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HOW TO SIMPLIFY THE ANALYTICS FOR INPUT-OUTPUT ACCOUNTABILITY MEASUREMENTS IN A REPROCESSING PLANT*

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ABSTRACT

An analytical approach to high-performance uranium and plutonium accountancy measurements in reprocessing input and output solutions is presented, which provides larger operational simplicity than the conventionally applied chemical methods. The proposed alternative is based on energy-dispersive absorption edge and fluorescence X-ray spectrometry, using the proven and reliable K-edge densitometry technique as reference method. Two X-ray densitometers developed for accurate and reliable uranium and plutonum analysis in both the feed and product solutions are described. Practical experiences and results from their performance evaluation on actual process solutions from a reprocessing plant are presented and discussed.

Ein Weg zur Vereinfachung der Analytik für die Bilanzierungsmessungen am Eingang und Ausgang einer Wiederaufarbeitungsanlage

ZUSAMMENFASSUNG

Für die mit hoher Genauigkeit durchzuführenden Uran- und Plutoniumbilanzierungsmessungen am Eingang und Ausgang einer Wiederaufarbeitungsanlage wird ein alternatives Meßverfahren vorgeschlagen, welches die Analytik gegenüber den traditionell verwendeten chemischen Analysenmethoden wesentlich vereinfacht. Das alternative Meßschema beruht auf den physikalischen Methoden der Röntgenabsorptiometrie und Röntgenfluoreszenzanalyse, wobei die erprobte und genaue K-Kantenabsorptiometrie als Referenzmethode eingesetzt wird. Es werden zwei Röntgenabsorptiometer beschrieben, die für genaue und zuverlässige Uran- und Plutoniumanalysen in den Eingangs- und Produktlösungen entwickelt wurden. Praktische Erfahrungen und Ergebnisse von deren Einsatz bei der Messung realer Prozeßlösungen aus einer Wiederaufarbeitungsanlage werden dargestellt und diskutiert.

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ABSTRACT

1. INTRODUCTION

Nuclear materials accountancy in a reprocessing plant requires - among other actions - primarily a precise quantitative determination of the uranium and plutonium fraction in the respective process solutions at the input and output.

Since the establishment and verification of the nuclear materials balance also forms the basis for both national and international nuclear materials control, the necessary analytical determinations have to be made as accurate as possible. It is evident that this particular aspect in most cases necessitates elaborate analytical methods in order to achieve the desired level of accuracy.

On the other hand, economical considerations as well as the steadily tightening safety regulations make it desirable to perform the necessary measurements in an efficient and - whenever possible - automated manner, requiring minimum human interference with the hazardous materials. This holds particularly for the analysis of the highly radioactive sample materials originating from the reprocessing headend.

When we are looking over the analyst's shoulder during his analytical work for nuclear materials accountancy, we quickly note that chemistry still prevails in his practical work. Undoubtedly, the chemical methods used have demonstrated the capability to provide the needed measurement accuracy. However, despite some recent improvements towards automation, the present analytics is still characterized by a number of direct interactions of the analyst with the materials under assay. Needless to mention what this kind of procedure implies in practice in view of the special types of analysis samples in a reprocessing plant.

In this paper we wish to demonstrate that there exists an alternative analytical approach to nuclear accountancy measurements in a reprocessing plant, which does the job as well, but in a very much simplified manner.

2. THE ALTERNATIVE APPROACH

In order to illustrate the possible degree of simplification with our proposed analytical alternative, let us pick out an important example of analysis, namely: the determination of the uranium and plutonium content in the dissolver solution at the reprocessing input. This analysis certainly represents one of the key measurements for nuclear accountancy within the nuclear fuel cycle.

It is well known that the technique of Isotope Dilution Mass Spectrometry (IDMS) is presently the preferred analytical method for determining the uranium and plutonium element concentration in the chemically complex dissolver solution. It is also known that IDMS is a quite elaborate, time-consuming and expensive technique, which requires a great deal of experience of the analyst, if reliable and accurate results are to be obtained. In fact, in this approach of analysis the analyst has to handle and treat the sample material in various manners as roughly sketched in the left part of Fig. 1. Altogether he has to proceed through about two dozens of individual steps before he finally can start to interpret his mass-spectrometer printout in terms of an uranium and plutonium concentration. By the way, the analyst's activities are also manifested in quite a substantial amount of radioactive analytical wastes.

The proposed alternative, shown on the right side of Fig. 1, is an X-ray spectrometer, where the required operator interactions involve not very much more than to transfer the sample for analysis - without any prior treatment - into the spectrometer, and to initiate the machine to start with the measurement. The X-rays then will do the job for the analyst, relieving him of a great deal of laborious analytical work. After some time the X-ray spectrometer will provide him the final results together with a realistic estimate for the analysis error. This alternative, approaching the situation of a 'pushbutton analysis', will definitely eliminate a number of inherent imponderabilities of the conventional IDMS analysis.

What are the X-rays doing in our spectrometer? They are actually employed in two different ways:

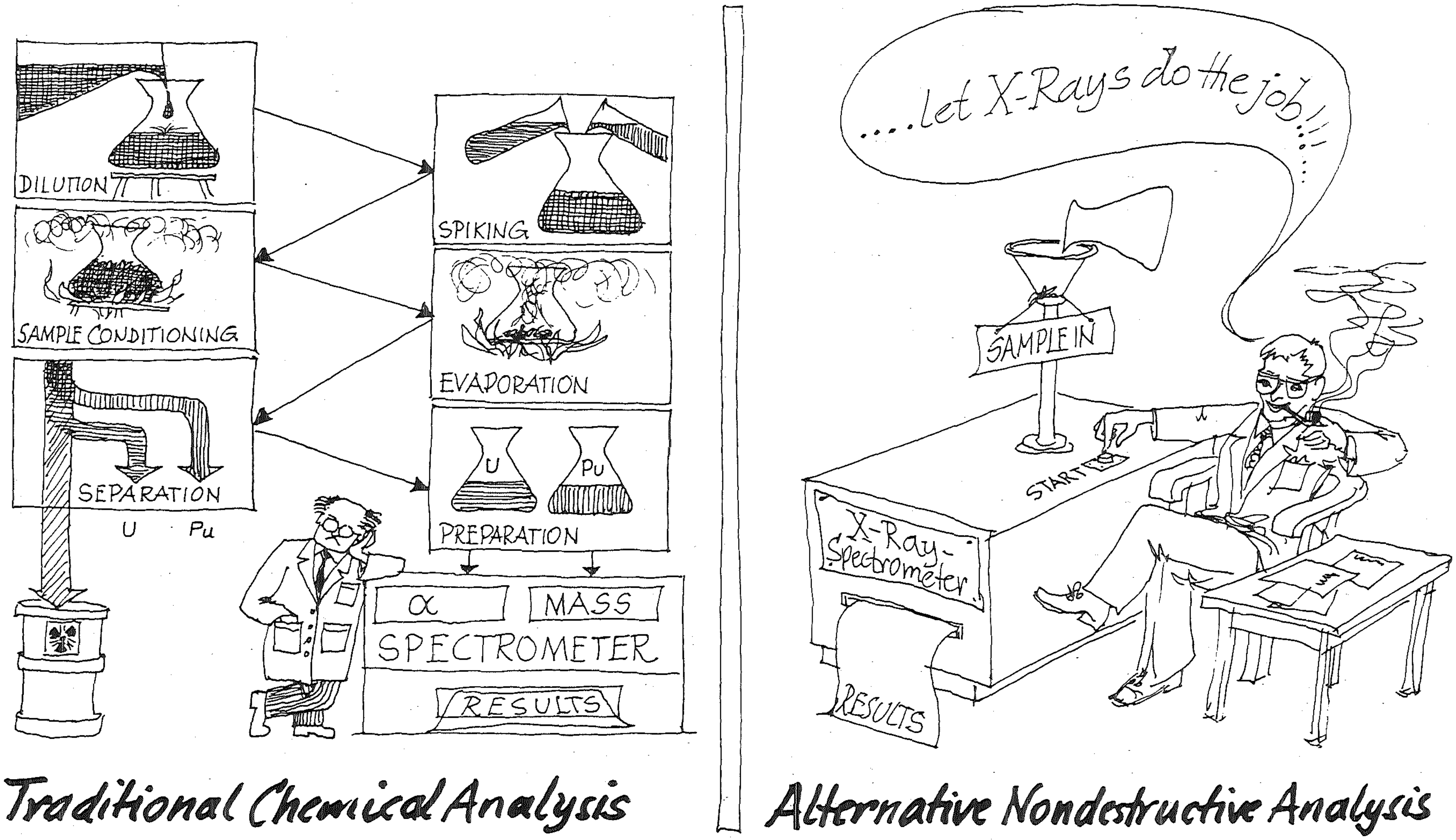

Fig. 1 Envisaged degree of simplification, illustrated at the example of reprocessing input analysis.

- First, external X-rays produced with an X-ray generator are transmitted through the solution samples for a measurement of their energy-differential attenuation at the K-absorption edge of those elements, whose fractional density has to be determined. That is what we colloquially call the 'K-edge densitometry' technique.
- Secondly, the external X-ray beam may be also used for the excitation of characteristic K X-rays from the heavy elements in the sample. This mode of analysis is the well-known X-ray fluorescence (XRF) technique.

Both X-ray techniques can be classified as nondestructive assay techniques, because they do not alter the samples during analysis. Further, the energetic X-rays ($E \gtrsim 100$ keV) used as measurement signals are also able to penetrate safe sample containments such as stainless steel or equivalents, which is of practical importance for in-plant operation.

The X-ray densitometers, developed at KfK and presented in this paper, are off-line instruments using discrete solution samples. However, the nondestructive nature of the assay techniques also recommend them for real in-line applications. Design examples of K-edge densitometers for in-line operation, monitoring nonstatic solutions, have been given at this Conference /1,2/.

3. K-EDGE DENSITOMETRY

The basic analytical method in our concept for simplified accountancy measurements in a reprocessing plant is the K-edge densitometry technique. During the past few years this technique has matured to a very reliable and accurate analytical method for the determination of heavy element concentrations in solutions /3/.

Description of the Method

The methodical basis of K-edge densitometry rests on the physical phenomena, that the photon attenuation suffers an abrupt change at the so-called 'absorption edge' of the atomic K-shell (as it does, of course, at the absorption edge energy of any other atomic shell). A photon continuum transmitted through a heavy element-bearing sample therefore shows a step-like transition at the K-absorption edge energy of the respective element. This characteristic feature is illustrated in Fig. 2, which shows a suitably tailored X-ray continuum after the transmission through samples containing different actinide elements. The K-absorption edge energies indicated in the measurement examples uniquely identify the nature of the element.

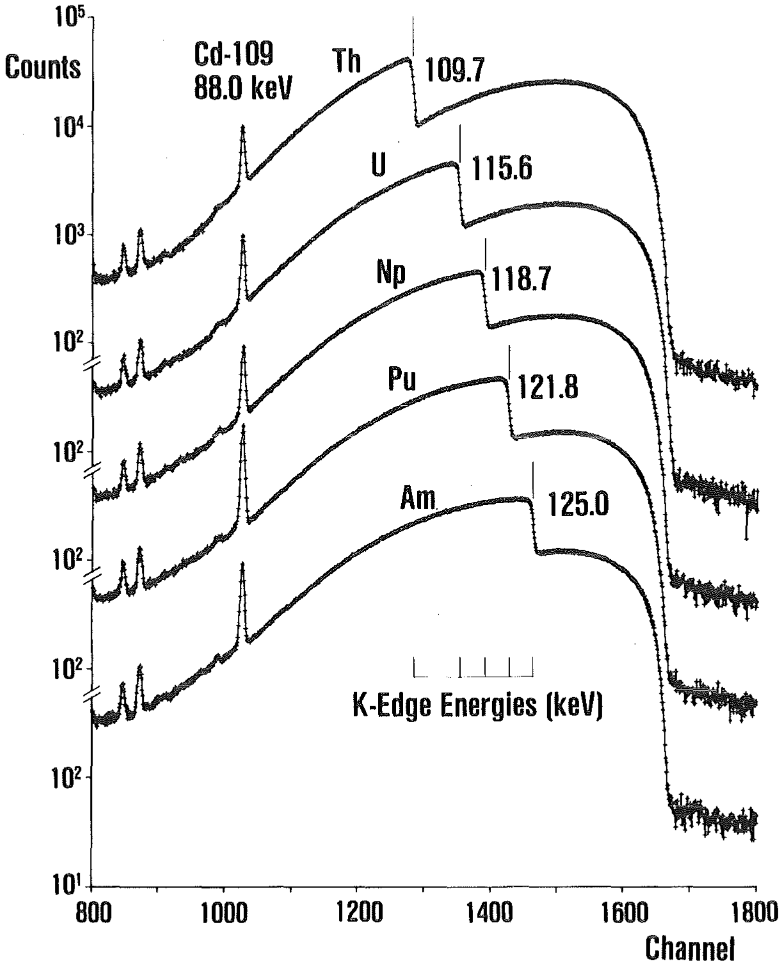

Fig. 2 K-edge spectra from actinide elements.
The gamma line at 88 keV originates from a ^{109}Cd source mounted close to the detector. It serves as reference line for digital stabilization of the analog electronics.

For quantitative analysis, K-edge densitometry requires two transmission measurements, one immediately below and one immediately above the absorption edge energy of the element of interest. The fractional density ρ_A of the analyte is related to the measured transmission ratio R by the densitometry equation

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

where $\Delta\mu_A$ and $\Delta\mu_M$ are the differences in the photon mass attenuation coefficients at the two transmission energies for the analyte and the matrix, respectively. ρ_M is the density of the matrix, and D is the sample thickness.

The effect of the matrix composition on the assay result, represented by the second term in the above expression, is in most cases of a very minor magnitude. The matrix effect can be even eliminated, if the transmission ratio is evaluated directly at the absorption edge energy of the analyte. In this case, $\Delta\mu_M$ becomes zero for all elements other than the analyte, while $\Delta\mu_A$ corresponds to the K-edge jump of the photon mass attenuation coefficient of the analyte. This approach of analysis becomes feasible with proper procedures for the evaluation of the measured spectral data.

For meaningful assays, K-edge densitometry requires, of course, homogeneous samples, so that the transmitted photon beam intercepts a representative portion of the sample. The technique is therefore most useful in solution assay applications.

Equipment Requirements

The experimental set-up for a K-edge densitometer is relatively simple. It requires four basic instrument components (Fig. 3):

1. A suitable photon source. The K-edge densitometers developed at KfK use an X-ray tube as a convenient photon source, which gives sufficient flexibility for different applications. Since the K-absorption edges of the actinides occur at

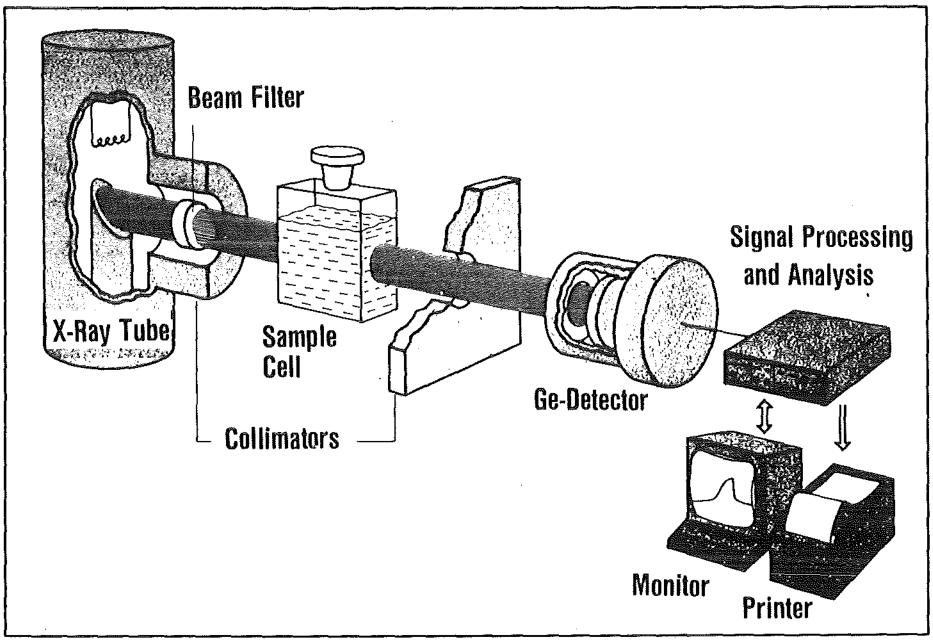

Fig. 3 Principal experimental set-up for a K-edge densitometer.

energies between about 110 and 125 keV, the X-ray unit must be capable to operate at voltages of about 140 to 150 kV. The X-ray beam extracted from the tube has to be suitably filtered and collimated for the transmission measurements.

2. A sample cell providing a well-defined path length for the photon beam. For the solution assays we are using disposable glass cells, whose path length is known to ± 2 μm. For densitometry measurements on radioactive samples such as plutonium, the sample cell is usually located in a glovebox or another type of α-tight containment.

3. A high-resolution photon detector with associated electronics. For K-edge densitometry at higher photon energies as required for the analysis of the actinide elements ($E > 100$ keV), a high-resolution, small planar Ge detector represents the best choice.

4. A computer- or microprocessor-based multichannel analyzer with standard pheripheral units for the collection and analysis of the transmitted photon spectra.

All of the above hardware components are commercially available standard units, used and proved in numerous research and industrial applications. They are assembled without specific modifications into the densitometer configuration.

Principal Features

From the measurement principle, and its practical realization, we can deduce a number of methodical features of K-edge densitometry, which are of practical importance:

- The method is element-specific and permits a direct analysis without any prior sample treatment.
- The determination of the element concentration is based on a ratio measurement, namely the ratio of photon transmissions above and below the K-absorption edge. This key feature lends great reliability to the technique and makes K-edge densitometry measurements relatively easy to interpret in quantitative terms.
- The analysis is relatively insensitive to matrix effects and independent of the chemistry of the samples. Because of the spectroscopy in the intense direct X-ray beam, K-edge densitometry is in particular also insensitive to the self-radiation from even highly radioactive samples, provided an X-ray tube is used as photon source for the transmission measurements.
- Unlike the analytical chemistry methods, K-edge densitometry provides comparable performance for all heavy elements. There exists, for example, no difference in measurement performance for uranium and plutonium.
- The calibration efforts for each element are reduced to the determination of a single physical constant, namely the difference $\Delta\mu$ of the photon mass attenuation coefficients across the K edge.

- K-edge densitometry measurements are easy to automate and operate, and they provide a number of possibilities for effective measurement control. This makes the analytics less prone to human influences and lends more objectivity to the assay results.

4. ANALYSIS OF REPROCESSING PRODUCT SOLUTIONS

The domain of K-edge densitometry is clearly bound to the analysis at higher concentration levels, say $\gtrsim$ 20g/l. It is therefore ideally suited for the assay of uranium and plutonium in the reprocessing product solutions, where the heavy element concentrations are typically ranging between about 100 and 500 g/l. In this range K-edge densitometry just exhibits its optimum performance.

The KfK K-Edge Densitometer

The main objective for the development of the KfK K-Edge Densitometer /4,5,6/ was to provide a means for timely and accurate safeguards verification measurements on the reprocessing product solutions, with the emphasis given, of course, to the analysis of the plutonium product. After an initial performance evaluation at KfK, the densitometer was then transferred in 1983 to the European Institute for Transuranium Elements (TUI), Karlsruhe, where it is now installed and operated.

The experimental configuration and the measurement geometry of the densitometer are detailed in the cross-sectional plan in Fig. 4. The shielded X-ray tube and the Ge detector are located on the opposite sides of a standard glovebox. The photograph in Fig. 5 gives an overall view of the present densitometer installation at TUI.

The only densitometer-specific modification to the glovebox consists of a horizontal perspex tube across the full length (80 cm) of the glovebox (Fig. 6), which connects the X-ray tube and the Ge detector. The tube confines the X-ray beam, and it incorporates a set of collimators for beam collimation and alignment

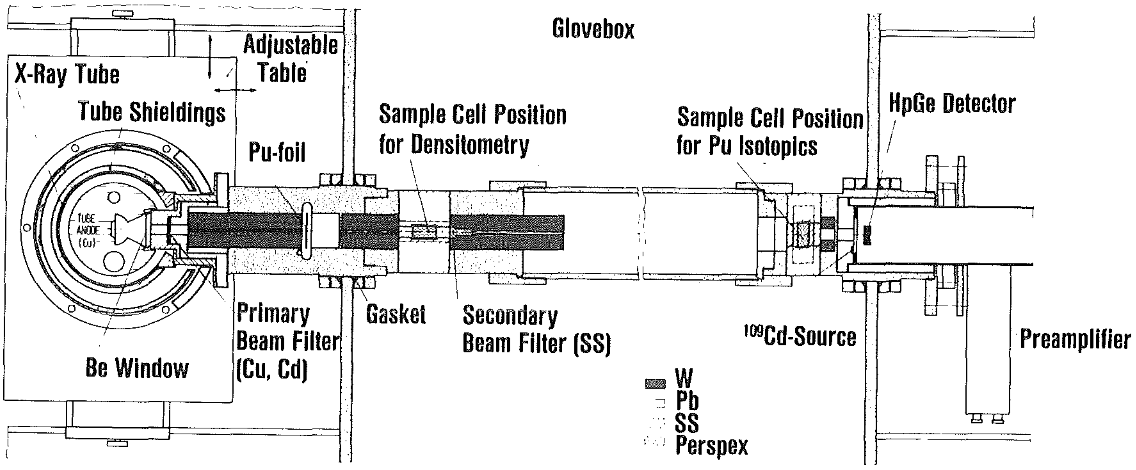

Fig. 4 Cross-sectional plan of the KfK K-Edge Densitometer.

as well as adapters for sample positioning. The 3 consecutive tungsten collimators at the front section - 10 cm, 5 cm and 10 cm long - have beam hole diameters of 0.2 cm, 0.25 cm and 0.3 cm, respectively. Beam filters of Cu, Cd and stainless steel tailor the X-ray beam to the desired distribution of photon flux vs. energy, with the intensity maximum being in the region of the K-edge energies of the actinides (see Fig. 2). The X-ray tube is operated at a constant potential of 145 kV.

Only two steps requiring operator interactions with the sample are necessary for an analysis: i) transfer of the sample into a disposable cuvette with specified transmission length, and ii) placement of the cuvette into the beam path. A sample adapter located just after beam entrance into the glovebox can accommodate cuvettes with a transmission length of up to 4 cm for the densitometry measurement (Fig. 7). Because of the relatively low rate of measurements in the present instrument, the samples are so far placed manually into the beam line. An automatic sample changing device, however, could be easily incorporated into the densitometer set-up, if required.

There is also provision made for the insertion of solid reference samples (sealed or unsealed foils) into the beam path for measurement control purposes. For easy access, the respective

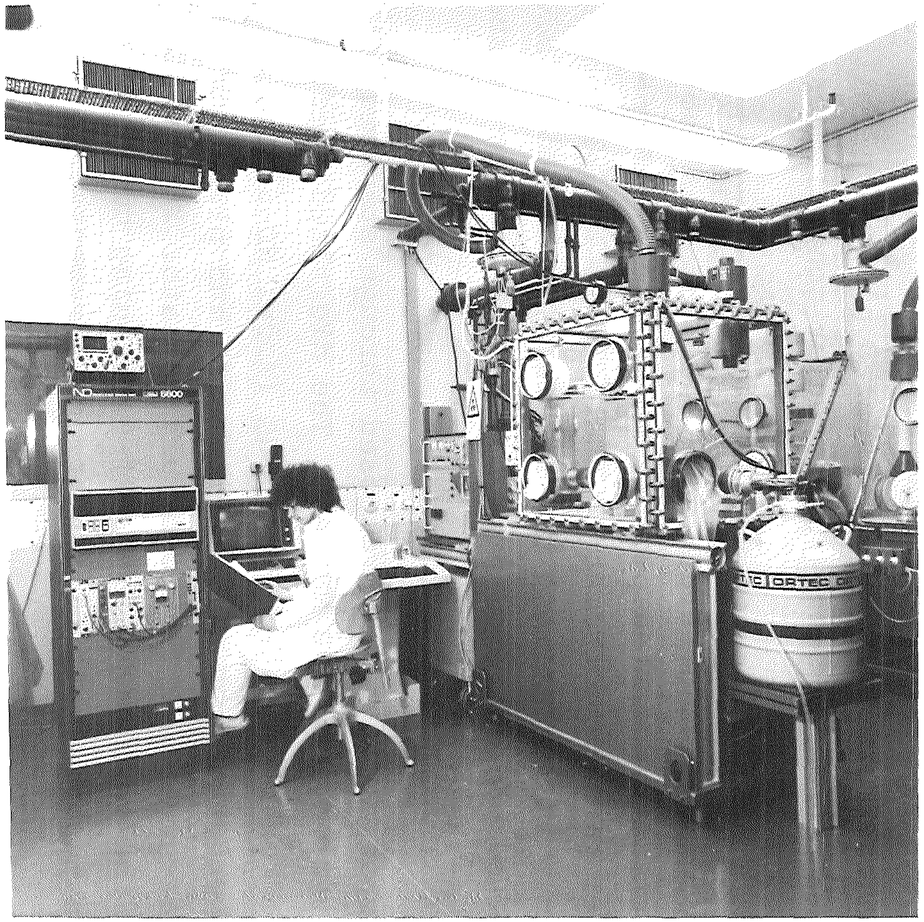

Fig. 5 Overall view of the KfK K-Edge Densitometer installed at TUI.

Fig. 6 View into the glovebox showing the beam tube with the sample adapters for densitometry (left) and Pu isotopic analysis (right).

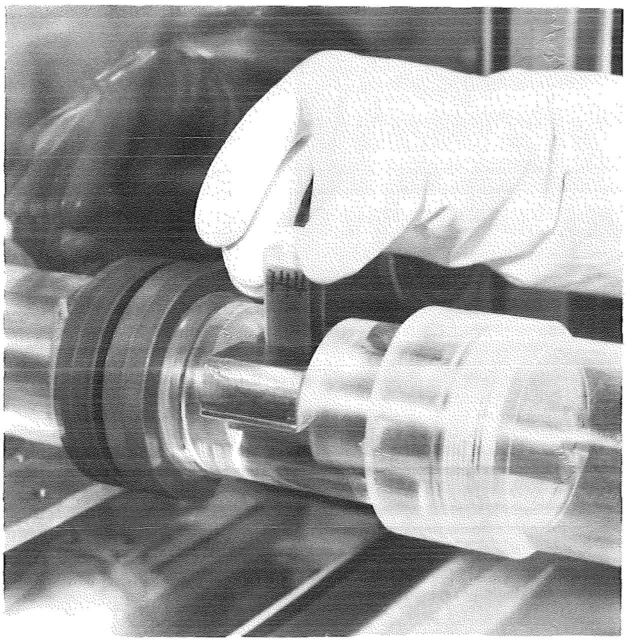

Fig. 7 Introducing a glass cell with sample solution into the measurement position for densitometry.

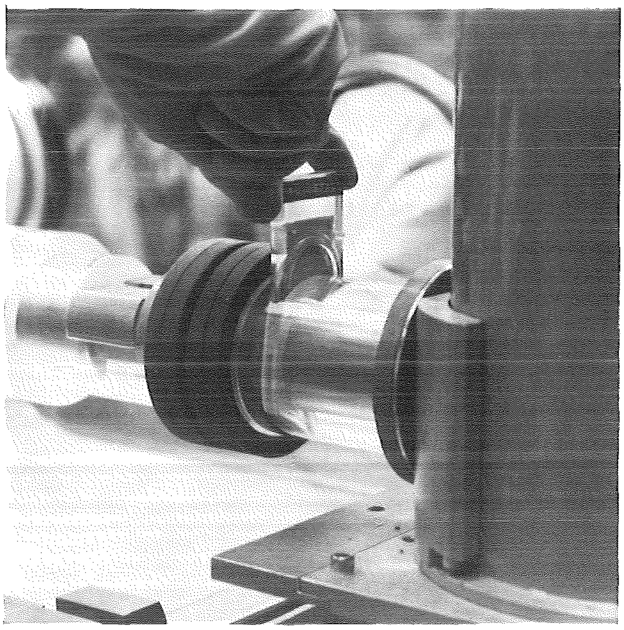

Fig. 8 Insertion of frame with encapsulated plutonium foil into the beam path for a control measurement.

measurement position is located outside the glovebox next to the X-ray tube. We are currently using a sealed plutonium foil mounted into a perspex frame (Fig. 8) for regular control measurements.

As an additional option the instrument also provides the possibility to determine nondestructively the plutonium isotopic composition of freshly separated plutonium /7/. This information is obtained from a gamma-spectrometric analysis of the plutonium self-radiation. For this measurement the sample vial has to be moved to another sample adapter located next to the Ge detector as shown in the densitometer plan in Fig. 4.

The detector signals are processed through standard NIM modules and digitized in a 400 MHz ADC. The digitized spectral data are accumulated on a computer-based MCA (Model ND-6600), on which the automated programs for the densitometry and plutonium isotopic measurements are running. The necessary operator interactions are prompted from the terminal via a self-explaining dialogue, which also enables nonspecialists to run the measurements.

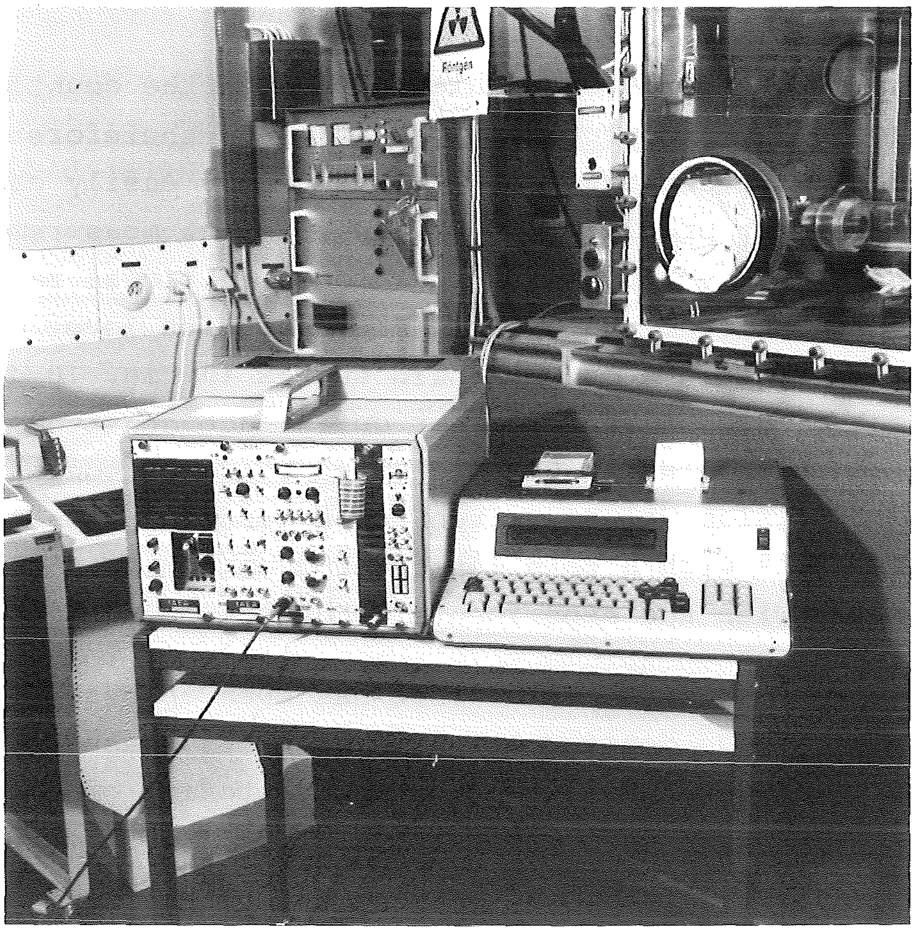

Fig. 9 Portable microprocessor-based MCA with associated terminal for independent data collection and analysis.

Alternatively, independent spectrum accumulation and evaluation is also possible on a separate microprocessor-based MCA unit with associated terminal. This compact data processing unit, which is based on developments of the Joint Research Centre, Ispra /8/, for automated NDA instrumentations, is shown in Fig. 9. The K-edge densitometry software, recently implemented at KfK on the dedicated program module of this low-cost portable system /9/, is identical to the software running on the resident computer of the densitometer. In the present application the compact MCA system is intended for parallel use by international safeguards inspectors as one of the possible means for authenticating the densitometer results evaluated with the resident data processing system.

Performance

K-edge densitometry is a technique based on the counting of statistical events. Its measurement precision is therefore largely determined by counting statistics. This can be easily calculated and quantitatively predicted for given relevant measurement parameters such as, e.g., counting time, processed signal rate, adopted procedure for spectrum evaluation, concentration level of the element to be determined etc. The solid curves in Fig. 10 describe the measurement precision expected for our K-edge densitometer for both uranium and plutonium in the indicated range of concentration. The predicted precision values, given for a counting time of 1000 s and for sample cells with a path length of 2 cm and 4 cm, respectively, fully agree with the experimentally determined data points.

The actual measurement performance has been assessed from comparisons between K-edge densitometry and chemistry results obtained from parallel analyses on both uranium and plutonium product solutions from the WAK reprocessing plant. In Fig. 11 we have plotted the ratios of densitometry and chemical assay results for the plutonium concentration of 8 consecutive plutonium product batches. The 4 chemical parallel analyses, which are all based on the AgO redox titration method, were independently performed at 4 different laboratories. For this intercomparison exercise the K-edge densitometer received 4 parallel samples from each plutonium product batch. The densitometry results represent the average measured from these 4 samples. Because of the large number of measurements (5 repeat measurements on each of the 4 parallel samples), the averaged densitometry results have a counting precision of better than 0.1 %.

The ratios to the 4 chemistry analyses are listed in Table 1. It can be seen that the average bias between K-edge densitometry and chemistry is below 0.1 % for the 4 data sets. The different magnitude of the calculated standard deviations, ranging between 0.15 % and 0.49 %, may be taken as measure for the quality of the respective chemistry data. It should be emphasized that the reported chemistry results refer to the real life situation of routine analytics.

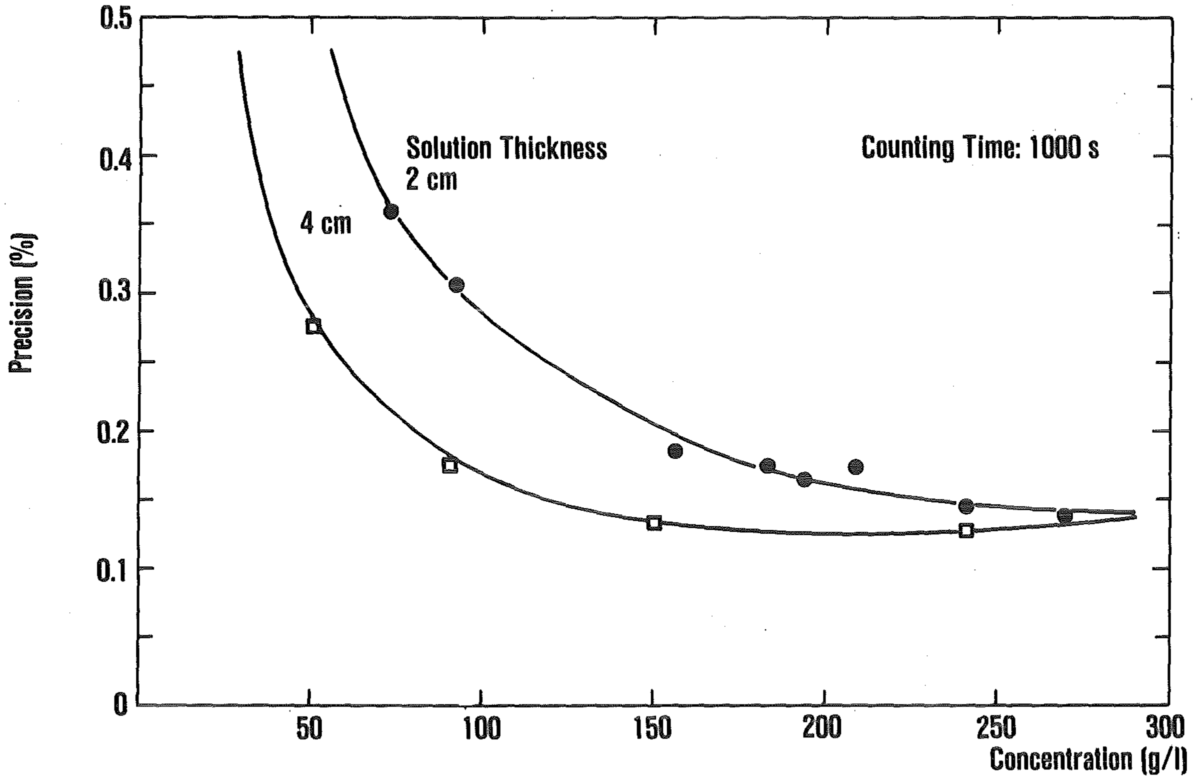

Fig. 10 Measurement precision for single-element analysis as a function of element concentration.

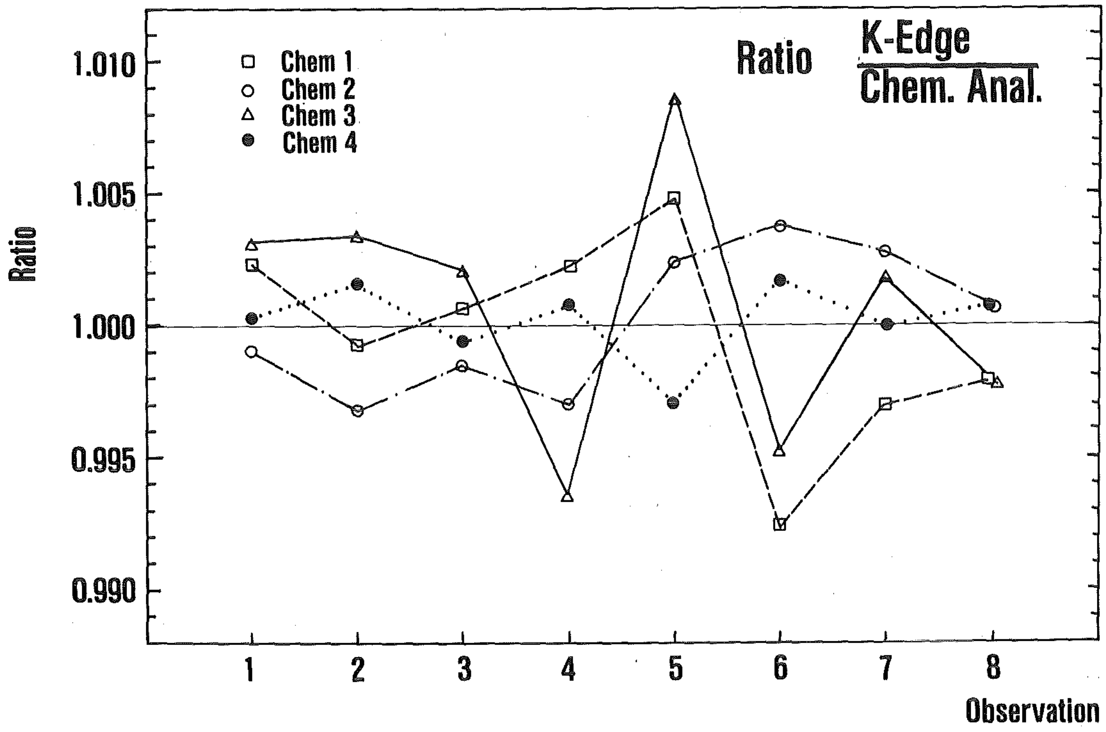

Fig. 11 Comparison between K-edge densitometry and 4 independent chemical analyses for plutonium concentration in 8 plutonium product batches.

Table 1 Comparison of K-Edge Densitometry Results with 4 Independent Chemical Analyses for Plutonium Concentration in Reprocessing Product Solutions.

Pu-Product Batch	Ratio of K-Edge Dens. and Chemical Analysis Results				
	K-Edge Dens. / Chem 1	K-Edge Dens. / Chem 2	K-Edge Dens. / Chem 3	K-Edge Dens. / Chem 4	K-Edge Dens. / Chem.Mean
1	1.0023	0.9990	1.0031	1.0003	1.0012
2	0.9992	0.9968	1.0034	1.0016	1.0002
3	1.0006	0.9985	1.0021	0.9994	1.0001
4	1.0022	0.9970	0.9936	1.0008	0.9984
5	1.0048	1.0024	1.0086	0.9971	1.0033
6	0.9924	1.0038	0.9953	1.0018	0.9983
7	0.9970	1.0028	1.0018	1.0000	1.0004
8	0.9979	1.0007	0.9978	1.0008	0.9993
Mean:	0.9996	1.0001	1.0007	1.0002	1.0002
Stand.Dev.:	0.0038	0.0027	0.0049	0.0015	0.0016

Table 2 Comparison of K-Edge Densitometry and Chemical Analyses for Uranium Concentration in Reprocessing Product Solutions.

U-Product Batch	Ratio of K-Edge Dens. and Chemical Analysis Results			
	K-Edge Dens. / Chem 1	K-Edge Dens. / Chem 2	K-Edge Dens. / Chem 3	K-Edge Dens. / Chem. Mean
1	0.9999	1.0015	1.0019	1.0011
2	0.9990	1.0015	1.0003	1.0003
3	0.9997	1.0004	1.0001	1.0001
4	0.9993	1.0029	1.0002	1.0008
5	1.0022	1.0034	1.0002	1.0019
6	1.0027	1.0041	1.0003	1.0024
7	1.0044	1.0074	1.0027	1.0048
8	0.9997	1.0044	0.9995	1.0012
9	0.9994	1.0039	1.0007	1.0013
Mean:	1.0007	1.0033	1.0007	1.0015
Stand.Dev.:	0.0019	0.0021	0.0010	0.0014

Results from comparison measurements on the uranium analysis in reprocessing product solutions are presented in a similar manner in Table 2. The K-edge densitometer results were obtained from 3 repeat measurements at 1000 s counting time on a single sample, which represents the normal measurement practice. They are compared with 3 independent chemical analyses from 3 different laboratories. The results in Table 2 show good agreement with 2 of the 3 chemical analyses, while one chemistry data set (Lab. 2) seems to be biased by about 0.3 %.

Both the uranium and plutonium assay in the K-edge densitometer is based on a calibration with carefully characterized reference solutions /10, 11/. The evaluation of the respective calibrations /12, 13/ has shown that for each element a single calibration constant is indeed sufficient for the quantitative interpretation of the K-edge densitometry measurements. From about 500 control measurements, which have been regularly performed over a period of about 30 months on the plutonium foil, we deduce an average constancy of the densitometer calibration of better than 0.15 % for long-term operation. This finding has the important practical consequence that the densitometer, once it has been calibrated, can be operated for longer periods (years) without spending efforts on frequent recalibrations.

5. ANALYSIS OF REPROCESSING INPUT SOLUTIONS

For K-edge densitometry it makes no principal difference, whether a relatively clean solution such as a purified reprocessing product, or a chemically highly complex and highly radioactive sample such as a reprocessing input solution of dissolved spent nuclear fuels is analyzed. In both cases the technique will equally provide an accurate and reliable assay, as long as the concentration level of the element to be determined is falling into the applicability range of K-edge densitometry ($\rho \gtrsim 20$ g/l).

Figs. 12 and 13 show examples of K-edge densitometry measurements on typical FBR- and LWR dissolver solutions. From both measurement examples it is evident that the technique can easily to-

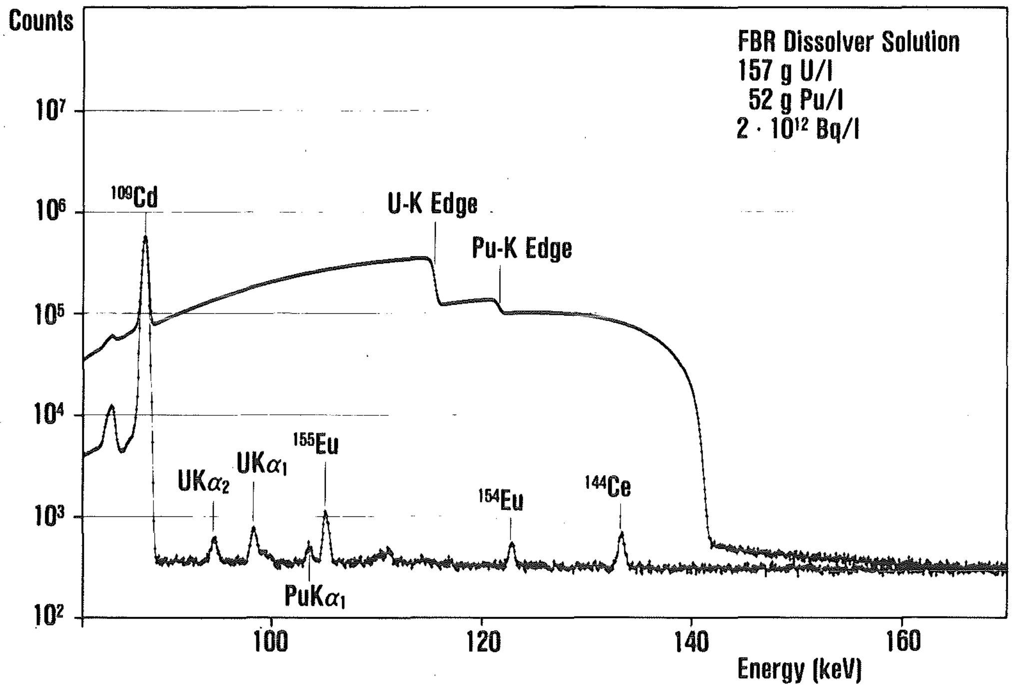

Fig. 12 X-ray transmission spectrum (top) and spectrum of passive radiation (bottom) measured from a FBR dissolver solution.

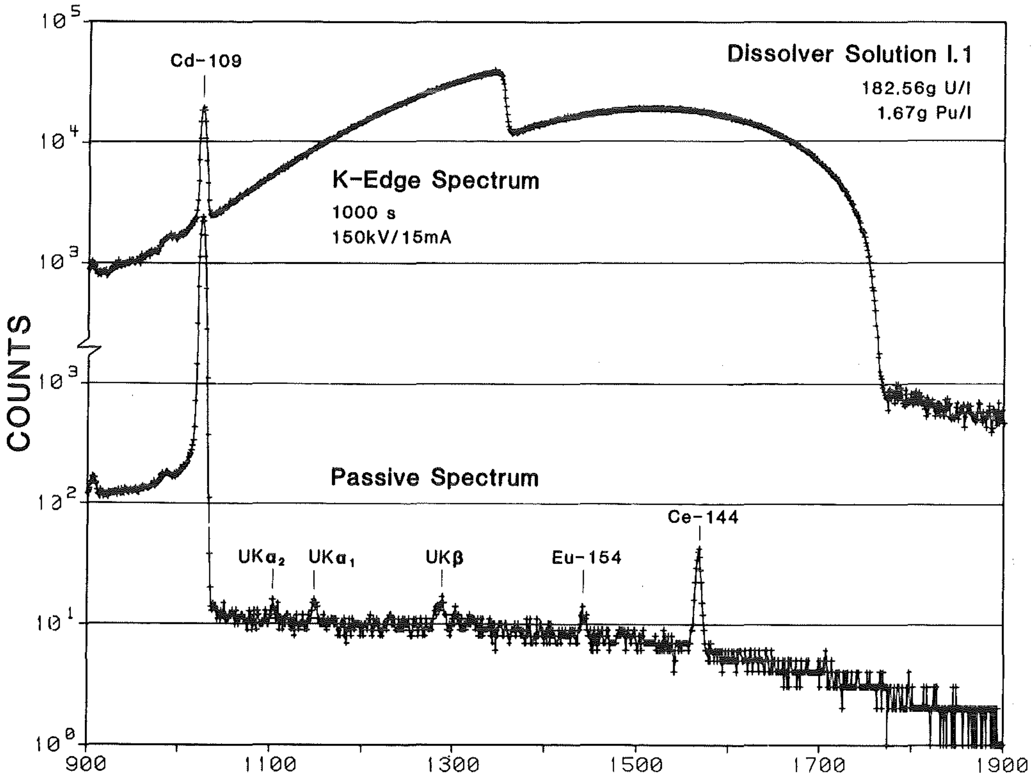

Fig. 13 X-ray transmission spectrum (top) and spectrum of passive radiation (bottom) measured with the K-edge detector in the Hybrid Instrument from a typical LWR dissolver solution (burnup 35GWd/MtU, cooling time 3 years).

lerate the high radiation level from dissolver solutions. In fact, the intensity of the sample self-radiation, shown in the bottom spectrum in the Figures, is 2 to 3 orders of magnitude below the intensity of the transmitted X-ray beam in the region of analysis around the K-absorption edge.

At small U/Pu ratios such as prevailing in FBR fuels, K-edge densitometry alone is capable to provide a simultaneous assay of both uranium and plutonium. This is not possible in LWR fuels, where the U/Pu ratio takes large values of typically $\gtrsim$ 100. In the latter case K-edge densitometry still provides a clean and distinct signal for the major element uranium as shown in Fig. 13, but it does not for the minor element plutonium.

Approach to LWR Dissolver Solution Analysis

For a simultaneous assay of uranium and plutonium in LWR dissolver solutions we have to make use of the second X-ray technique mentioned before, namely X-ray fluorescence analysis (XRFA). It is well known that XRFA exhibits a much larger dynamic range, making simultaneous assays possible at large element ratios.

The top curve in Fig. 14 shows the tube-excited XRF spectrum from the same LWR dissolver solution, which in Fig. 13 has been analyzed in the K-edge densitometry mode. Besides the abundant uranium K X-rays we also notice a distinctly resolved X-ray signature from plutonium (PuKα_1-line), which at the given U/Pu ratio of 110 can be clearly detected. The uranium and plutonium X-rays induced by the primary X-ray beam from the tube are about a factor of 100 more intense than the characteristic X-rays excited by the sample self-radiation, which is spectroscopied in the bottom curve in Fig. 14. From the measurement example given in this Figure it is also evident that the XRF analysis, although being more sensitive to the radioactivity of the fission products than K-edge densitometry, can still tolerate the typical radiation level of even relatively shortly cooled (2-3 years) medium to high-burnup LWR fuels. The only fission product gamma line detectable in the region of the uranium and plutonium K X-rays, the 105.3 keV line from ^{155}Eu, is well resolved from the PuK$_{\alpha 1}$ line and does not interfere with the analysis.

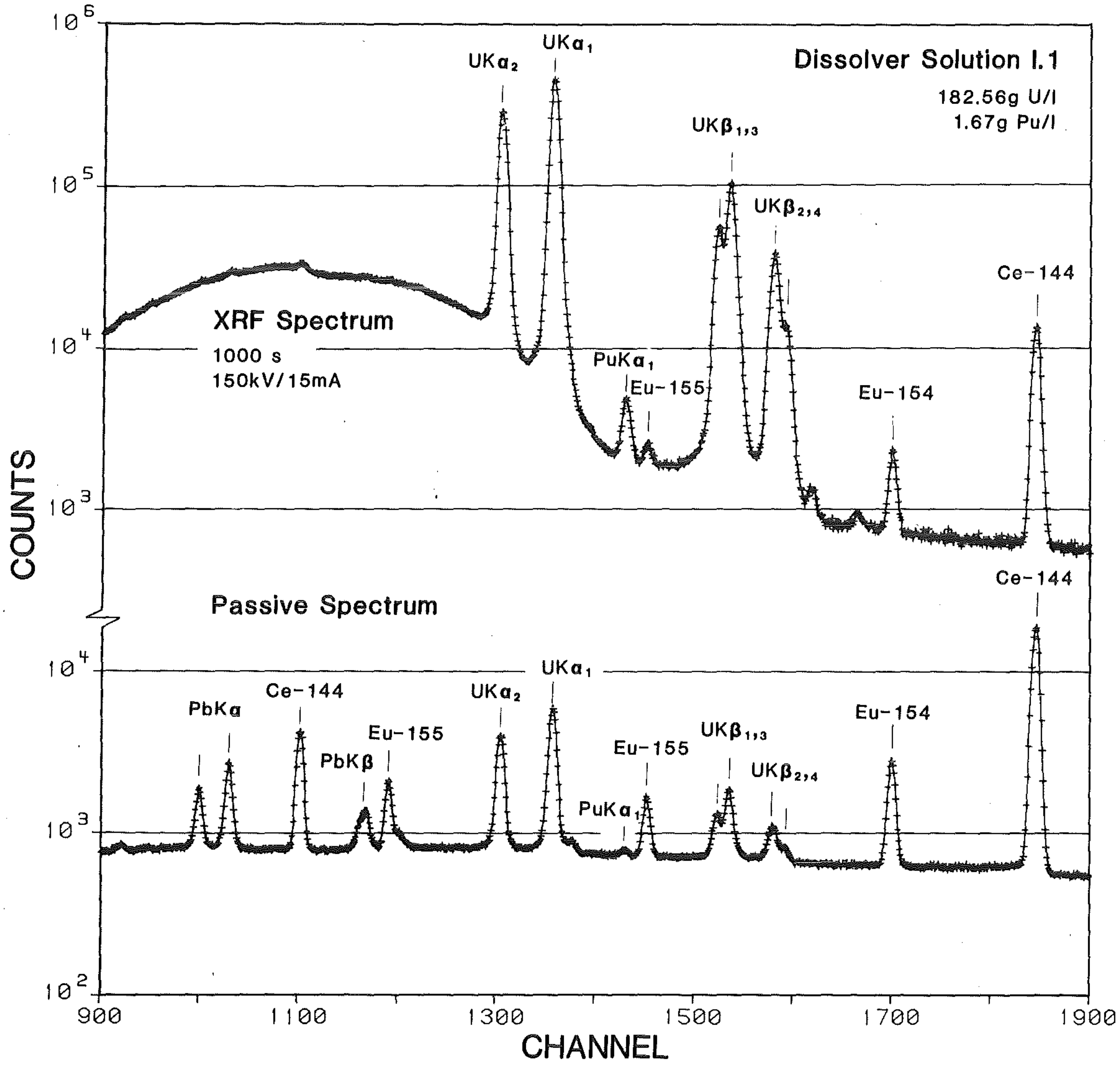

Fig. 14 Excited XRF spectrum (top) and spectrum of passive radiation measured with the XRF detector in the Hybrid Instrument from a typical LWR dissolver solution (same as in Fig. 13).

In principle XRFA alone would be sufficient for the uranium and plutonium assay in the dissolver solution. The traditional difficulty with XRFA, however, is the problem of measurement accuracy. To derive an accurate assay result from a measured X-ray peak intensity, which in fact is influenced by a number of parameters other than the concentration of the respective element, is obviously more difficult and less reliable than the quantitative interpretation of a K-edge densitometry measurement, where the element concentration is simply deduced from a measured transmission ratio. In order to achieve and to maintain the level of measurement accuracy and reliability needed for uranium and plutonium accountancy measurements, we therefore use both techniques in combination in our X-ray spectrometer for dissolver solution analysis. In this approach the proven K-edge densitometry technique provides the reference basis in terms of an accurately determined uranium concentration, while the XRF analysis is only used for the U/Pu ratio measurement. *The whole assay process for uranium and plutonium in dissolver solutions is thus simply reduced to the measurement of two ratios:*

- the ratio of X-ray transmissions at the K-edge of uranium, and
- the intensity ratio of the fluoresced $K\alpha_1$ X-rays from uranium and plutonium.

The Hybrid K-Edge/K-XRF System

A Hybrid K-Edge/K-XRF Solution Assay System, specially designed for dissolver solution analysis, has been recently developed at KfK /14/. This instrument is now installed at one of the hot cells at TUI for a performance evaluation with real reprocessing input solutions from the WAK Reprocessing Plant.

Fig. 15 shows the layout of the Hybrid Instrument. For simultaneous K-edge densitometry and XRFA one has just to add a second Ge detector to a basic K-edge densitometer set-up. The additional XRF detector is advantageously located at the largest possible backward angle relative to the direction of the primary X-ray beam. In this geometry the primary X-rays, which to a large extent are inelastically scattered from the solution sample, are energetically shifted below an energy of about 100 keV, provided the X-ray tube is operated at voltages not larger than about 160 kV. In this way it is possible to achieve the low background needed for an accurate determination of the $K\alpha_1$ X-ray from the minor element plutonium (see Fig. 14).

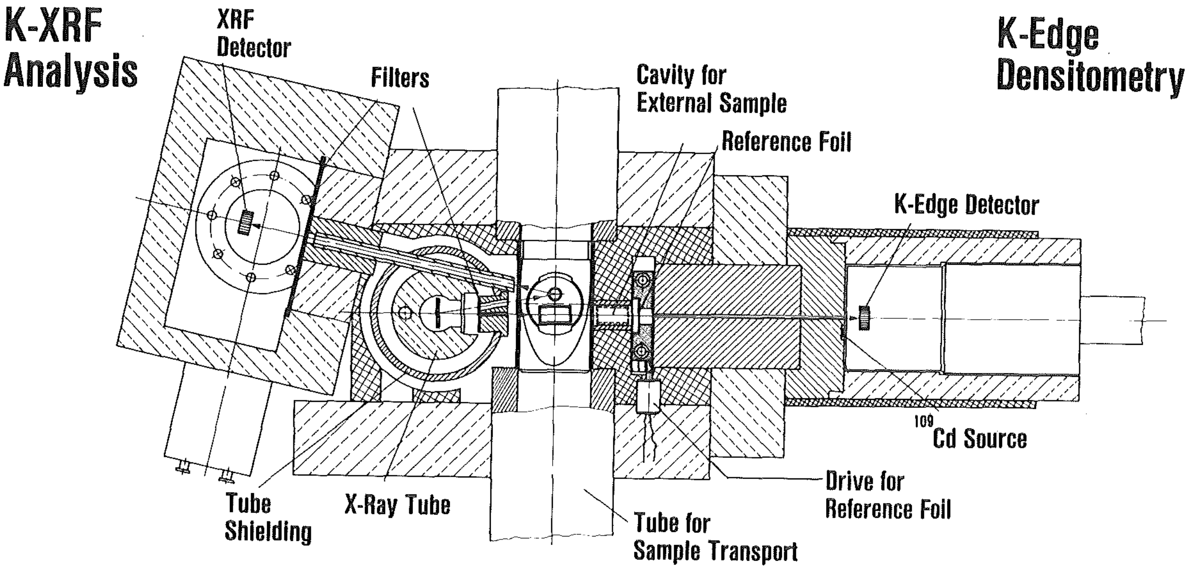

Fig. 15 Cross-sectional plan of the Hybrid Instrument.

The instrument uses a tandem sample, consisting of a 2 cm glass cuvette with accurately known path length for K-edge densitometry, and a thin-walled 1 cm diameter polyethylene capsule for XRFA. The separate XRF cell has been chosen in order to optimize the signal-to-background ratio for the more critical fluorescence measurement. Both sample cells are located at 8 cm distance from the focal spot of the X-ray tube. They are irradiated by two separate collimated X-ray beams, filtered by 1 mm Cd for the XRF analysis, and additionally by 15 mm of stainless steel for K-edge densitometry. The straight-through X-ray beam for K-edge densitometry is highly collimated through a 12 cm long, 0.08 cm diameter tungsten collimator located between sample and detector. A uranium metal foil mounted into a motor-driven frame can be inserted into the beam path for measurement control purposes. The XRF detector, located at a backward angle of 157° with respect to the primary X-ray beam directed towards the XRF cell, views its sample through a 14 cm long, 0.6 cm diameter tungsten collimator.

The relatively compact set-up, shown in the photograph in Fig. 16, is installed at the backside of the hot cell. It is built around a stainless steel tube used for sample transport, which ex-

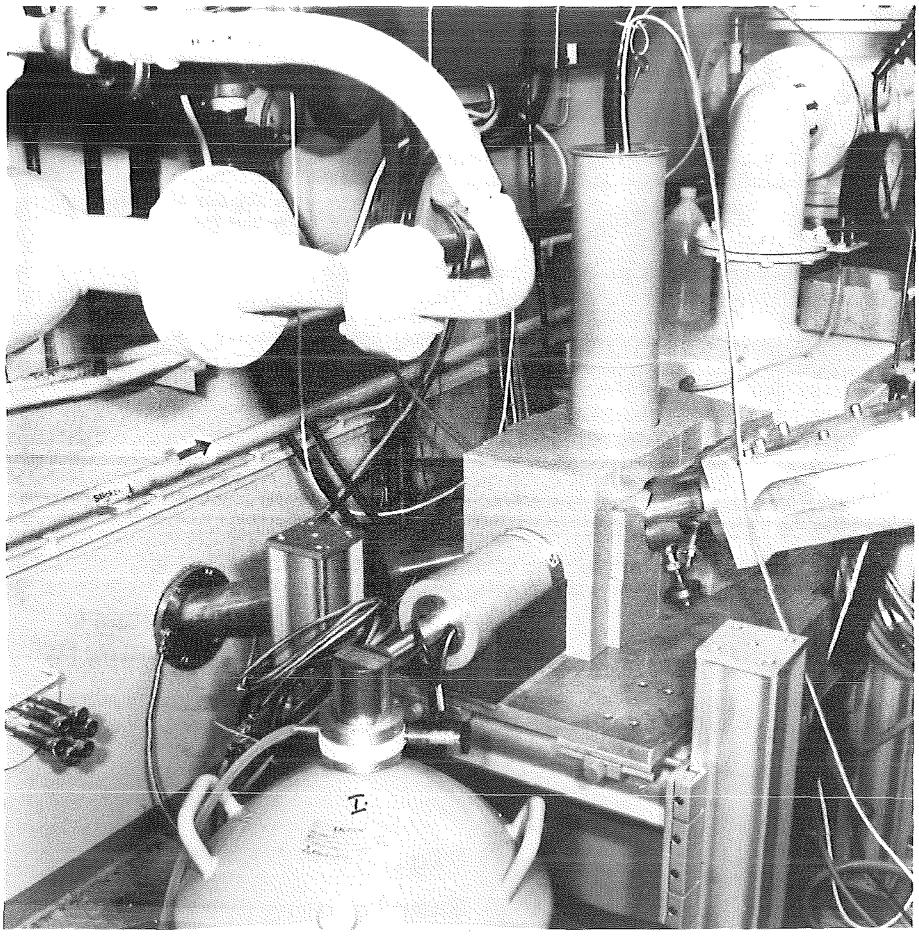

Fig. 16 Photograph of the Hybrid Instrument located at the backside of a hot cell at TUI.

tends through the biological shield into the interior of the hot cell (Fig. 17).

What has the analyst to do, when he receives a dissolver solution in the hot cell for a determination of the uranium and plutonium concentration? He just has to pipette a total sample volume of about 2.8 ml directly into the two sample vials located in a polyethylene capsule, and to load this capsule into the sample conveyor, which carries the samples from the interior of the hot cell to the instrument (Fig. 18). During the following automated analysis the samples remain safely contained inside the stainless steel tube of the sample transport system. The safe sample containment eliminates any contamination risks and permits full ac-

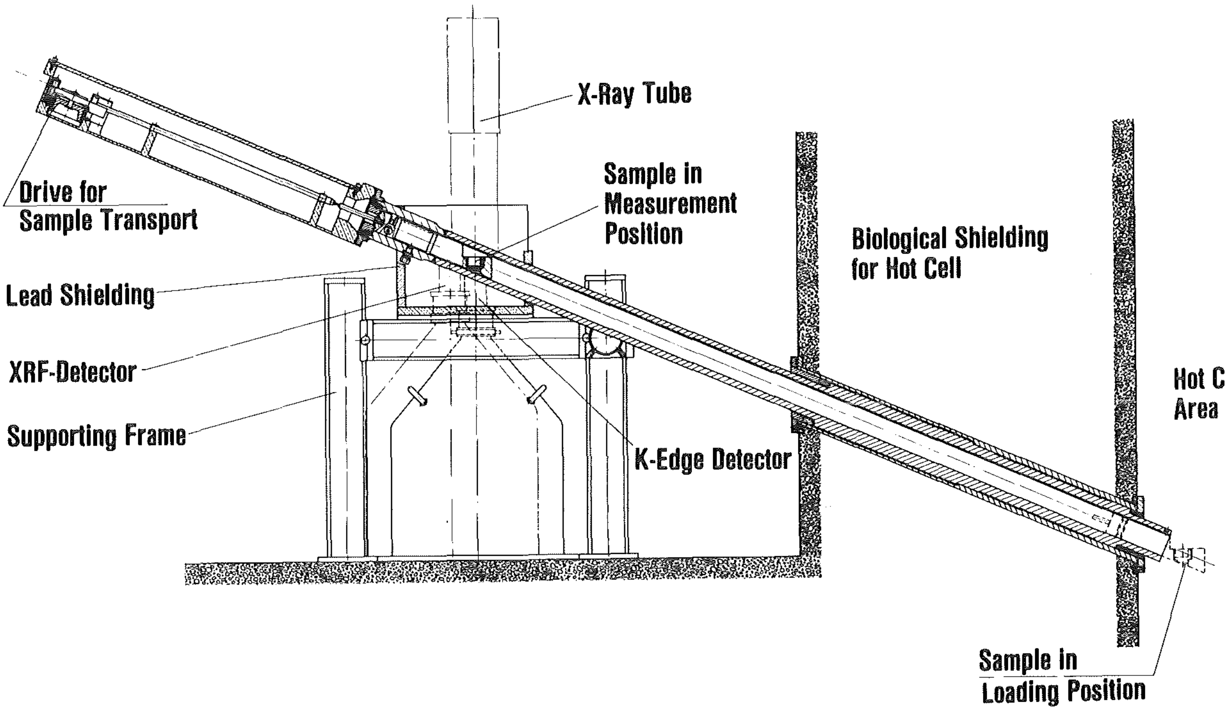

Fig. 17 Plan of the Hybrid Instrument installation at TUI.

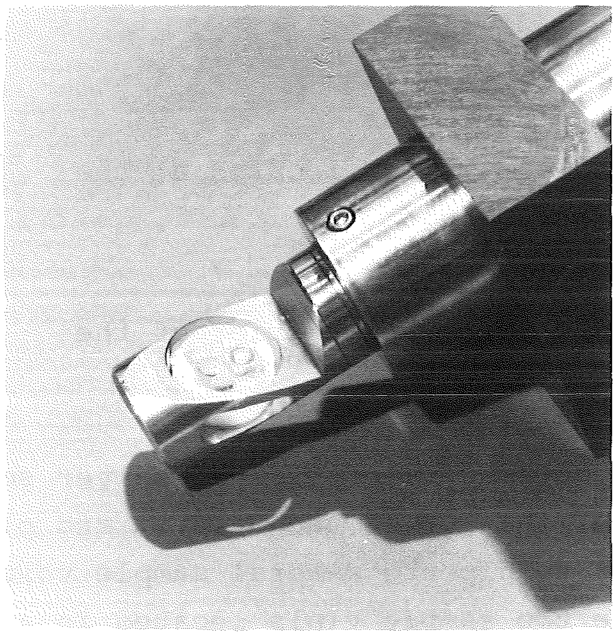

Fig. 18
Sample conveyer accommodating the polyethylene capsule (cover removed) with the 2 sample vials. The smaller glass cell for XRF analysis shown in the Figure has been later replaced by a polyethylene capsule.

cess to the instrument even during a measurement. The standard measurement procedure includes 3 repeat runs at 1000 s counting time each, resulting in a total analysis time of about 1 hour.

Performance Characteristics

The overall performance of the Hybrid Instrument depends, of course, on the individual performance characteristics of the two combined X-ray techniques. An important experimental factor, which determines to some extent the performance of X-ray tube-based K-edge densitometry and XRFA in terms of measurement precision, is the spectral distribution of the interrogating X-ray beam extracted from the tube. When operated individually, both methods would require somewhat different X-ray tube voltages for optimum measurement precision. In the Hybrid Instrument, where the K-edge densitometry and XRF measurements are simultaneously performed with the same X-ray tube as photon source, one has therefore to find a compromise for the tube operating conditions in order to optimize the system's overall performance.

The adopted compromise for the Hybrid Instrument is a tube voltage of 150 kV, with the tube current normally fixed to 15 mA. These ratings correspond to about 75 % of the maximum tube power (160 kV, 19 mA) available from the X-ray unit. The applied tube voltage is about 10 kV above the value required for optimum K-edge densitometry precision for uranium, and about 5 kV below the value which provides optimum performance for the U/Pu ratio measurement from fluorescence.

For the given experimental conditions, including the procedures for spectrum evaluation, a measurement precision of 0.25 % (1σ) for uranium is obtained from the K-edge densitometry measurement on a representative LWR dissolver solution ($\rho_U \simeq 200$g/l, U/Pu $\simeq$ 100) in a 1000 s counting time. At the same time the U/Pu ratio is evaluated from the XRF spectrum with a 1σ-precision of about 1 %.

Useful informations on typical performance characteristics have been obtained from the evaluation of the initial calibration measurements /13/. These have been carried out on various types of carefully characterized reference solutions, which included both pure uranium solutions, synthetic U/Pu mixtures without fission products, and highly active input solutions. The reference values for the U and Pu concentrations in the solutions were based on independent chemical analyses at 3 different laboratories /11/.

The evaluation of the calibration data for K-edge densitometry has shown, that the uranium determination in the different types of solutions is actually accomplished with a single calibration constant $\Delta\mu$. This proves the expected immunity of the K-edge densitometry technique to matrix effects. To what extent the presence of fission products and plutonium in a LWR dissolver solution will affect the measured uranium concentration is graphically shown in Fig. 19. The expected (negative) bias, shown in the Figure as a function of burnup, is based on the assumption that the transmission ratio is evaluated at energies, which are separated by 4 keV across the uranium K-edge. Even for this conservative experimental approach the reduction of the measured uranium concentration in the input solution, compared to the result from a pure uranium solution, will be less than 0.2 %

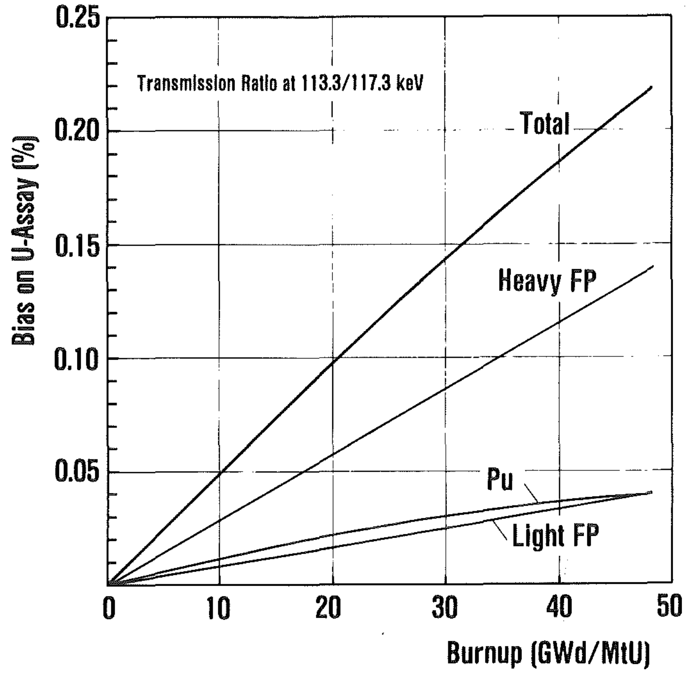

Fig. 19 Calculated percentage reduction of measured uranium concentration due to the presence of fission products and plutonium in LWR input solutions as a function of fuel burnup.

for burnup's up to 40 GWd/MtU. This small bias, which is reliably estimated from known physical parameters, can be easily taken into account in the analysis.

Similarly, the calibration results for the U/Pu ratio determination from the fluorescence spectra have shown that, given about the same total heavy element concentration, the same calibration factor applies for the conversion of the measured peak area ratio $UK\alpha_1/PuK\alpha_1$ into the U/Pu element ratio for both the synthetic U/Pu mixtures without fission products and for the real input solutions. However, the typically much larger sensitivity of XRFA, as compared to K-edge densitometry, to variations of the sample composition has the consequence, that even for the more simple and easier to interpret element ratio measurement corrections have to be taken into account for changes of the total heavy element concentration. This is because the interrogating X-ray beam, while passing through the heavy metal-bearing sample, suffers a change of its spectral distribution in the sense, that the X-ray beam will be slightly hardened. As a result, the excitation probability for emission of plutonium K X-rays will slightly increase relative to that for uranium with increasing total heavy element concentration. Therefore the XRF calibration factor, which is physically described by the ratio of excitation probabilities for emission of $UK\alpha_1$ and $PuK\alpha_1$ X-rays in the primary beam, will slightly decrease with increasing total heavy element concentration.

The expected variation of the calibration factor $R_{U/Pu}$ with the uranium concentration in the Hybrid Instrument, calculated for a fixed U/Pu ratio of 100 and for a 1 cm thick solution layer, is shown in Fig. 20. We note from the Figure that $R_{U/Pu}$ changes by about 2 %, when the uranium concentration is varied from 100 to 300g/l. The dependence is well approximated by an exponential function, and the necessary corrections are incorporated into the data analysis. Fortunately, variations of the U/Pu ratio within the range reasonably to be expected for LWR fuels, as well as the levels of fission products and changes of the nitric acid density, have a negligible effect on the XRF calibration factor $R_{U/Pu}$.

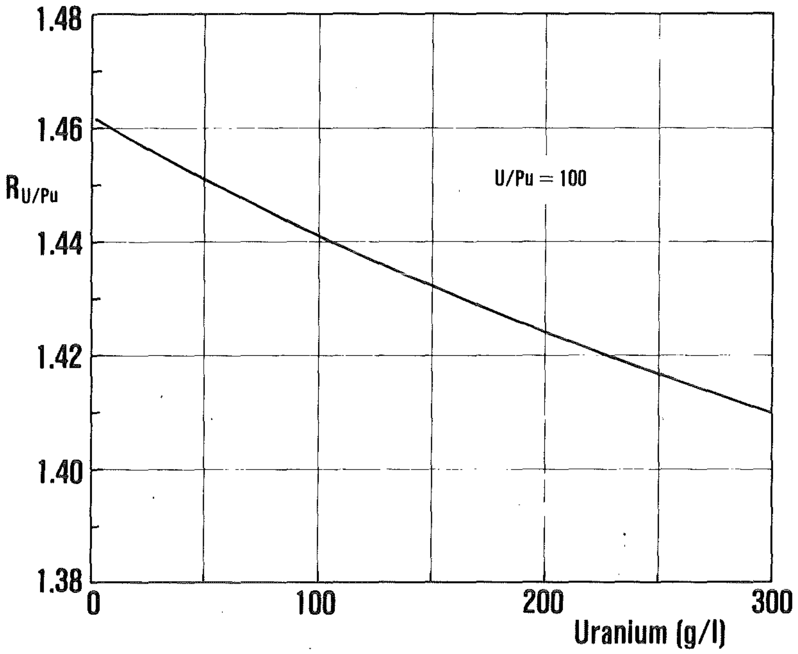

Fig. 20 Dependence of the XRF calibration factor $R_{U/Pu}$ for the U/Pu ratio measurement on the uranium concentration (assumed ratio U/Pu = 100).

It should be mentioned that the dependence of the calibration factor $R_{U/Pu}$ on the heavy element concentration as shown in Fig. 20 solely arises from the excitation process. The different self-attenuation of the fluoresced UKα_1 and PuKα_1 X-rays is automatically corrected for each measured XRF spectrum by the establishment of an overall relative detection efficiency curve using informations from the measured uranium K series X-rays.

From its physical meaning, the calibration factor $R_{U/Pu}$ will strongly depend, of course, on the applied tube voltage. This is shown in Fig. 21, which gives the expected ratio of excitation probabilities for emission of UKα_1 and PuKα_1 X-rays as a function of tube voltage. The curve has been calculated for the experimental conditions (beam filtration, sample size) in the Hybrid Instrument. Of practical importance is the differential change of $R_{U/Pu}$ at the adopted operating voltage of 150 kV, which is about 1.1 % per kV change. Based on the voltage stability

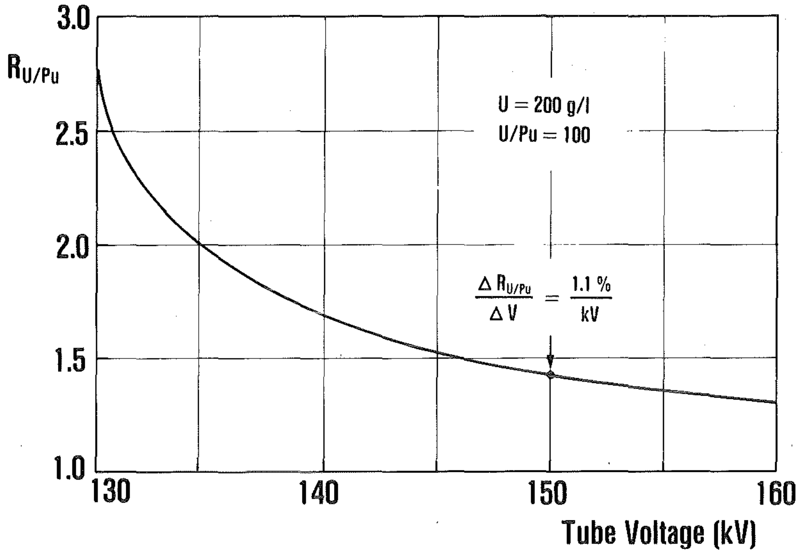

Fig. 21. Ratio of excitation probabilities for emission of $UK\alpha_1$ and $PuK\alpha_1$ X-rays as a function of tube voltage, calculated for the experimental conditions in the Hybrid Instrument.

of 0.1 % specified for the X-ray unit we then can assume, that the produced intensity ratio of $UK\alpha_1$ and $PuK\alpha_1$ X-rays, from which the U/Pu element ratio is derived, remains constant within 0.15 %. The actual effective tube voltage during the analysis is monitored within 0.1 kV from the endpoint of the measured X-ray continuum in the K-edge densitometry spectrum.

Demonstration on Real Input Solutions

Routine measurements with the Hybrid Instrument on real input solutions from the WAK reprocessing plant have been recently started, aiming at a thorough performance evaluation of the instrument from measurements on actual process solutions. During the hot testing period the instrument has so far demonstrated its operational simplicity for reliable and timely uranium and plutonium elemental assays in input solutions.

The quality of the measurements is estimated from comparisons with 3 independent IDMS analyses, performed on parallel samples from the same dissolver solution. At present, data are available from measurements on about 40 input samples. For these the average scatter (1σ) between the results from the Hybrid Instrument and the different IDMS analyses ranges between 0.4 and 0.7 % for uranium, and between 0.7 and 1.0 % for plutonium. This is well within the range of the estimated combined uncertainties of the two methods, and the values are similar to the spread observed among the different IDMS analyses. Outliers as occasionnally observed in the IDMS analyses have not been identified within the set of results obtained from the Hybrid Instrument during the first 6 months of operation.

The initial results indicate, however, an average positive bias of about 0.5 % for both uranium and plutonium between the nondestructive X-ray measurements in the Hybrid Instrument and the analysis results from IDMS. The origin of this bias has most probably to be ascribed to the problem of undissolved residues in the dissolver solutions, which will be - at least partly - covered by the nondestructive X-ray measurements, but not with the established procedure of the parallel IDMS analyses. This point is being further investigated in the continuing program for the performance evaluation of the Hybrid Instrument.

6. SUMMARY

The proposed analytical alternative for input-output accountability measurements in a reprocessing plant represents a purely nondestructive assay approach, based on energy-dispersive absorption edge and fluorescence X-ray spectrometry. These physical methods have demonstrated that they are able to measure, individually or in combination, very accurately and reliably the uranium and plutonium concentration in both the feed and product streams. The analysis results are achieved in a straightforward, economic and timely manner with:

- a minimum of sample handling;
- a direct measurement, eliminating any sample treatment procedures prior to the analysis;
- methods of analysis which neither depend on the chemistry of the samples nor on the nature of the element to be measured;
- a single instrument and a single reference method, namely K-absorption edge spectrometry, for both the uranium and plutonium input and output analysis;
- a high degree of automation, not requiring highly skilled personnel;
- only a fraction of the nuclear wastes generated with the conventional chemical methods.

It is emphasized that the increased operational simplicity is not gained at the expense of a corresponding loss of measurement performance. There are sufficient experimental data available, indicating comparative quality of the physical and the conventional chemical methods. This holds particularly when the 'true life situation' encountered in day-to-day routine analytics is considered. It is evident that the direct nondestructive measurements are less prone to human errors of the analyst, and that they also permit a more stringent control and assessment of measurement errors.

The technique of X-ray absorptiometry at the K-absorption edge has been realized in two different prototype instruments. One of these instruments, specially designed for uranium and plutonium analysis in reprocessing input solutions, couples this technique with the simultaneous spectrometry of fluoresced K X-rays ('Hybrid Instrument'). Both instruments have been subject of a thorough performance evaluation with actual reprocessing input and output solutions. Practical experiences and results from realistic applications have been presented and discussed.

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