

CaCO ₃ taken, g.	CaSO ₄ found, g.	CaO found, %	Variance from calcd., %
0.6407	0.8737	56.17	+0.14
.7179	.9783	56.13	+ .10
.6770	.9201	55.98	- .05

SUMMARY OF THE RESULTS

CaO found by %	Carbonate method	Ignition of spar	Detn. as sulfate	Calcd.
	56.105	56.11	56.09	56.03

Hinrichsen² determined the atomic weight of calcium by igniting an Iceland spar similar to the sample used by us. It contained 0.03% of ferric oxide. Using, in all his determinations, over 130 g. of the spar he found 56.068% of calcium oxide, including the trace of ferric oxide.

Summary

Calcium may be determined accurately as the carbonate by igniting the oxalate in a current of carbon dioxide under suitable temperature control. The method gives results as good as or better than the method depending on the conversion of the oxalate to oxide. It has the advantages over the oxide method that the carbonate can be weighed without danger of taking up moisture or carbon dioxide, and the precipitate of oxalate can be filtered on a porcelain Gooch crucible, thereby saving time in filtration and avoiding the use of a platinum crucible for ignition.

On account of the accuracy and speed of the method, the writers believe that it may often be substituted to advantage for the rapid method of determining calcium by titrating the oxalate with permanganate.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE SEVERANCE CHEMICAL LABORATORY OF OBERLIN COLLEGE]

THE ADSORPTION OF SULFIDES BY COLLOIDAL CHROMIUM HYDROXIDE

BY HARRY N. HOLMES AND MELVIN A. DIETRICH

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In Sneed's method¹ of qualitative analysis for the hydrogen sulfide group mercuric sulfide is dissolved with the sulfides of arsenic, antimony and tin, contrary to the usual custom. The reagent used is a solution of sodium hydroxide and the sulfides of sodium. The sodium hydroxide prevents hydrolysis of the soluble compound, Hg(SNa)₂, and the consequent precipitation of mercuric sulfide. The method calls for the later addition of ammonium chloride which so represses the ionization of the base that hydrolysis of Hg(SNa)₂ then takes place, thus permitting the precipitation and separation of mercuric sulfide at the proper time.

² Hinrichsen, *Z. physik. Chem.*, **39**, 311 (1901).

¹ Sneed, *THIS JOURNAL*, **40**, 187 (1918).

In our Laboratory it was often observed that the mercuric sulfide failed to precipitate when expected. Investigation disclosed the fact that this was true only when the "unknown" contained a chromium salt.

It was suspected that the solution of the chromium salt contained some colloidal chromium hydroxide (because of hydrolysis) and that this was adsorbed by the sulfides precipitated in Group II. In such an event this chromium hydroxide would naturally be peptized again by the sodium hydroxide of the Sneed reagent at the same time that the mercuric sulfide was dissolved as $\text{Hg}(\text{SNa})_2$. Upon addition of ammonium chloride any mercuric sulfide formed by "permitted" hydrolysis would normally be precipitated. However, any colloidal chromium hydroxide present must adsorb the negatively charged particles of mercuric sulfide and carry them into suspension, thus interfering with an interesting method of analysis.

The ability of colloidal chromium hydroxide to adsorb mercuric sulfide was clearly demonstrated by passing hydrogen sulfide into a hot solution (made 0.5 *N* with hydrochloric acid) containing 13.5 g. of mercuric chloride and 69 g. of green chromium chloride per liter. Mercuric sulfide failed to precipitate. The solution turned black and ran through a filter paper. To show that this suspension was a positive colloid (chromium hydroxide), in spite of the evident adsorption of mercuric sulfide, we precipitated it by the addition of 15 cc. of 0.05 *N* potassium ferrocyanide solution to 20 cc. of the colloid. As much as 90 cc. of 0.05 *N* potassium sulfate was required for precipitation. Saturation of the solution with potassium chloride failed to cause precipitation. The effect of the tetravalent negative ferro-cyanide ion was conspicuously greater than that of the negative ions of lower valence.

To reverse the adsorption order we passed hydrogen sulfide into a hot solution (made 0.5 *N* with hydrochloric acid) containing 50 g. of mercuric chloride and 10 g. of green chromium chloride per liter. Mercuric sulfide precipitated and carried down a part of the chromium.

This is somewhat similar to the work of Fischer and Herz.² They added sodium hydroxide to solutions containing ferric chloride and chromic sulfate mixed in various proportions. When iron was in excess a brown precipitate of ferric hydroxide carried down all of the chromium hydroxide in spite of the peptizing action of an excess of sodium hydroxide or chromium hydroxide. When chromium was in excess no precipitation occurred. The peptized chromium hydroxide adsorbed the ferric hydroxide and carried it into suspension.

We observed that solutions freshly prepared for analysis, one day old at most, never caused the adsorption difficulties mentioned unless the weight ratio of chromium chloride to mercuric chloride decidedly exceeded 2:1. Yet 48 hours after green chromium chloride had been dissolved in the solution containing mercuric chloride a satisfactory analytical separa-

² Fischer and Herz, *Z. anorg. Chem.*, **31**, 352 (1902).

tion could not be made if the ratio of chromium chloride to mercuric chloride was as great as 1:3.5. This aging effect pointed to an increase in the amount of colloidal chromium hydroxide formed by hydrolysis.

To test this theory we selected a series of solutions ranging from a content of 5.75 g. of green chromium chloride with 13.5 g. of mercuric chloride to 69 g. of chromium chloride with 13.5 g. of mercuric chloride per liter. When aged for 48 hours all of these solutions (made 0.5 *N* with hydrochloric acid) showed very cloudy filtrates after treatment with hydrogen sulfide. The mercuric sulfide was adsorbed and suspended by colloidal chromium hydroxide. Similar solutions, aged for 48 hours, were then boiled for two minutes with equal volumes of 6 *N* hydrochloric acid, neutralized cautiously (while being stirred rapidly) with dil. ammonium hydroxide and analyzed by the hydrogen sulfide method. In each case the separation of mercury from chromium was satisfactory; the mercuric sulfide precipitated cleanly yielding a clear, green filtrate. Evidently hydrolysis of chromium chloride had been driven back by the excess of acid.

It was further observed that solutions containing as much as 90 g. per liter of chromium sulfate with 13.5 g. of mercuric chloride could be analyzed without difficulty even when 96 hours old. The inference that there was little, if any, colloidal chromium hydroxide in a chromium sulfate solution called for confirmation. Consequently we dialyzed 0.1 *M* solutions of the chloride, the nitrate, the acetate and the sulfate of chromium by Neidle's rapid method of hot dialysis.³ After four days of dialysis, the green colloidal hydroxide remaining in the dialyzer was evaporated, ignited and weighed. The fraction of each salt that had been hydrolyzed was readily calculated, and found to be 47.22% for chromic chloride, 42.73% for chromic nitrate, 20.15% for chromic acetate and 0.59% for chromic sulfate. This evidence strengthens the theory that solutions of chromium sulfate contain but little colloidal hydroxide.

As stated before, an aged solution (48 hours) containing as much as 5.75 g. of green chromium chloride with 13.5 g. of mercuric chloride yielded a cloudy filtrate on treatment with hydrogen sulfide, due to the suspension of mercuric sulfide. When an equivalent weight of cadmium chloride was substituted for the mercuric chloride similar results were obtained. Cadmium sulfide was adsorbed and suspended by colloidal chromium hydroxide. When an equivalent weight of cupric chloride was substituted, however, cloudiness in the hydrogen sulfide filtrate did not appear until the concentration of chromium chloride was increased to 11.5 g. per liter.

Solutions of aluminum chloride containing as much as 59 g. per liter and of ferric chloride containing 67 g. per liter showed relatively small suspending power towards the sulfides of the copper group under hydrogen sulfide treatment.

³ Neidle, *THIS JOURNAL*, **38**, 1270 (1916); **39**, 71 (1917).

To compare the effect of hydrogen, sulfate, chloride and sodium ions a series of five solutions containing 12 g. of green chromium chloride and 45 g. of mercuric chloride per liter was allowed to age for two months to permit considerable hydrolysis of the chromium salt. Four of the solutions were then boiled for two minutes with equal volumes of some acid or salt, as indicated in Table I. The fifth was boiled and treated with hydrogen sulfide without added acid or salt.

TABLE I
EFFECT OF CERTAIN IONS

Soln. added	6.0 N HCl	1.5 N H ₂ SO ₄	1.5 N Na ₂ SO ₄	1.5 N NaCl	None
H ₂ S filtrate	Clear	Clear	Clear	Sl. cloudy	Very cloudy

Clearly, the hydrolysis of chromium chloride is retarded by hydrogen ions and even more by sulfate ions but is far less influenced by chloride or sodium ions. It was also observed that dilution and boiling aided hydrolysis somewhat. Probably it is more nearly correct to state that the change from the green to the violet form of chromium chloride is fundamental to the ultimate formation of colloidal chromium hydroxide.

Conductivity measurements by Werner and Gubser⁴ show that freshly prepared solutions of the green chloride gradually change to the violet form. The green form ionizes to yield $\text{CrCl}_2(\text{OH}_2)_4^+$ and chloride ion.

With this complex positive ion, there is small chance for the formation of colloidal chromium hydroxide. The violet form ionizes to yield $\text{Cr}(\text{OH}_2)_6^{+++} + 3 \text{Cl}^-$. Such a simple hydrated chromium ion can readily form the colloidal hydroxide by hydrolysis. Povarnin⁵ stated that the retardation of the hydrolysis of chromium sulfate produced by SO_4^{--} is greater than that caused by Cl^- . The importance of ion influence has also been indicated by Lamb.⁶

Summary

It has been shown that precipitation of certain sulfides by hydrogen sulfide in 0.5 N hydrochloric acid solution containing chromium chloride may be prevented by adsorption of the sulfides on colloidal chromium hydroxide formed by hydrolysis of the chloride. This occurs in freshly prepared solutions containing chromium chloride and mercuric chloride in excess of the ratio 2:1. Hydrolysis increases on standing and precipitation after 48 hours does not occur when the ratio is as low as 1:3.5. The hydrolysis of the chloride is retarded by sufficient concentrations of hydrogen and sulfate ions. Hydrolysis of chromium sulfate is so slight that there is no interference in the precipitation of sulfides in a solution containing chromium sulfate. Solutions in which marked hydrolysis has occurred are

⁴ Werner and Gubser, *J. Chem. Soc.*, **80**, [2] 453 (1901); *Ber.*, **34**, 1579 (1901).

⁵ Povarnin, *J. Russ.-Phys. Chem. Soc.*, **41**, 1014 (1909).

⁶ Lamb, *THIS JOURNAL*, **28**, 1710 (1906).

reversed by boiling them for two minutes after making 3 *N* with hydrochloric acid.

OBERLIN, OHIO

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY AT CORNELL UNIVERSITY]

HYDRONITRIC ACID AS PRODUCT OF DESOLVATION OF AMMONONITRIC, HYDRAZONITROUS AND AMMONO-HYDRAZONITROUS ACIDS. EXPERIMENTAL FORMATION OF SODIUM TRINITRIDE BY AMMONOLYSIS OF SODIUM NITRATE WITH SODIUM AMIDE¹

BY A. W. BROWNE AND FRANK WILCOXON

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It was first suggested by Turrentine² that hydronitric acid, an "ammonated nitride of nitrogen," may be regarded as the analog in the well-known ammonia system of compounds,³ of nitric acid, a hydrated oxide of nitrogen, in the water system. This analogy has been recognized by Franklin, who uses the name ammononitric acid for hydronitric acid and who has submitted various lines of experimental evidence⁴ in support of the idea. From a slightly different viewpoint, workers in this Laboratory⁵ have long regarded the trinitrides, or pernitrides, as nitridizing agents analogous to the peroxides, and have considered nitric and nitrous acids, with their chemical aggregates of oxygen and nitrogen atoms, as intermediate in composition and character between hydrogen pernitride and hydrogen peroxide.

Certain experimental evidence seems to indicate that hydronitric acid may be more closely akin to nitrous than to nitric acid. The authors have found, for example, that iodine is not liberated in appreciable amount on addition of 1% solutions of nitric acid to hydriodic acid, although readily liberated by 1% solutions of either nitrous acid or hydronitric acid. Since the latter substance is not theoretically derivable, however, from normal ammononitrous acid, $N(NH_2)_3$, by removal of ammonia, and has never

¹ This article is respectfully dedicated by the authors to Professor L. M. Dennis, and will be reprinted as Article No. 1 in The Louis Munroe Dennis Quarter Century Volume to be published in 1928 in commemoration of the completion by Professor Dennis of twenty-five years of service as Head of the Department of Chemistry at Cornell University. The current article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by Frank Wilcoxon in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

² Turrentine, *THIS JOURNAL*, **34**, 385 (1912).

³ Franklin, (a) *ibid.*, **27**, 820 (1905); (b) *Am. Chem. J.*, **47**, 285 (1912); (c) *Proc. Eighth Int. Cong. Appl. Chem.*, **6**, 119 (1912); (d) *THIS JOURNAL*, **46**, 2137 (1924).

⁴ Franklin, (a) *Science*, **56**, 28 (1922); (b) Ref. 3 d, p. 2142.

⁵ Browne and Welsh, *THIS JOURNAL*, **33**, 1728 (1911). Goldberg, *ibid.*, **34**, 886 (1912). Browne and Hoel, *ibid.*, **44**, 2116 (1922).