having one duplicate, to the condition where calcium is ready for precipitation as oxalate.

Summary.

A more rapid and accurate method is recommended for the determination of calcium in the ash of agricultural products. It consists essentially in removing the phosphorus as ammonium phosphomolybdate from an acid solution of the ash, and precipitation of calcium from the filtrate as calcium oxalate, either directly or after the removal of the excess of molybdenum as sulfide. Since no advantage was found in removing the molybdenum, it is recommended that this step be omitted.

A comparison of this method with the so-called basic acetate method in common use brings out the following points in its favor:

1. It yields more accurate and concordant results than the basic acetate method.
2. No attention need be given to the maintenance of exact neutrality of the solution.
3. The volume of the filtrate resulting from the precipitation of phosphorus can be kept reasonably small, so that no evaporation is necessary.
4. The time required for the determination is greatly shortened.
5. Phosphorus and calcium may be determined in the same aliquot.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF ILLINOIS.]

A SYSTEMATIC SEPARATION OF THE ANIONS OF GROUP I. ANIONS WHOSE SILVER SALTS ARE INSOLUBLE IN NITRIC ACID.[1]

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The customary methods for the examination and separation of the acids depend mainly upon various group reactions, followed by specific tests for one or the other anion, combined with a process of elimination based upon the results of the analysis for the cations. For a limited number of anions special methods of separation have been worked out in detail, as for instance for certain of the acids containing sulfur. The literature on the separation of the halogens Cl, Br, I, is quite voluminous and in this particular case a choice of various satisfactory methods of separation is possible. On the whole these methods are, however, limited in scope and very little work has been done upon systematic methods for the separation of the anions.[2]

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[1] Portions of this work were submitted by Mr. H. A. Winkelmann in partial fulfilment of the requirements for the degree of Master of Science in Chemistry in the Graduate School of the University of Illinois, June, 1915.

[2] The lack of such a systematic procedure is shown particularly by the errors and confusion resulting from the customary method of attack in the hands of students

The classification of acids into groups according to their reactions with silver and barium salts, frequently used in texts on qualitative analysis is ascribed to Bunsen in 1878, and is used practically unchanged. In 1900 Abegg and Herz[1] described, very briefly, a separation of the anions based upon the solubility of the calcium, barium and zinc salts and the volatility of various acids.

Quite recently A. A. Noyes,[2] published the most comprehensive scheme of separation of the anions so far elaborated. The fundamental idea of this method is the separation of the volatile and nonvolatile acids in various stages by distillation after addition of phosphoric acid. The more volatile acids, such as hydrocyanic acid, are collected in the first distillate, the less volatile in the second. The various portions are then examined for specific reactions of one or the other acid, without attempting to effect a further separation. The method is, in many respects, ideal and very effective, and a very great improvement upon the method of trial and failure indicated above.

In cases in which the nature of the mixture is such that interaction between the various constituents is possible, the prolonged heating during distillation will hasten and extend decomposition, with resulting decrease of directness or certainty in the results.[3]

The part of the investigation here described has to do with the first group of acids, in the following classification:

I. Anions which give silver salts insoluble in dilute nitric acid, but whose barium salts are soluble in water or acids.

II. Anions which give silver salts difficultly soluble in neutral solution, but readily soluble in dilute nitric acid, and whose barium salts are readily soluble.

III. Anions which give silver and barium salts insoluble in water alone, but soluble in the presence of dilute nitric acid.

IV. Anions which give salts of silver and barium readily soluble under all conditions.

V. Anions which give silver salts soluble in water, but whose barium salts are insoluble, even in the presence of nitric acid.

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first confronted with the problem of recognizing, and distinguishing between the various negative radicals in an unknown mixture. While they obtain a fairly comprehensive view of the relations between the various metallic elements in their reactions, this is not true of the nonmetallic elements.

[1] *Z. anorg. Chem.*, **23**, 236 (1900).

[2] THIS JOURNAL, **34**, 609 (1912).

[3] The fact that each distillation with phosphoric acid entails destruction of the distillation flask does not involve more than a slight inconvenience in individual cases; where the method is, however, to be applied repeatedly by large numbers of students, this factor does become one which it is desirable to eliminate.

The anions included in this first group are Cl^-; Br^-; I^-; CN^-; CNS^-; $Fe(CN)_6^{III}$; $Fe(CN)_6^{IV}$; $S^=$.

The first step in the problem consisted in the examination of the solubility data of the salts of the various anions, either in neutral, acid or alkaline solutions and in the presence of various salts. While it was a simple matter to find numbers of insoluble salts, the compounds available rapidly narrow down in number, either because they are not suitable for purposes of separation, or because the solubilities referred to pure salts in equilibrium with pure water, conditions which are not applicable always to the conditions of an analysis. For this reason a number of the cases examined as promising, but found to be unsatisfactory, are briefly described as a matter of record. The effect of the complications introduced in the course of analysis is shown by the results tabulated under these and various other metals further on.

Ferrocyanides and Ferricyanides.—The plan which first suggested itself was to add metallic zinc to the mixture of the silver salts of the acids. The silver salts would thus be reduced with the production of metallic silver and the corresponding zinc salts. The zinc ferrocyanide and ferricyanide being insoluble, would remain with the reduced silver and unused zinc, the remaining zinc salts being left in solution. This method lost in sensitiveness as a result of the occlusion of some of the other anions by the metallic silver or zinc. In addition,[1] metallic zinc, when acting on potassium ferricyanide, will reduce the same, yielding some ferrocyanide, and in part replacing iron in the complex.

This procedure would have been more in harmony with the steps to be anticipated in the succeeding groups, since the first group could thereby be removed as a whole, but was not found feasible. The difficulty was overcome by adding zinc nitrate to the solution before adding silver nitrate. The insoluble zinc ferrocyanide and ferricyanide are precipitated, leaving the remaining acids of the first group in solution, from which they are precipitated by silver nitrate. Experiments performed to determine the sensitiveness of this method showed that in a solution containing dilute nitric acid, 0.05 mg. of ferricyanide, or ferrocyanide, in 10 cc. total volume, gave a decided precipitate, while 0.02 mg. could still be detected by an experienced observer. The separation of the two zinc salts was found to be readily effected by means of ammonium hydroxide, and will be described under the general procedure.

The Remaining Anions.—Having precipitated the silver compounds of Cl^-, Br^-, I^-, CN^-, CNS^-, and $S^=$, the next step was to determine upon a process of separation and identification. The following steps were investigated for their usefulness:

A. Ammonium Hydroxide.—Since ammonium hydroxide is a good sol-

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[1] *vide* G. McP. Smith, *Z. anorg. Chem.*, **82**, 65 (1913).

vent for some silver salts, the possibility of its use for the separation was examined. Silver iodide and sulfide were found to be insoluble under all conditions. The solubility of the silver salts under examination depends considerably upon conditions, as is well known, making necessary a careful control of the variables. For example, silver chloride is easily soluble in dilute ammonium hydroxide, whereas the bromide is but slightly so, but its solubility increases materially with the concentration of the ammonia. The thiocyanate is soluble only in concentrated ammonia. The ammonium cyanide, on the other hand, is very unstable, so that even if a separation is obtained, there is danger of decomposition in subsequent manipulations.

One of the fundamental objections to this method is the unreliability of results which depend upon extraction of a more soluble substance from an admixture containing less soluble substances. This is never possible with mathematical precision, and, unless the differences in solubility are very great, it is not evén possible for practical purposes. Given large quantities of two constituents, for instance silver bromide and silver iodide, such a method gives decided results. But at the extremes of the range of mixtures, the results are of necessity erroneous. Thus a large quantity of iodide will prevent solution of small percentages of bromides, and conversely, small percentages of iodide will dissolve with the larger portion of bromide. Methods of separating the silver halides by means of ammonium hydroxide do not seem to have obtained wide application, although several have been described. For these reasons, the method was abandoned after a brief examination of its possibilities.

B. Lead Salts.—The behavior of the lead salts of this group of acids was examined with the view to separating iodine as lead iodide, after the reduction of the silver salts. The following table shows the behavior of lead acetate added to a neutral and acid solutions of the anions:

TABLE I.—BEHAVIOR OF LEAD ACETATE WITH VARIOUS SALTS[1] (VOL. 10 CC.).

	Solution neutral.					Solution acid (1–2 cc. dil. HNO_3).				
	1 mg.	3 mg.	5 mg.	7 mg.	10 mg.	1 mg.	3 mg.	5 mg.	7 mg.	10 mg.
KCl	+	+	+	+	+	—	—	—	—	—
KBr	+	+	+	+	+	—	—	—	—	—
KI	+	+	+	+	+	—	—	—	+	+
KCN	+	+	+	+	+	—	—	—	—	—
KCNS	+	+	+	+	+	—	—	—	—	—

The results given in Table I show that this salt does not offer a satisfactory means of separation, since in neutral solutions a precipitate was obtained in every case, while in an acid solution, 7 mg. of iodide yielded only a slight precipitate and 10 mg. only a fair one. Even if the lead iodide separation had been practicable, the lead would again have to be removed

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[1] In this and subsequent tables a plus sign indicates a positive test and a minus sign a negative result.

after proceeding with another step. Such an extra step increases the liability of losing small amounts of the acid, which was considered an added disadvantage in the use of lead.

C. Mercurous Salts.—The insoluble halide compounds of univalent mercury were next examined for their usefulness. One milligram of chloride or bromide ion in 10 cc. of a solution acidified with nitric acid gave, as anticipated, a decided precipitate with mercurous nitrate. Corresponding or larger quantities of the iodides, cyanides or thiocyanates gave precipitates from neutral solutions which readily redissolved upon acidification or addition of excess $HgNO_3$. In fact, even the mercurous chloride dissolves in a large excess of mercurous nitrate in an acidified solution. In the hope of separating the constituents of the silver precipitate by treatment with mercurous nitrate, AgCl, AgBr, AgI, AgCN and AgCNS were digested with $HgNO_3$. The precipitates were found to be reduced, the presence of mercurous chloride and bromide in the precipitate being indicated by the blackening of the residue by ammonia. The remaining three anions were found in the mercurous solution. Part of the chloride and of the bromide were, however, also in solution, the recovery of the cyanide ion was not satisfactory and the method involved subsequent removal of mercury for further steps. This procedure was therefore abandoned in favor of the formate reduction.

D. Formate Reduction.—In order to effect a separation of the precipitated silver salts, various reducing agents were investigated. Copper and metallic zinc reduce all of the silver compounds with the exception of the sulfide. Formaldehyde in alkaline solution acts in the same manner. Formates in acid solution give slow and incomplete reduction. It was soon found that with proper control of the alkalinity a satisfactory separation of chlorine could be obtained. The iodide of silver is the most resistant and even with the greatest concentration of alkali, silver iodide is practically unaffected. With solutions containing 15% of sodium hydroxide the reduction of silver chloride to metallic silver is very rapid, 200 mg. of silver chloride being completely reduced by warming a few minutes, whereas the bromide is only very slightly affected. In a solution which contains about 8% of sodium hydroxide and sodium formate, silver chloride was completely reduced in 10 minutes' boiling, while the bromide is unaffected even after much longer treatment. The cyanides and thiocyanates were reduced under the same conditions. Cyanides caused some difficulty by dissolving in the known fashion in the alkali, so that the filtrate from the silver residue contained some silver cyanide in addition to sodium cyanide. This caused some difficulty in the succeeding manipulations, which was later overcome by removing the silver cyanide from the silver chloride, bromide, iodide, and thiocyanate before reduction. This can be very effectively done by treatment with a solution of a mercuric salt, without dissolving any of the other silver compounds, which behavior furnishes, at the same time, a very satisfactory method of isolating and detecting the cyanide radical. The reaction depends upon the fact that mercuric cyanide is dissociated to an abnormally low extent into cyanide ion, as the well-known anomalous behavior of mercury cyanide indicates. If silver cyanide is digested with mercuric nitrate or sulfate it immediately dissolves, or conversely, in the presence of mercuric salts cyanides do not precipitate silver salts. This behavior is most pronounced with cyanides, the remaining anions of this groups precipitating the corresponding salts of silver even in the presence of mercury, provided certain precautions are observed.

In connection with these experiments the ferri- and ferrocyanide of silver were also subjected to reduction by means of formates in the presence of alkalies, with the view to include these two ions in the silver precipitate for further treatment. This would then have avoided the precipitation of these two anions by means of the zinc before adding silver nitrate. The procedure was not however applicable. The two silver salts were reduced, but the alkaline filtrate gave either uncertain, or negative, tests for ferrocyanide or ferricyanide. Here, as with such reducing agents as copper and zinc, the complex cyanide radical suffers disruption yielding, among other things, the cyanide ion. This behavior made it necessary to remove the complex cyanides at the beginning of the separation.

Applying, then, sodium formate as a reducing agent to the mixture of silver salts, after dissolving silver cyanide by means of a mercuric salt, causes reduction of silver chloride and silver thiocyanate, with the formation of metallic silver in the residue, and the corresponding sodium salts in solution. From this solution the thiocyanate can readily be precipitated as cuprous thiocyanate under the proper conditions, and the filtrate from this precipitate tested for chloride by means of silver nitrate.

The residue from the reduction contains metallic silver and any silver bromide, iodide and sulfide originally present.

Cuprous Salts.—The original procedure which was developed entailed the separation of chloride, bromide, cyanide and thiocyanate after the silver salts had been converted into the corresponding sodium salts by means of reduction with formate. The precipitation of copper thiocyanate is a well-known quantitative method. It remained to be seen how the chloride and bromide behaved under the conditions of separation. It was found that, in the presence of sulfurous acid, 100 mg. of chlorine or bromine (as potassium salts) are held in solution. Under the same conditions 0.02 mg. of CN or CNS give a decided precipitate.[1]

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[1] While working on this method a paper by Curtman and Wickoff, THIS JOURNAL, 37, 298 (1915), appeared, treating the determination of bromides in the presence of cyanides, thiocyanates and ferricyanides. The results there were in harmony with

While this gave a satisfactory separation from bromine the question of separation of the cyanide and thiocyanate still remained, and caused considerable difficulty. The cobalt and nickel salts offered some hope for a separation but were rejected after trial. The cyanide may be converted into Prussian blue in one part of the solution and the characteristic ferric thiocyanate reaction obtained in another, but this was not all that could be desired, particularly when both constituents were present in rather large quantities. Fortunately, later work showed that the removal of the cyanide at an earlier stage of the procedure eliminated this difficult separation and this was therefore accepted as a welcome simplification of the process.

As a consequence of these results the best procedure was decided to consist in limiting this separation by means of cuprous salts to the removal of thiocyanates from chlorides. This process can be conveniently and accurately carried out and the other anions are provided for at other stages of the procedure.

PROCEDURE.

Precipitation of Ferricyanides and Ferrocyanides.

Procedure I.—Add one to three cc. of dilute nitric acid to a nearly neutral mixture of acids, and *immediately* enough zinc nitrate to insure complete precipitation of the ferricyanide and ferrocyanide and shake the solution vigorously. Completeness of the precipitation is indicated by a noticeable change in the character of the precipitate, which is colloidal at first but coagulates more readily when excess of precipitant is present. When sufficient ferricyanide is present to color the solution, there is a fairly sharp end point, consisting in the discharge of the yellow color. When not enough zinc nitrate is present the solutions are colloidal; an excess of zinc nitrate to insure complete precipitation of the ferricyanide and ferrocyanide is advantageous. One to two grams of ammonium nitrate hasten coagulation of the colloidal precipitate and should be added if difficulty is experienced in filtering.

Heating the solution should be avoided, since it increases the tendency of the precipitate to become colloidal, and would cause loss of hydrocyanic acid. Ageing always favors the separation of colloidal precipitates, and should the precipitate run through the filter, which for this case should be a fairly close-grained one, it may be set aside for a short period and will then usually be found to have changed sufficiently to permit satisfactory filtration. The *same effect* may be obtained more rapidly by shaking the suspended precipitate energetically in a stoppered flask. Shaking, in effect, simply hastens the ageing of the colloid and is very

our experience and showed that 2 mg. of bromine could be detected in the presence of as much as 500 mg. of the other constituents by applying the cuprous salt separation previous to the test.

effective in producing a precipitate which does not run through the filter.

When iodides and ferricyanides are both present, iodine will be liberated slowly. This does not interfere with the subsequent detection of iodine. In order, however, to check appreciable reduction of the ferricyanide to ferrocyanide the zinc nitrate should be added immediately, or, preferably, the nitric acid should be added first to the zinc nitrate and the two reagents added to the solution in one operation.

After washing the zinc precipitate on the filter several times with a few cubic centimeters of a dilute ammonium nitrate solution (rejecting all but the first washing), pour 10 cc. of a warm 3% NaOH solution through the filter. This is sufficient for quantities up to 200 mg. of each of the two salts, which dissolve, yielding the alkali ferri- and ferrocyanide and sodium zincate. Add to the resulting solution 5 cc. of a 5% ammonium nitrate solution, a few drops of zinc nitrate solution to provide excess zinc ion, and shake vigorously. The zinc ferrocyanide is precipitated as a gelatinous white precipitate. This precipitate is quite characteristic. It may, if desired, be further characterized by the conversion into the cupric or ferric ferrocyanide. The red cupric ferrocyanide is to be preferred, since it is just as sensitive and cannot be confused with the ferrous ferricyanide as the ferric ferrocyanide may. In either case, the ferrocyanide of zinc is dissolved in a small quantity of NaOH solution, the copper or iron is added and the solution then acidified. This is preferable to acidifying first, particularly when only small quantities are present, since the zinc ferrocyanide, when once formed, is not converted into the copper or iron salt very rapidly.

The ferricyanide is identified by acidifying the filtrate from the zinc ferrocyanide with dilute hydrochloric acid, and adding 1–2 cc. of potassium iodide solution (which should not give free iodine upon acidification), and 0.5–1 cc. of $CHCl_3$ or CCl_4. The ferricyanide is reduced, giving free iodine in the $CHCl_3$ layer.

$$2K_3Fe(CN)_6 + 2KI = 2K_4Fe(CN)_6 + I_2.$$

The voluminous nature of these zinc precipitates adapts them particularly well to quantitative approximations. A series of seven precipitates obtained in the regular course of analysis and varying from 100 to 1 mg. in approximately even steps, were corrrectly estimated by four out of five observers entirely unused to the method. The same thing is true of the ferricyanide of zinc.

The iodide reaction develops rather slowly with small quantities (0.5 mg.) of ferricyanide but it is recommended in preference to the test with ferrous iron.

A ferric salt gives with a ferrocyanide a blue precipitate of ferric ferrocyanide, but not with ferricyanide. A ferrous salt gives with a ferricyanide a similar blue precipitate of ferric ferrocyanide. It gives with ferrocyanide a white precipitate of ferrous ferrocyanide when no ferric salt is present, but a blue one after exposure to the air. In order to distinguish the ferricyanide from ferrocyanide with a ferrous salt the solution must be fresh, that is, free from ferric salt. The reaction with potassium iodide is to be preferred for the reason that there is no possibility of confusion with ferrocyanide due to faulty separation. When applying this test for small quantities, it is necessary to bear in mind that commerial iodides usually contain traces of iodates and will consequently give traces of free iodine on acidification. A reagent which will not liberate iodine upon acidification may very conveniently be made by boiling a neutral, or but faintly acid, solution of potassium iodide with metallic magnesium.

The oxidation of iodides by ferricyanides is slow, and in testing for small quantities, time must be given for the iodine to be liberated. As in the case of ferrocyanide, a fairly accurate quantitative estimation can be made even by one unused to the method when amounts from 100 to 1 mg. are used.

The results obtained during experimentation on the above separation are given in Table II.

Table II.—Sensitiveness of Test with Zinc Nitrate in Presence of Dilute HNO_3 (Vol. 10 Cc.).

Milligrams.	10	8	6	4	2	0.5	0.1	0.02
$K_3Fe(CH)_6$....	+	+	+	+	+	+	+	+
$K_4Fe(CN)_6$....	+	+	+	+	+	+	+	+

Reliability of Separation for 0.1 Mg. in the Presence of 200 Mg. of any One of the Remaining Anions of this Group (Vol. 10 Cc.):

$K_3Fe(CN)_6$....	+	+	+	+	+	+	+	+
$K_4Fe(CN)_6$....	+	+	+	+	+	+	+	+

Precipitation of Silver Salts.

Procedure II.—The filtrate from the zinc precipitation is treated with silver nitrate until no further precipitate forms. If cyanides are present in appreciable quantities the disappearance of the odor of hydrocyanic acid indicates completeness of precipitation. A slight excess of silver nitrate is added, the precipitate is coagulated by shaking, and the solution is removed by decantation or filtration. The precipitate is washed with distilled water containing a few drops of nitric acid until the washings are practically free from silver. Reject all but the first washings. The solution contains the acids of subsequent groups. The precipitate is examined for Cl^-, Br^-, I^-, CN^-, CNS^-, and $S^=$.

Separation of Cyanide.

Procedure III.—To the precipitated silver salts contained in a beaker, after having removed excess of water, add 2 cc. of a 2 molar solution of mercuric acetate containing 5% of acetic acid. Digest 15 minutes on the steam bath (the solution may be permitted to evaporate to dryness). Add 2 cc. of a 2 molar sodium acetate solution and dilute to 20 cc. and filter. The filtrate contains the cyanide as a complex mercury compound. H_2S is passed into this until mercury has been completely precipitated and the mercuric sulfide is removed by filtration. The filtrate is made alkaline with a few drops of sodium hydroxide, enough ammonium polysulfide is added to color the solution yellow (2–5 drops are sufficient unless very large quantities of cyanides are present) and it is then digested on the steam bath, preferably until the liquid has evaporated.

Enough dilute sulfuric acid is added to decompose the excess polysulfide. In the filtrate from this, which now contains thiocyanic acid, the blood-red color of ferric thiocyanate is obtained upon addition of ferric salts. (See Table VI.)

All of the halogen salts of silver dissolve in mercuric salts with the formation of highly complex mercuric compounds. Thus, in a solution containing one mol of $Hg(NO_3)_2$ and one mol of HNO_3, 7 g. per liter (0.05 mol) of silver chloride, 7 g. (0.04 mol) of silver bromide and 25 g. (0.11 mol) of silver iodide will dissolve.[1]

The compounds formed are, according to the conditions, any one or all of the following: $HgHgCl_4$, $HgHgCl_2(NO_3)_2$, $AgHgCl_2(NO_3)_2$. As may be noted on comparing the remaining halides, the complex formation increases toward the iodide, *i. e.*, as the acid grows weaker. With the very weak hydrocyanic acid the complex formation is very much greater still, the CN^- being used up quantitatively to form either the $Hg(CN)_4^{=}$ or the $Hg(CN)_3^-$ ion.[2] If, instead of using mercuric salts of the strong acids, the acetate is used the complex cyanide alone is formed, *i. e.*, only silver cyanide and not the chloride dissolves. (A trace of chloride, and more iodide, dissolves if a slight amount of acetic acid is present, either added or from hydrolysis, but this is completely stopped by the addition of sodium acetate to the solution, so that not even 0.2 mg. of iodine dissolves in 300 times as much mercuric acetate.) In effect, then, mercuric acetate is less complex than mercuric cyanide and more so than the remaining halogen compounds and this makes the separation possible. The addition of the sodium acetate after digestion with the acid solution of mercuric acetate is necessary to precipitate the last traces of the other halides.

For the final characterization of the cyanide, the thiocyanate conversion works well, 0.1 mg. being detected without difficulty. Removal of mercury from the solution by means of more electropositive metals and conversion of the cyanide into ferrocyanide gave erratic results under the conditions prevailing and is not to be recommended here.

Separation of Chloride and Thiocyanate.

Procedure IV.—To the washed silver salts, from which the cyanide has been removed (excess water should be decanted), add 10–15 cc. of an 8% sodium hydroxide solution and 1 g. of sodium formate and boil a short time in a covered receptacle (5 to 10 minutes). Dilute to 20 cc., decant or filter and test the filtrate for chlorine and thiocyanate as follows: very nearly neutralize the solution with dilute sulfuric acid, completing the neutralization with sulfurous acid. To the acid solution, which should smell decidedly of SO_2, add copper sulfate solution drop by drop until no more copper thiocyanate is precipitated. Filter, dissolve the precipitate in hydrochloric acid and add a ferric salt to obtain the red ferric thiocyanate. To the filtrate from the cuprous thiocyanate add dilute nitric acid equivalent in quantity to the sulfurous acid previously added, heat until the SO_2 is driven off and add silver nitrate until no more silver chloride forms. (See Table VI.)

The precipitation of thiocyanates by copper in a reducing solution is very nearly complete, only 5×10^{-5} g. dissolving in a liter. If desired, a separate portion of the solu-

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[1] Morse, *Z. physik. Chem.*, **41**, 707 (1902).

[2] Sherrill, *Ibid.*, **43**, 705 (1903); **47**, 103 (1904).

tion may be tested for thiocyanate directly with a ferric salt. If found present it must first be removed before testing for chloride.

Formic acid reduces silver chloride to metallic silver much more readily than it does the bromide or the iodide. The speed of reduction varies considerably with the concentration of the sodium hydroxide. For this reason the solution should not be allowed to concentrate to an appreciable extent while heating. For the reduction it is advisable to prepare a reducing solution containing 8 g. NaOH and 10 g. of H.COONa (chlorine free) per 100 cc. and to use 20 cc. of this solution. With the concentrations given, silver chloride is completely reduced in 10 minutes' vigorous boiling, while silver bromide is not affected. With a 15% sodium hydroxide solution and as much as a half hour's boiling silver bromide is partially reduced (a few per cent of 200 mg. for instance) while silver iodide is not appreciably reduced even in 33% NaOH on long extended boiling. The silver thiocyanate behaves toward the reduction as the chloride does, forming sodium thiocyanate, which dissolves, and metallic silver.

Separation of Bromide and Iodide.

Procedure V.—The precipitate which remains contains silver bromide, iodide (and sulfide) and in addition the metallic silver resulting from the previous reduction. It is covered with a few cubic centimeters of concentrated ammonia and metallic copper in powder form (molecular copper) is added. The reduction of the bromide and iodide is instantaneous, the corresponding cuprous salts going into solution. If a precipitate of basic copper salts is formed more NH_4OH must be added. Silver sulfide remains behind. The filtrate is neutralized with sulfurous acid and an excess of dilute sulfuric acid is added. If iodine is present white copper iodide is precipitated. This is collected on the filter (shake precipitate to coagulate) and the iodine, after dissolving the cuprous iodide in hydrochloric acid, is liberated by chlorine water (or HNO_2, H_2O_2 or $FeCl_3$) and dissolved in carbon tetrachloride giving a violet color.

To the filtrate from the copper iodide, which contains the bromide, nitric acid is added and the solution is warmed until most of the SO_2 has been driven off. Addition of silver nitrate then causes formation of yellowish silver bromide. (See Table VI.)

The precipitation of copper as cuprous iodide is a well-known quantitative method, the solubility of Cu_2I_2 in water being only 3×10^{-4} g. per liter. Under the same conditions 100 mg. of bromine are not precipitated. The characterization of the precipitate is hardly necessary unless it is feared that the thiocyanate was not completely removed in the previous step, or unless unusually large quantities of bromide were taken.

Detection of Sulfide.

Procedure VI.—The silver residue from the reduction contains the sulfide. It is completely dissolved in nitric acid. The silver sulfide dissolves with formation of sulfuric acid, which, after dilution to 100 cc. is precipitated as white barium sulfate upon addition of barium nitrate.

Numerical Data.

TABLE III.

Formate Reduction.

4 Millimols of the silver salts (AgCl, AgBr, etc.) 2 g. H.COONa + NaOH (vol. 20 to 40 cc.).

% NaOH.	6.	8.	11.	14.	16.	18.
AgCl	Not complete	Reduced	Reduced	Reduced (10 min.)	Reduced	Red. cold
AgCN, AgCNS	......	Reduced	......	......	......	......
AgBr	Not red.	Not red.	Not red.	Not red.	Trace red.	Slight red. in $2^1/_2$ hr.
AgI	......	......	......	......	No trace of reduction.	

TABLE IV.

Rate and completeness of reduction with copper powder.

200 mg. (8 millimols) Cl^-, Br^-, I^-, CN^-, CNS^- as the silver salts, freshly precipitated and washed. Various ions were taken separately.

Set. 1. Copper, about equal in volume to the silver precipitate and distilled water. The silver salts are reduced rapidly to metallic silver.

Set. 2. Same as 1, and 1 cc. of conc. ammonia added. The reduction is very rapid (less than 10 minutes). The residues of silver and copper after washing dissolved without a trace of residue in dilute nitric acid. If air is excluded during the operation the ammonia solution contains the cuprous compounds.

Set. 3. Same as 1 but carried out in presence of dilute sulfuric acid. Reduction takes place much more slowly and is not complete, even on long standing.

Set 4. Similar trials with Pb as reducing agent gave unsatisfactory results.

TABLE V.

Mercuric salt separation of cyanides.

Solubility of silver salts.—To 5 cc. of 0.5 *M* $HgNO_3$ about 1 cc. of 1.5 *M* $AgNO_3$ was added. In order to obtain a precipitate, 2.5 mg. Cl^-, 0.8 mg. Br^-, 4 mg. I^-, no pptd. CN^-, 1 mg. CNS^- were added before a precipitate formed. Addition of sodium acetate caused immediate precipitation of the dissolved silver salt, except in the case of AgCN.

Similar behavior was noted with $HgSO_4 + H_2SO_4$ solution.

To 20 cc. of 0.2 *M* mercuric acetate a few drops of acetic acid and silver nitrate was added. In order to obtain a precipitate the following amounts of halogen were necessary: 0.4 mg. Cl^-; 0.5 mg. Br^-; 0.6 mg. I^-; no ppt. w. CN^-; 0.2 mg. CNS^-. To the same solution 2 cc. 2 *M* sodium acetate were added. Precipitates were obtained with 0.04 mg. Cl^-; 0.04 mg. Br; 0.02 mg. I^-; no ppt. w. CN^-; 0.01 mg. CNS^-. The precipitates obtained under the last conditions were practically as strong as the blanks obtained without $HgC_2H_3O_2$ in distilled water.

TABLE VI.

Sensibility of procedure as outlined with the various ions.[1] A long series of tests was made with varying quantities. Only the minimum amounts used are tabulated. Figures represent milligrams.

	Cl^-.	Br^-.	I^-.	CN^-.	CNS^-.	$Focy^{\equiv}$.	$Ficy^{=}$.
Other ions absent	0.04	0.04	0.02	0.05	0.05	0.02	0.02
200 mg. of any other ion present	0.10	0.10	0.10	0.10	0.10	0.10	0.10

TABLE VII.

Constitution of unknown solutions analyzed.

Mg.	A.	B.	C.	D.	E.	F.	G.	H.
Cl^-	100	0	1	10	20	40	60	80
Br^-	80	100	0	1	10	20	40	60
I^-	60	80	100	0	1	10	20	40
CN^-	40	60	80	100	0	1	10	20
CNS^-	20	40	60	80	100	0	1	10
$Ficy^{=}$	10	20	40	60	80	100	0	1
$Focy^{\equiv}$	1	10	20	40	60	80	100	0
Total	310							

Sets of solutions constituted as shown in Table VII were prepared and analyzed by H., J., and W., the contents being unknown to the analyst at the time. Since the results were uniformly correct they are not reproduced in detail. In Solution B chlorine was found in small amounts in every instance. This error is only an apparent one however, since the other salts present, while of high grade commercial quality were not chlorine-free. Thus no sample of cyanide was found during the course of the work which did not contain chlorine. In solution C, which contained 80 mg. I, one analyst reported a trace of bromine. In Solution H, ferrocyanide was twice reported although not added. Reduction of the ferricyanide by the hydriodic acid present, or a content of ferrocyanide in the ferricyanide, accounts for this. Otherwise the results obtained were correct.

Summary.

A procedure is described in which any mixture of the ions Cl^-, Br^-, I^-, CN^-, CNS^-, $FeCy_6^{=}$, $FeCy_6^{\equiv}$ may be systematically separated with quantitative approximation.

Data in support of the proposed methods are furnished. The separations given are adequate when the respective ions form 0.01 to 0.0001 of the total, varying somewhat with the ion in question.

The procedure may be represented schematically by Table VIII, in which the compounds listed are empirical designations and an underscored substance indicates a precipitate. The numbers indicate the corresponding procedure:

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[1] For convenience in these tables, ferrocyanide is designated by Focy and ferricyanide by Ficy.

TABLE VIII.

I. $Zn(NO_3)_2 + HNO_3$	$\underline{Zn_2Focy}$	$\underline{Zn_3Ficy_2}$	$Zn(CN)_2$	$Zn(CNS)_2$	$ZnCl_2$	$ZnBr_2$	ZnI_2	H_2S
$NaOH$	Na_4Focy	Na_3Ficy						
NH_4OH	$\underline{Zn_2Focy}$	$(NH_4)_3Ficy_2$	↓	↓	↓	↓	↓	↓
HNO_3		$\underline{Zn_3Ficy_2}$						
II. $Ag(NO_3)_2$			$\underline{AgCN}$	$\underline{AgCNS}$	$\underline{AgCl}$	$\underline{AgBr}$	$\underline{AgI}$	$\underline{Ag_2S}$
III. $Hg(C_2H_3O_2)_2$			$Me_2Hg(CN)_4$	$\underline{AgCNS}$	$\underline{AgCl}$	$\underline{AgBr}$	$\underline{AgI}$	$\underline{Ag_2S}$
IV. $HCOONa + NaOH$				$NaCNS$	$NaCl$	$\underline{AgBr}$	$\underline{AgI}$	$\underline{Ag_2S}$
V. $Cu + NH_4OH$						$Cu(NH_3)_2Br$	$Cu(NH_3)_2I$	$\underline{Ag_2S}$
VI. HNO_3								Ag_2SO_4
	↓	↓	↓	↓	↓	↓	↓	↓
	$\underline{Fe_4Focy_3}$	$H_3Fe(CN_6)$ I_2	$HCNS$ $Fe(CNS)_3$	$\underline{Cu(CNS)_2}$ $Fe(CNS)_3$	$\underline{AgCl}$	$\underline{AgBr}$ Br_2	$\underline{Cu_2I_2}$ I_2	$\underline{BaSO_4}$

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