

Systematic Analysis of the Metallic Ions by the Alkaline Method

—An Attempt on Experiments in General Chemistry—

By

SHIZUE ODA

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In analytical practice for the students, a method for the systematic separation of cations has been proposed using non-sulfide as the group reagents. This procedure was named the alkaline method, and was designed with the caution so as not to contaminate the environment, employing only the usual laboratory reagents and apparatus. Except for the six poisonous metals such as As, Cd, Hg, Bi, Sb, and Cr, seventeen kinds of common cations were divided into five groups by hydrochloric acid, ammonium hydroxide, sodium sulfite, and sodium hydroxide, and were detected succeedingly.

Introduction

There are various methods devised by A. A. Noyes and W. C. Bray^{1),2)}, by G. Vortmann^{3),4)}, by S. Takagi^{5),6)}, by P. W. West^{7),8)} by T. Kiba^{9)~12)}, and by other workers, for the systematic separation of cations. However, the method in which hydrogen sulfide is used or formed in the course of the operations are undesirable, because the reagent has the poisonous property, a bad odor, and the corrosive action to metals in the room. In the cases of non-sulfides, the manners are not popular on the performance, and alternate contaminations for the environment are also presumable.

The method reported in this paper was designed with the environmental and analytical restrictions, that is, the toxic ions and reagents, concentrated acids and alkalines, and special reagents and apparatus were not used. This method required the comparatively small amounts of samples and only the usual operations.

Materials and Methods

Samples and Reagents—

Seventeen kinds of common cations: silver, lead, tin, aluminium, manganese, iron, cobalt, nickel, copper, zinc, magnesium, calcium, strontium, barium, sodium, potassium, and ammonium were applied as the samples. In these metals, only tin was chloride, and the others were nitrates. Six cations: arsenic, antimony, bismuth, cadmium, mercury, and chromium were not included in this procedure.

Sample solutions containing 5 mg/ml of each ions were prepared.

The concentrations of the reagents used here are as follows:

Acids

hydrochloric acid	HCl	3	N
nitric acid	HNO ₃	4	N
sulfuric acid	H ₂ SO ₄	2	N
acetic acid	HOAc	6	N
hydrogen peroxide	H ₂ O ₂	3	%

Bases

ammonium hydroxide	NH ₄ OH	6	N
sodium hydroxide	NaOH	4	N

Salts

sodium carbonate	Na ₂ CO ₃	1	M
sodium sulfide	Na ₂ S · 9H ₂ O	1	M
sodium sulfite	Na ₂ SO ₃ · 7H ₂ O	2/5	M
disodium hydrogen phosphate	Na ₂ HPO ₄ · 12H ₂ O	1/3	M
sodium hexanitrocobaltate(III)	Na ₃ Co(NO ₂) ₆	1/2	M
potassium iodide	KI	1/2	M
potassium hexacyanoferrate(II)	K ₄ Fe(CN) ₆ · 3H ₂ O	1/8	M
ammonium chloride	NH ₄ Cl	3	M
ammonium acetate	NH ₄ Ac	3	M
ammonium oxalate	(NH ₄) ₂ C ₂ O ₄ · H ₂ O	1/4	M
ammonium thiocyanate	NH ₄ SCN	4/3	M

(sodium bismuthate is a solid reagent.)

Organic reagents

aluminon (ammonium aurintricarboxylate)

C₂₂H₂₃N₃O₉ 0.5 %

dimethylglyoxime C₄H₈O₂N₂ 1 % in ethanol

oxine (8-hydroxyquinoline)

C₉H₇ON 1 % in ethanol

EDTA (disodium ethylenediaminetetraacetate)

C₁₀H₁₄O₈N₂Na₂ · 2H₂O 10 %

(The commercial ethanol and acetone are used in this method.)

The required apparatus are simple and those used commonly in the laboratory.

Procedures—

Take 4–5 ml of the sample solution containing all cations and add dilute hydrochloric acid. (Group I). Silver and lead ions precipitate as chlorides. Carry out the separation and detection of these metals in Group I by the usual method.

Table 1. Group separation of the metallic ions by alkaline method

Group No.	I	II	III	IV	V
Precipitants and Procedure	HCl	excess NH ₄ OH H ₂ O ₂ Boil	Na ₂ SO ₃ Heat	excess NaOH Heat	— Concentration
Cations	Ag ⁺ Pb ²⁺	Mn ²⁺ , Fe ³⁺ , Al ³⁺ , Sn ⁴⁺ , Mg ²⁺ (Pb ²⁺)	Ba ²⁺ , Sr ²⁺	Cu ²⁺ , Co ²⁺ , Ni ²⁺ , Ca ²⁺ (Mg ²⁺)	Zn ²⁺ , K ⁺ (Na ⁺ , NH ₄ ⁺)

Chart 1. Analysis of Group II

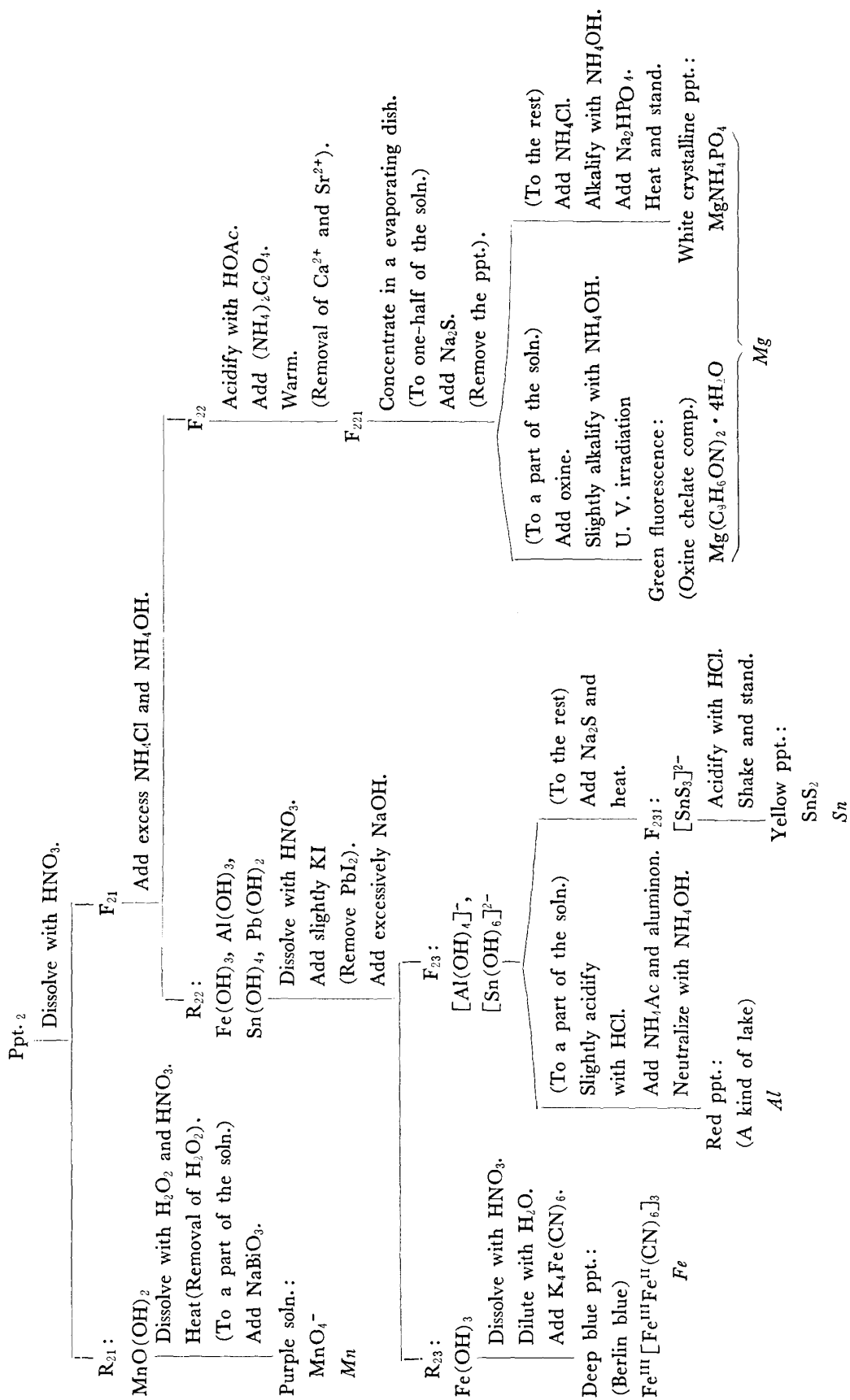
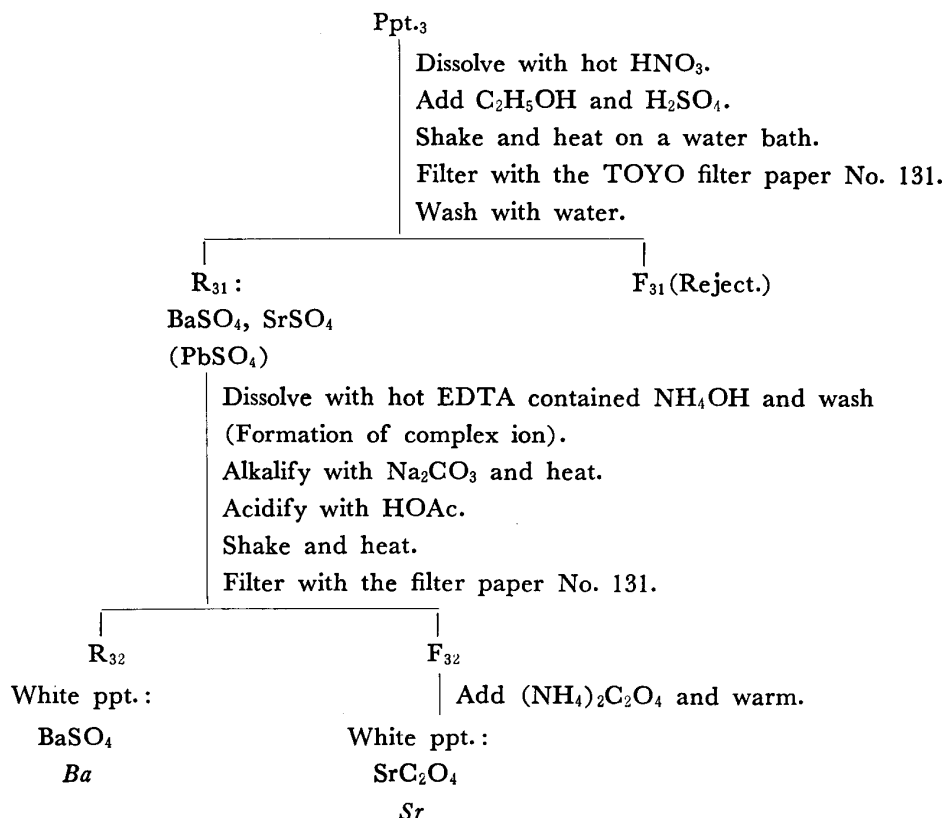


Chart 2. Analysis of Group III



Add a large excess of ammonium hydroxide and about 2 ml of hydrogen peroxide to the filtered solution. Boil and filter. (Group II). Manganese, iron, aluminium, tin, magnesium, and a part of lead precipitate. (Ppt.₂ in Chart 1.).

After acidification of the filtrate with acetic acid, add an adequate amount of sodium sulfite, heat and filter. (Group III). Barium and strontium precipitate as sulfites. (Ppt.₃ in Chart 2.).

To the filtrate, add a large excess of sodium hydroxide, heat with care of bumping and filter. (Group IV). Copper, cobalt, nickel, and calcium precipitate here, and magnesium also if it is not separated into Group II. (Ppt.₄ in Chart 3.).

Concentrate the solution (Filtrate₄ in Chart 4.), which is free from all the precipitates of Group I-IV, and filter. (Group V₁). In this filtrate, zinc remains as the soluble complex ion, and alkaline metals and ammonium ions also are contained. (F₅ in Chart 4.). However, sodium and ammonium ions have to be detected from the original sample solution, because of the addition of these ions as the reagents. (Group V₂, Chart 5.).

The outline of this method is shown in Table 1, and the analytical procedures of Group II-V are successively described in Chart 1-5.

In order to simplify these treatments, the solubilizations of all the precipitates are carried out by pouring the reagents over those in a funnel. The TOYO filter paper No. 131 (for qualitative analysis) described in Chart 2 and Chart 3 (Group III and IV) is employed when the fine precipitates (barium sulfate and the like) have to be retained. However, it is necessary to re-filter for the complete separation.

The general description of washing of the precipitates is omitted in all Charts, except for the necessity of the particular notice. In the Charts, R is the simple notation for the

Chart 3. Analysis of Group IV

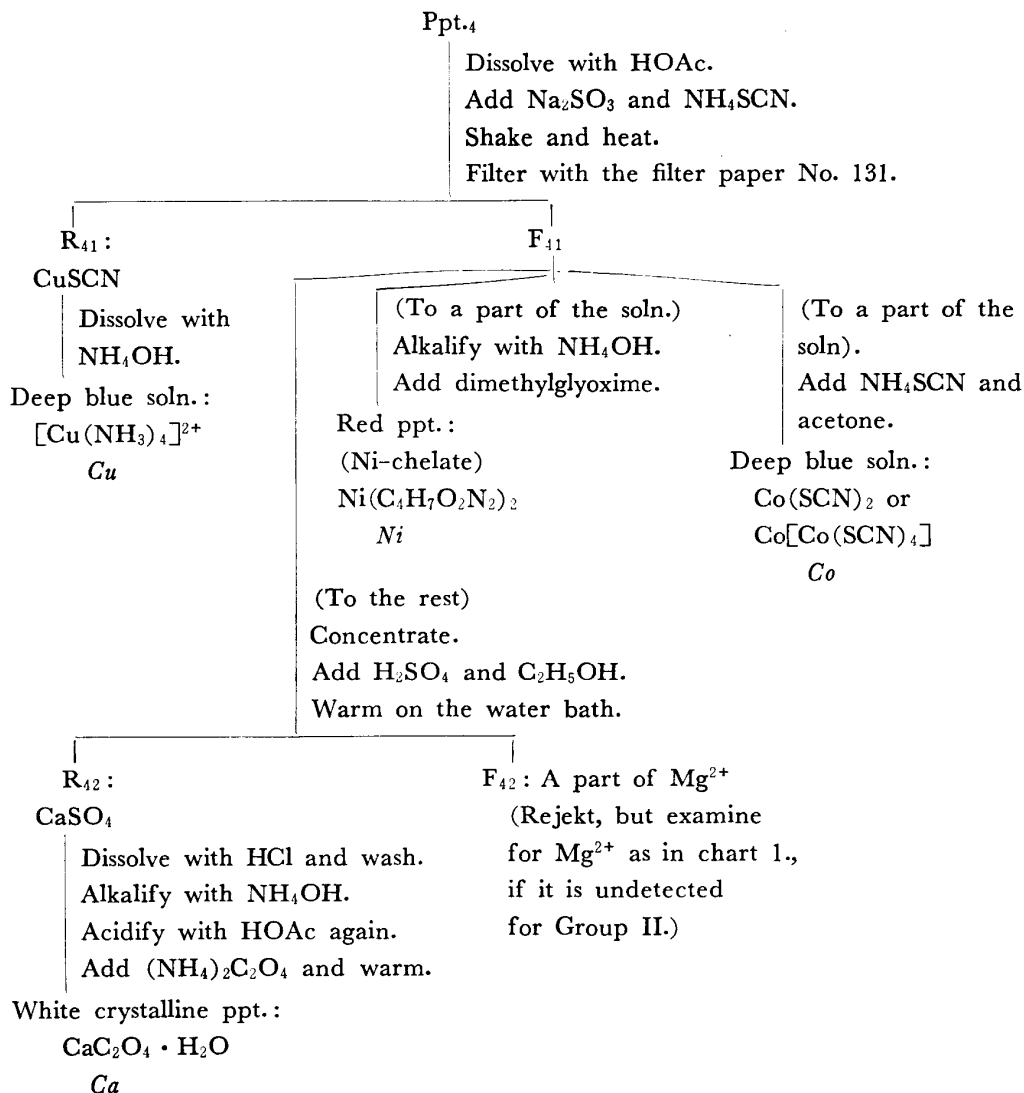


Chart 4. Analysis of Group V₁

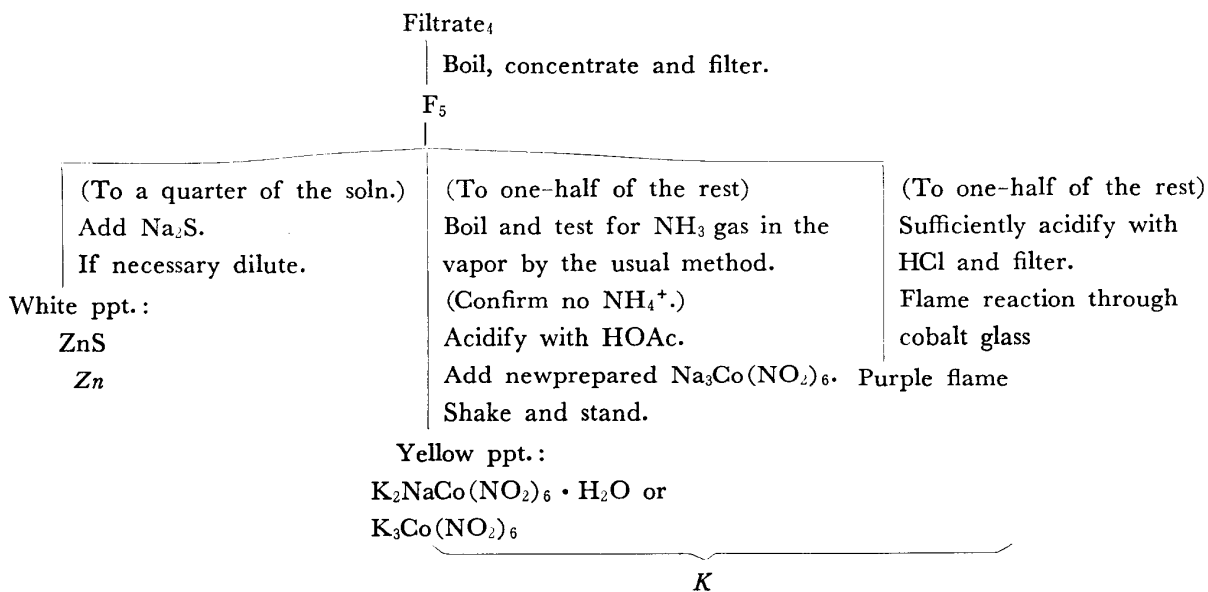
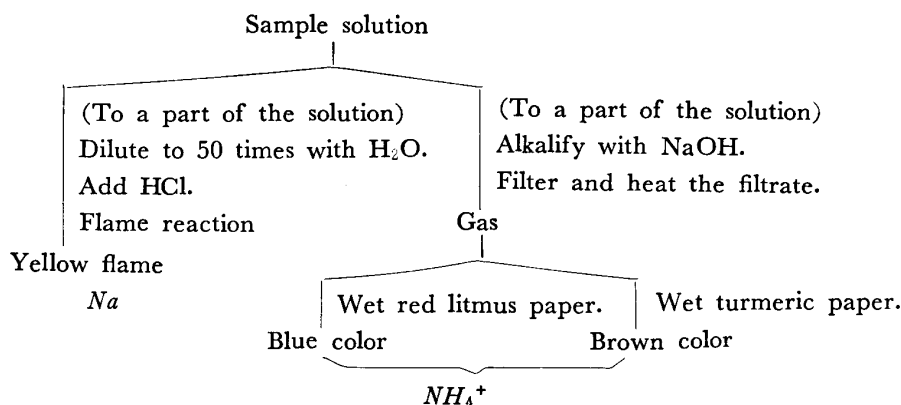


Chart 5. Analysis of Group V₂

residue, and F is the filtrate. The first subscript of these notations shows the Group number.

Results and Discussion

All the seventeen kinds of cations were detected from the two sample solutions: one included all cations except for tin ion, and the other did not contain only the two cations (silver and lead) of Group I, owing to hydrochloric acid which is necessary to dissolve tin in the sample solution.

In the course of the separation into Group II, the cations change from the lower ionic valence to the higher by the reaction with hydrogen peroxide, and cobalt ion also changes to hexaamminecobalt (III) ion $[\text{Co}(\text{NH}_3)_6]^{3+}$ at the same time.

The precipitates of Group II (Ppt.₂) are mainly hydroxide of iron, aluminium, tin, magnesium, and lead, and hydrated manganese dioxide. Precipitation of magnesium in Group II was not complete under usual conditions of the solution, and magnesium ion was held in Group IV, but well enough to be detected anyway. For the identification of magnesium, not only the precipitation reaction with disodium hydrogen phosphate, but also the observation of the fluorescence with oxine were used because it is possible to precipitate other impurities by the reagent. The rest of lead ion precipitated insufficiently in Group I owing to its considerable solubility, is included in Group II and disturbs the precipitation reaction of stannic sulfide for the detection of tin. Instead of using potassium chromate to remove this ion, potassium iodide was adopted. However, it should be replaced by new other reagents, for iodine is produced from this reagent in some cases. A part of calcium and strontium also enter into this Group, but they are removed before the detection of magnesium.

Analysis of Group III is based on a fact that the precipitate of barium sulfate is dissolved with hot EDTA containing ammonium hydroxide because of the formation of the soluble complex ion, and this sulfate is reprecipitated with acid. A slight amount of lead, calcium, and other contaminants in Group III are removed during the operations.

The precipitates of Group IV are hydroxide of copper, cobalt, nickel, calcium, and magnesium, and such by-products as calcium carbonate prepared by carbon dioxide in the air. A part of calcium was precipitated by sodium sulfite as calcium sulfite, and was mixed with cuprous thiocyanate of R₄₁, but did not disturb the detection of copper ion. Cobalt changed to the dark colored complex ion by ammonium hydroxide and hydrogen peroxide during of the separation of Group II, and reverted to the pink solution of the lower

valent ion by the reducing action of sodium sulfite. In the reaction to detect cobalt, slight acidification or neutralization of the solution is effective to protect from the variety of colors. Analysis of magnesium in Group IV is practiced for F_{42} as F_{221} in Chart 1 (Group II).

By concentration and filtration of Filtrate₄ in Chart 4, most of the impurities in Group V were removed from F_5 (Chart 4), and zinc was detected certainly. At the same time, ammonium ion, which reacted similarly with the reagent for the detection of potassium, also was removed. The detection of sodium is the utilization of the flame reaction which is exceptionally sharp for sodium. And there is not yet a good precipitation reaction for this cation without using the expensive reagents. The detection of ammonium ion by the evolution of ammonia gas is sensitive unexpectedly when the litmus paper is used, e. g., NH_4^+ was detected with one drop of 5 mg/ml by the micro method, because the pH range of color change of litmus lies so far to the acid side.

The Alkaline Method is simple on actual operations and arrangements as is described above. The character of this method is that the ions of alkaline earth metals were divided into three groups by using sodium sulfite. Compared with other well-known methods in which these cations are collected in the latter half of the Groups, the present method is advantageous for detecting these cations. Actually, in those method, there are the difficult points: the trouble of detection for alkaline earth groups, the treatment of the colloidal precipitate of nickel from the alkaline solution, and so on. These points are out of the question in the present one. However, this method has a few defects: the caution for handling of alkaline solution, increasing volume of the solution, etc., and still leaves some problems to be solved.

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