URANIUM ISOTOPE RATIO MEASUREMENTS IN FIELD SETTINGS

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ABSTRACT

We have developed a technique for uranium isotope ratio measurements of powder samples in field settings. Such a method will be invaluable for environmental studies, radioactive waste operations, and decommissioning and decontamination operations. Immediate field data can help guide an ongoing sampling campaign. The measurement encompasses glow discharge sputtering from pressed sample hollow cathodes, high resolution laser spectroscopy using conveniently tunable diode lasers, and optogalvanic detection. At 10% ^{235}U enrichment and above, the measurement precision for $^{235}U/(^{235}U+^{238}U)$ isotope ratios was $\pm 3\%$; it declined to $\pm 15\%$ for 0.3% (i.e., depleted) samples. A prototype instrument was constructed and is described.

Measurement scenario

Conventional methods for measuring isotope ratios are seldom amenable to field use. They can be difficult and time consuming, involving sample dissolution, filament loading (for thermal ionization mass spectrometry), and ion count logging and interpretation. These laboratory techniques are sensitive, amenable to a suite of interesting analytes, and can provide isotope ratios at a precision of $\pm 0.1\%$ or better. However, laboratory-based mass spectrometry is expensive, requires highly skilled operators, and often results in a substantial time delay before learning the results. A sampling campaign would be greatly expedited if on-the-spot analyses were possible, even if the measurements made were only at modest precision ($\pm 10\%$). Samples with unusual enrichments discovered by this means would allow the sampling to be concentrated on interesting locations. The interesting samples could be forwarded to a laboratory for more precise analysis.

Measurement technique

We have demonstrated a simple technique, glow discharge optogalvanic spectroscopy,[1,2,3] for use in instances where only modest accuracy and precision are required. With this method isotopic abundances are determined using high resolution optical spectroscopy instead of spatial or temporal separation of the masses. Sampling is accomplished without dissolution or any other pretreatment; sample powders are pressed with a conducting binder to form hollow cathodes. These are sputtered in a low pressure argon dc glow discharge to produce analyte atoms in the gas phase. Only modest vacuum conditions are required, as the operating pressure is approximately 1000 Pa (i.e., a few Torr). The optogalvanic effect is used to quantify the isotopic abundances. As the wavelength of a single longitudinal mode laser is tuned through absorption features of the discharge gas, optical energy is deposited; this results in a change in the ionization equilibrium of the plasma, that is detected as a discharge impedance change. The laser beam is modulated using a mechanical chopper, and impedance changes are measured using a lock-in amplifier that processes the ac component of the cathode voltage. Integration of the areas under the resolved spectral signatures of the isotopes yields the abundances. Use of the optogalvanic technique for isotope

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ratio determinations has been considered in the past by others.[4,5,6] The aspect that affords practicality to the method described here is that a semiconductor diode laser can be employed as the source. Diode lasers are rugged, and their output wavelength is conveniently tuned by varying the device temperature and/or the drive current.[7]

Figure 1 illustrates a uranium line (776.2 nm) that exhibits an isotope spectral shift sufficiently large for facile determination of isotope ratios. The observed linewidth is Doppler limited and is generally < 1 GHz full width at half maximum (FWHM). The sample was depleted uranium metal (0.3% ^{235}U), corresponding to the lowest abundance expected for field measurements. The signatures corresponding to ^{235}U and ^{238}U are fully resolved. Other uranium lines with smaller isotope shifts (< 1 GHz) are less desirable because of spectral overlap of the isotope features. Since the isotope shift for this line is large, the ^{235}U signal can be measured unambiguously. The laser used for this particular spectrum was a titanium:sapphire laser, but was attenuated to an output power of 30 mW to simulate the robust tunable diode lasers to be employed for field measurements. At the position indicated in the figure, the measurement sensitivity was increased ten-fold. The signatures shown that correspond to ^{235}U and ^{238}U are distinct and separated. By integrating the signal areas, we found the $^{235}U/(^{235}U+^{238}U)$ ratio to be 0.0034. A benchmark ratio for this sample measured using thermal ionization mass spectrometry was 0.0027.

Measurement Accuracy and Precision:

To evaluate the utility of optogalvanic spectroscopy for uranium isotope ratio measurements, four cathodes (fabricated from a ^{235}U enriched oxide powder, a ^{235}U enriched metal, a natural metal powder, and a ^{235}U depleted fluoride powder) were prepared. By choosing four different isotopic compositions and three different uranium compounds, samples were addressed with a wide variety of characteristics.

Figure 2 shows a calibration curve developed from data recorded using the 776.2 nm uranium line. The measured $^{235}U/(^{235}U + ^{238}U)$ values are plotted versus either certified values or versus thermal ionization mass spectrometric values. Eleven isotope ratio measurements were made for each cathode. The error bars correspond to $\pm1\sigma$ relative standard deviation. The data show a good linear fit with an R value of 0.99986 for a line with slope 1.019 and y-intercept 0.0018. For the four samples analyzed, the percent relative error with respect to the thermal ionization measurements ranged from 2.38% for the nominally 20% enriched ^{235}U sample where the ^{235}U signal-to-noise ratio was > 500 to 1, to greater than 30% error for the natural and depleted samples where the signal-to-noise ratio was < 5 to 1. The use of a more powerful laser diode (42 mW) operating at 831.8 nm, resulted in an improved accuracy (3.7%) and precision (8%) for a depleted uranium metal powder sample. This is the direct result of the more powerful diode laser and the stronger optogalvanic transition.

Run-to-run, day-to-day and sample-to-sample precision (repeatability) were also evaluated using a 20% enriched sample. Seventy-seven $^{235}U/(^{235}U + ^{238}U)$ determinations were made over 7 days with 3 different sample cathodes. Each measurement was the average of eleven $^{235}U/(^{235}U + ^{238}U)$ ratios. The run-to-run precision (1σ for n=11) ranged from $\pm1.9\%$ to $\pm5.5\%$ over five consecutive days. Sample-to-sample precision (three different cathodes) was $\pm3.5\%$ RSD. The ratios show no trends or biases, varying about a mean of 0.21.

Discharge conditioning and sample matrix effects

A strong dependence of the optogalvanic signal strength on the quality of the discharge was noted, most likely due to the presence of water and other gaseous impurities. To improve the signal, several measures were taken: a feed gas purification cartridge, a discharge cell non-evaporable getter, and tantalum metal (a gas phase getter) incorporated into pressed sample cathodes. All of these methods improved the optogalvanic signal strength to a certain degree.

The effect of adding contaminants to the uranium sample on the optogalvanic isotope analysis was examined by recording optogalvanic spectra for samples to which soil had been added. Samples containing 1:1:1:1 by weight U_3O_8 (3% 235U):soil:silver:tantalum were prepared and examined. The soil used was a NIST standard reference material (dried Buffalo river sediment, SRM No. 2704). The optogalvanic signal recorded for these samples was approximately 5- to 10-fold weaker, relative to a comparable U_3O_8/Ag/Ta sample. Thus, the precision observed for the isotope ratio measurement was ±15%. That precision is comparable to the precision observed for measurement of pristine, depleted uranium samples. Thus, soil added to the sample did indeed degrade the measurement.

Prototype instrument

Based on the successes of our laboratory measurements, a van-portable prototype instrument was designed and assembled (Figure 3). The availability of standard 115 volt AC power has been assumed for this initial prototype. The prototype instrument weight and power consumption are approximately 98 kg and 655 Watts, respectively.

The prototype instrument was tested by determining a uranium isotope ratio for an enriched uranium oxide (20% 235U) in a silver/tantalum binder sample cathode . A single scan of the spectrum was recorded under computer control, along with signals from the instrument's wavelength monitor that assures the operating wavelength. The measured 235U/(235U+238U) ratio was 19.0%, in excellent agreement (5.0% error) with the true value. No multiple-scan signal averaging was required to obtain this ratio. For a set of three consecutive scans, the measured precision was ±10%.

Summary

We have developed a technique and instrument for uranium isotope ratio determinations in field settings. Such a technique will be invaluable for on-site analyses during DD&R operations. The method encompasses glow discharge sputtering from pressed sample hollow cathodes, high resolution laser spectroscopy using conveniently tunable diode lasers, and optogalvanic detection. Using this technique, analytical figures of merit were determined for 235U/(235U+238U) isotope ratio measurements for uranium samples with enrichments as low as "depleted" (0.3% 235U). A prototype instrument was constructed. This instrument can be transported in a van to remote locations. It currently requires 115 V line power, but could easily be adapted to fully remote use with the addition of a battery or generator power source. The prototype instrument was successfully tested by analyzing an enriched uranium oxide sample. Further development will center on reducing the sample size required for this measurement.

References

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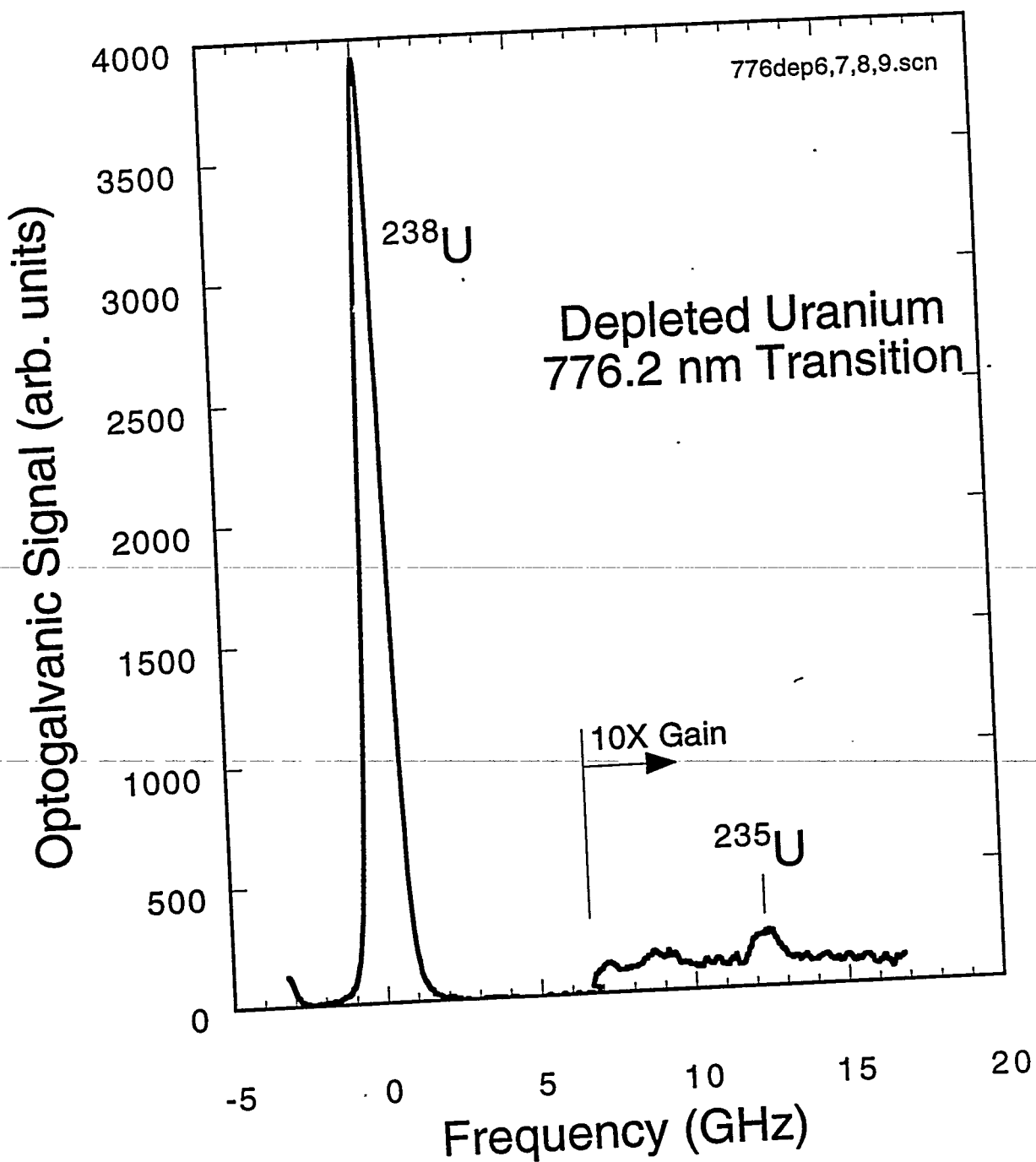
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Figure Captions:

Figure 1. Averaged optogalvanic signal for 3 spectral scans near 776 nm for a depleted (0.3% ^{235}U) uranium metal/silver sample cathode. The detection gain was increased 10-fold at the indicated position.

Figure 2. The measured ^{235}U / (^{235}U + ^{238}U) ratio versus the reference value (certified value or thermal ionization mass spectrometric measurement) for four uranium compounds and enrichments.

Figure 3. Photograph of the prototype instrument for isotope ratio measurements.

Figure 1.
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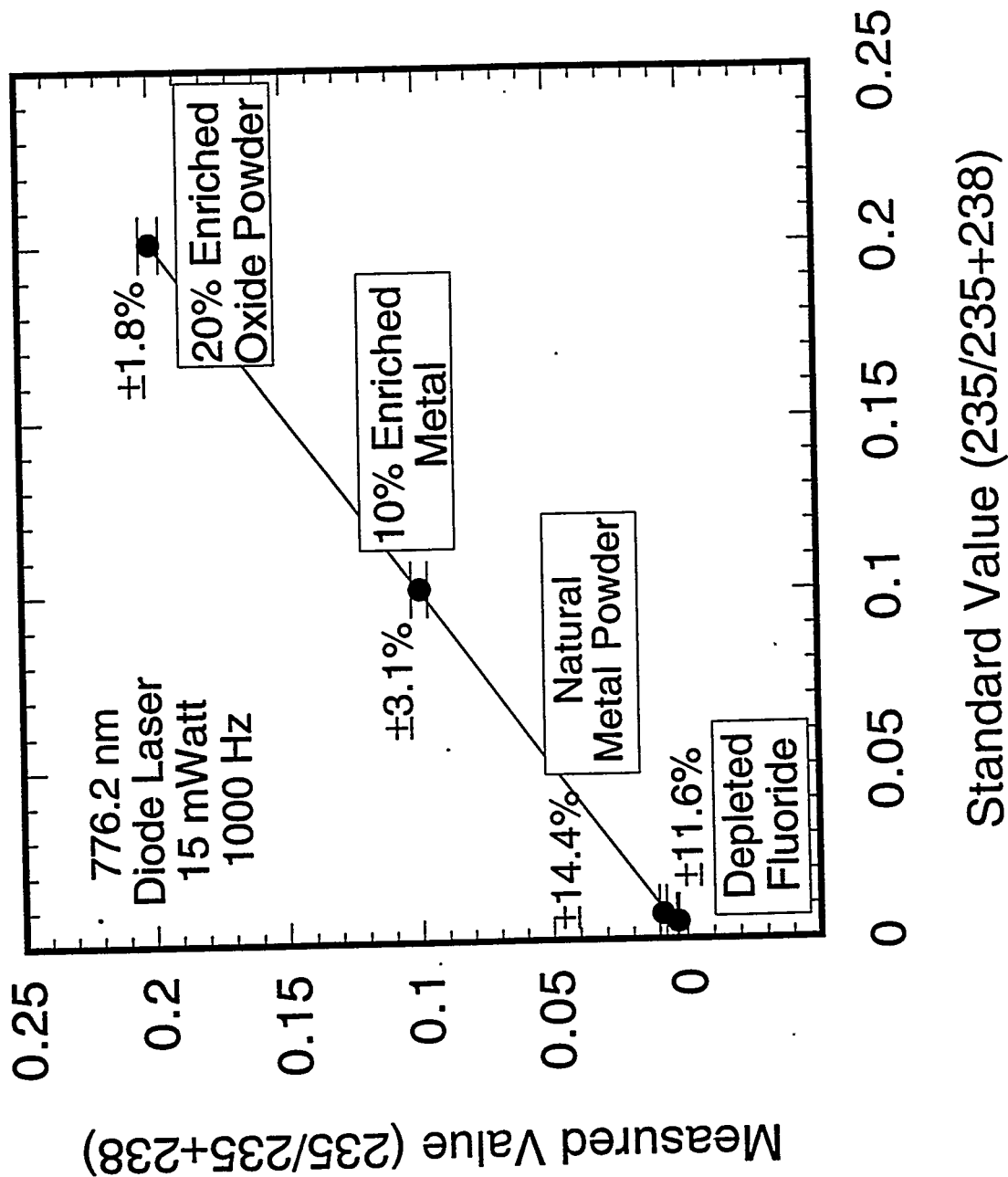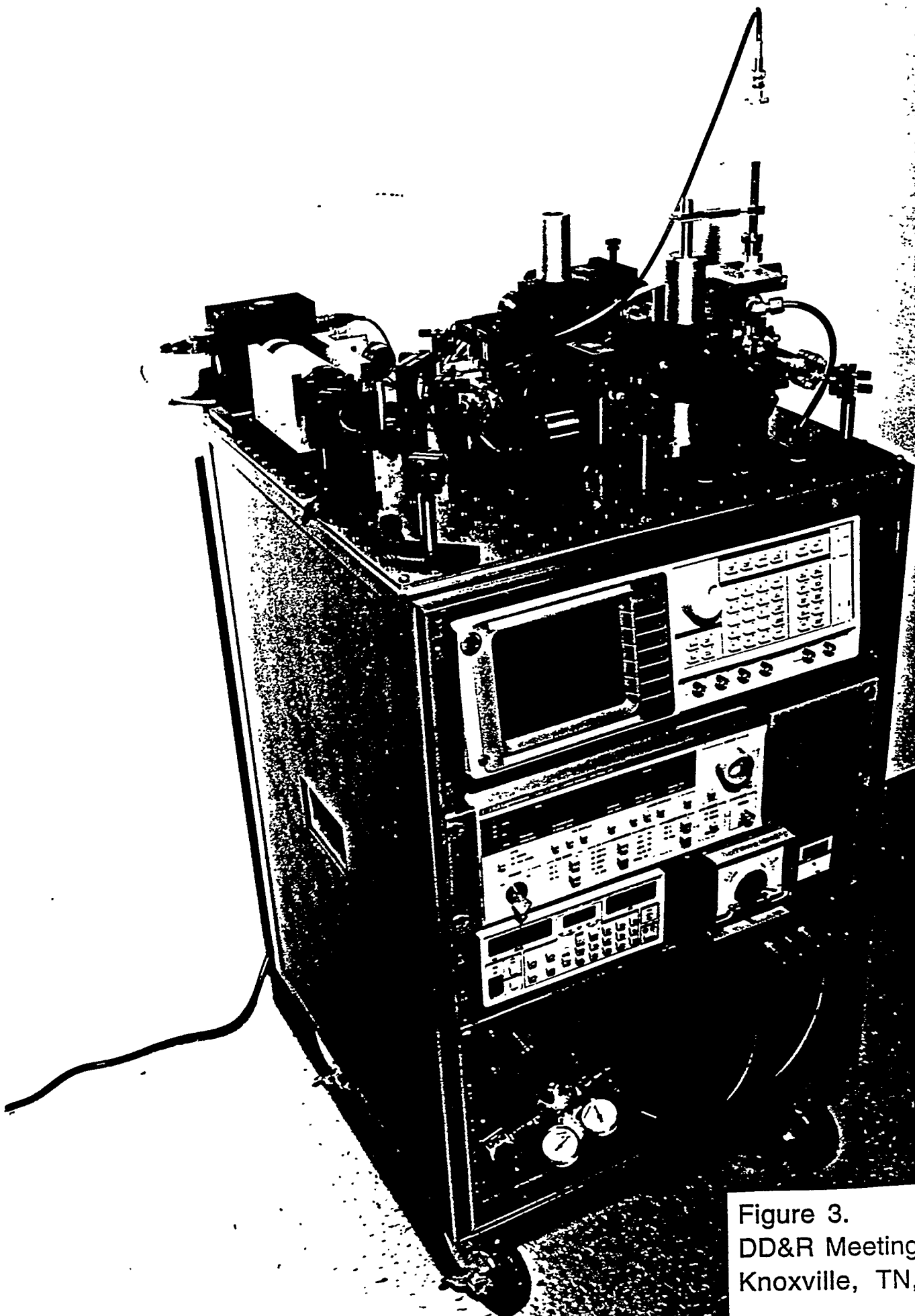Uranium Isotopic Measurement: Linearity and Precision

Figure 2.
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Figure 3.
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