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MONOCHROMATIC WAVELENGTH DISPERSIVE X-RAY FLUORESCENCE PROVIDING SENSITIVE AND SELECTIVE DETECTION OF URANIUM

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ABASTRACT

Monochromatic wavelength dispersive X-ray fluorescence (MWDXRF) is a sensitive and selective method for elemental compositional analyses.[1-3] The basis for this instrumental advance is the doubly curved crystal (DCC) optic. Previous work has demonstrated the feasibility of sensitive trace element detection for yttrium as a surrogate for curium in aqueous solutions.[1] Additional measurements have demonstrated similar sensitivity in several different matrix environments which attests to the selectivity of the DCC optic as well as the capabilities of the MWDXRF concept. The objective of this effort is to develop an improved Pu characterization method for nuclear fuel reprocessing plants. The MWDXRF prototype instrument is the second step in a multi-year effort to achieve an improved Pu assay. This work will describe a prototype MWDXRF instrument designed for uranium detection and characterization. The prototype consists of an X-ray tube with a rhodium anode and a DCC excitation optic incorporated into the source. The DCC optic passes the RhKα line at 20.214 keV for monochromatic excitation of the sample. The source is capable of 50 W power at 50 kV and 1.0 mA operation. The x-ray emission from the sample is collected by a DCC optic set at the ULα line of 13.613 keV. The collection optic transmits the ULα x-rays to the silicon drift detector. The x-ray source, sample, collection optic and detector are all mounted on motion controlled stages for the critical alignment of these components. The sensitivity and selectivity of the instrument is obtained through the monochromatic excitation and the monochromatic detection. The prototype instrument performance has a demonstrated for sensitivity for uranium detection of around 2 ppm at the current state of development. Further improvement in sensitivity is expected with more detailed alignment.

INTRODUCTION

Previous work has provided the background for improved Pu assay within nuclear reprocessing plants [1]. Both the feasibility and potential for highly sensitive and selective detection of actinide elements were demonstrated with a measured limit of detection of the Cm spectroscopic surrogate Y of 0.29 ppm at 14.96 keV [1, 2]. While the Y effort utilized a breadboard system, this work will highlight the capabilities of a research grade prototype instrument encompassing a 2 channel system for yttrium and uranium. The existing Y DCC optic at the Kα line of 14.96 keV was used with a new U DCC optic at the U Lα line of 13.61 keV.

The point of the current effort is to demonstrate MWDXRF capabilities on actinide elements for both selectivity and sensitivity. The objective is to elucidate the necessary hardware configuration to obtain the desired sensitivity for single digit ppm detection limits. The comparison of the Y Kα and the U Lα DCC collection optic performance will guide future efforts in developing this technology for improved safeguards measurements. This work reports on the preliminary efforts of the just built prototype instrument and initial measurements of selected model samples.

MWDXRF

The advantages of the MWDXRF method are highlighted in this work. The use of doubly curved crystals [3] is critical for attaining the desired sensitivity as well as spectroscopic selectivity which cannot be achieved with other x-ray optical arrangements. The MWDXRF method depends upon DCC optics for both excitation of the sample and collection of the emitted x-ray fluorescence. A single channel instrument consists of a point-focusing DCC excitation optic mounted directly on a low power x-ray tube. The DCC excitation optic creates a high flux, monochromatic x-ray source for exciting x-ray fluorescence from samples. The excitation spot is several hundred micrometers in diameter and depends upon the source spot size. The collection DCC optic is fixed at a specific energy collects the appropriate analyte x-ray emission and focuses it onto the detector. The energy resolution of the collection optic can range from +/-2 to over +/-100 eV depending upon the energy desired and the quality of the crystal.

EXPERIMENTAL

The excitation DCC optic has the following characteristics: crystal: Si<220>, geometry: Johann geometry, focusing energy: 20.2 keV (Rh-Kα1), source optic distance: 181.5 mm, solid angle: 1.2° x 51.2° flux with 50W source: 4x10e8, focal spot size: 190 µm x 250 µm, reflection efficiency: estimated 5%.

The Y collection DCC optic has the following characteristics: crystal: Si<220>, geometry: Johann geometry, focusing energy: 14.957 keV(Y-Kα1), sample optic distance: 172.7 mm, solid angle: 2.4° x 68°, focal spot size: on detector 400 x 500 µm, reflection efficiency: estimated 5%.

The uranium collection DCC optic has the following characteristics: Si<400>, geometry: log spiral, focusing energy: 13.61 keV (U-Lα1), sample optic distance: 146.4 mm, solid angle: 6.4° x 104°, focal spot size: on detector 1008 x 1350 µm, reflection efficiency: estimated 2%

The assembled MWDXRF prototype system consisted of an XOS X-beam Rh 50 W X-ray tube (East Greenbush, NY) operated at 50 kV and 1 mA equipped with the excitation DCC noted above as the X-ray source. The X-ray tube was controlled with a XOS PCS50 power control system connected via an Ethernet connection to the PC. The detector was a Vortex-EX Si drift detector (SII

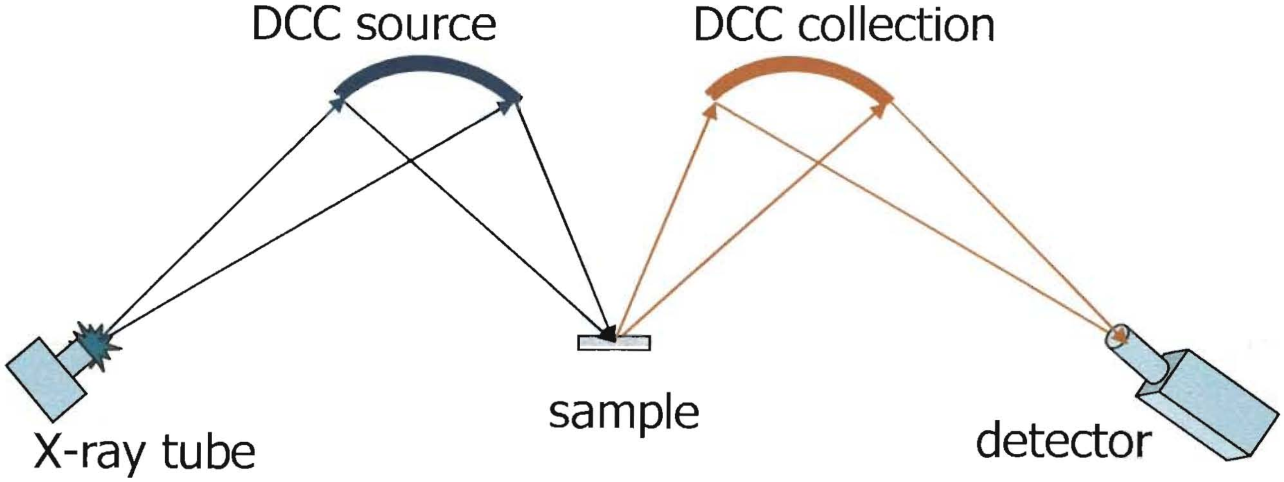

Figure 1. Schematic diagram of a single channel MWDXRF prototype setup.

NanoTechnology Inc., Chuo-ku Tokyo, Japan) with a 50 mm^2 detector area and a 300 μm thick Si layer. A schematic of a single channel of the experimental setup is shown in Figure 1. The source, source DCC optic, sample, DCC collection optic and detector were all mounted on translation stages (Newport model URS100BCC (Rotation), and 443 Series, Newport Corporation, Irvine, CA) along with Newport actuators TRA25CC. The stages allowed precise alignment of the components. The stages were controlled with a Newport XPS 8 channel motion controller via an Ethernet interface connected to a PC. Data collection from the Vortex detector was done using the vendor supplied software via USB connection.

The samples were prepared by depositing different volumes of droplets of aqueous solutions onto polypropylene films (4 μm thick, Ultralene, Chemplex Industries, Palm City, FL). The known concentration of the solution along with the volume deposited, provides the total mass of the analyte in the deposit. The stock solutions 10 mg/mL (unless otherwise noted in the text) were obtained from High Purity Standards (Charleston, SC).

RESULTS

The monochromatic excitation provides several advantages as noted previously [1]. The increased x-ray photon flux at the monochromatic excitation energy of 20.2 keV provides a relatively clean spectroscopic excitation source. This reduces the background and increases the signal to noise ratio improving the sensitivity of the XRF analysis. A more detailed comparison of monochromatic vs. Bremsstrahlung excitation will be discussed later.

The spectrum of a 1 microliter, 1000 ppm U solution deposit on polypropylene is shown in Figure 2. Since this is preliminary data, the detector is not yet equipped with an aperture to restrict scatter, therefore a small iron peak around 6.4 keV and the tube Compton scatter between 18-20 keV is visible. We obtained a calculated limit of detection of 1.7 ppm U for a collection time of 100 Lsec,

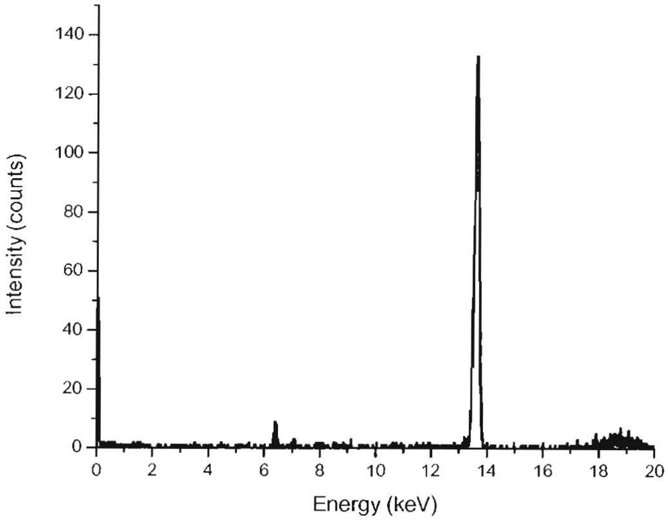

Figure 2. Spectrum of 1 microliter deposit of 1000 ppm U with 100 Lsec acquisition collected with prototype MWDXRF.

based on the integrated peak intensity of the U Lα line at 13.61 keV of 2,543 counts. The nominal integrated background intensity collected for 100 Lsec was only 2 counts. The 1.7 ppm detection limit exceeds our MWDXRF target of 10 ppm by a factor of 6. It should be noted that the excitation spot size is only ~200 micrometers in diameter, while the deposit measures ~600 micrometers in diameter. The total mass of U in the nominal 600 micrometer diameter deposit is 1 microgram. The difference between the excitation area and the deposit area is over a factor of 10^2. Hence, assuming a uniform deposition, which we know is not correct from mapping the U distribution in the deposit, a sub-ppm detection limit appears to be assured.

A two channel system is demonstrated in Figure 3. A deposit of 1 microliter each of 10k ppm uranium and yttrium solutions was prepared. The difference in intensity between the U and Y is an indication that the deposit is not uniform. Each spectrum was collected for 100 Lsec separately and overlaid to give the composite figure. The fact the deposit is not uniform was confirmed with elemental maps. The actual deposit is not circular and has a significant tail. The deposition area is larger than the 1k ppm deposit for the uranium in Figure 2.

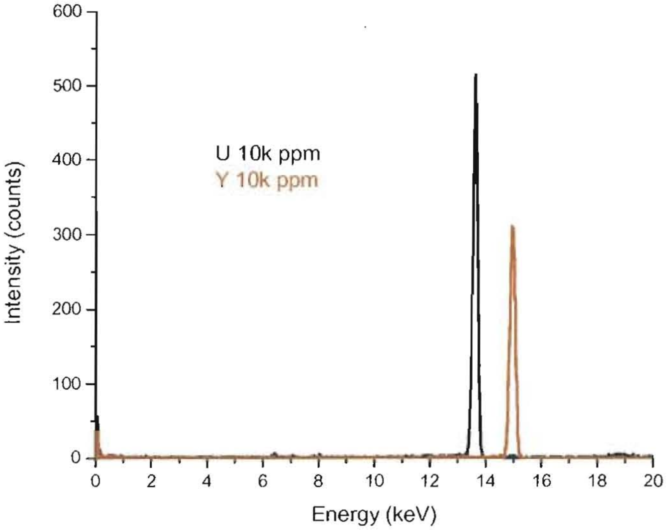

Figure 3. Composite overlay of 2 channel detection of Y and U deposits, 1 microliter each of 10k ppm, with prototype MWDXRF.

In order to demonstrate the selectivity of the MWDXRF instrument, one microliter each of 10k ppm aqueous U and Y was deposited onto a deposit of NIST SRM 2704, Buffalo River Sediment. This spiked sample simulates a high mass dried solids deposit which would be expected of a reprocessing deposit. Such a deposit would exhibit a high background from the low Z elements present along with low levels of elements around the energy range of interest. Table 1, lists the elements present along with the concentrations. It is clear from Table 1. there are significant concentrations of low Z elements which would generate a significant background. A comparison of the monochromatic excitation of the spiked SRM2704 and the Bremsstrahlung excitation from a polycapillary optic is shown in Figure 4 along with the MWDXRF spectrum of uranium in the spiked sample. It is clear that the monochromatic excitation results in a significantly lower background. While the MWDXRF spectrum shows an even cleaner background, showing only the scatter (noted earlier) which would be eliminated with an aperture on the detector. The overlay of the 3 different spectra in Figure 4 clearly shows the advantage of using MWDXRF for actinide detection. The sensitivity of the detection is calculated to be in the single digit ppm level since the U deposit in not uniform. The elemental maps shown in Figure 5 of the 2704 Buffalo River Sediment spiked deposit clearly delineates heterogeneity both the SRM deposit as well as the aqueous spike samples. The aqueous U and Y spikes dried almost circular, while the SRM was slightly tear shaped to the right. The Y was mainly on the left of the deposit while the U appears to be concentrated around the perimeter.

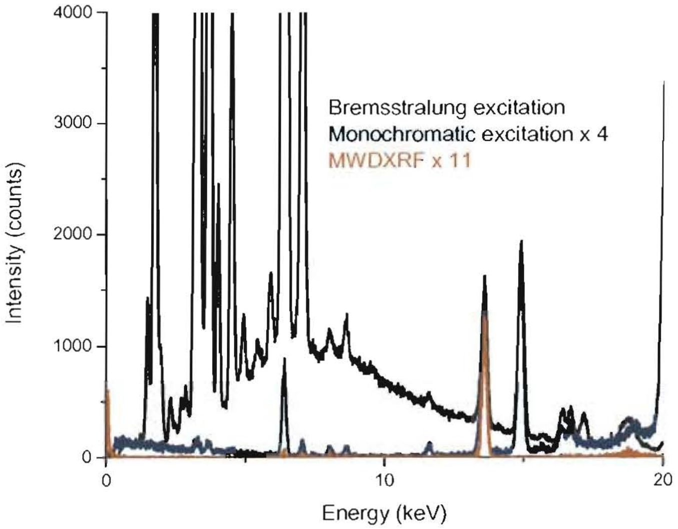

Figure 4. Overlay of spectra for NIST SRM 2704 spiked deposit with 1 microliter of 10k ppm aqueous U and Y solutions. (Black trace) Bremsstrahlung excitation, (blue) monochromatic excitation and (red) MWDXRF monochromatic excitation and DCC detection.

Element	Concentration (wt%)	Element	Concentration (μg/g)
Al	6.11	Ba	414
Ca	2.60	Cr	135
C	3.348	Cu	98.6
Fe	4.11	Pb	161
Mg	1.20	Mn	555
K	2.00	Zn	438
Si	29.08	Rb	100
Na	0.547	Sr	130
Ti	0.457	Zr	300

Table 1. Elemental concentrations of selected elements in NISTS SRM 2704 Buffalo River Sediment.

CONCLUSIONS

The MWDXRF prototype is operational for 2 channel data acquisition. The 2 channel operation is not simultaneous at this time. The 2 channels available at this time are uranium and yttrium. Both have calculated limits of detection around 2 ppm for a dried aqueous deposit of 10k ppm. This detection limit is below our target of 10 ppm. The selectivity and sensitivity have been demonstrated by spiking a NIST SRM to mimic the high mass dried solids of a reprocessing solution. Since the deposits are known to be heterogeneous we expect to achieve sub-ppm sensitivity for U with improvements in alignment and droplet deposition. We expect to achieve similar detection limits for Pu, which will allow the direct determination of Pu in reprocessing solutions and provide more accurate measurements of Pu concentrations for safeguards efforts.

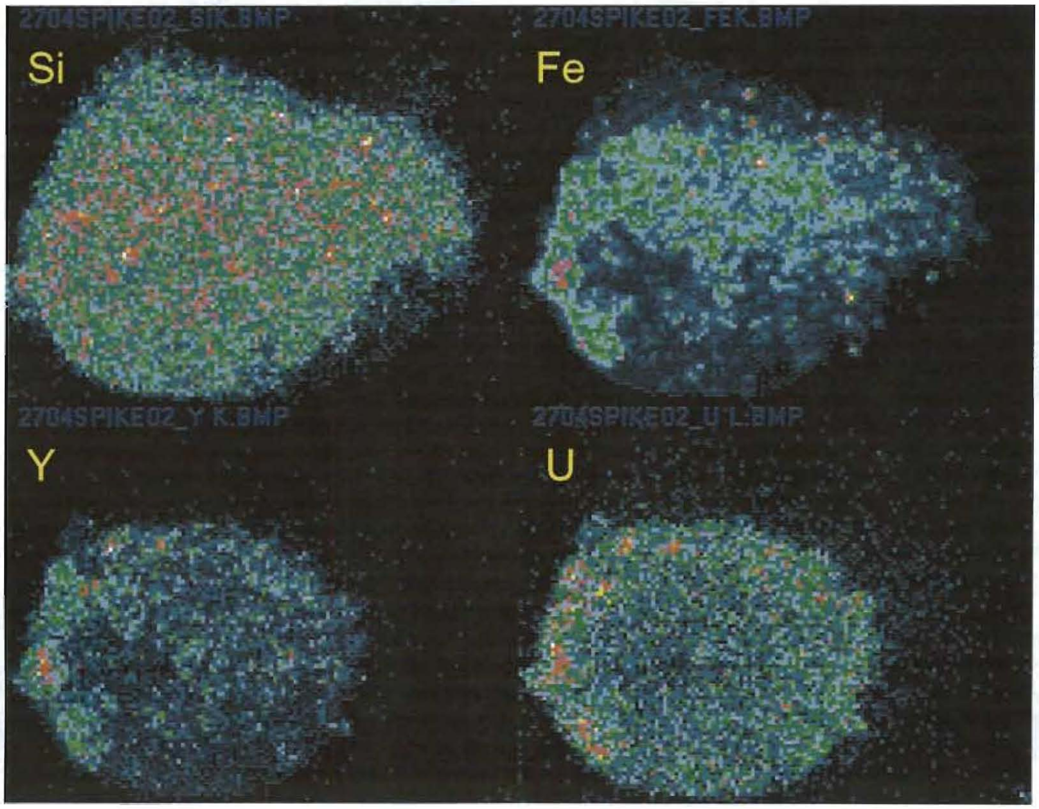

Figure 5. Elemental maps of NIST SRM 2704 spiked deposit showing distribution of the SRM elements Si and Fe and the spike elements U and Y.

The next step in with this prototype instrument is the addition of a thorium collection optic to simulate the detection of Pu and Cm concentrations in actual reprocessing solutions.

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REFERENCES

1. Improved Pu Assay Using A Novel Monochromatic Wavelength Dispersive X-Ray Fluorescence Instrument, George J. Havrilla, Michael Collins, Velma Montoya, Zewu Chen and Fuzhong Wei, INMM 50th Annual Meeting Proceedings, 2009.
2. Detection Limits for Actinides in a Monochromatic, Wavelength-Dispersive X-Ray Fluorescence Instrument, Michael Collins, George J. Havrilla, , INMM 50th Annual Meeting Proceedings, 2009.
3. Doubly Curved Crystal (DCC) X-ray Optics and Applications, Zewu Chen and Walter M. Gibson, Powder Diffraction, 2002, 17, 99-103.