# Chemistry

T. I. Sendulskaya and M. Ya. Shpirt

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## Abstract

## Full Text

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**T. I. Sendulskaya and M. Ya. Shpirt**

# On the Coprecipitation of Microquantities of Germanium with Ferric Hydroxide

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Recently, works have appeared explaining the coprecipitation of various metals with insoluble hydroxides by the ion-exchange properties of the latter ([1]). In most studies dealing with the adsorption properties of ferric hydroxide, the coprecipitation with it of various divalent cations is considered. A summary of these is given by Kurbatov and co-workers ([2]). A considerably smaller number of reports is devoted to the coprecipitation with ferric hydroxide of elements present in aqueous solutions in the form of anions. Among these, the works of Plotnikov ([3],[4]) on the coprecipitation of selenium and tellurium with $Fe(OH)_3$ should be noted.

**Table 1**

*Effect of temperature on the coprecipitation of germanium*

| Temperature, °C | Coprecipitation Ge, % |
|---|---|
| 20 | 99 |
| 40 | 97 |
| 70 | 100 |
| 80 | 99 |

Summarizing the results obtained, it may be noted that, in the case of an adsorption or ion-exchange mechanism of coprecipitation, complete precipitation of metals is achieved over a comparatively long time ([2]) at ratios Me : Fe  1 : 1000; moreover, increasing the concentration of the foreign electrolyte reduces the completeness of precipitation.

In the chemical determination of germanium, the method of its coprecipitation with ferric hydroxide is often used ([5]). In this case, not only is germanium separated from the main quantity of Cu, Zn, Cr, etc., but it is also considerably concentrated in the solutions formed after dissolving the hydroxide with coprecipitated germanium in dilute hydrochloric acid. Meanwhile, the literature contains no data concerning the mechanism of coprecipitation and the influence of various factors on the completeness of coprecipitation of microquantities of germanium with ferric hydroxide.

In the present communication, results are given of studies on the coprecipitation of germanium—present in solution in the form of germanic acid, the anion $HGeO_3'$, and, possibly, $Ge_5O_{11}''$ ([6])—with ferric hydroxide as a function of temperature, the time of contact of the precipitate with the solution, the amount of hydroxide introduced, the concentration of germanium, and the pH of the solution.

**Table 2**

*Effect of the time of contact of the precipitate with the solution on the completeness of coprecipitation of germanium*

| Duration of contact of the precipitate with the solution, min | Coprecipitation Ge, % |
|---:|---:|
| 2 | 99 |
| 5 | 98 |
| 10 | 102 |
| 30 | 99 |
| 60 | 103 |
| 120 | 101 |
| 24 hours | 100 |

Tables 1 and 2 give data on the influence of temperature and of the time of contact of the precipitate with the solution on the completeness of coprecipitation of germanium (Ge concentration 1 $\gamma$/ml; pH 8; Ge : Fe = 1 : 100). From the data presented it is evident that the completeness of coprecipitation of germanium is the same in the temperature interval—

in the temperature range from 20 to 80°, complete coprecipitation within the experimental error is achieved already after two minutes' contact of the solution with the precipitate, and germanium is not released back into the solution even upon prolonged contact of the solution with the precipitate.

In studying the dependence of germanium coprecipitation on the Ge : Fe ratio (Fig. 1), it may be noted that even at ratios Ge : Fe = 1 : 20 (at a germanium concentration of 1 $\gamma$/ml) complete coprecipitation of germanium with the hydroxide is attained, and decreasing this ratio does not lead to dissolution of germanium.

**Fig. 1.** Dependence of Ge coprecipitation on the amount of iron hydroxide. pH 8; $t = 70°$; Ge conc. 1 $\gamma$/ml: 1 —without addition of $(NH_4)_2SO_4$; 2 —in 2% $(NH_4)_2SO_4$ solution.

**Fig. 2.** Effect of Ge concentration in solution on completeness of precipitation by iron hydroxide. pH 8; $t = 70°$; 1 —Ge : Fe = 1 : 100, without $(NH_4)_2SO_4$; 2

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Fig. 2. Effect of Ge concentration in solution on completeness of precipitation by iron hydroxide. pH 8; t = 70°; 1 —Ge : Fe = 1 : 100, without $(NH_4)_2SO_4$; 2 —Ge : Fe = 1 : 100 in 2% $(NH_4)_2SO_4$ solution; 3 —Ge : Fe = 1 : 1000, in 2% $(NH_4)_2SO_4$ solution

Figure 2: Fig. 2. Effect of Ge concentration in solution on completeness of precipitation by iron hydroxide. pH 8; t = 70°; 1 —Ge : Fe = 1 : 100, without $(NH_4)_2SO_4$; 2 —Ge : Fe = 1 : 100 in 2% $(NH_4)_2SO_4$ solution; 3 —Ge : Fe = 1 : 1000, in 2% $(NH_4)_2SO_4$ solution

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Addition of ammonium sulfate to the solution, on the one hand, does not decrease the degree of germanium precipitation at small Ge : Fe ratios; on the other hand, it increases the degree of germanium precipitation at large ratios, probably owing to better coagulation under these conditions.

From the experimental data presented in Fig. 2, it may be concluded that practically complete coprecipitation of germanium with the hydroxide can be achieved at germanium concentrations of 0.01 $\gamma$/ml at a Ge : Fe ratio of 1 : 1000 in 2% $(NH_4)_2SO_4$ solution; consequently, the use of iron hydroxide may serve, in the analysis of highly dilute solutions, as a preliminary concentrator of germanium (by approximately 100-fold). At a Ge : Fe ratio of 1 : 100, probably because of insufficient coagulation of the hydroxide in such dilute solutions, completeness of coprecipitation is achieved only starting from 0.05 $\gamma$/ml.

**Fig. 3.** Dependence of coprecipitation of germanium (1) and iron hydroxide (2) on the pH of the system. Ge conc. 1 $\gamma$/ml; Ge : Fe = 1 : 100, $t = 70^\circ$, 1 —percent precipitation of Ge, 2 —percent precipitation of Fe.

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The dependence of germanium coprecipitation on the pH of the solution is shown in Fig. 3. Completeness of coprecipitation is attained in the interval from pH 6 to 9.5. From Fig. 3 it is seen that complete precipitation of iron in the form of the hydroxide is reached earlier than 100% coprecipitation of germanium on it, whereas at pH $> 9.5$ part of the germanium remains in solution, while the amount of precipitated hydroxide does not change. Thus, the use of coprecipitation with iron hydroxide makes it possible to determine germanium in highly dilute solutions ($\geq 0.01\ \gamma$/ml).

The data presented indicate that what occurs is probably not adsorption of germanic acid by ferric hydroxide, but coprecipitation with it of iron germanates that are insoluble at pH 6–9.5. The following facts support this: the rapidity of complete coprecipitation, the independence of the completeness of coprecipitation from the concentration of a foreign electrolyte, and the attainment of complete coprecipitation at comparatively large Ge : Fe ratios.

## Experimental Part

The working solutions were prepared from chemically pure reagents in distilled water. Germanium was used in the form of a solution of germanium dioxide in water acidified with hydrochloric acid to pH 5. Iron was added in the form of an aqueous solution of ferric ammonium alum. Precipitation of the hydroxide was carried out by adding ammonia dropwise to the prepared solution.

The amount of germanium coprecipitating with ferric hydroxide was determined as follows: after filtration, the hydroxide formed was dissolved on the filter in a small amount of 4 N hydrochloric acid. From an aliquot portion of the resulting solution, germanium was extracted with carbon tetrachloride by the method of Nazarenko et al. ([7]) and colorimetrically determined on a FEKM-57 instrument with light filter No. 4 (transmission maximum 508 m$\mu$). The relative error of the measurements did not exceed $±$5%. For measuring the pH of the solutions, an LP-5 potentiometer was used.

Institute of Fossil Fuels
Academy of Sciences of the USSR

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## References Cited

[1] K. Kraus, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, A/Conf. 15 (p) 1832 USA, June, 1958. [2] M. N. Kurbatov, G. B. Wood, J. D. Kurbatov, J. Phys. Chem., 55, 1170 (1951). [3] V. I. Plotnikov, ZhKh, 3, No. 8, 1761 (1958). [4] V. I. Plotnikov, ZhKh, 5, No. 3, 731 (1960). [5] T. A. Kryukova, S. I. Sinyakova, T. V. Aref' eva, *Polarographic Analysis*, Moscow, 1959. [6] Lourijsen-Teyssedre, Bull. Soc. chim. France, No. 9,

1118 (1955). [7] V. A. Nazarenko, N. V. Lebedeva, R. V. Ravitskaya, Zav. lab., No. 1 (1958).

*Note: Figure translations are in progress. See original paper for figures.*