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OPTIMIZATION OF WET DIGESTION PROCEDURE OF BLOOD AND TISSUE FOR SELENIUM DETERMINATION BY MEANS OF ^{75}Se TRACER

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OPTIMIZATION OF WET DIGESTION PROCEDURE OF BLOOD AND TISSUE FOR SELENIUM DETERMINATION BY MEANS OF ^{75}Se TRACER

ZASTOSOWANIE WSKAZNIKA ^{75}Se W CELU OPRACOWANIA OPTYMALNEGO SPOSOBU MINERALIZACJI KRWI I TKANEK DLA OZNACZANIA ZAWARTOŚCI SELENU

ПРИМЕНЕНИЕ ИНДИКАТОРА ИЗОТОПА ^{75}Se С ЦЕЛЮ РАЗРАБОТАНИЯ ОПТЫМАЛЬНОГО СПОСОБА МИНЕРАЛИЗАЦИИ ТКАНИ И КРОВИ ДЛЯ ОПРЕДЕЛЕНИЯ КОНЦЕНТРАЦИИ СЕЛЕНА

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Summary

Selenium-75 tracer has been used for optimization of analytical procedure of selenium determination in blood and tissue. Wet digestion procedure and reduction of selenium to its elemental form with tellurium as coprecipitant have been tested. Recovery of selenium obtained with the use of optimized analytical procedure amounts up 95 % and precision is equal to 4.2 %.

Streszczenie

Zastosowano wskaźnik radioizotopowy ^{75}Se w celu opracowania optymalnego sposobu mineralizacji i wzbogacenia w próbkach krwi i tkanek do oznaczenia zawartości selenu. Badano dwa sposoby mineralizacji próbek biologicznych i redukcji selenu IV do postaci elementarnej. Dla metody optymalnej otrzymano odzysk ^{75}Se równy 95 % oraz precyzję (1s) wynoszącą 4,2 %.

Резюме

Применено радиоактивный индикатор изотопа ^{75}Se с целю разработания оптыиального спосрба минерализации и обогощения образцов ткани и крови для определения концентрации селена. Исследовано два метода минерализации биологических образцов и редукции селена IV к елементарному виду.Для оптымального метода получено 97% найденную величину и точность /I с/ 4.2%.

INTRODUCTION

Growing concern over selenium as essential nutrient has resulted in need for analytical method of determination of this element in animal and human blood and tissue as well as in environmental material. The spectrofluorometric, spectrophotometric and X-ray fluorescence methods of analysis offer an easy and sensitive way of determining selenium. Unfortunately direct analysis of biological material /even lyophylized/ is not feasible for part per billion concentrations. Therefore a preliminary chemical enrichment has to be undertaken before attempting analysis. Wet digestion has been the most generally used for destroying organic matter prior to determining Se by any of above mentioned methods. However high volatility of selenium compounds can cause serious losses via volatilization at wet digestion and other stages of analytical procedure.

Strausz et al. [1] proposed using a mixture of nitric and sulphuric acid while Cummins et al. [2] a mixture of perchloric and sulphuric acid with sodium molybdenate as catalyst, followed by reduction selenium to its elemental form. Both procedures of wet digestion have been tested by us with the use of radiotracer ^{75}Se and the optimized procedure has been chosen for selenium preconcentration.

EXPERIMENTAL

First procedure

Chemical reagents - $Na_2{}^{75}SeO_3$ solution of activity about 5 uCi/ml

digestion mixture: HNO_3 /conc./ + H_2SO_4 /conc./ 3:1

copper sulphate solution /15 mgCu/ml/

0.0250 g of tellurium oxide /TeO_2/ dissolved in HCl /conc./ and adjusted to 200 ml /0.1 mg Te/ml/

reducing agent: 120 ml of H_2O, 20 ml H_2SO_4 /conc./ 4 g NaCl, 8 g hydroxylamine hydrochloride, 8 g $SnCl_2$ /dihydrate/ - the volume adjusted with water to 200 ml.

All chemical reagents were "pro analysi".

Two grams of lyophylized blood were put into a screw cap polyethylene bottle and spiked with a 1 ml of $Na_2{}^{75}SeO_3$ solution. 10 ml of digestion mixture were added and allowed to stand overnight, then kept on a water bath at 60°C for a period of 4 hours. After diluting with water to 50 ml, the solution was simmered to remove the nitrogen oxides. After cooling two samples, each of 1 ml volume, were taken out for activity measurement. A single channel spectrometer with a well NaI/Tl scintillation counter was used. After activity measurement had been completed the samples have been poured back into main solution.

Then, 15 mg of copper and 400 ug of tellurium as coprecipitant, and 15 ml of reducing agent were added. The solution was allowed to stand for about 30 min. and a precipitate formed was filtered by a membrane filter 0.60 um pore. Then the count rates of solution and precipitate on the filter were measured separately. Losses of selenium due to digestion were small - and did not exceed 5 per cent. However, the mean recovery of selenium in precipitate, obtained from the results of ten blood samples, was only 59 %. The spread of results ranged from 47 to 65 %. It is probable that such a low temperature wet digestion does not result in complete destroying of organic matter and therefore the recovery of selenium is so poor.

Second analytical procedure

Digestion mixture - 10 g of sodium molybdenate is dissolved in 150 ml of bidistilled water then 150 ml of H_2SO_4 /conc./ is added. After cooling 200 ml of 70 % perchloric acid is added.

Two grams of lyophylized or 10 g of fresh blood were put into a round bottom flask /150 ml volume/ together with 40 ml of digestion mixture and 1 ml of $Na_2{}^{75}SeO_3$ solution. Then the mixture was heated at the open flame during about 1 h. The temperature was controlled and did not exceed 160°C. The solution obtained was colourless and clear. After cooling

and diluting with water to fourfold volume, two 1 ml samples were taken for activity measurement. Practically no losses of selenium tracer have been observed. The solution was allowed to stand overnight and then the reduction of selenium was carried out in the same way as previously but with the use of 40 ml of reducing agent instead of 15 ml. Then the activities of precipitate and filtrate were measured. The recovery of selenium was better than before but it amounted only about 80%.

In further experiment one analytical step has been added. The solution after digestion and diluting has been boiled in order to remove chlorine. This improved the results. Nearly complete recovery was obtained when the solution after digestion has been diluted 6 times instead of 4 times only. When the solution is too acid the precipitation of tellurium coprecipitant is not complete because it is partially dissolved in sulphuric acid [3].

RESULTS AND DISCUSSION

The results obtained with the use of second optimized analytical procedure are listed in Table 1.

TABLE 1. The recovery of selenium-75 at optimized analytical procedure

Sample	Wet digestion recovery [%]	Selenium found in precipitate [%]
1	99.20	96.6
2	100.0	100.0
3	99.3	94.8
4	99.4	99.5
5	98.4	97.9
6	100.0	88.3
7	98.0	90.6
8	98.5	90.7
9	98.1	92.9
	mean value - 99.0 %	mean value - 94.6 %
	stand.dev. s - 0.77%	stand.dev. s - 4.2 %

It is seen that the use of a mixture of perchloric and sulphuric acid with sodium molybdenate for wet digestion or organic matter followed by reduction of selenium to its elemental form by a mixture of stannous chloride and hydroxalamine hydrochloride result in very good recovery of selenium.

This procedure followed by energy dispersive X-ray fluorescence method has been used by us for the determination of selenium in human blood, animal tissue /kidney and liver/ some kinds of fodder and raw sodium chloride [4]. It is worthwhile to mention that above described analytical procedure is especially suitable when X-ray fluorescence method is used, because the precipitate of selenium obtained on a surface of membrane filter is not subjected to any additional chemical treatment but can be directly measured by X-ray system.

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