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STUDY ON PALLADIUM DETERMINATION BY NEUTRON ACTIVATION ANALYSIS

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ABSTRACT

This study presents results of Pd determinations in neutron activation analysis of spiked biological tissues and CCQM-P63 automotive catalyst. Pd spiked biological tissues of bovine muscle and liver were prepared using a blender with titanium blades and Pd solutions. These materials obtained in a past form were freeze-dried and homogenized before the analysis. Thermal and epithermal neutron activation analyses were applied in these determinations. Separations of Pd from interfering elements were also carried out using solvent extraction and solid-phase extraction techniques, before the irradiations with epithermal neutrons. The irradiations were carried out at the IEA-R1 nuclear research reactor under thermal neutron flux of about 4 x 10^{12} n cm^{-2} s^{-1} during 4 and 16 h for thermal and epithermal irradiations, respectively. The gamma activities of ^{109}Pd of the irradiated samples and Pd standard were measured using an HGe detector coupled to a gamma ray spectrometer. Results obtained in these analyses indicated that the epithermal irradiation presented higher sensitivity, due to the reduction of interferences. The pre-separation procedure of solid-phase extraction applied also yielded low detection limit. Comparisons made between the Pd results obtained using different procedures of neutron activation analysis indicated a good agreement. The analyses carried out in replicates also indicated a good precision with relative standard deviations varying from 1.2 to 14 %.

1. INTRODUCTION

Palladium is an element belonging to the platinum element group (Pt, Rh, Ir, Os and Au). This element is found at low concentrations in several matrices. Thus its determinations are very difficulty. As such the development af analytical technique for Pd determination has been a challenge for researchers.

Pd determination is of special interest since this element is a new contaminant to the environmental with the introduction of automobile catalyzers containing elements of the platinum element group. Pd is also being studied by the medical field to be used as possible new antitummoral drug [1,2].

Several techniques have been developed to determine Pd in different matrices such as neutron activation analysis (NAA)[3-5], inductively coupled plasma mass spectrometry (ICP-MS)[6-8], atomic absorption spectrometry (AAS)[9], optical emission spectrometry (OES)[10], graphite furnace atomic absorption spectrometry (GFAAS)[11-12] and X-ray fluorescence (XRF)[13].

NAA which is used to determine numerous elements but in the case of the Pd there is a certain difficulty. The only radioisotope that can be measured is ^{109}Pd with half life of 13.7 h and a gamma ray energy of 88.03 keV. This peak is located in a spectrum region of low energy where occurs interferences of X rays peaks, "bremsstrahlung" radiation, as well as Compton effect of ^{24}Na high activity.

This paper presents results obtained in the determination of Pd in biological tissue samples and automotive catalyst using thermal and epithermal neutron activation analysis, separately. Pre-separations of Pd from interfering elements were also undertaken before irradiations.

2. EXPERIMENTAL

Biological reference material with certified values for Pd is not presently commercialized [14]. The only material that was available in the past was the Bowen's Kale which can no longer found. The solution was to prepare a homemade biological material containing Pd for the study.

2.1. Preparation of Pd Spiked Biological Materials

To prepare these materials bovine muscle and liver were acquired from a local butchery. First the materials such as skin and fat of these samples were removed using a titanium knife. Once cleaned these samples were cut into small pieces that were then ground using a blender with titanium blades, and the muscle and liver tissues were obtained in a past form. For Pd spiked muscle tissue sample, 70 mL of 11.4 mg L^{-1} Pd solution was added to 120 g of bovine muscle past and mixed in a blender again. In the case of liver, the Pd spiked material was prepared using 150 g of liver and 40 mL of 9.8 mg L^{-1} Pd solution.

These Pd spiked samples were freeze-dried and in this process, weight losses of 75.1 and 86.3% for Pd spiked biological tissues of bovine muscle and liver, respectively. Then the dried materials were homogenized manually in the teflon recipient to obtain in a powdered form.

2.2. Reference Materials

The reference material analyzed in the present study was a sample of automobile catalyst CCQM-P63, of the Proficiency Test from *Comité Consultatif pour la Quantité de Matière.*

2.3. Preparation of Pd Standards

Pd standard solution provided from Spex Certiprep Chemical (USA) was used to obtain diluted solution. From a certified standard solution of 1002.5 ± 3 mg L^{-1}, a diluted solution of 100.25 µg mL^{-1} Pd solution was prepared using MILLI-Q purified water for dilution. 50 µL of this diluted solution were pipetted onto sheets of Whatmam n° 40 filter paper. After drying at room temperature in a desiccator, the sheets were placed in clean polyethylene involucres and irradiated with the samples.

2.4 Procedure for Instrumental Thermal and Epithermal Neutron Activation Analysis

About 150 mg of sample weighed and heat-sealed in polyethylene involucres were irradiated at the IEA-R1 nuclear reactor, together with Pd standard. For irradiation the samples and standard were placed in an aluminum device. In the case of epithermal irradiation, the samples and standard were placed in a cadmium capsule and this in an aluminum device. Periods of 4 and 16 h were used for thermal and epithermal irradiations, respectively. The thermal neutron flux utilized was about 4 10^{12} n cm^{-2} s^{-1}. After about 60 h of decay time, samples and standard were mounted individualy in stainless steel planchets and measured using an HPGe detector coupled to an integrated signal processor (model 1510) both from Canberra. The resolution (FWHM) of the system was 0.99 keV for 122 keV of the ^{57}Co and of 1.78 keV for 1332 keV gamma-ray of ^{60}Co. The software S100 from Canberra was used to acquire spectra data and the VERSAO2 program was used to process the gamma spectra. From this program, counting rate and gamma-ray energies was obtained for radioisotope identification. The photopeak of 88.03 keV of ^{109}Pd (half life = 13.7 h) was used to calculate Pd concentration by comparative method.

2.5 Pre-separation of Pd before Epithermal Neutron Activation Analysis (ENAA)

The separation methods of palladium from interfering elements in this study were, solvent extraction and solid phase extraction applied before ENAA.

2.5.1. Pre-separation of Pd using solvent extraction technique

Pd pre-separation using solvent extraction was based on the paper presented by Byrne[5]. About 300 mg of the sample was dissolved in a Savilex Teflon flask using 4 mL of concentrated HNO_3. This mixture was left to rest for 5.5 h. After this time, 1 mL of H_2O_2 was added and left overnight. The following day, the contents were heated in a digestor block for 3 h at 90 ^{o}C.

The resulting solution was placed in a separation funnel, 1 mL of 0.1 M EDTA solution and 0.5 mL of dimethylglyoxime (DMG) solution were added. The DMG solution was prepared dissolving this complexant in ethanol. The funnel was agitated manually. After 15 min rest, 5 mL of chloroform were added and the funnel was agitated again.

The separation of the phases was obtained by decantation. The organic phase was removed and 2.5 mL of chloroform was added to the remaing aqueous phase. Both organic phases containing Pd were then mixed together and washed using two portions of 5 mL of 0.2 M HCl. The organic phase was collected in a 10 mL volumetric flask. The volume was completed adding chloroform. Aliquot of 250 µL of this chloroform solution containing Pd were pipetted into a polyethylene capsule from Vrije Universiteit, Amsterdam, Netherlands. The pipetted salution was dried using an infrared lamp. The Pd standard solution for irradiation was prepared by pipetting the standard solution in a capsule. The content of Pd in the sample was performed by ENAA as decribed in item 2.4.

2.5.2. Pre-separation of Pd using solid-phase extraction

Pd pre-separation in a reversed phase column was performed based on the paper published by Schwarzer et al.[3]. In this procedure Pd was retained in a solid-phase of the Phenomenex model SPE-Strata C18-E extraction cartridge.

The extraction cartridge was prepared by percolation of 10 mL of N,N-diethyl-N'-benzoyl-thiourea (DEBT) complexant dissolved in a 1% concentration of DEBT in a water and methanol mixture in a proportion of 0.9:1 (volume/volume). The cartridges containg DEBT absorved were then washed by percolation of 5 mL of purified water MILLI-Q. The dissolved sample was passed through the column to retain Pd. 5 mL of a 6.5% HNO_3 solution was passed through the column to eliminate the interfering elements. In order to remove Pd from this column, 10 mL of ethanol p.a was used as an eluent. 250 µL of ethanol solution containg Pd was dried in polyethylene capsule for ENAA.

3. RESULTS AND DISCUSSION

Results obtained in the analyses of Pd in Pd spiked biological tissues are presented in Table 1. In this Table are also presented the detection limit values evaluated according to Currie criteria [15].

Table 1. Pd concentrations obtained in Pd spiked biological tissues

Sample	Method of Analysis	Pd Mean ± SD[a] (n)[a] (µg g^{-1})	RSD[b] (%)	Detection limits (µg g^{-1})
Bovine muscle	NAA, instrumental	22.9 ± 3.2 (4)	14.0	11.0
	ENAA, instrumental	17.9 ± 1.6 (8)	8.9	0.4
	SPE[c] + ENAA	16.9 ± 0.2 (3)	1.2	0.07
	SE[d] + ENAA	16.2 ± 0.5 (3)	3.1	0.09
Bovine liver	NAA, instrumental	< 12	-[e]	12.0
	ENAA, instrumental	13.3 ± 0.3 (3)	2.3	0.4

[a.] aritmethic mean and standard deviation. n indicate number of determinations; [b.] relative standard deviation; [c.] solid-phase extraction; [d.] solvent extraction; [e.] - indicate non determined value.

Results obtained for Pd spiked bovine muscle and liver indicate good precision with relative standard deviations varying from 1.2 to 9.0%. The less precise result was obtained by instrumental NAA due to the interference of ^{24}Na formed. In Bovine liver sample the peak of ^{109}Pd was not detectec when instrumental NAA was used. On the other hand the instrumental analysis using epithermal neutron irradiations provided results with good precision when compared with those obtained using thermal irradiations. In epithermal neutron irradiation there is reduction of interference problems since the resonance integral values of interfering elements, such as Na, are lower than their thermal neutron cross sections. Besides ^{108}Pd isotope presents high resonance integral value when compared its thermal neutron cross section.

In Table 2 is present results obtained for CCQM-P63 automotive catalyst together with preliminary data presented by proficiency test participants. As can be seen in Table 2 this automotive catalyst sample presents high content of Pd so this element could be determined by instrumental NAA. Results obtained in this sample showed also good precision with relative standard deviations lower than 10.5%. Certified value for Pd determination for this sample was not published yet. Thus, our results were compared with preliminar results present by 21 laboratory participants in this proficience test. The results obtained in this study are very close to this preliminary result. However only the values obtained by instrumental methodology are within the preliminary range data.

Table 2. Pd concentrations obtained in automotive catalyst CCQM-P63

Sample	Method of Analysis	Pd Mean ± SD[a] (n)[a] (μg g^{-1})	RSD[b] (%)	Detection limits (μg g^{-1})
Automotive catalyst	NAA, instrumental	2372 ± 249 (4)	10.5	400.0
	ENAA, instrumental	2609 ± 65 (4)	2.5	13.7
	SPE[c] + ENAA	2200 ± 200 (3)	9.1	5.4
	SE[d] + ENAA	1919 ± 53 (3)	2.8	5.7

[a.] aritmethic mean and standard deviation. n indicate number of determinations; [b.] relative standard deviation; [c.] solid-phase extraction; [d.] solvent extraction.

Results obtained in this study (Tables 1 and 2) show that the results obtained using Pd pre-separation procedures are slightly lower than those obtained by instrumental methodology. These results indicate the necessity to evaluate the recovery yield of Pd in order to correct resulting from Pd loss occurred in separation steps.

Detection limits presented in Table 1 and 2 indicate that these values depend on the matrix and method of analysis. The lowest detection limits were obtained when the Pd was analyzed using pre-separation procedure followed by ENAA.

4. CONCLUSIONS

The results obtained in this study indicate that ENAA is more appropriate than instrumental NAA for Pd determination due to the reduction of the interference problems. The detection limit values indicated that the Pd separation before ENAA provides an increase of the sensitivity. The solid-phase extraction allowed obtaining the lowest values of Pd detection limit.

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