# Studies on the Separation of Arsenic from Iron by Ion-Exchange Resin

By Yukichi YOSHINO

(Received July 18, 1950)

Although arsenic is an amphoteric element, it has been said that aqueous or dilute hydrochloric acid solution contains arsenic as arseneous or arsenic acid. For the purpose of separating arsenic from iron using cation-exchange resin, the author has made a series of fundamental experiments. It was proved that the trivalent arsenic could be separated quantitatively from ferrous iron, while the separation of quinquevalent arsenic from ferric iron, though theoretically possible, was unpracticable, which seemed perhaps due to the formation of unstable ferric-arseno complex. As an example of practical applications of the method, the content of arsenic as well as iron and sulfur in an arsenopyrite was determined using ion-exchange resin. The results obtained agreed with those of hydrogen sulfide method of separation.

## Experimental

The Resin: Cation-exchanger of commercial phenolsulfonic acid type. Ten grams of 30 meshed resin was conveniently equipped in a 50 cc. burette. The flow method was adopted and the rate of flow was 2—3 cc. per minute throughout the experiments. The exchange capacity of the resin was 1.84 milliequivalents per gram with respect to hydrogen ion.

**Experiment I. The Behavior of Arsenic Solution in Passing through the Column of Resin.**—The resin was previously saturated with 1*N*-sodium chloride or 1*N*-hydrochloric acid and washed thoroughly with distilled water. Various amounts of standard solutions of arseneous and arsenic acid respectively were added to the column of resin. The filtrate and washing water were received in a measuring flask of 150 or 250 cc. of capacity and the flask was filled up to the mark. The aliquot portions of the filtrate were taken and the amount of arsenic was determined iodometrically as follows:

In case of arseneous acid: The sample solution is neutralized with an excess of sodium bicarbonate and then titrated with 0.01*N*-iodine solution using starch as an indicator.

In case of arsenic acid: The method of determination of arsenic acid(1) is just the reverse of the case of arseneous acid, that is, an excess of potassium iodide is added to the strongly acid solution of quinquevalent arsenic and liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. In this case, however, the strong acidity of the sample solution is apt to promote the decomposition of potassium iodide and to give the intermediate pink color at the end point of titration. Therefore, special cautions were taken as follows.

Concentrated hydrochloric acid and distilled water are previously boiled and freed from chlorine and air. To ten cc. of the sample solution, add concentrated hydrochloric acid so as to give 6*N* with respect to acidity. Throughout the procedure, a stream of carbon dioxide is led to the solution. Add 1 g. of solid potassium iodide and keep it on standing for five minutes. The liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution. When the end point is near, the solution is diluted with water to 2*N* of acidity and 5 drops of 0.5 per cent starch solution is added and titration is carried out to the end point indicated by the change of color from blue to pink. Using this procedure, the blank value can be kept within 1 or 2 drops in every titration.

The results of such experiments are given in Table 1.

Table 1

Titrated Values of Arsenic after Passing through the Column of Resin

| | No. of Expts. | *p*H | Amts. of arsenic, mg. As | | Error, % | Remarks |
|---|---|---|---|---|---|---|
| | | | taken | found | | |
| $AsO_3^{---}$ | 1 | 2.4 | 93.64 | 93.57 | −0.07 | Na-R*→ 250 cc.** |
| | 2 | 1.8 | 56.18 | 55.91 | −0.51 | Na-R → 150 cc. |
| | 3 | 1.8 | 56.18 | 56.29 | +0.20 | H-R → 250 cc. |
| $AsO_4^{---}$ | 4 | 1.8 | 102.0 | 101.8 | −0.20 | Na-R → 250 cc. |
| | 5 | <1.0 | 102.0 | 100.8 | −1.18 | Na-R → 250 cc. |
| | 6 | 1.4 | 102.0 | 102.4 | +0.39 | H-R → 250 cc. |

* Na-R and H-R show the types of resin saturated with $Na^+$ or $H^+$ respectively.

** Total volume of effluent.

Table 1 shows that both trivalent and quinquevalent arsenic can be passed out through the bed without any loss. Moreover their behavior seems to be independent of the types of resin (Na-R or H-R). These results may enable us to

---

(1) L. Rosenthaler, *Z. anal. Chem.*, **45**, 596 (1906); **61**, 222 (1922); I. M. Kolthoff, *Z. anal. Chem.*, **60**, 393 (1921); **62**, 137 (1923).

conclude that arsenic of both valency in the dilute hydrochloric acid solution can be treated as anions.

**Experiment II. Separation of Arseneous Acid from Ferrous Iron.**—The mixed solution of various amounts of arseneous acid and ferrous ammonium sulfate solution was flowed into the column of resin and the filtrate and washing water were collected and made up to a definite volume, say 250 cc., aliquot portions of which were taken and arseneous acid was determined by titrating with 0.01*N*-iodine solution. Distilled water of 100 to 150 cc. was proved to be sufficient for washing. The test of iron in the effluent with dimethylglyoxime or ammonium thiocyanate revealed no reaction at all.

These results show that arseneous acid could be quantitatively separated from ferrous ion as is given in Table 2.

Table 2

Separation of Arseneous Acid from Ferrous Iron

| No. of Expts. | $p$H | Iron added, mg. Fe | $AsO_3{}^{---}$ taken, mg. As | $AsO_3{}^{---}$ found, mg. As | Error, % |
|---|---|---|---|---|---|
| 1 | <1 | 94.69 | 18.73 | 18.60 | −0.69 |
| 2 | 1.9 | 59.53 | 37.46 | 37.58 | +0.32 |
| 3 | 0.9 | 59.53 | 37.46 | 37.31 | −0.30 |

**Experiment III. Separation of Arsenic Acid from Ferric Iron.**—A mixture of ferric chloride (94.41 mg. as Fe) and arsenic acid (100 mg. as As) was poured into the column of resin and, to prevent the formation of ferric arsenate precipitate, washed with 0.01*N*-hydrochloric acid solution. But, in this case, the amount of arsenic found in 250 cc. of effluent was about 80 per cent of that originally present. Sncceessive washing with distilled water showed the gradual flowing-out of arsenic remained in the column. Table 3 gives the amounts of arsenic found in the filtrate at each step of washing.

About 2000 cc. of water was necessary for washing until the filtrate ceased to show blue coloration with ammonium molybdate reagent.⁽²⁾

Table 3

Relation between the Volume of Washing Water and the Amount of Arsenic Found in the Filtrate

| cc. of washing water | ~250 | 250 ~500 | 500 ~750 | 750 ~1000 |
|---|---|---|---|---|
| $AsO_4{}^{---}$found, % | 80.33 | 15.84 | 2.25 | 1.31 |

| cc. of washing water | 1000 ~1250 | 1250 ~1500 | 1500 ~2000 | Total As found |
|---|---|---|---|---|
| $AsO_4{}^{---}$found, % | 0.13* | 0.01* | 0.01* | 99.88 |

* determined colorimetricaly with "molybdenum blue" method.

The amount of iron in the filtrate when tested by means of ammonium thiocyanate in the dilute nitric acid medium proved to be trace amount. Between $p$H 0.9 and 2.0, a number of experiments was made varying mixing ratio Fe/As, flow rate and the types of resin (H-R, Na-R or $NH_4$-R)., but none of them proved to be effective for complete separation of arsenic acid from ferric ion. These results seem to suggest that such behavior of arsenic acid might be attributed to some interaction between ferric ion and arsenic acid.

To clarify the state of affairs, following experiment was carried out. Into the column of 5 g. of resin which was previously saturated with ferric ion, a definite amount of arsenic acid (30 mg. as As) was poured. The filtrate and washing water were collected to a definite volume. The arsenic found in the effluent was 71.8 and 81.3 per cent respectively when the volume of the latter reached to 550 cc. and 1050 cc. On the other hand, a little iron (about a few mg. of ferric ion) was found in the filtrate.

In contrast to above mentioned case, when 56.18 mg. (as As) of arseneous acid passed through the column of 5 g. of resin which was previously saturated with ferric ion, the amount of arseneous acid in 150 cc. of filtrate was found to the extent of 98.2 per cent.

We may hereby conclude that a part of arsenic acid might form some complex ion⁽³⁾ with ferric iron in the solution. But owing to the relatively weak linkage, the complex ion is gradually dissociated along with the adsorption of ferric ion by the resin and consequently the flowing-out of arsenic acid takes place.

Even in case of oxidized state of arsenic and iron, it was shown that the separation of arsenic from ferric ion was possible when treated previously with sulfur dioxide. The process is as follows. The solution containing both ferric ion and arsenic acid, after being reduced by leading a stream of sulfur dioxide, is poured into the column of resin. The filtrate and washing water are collected to a definite volume, an aliquot portion of which is oxidized with bromine water. The excess of the latter is expelled by heating.

When cooled, 1 g. of potassium iodide is added and the liberated iodine is titrated with 0.01*N*-sodium thiosulfate solution as mentioned in Experiment I. Table 4 gives the results of such experiments.

Table 4

Separation of Arsenic Acid from Ferric Ion after Reducing with Sulfur Dioxide

| $Fe^{+++}$ added, mg. Fe | Amts. of arsenic acid, mg. As | | Error, mg. As |
|---|---|---|---|
| | taken | found | |
| 94.4 | 102.0 | 102.3 | 0.3 |
| 94.4 | 15.3 | 15.7 | 0.4 |

---

(2) Denigès, *Compt. rend.*, **171**, 802 (1920); Emill Trug and A. H. Meyer, *Ind. Eng. Chem., Anal. Ed.*, **1**, 136 (1929).

(3) L. Dede, *Z. anorg. Chem.*, **125**, 28 (1922).

**Analysis of Arsenopyrite using Ion-Exchange Resin.**—As mentioned above, the separation of arseneous acid from ferrous ion is quantitatively carried out. As an example of practical applications, the analysis of an arsenopyrits(4) was tried using ion-exchange resin.

About 0.7 g. of fine powdered sample is weighed out and transfered into a casserol. After digesting with 5 cc. of conc. nitric acid, 5 cc. of bromine is added in portions, while the solution is warmed on a water-bath. When all the sulfur is converted to sulfate, 5 cc. of conc. hydrochloric acid is added and dried up. This is repeated once more. Then, the residue is treated with a small volume of dilute hydrochloric acid and water. The insoluble matter and silica are filtered off. The filtrate is made up to 100 cc.

Determination of Arsenic: An aliquot portion of the sample solution, say 20 cc., is taken and treated with sulfur dioxide. The same procedure as mentioned in the preceeding paragraph is adopted.

Determination of Iron: The adsorbed iron is eluted out with about 100 cc. of $4N$-hydrochloric acid. The elute is evaporated to a small volume, to which a few drops of 1 per cent potassium permanganate solution are added. The solution is heated and the iron is reduced with stannous chloride and then determined volumetrically with $0.05N$-potassium permanganate solution using Zimmermann-Reinhardt's solution.(5)

Determination of Sulfur: Another portion of the sample solution is poured directly into the column of resin and washed with 150 cc. of water. The sulfate ion in the filtrate is precipitated with 10 per cent barium chloride solution and weighed as barium sulfate.

In order to check the results obtained, the sample was analysed by the usual method as follows:

After separating arsenic from iron with hydrogen sulfide, the element was determined volumetrically by conversion to silver arsenate and titration as in Volhard's method.(6)

From the filtrate of arseneous sulfide, iron was determined volumetrically with $0.05N$-potassium permanganate solution as in the case of resin method. Sulfur was estimated gravimetrically as barium sulfate after separating it from iron with ammonia. Table 5 shows the data of these experiments. The results obtained are in fairly good agreement with each other.

Table 5

Data of Analysis of an Arsenopyrite

| | Resin method, % | Common method, % |
|---|---|---|
| As | 43.89 | 43.64 |
| Fe | 34.13 | 34.30 |
| S | 21.11 | 21.25 |
| Total | 99.13 | 99.19 |

The author wishes to express his appreciation for kind guidance of Prof. Eiiti Minami of the University of Tokyo. He is also indebted to Dr. M. Honda for his advice and to Dr. H. Minato for supplying him with arsenopyrite samples and making mineralogical examination of them.

*Chemical Institute, Faculty of Culture,*
*the University of Tokyo, Tokyo*

---

(4) The sample is from the Iname mine, Aichi Prefecture.

(5) C. Zimmermann, *Ber.*, **14**, 779 (1881); C. Reinhardt, *Z. anal. Chem.*, **36**, 794 (1897).

(6) W. Eschweiler and W. Röhrs, *Z. angew. Chem.*, **36**, 464 (1923).