Deep appreciation is hereby expressed to Professor Hopkins for the loan of material for the investigation; to the National Research Council and International Education Board for furnishing funds to allow a continuation of this work in Europe, and also to Professor Georges Urbain of the Sorbonne whose kindly advice and interest was a source of inspiration at all times.

Summary

1. As mentioned in the historical part of this paper, it was feared that there was a possibility of loss of illinium during original extraction of double sulfate residues. As the material used had been extracted with a 50% solution of sodium hydroxide, the foregoing experiments show that there is a possibility of loss of rare earths at this point.
2. A method has been outlined whereby using a sodium hydroxide solution, practically theoretical results—as compared with an accurate quantitative determination—have been obtained for amounts up to 300 g.
3. An equally efficient method for larger amounts, involving fusion with sodium carbonate, has been described.
4. The use of nitric acid and hydrogen peroxide is recommended for the extraction of commercial hydrated oxides. Hence, if the original material is extracted by any of the above methods, all of the rare earths, including illinium, should be found in the extract. All undissolved residues are, however, being investigated.

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[CONTRIBUTION FROM THE BIOCHEMIC DIVISION, BUREAU OF ANIMAL INDUSTRY, U. S. DEPARTMENT OF AGRICULTURE]

DICHLORO-AMINE

BY ROBERT M. CHAPIN

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Available evidence for the existence of dichloro-amine, $NHCl_2$, including the most recent,[1] rests upon incidental observations made in the course of work on nitrogen trichloride. The conditions necessary for the formation of the substance remain undefined, while methods for its separation from the two other reaction products are lacking.

The nature of the product obtained through chlorination of an excess of ammonium ions is known to depend upon the reaction of the solution, acidity leading toward nitrogen trichloride and alkalinity toward monochloro-amine. It will be shown here that when the reaction is effected through rapid mixing of sufficiently cool and dilute buffered solutions, with ammonium ions always in excess, the nature of the product is governed solely by the concentration of hydrogen ions. In solutions more alkaline

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[1] W. A. Noyes, THIS JOURNAL, **42**, 2173 (1920).

than slightly above *P*H 8.5 nothing but monochloro-amine was found; below *P*H 4.4 nitrogen trichloride is produced with only a trace of chloro-amine; between *P*H 4.4 and 8.5 graduated mixtures of the two chloro-amines result. That is, while the shift between nitrogen trichloride and dichloro-amine is sharp near *P*H 4.4, there is a considerable range over which the two chloro-amines coexist in a ratio ultimately fixed by the hydrogen-ion concentration. Accordingly an acidified solution of monochloro-amine becomes proportionately converted to dichloro-amine on storage.

In the physical properties of odor, volatility from aqueous solution and relative solubility in various immiscible solvents, dichloro-amine is intermediate between nitrogen trichloride and monochloro-amine. Like these two it liberates iodine from an acidified solution of potassium iodide, and may be thus determined when free from both of the others. Removal of contaminating nitrogen trichloride is easily effected with little loss of chloro-amine by shaking out the aqueous solution with successive small proportions of carbon tetrachloride, but no way for removing contaminating monochloro-amine was found other than conversion to dichloro-amine by subjection to a sufficiently low hydrogen-ion concentration.

Mixtures of the two chloro-amines that are free from nitrogen trichloride may be assayed by determining the apparent partition ratio in an appropriate immiscible solvent, either chloroform, carbon tetrachloride or pure ether, and comparing the result with the partition ratios of the two pure substances in that solvent.

Experimental

The solutions of chlorine and of ammonium ions were mixed expeditiously and the products were stored in the dark at room temperature. The buffers employed in the preparations were acetate, phosphate or borate mixtures, which are resistant to chlorine. Hydrogen-ion concentrations were determined colorimetrically by standard methods (Clark) with the indicators methyl red, brom thymol blue, cresol red and thymol blue (alkaline range). Errors from bleaching could be sufficiently avoided by rapid work except that nitrogen trichloride required previous removal by carbon tetrachloride. Any solution to be analyzed for "available chlorine" was pipetted (tip beneath surface) into a flask already charged with a dilute iodine-free mixture of potassium iodide and the necessary excess of hydrochloric acid, with constant swirling. All extractions and subsequent analyses, once started, were put through as expeditiously as possible.

Experiment 1.—The ammonium solution, 250 cc., was 0.1 *M* ammonium acetate brought to the desired *P*H by acid or alkali and in many cases carrying additional buffer. The chlorine solution, 250 cc., had been brought to the same *P*H by calculated addition of buffer to 100 cc. of chlorine water carrying 0.4 to 0.6% chlorine.

After admixture, storage and determination of the *P*H, the whole solution was thoroughly shaken with 10 cc. of carbon tetrachloride in a separatory funnel. A little of the carbon tetrachloride was discarded to rinse the stem of the funnel, then 5 cc. of the remainder was added to acidified potassium iodide and titrated with 0.01 *N* sodium thiosulfate. After expulsion of sludge, extraction and titration were repeated until the slightness of the difference between successive results proved the absence of nitrogen trichloride.

Following extraction with carbon tetrachloride, the apparent partition ratio of the chloro-amine in chloroform was determined, 25 to 30 cc. of each liquid being thoroughly shaken together, and 20 cc. of each phase being titrated in acidified potassium iodide solution with 0.01 *N* thiosulfate. Many of these determinations were made in duplicate.

The results of Expt. 1 are contained in Table I. Owing to the formation of acid in the reaction, the final *P*H usually fell below the calculated initial *P*H to a degree dependent upon the nature and proportion of buffer present. There appears a marked difference in the solubility and hence in the nature, of the substances extracted by carbon tetrachloride from Preparations A and B, respectively. The partition ratio in chloroform of Preparation A was not determined because the total available chlorine remaining after the fourth carbon tetrachloride extraction required only 3.8 cc. of 0.01 *N* thiosulfate per 50 cc.

TABLE I

INFLUENCE OF HYDROGEN-ION CONCENTRATION UPON PRODUCTS IN EXPERIMENTS 1 AND 2

Expt.	Prep.	Init. *P*H, calcd.	Final *P*H, detd.	Time, hours	$Na_2S_2O_3$ titr. of CCl_4 extracts			Part. ratio, $\frac{CHCl_3}{aq.}$	$\frac{D.c.a.\text{-}Cl}{Total\ c.a.\text{-}Cl}$, %
					1	2	3		
1	A	4.3	4.4	0.75	136.5	26.3	4.8[a]		
	B	4.6	4.4	.75	8.0	7.8	7.7	1.87	99.8
	C	7.0	5.5	1.25	5.9	5.7		1.63	92.9
	D	8.0	6.5	1.25	4.6	4.3		0.99	
			6.4	21.5				.98	65.5
	E	8.0	7.0	3	1.85	1.75		.68	45.2
	F	8.0	7.3	1.5				.66	43.7
	G	8.0	8.0	1.25	1.35			.28	3.5
	H	8.4	8.5	0.75	0.9			.252	0.4
	I	9.2	8.9	.75	.9	0.9		.249	.0
		(detd.)							
2	A	4.2		20	12.4	2.15	0.7		
	B	4.6	4.4	21	6.6	6.4		1.90	100.0
	C	4.8	4.7	22	7.05	6.9		1.87	99.8
	D	4.9	4.8	18.5	6.25	6.05	5.95	1.86	99.5
	E	5.3	5.2	43	4.25	4.2		1.86	99.5
	F	5.5	5.3	44	3.8	3.75		1.84	99.0
	G	>9	>9	2				0.25	0.0

[a] Titration of fourth CCl_4 extract = 1.2 cc.

Experiment 2.—This experiment shows the effect of acidification upon monochloro-amine. The ammonium solution contained 30 cc. of 10% ammonium sulfate and 5 cc. of *N* sodium hydroxide in 200 cc. The chlorine solution contained 100 cc. of chlorine water and 20 cc. of *N* sodium hydroxide in 200 cc. After admixture and standing for one hour, a predetermined quantity of 0.5 *N* acetic acid was added and the *P*H was immediately determined. Other determinations were made after a further interval, as shown in Table I. As in Expt. 1, Preparations A and B on either side of *P*H 4.4 yielded different substances to extraction by carbon tetrachloride. It is also evident that monochloro-amine held at *P*H 4.4 to 5.3 undergoes extensive conversion to dichloro-amine.

Experiment 3.—The rate of the formation of dichloro-amine from chlorine and ammonium ions at a favorable *P*H was next investigated. Mixtures were made as in Expt. 1 at a calculated initial *P*H of 4.9. The results are contained in Table II. Residual Preparation B after standing for a total of three hours was extracted twice with carbon tetrachloride. The obtained titrations of 9.50 and 9.25 cc. of 0.01 *N* thiosulfate showed freedom from nitrogen trichloride. Accordingly, the reactions leading to dichloro-amine under the most favorable conditions require at least one to two hours for completion.

TABLE II

INFLUENCE OF TIME UPON FORMATION OF DICHLORO-AMINE IN EXPERIMENT 3

			Partition in CCl_4			Partition in $CHCl_3$		
Prepn.	Time, min.	*P*H, detd.	CCl_4 phase; titrn.	Aq. phase; titn.	$\frac{CCl_4}{aq.}$	$CHCl_3$ phase; titrn.	Aq. phase; titrn.	$\frac{CHCl_3}{aq.}$
A	2		29.0	42.4	0.68			
	17		26.7	36.3	.74			
	60	4.7	26.0	32.8	.79			
	120		24.3	30.1	.81			
B	15					47.2	26.3	1.79
	60		24.2	28.1	.86	44.6	23.7	1.88
	120	4.6	22.6	26.6	.85	44.0	23.7	1.86

Experiment 4.—Marckwald and Wille[2] found the partition ratio of monochloro-amine between ether and water to be near unity. To determine that of dichloro-amine, portions of Preparation B of Expt. 3 after the two extractions by carbon tetrachloride were shaken with ether, free from peroxide and alcohol, and the partition ratio was determined as before described, except that only 10 cc. of the ether layer was pipetted out, and this was discharged into 10 cc. of carbon tetrachloride underlying the acidified potassium iodide in the flask in order to sink the non-aqueous solvent. Two trials gave partition ratios of 47.5 and 47.0.

On the assumption that dichloro-amine was the sole product present at a *P*H slightly above 4.4, the previous experiments indicate the following partition ratios

Monochloro-amine in chloroform	0.25
Dichloro-amine in chloroform	1.88
Dichloro-amine in carbon tetrachloride	0.85
Dichloro-amine in ether	47.3

From the partition ratios of the two pure chloro-amines in chloroform, the percentage of dichloro-amine chlorine in total chloro-amine chlorine

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[2] Marckwald and Wille, *Ber.*, **56**, 1319 (1923).

may accordingly be calculated from the apparent partition ratio, R, of a mixture by the formula

$$44.2 = \frac{4R - 1}{R + 1}$$

Application of this formula gave the results in the last column of Table I.

Experiment 5.—With respect to the determination of the chlorine–nitrogen ratio in the supposed dichloro-amine, the work of Noyes[1] on nitrogen trichloride indicated that transfer of the substance to an immiscible solvent would be the best means for purification from ammonium salts and chloride. For the actual analysis the methods of Marckwald and Wille[2] for monochloro-amine were followed as closely as possible.

Preparations were made as in Expt. 1 but with the chlorine water increased to 150 or 200 cc. After one hour the P_H was found to lie between 4.5 and 4.7 and freedom from nitrogen trichloride was proved by two extractions with carbon tetrachloride. Dichloro-amine was then extracted with 125 cc. of peroxide-free ether. The ether extract was transferred to a small separatory funnel and washed four times with 10 to 15 cc. of acetate buffer of P_H 4.5, though the last wash was not removed. The second and third washings afforded only opalescences with silver nitrate solution.

From the clear ether layer 50 cc. was pipetted into a 200-cc. volumetric flask containing 35 to 50 cc. of strong aqueous sulfur dioxide, while 10 cc. was pipetted into a glass-stoppered flask charged with acidified potassium iodide and 10 cc. of carbon tetrachloride. The liberated iodine in the latter flask was at once titrated with 0.1 N sodium thiosulfate.

The flask containing sulfur dioxide and ethereal solution was stoppered and frequently shaken for one-half hour; then the ether and evident excess of sulfur dioxide were gently boiled off. Half of the cooled solution was taken for cold precipitation of silver chloride and half for distillation of ammonia into 0.1 N acid. The results in Table III appear adequate to identify the substance as well as to prove the applicability of the assay method for "available chlorine."

TABLE III

ANALYTICAL RESULTS ON DICHLORO-AMINE SOLUTIONS IN EXPT. 5

				Results in g. per 100 cc.			
Prepn.	$Na_2S_2O_3$, titrn.	AgCl, g.	NH_3, titrn.	"Avail. Cl"/2	Total Cl	N	At. ratio, total Cl/N
A	16.19	0.2945	10.10	0.2870	0.2914	0.0566	2.034
B	12.09	.2147	7.50	.2144	.2125	.0420	1.998

Experiments on the germicidal powers of dichloro-amine have been begun in these Laboratories.

Summary

Dichloro-amine is produced by chlorination of excess ammonium ions at P_H 4.4 to 8.5, being practically the sole ultimate product at P_H 4.5 to

5.0, and, likewise, by corresponding acidification of monochloro-amine solutions. It was identified through its behavior with immiscible solvents and by its chlorine–nitrogen ratio.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE DETERMINATION OF FERROUS IRON IN SILICATE ROCKS. II. ELECTROMETRIC

BY BYRON A. SOULE

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In a previous article[1] it was shown that the ferrous iron content of silicate rocks can be determined by decomposing the sample with hydrofluoric acid in a pyrex glass flask, diluting with a solution of boric acid and titrating with standardized potassium permanganate. The method has two advantages over that commonly used: (a) the course of decomposition can be watched, and (b) solution and titration are conducted in the same vessel. The most significant disadvantage is that a correction must be applied for the permanganate reduced by dissolved glass constituents.

A consideration of the composition of pyrex glass[2] suggested that arsenic might be the only disturbing element. It was therefore decided to try ceric sulfate as the oxidizing agent, Willard and Young[3] having reported that the titration is not affected by a moderate amount of arsenious acid. The results obtained were satisfactory and led to the development of the method herein advocated.

Materials

Apparatus.—The decomposition flasks were of two sorts: (1) ordinary 250-cc. pyrex glass suction flasks, each having an especially made, well fitting, glass stopper provided with an outlet tube 1 cm. in diameter and bent sharply at the lower end to almost touch the side of the flask; (2) 250-cc. transparent, fused quartz, Erlenmeyer flasks with similar stoppers.

Titrations were conducted with the aid of a bimetallic electrode system similar to that suggested by Furman and Wilson.[4] The resistance used was 240,000 ohms. The electrodes were prepared from pieces of No. 27 B. and S. gage platinum wire and silver wire[5] annealed at 100–105°, then sealed into the ends of glass tubes as usual. About 3 cm. of the platinum and 6 cm. of the silver wire projected. When not in use the anode was kept in a solution of ceric sulfate and the cathode in dilute ammonia water.

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[1] Soule, THIS JOURNAL, 50, 1691 (1928).

[2] U. S. Bureau of Standards Tech. Paper 107, p. 8.

[3] Willard and Young, THIS JOURNAL, 50, 1335 (1928).

[4] Furman and Wilson, *ibid.*, 50, 277 (1928).

[5] This work was nearing completion when the article by Brann and Clapp, *ibid.*, 51, 39 (1929), appeared.