Study of Precipitation in Neutron Activation Analysis (III) Separation of Cuprous Iodide in Determination of Copper in Biological Material

M. RAKOVIČ

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

The author investigated the possibility of copper determination in various animal tissues by activation analysis by the use of the one-step separation in the form of cuprous iodide. This simple separation combined with analysis of decay curves is quite sufficient in practice. This fact is verified by the measured decay and absorption curves and by tracing experiments.

In recent communications [1, 2] the coprecipitation of sodium with potassium perchlorate and the coprecipitation of iron with cobaltic 1-nitroso-2-naphtholate have been studied. In this part of the research programme the author tried to elaborate simple precipitation of copper in order to use it in activation analysis of biological material.

At the present time we often meet the general refusal of precipitation in activation analysis based on the assumption that the precipitation is connected with coprecipitation of radioactive impurities. But such an assumption is of no practical importance if it is not supported by quantitative data. It is necessary to estimate: which elements are coprecipitated, what is the yield of coprecipitation and what will be the influence of coprecipitation on the result of activation analysis. In the estimation of this influence the yield of coprecipitation, the nuclear data important for activation and measurement and the approximate concentrations of the determined and coprecipitated element, have to be considered. Then it may be concluded that, either the coprecipitation seriously influences the result of analysis and the method in question must not be used, or the result of analysis is not changed (within the limits of required accuracy) and the coprecipitation may be neglected in practice.

According to the authors opinion the refusal of precipitation in activation analysis is also caused by many communications (published about the year 1950) where often many useless separation steps had been used. In the investigation of new method of activation analysis, it is necessary to verify the radiochemical purity after the separation steps used. On the other hand in the case that many separation steps were chosen, it is also necessary to give the evidence, that all of them are important. In addition to this fact, in many of these recent communications the individual separation steps are connected with the high yield of coprecipitation, because authors had used classical procedures from gravimetry and had not tried to improve the radiochemical purity by the changes of certain conditions (pH, the concentration of holdback carrier, etc.).

The following nuclear reaction was used in determination of copper:

$$^{63}\mathrm{Cu}(\mathrm{n}, \gamma)^{64}\mathrm{Cu}.$$

The relative isotopic abundance of the target nuclide is 69.1 %, the activation cross

section is 4.5 barn [3]. The half-life of the radionuclide ^{64}Cu is 12.8 hours. It emits the electrons (39 %) with maximal energy of 0.571 MeV and the positrons (60 %) with maximal energy of 0.657 MeV. Only in about 0.5 % of all decays the electron capture may be observed. This electron capture is connected with emmision of one γ quantum [4].

Experimental

The dried biological samples were weighed and wrapped in an aluminium foil. For preparation of standards the dishes from aluminium foil were manufactured. About 0.2 ml of the solution of cupric sulphate was dropped on the dish (0.2 ml of the solution contained 0.5 μg of copper). The solution in the dish was weighed, evaporated and the edges of the dish were bent inside. Together with samples and standards the empty dishes were prepared for activation. Samples, standards and empty dishes were activated in a thermal column (density of the neutron flux 10^{12} n cm^{-2} s^{-1}) during 20 hours. After activation the following chemical procedure was carried out.

A porcelain dish was prepared for every sample. In this dish the solution of cupric sulphate containing 50 mg of copper (as a carrier) was evaporated. The sample was dissolved in the mixture of acids (hydrochloric acid, nitric acid, and perchloric acid 1 : 3 : 1). Several drops of hydrogen peroxide were added during the decomposition. After evaporation 1 ml of hydrochloric acid was added and the new evaporation was performed in order to remove the remains of oxidizing acids. 0.2 g of sodium chloride and 1 g of ammonium phosphate (dibasic) were added (as holdback carriers) to the evaporation. After elution by 50 ml of water the solution was filtered in order to remove the remains which did not undergo the decomposition (fat) and put in the new porcelain dish. 1.5 g of potassium iodide was added. The mixture was evaporated on the water bath to dry. After elution by 100 ml of water the precipitate of cuprous iodide was filtered through a weighed filter crucible, washed by water, dried at 130 °C and weighed.

The precipitates obtained from individual samples were measured by a Geiger—Müller counter at various times to obtain the decay curve. Simultaneously the counting rates of standards and of empty dishes were measured. The activity of empty dishes (equals about 1/6 of the activity of standard) was subtracted as a background.

In order to control the radiochemical composition of the precipitations, the absorption curves of precipitates together with absorption curves of radiocopper ^{64}Cu and radiophosphorus ^{32}P were measured.

In the second experiment the author tried to establish what share of the total activity (after the decay of radiocopper) corresponded to radiophosphorus ^{32}P. The precipitates were decomposed by nitric acid and radiophosphorus was precipitated as ammonium phosphomolybdate. The activity of this precipitate was measured by a Geiger—Müller tube and was compared with the activity of cuprous iodide before its decomposition. In the third experiment the cuprous iodide was precipitated (under the same conditions as in the case of the biological material) in the presence of radiosodium ^{22}Na as a tracer. Various amounts of sodium chloride (as a holdback carrier) were added.

In the last experiment the influence of holdback carrier on coprecipitation of phosphorus was studied by a similar technique as in the previous experiment in the case of sodium. Radiophosphorus ^{32}P was used as a radioactive tracer.

Results

The decay curves can be seen in Fig. 1. Curve *1* is the decay curve of cuprous iodide separated from activated blood. For other tissues similar decay curves were obtained. After the subtraction of the dashed extrapolated line from the curve *1*, the straight line (in semilogarithmic plot) results. It is parallel with the straight line for the standard of copper (curve *2*).

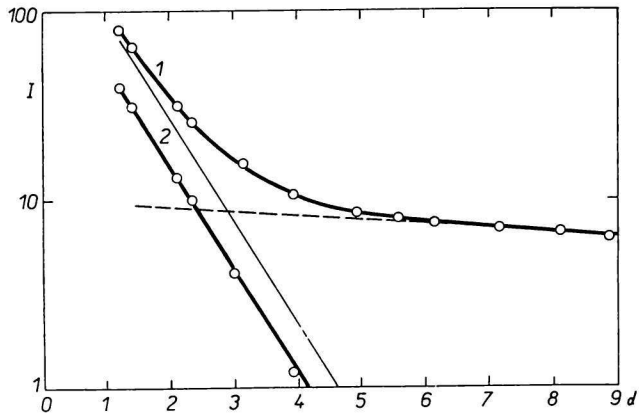

Fig. 1. The counting rate I (c. p. s.) measured by the Geiger—Müller tube in dependence on time (in days d). *1.* the decay curve of the Cu_2I_2 preparation separated from the activated sample of blood; *2.* the decay curve of the copper standard.

In Fig. 2 the absorption curve (obtained also for precipitate from activated blood) is given. The experimental points are demonstrated as crosses. Simultaneously the absorption curves of radiophosphorus ^{32}P (full circles) and radiocopper ^{64}Cu (empty circles) are given. The course of absorption curves of precipitates obtained from other tissues was also between the curves of radiophosphorus and radiocopper.

The experiment studying the activity of phosphorus in cuprous iodide (after the decay of radiocopper) showed, that practically 100 % of the activity measured before the decomposition of the precipitate, entered the precipitate of ammonium phosphomolybdate.

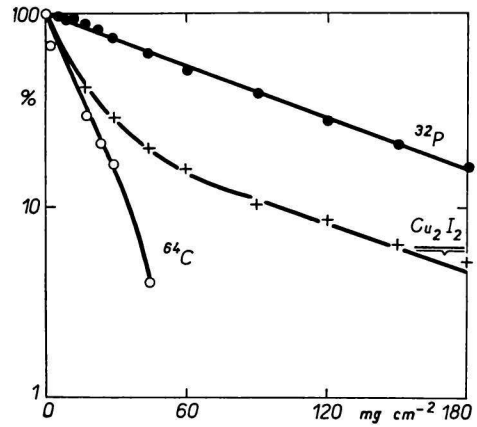

Fig. 2. The counting rate (in percentage from the value measured without filtration) in dependence on the thickness of aluminium foils used as filters, measured by the Geiger—Müller counter. The full circles — experimental points obtained for radiophosphorus ^{32}P, the empty circles — experimental points obtained for radiocopper ^{64}Cu, the crosses — experimental points obtained for Cu_2I_2 preparation separated from activated blood.

The influence of sodium holdback carrier on the coprecipitation of radiosodium is obvious from Fig. 3.

Fig. 4 demonstrates the yield of coprecipitation of phosphorus with cuprous iodide in dependence on the amount of the holdback carrier. Whereas Fig. 3 was plotted in linear coordinates, Fig. 4 was plotted in logarithmic ones.

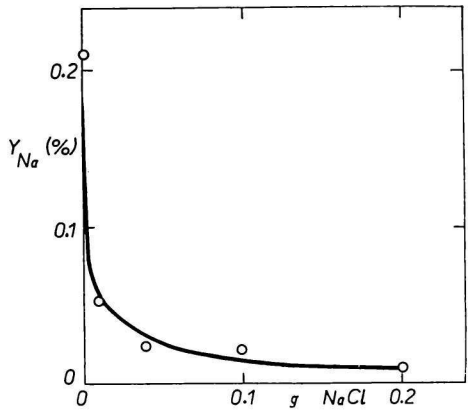

Fig. 3. The influence of the amount of phosphorus holdback carrier (g P) on the yield of coprecipitation of phosphorus (Y_P, in percentage).

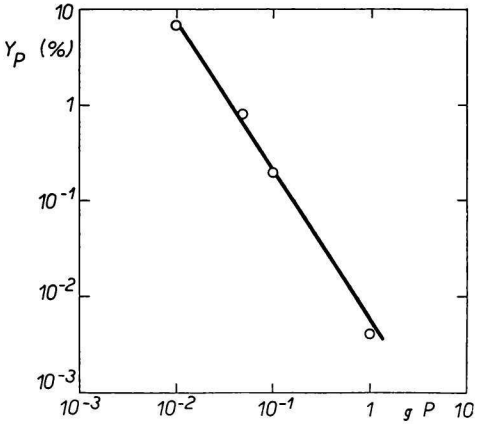

Fig. 4. The influence of the amount of sodium holdback carrier (g NaCl) on the yield of coprecipitation of sodium (Y_{Na}, in percentage).

Experimental decay curves were decomposed. The decomposition is demonstrated in Fig. 1. The activity of radiocopper was extrapolated to the time $t = 0$, adjusted in relation to the chemical yield and the concentrations of copper in individual tissues were calculated by comparison with the activity of standard at the time $t = 0$. Two samples of individual kinds of tissues (weighing 0.1—1 g of dry weight) were analyzed. The results are summarized in Tab. 1.

Table 1

Results of determination of copper in various tissues of white laboratory rats

Tissue	The concentration of copper (μg of Cu per 1 g of dry tissue)	
	I	*II*
blood	6.2	6.3
liver	12.0	9.3
kidney	16.1	16.9
spleen	5.6	5.8

Discussion

The course of the decay curve shows, that the activity of the precipitate isolated from activated biological tissue consists mainly of 2 components. The component showing the shorter half-life was identified as radiocopper ^{64}Cu. The long-lived one corresponds to coprecipitated radiophosphorus ^{32}P. The influence of phosphorus can be expected. Due to the composition of the biological material the following activities are prevailing: radiochlorine (short-lived), radiopotassium and radiosodium (half-lives about 12—15 hours) and radiophosphorus (long-lived, 14.3 days). The course of the absorption curve is also in good agreement with the fact, that the long-lived activity belongs to radiophosphorus. Finally this fact was exactly verified by the experiment in which radiophosphorus was separated from cuprous iodide after the decay of radiocopper.

The decay curve must not be considered as a sufficient criterion of the radiochemical purity when the impurities have not sufficiently different half-life from the half-life of the separated radionuclide.

In our case the possible presence of alkali elements as impurities was considered. The half-lives of radionuclides ^{42}K and ^{24}Na are not sufficiently different from the half-life of radiocopper ^{64}Cu. Thus the trace experiment was provided. Its results are shown in Fig. 3. Considering the yield of coprecipitation, nuclear data of sodium and copper, and average concentration of these 2 elements in biological material, we can evaluate, that the influence of coprecipitated sodium on the results of determination of copper does not exceed 1 relative %. Such an increase of the result is admissible within the limits of the reguired accuracy. As far as potassium is concerned, the trace experiment was not performed, but it is not necessary to expect the higher coprecipitation of potassium than this one of sodium, and the concentration of potassium is lower than this one of sodium in many animal tissues. In addition to these facts the substancial influence of radiopotassium should be obvious from the course of the absorption curve (Fig. 2). In our recent communication [5], we showed, that on the basis of absorption beta curve the β activity of potassium can be distinguished from that of sodium. In the case of copper the conditions are much more advantageous then in the case of sodium, because the β radiation of copper is much softer than the β radiation of sodium.

Figures 4 and 3 show, that the influence of the amount of the holdback carrier on the purity of the precipitate is very important. Thus the choice of the random amount of the holdback carrier (as one can read in many communications) is incorrect.

The procedure described is very simple. The author proved, that the one-step separation by precipitation is sufficient. The evaporation of the mixture after the addition of the precipitating agent is the mostly time consuming procedure. But this fact cannot be considered as the serious disadvantage of the method, because several samples are usually analyzed simultaneously, and the half-life of radiocopper is not extremely short.

STUDIUM SRÁŽECÍCH POSTUPŮ PRO ÚČELY NEUTRONOVÉ AKTIVAČNÍ ANALYSY (III)
SEPARACE JODIDU MĚĎNÉHO PŘI STANOVENÍ MĚDI V BIOLOGICKÉM MATERIÁLU

M. Rakovič

Katedra lékařské fysiky a nukleární mediciny Fakulty všeobecného lékařství Karlovy university, Praha

V práci je prokázáno, že jednostupňová srážecí separace mědi ve formě jodidu měďného plně postačí při stanovování mědi v živočišných tkáních neutronovou aktivační analysou. Po aktivaci a po provedení této separace se separovaná sraženina měří pomocí GM trubice v různých časových intervalech. Získá se tak rozpadová křivka, skládající se ze dvou komponent. Po odečtení dlouhodobější komponenty, která přísluší radionuklidu fosforu ^{32}P, obdrží se rozpadová křivka, která se plně shoduje svým průběhem s rozpadovou křivkou standardu mědi. Její extrapolací k nule se zjistí počáteční aktivita radionuklidu mědi ve vzorku a po přepočtu, vzhledem k chemickému výtěžku, se srovnáním s počáteční aktivitou standardu zjistí obsah mědi ve vzorku. Pro zhotovení standardu autor doporučuje odpařování roztoku síranu měďnatého na miskách zhotovených z hliníkové fólie. Standardy se aktivují spolu s prázdnými miskami a po aktivaci se aktivita prázdných misek místo pozadí odečítá od aktivity misek s odparky.

Identifikace radionuklidu fosforu, jako koprecipitované složky byla prokázána nejen z průběhu rozpadové a absorpční křivky, ale též pokusem o separaci fosforu po vymření aktivity radionuklidu mědi a po rozkladu sraženiny jodidu měďného. Fosfor byl v tomto případě separován jako molybdátofosforečnan amonný.

Pomocí radioaktivních indikátorů ^{32}P a ^{22}Na byl sledován vliv množství zadržujícího nosiče na výtěžek koprecipitace fosforu a sodíku. Tento vliv je značný, a je proto důležitá volba správného množství zadržujícího nosiče.

ИЗУЧЕНИЕ ПРОЦЕССОВ ОСАЖДЕНИЯ ДЛЯ ЦЕЛЕЙ НЕЙТРОННОГО АКТИВАЦИОННОГО АНАЛИЗА (III)
ВЫДЕЛЕНИЕ ИОДИДА ОДНОВАЛЕНТНОЙ МЕДИ РПИ ОПРЕДЕЛЕНИИ МЕДИ В БИОЛОГИЧЕСКОМ МАТЕРИАЛЕ

М. Ракович

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

В работе указывается, что одностепенное осадительное выделение меди в виде иодида одновалентной меди совершенно достаточно при определении меди в тканях животных нейтронным активационным анализом. После активирования и после такого отделения активность отделенного осадка измерялась с помощью счетчика Гейгера—Мюллера в различных интервалах времени. Так была получена кривая распада, состоящая из двух компонентов. После вычитания долгоживущего компонента, который относится к радиоизотопу фосфора ^{32}P, получится кривая распада, которая полностью совпадает с кривой распада стандарта меди. При экстраполировании этой кривой до нуля находится первоначальная активность радиоизотопа меди в образце и после пересчета,

с учетом химического выхода по сравнению с первоначальной активностью стандарта, находится количество меди в образце. Для приготовления стандарта автор рекомендует выпаривать раствор сульфата меди в мисках, сделанных из алюминиевой фольги. Стандарт активируется вместе с пустыми мисками и после активирования активность пустых мисок вместо фона вычитается из активности мисок с осадком.

Присутствие радиоизотопа фосфора как осажденного компонента было доказано не только из хода кривой распада и кривой поглощения, но также и выделением фосфора после исчезновения активности радиоизотопа меди и после разложения осадка иодида одновалентной меди. Фосфор был выделен в виде молибдатофосфата аммония.

Перевела Т. Диллингерова

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The address of the author:
Doc. Ing. Miloslav Rakovič, CSc., Praha 2, Salmovská 3.