[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WASHINGTON SQUARE COLLEGE, NEW YORK UNIVERSITY]

SEPARATION AND IDENTIFICATION OF THE ALKALI AND ALKALINE EARTH METALS USING ISOAMYL ALCOHOL

BY HERMAN YAGODA

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Introduction

The method employed for separating and identifying sodium, potassium, magnesium, calcium, barium and strontium in the usual scheme of qualitative analysis for those ions is to precipitate the calcium, barium and strontium as carbonates from ammoniacal solution using a highly concentrated solution of ammonium carbonate as reagent, and leave sodium, potassium and magnesium in solution,[1] or to use ethyl alcohol along with the ammonium carbonate and thereby cause magnesium to precipitate along with the alkaline earth carbonates.[2] These separations, in general, are satisfactory, but require considerable time to execute.

The basis of the method of analysis here proposed is that the bromides of sodium, potassium and barium are insoluble in isoamyl alcohol (commonly called amylic or simply amyl alcohol) and that calcium, strontium and magnesium bromides are soluble in that alcohol. An advantage of this separation, from the qualitative point of view, is that traces of sodium, such as are usually introduced during the course of analysis from the glassware and reagents remain in solution along with the soluble bromides; therefore, if further analysis of the insoluble portion reveals the presence of sodium, it may be assumed with assurance that the sodium so found is not foreign to the sample being analyzed. Also, as barium is a metal of relatively rare occurrence, the presence of a portion of salt insoluble in the isoamyl alcohol may usually be taken as an indication of the presence of alkali salts in the sample.

Apparatus

The apparatus required for this separation of the metals into two groups and for the subsequent analysis of each group consists of: (1) a 30-cc. pyrex glass beaker and an iron or nickel crucible 1.5″ in diameter. The metal crucible both serves as an air-bath for the beaker, preventing spattering of the liquid being heated, and also keeps the bottom of the beaker free from films of dirt which make difficult the detection of small residues left by the evaporation of liquids (see Fig. 1); (2) the filtering apparatus—

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[1] Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., 1929, Vol. I, 5th ed., pp. 118–120.

[2] Bray, THIS JOURNAL, 31, 611 (1909); Noyes, "Qualitative Chemical Analysis"; Noyes and Bray, "A System of Qualitative Chemical Analysis for the Rare Elements," p. 236.

a side-necked test-tube, or small suction flask, in which a small test-tube is placed to catch the filtrate and (3) a 1-cc. and a 3-cc. pipet.

The use of this small apparatus keeps the substance being analyzed in a concentrated form with the result that small samples may be taken for investigation and the time of analysis greatly shortened thereby.

Procedure for the Separation and Identification of the Alkali and Alkaline Earth Metals.—The solution, which has been freed from members of the first, second and third groups in accordance with the customary procedure, is boiled until all hydrogen sulfide gas is expelled, and (then until) its volume is about 5 cc. (a). At this point the liquid is filtered into the small 30-cc. beaker, 1 cc. of 16 *N* nitric acid is added, and the solution is evaporated to dryness. The heating is then continued until all ammonium compounds are volatilized (b).

The residue in the beaker is treated with 1 cc. of concentrated hydrobromic acid (48.5% HBr, approximately 8 *N*) and evaporated to dryness, avoiding strong overheating (c). When cool, the residue is pulverized with the stirring rod, 3 cc. of isoamyl alcohol is added, the mixture is heated to ebullition and maintained at boiling for about half a minute. The mixture is cooled to room temperature and filtered. The *Filtrate* contains magnesium, strontium and calcium bromides; the *Residue* consists of sodium, potassium and barium bromides.

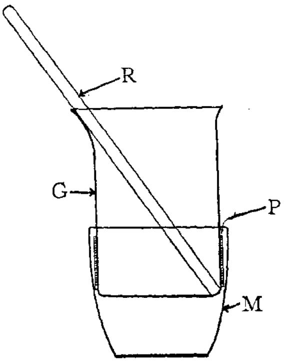

Fig. 1.—Apparatus for digestion and evaporation processes. G, 30-cc. glass beaker; R, glass rod; P, asbestos paper; M, metal crucible.

The *Residue* is washed with a few drops of isoamyl alcohol and then subjected to a preliminary flame test examination (d). The appearance of the characteristically colored flame given by any one of the metals may be taken as a test for the presence of that element and its relative quantity may be judged from the size of the residue left by the isoamyl alcohol. Where the residue consists of a mixture of the two alkali metals and barium, a simple qualitative separation may be made as follows. The residue is dried, the bromides removed from the filter paper into a small test-tube, 1–2 cc. of 95% ethyl alcohol and two drops of concentrated hydrobromic acid are added to the tube, the mixture brought to a boil, cooled and then filtered (e). The residue consists chiefly of potassium bromide, which may be dissolved in 1 cc. of water and the solution further tested for potassium with the aid of sodium cobaltinitrite reagent. The alcoholic filtrate contains sodium and barium bromides. Add 0.5–1 cc. of 12 *N* hydrochloric acid to the solution; a crystalline precipitate of sodium and barium chlorides forms immediately in the presence of appreciable quantities of either of the salts. Cool under running tap water, filter off the crystalline precipitate, saving the filtrate (f), and test the salts in the Bunsen flame. If the color of the flame indicates the presence of barium, as well as that of sodium, the presence of the barium may be further confirmed by dissolving the chlorides in 2 cc. of water and adding a few drops of dilute sulfuric acid; in the presence of barium, a white precipitate of barium sulfate will form.

The *Filtrate* of magnesium, strontium and calcium bromides dissolved in the isoamyl alcohol is evaporated to dryness, 0.5 cc. of 16 *N* nitric acid is added and the solution is again evaporated to dryness (g). The dry salts are heated strongly (h) until reddish brown fumes of nitrogen peroxide are no longer evolved (i), then cooled, pulverized with the stirring rod, leached with 3 cc. of water, boiled and filtered. The residue is a mixture of oxide and hydroxide of magnesium, which may be confirmed further by dissolving it in a few drops of hydrochloric acid (j) and then testing the solution with ammonium phosphate in the usual manner (k).[3] The aqueous filtrate is evaporated to dryness, a residue indicating the presence of either strontium or calcium. Cool, and when cold add 1 cc. of 16 *N* nitric acid, stir for a few minutes and then filter through a paper previously moistened with nitric acid. The crystalline residue is strontium nitrate; this is washed with 0.5 cc. of 16 *N* nitric acid and further confirmed by any of the usual methods.[4] Hillebrand and Lundell suggest this method for the quantitative separation of strontium from calcium.[5] The presence of calcium in the filtrate may be determined by making the solution ammoniacal, and adding several drops of a saturated solution of ammonium oxalate to the hot alkaline liquor; a white precipitate of calcium oxalate indicates the presence of calcium.

Notes on the Procedure

(a) The only acid radicals present in the solution should be either nitrates or chlorides. Sulfates, if present, are easily removed by treatment with lead nitrate solution, filtering off the lead sulfate and removing the excess lead ion with hydrogen sulfide. As nitrates are converted more readily to bromides than chlorides, it is best first to evaporate the residue with 1 cc. of 16 *N* nitric acid, when preliminary tests indicate the presence of considerable sodium chloride.

(b) Only a small quantity of ammonium salts will be present at this stage of the analysis as most of them are usually introduced in the precipitation of the fourth group by a concentrated solution of ammonium carbonate. Absence of any appreciable white residue may be taken as proof of the absence of Na^+, K^+, Ba^{++}, Mg^{++}, Sr^{++} and Ca^{++}.

(c) Overheating will decompose magnesium bromide. If this has occurred, the insoluble magnesium compound may be brought back to solution by adding a drop of concentrated hydrobromic acid to the isoamyl alcohol used in the separation.

(d) The bromides of sodium, potassium and barium yield the characteristically colored flames more readily than the chlorides.

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[3] *Cf.* Carl Otto, THIS JOURNAL, **48**, 3016 (1926).

[4] S. G. Rawson, *J. Soc. Chem. Ind.*, **16**, 113 (1897).

[5] "Applied Inorganic Analysis," John Wiley and Sons, New York, **1929**, p. 491.

(e) If the residue left by the isoamyl alcohol is small, only 1 cc. of ethyl alcohol should be used in making the separation. Very small residues are best handled at this point by placing the small filter paper in the tube and digesting it with the alcohol along with the bromide salts. By properly folding the paper the potassium may be kept on it, and then removed for further examination by leaching the paper with water.

(f) Where the presence of potassium in quantities less than 1 mg. is sought and more than 2 cc. of ethyl alcohol was used in the separation, this filtrate should be evaporated to dryness and the residue subjected to a flame test.

(g) The nitric acid removes traces of organic matter left by the decomposition of the isoamyl alcohol. Negligibly small residues will usually appear at this point even in the absence of Mg^{++}, Ca^{++} and Sr^{++} owing to the solution by the isoamyl alcohol of Na^+, K^+ and Ba^{++} to the extent of less than one milligram of total metal.

(h) A gas flame about one inch high and whose tip just covers the base of the crucible will be found convenient for most of the heating processes in this procedure. For the decomposition of the magnesium nitrate, however, the flame should be about three inches high and of sufficient intensity to maintain the portion of the crucible below the beaker at a red heat. The decomposition process may be followed by noting the evolution of nitrogen dioxide vapors, whose color is made very pronounced by the white background of magnesia.

(i) Magnesium nitrate decomposes at a temperature much below the melting point of either strontium or calcium nitrate, neither of the latter showing any tendency to decompose at their respective melting points.

(j) Where such magnesium is present, the magnesium oxide cakes and a portion of it adheres to the scratches in the bottom of the beaker. In such cases, after the leaching and filtration, the hydrochloric acid should be added first to the beaker so as to dissolve the remaining magnesia, and then that liquor is poured through the magnesia on the filter paper.

(k) Owing to the absence of ammonium salts the magnesium ammonium phosphate precipitates without any difficulty.

(l) Strontium nitrate not being very volatile does not give a good flame test. The residue should therefore be moistened with hydrochloric or hydrobromic acid before applying the flame test. The formation of a persistent turbid liquid is in itself a delicate test for strontium, as the nitrate residue dissolves very readily in cold nitric acid when only calcium is present, forming a clear solution.

Experimental Basis of the Procedure

All the salts used in this study were prepared and purified by well-known methods. The isoamyl alcohol employed for the solubility measurements boiled between 129–130°; a C. P. product was used without further purification in studying the separations qualitatively. The 95% ethyl alcohol used in this work had a specific gravity of 0.7999.

The solubility data assembled in Tables I to V were obtained by evaporating approximately 5-cc. portions of saturated solution of known weight in small quartz dishes and determining the weight of the solid residue left in the dish by difference. The solvent was prepared by diluting approximate quantities of concentrated hydrobromic acid with the alcohol in question and then measuring its acidity by titration with standard alkali. The solutions were prepared by digesting portions of the solvent with an excess of solute, raising the mixture to a boil, immediately cooling for a moment under tap water and then allowing the system to reach equilibrium at a slower rate in a thermostat at 25°. This method of preparing the solution, though giving a slightly supersaturated one, was thought advisable in so far as it duplicated conditions as directed in the procedure.

TABLE I

SOLUBILITY OF THE DIFFERENT BROMIDES IN ISOAMYL ALCOHOL AT 25° (SP. GR. OF SOLVENT, 0.805)

Salt	G. of salt per cc. of solvent	Mg. of metal per 3 cc. of solvent
NaBr	0.00085	0.67
KBr	.000014	.014
$BaBr_2$	.00013	.017
$SrBr_2$	.305	324.0
$MgBr_2$	Very soluble	
$CaBr_2$	Very soluble	

The solubility data show that a satisfactory separation of the above salts into two groups can be effected by isoamyl alcohol.

TABLE II

SOLUBILITY OF SODIUM BROMIDE IN ISOAMYL ALCOHOL CONTAINING HYDROBROMIC ACID, AT 25°

Normality of solvent	Sp. gr. of solvent	G. of NaBr per cc. of solvent	Mg. of metal per 3 cc.
0	0.805	0.00085	0.67
0.066	.8166	.00124	0.84
.181	.8262	.00174	1.17
.463	.850	.00274	1.83
.764	.8754	.0039	2.61

The data in Table II show that the solubility of sodium bromide in isoamyl alcohol cannot be diminished by the addition of hydrobromic acid to the solvent.

The solubility data in Tables III and IV show that the addition of hydrobromic acid to ethyl alcohol causes the solubility of sodium bromide to increase steadily, whereas, in the case of potassium bromide, the solubility first diminishes, and then upon further addition of acid increases. The

TABLE III

SOLUBILITY OF SODIUM BROMIDE IN 95% ETHYL ALCOHOL AT 25°

Normality	Sp. gr.	G. of NaBr per g. of solvent	Mg. of Na per cc. of solvent
0	0.7997	0.0397	7.1
0.100	.810	.0404	7.4
.162	.815	.0425	7.8^-
.204	.820	.0425	7.8
.337	.833	.0448	8.3
.629	.862	.0457	8.8
.800	.878	.0435	8.5^+
.954	.893	.0455	9.1

Table IV

Solubility of Potassium Bromide in 95% Ethyl Alcohol at 25°

Normality	Sp. gr.	G. of KBr per g. of solvent	Mg. of K per cc. of solvent
0	0.7997	0.00289	0.76$^-$
0.050	.805	.00191	.50$^+$
.100	.810	.00165	.44
.204	.820	.00162	.43$^+$
.400	.839	.00176	.48$^+$
.537	.853	.00186	.52
.800	.878	.00190	.60
.954	.893	.00242	.71

solubility of potassium bromide is a minimum when the acidity of the alcohol is 0.2 N in hydrobromic acid; under these conditions the solvent will dissolve 43 mg. of sodium bromide and 1.6 mg. of potassium bromide per cc.

Table V

Solubility of Salts in 95% Ethyl Alcohol 0.2 N in Hydrobromic Acid at 25°

Salt	G. of salt per cc. of solvent	Mg. of metal per cc. of solvent
KBr	0.0016	0.44
NaBr	.043	7.8
$BaBr_2$	.022	10.0
KCl	.0042	2.2
NaCl[a]	.00094	0.37
$BaCl_2$[a]	.00026	.17

[a] Figures refer to the solubility in a solution obtained by adding 1 cc. of 11.2 N hydrochloric acid to 2 cc. of saturated solution of sodium bromide or barium bromide in the above ethyl alcohol.

The data of Table V show that a qualitative separation of potassium from sodium and barium may be effected by solution of the last two in ethyl alcohol 0.2 N in hydrobromic acid; that sodium chloride and barium chloride precipitate almost quantitatively upon addition of concentrated hydrochloric acid to the alcoholic solution of the bromides; also, that the solvent can dissolve more potassium chloride than is formed by the reaction of the hydrochloric acid upon the small quantity of potassium bromide that enters into solution along with the sodium and barium bromides.

Qualitative Study of Procedure

Solutions of the chlorides of sodium, potassium, barium, magnesium, strontium and calcium were prepared of such strength that 1 cc. of the solution contained 10 mg. of the metal. Definite volumes of these solutions were mixed together and then analyzed in accordance with the proposed procedure. The samples so analyzed are tabulated in Table VI, the numbers representing the milligrams of the metal present in the sample.

Conversion of Salts to Bromides with Concentrated Hydrobromic Acid.—The utility of the procedure depends upon the ease with which the

TABLE VI

ANALYTICAL DATA

	No. 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Na^+	10	..	..	..	..	20	..	..	..	..	..	50	..	..	..	..	50	5	..	2
K^+	5	..	20	..	10	..	20	..	..	..	..	..	25	..	..	..	..	10	2	5
Ba^{++}	10	..	..	10	..	..	..	20	..	..	..	..	..	50	..	..	..	5	..	2
Mg^{++}	10	..	..	10	..	..	..	..	..	50	..	..	..	..	25	25	..	5	20	2
Ca^{++}	10	..	5	..	20	..	..	..	..	..	50	..	25	..	25	..	50	20	5	30
Sr^{++}	5	50	10	..	..	..	..	..	20	..	..	..	..	..	..	25	..	5	10	5

acid radicals, commonly associated with the metals, can be converted to bromides with concd. hydrobromic acid. Definite weights of different salts were taken such that 50 mg. of metal was present in each case and evaporated to dryness with 1 cc. of hydrobromic acid in the apparatus of Fig. 1. The residue was then tested qualitatively for the replaced acid constituent. The results are shown in Table VII.

TABLE VII

EXPERIMENTAL RESULTS

Salt	Number of treatments	Quantity of replaced radical	Salt	Number of treatments	Quantity of replaced radical
$SrCl_2{\cdot}4H_2O$	1	None	$NaNO_3$	1	Trace
KCl	1	Trace	$BaCl_2{\cdot}2H_2O$	1	Trace
NaCl	1	Fairly large	$CaCl_2{\cdot}6H_2O$	1	Trace
NaCl	2	Small	$MgCl_2{\cdot}6H_2O$	1	None

The presence of sulfates interferes with this separation of the alkali and alkaline earth metals. If present, the sulfates are best removed by treating the filtrate from the third analytical group with a lead nitrate solution, filtering off the lead sulfate and then removing the excess lead ion by saturating the solution with hydrogen sulfide gas.[6] The alkaline earth sulfates, being insoluble in water, will precipitate at an early stage of the analysis of the sample. These sulfates are first converted to carbonates by boiling with a concentrated sodium carbonate solution;[7] the carbonates are then dissolved in dilute hydrobromic acid and the solution is joined with the alkali bromides.

The treatment of the bromides of barium, potassium and sodium with ethyl alcohol is not made with the view of quantitatively separating the sodium and barium from potassium, but to get a solution (most frequently containing sodium only) from which sodium and barium can be precipitated with as simple a reagent as concentrated hydrochloric acid.

Summary

A method for separating and identifying a mixture containing sodium, potassium, barium, magnesium, strontium and calcium has been proposed whose essential features are as follows.

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[6] Noyes and Bray, "Qualitative Analysis for the Rare Elements," p. 254.

[7] Noyes and Bray, *ibid.*, p. 51.

SCHEME OF ANALYSIS OF THE ALKALI AND ALKALINE EARTH METALS

<table>
<tr><td colspan="7">Solution of nitrates or chlorides of Na, K, Ba, Mg, Sr and Ca; evaporate to dryness, add 1 cc. of 8 N HBr, boil off acid, cool, pulverize residue, digest with 3 cc. of isoamyl alcohol and filter.</td></tr>
<tr><td colspan="4">Residue.—NaBr, KBr and $BaBr_2$: Make flame test. Boil residue with 1–2 cc. of ethyl alcohol, add 1–2 drops of 8 N HBr, cool and filter.</td><td colspan="3">Filtrate.—$MgBr_2$, $CaBr_2$ and $SrBr_2$. Boil off the isoamyl alcohol, add 0.5 cc. of 16 N HNO_3 and evaporate to dryness. Residue: $Mg(NO_3)_2$, $Ca(NO_3)_2$ and $Sr(NO_3)_2$. Heat strongly, cool, add 3 cc. of water, boil and filter.</td></tr>
<tr><td rowspan="3">Precipitate.—Chiefly KBr. Dissolve in 1 cc. of water and add 2 cc. of $Na_3Co(NO_2)_6$ reagent. A yellow ppt. confirms the presence of potassium.</td><td colspan="3">Solution.—Contains NaBr and $BaBr_2$. Add 0.5–1 cc. of 12 N HCl, cool and filter.</td><td rowspan="3">Residue.—MgO and $Mg(OH)_2$. Redissolve in 1 cc. of 6 N HCl, add 1 cc. of 1 N $(NH_4)_2HPO_4$ soln. and 2 cc. of 16 N NH_4OH. A white precipitate of ($MgNH_4PO_4$) confirms the presence of magnesium.</td><td colspan="2">Filtrate.—Contains $Ca(NO_3)_2$ and $Sr(NO_3)_2$. Evaporate to dryness, cool, add 1 cc. of 16 N HNO_3, stir and filter, moistening paper with nitric acid.</td></tr>
<tr><td colspan="2">Precipitate.—Mixture of NaCl and $BaCl_2$. Make flame test. Dissolve salts in 1 cc. of water, add a few drops of 6 N H_2SO_4. Boil and filter.</td><td rowspan="2">Filtrate.—May contain a trace of potassium.</td><td rowspan="2">Precipitate.—$Sr(NO_3)_2$: Moisten with 12 N HCl and test in flame.</td><td rowspan="2">Filtrate.—$Ca(NO_3)_2$: Make alkaline with 16 N NH_4OH, add 1 cc. of saturated $(NH_4)_2C_2O_4$ soln. White precipitate confirms calcium.</td></tr>
<tr><td>Precipitate.—$BaSO_4$: Confirms presence of barium.</td><td>Filtrate.—Na_2SO_4: Evaporate, moisten residue with 12 N HCl and test in gas flame.</td></tr>
</table>

1. The conversion of the chlorides or nitrates to bromides with 8 *N* hydrobromic acid.
2. Separation of sodium, potassium and barium bromides from magnesium, strontium and calcium bromides using isoamyl alcohol.
3. Separation of sodium and barium bromides from potassium bromide using ethyl alcohol.
4. Precipitation of sodium and barium chlorides with 12 *N* hydrochloric acid from the ethyl alcohol solution.
5. Separation of magnesium from calcium and strontium by ignition of the nitrates.
6. Separation of strontium from calcium by dissolving calcium nitrate in 16 *N* nitric acid.

NEW YORK CITY, N. Y.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

STUDIES ON THE PERIODIC SYSTEM. III. THE RELATION BETWEEN IONIZING POTENTIALS AND IONIC POTENTIALS

BY G. H. CARTLEDGE

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In the preceding papers of this series[1] the author has developed a quantitative periodic function, the ionic potential ϕ, which is defined as the ratio of the charge of an atomic ion to its crystal radius, that is

$$\phi = \frac{z}{r} \tag{1}$$

In the previous papers the numerical values of the ionic potentials were calculated in arbitrary units, taking z as the valence and r as the ionic radius in Ångström units. It has been shown that the values of the ionic potential may be used to trace the order of variation in numerous properties of ions and compounds, such as the development of acidic properties of hydroxides, the electrical conductance and volatility of chlorides, and others. It is the purpose of the present paper to show the relationship between the ionic potential and the ionizing potential; from this relationship it is found that information regarding the polarizability of the ions may be obtained.

In order to make the desired comparisons it will be convenient to express the ionic potential in volts. The potential of a positive ion of valence z and charge ze e. s. u. is ze/r_c in electrostatic units, if r_c is the ionic radius in cm. As the volt is one three-hundredth of the electrostatic unit of potential, we have for ϕ_v, the ionic potential in volts

$$\phi_v = 300\,\frac{ze}{r_c}\ \text{volts} \tag{2}$$

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[1] Cartledge, THIS JOURNAL, **50**, 2855, 2863 (1928).