Dinuclear metal-metal bonded complexes have attracted great attention because of their chemical reactivity, high catalytic activity in many reactions [1]. These complexes, mainly rhodium, ruthenium and rhenium are also known for their cytostatic properties [2] since the 1970s and are among the most promising non-platinum anticancer complexes [3]. It was shown that dirhodium tetraacetate exhibits appreciable cytostatic activity against a variety of cell lines, including L1210 tumor, sarcoma 180, Ehrlich ascites, P388 lymphocytic leukemia, etc. Among the recognized non-platinum antitumor agents are dinuclear carboxylates species of Rh, Re, and Ru.

Some years ago it was elucidated that Rh(II)-Rh(II) carboxylate can interact with DNA giving a biologically active metal-metal bonded system, which is the primary target in the design of replacements for platinum anticancer agents [4]. To elucidate the possible binding modes of DNA to the dirhodium core Rh-Rh, interactions with nucleobases, nucleotides, dinucleotides were studied. Our recent investigations proved (data not published), that some types of the Rh complexes prepared in the laboratory of the Department of Organic Chemistry at ELTE can get into the cells, and these findings are in good correlation with the biological data. The experimental data obtained at HASYLAB beamline L will help to understand the mechanism of the biological effect of Rh complexes.

X-Ray Absorption Near Edge Structure (XANES) analysis in combination with Synchrotron Radiation induced Total reflection X-Ray Fluorescence (SR-TXRF) acquisition was used to determine the oxidation state of Rh in human cancer cells. The applied geometry enables the acquisition of two types of spectra using a single method of sample preparation and the same reflector: the TXRF spectrum yielding elemental analytical information as well as the XANES spectrum containing information on the oxidation state and molecular environment of Rhodium. The big advantage of the investigation using SR-TXRF-XANES is the reduction of the sample preparation to a minimum: the cells available in a suspension can be directly pipetted in the Si reflectors, dried, inserted in the vacuum chamber and measured. XANES spectra of several dirhodium complexes were recorded and compared with those obtained on different cell lines.

Following the successful analysis of Fe in cancer cell lines reported in HASYLAB report 2009 and 2010, and published in ref [5], the same procedure was used for analysis of Rh in cell lines. The SR-TXRF setup – a vacuum chamber with an 8 stage sample changer - installed at Beamline L with the 50mm² Silicon Drift detector available there was used for the experiments [6]. The absorption spectra were recorded by tuning the energy of the incident beam across the K absorption edge of Rh using the Si(111) double monochromator. The evaluation of the XANES spectra was performed as a fingerprint method by comparison of the measurements of the unknown samples to those of the standards.

Preliminary evaluation of data collected at HASYLAB Beamline L in August 2011 (Fig.1) shows the feasibility of SR-TXRF-XANES analysis for Rh in cell lines. Our first results show clear differences between the cellular Rh forms with or without biological effect.
Figure 1: Investigation of the XANES spectra of two samples, labeled ‘Cell l2’ and ‘Cell l4’.
Left: Cell l2 fits Standard l2 very well (l2 type Rh complex with high intracellular concentration and promising biological effect)
Right: Cell l4 shows a clear edge-shift versus all measured standards (l4 type Rh complex with high intracellular concentration and negligible biological effect)

References