

NATURALISATION OF PPB RANGE IRIIDIUM DETERMINATION BY INSTRUMENTAL NEUTRON ACTIVATION IN HUNGARY

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ABSTRACT

The determination of iridium is the most commonly used scanning technique in the search for chemical impact markers. Until now Ir was not on the list of the standardized and measured elements in Hungary by neutron activation. As the naturalisation of the technique, we calibrated and tested the iridium detection at the Technical University of Budapest. The calculated k factors are the following: 50 mm sample–detector distance at 316 keV, 3.03; at 468 keV, 0.788; in-well geometry at 316 keV, 33.9; at 468 keV, 13.3. The calculated detection limit of iridium is 1×10^{-9} grams at the most sensitive irradiational and detectional parameters at the Technical University of Budapest. This value combined with the mass of the irradiated sample yields ca. 1 ppb iridium as the lowest concentration that can be detected without chemical preconcentration.

INTRODUCTION

The determination of iridium is the most commonly used scanning technique in the search for chemical impact markers. This element can be determined with greater sensitivity and more ease than any of the other PGEs (platinum group elements). Thus Ir acts as a marker for the other PGEs, by which, if an iridium anomaly is found, the complete platinum group can also be analysed to decide about the origin. The most commonly used technique to measure Ir content is the Instrumental Neutron Activation Analysis (INAA) (Montanari and Koeberl, 2000).

Neutron Activation Analysis uses the decay of the Ir-192 radioactive isotope, which forms from the Ir-191 stable isotope by capturing a neutron. The Ir-192 undergoes β -decay with 73.831 days of half-life. This β -decay is followed by a few characteristic γ -radiations. The two most intense γ -peaks are at 316.51 keV energy with 83.1% abundance and at the 468.07 keV with 47.6% abundance (Blaauw, 1996).

MEASUREMENT PARAMETERS

NAA measurements have been performed at the Institute of Nuclear Techniques of Technical University of Budapest since 1971. The analyses of geological samples started in the mid 1970's. Until now the Ir was not on the list of the standardized and measured elements. The detection of iridium in ppb concentration range was important because of the emerging impact-geological research activities in Hungary. There was only one master's thesis (Balogh, 1994), which purposed to determine the k factor for iridium measurements at 316 keV with 50 mm sample-detector distance (Fig. 1).

When using the comparator method, the k factor determination is important, because this factor shows the specific intensity of the elements relative to a chosen

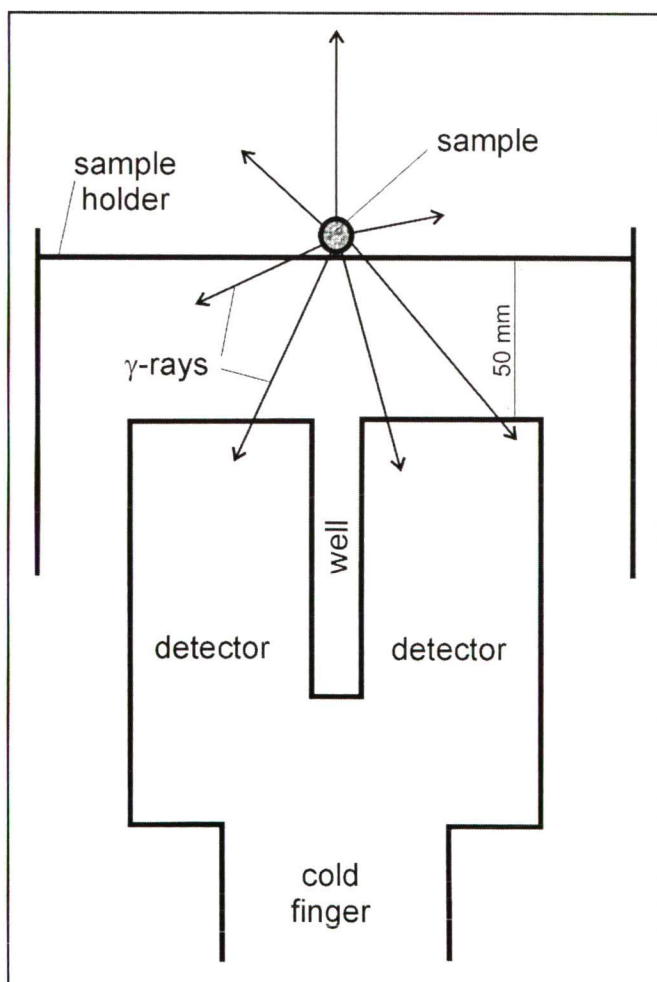


Fig. 1. Sample–detector configuration at 50 mm sample–detector distance.

comparator element. In this case there is no need to prepare standards every time for the detected elements. In the institute the comparator element is gold. Thus only a piece of gold is given to the samples every time, but many elements can be analysed.

A swimming-pool type thermal reactor is in the institute which has a thermal neutron flux density of $2 \times 10^{12} \text{ n cm}^{-2} \text{ s}^{-1}$. We had opportunity for maximum 8 hours irradiation at this neutron flux. To the γ -ray spectrometry a HPGe well-type detector (Canberra) was used, which has a 20.5% relative efficiency and 1.95 keV resolution (FWHM) at 1333 keV energy (Molnár et al., 1993). The detection time ranged between 60 000 to 150 000 s.

DEVELOPMENT OF METHODOLOGY

New geometry

We had to change the geometry of the detection because of the small amount of the samples and the low concentrations of iridium. We used the „in-well geometry” of the detector (Fig. 2), which can detect the radiation from almost the full 4π solid angle.

We measured a natural iridium standard in both geometries. This standard was the Cretaceous-Tertiary Fish Clay from Stevns Klint, FC-1, which has 32 ± 2 ppb iridium content (Gwozdz et al., 1992).

Change in the detected γ energy

From previous measurements and from the personal communication of professor Koeberl (Univ. of Vienna) it turned out that chromium and protactinium (which forms from thorium) contained by geological samples cause a perturbation at 316 keV for the iridium determination. This is basically due to the largest intensity γ -radiation of chromium at 320.1 keV, thus it is recommended to measure these samples at 468 keV, where there are no interacting peaks of any of the above elements. Therefore, we determined the k factors for both geometries at 468 keV energy also. At first we prepared a diluted aqueous solution from iridium-chloride ($\text{IrCl}_4 \cdot 6\text{H}_2\text{O}$) thus excluding any interfering element. By using the γ -ray intensities of the iridium, we could easily determine the k factors after the irradiation of the solution. The calculated k factors are the following: 50 mm sample-detector distance at 316 keV, 3.03; at 468 keV, 0.788; in-well geometry at 316 keV, 33.9; at 468 keV, 13.3 (Table 1).

Table 1. The k -factors determined at different wavelengths and geometries.

Sample-detector geometry	wavelength	k factor
50 mm sample-det.	316 keV	3.03
50 mm sample-det.	468 keV	0.788
in-well geometry	316 keV	33.9
in-well geometry	468 keV	13.3

CHECKING AND TEST APPLICATION OF THE NATURALISED TECHNIQUE

To check the k factor at 468 keV at in-well geometry, we did measurements in the Stevns Klint Fish Clay, which has 32 ± 2 ppb iridium content (Gwozdz et al., 1992). We measured 30.7 ± 1 ppb and 32.9 ± 1 ppb values with this

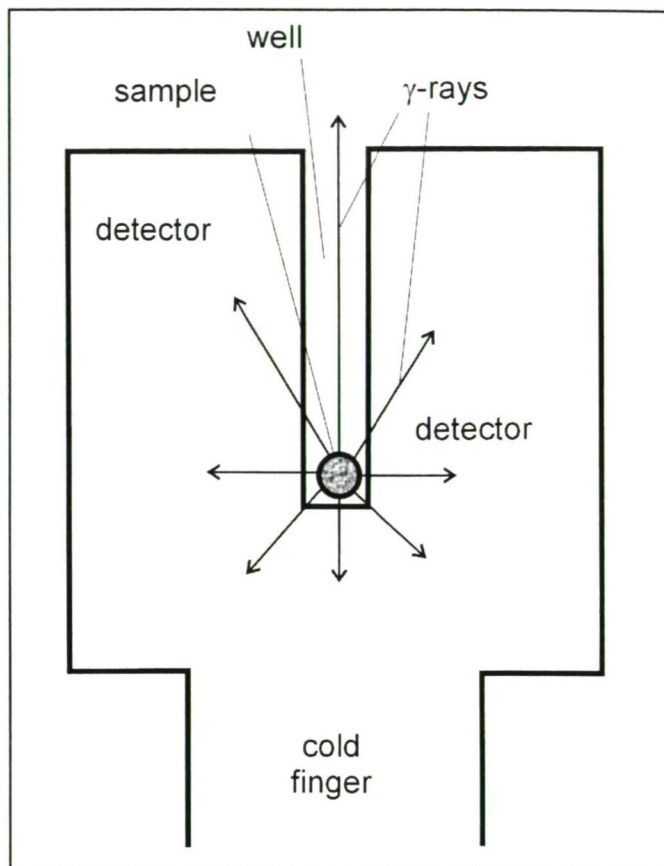


Fig. 2. Sample-detector configuration at „in-well geometry”.

standard. (The accuracy of our data is estimated from the determination of the peak area, thus this is the minimum error of the measurement.) (Table 2)

Table 2. Iridium content of the Stevns Klint Fish Clay.

Stevns Klint Fish Clay	sample No.	Ir concentration
Gwozdz et al., 1992	FC-1	32 ± 2 ppb
this paper	1	30.7 ± 1 ppb
	2	32.9 ± 1 ppb
	average	31.8 ± 2 ppb

We performed measurements on a Cretaceous-Tertiary boundary clay from an Italian section at Fonte d’Olio (Umbria-Marche basin). We collected the samples in May, 2000 from the Qualigotti quarry, which is located some 12 km to southward from Ancona. This section has the highest iridium content, 10.29 ± 0.48 ppb (Montanari, 1991) in the region. Here we separated the clay to two parts, a lower third and the upper two thirds of it.

The lower third of the clay is sample „a”, the upper two thirds of it is sample „b”. We obtained 8.4 ± 1 ppb iridium content on the bulk sample „a” and 8.0 ± 1 ppb on sample „b” in very good agreement with ICP-MS data from the Humbolt Institute, which is 8.4 ppb measured on an unseparated bulk sample from the same location (Roald Tagle pers. comm.).

APPLICATION AND DEVELOPING POSSIBILITIES

The calculated detection limit of iridium is 10^{-9} g at the above mentioned irradiational and detectional parameters.

This value combined with the mass of the irradiated sample yields 1 ppb iridium as the lowest concentration that can be detected. Using chemical enrichment before or after the irradiation, this detection limit can be reduced to ppt range. Now we are working on this problem.

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