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LOW LEVEL DETERMINATION OF MANGANESE IN BIOLOGICAL REFERENCE MATERIALS BY NEUTRON ACTIVATION ANALYSIS

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A simple method was developed for the low level determination of manganese in biological materials by neutron activation analysis with radiochemical separation based on manganese dioxide precipitation. Precision and accuracy of the method were tested by analyses of IAEA reference materials Animal Muscle H-4, Milk Powder A-11, Freeze Dried Animal Blood A-13, Horse Kidney H-8, and Mixed Human Diet H-9. Interferences from iron and cobalt were also evaluated.

INTRODUCTION

Manganese belongs to elements that are essential in trace concentrations for all living organisms, especially for mammals. It is bound in a large number of metalloproteins and metalloenzymes and acts as a catalyst of many processes, mostly redox ones, and as an enzyme activator[1,2]. Manganese levels in some body tissues and/or fluids are very low and accurate determination of the element is associated with severe analytical

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difficulties. Human plasma or serum manganese concentration may give a true picture of the problem. Although these fluids belong to the most thoroughly analyzed ones and a rather small range of mean values, around 0.5-0.6 $ng.ml^{-1}$, is expected in healthy individuals due to the homeostatic control, a great variation in the mean values, up to 34 $ng.ml^{-1}$, are still being published[3]. The main reason for the controversially high results should be seen in contamination problems during the sampling and analytical process.

Quality control of the analytical process can be pursued with the aid of suitable reference materials. However, biological reference materials with reliably specified manganese concentrations in the sub-$\mu g.g^{-1}$ region are available only at very limited choice[4]. Also certification of manganese concentrations in this region in the International Atomic Energy Agency /IAEA/ reference materials Animal Muscle H-4 and Milk Powder A-11 from interlaboratory comparisons yielded only unsatisfactory results and revealed again analytical and evaluation problems involved[5]. Follow-up analyses were carried out by several authors[5,6] and a program has been promoted by the IAEA to elucidate concentration of manganese and other trace elements of interest in these reference materials[7].

Neutron activation analysis plays a very important role for accurate and precise determination of very low element concentrations as a method less susceptible to laboratory-dependent systematic errors than other trace-element techniques[5,8]. Therefore, a simple radiochemical neutron activation method was developed for low level manganese determination in biological materials. In this work, the method was used for the manganese determination in the above mentioned and several other IAEA biological reference materials.

EXPERIMENTAL

Irradiation of samples and standards

Samples of reference materials amounting to 150-200 mg were sealed into polyethylene /PE/ vials pre-cleaned with high purity nitric acid /1+1/ and deionized water prior to irradiation. The manganese standard for irradiation was prepared by dissolution of 99.9% metal /Koch Light, Ltd./ in nitric acid and by pipetting aliquots onto a small piece of filter paper. After drying, the filter paper containing 10 μg of manganese was sealed into the PE vials. The samples and standards were irradiated along with flux monitors /10 μg of gold/ for 1-3 min with the aid of a pneumatic facility in a core of a VVR-S reactor of the Nuclear Research Institute /NRI/, Řež in which the thermal neutron flux density amounted to 3×10^{13} $n.cm^{-2}.s^{-1}$.

Radiochemical separation

Procedure A. The samples and standards were removed from PE irradiation vials and mineralized in a mixture of 5 ml 65% HNO_3 + 2 ml 70% $HClO_4$ by heating for 20 min at 230 °C in the presence of 1 mg Mn^{2+} inactive carrier Then, the remaining solution /about 1 ml/ was diluted with 100 ml of hot water to about 0.1M $HClO_4$ and MnO_2 was precipitated by addition of 3 ml of a 5% $/NH_4/_2S_2O_8$ solution and boiling it for 2-3 min. The precipitate was filtered off with the aid of a membrane ultrafilter Synpor No. 3 with a pore diameter of 1.5 μm /Barvy a laky, Czechoslovakia/ and washed with dilute nitric acid /1+10/.

Procedure B. In contrast to procedure A, the solution of dilute perchloric acid obtained after decomposition

of the samples was neutralized with NH_4OH to pH 6-9 before precipitation of MnO_2.

Both procedures provided about the same manganese yield, typically in the range 90-95%, as was ascertained by reactivation after a measurement of each sample. Procedure B was usually employed because it yielded a precipitate more suitable for filtration.

The manganese standard for counting contained 0.1 μg of radio-manganese and was prepared from the irradiated standard by 100-times dilution of the solution obtained after mineralization in order to be able to neglect the manganese content of the filter paper.

The whole radiochemical procedure can be completed within 25-30 min.

Nuclear data and counting

The radioisotope ^{56}Mn employed for manganese determination /activation cross section for thermal neutrons, σ_{th}, 1330±20 fm^2; half-life, T = 2.58 h; the most intensive γ-line 846.9 keV/[9] originates not only from the analytical reaction with thermal neutrons $^{55}Mn/n,\gamma/^{56}Mn$ but also from two interfering reactions with fast neutrons $^{56}Fe/n,p/^{56}Mn$ and $^{59}Co/n,\alpha/^{56}Mn$ /activation cross sections for fast neutrons, σ_{fast}, 0.107±0.008 fm^2 and 0.0156±0.0009 fm^2, respectively/[9]. Interfering formation of ^{56}Mn was determined by irradiation of about 100 mg of high purity metals /99.9% Fe, Koch Light, Ltd., 99.9% Co, Johnson and Matthew/ in a cadmium box /wall thickness 0.75 mm/. The irradiation yielded an apparent manganese content 39.1 μg Mn/g Fe for the former and 5.9 μg Mn/g Co for the latter interfering reaction.

Measurements of γ-ray spectra were performed with a coaxial Ge/Li/ detector /11.8% relative efficiency, re-

solution FWHM 2.7 keV for the 1332.5 keV γ-rays of ^{60}Co, NRI, Řež/ coupled to a Plurimat 20 multichannel analyzer with a Multi-8 built-in computer /Intertechnique, France/. The samples and standards were measured on the cap of the detector for 15-30 min.

RESULTS AND DISCUSSION

The radiochemical method developed for low level manganese determination represents a simple, quick and robust procedure. The chemical yield of manganese is very high, above 90%, and stable in the pH range 1-9. The MnO_2 precipitate contains almost no radioactive admixtures /only quite negligible traces of ^{24}Na were observed/ and forms a thin and homogeneous layer on the membrane ultrafilter suitable for reproducible counting close to the detector. Thus, favourable detection limit, based on the 3σ criterion, was achieved amounting to 10 pg of manganese for 3 min of irradiation, 30 min decay, and 30 min counting times /in absence of iron and cobalt/.

Results of the manganese determination in IAEA reference materials Animal Muscle H-4 /Ref. 10/, Milk Powder A-11 /Ref. 11/, Freeze Dried Animal Blood[12], Horse Kidney H-8 /Ref. 13/, and Mixed Human Diet H-9 /Ref. 14/ are summarized in Table 1. Besides the corrected values for the interfering contribution of iron and cobalt, the uncorrected ones are also given in order to show an effect on the accuracy of the results. It can be seen from Table 1 that the interfering influence of cobalt can be neglected for all samples analyzed owing to very low abundances of the element. The same is almost valid for the iron interference excepted for the

TABLE 1

Manganese content in IAEA biological reference materials

Reference material	Manganese content, $\mu g.g^{-1}$ /dry weight/					
	This work				IAEA value	
	Mean[a] uncorr.for Fe contribution	Mean[b] uncorr.for Co contribution	Mean ± S.D. /N/[c]	S.D. /%/[r]	Mean[d] / CL	New[7] Mean ± S.D. /N/[c]
Animal Muscle H-4[10]	0.474	0.472	0.472±0.0282 /7/	6.0	0.52 / 0.48-0.55	0.466±0.042 /3/
Milk Powder A-11[11]	0.258	0.258	0.258±0.0138 /7/	5.3	0.377 / 0.296-0.457	0.257±0.006 /3/
Freeze Dried Animal Blood A-13[12]	0.125	0.031	0.031±0.0026 /7/	8.4	-	-
Horse Kidney H-8[13]	5.92	5.91	5.91 ± 0.203 /5/	3.4	5.72 / 5.46-5.99	-
Mixed Human Diet H-9[14]	12.1	12.1	12.1 ± 0.24 /5/	2.0	11.84 / 11.44-12.25	-

a - Interference contribution due to the mean content of Fe /$\mu g.g^{-1}$/: 49 in H-4, 3.6 in A-11, 2400 in A-13, 262.3 in H-8, 33.9 in H-9.

b - Interference contribution due to the mean content of Co /$ng.g^{-1}$/: 8 in H-4, 5 in A-11, ? in A-13, 120.9 in H-8, 45.5 in H-9.

c - Mean ± standard deviation /number of replicates/.

d - Mean/confidence limit for the mean of population for probability level 0.95.

case of the manganese determination in Freeze Dried Animal Blood A-13 where the uncorrected value exceeds the true one by a factor of 4. Therefore, for samples with an unfavourable Mn/Fe ratio, such as blood, the interfering contribution of iron should be carefully evaluated especially when irradiation is carried out in a not very well thermalized neutron flux, such as in the core of the VVR-S reactor.

The precision of the analyses, expressed as a relative standard deviation in per cent, amounts to 2-3% for the manganese contents in the $\mu g.g^{-1}$ range /which can, of course, be determined by instrumental neutron activation analysis, too/ and decreases consistently with counting statistics for lower manganese contents. However, it can be pointed out that our results and also variation of the new IAEA value[7] indicate that manganese distribution in Animal Muscle H-4 seems to be a little less homogeneous than in other reference materials.

The accuracy of the method can be inferred from a comparison of our results with the IAEA certified and new values[7,10-14]. For the reference materials Horse Kidney H-8 and Mixed Human Diet H-9, about 2-3% higher values were obtained compared to the IAEA provisionally certified mean values[13,14]. Even a better agreement was found with the new IAEA results[7] for Animal Muscle H-4 and Milk Powder A-11. Our results for the latter reference material also agree very well with a value of about 0.28 $\mu g.g^{-1}$ of manganese suggested by De Goeij et al.[5] after scrutinizing the originally certified value[11] and also with a value of 0.25 $\mu g.g^{-1}$ of manganese reported by Iyengar et al.[6]. Thus, independently of the IAEA and other revision analyses, results of this work indicate a need for

revision of the originally certified manganese values in Animal Muscle H-4 /Ref. 10/ and Milk Powder A-11 /Ref. 11/. No comparison can be done for the manganese concentration determined in Freeze Dried Animal Blood A-13 because no IAEA value is available[12], until now. However, a fairly good agreement was found with the value of 0.0353 ± 0.0031 $\mu g.g^{-1}$ of manganese reported by Versieck[15]

It is felt that certification of the manganese content in Freeze Dried Animal Blood A-13 would be of considerable importance since no other blood reference materials are available with a certified manganese value excepted for NBS RM 8419 Bovine Serum with a recommended concentration of 2.6 $ng.\ell^{-1}$ of manganese[4].

*

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