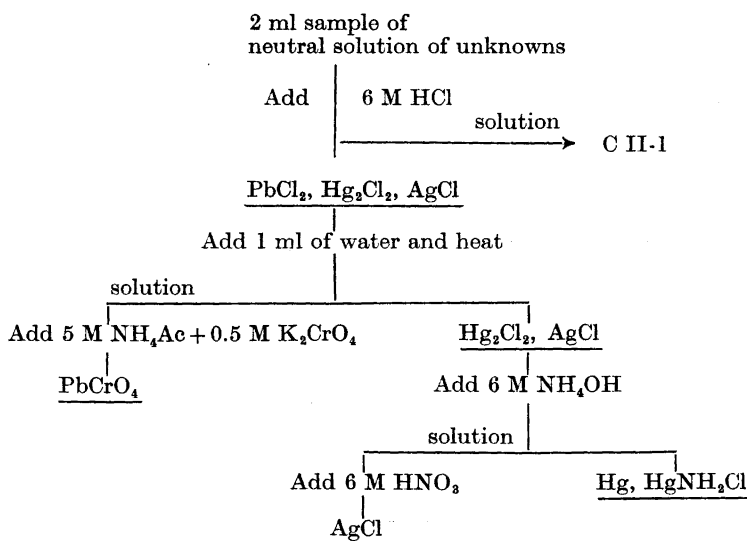
Several systematic analytical schemes have been presented in the literature for the analysis of anions in groups, but they are mostly complicated and laborious.<sup>7</sup> In the scheme presented here, the anions are not grouped on the basis of their analytical properties but are mainly listed in the order in which they are effectively identified. This has been made possible by the relatively small numbers of anions that has been selected for identification by the scheme.<sup>5,6</sup>

The anions of group I give gaseous products when they are treated with acid reagents and they are identified directly in the original sample in a simple gas detection unit. Also the presence of ammonium ion in the sample can be detected at this stage. Anions of group II are identified by means of the customary reactions in a solution of the sample from which heavy metals have been replaced by an alkali metal.<sup>7</sup>

### Identification of cations

Investigation of the cations is begun directly on the original sample of unknowns if it is a solution or as a solution obtained by dissolving the sample in dilute mineral acid or base. If the sample contains a phase that dissolves with difficulty or if such a phase is formed when the sample is dissolved in dilute acid or base, it is separated from the other components of the sample, dissolved and examined separately.

*Scheme 1. Precipitation and identification of group I cations.*



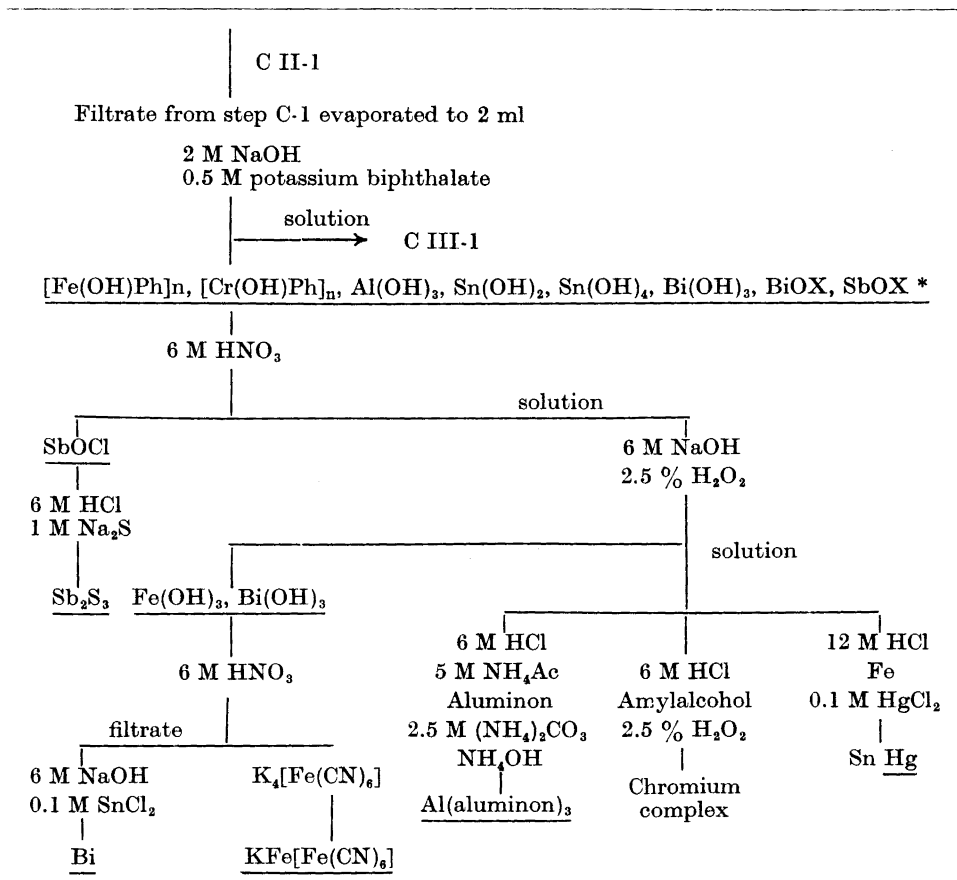
Customary tests are applied to identify the ions.<sup>4,7</sup>

*Examination of cation group I.* The tests are carried out on a practically neutral solution of the sample of unknowns. If the solution must be neutralized, this is done either with 6 M nitric acid or with 6 M sodium hydroxide.

The actual analysis is begun by taking a sample of the solution that is about 2 ml in volume and adding 6 M hydrochloric acid. If care is taken to avoid adding an excess of the reagent and the solution is cooled near 0°C before the precipitate is collected by filtration, the metals of the first group and lead are precipitated almost completely as chlorides. In the analytical schemes presented below, the precipitated compounds are underlined.

*Examination of cation group II.* Tests for the presence of cations of this group are done on the filtrate (C II-1) collected after the cations of group I have been precipitated from the solution of the sample of unknowns which

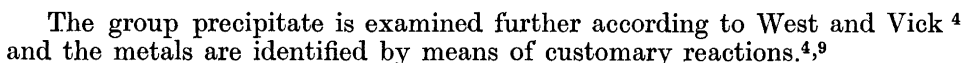
Scheme 2. Precipitation and identification of group II cations.



\* Where X = Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, or some other anion depending on the composition of the solution. The presented evaporations are the most probable ones.

The metals are identified by customary tests.<sup>4,7</sup>

**Scheme 3.** Precipitation and identification of cations of group III.



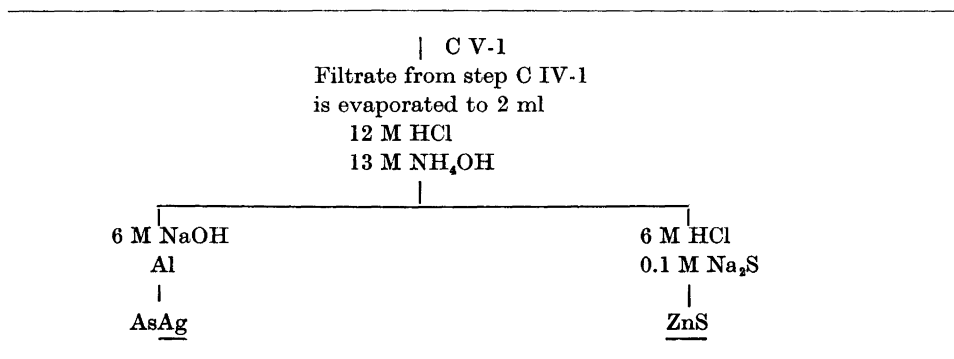


*Examination of cation group III.* A saturated sodium fluoride solution is added to the filtrate collected after the precipitation of cations of group II and the solution is allowed to stand for at least 5 min with occasional stirring. The solution and precipitate are cooled near 0°C before the precipitate is collected by filtration.

*Identification of group IV cations.* The filtrate remaining after the cations of group III were precipitated is made clearly alkaline and the solution is evaporated until its volume is 2 ml, during which any ammonia present volatilizes. The cations of group IV precipitate mainly as hydroxides or oxides.

*Examination of cation group V.* The filtrate collected after precipitating group IV is evaporated to a volume of 2 ml and acidified with hydrochloric acid. (Phthalic acid may precipitate at this stage, but is removed by filtration.) Ammonia is then added; in rare cases tin that has been transferred from cation group II may precipitate as stannous hydroxide. The solution is tested for the presence of arsenic and zinc.<sup>4,7</sup>

Scheme 5. The examination of cation group V.



*Examination of cation group VI.* Tests for cations of this group are carried out on the original sample of unknowns in the order given in Scheme VI.

### SUMMARY

The main advantages of the described analytical system involving the use of phthalate ion as a precipitating agent may be summarized as follows.

1. No difficulties are encountered in precipitating copper(II) and tin(II)-ions as when benzoic acid is used as precipitating agent.<sup>4</sup>

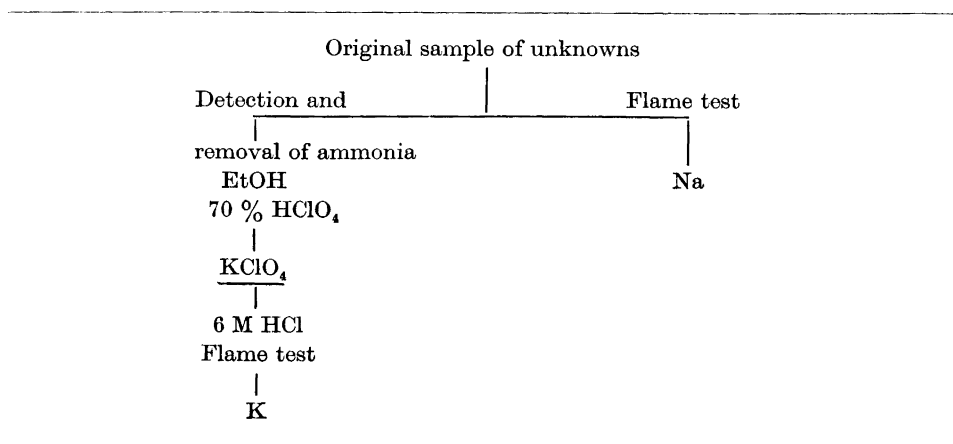
2. Dibasic phthalic acid has a wider buffer range than monobasic benzoic acid and therefore the precipitation conditions are more easily controlled.

3. The formed heavy metal precipitates settle rapidly and are easily collected. In these respects the precipitates are at least as good as the precipitates obtained with benzoic acid.

4. The formation of soluble phthalate or hydroxo complexes is avoided by immediate separation.

5. Phthalic acid is only about half as expensive as benzoic acid and ten times cheaper than thioacetamide.

*Scheme 6.* The examination of cation group VI.



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