

Study of Precipitation in Neutron Activation Analysis (II) Coprecipitation of Iron by Cobaltic 1-Nitroso-2-naphtholate

M. RAKOVIČ

*Department of the Medical Physics and Nuclear Medicine, Medical Faculty,
Charles University, Prague*

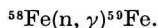
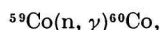
The yield of coprecipitated iron is studied in dependence on the amount of carrier and on the acidity of the solution when precipitating cobalt as its 1-nitroso-2-naphtholate. The possibility to apply the principle of the substoichiometric separation is also taken into account. The efficiency of preliminar hydrolytic separation of iron is verified.

In the recent communication [1] the authors have studied the coprecipitation of sodium by potassium perchlorate. In this communication the coprecipitation of iron by cobaltic 1-nitroso-2-naphtholate was followed. Authors tried to elaborate the simple precipitations for the use in activation analysis of several elements. Regarding 3 following facts, coprecipitation of iron is of main importance when precipitating 1-nitroso-2-naphtholate of cobalt:

1. The appreciable coprecipitation has to be expected due to the chemical similarity of these elements.

2. In many kinds of samples (iron alloys, iron meteorites, minerals, biological materials, etc.) the concentration of iron exceeded very much the concentration of cobalt.

3. Thermal neutrons activate cobalt and iron as follows:



The energies of γ rays of final radionuclides are similar (radiocobalt 1.17 and 1.33 MeV, radioiron 1.29 MeV [2]). Using the long-lived radionuclide ^{60}Co in determination of cobalt, the resolution of these two elements by scintillation γ spectrometer cannot be expected.

Experimental

Solution of cobaltous chloride (containing 6 mg Co per ml) was prepared.

The classical precipitation [3] of cobaltic 1-nitroso-2-naphtholate was used and we changed certain conditions of precipitation. 5 ml of cobaltous salt (corresponding 30 mg of Co) was diluted to the volume of 20 ml, 10 drops of hydrogen peroxide were added and the solution was boiled for a short time. Further 10—70 ml of acetic acid, 0—2.5 mg of iron in the form of iron trichloride as the holdback carrier and 0,1 mCi of radioiron ^{59}Fe of high specific activity was added and then the final volume was adjusted to 200 ml by the addition of water. In precipitation various amounts (2—20 ml) of 2 % 1-nitroso-2-naphthol in 50 % acetic acid were used. After the addition of the precipitating agent the mixture was heated to the boiling point and after sedimentation of the precipitate

it was filtered by a weighed filter crucible. The precipitation was washed by hot 33 % acetic acid, dried at 130 °C and weighed in order to estimate the chemical yield.

The yield of coprecipitated iron was determined on the basis of measurement of counting rates of the precipitate and of the standard by NaI(Tl) scintillation counter.

The reproducible results were reached when using the preparation of 1-nitroso-2-naphthol of the grade of purity p. a. or the preparation of this compound synthesized from 2-naphthol recrystallized from water solution. The compounds of the worse grades of purity were not suitable.

In the experiment studying the preliminary hydrolytic precipitation of iron, radiocobalt ^{60}Co or radioiron ^{59}Fe was added as a radioactive tracer. In the first case the losses of cobalt by coprecipitation were estimated. In the second one the activity of the solution yielded the information concerning the completeness of the separation of iron.

The precipitation by ammonium acetate was chosen in hydrolytic separation. 100 ml of the solution containing 0.1 g of iron, 30 mg of cobalt and the radioactive tracer (radiocobalt or radioiron) was neutralized by sodium hydrogen carbonate to the appearing of the small quantity of precipitate which was subsequently dissolved by adding one drop of hydrochloric acid. The solution of 2 g of ammonium acetate in 50 ml water was added, the mixture was diluted by hot water to the volume of 300 ml, heated to the boiling point, filtered and washed by hot water.

Results

In Fig. 1 one can see the results of the experiment concerning the substoichiometric conditions of precipitation. The direct proportionality between the yield of cobalt and the amount of the precipitating agent is fairly reproducible. The addition of the higher quantity than 14 ml of the solution does not further influence the yield. The curve Y_{Co} shows the similar dependence of the amount of coprecipitated iron. Using the superfluous amount of the agent, about 100 % of cobalt and 30 % of iron originally present in the solution is obtained. But when precipitating by a substoichiometrical amount (corresponding to the 50 % yield of the precipitated cobalt) 50 % of cobalt and 5 % of iron is obtained. Thus the ratio expressing the efficiency of separation is 3 : 1 in the separation by the superfluous amount and 10 : 1 by the substoichiometric amount. The amount of acetic acid was 50 ml in this experiment.

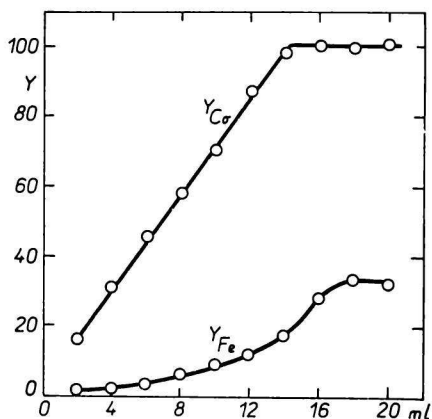


Fig. 1. The yield of coprecipitated iron (Y_{Fe}) and precipitated cobalt (Y_{Co}), in percentage, in dependence on the amount of precipitating agent (in ml).

In following experiments 8 ml of the solution of precipitating agent was used.

Fig. 2 shows the influence of acetic acid on coprecipitation of iron. The curve Y_{Co} shows, that the losses of cobalt due to the partial solubility of the precipitate in acetic acid are not important and the decrease of the amount of coprecipitated iron is of high significance. Thus in further experiments 70 ml of acetic acid were used.

The experiments described above were carried out without the holdback carrier. The influence of the holdback carrier is apparent from the Fig. 3. The decrease of the coprecipitated iron is significant, but it ranges only within 6–7 % whereas the various amounts of acetic acid suppress the yield of coprecipitation to 5–50 %. That is why the scattering of experimental points is higher than in Fig. 2.

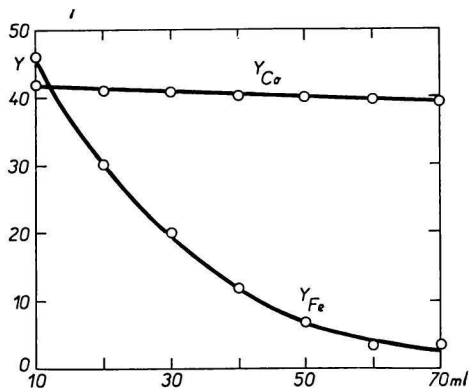


Fig. 2. The yield of coprecipitated iron (Y_{Fe}) and precipitated cobalt (Y_{Co}), in percentage, in dependence on the amount of acetic acid present in the given volume (in ml).

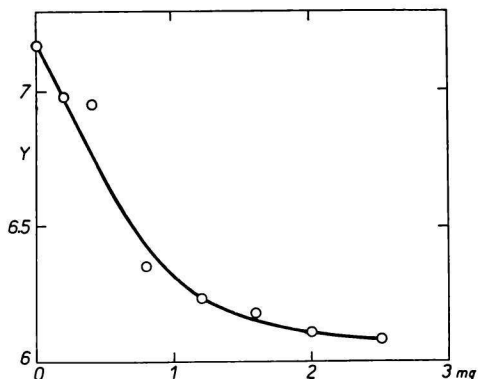


Fig. 3. The yield of coprecipitated iron (Y), in percentage, in dependence on the amount of the holdback-carrier (in mg) present in the given volume.

The experiment concerning the preliminar hydrolytic separation of iron showed, that in the solution remained 0.188 of the originally present iron. The losses of cobalt were negligible. The precipitate contained 0.308 % of the cobalt originally present.

Discussion

The communication shows that on the basis of study of conditions of precipitation it is possible to evaluate quantitatively the yield of coprecipitation. Such an evaluation is very important because it enables to appreciate the practical significance of certain precipitation method. The precipitating methods are often underestimated basing on the existence of coprecipitation of certain element. But this fact alone is of no importance when the rate of coprecipitation is not evaluated quantitatively.

It was shown, that using suitable conditions in precipitation, the ratio of yield $Y_{Fe} : Y_{Co}$ can be diminished to 1 : 10 and using the preliminar hydrolytic separation

of iron, the precipitate is obtained (in 2 separation steps) containing about 0.02 % of the originally present iron (in relation to 100 % yield of cobalt).

This value may be used as the basis in the appraisal of the possibility of determination of cobalt by this method in certain kind of material, where the ratio of concentrations of cobalt and iron is approximately known.

The substoichiometric principle of separation proposed in activation analysis by J. Růžička and J. Starý [4] and N. Suzuki and K. Kudo [5] has been studied mainly for extraction and ion-exchanger separations. In this communication the substoichiometric principle of the separation was used successfully for precipitation. It was possible due to sufficient insolubility of the precipitate.

The communication is one part of the research program studying the possibility to use precipitation in simple separation of various elements from activated biological material. In the case of copper and arsenic (to be published in this magazine) the author found the one step precipitation as sufficient and therefore he pointed out at the advantage of precipitation of these elements. This communication, studying the precipitation of cobalt, showed that at least 2 separation steps are necessary. It is obvious, that it will be advisable to consider also other separation methods. May be, that e. g. the extraction of 1-nitroso-2-naphtholate can yield sufficiently pure preparation after one-step separation.

STUDIUM SRÁŽECÍCH POSTUPŮ PRO ÚČELY NEUTRONOVÉ AKTIVAČNÍ
ANALYSY (II)
KOPRECIPITACE ŽELEZA PŘI SRÁŽENÍ
1-NITROSO-2-NAFTOLÁTU KOBALTITÉHO

M. Rakovič

Katedra lékařské fyziky a nukleární medicíny Fakulty všeobecného lékařství
Karlovy university, Praha

Snižíme-li zvolením vhodných separačních podmínek při srážení 1-nitroso-2-naftolátu kobaltitého poměr výtěžků $Y_{Fe} : Y_{Co}$ na hodnotu asi 1 : 10 a zavedeme-li předběžné hydrolytické oddělení železa, obdržíme ve dvou separačních stupních sraženinu, která obsahuje asi 0,02 % z původně přítomného množství železa (vztaženo na 100 % výtěžek kobaltu).

ИЗУЧЕНИЕ ПРОЦЕССОВ ОСАЖДЕНИЯ ДЛЯ ЦЕЛЕЙ НЕЙТРОННОГО
АКТИВАЦИОННОГО АНАЛИЗА (II)
СОСАЖДЕНИЕ ЖЕЛЕЗА ПРИ ОСАЖДЕНИИ 1-НИТРОЗО-2-НАФТОЛАТА
ТРЕХВАЛЕНТНОГО КОБАЛЬТА

М. Ракович

Кафедра врачебной физики и ядерной медицины Факультета общей медицины
Университета Карла, Прага

Выбором подходящих условий разделения при осаждении 1-нитрозо-2-нафтолата трехвалентного кобальта понизилось отношение выходов $Y_{Fe} : Y_{Co}$ до значения, приблизительно, 1 : 10. Железо было предварительно гидролитически отделено, после

чего получили двухступенным разделением осадок, который содержит, приблизительно, 0,02 % первоначально присутствующего железа (отнесено к 100 %-ному выходу кобальта).

Перевела Т Диллингерова

REFERENCES

1. Rakovič M., Procházková Z., *Chem. zvesti* **20**, 293 (1966).
2. Strominger D., Hollander J. M., Seaborg G. T., *Revs. Modern Phys.* **30**, 585 (1958).
3. Mayr C., Feigl F., *Z. anal. Chem.* **90**, 15 (1932).
4. Růžička J., Starý J., *Talanta* **10**, 287 (1963).
5. Suzuki N., Kudo K., *Anal. Chim. Acta* **32**, 456 (1965).

Received February 10th, 1968

The address of the author:

Doc. Ing. Miloslav Rakovič, CSc., Praha 2, Salmovská 3.