

Analysis of Highly Active Waste of Nuclear Fuel Reprocessing

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A K-edge densitometer combined with X-ray fluorescence analysis has been adapted to a hot cell for the analysis of highly radioactive samples.

The ICP-MS is a new instrument for multi-element and isotope analysis, which can be used to analyse fission products and actinides. For this purpose we have changed the configuration of a commercial system, installed the nebulizer in a hot cell and the torch box in a glove-box. The mass-spectrometer is mounted on to one wall of the glove-box whereas all the electronics and the personal computer are outside and accessible to the operator.

K-Edge Densitometry

K-edge densitometry is a versatile non-destructive technique which can be used to measure the concentrations of uranium and plutonium in solution. The device developed at KfK [Ref. 1+2] analyses the uranium and plutonium concentrations in the output and the uranium concentration in the input of a reprocessing plant. When combined with X-ray fluorescence this technique is also able to determine low concentrations of plutonium as is found in the reprocessing dissolver solution. The two instruments have been installed at the European Institute for Transuranium Elements for a thorough field testing.

K-edge densitometry is based on the abrupt change of the transmitted X-ray intensity at the absorption-edge of the atomic K-shell. The step-like transition is seen from the K-edge spectra taken for different actinide elements [Fig. 1].

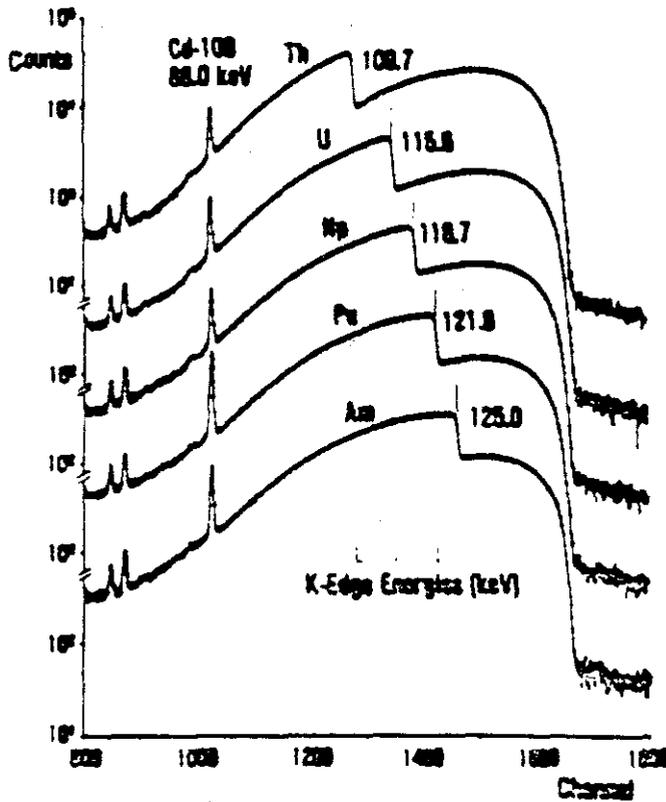


Fig. 1: K-edge spectra from actinide elements. The gamma line at 88 keV originates from a ¹⁰⁹Cd source mounted close to the detector. It serves as reference line for digital stabilisation of the analog electronics.

The fractional density, ρ_A of the dissolved transuranium element is given by the measured transmission ratio, R (determined directly above and below the absorption-edge energy) as follows:

$$\rho_A = \frac{\ln R}{\Delta\mu_A \cdot D} + \frac{\Delta\mu_M}{\Delta\mu_A} \cdot \rho_M$$

where $\Delta\mu_A$ and $\Delta\mu_M$ are the differences in the photon mass attenuation coefficients (at the two transmission energies) for the transuranium element and the matrix. ρ_M is the matrix density and D the sample thickness.

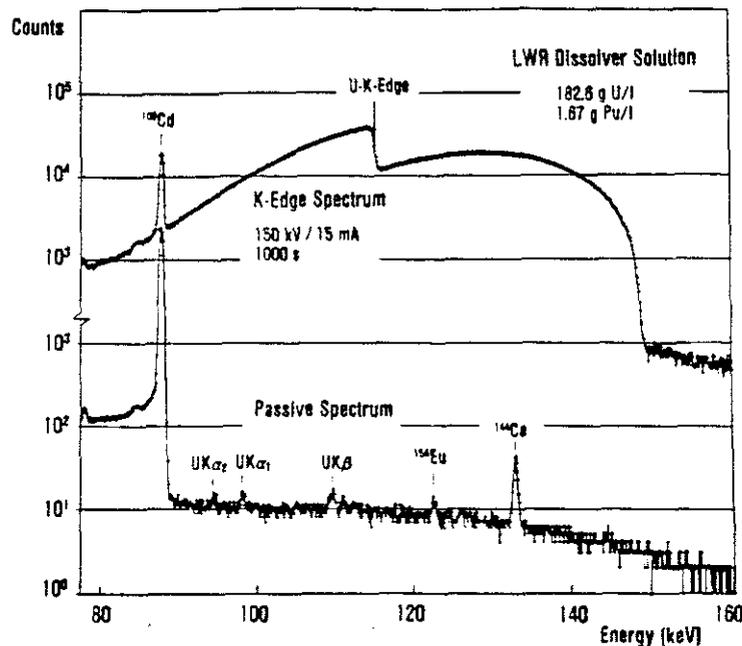


Fig. 2: Absorption edge spectrum (top) and passive spectrum (bottom) from a representative LWR dissolver solution (fuel burnup 35 GWd/tU, cooling time 3 years).

The concentration of uranium in the solution of a dissolved spent fuel can be analysed without interference from its radioactivity. In *fig. 2* the passive spectrum of the typical LWR fuel is shown in comparison to the absorption edge spectrum. The plutonium concentration is on the order of 1% of that of uranium so that the X-ray fluorescence (XR) is used instead. This well proven technique is used in the energy dispersive mode: a spectrum for a typical spent LWR fuel is given [*Fig. 3*]. The combination of the two techniques eliminates the need of the internal standard usually required for X-ray fluorescence analysis. Hence the accuracy of the uranium and plutonium analysis is mainly determined by the capability of the XRF-technique.

A schematic plan of the present instrument installation at the European Institute for Transuranium Elements is shown in *fig. 4*. The instrument is located outside a hot cell facility. It is connected to the interior of the hot cell through a tight stainless steel tube, which serves for sample transport.

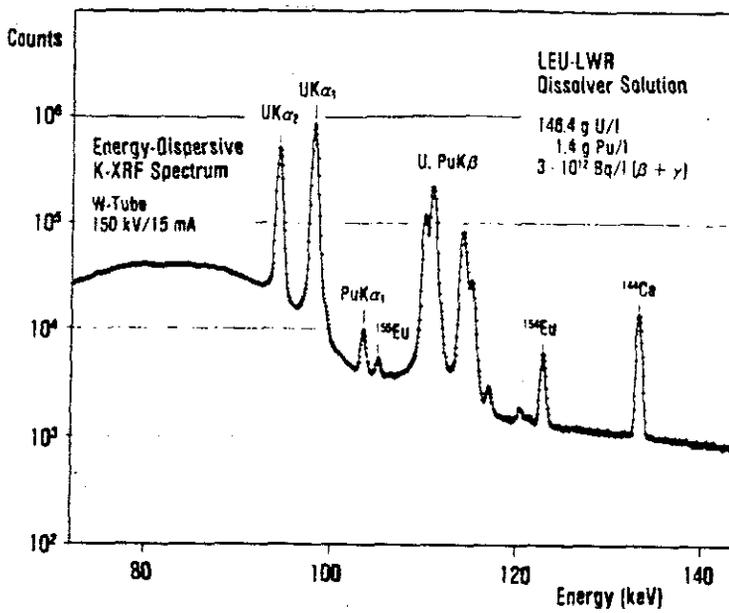


Fig. 3: Tube-excited XRF spectra from a LWR dissolver solution. Energy-dispersive K-XRF spectrum.

The two X-ray methods incorporated into the instrument use a single X-ray tube as photon source. The tube, operated at a potential of 150 kV and at tube currents between about 10 and 15 mA, irradiates with two separate X-ray beams a dual sample consisting of a 2 cm glass cell for K-edge densitometry, and a 1 cm diameter polyethylene capsule for XRF. The straight-through X-ray beam for K-edge densitometry is highly collimated through a 12 cm long, 0.08 cm diameter tungsten collimator. The XRF-detector, which is located at the largest possible backward angle relative to the primary beam direction, views the XRF cell through a 14 cm long, 0.6 cm diameter tungsten collimator.

Both detectors are standard planar HpGe detectors. They are operated at total counting rates between about 20 000 and 50 000 cps. The detector signals are digitized in two 400 MHz ADC's, and accumulated and analysed simultaneously on a computer-based data acquisition and analysis system.

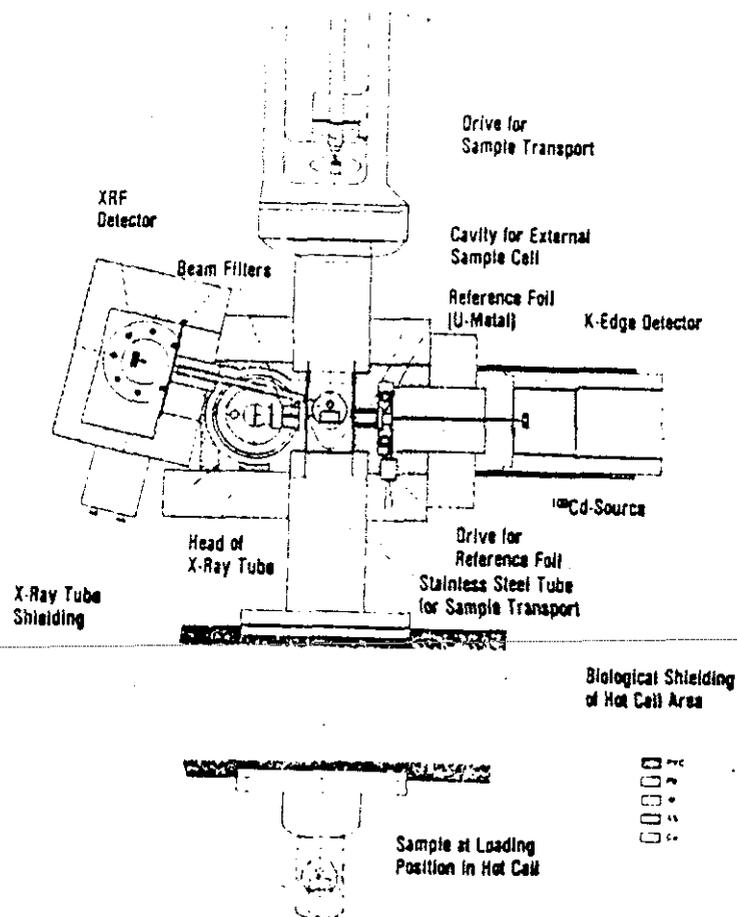


Fig. 4: Schematic plan of the hybrid K-edge / K-XRF instrument

Inductively coupled plasma mass-spectrometry

The ICP-MS is a relatively new technique for multi-element and isotope analysis in solution. It consists of an inductively coupled plasma coupled with a mass-spectrometer.

A solution containing the elements to be analysed is nebulized and carried by an argon stream into an plasma at a power of 1.2 KW where it is completely atomised and ionised.

All the elements of the periodic table are ionised under these conditions. The ion pass through an interface and reach a quadrupole mass filter. The quadrupole can be scanned to detect simultaneously all the elements and their isotopic distribution, with a sensitivity in the range of ng/ml and a linearity of 5 orders of

magnitude. Spectra are very simple even in complex matrices because each element is detected at its own mass value; little interference is found from isobaric overlap and from the presence of oxides and doubly charged ions. This instrument can be used in nuclear analytical chemistry for the analysis of fission products and actinides: for this specialised task no commercial instrument is presently available.

In collaboration with Perkin Elmer we changed the configuration of a commercial instrument and designed a new installation with which it is possible to analyse radioactive samples.

Depending on the different level of contamination to be expected in different parts of the instrument we have rebuilt it in a way more suitable for radioactive samples [Fig. 5]. The nebulized sample is carried by a stream of argon along a five meter pipe from the hot cell to the plasma torch box which is mounted in a glove-box.

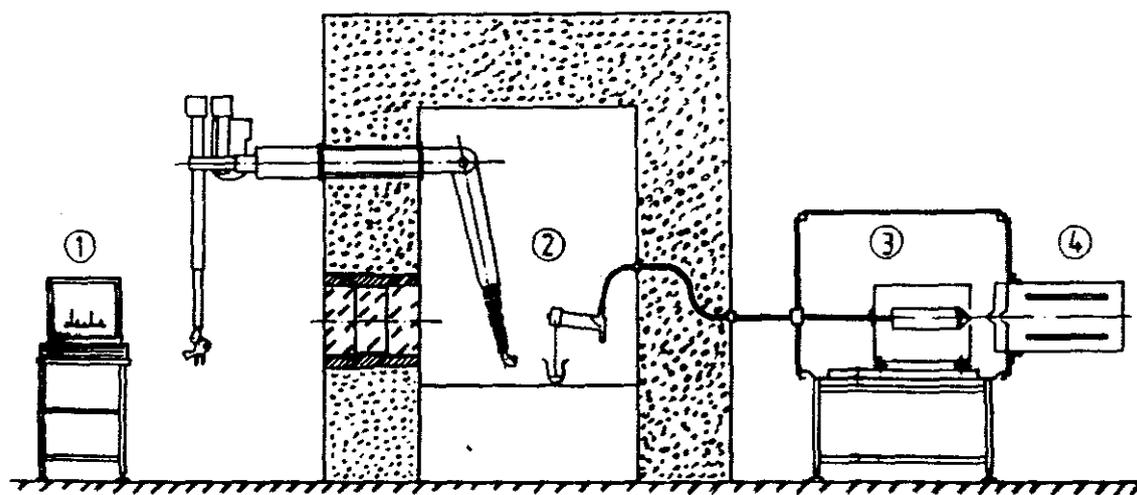


Fig. 5: Scheme of ICP-MS connected to Chemical Hot Cell Facility
(1) Personal computer ; (2) Nebulizer ; (3) Torch Box ; (4) Quadrupole Mass Spectrometer.

The glove-box is provided with extraction system, cooling and filters. The interface between flux, plasma torch and the MS consists of two nickel cones with small holes and is mounted on the stainless steel wall of the glove-box. This part is in contact with the plasma under operating conditions and is accessible for cleaning and maintenance.

The mass-spectrometer itself is mounted at the external side of the stainless-steel wall of the box just behind the interface; this part is considered not to be contaminated because only very few ions coming from the bulk of the plasma can reach the quadrupole and the multiplier.

All the electronics (RF generator, ICP-MS control units) are separated from the rest of the mechanical parts as is the computer used for the data acquisition and for instrument control.

With this new configuration it is possible to analyse all the isotopes up to 300 Daltons in highly radioactive solutions with a sensitivity in the range of 1 ppb.

Our aim is the characterisation and determination of the concentration of fission products in H.L.W. solutions and in spent fuel; the analysis of actinides in solution, characterisation of conditioned H.L.W. and analysis of leaching solutions.

The performance of the instrument installed with the new configuration will be tested at the end of July with inactive samples and in September with radioactive samples coming from the hot cell.

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