Study of Precipitation in Neutron Activation Analysis. IV. Separation of Arsenic(V) Sulphide or Silver Arsenate in Determination of Arsenic in Biological Material

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In the present work the possibility of determining arsenic in animal tissues by simple precipitation separation of arsenic(V) sulphide or silver arsenate is studied. The decay curves obtained from measurements carried out by a scintillation counter indicate radiochemical purity, which, for practical purposes, is quite satisfactory. The precipitation of silver arsenate is less suitable since a greater part of the radiophosphorus ^{32}P occurs in the solid phase.

In our last communication [1] we showed, using the example of the cuprous iodide, that the precipitation separation may be very well used in the neutron activation analysis. In the present work we tried to prove the same for arsenic.

The only natural radionuclide of arsenic, ^{75}As, [2] is activated with thermal neutrons by the reaction

$$^{75}As(n, \gamma)^{76}As.$$

The cross section of the reaction is 5.6 barns. The generated radionuclide ^{76}As is a β- and γ-emitter [3] with half-life 26.4 hours. The energetic maxima of the β-radiation are: 2.95 MeV (51%), 2.41 MeV (31%), 1.76 MeV (16%) and 0.36 MeV (3%). The first maximum, 2.95 MeV, represents the pure β-decay. The other β--particle emissions (about 50% of all decays) take place together with γ-rays emission. The γ-decay from higher energetic levels occurs in cascades and five energies [3] are discerned here. The most frequent is the energy 0.561 MeV.

Experimental

Samples of dried animal tissues, ranging from 0.01 to 0.1 g, were weighed and wrapped in aluminium foils. Dishes of aluminium foils were prepared for standard specimens. About 0.2 ml of ammonium arsenate solution was put dropwise into the dish which was weighed before and after filling with the solution. The solution was evaporated and the dish edges were bent inside. In 0.2 ml of the solution, 1 μg arsenic was contained. Together with samples and standards, the empty dishes were also prepared for activation. The whole was irradiated in a thermal column of a reactor at a flux of 10^{12} neutrons $cm^{-2}\ s^{-1}$ for 20 hours. After activation, the samples were chemically processed as follows.

First, for each sample a porcelain dish was prepared from which the solution of ammonium arsenate containing 100 mg of arsenic as carrier, was evaporated. The samples were decomposed by a mixture of acids (hydrochloric, nitric and perchloric acid

in the ratio 1 : 3 : 1) containing a few drops of hydrogen peroxide, and subsequently they were allowed to evaporate.

When trying to achieve the precipitation of silver arsenate, the residue was extracted with 50 ml water and filtered into a beaker. After neutralization with methyl red the precipitation with a slight excess of 0.1 N silver nitrate was performed. The mixture with the precipitate was boiled, filtered after cooling down through a weighed filtration crucible, the precipitate was washed with distilled water, dried at 105°C and weighed.

Attempting to achieve the precipitation of arsenic(V) sulphide, the mineralization residue was extracted with 50 ml water, filtered into an Erlenmeyer flask (250 ml), 100 ml of cooled concentrated hydrochloric acid was added while the whole was being cooled so that the temperature should not exceed 0°C. After subsequent precipitation with gaseous hydrogen sulphide, the reaction mixture was stoppered and allowed to rest. After two hours it was filtrated through a filtration crucible, washed with cold water and the precipitate was weighed.

The decay curves of the precipitated arsenic(V) sulphide and silver arsenate were plotted basing on a scintillation detector measurement over a range of time intervals. Standard, samples and the activated dishes were submitted to these measurements, too. The activities of the empty dishes were substracted from those of dishes containing standards as background.

The crystal diameter was 38 mm. Copper filters in total thickness of 2640 mg cm^{-2} were placed between the crystal and the sample so as to eliminate the β-radiation. The impulses were recorded by the Soviet apparatus Volna.

With regard to a relatively very high content of the radionuclide ^{24}Na in the activated biological material, a tracer test was performed in order to check the coprecipitation of sodium with arsenic(V) sulphide. In this test, 0.1 g of non-activated blood was taken, the radionuclide ^{22}Na, in the form of sodium chloride, was added as radioactive tracer and afterwards the same procedure as in the case of the activated sample was carried out. The isolated precipitate was measured with the scintillation counter and the yield of the coprecipitated sodium was evaluated by comparison with the standard.

Results and Discussion

In Fig. 1 we can see the decay curves obtained by measuring the counting rate on the precipitates with a scintillation counter. On the perpendicular axis, the impulse frequency (imp s^{-1}), on the horizontal coordinate time in days are plotted.

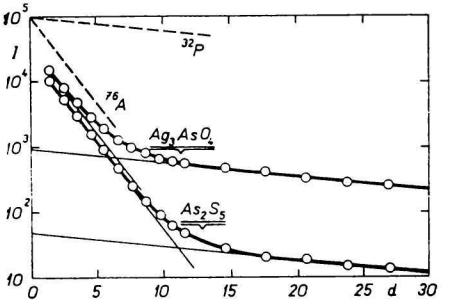

Fig. 1. Dependence of counting rate I (imp s^{-1}), measured by a scintillation counter, on time (in days d) for silver arsenate and arsenic(V) sulphide precipitated from activated samples (dry weight about 0.1 g), of rat blood. The circles designate the experimental points, the heavy and the light lines designate the experimental curves and the analysis of these curves, respectively. The dashed line indicates the theoretical course of the decay of the radionuclides ^{32}P and ^{76}As.

The experimental points are marked by circles. The analysis of both experimental curves is also shown in Fig. 1; the dashed straight line designates the theoretical decay curve for the decay of the radionuclides ^{32}P and ^{76}As.

The curves for blood specimen are shown in Fig. 1 as representative examples. Similar curves were obtained for samples of rat livers, spleen and kidneys.

The attempt to find the amount of coprecipitated sodium showed that in the precipitate, about 1.4×10^{-4} % of the sodium originally present in the sample, enters the precipitate.

The decay curve obtained for the precipitate of silver arsenate indicates that the abundance of the long-lived portion is remarkable. The half-life of this component conforms to that of the radionuclide ^{32}P. Substracting this component we obtain a straight line in the semilogarithmic coordinates, which is indicative of the decay of the radionuclide ^{76}As. Hence it follows that chemical separation of silver arsenate may be used only in combination with the analysis of the decay curve. The separation of the arsenic(V) sulphide is more suitable.

From the decay curve of the arsenic(V) sulphide it can be seen that only a very small portion (far less than 1%) of the long-lived component is present, which is again the radionuclide ^{32}P. The first part of the decay curve practically agrees with the decay of ^{76}As.

The course of the decay curve proves that the influence of the long-lived activity may be considered as negligible. As to the influence of the short-lived activity, we investigated the coprecipitation of the radionuclide ^{24}Na. From the yield, from the average concentration of sodium and arsenic in the animal tissues [4] and from the nuclear activation data for these elements [2] we calculated that the activity of the coprecipitate can make about 1.43% of the activity of the precipitate in the moment when the precipitation is finished. After 5 days, this being about the time corresponding to the mean of the first linear part of the decay curve, this ratio changes more than by ten times in favour of arsenic.

When precipitating from a strongly acid medium, the precipitation of copper sulphide can be assumed too. Anyway, we need not be afraid of the influence of copper on the determination results. We were able to measure the activity of the precipitated cuprous iodide in the course of our previous work [1] under conditions identical with those under which the measurement for arsenic was carried out. In this case, the copper yield approached 100%. The activity of copper ^{64}Cu made 7.3 c.p.s., whereas the activity of arsenic isolated from about the same amount of activated blood was $10^3 - 10^4$ c.p.s. As we see, the activity of the radionuclide ^{64}Cu is negligible. This is surely due to the decay scheme of this radionuclide [3].

From the above said it follows that the one-step precipitation separation of arsenic(V) sulphide is quite satisfactory for determination of arsenic in biological material. The arsenic content determined in the blood of white laboratory rats made 3.45 μg per 1 g of dry weight.

References

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