

found readily undergoes hydrolysis and for this reason it cannot be used for purifying thulium.

The absorption spectrum of an alcoholic solution of the acetylacetonate differs from aqueous solutions of other salts, such as the nitrate and chloride. The difference is shown more especially by the blue band, which in the case of the acetylacetonate is most intense on the side towards the red, whereas the nitrate in aqueous solution gives the most intense part on the violet side.

Thulium Phenoxyacetate, $(CH_2(C_6H_5O)COO)_6Tm_2 \cdot 6H_2O$.—Thulium hydroxide was dissolved in a solution of phenoxyacetic acid in dilute alcohol. The clear liquid was evaporated, the crystals were separated upon a Hirsch funnel and washed with water. The crystallin mass was well stirred with 95 per cent. alcohol after which an equal volume of ether was added. The phenoxyacetate was again filtered and washed with ether. This compound is very voluminous, sparingly soluble in water and soluble in alcohol. By a simple ignition it was found that the thulium oxide amounted to 28.58 per cent.

Thulium Nitrate, $Tm_2(NO_3)_6 \cdot 8H_2O$.—This was obtained by dissolving thulium oxide in nitric acid and evaporating to a small bulk. After a slight excess of fuming nitric acid had been added, the nitrate crystallized out. This compound is deliquescent. When it was dried over sulfuric acid and analyzed, it gave the following results: $Tm_2O_3 = 45.24$ per cent.; calculated $Tm_2O_3 = 45.12$. This compound therefore contains eight molecules of water of crystallization. Most of the rare earth nitrates contain ten or twelve molecules of water. Thulium nitrate resembles "old ytterbium" nitrate, since Astrid Cleve gave 8 H_2O as the amount of hydration of the latter salt.

Thulium nitrate can readily be crystallized from nitric acid. The fractionation of the simple nitrates from nitric acid was first proposed by Demarcay and since then has been used with great success by Urbain and others. At this end of the series the nitrates are very soluble and strong nitric acid must be used during the fractional crystallization.

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VOLHARD'S METHOD FOR THE ESTIMATION OF CHLORINE IN POTABLE WATERS.

BY A. T. STUART.

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The Volhard method, as is well known, requires the addition of an excess of standard silver nitrate solution to the sample under investigation. The precipitated silver chloride is filtered off and the excess of silver nitrate remaining in the filtrate is determined by titration with standard potassium thiocyanate, using a ferric salt as indicator.

It has been suggested that this method be adopted for the determination of chlorine in drinking waters where exceptional accuracy is desired and where the end point by the "Chromate" method is obscured or interfered with by natural color and dissolved peaty matter in the water.¹ In applying this method to water of this type the writer encountered discrepancies which invited further investigation.

Solutions were made as follows:

Silver nitrate of such strength that 1 cc. = 0.001 gram chlorine; *potassium thiocyanate* of equivalent strength; *nitric acid* freed of oxides of nitrogen by boiling.

The *indicator* was prepared by dissolving a known amount of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in water, oxidizing with nitric acid, evaporating to dryness with sulphuric acid and neutralizing the excess of this with ferric carbonate and filtering. The filtrate was so diluted that the solution contained 1 per cent. $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$.

Titrations were made in a flat porcelain dish and the volume always kept constant. A similar dish was placed alongside in which a like amount of silver thiocyanate was precipitated. This aided in the determination of the end point. In all cases 2.00 cc. silver nitrate (representing the excess in any determination) were run in from a 2 cc. pipette graduated to $\frac{1}{50}$ cc. The indicator was carefully measured in each case and the potassium thiocyanate run in from a similar pipet of 2 cc. capacity. Five cc. of nitric acid were added in each case.

READINGS TABULATED.					
Water.	Indicator.	KCNS.	Water.	Indicator.	KCNS.
100	0.1	4.0?	95	5.0	1.92
100	0.2	3.0?	95	6.0	1.90
100	0.3	2.6?	95	7.8	1.90
100	0.4	2.4	93	8.0	1.87
100	0.5	2.3	90	10.0	1.80
100	0.6	2.2	85	15.0	1.75
100	0.7	2.15	80	20.0	1.60
100	0.8	2.15	75	25.0	1.51
100	0.9	2.12	70	30.0	1.44
100	1.0	2.09	65	35.0	1.35
100	1.2	2.07	60	40.0	1.25
100	1.4	2.05	50	50.0	1.05
100	1.6	2.05	40	60.0	0.86
100	1.8	...	30	70.0	0.67
100	2.0	2.05	20	80.0	0.48
100	2.5	2.02	10	90.0	0.28
100	3.0	2.00	..	100.0	0.08
100	4.0	1.94	..	104.0	...
			..	110.0	...

¹ "The Volhard Method for the Determination of Chlorine in Potable Waters." Shutt and Charlton, Proceedings Royal Society, Canada, 1905.

These results are plotted in Fig. 1.

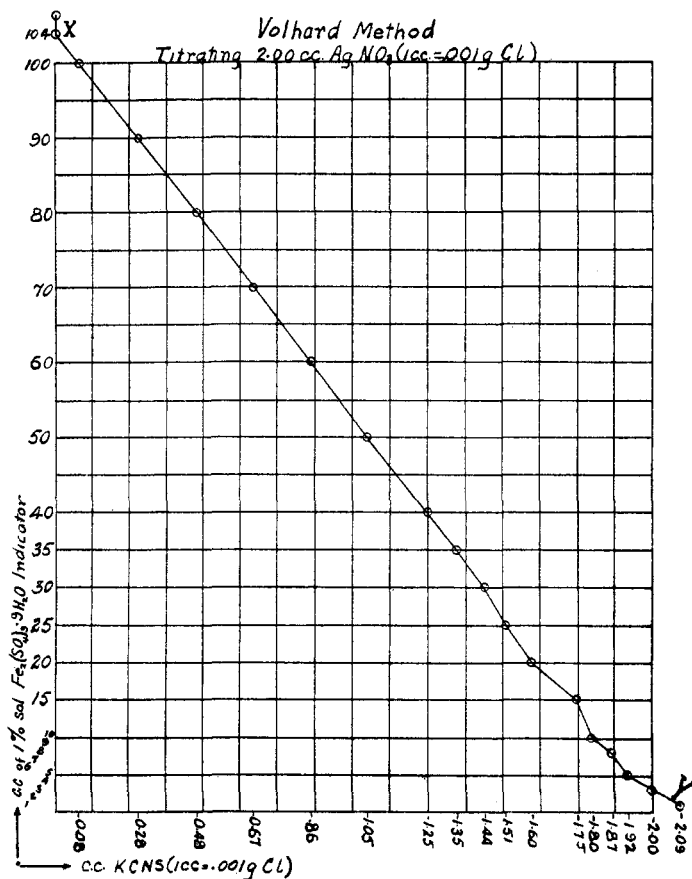
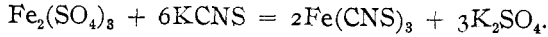


Fig. 1.

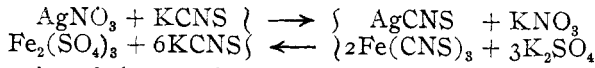
The above curve includes all cases of course, both extreme and otherwise, but clearly illustrates the influence of "mass action," whereby it is seen that if the concentration of the ferric salt is so increased it will completely drive the reaction in the other direction and leave the silver nitrate unacted upon. In applying this method it was expected that the silver thiocyanate formed, being insoluble, would be precipitated out of the phase in which the reaction takes place and thus allow it to go in the one direction. However, it is considered that the small amount remaining in solution sets up a series of equilibria which are represented in the curve. Referring to Fig. 1, at the point "Y," close to the axis, the concentration of the ferric salt is very low and hence the reaction is almost complete between:



At the point "X," near the axis, the concentration of the ferric salt is very great and the first addition of potassium thiocyanate reacts with the ferric salt to give a red color:



At points between "X" and "Y" there is a series of equilibria set up representing a combination of the two equations:



The end point of the reaction is also necessarily influenced to a certain extent by the dissociation in solution of the red ferric thiocyanate, represented as follows:

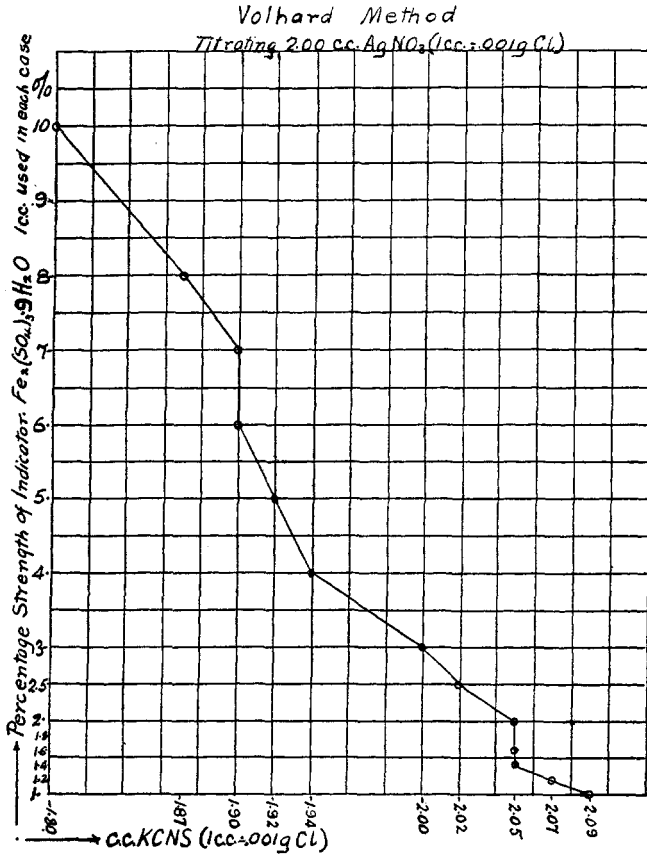
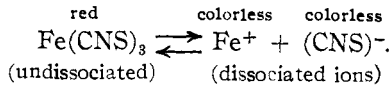


Fig. 2.

Thus on the addition of the *first slight* excess of potassium thiocyanate a red color may not be produced since the concentration of the ferric thiocyanate is so low that it is completely dissociated into colorless ions and the undissociated, and red ferric thiocyanate may not be formed until the concentration of the $(\text{CNS})^-$ ion drives the reaction in that direction. This point is indicated by the curve in Fig. 1, for at the extremity "Y" it is found necessary to add potassium thiocyanate even to the extent of 3 and 4 cc. On the other hand, at the extremity "X," where the concentration of the Fe ion is very great, the slightest addition of $(\text{CNS})^-$ ion immediately reacts to form the undissociated red ferric thiocyanate.

To eliminate extreme cases and further illustrate results within practical working limits a second curve is drawn. One axis represents *one cc.* of indicator of various per cent. strengths and the other the potassium thiocyanate required.

The figures indicate that in titrating 2 cc. silver nitrate, using 1 cc. of indicators of various strengths from 1 to 10 per cent., the reading may vary between 1.80 cc. and 2.09 cc. This, of course, represents an error not permissible for work of extreme accuracy and involving in its limits 2.9 parts per million of chlorine.

From the above it is concluded that the method is only applicable when very small amounts of silver nitrate—not greater than 0.2 cc.—in excess of that required are added. Under such conditions and those previously mentioned, the plus or minus error for a water containing say 10 parts per mil. would be within 0.5 part per mil., but in no such case is the method applicable when attempts are made to differentiate between fractional parts per million.

To investigate to what extent this influence is exerted in cases of solutions of more ordinary concentration the following results were obtained with *decinormal* solutions:

Water.	HNO_3 .	AgNO_3 .	Indicator.	KCNS.
100	5	2	0.1	2.5?
100	5	2	0.5	2.05
100	5	2	1.0	2.00
100	5	2	5.0	1.95
90	5	2	10.0	1.92
75	5	2	25.0	1.87
50	5	2	50.0	1.70
25	5	2	75.0	1.58
..	5	2	100.0	1.42
90	5	10	1.0	10.05
80	5	10	10.0	10.00
65	5	10	25.0	9.85
50	5	10	50.0	9.70
..	5	10	100.0	9.50
65	5	25	10.0	24.70
..	5	25	100.0	24.30

Although a variance is quite noticeable when examining solutions of *ordinary* strength, it may not be considered of sufficient practical importance to seriously interfere with the use of this method. It would, however, be necessary to take particular care that a very slight excess only of silver nitrate is present.

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THE SIGNIFICANCE OF THE PERIODIC LAW.

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The physical significance of the periodic law has been the subject of much speculation and of many important investigations. The conclusion seems inevitable that the chemical elements have been built up step by step, from some simpler substance or substances, but thus far all attempts at identifying the original substance have failed. Meanwhile, the discovery of radioactivity and the successive disintegrations of the uranium and thorium atoms seem to have shown us how these atoms were originally put together. In this process we see one elementary atom changing into another of lower atomic weight by releasing one or more alpha particles or one or more negative electrons, or in some cases, perhaps, by giving off both an alpha particle and an electron in a single change. Since the electron has but little, if any, influence upon the atomic weight, we find these successive atoms differing in atomic weight by four or eight, or in the case where only an electron is set free we may have two successive atoms with the same atomic weight but with different chemical properties.

Since the disintegration products of uranium seem to fall into their proper positions in the periodic series and to have properties analogous to the other members of their periodic groups, radium, for example, showing the characteristic properties of the barium group and emanation forming an inert gas of the argon group, it would seem to follow that the other elements of these groups must in the same way be formed by adding alpha particles and electrons to elements of lower atomic weight.

A difficulty in constructing the elementary series in this way arises from the fact that the atomic weights of successive elements do not increase by four or by multiples of four. This difficulty is largely overcome for a considerable part of the series, by assuming two parallel lines of development, one line starting from helium and one from lithium. In the following table the elements have been arranged in two series from that point of view, the attempt being made to select the elements which would most nearly meet the atomic weight requirements: