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Development of Laser-Based Resonance Ionization Techniques for 81-Kr and 85-Kr Measurements in the Geosciences, II

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Table of Contents

Summary

The establishment of a facility for measurement of rare ^{81}Kr and ^{85}Kr isotope concentration in hydrogeologic samples, and isotopic composition of minute quantities of krypton and xenon from extraterrestrial samples, is described. This required development and refinement of an emerging mass spectrometric-based analytical technique, securing of laboratory space and equipment, and development of complementary funding sources to support the work.

The analytical process consists of (1) collecting the groundwater sample, (2) degassing the water sample, (3) separating Kr from the recovered gases, (4) isotopic enrichment to reduce interfering isotopes by 10^5, (5) a second isotopic enrichment of 10^4, and (6) detecting the rare krypton isotope in a time-of-flight mass spectrometer. All equipment is installed and operating at the Institute for Rare Isotope Measurements that was established at the University of Tennessee, with only some additional adjustment and testing of the last step (6, above) remaining to be completed.

Collaborations have been established with a number of researchers and organizations world-wide. A researcher from abroad has already spent a year at the facility, while another from the US, is planning to arrive in May for the remainder of 2001. Groundwater samples have been collected from a number of carefully chosen settings and been partially processed, which once measured, will verify that reliable age-determinations are possible with this technique. Extraterrestrial samples are in-hand, awaiting analysis once background levels in the new system improve. The facility is entering its next phase with preparation and submission of funding requests whose emphasis shifts from instrumentation development towards answering questions using analytical capabilities that were previously unavailable.

A total of twelve students, six graduate and six undergraduates were involved in the work. The diversity of the equipment developed, and the broad range of research fields addressed by the inter-disciplinary nature of the applications possible with the increased analytical sensitivity, has provided them with an unusually rich learning experience. This includes both developing a variety of laboratory skills, and gaining an understanding of current research problems in a number of fields.

Introduction

The emerging analytical technique based on "Resonance Ionization" has demonstrated the potential of lowering detection limits to the few-atom level. The methodology is technically very challenging, and as no commercial instrumentation is available, only a handful of laboratories world-wide practice it. The purpose of the research reported herein was to develop and refine the instrumentation, and to provide the facilities, to measure small quantities (i.e., few thousand, or less, atoms) of the very rare ^{81}Kr and ^{85}Kr isotopes, and isotopic abundance of the major krypton isotopes, again, at the few thousand, or less, atom level. The capability of making such measurements is not available anywhere else, and if successful, could provide dramatic new research capabilities in the fields of hydrogeology, glaciology and planetary sciences, to name a few.

For example, in hydrogeologic studies of young (<50 a) aquifers, environmental tracers, such as ^{3}H and CFCs, which are present in the atmosphere, and hence in precipitation, travel downwards with the infiltrating groundwater. If the "age" of the water at several different depths below the water table can be determined, then important hydrogeologic parameters, such as recharge rate and potential for pollution intrusion, can be directly calculated. Environmental tracers can be used to determine the average downward flow rate in the aquifer, so the effects of variability in hydraulic conductivity and gradient are effectively integrated in the measurement of groundwater age. Hence, these methods are well suited for use in heterogeneous settings.

However, measurements based on these tracers are problematic because of a variety of factors related to either historic variations of their concentration in the atmosphere (in the case of ^{3}H), or biogeochemical reactions in the subsurface (in the case of CFCs). As a result, recharge rate measurements based on these methods contain a lot of uncertainty, or require detailed hydrogeochemical studies utilizing nests of many wells installed at different depths.

What is needed is an environmental tracer that can provide an accurate groundwater "age" utilizing samples from a single well, or at most, a pair of wells. Characteristics of an ideal groundwater tracer are: 1) its input concentration history should be known and not sensitive to local or seasonal variation; 2) it should be non-degradable or should decay at a known rate; 3) it should be unaffected by interaction with the aquifer and have no subsurface sources; 4) collection and analysis of samples should be practical, and 5) interpretation of results should be simple and unambiguous. With a tracer meeting the above criteria, it would become economically feasible to map recharge rates over large areas, preferably using existing wells, so that variations in recharge rates could be explicitly included in water balance and aquifer utilization models.

At 1.14 ppm, krypton is a trace constituent of the earth's atmosphere. Two of its radioactive isotopes, cosmogenic ^{81}Kr (231 ka half-life, 10^{-13} isotopic abundance) and anthropogenic ^{85}Kr (10.8 a half-life, 10^{-11} isotopic abundance) have long been considered potentially ideal environmental tracers, but have seen almost no use because no practical analytical methodology was available.

The half-life of Kr-81 is much greater than any known geomagnetic cycles that could modulate cosmic-ray intensities, and hence, atmospheric production rates. That, together with the atmosphere being by far the largest reservoir of Kr on earth, with no significant sources or sinks, implies that the concentration of Kr-81 should be constant over very long time periods. In addition, no mechanisms for underground production, nor any anthropogenic sources, have been identified (Lehmann et al., 1993). The 20,000 to 1,000,000 year age-dating range of krypton-81 is a very good match to studies of very old ground water, important in site-selection of hazardous-waste repositories, and of polar ice, important in evaluating long-range climate changes. Finally, it is anticipated that Kr-81 "ages" will not require the many corrections that are necessary in the interpretation of ^{36}Cl, ^{234}U/^{238}U or ^{4}He ages (Froelich et al., 1991). Therefore, hydrogeologists have for many years considered Kr-81 a "perfect" tracer for this time interval.

Because there are less than 1,200 Kr-81 atoms in a one-liter modern groundwater sample, decay-counting methods are a practical impossibility. (In principle, $>10^7$ liters of water would be required.) Therefore, a method had to be developed to count the Kr-81 atoms directly. Tandem-Accelerator Mass Spectrometry (AMS) cannot be used because krypton does not form negative ions. It wasn't until the development of *R*esonance *I*onization *S*pectroscopy, (RIS) a concept that in principle could detect a single atom of one element in an extremely large background of other elements and molecules, that serious consideration was given to utilizing some of the rare atmospheric constituents, such as Kr-81, in earth and planetary science research. The pioneering work on RIS was done in the early 1970s by groups lead by G.S. Hurst at the Oak Ridge National Laboratory (Hurst et al., 1975; Payne et al., 1975) and V.S. Letokhov at the Institute of Spectroscopy (Ambartzumian and Letokhov, 1972) of the Russian Academy of Sciences. The key to RIS is the use of tunable lasers to selectively and efficiently excite by resonant photon absorption atomic states unique to the chosen element. Ionization of the specified element can then occur at the exclusion of all other constituents of the sample, bringing detection limits down to the single-atom level (Hurst et al., 1977). A review by Payne et al. (1994) provides a useful overview of both theory and experimental aspects of resonance ionization, as applied to mass spectrometry.

Combining RIS with several steps of isotopic enrichment made detection of a rare isotope, such as Kr-81, feasible. The first-ever quantitative measurement of Kr-81 from a ground water sample (Thonnard, et al., 1987; Lehmann, et al., 1991) was made using the method conceived at Oak Ridge National Laboratory (Hurst, et al., 1985; Lehmann, et al., 1985) and put into practice at Atom Sciences, Inc. (Willis et al., 1989) The ground water measurements were followed by the first-ever age determination of ancient ice using Kr-81. (Craig, et al., 1990) These measurements started with 40 liters of water, and 70 kg of ice, respectively, and ended with counting the few thousand remaining Kr-81 atoms using RIS. This is the basis for the method that has been developed further at the Institute for Rare Isotope Measurements (IRIM) of the University of Tennessee, (Thonnard and Lehmann, 1995) with refinements to make the process more reliable for applications in the earth and planetary sciences. Recently, Kr-81 was measured with a Cyclotron-based AMS technique (Collon, et al., 1999) in four samples from the Great Artesian Aquifer in Australia (Collon, et al., 2000) but the efficiency is so low that 16,000 liters of water had to be processed for each measurement. It is not yet clear if the efficiency can be increased to bring sample-size requirements in par with the approach being pursued at IRIM.

Similarly, krypton-85 has great potential for use as a young (0.1 to 40 year age-dating range) groundwater tracer. It is not affected by many of the factors (declining source concentration, reaction with soil or groundwater, temperature-dependence) that limit the present or future usefulness of tritium or CFCs. (See Table 1.) In contrast to tritium, the monotonic increase of Kr-85 in the atmosphere since 1950, due principally to reprocessing of nuclear fuel, results in a direct relationship between measured Kr-85 concentration and age, (Figure 1., Smethie, et al., 1992) hence a single measurement represents a unique age. As krypton measurements result in the *isotopic ratio* of Kr-85 to the stable krypton isotopes in the sample, changes in solubility and recovery or processing losses cancel and do

TABLE 1

Comparison of ^{85}Kr, ^{3}H and CFCs to an "Ideal" Groundwater Tracer:

Its atmospheric concentration history should be known and not extremely variable		
^{85}Kr (++)	^{3}H (—)	CFCs (++)
It should be non-degradable or should decay at a known rate		
^{85}Kr (++)	^{3}H (++)	CFCs(—)
It should not interact with the aquifer and have no surface or subsurface sources		
^{85}Kr (++)	^{3}H (+)	CFCs (—)
Collection and analysis of samples should be practical		
^{85}Kr (— to 0)	^{3}H (++)	CFCs (++)
Interpretation of results should be simple and unambiguous		
^{85}Kr (++)	^{3}H (—)	CFCs (—)

Legend

(++) = VG
(+) = G
(0) = Ave
(-) = P
(—) = VP

Adapted from McMaster et al. (1995).

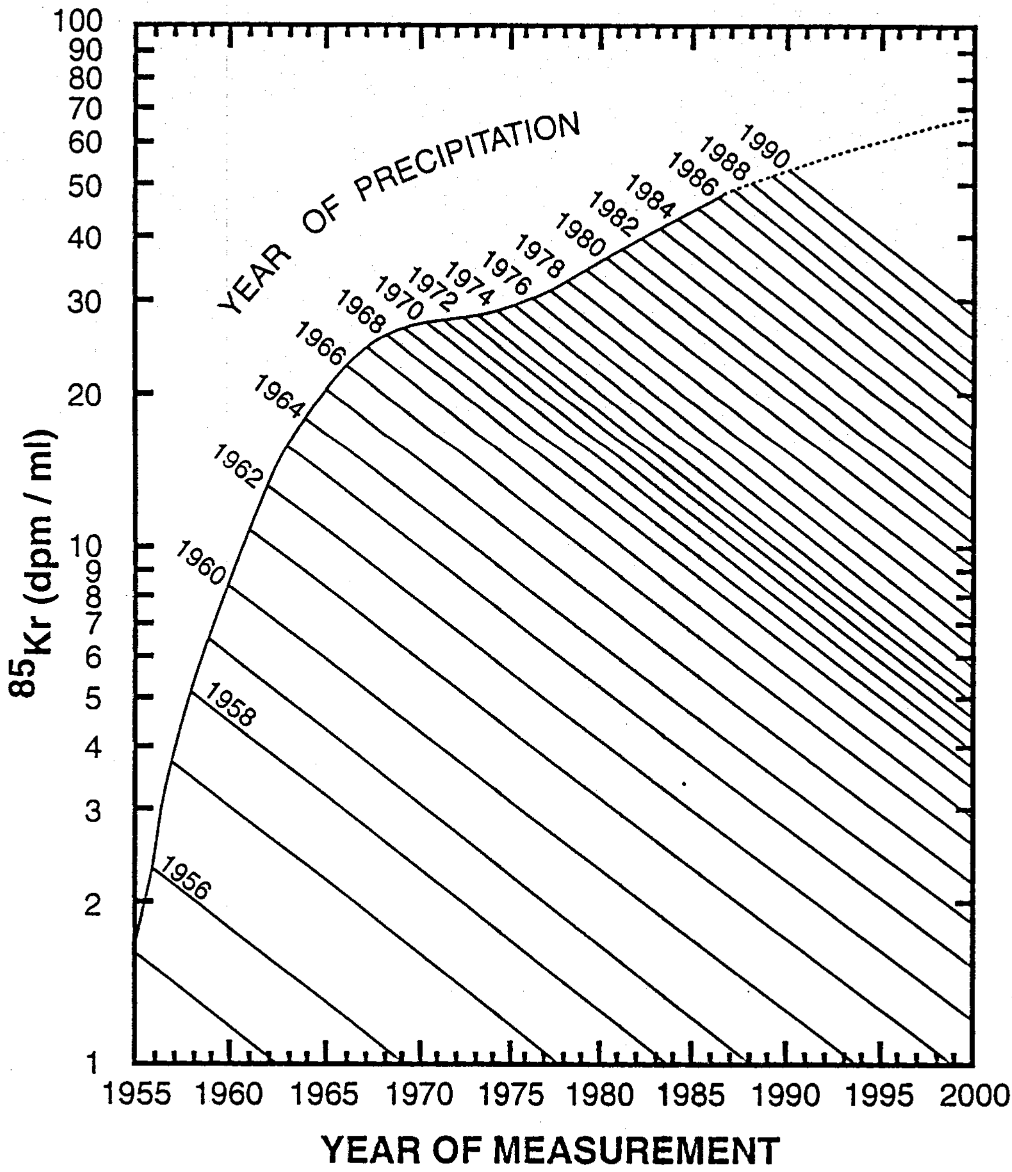


Figure 1. The atmospheric krypton-85 activity, in disintegrations per minute per ml Kr, has been rising continuously since the beginning of the nuclear age. Combining this with the decay of Kr-85, (represented by straight lines in this semi-logarithmic plot) results in a unique date of isolation from the atmosphere being assignable to the Kr-85 concentration measurement from a single groundwater sample. (Adapted from Smethie, et al., 1992)

not affect the accuracy of the measurement. Therefore, for the applications discussed above, Kr-85 has a substantial advantage over other methods because a reliable, non-ambiguous groundwater "age" can be determined from a single groundwater sample, often taken from an existing well.

The principal impediment to the widespread use of Kr-85 has been the difficulty in carrying out analyses, and the relative lack of well-documented field applications of this method. Until recently, the only available analytical method was decay counting, and because of the low atmospheric concentration, required 120 to 250 liter water samples and low-level counting for up to a week (Rozanski and Florkowski, 1979; Smethie, et al., 1992; Ekwurzel,et al., 1994). The development by the PI, and co-workers, of the laser-based resonance ionization methodology for Kr-85 and Kr-81 analyses, has reduced the water requirement to 3 to 10 liters for Kr-85, and 10 to 20 liters for Kr-81, at a cost feasible for use as an investigative tool, making them viable tracers for hydrogeology.

This technique, implemented at the Institute for Rare Isotope Measurements of The University of Tennessee under sponsorship of NSF and several other federal agencies is a multi-step process starting with (1) collecting the groundwater sample, (2) degassing the water sample, (3) separating Kr from the recovered gases, (4 & 5) two isotopic enrichments reducing interfering isotopes by $>10^9$, and (6) detecting the rare krypton isotope in a time-of-flight mass spectrometer. (Figure 2.) The sensitivity, element specificity, and immunity to isobaric interference of resonance ionization (~100 Kr-85 atom detection limit, Thonnard, et al., 1992) is necessary to detect the few thousand analyte atoms remaining in the sample, as shown in Figure 3. More detail on each of the processing steps is given in Figures 4. through 9.

Another major application is in the field of planetary sciences. Some of the earliest relics from the time of formation of the Solar System are micron-sized grains of refractory material (SiC) imbedded in the most primitive (undifferentiated) meteorites. Some of these grains retain minute quantities of noble gases trapped as they formed in their parent star. Determination of the krypton and xenon isotopic abundances for the few-thousand noble gas atoms in these grains can elucidate some of the nucleosynthesis processes that occurred. Measurement of these samples only requires use of the final processing step, Figure 9.

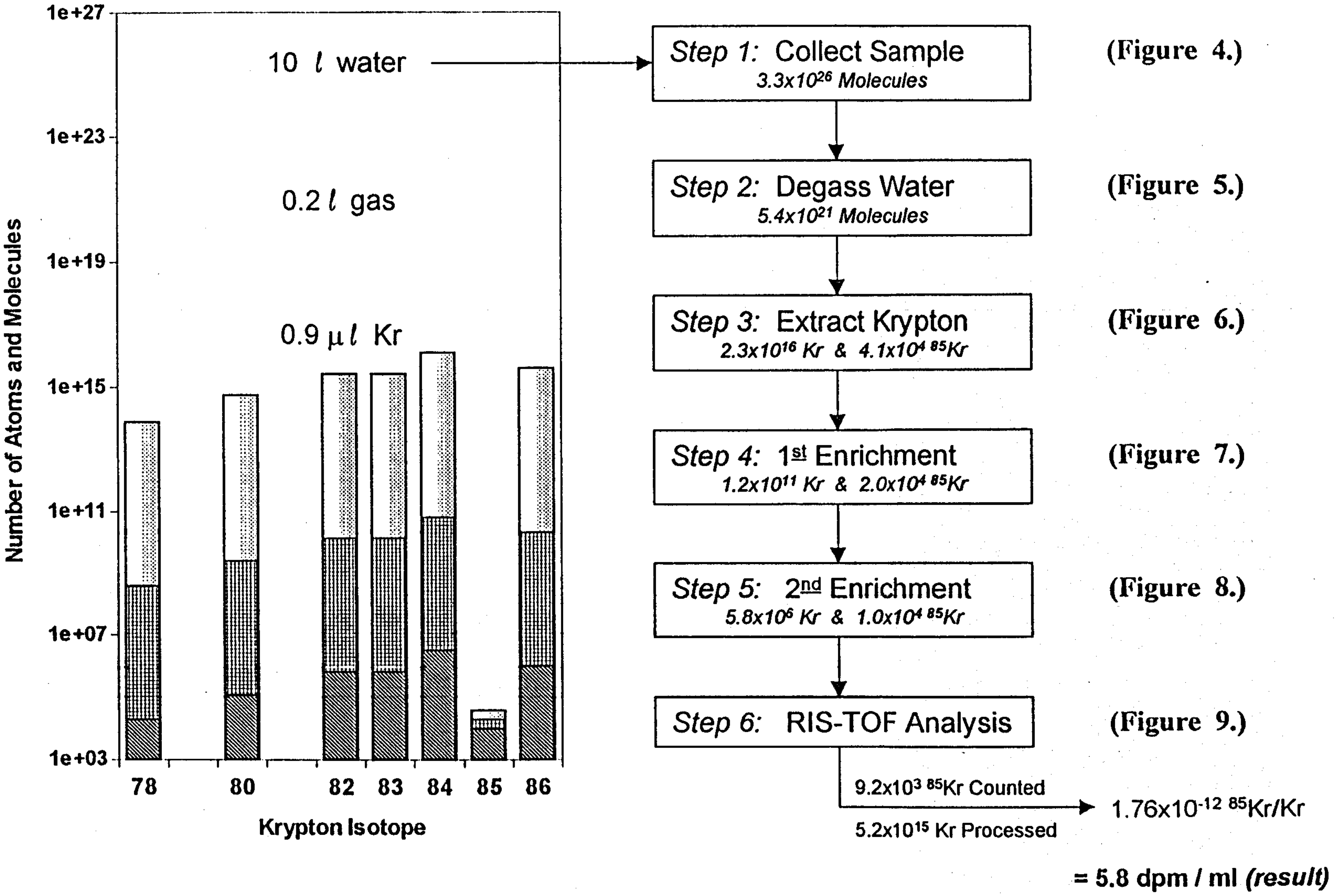


Figure 2. Graphical illustration of the multi-step process being implemented at IRIM to measure the concentration of the rare krypton isotopes in environmental samples. This illustration utilizes the current measured efficiency of each processing step set-up at IRIM, and tracks the processing of a 10 *l* groundwater sample from an aquifer recharged in 1975 at 10 °C, 1006 mbar barometric pressure and 50% relative humidity through all steps required to determine its ^{85}Kr/Kr ratio. Details on the process and hardware used is given in the figures called out to the right of each step. Note that the measurement spans a range greater than 10^{22} orders-of -magnitude.

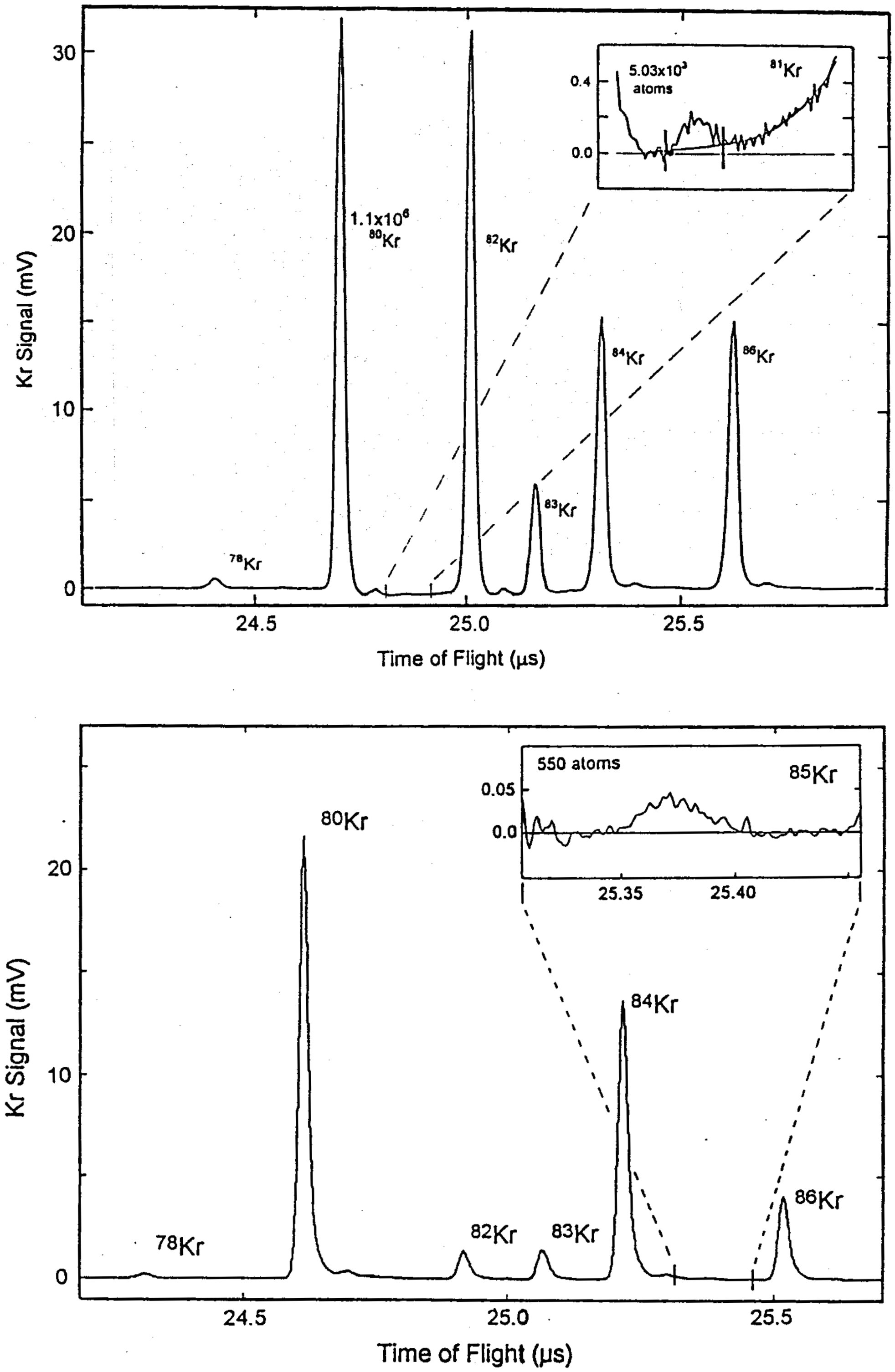


Figure 3. Sensitivity of *R*esonance *I*onization *M*ass *S*pectrometry (RIMS) illustrated by the signal recorded from environmental samples in which only 5,030 Kr-81 atoms (upper, Craig, et al., 1990) and 550 Kr-85 atoms (lower, Thonnard, et al., 1992) were present in the mass spectrometer. These data were obtained earlier with the mass spectrometer now being set-up at IRIM after multi-step processing similar to what is shown in Figure 2. A 100-atom 3-σ detection limit can be inferred from the noise in the Kr-85 mass spectrum.

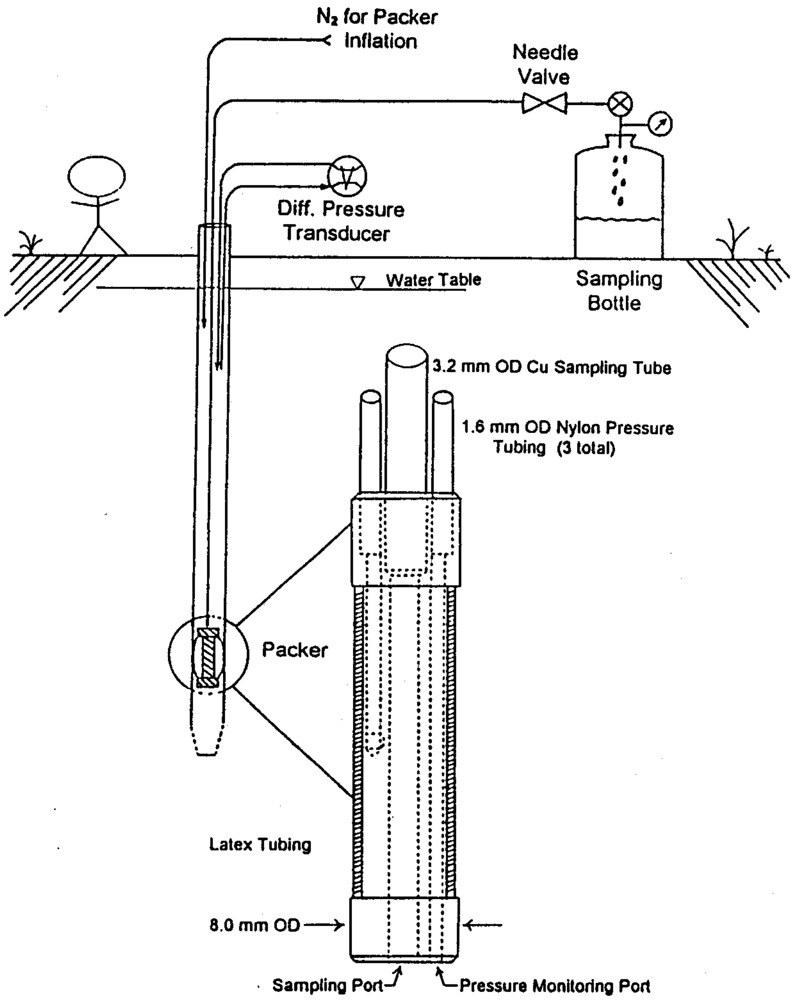


Figure 4. Shallow-well sampling system with miniaturized packers for the piezometers at the Sturgeon Falls, Ontario, site of the University of Waterloo. To avoid contaminating the formation, two well-volumes were pumped with the water pick-up ~0.5 m below the water-level before slowly inserting the packer to within 0.5 m of the screen and inflating it Additional purging of one to two well-volumes, with the flow-rate adjusted by setting the differential pressure to a 0.5 to 1 m head drop, was done before collecting 20 *l* into evacuated glass sampling bottles. Deeper wells will require a pump at the packer.

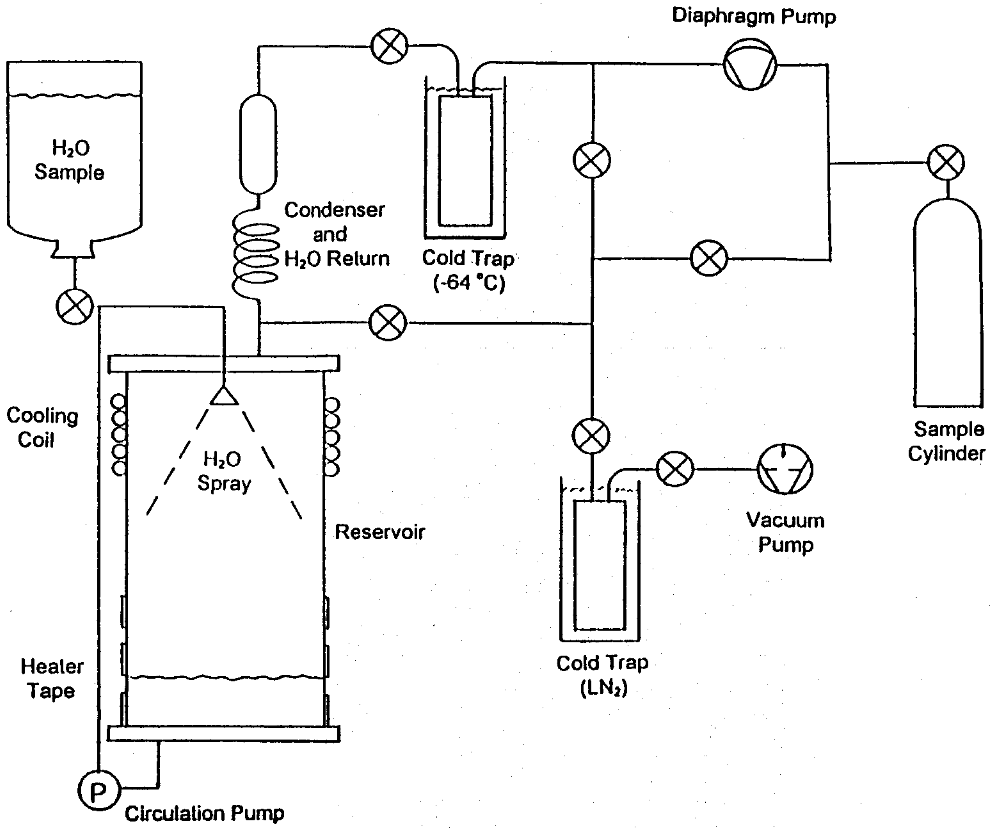


Figure 5. High-efficiency water degassing system for 20 *l* samples. Gases are stripped and transferred by the diaphragm pump to the evacuated sample cylinder in three phases. First, as the gases in the bottle head-space are being pumped out, next during degassing of entering water sprayed into the evacuated 50 *l* reservoir, and finally, from degassing of sprayed circulating water. The condenser and -64 °C trap remove water and CO_2. The water is heated to 25 °C and He added to improve degassing and gas transfer efficiency. More than 95% of the gases dissolved in the sample are recovered. Alternately, gases released as water sprays continuously into the reservoir are transferred to the cylinder while pumping water continuously out of the bottom of the reservoir. This latter operating mode is faster, but recovers only ~ 70% of the dissolved gases. The LN_2-trapped vacuum pump evacuates the various components before use and assures leak-free operation.

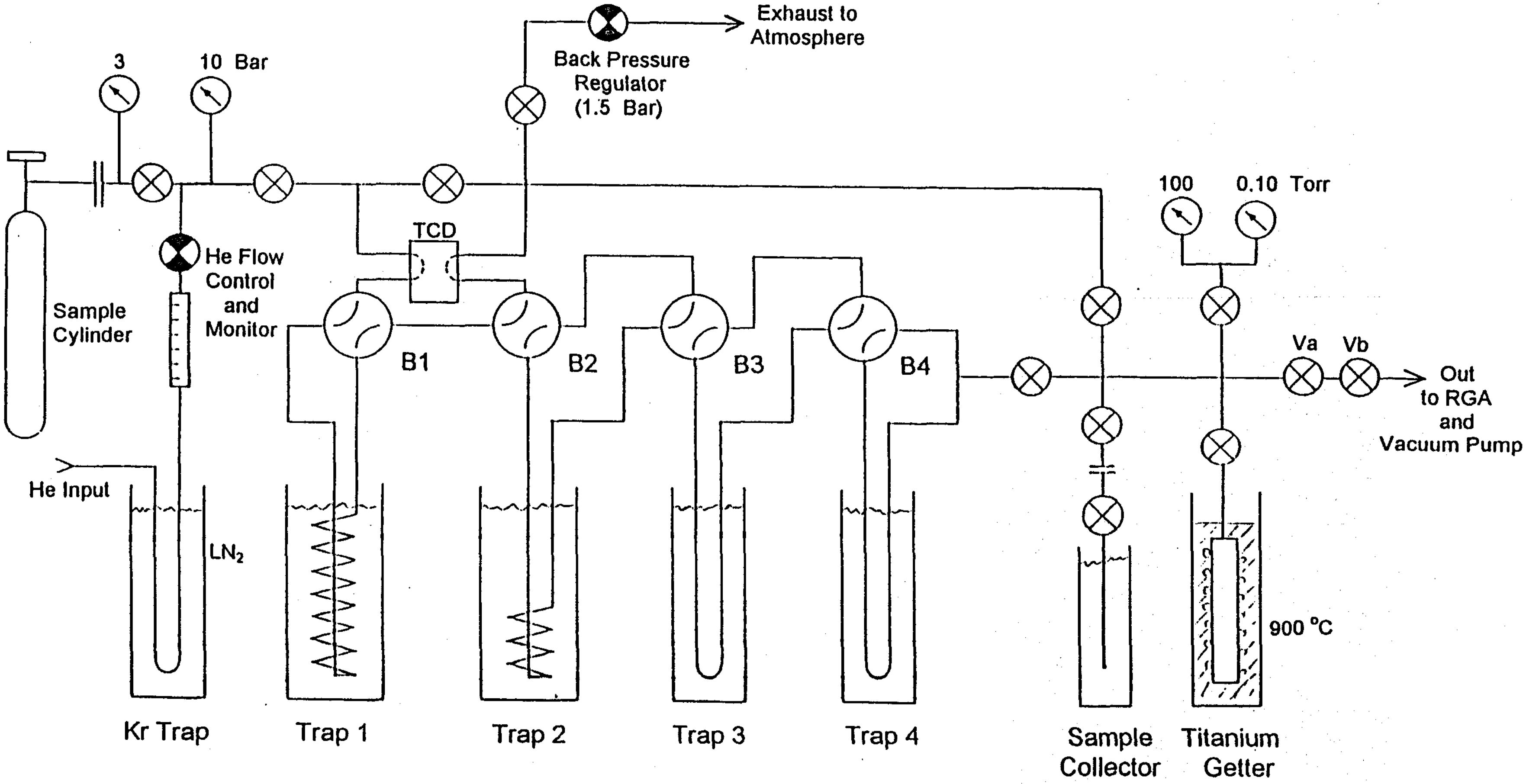


Figure 6. Schematic representation of the Krypton-Air Separation System. The system is based on cryogenic trapping of the gases at 77 K (LN$_2$) on activated charcoal traps, followed by gas chromatographic separation at 100 °C (boiling H_2O). After heating under vacuum at 300 °C for at least 4 hours, all traps and the sample collector are chilled to 77 K. The gases in the sample cylinder are then drawn slowly (~40 min) through Trap 1 with the vacuum pump. A helium flow is then established through Trap 1 and out the Back Pressure Regulator. The LN$_2$ on Trap 1 is replaced with boiling H_2O, causing the trapped gases to release from Trap 1 with delays proportional to their mass and are exhausted through the Back Pressure Regulator. After an appropriate delay, (established earlier with Kr-spiked test samples detectable with TCD, the thermal conductivity detector) valve B2 is switched to collect the Kr in the sample on Trap 2. This process is repeated for Traps 3 and 4, after which the He is pumped off and the remaining sample transferred to the Sample Collector. A Ti getter removes any remaining active gases, and the amount is determined from the pressure indicated on a capacitance manometer. The purity is confirmed by RGA analysis of a small aliquot trapped between Va and Vb. More than 98% of the krypton in a 0.1 to 10 *l* gas sample is recovered, while the Kr concentration is raised from ~1 ppm to >95%.

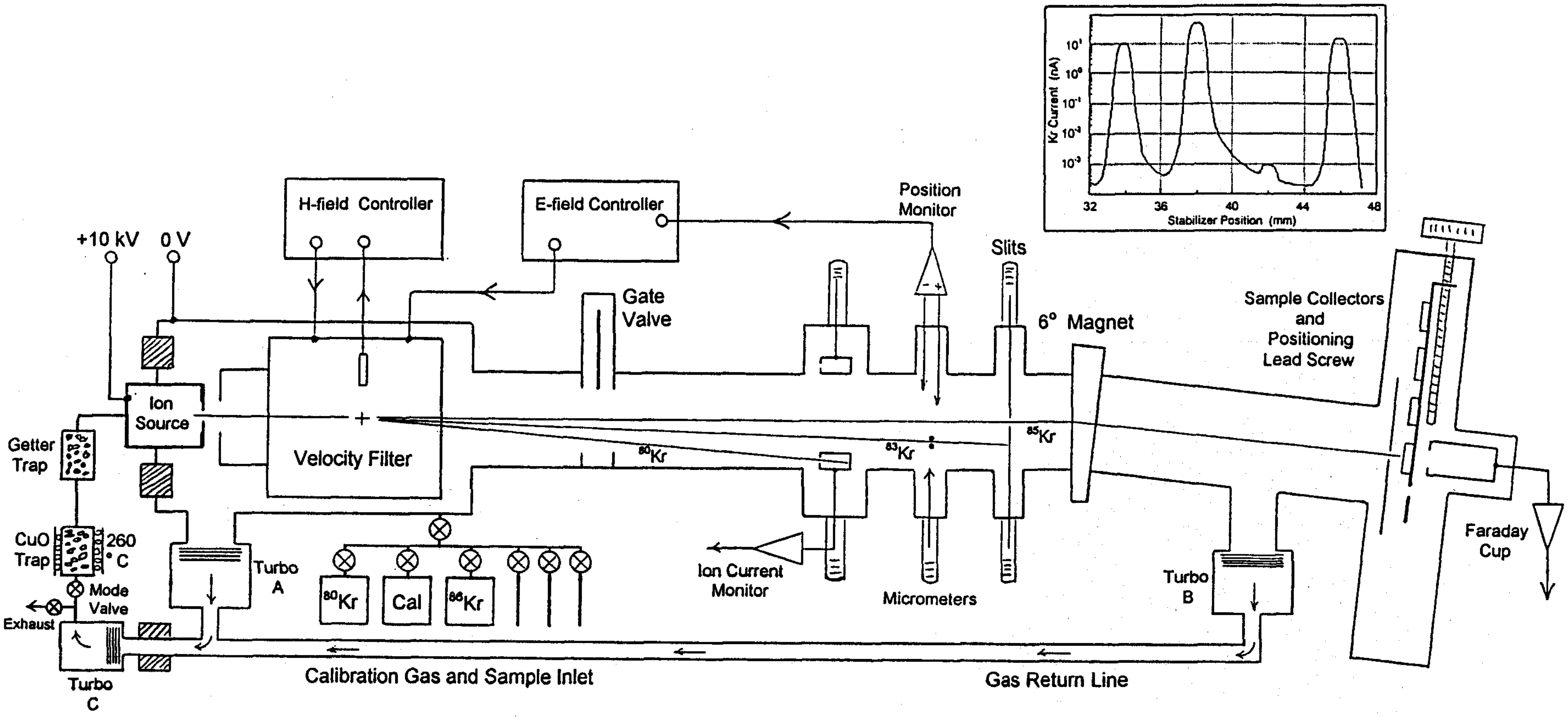


Figure 7. Schematic representation of the 1st Enrichment System used to reduce interfering isotopes by a factor of 10^5, while collecting >50% of the desired isotope. In standby, with mode valve set to exhaust, system pressure is $<3\times10^{-10}$. To enrich, mode valve is set to recirculation and ~1 μℓ of sample introduced, resulting in ~100 nA total Kr^+ current. Neutral Kr is returned to the source by magnetic-bearing Turbos A & B, whose output is further compressed by Turbo C. A Hall probe stabilizes the Velocity Filter magnetic field, while two 0.5 mm dia wires, separated by 1.0 mm straddle the ^{83}Kr beam, providing feedback to stabilize the electric field, and hence, the dispersed beams. The "locked" beam can be scanned across the slits and defining aperture by moving the wires, verifying the position of the Kr isotopes. After ^{85}Kr (or ^{81}Kr) is centered in the slits, the movable faraday cup is centered on ^{80}Kr (or ^{86}Kr) to continuously monitor the beam current. Starting sample size can be determined from the major isotope ratios by adding an aliquot of ^{80}Kr. (or ^{86}Kr) After blanking the beam to position an aluminized sapphire collector at the defining aperture, enrichment starts by implanting the 10 keV Kr ions into the Al, where they are retained indefinitely with 100% efficiency. After processing 50% of the sample, (~10 h) a 1×10^{11} ^{80}Kr (^{86}Kr) "spike" is implanted for calibration. A scan over the 83 through 86 mass region (inset) shows the smooth, flat-topped peaks and $>10^5$ abundance ratio; the 1 pA peak at mass 85 is from $^{84}KrH^+$.

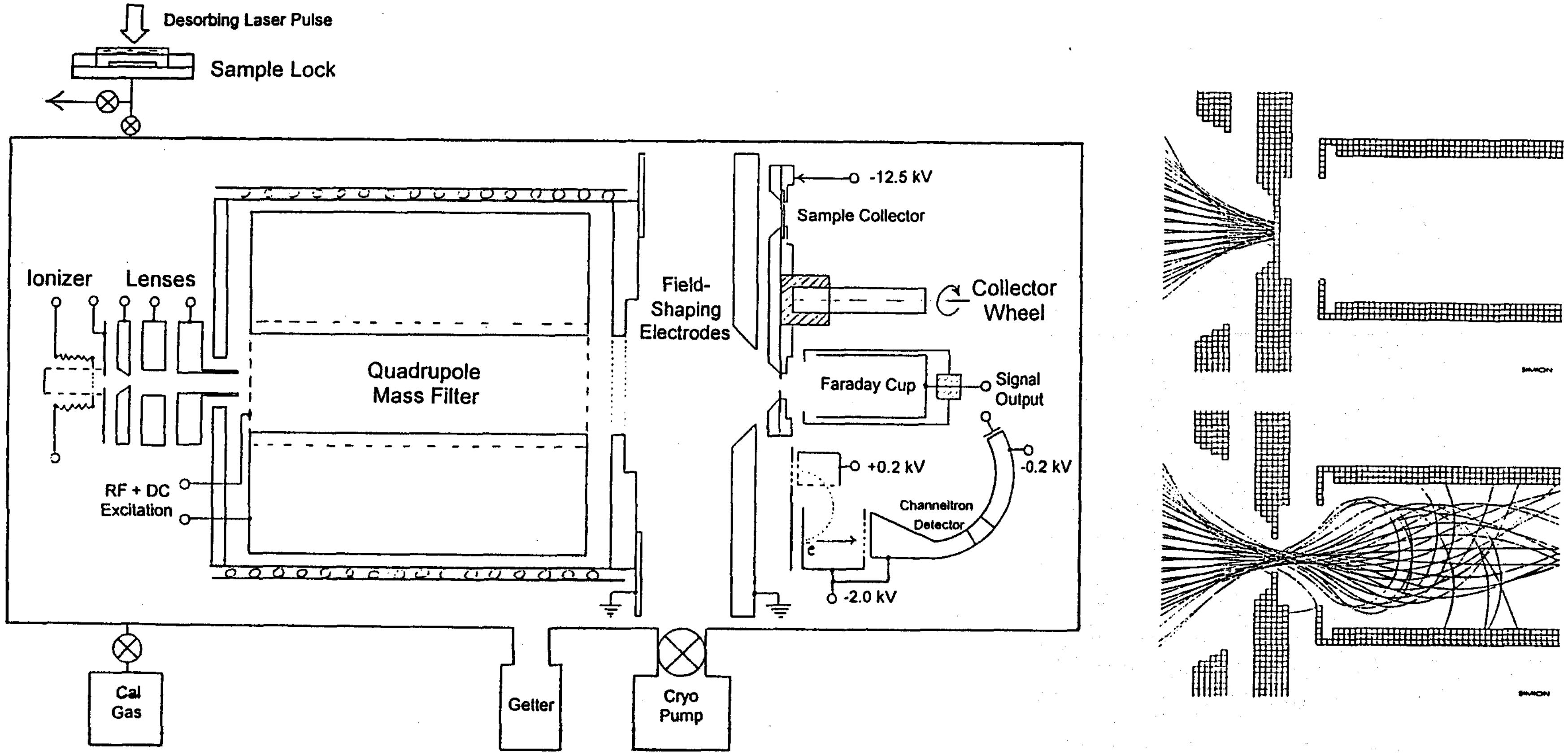


Figure 8. Schematic of the 2nd Enrichment System. Krypton from the first enrichment step is released by flash-evaporation of the Al coating on the sapphire collectors with a single Nd:YAG laser pulse at ~1 J cm^{-2} energy density. (~10^{8} W cm^{-2}) A single pulse produces less background as there is no transmitted beam, and significantly less scattered beam, to desorb Kr from other surfaces. The residual gas in the static system is ionized by electron impact, and a collimated 10 to 15 eV beam injected into the Quadrupole Mass Filter. The noble gas atoms rejected by the filter are neutralized upon striking the poles and returned (in principle) to the source for reprocessing. (Tests showed that keeping the poles hot reduced retention.) Virtually all of the ions making it through are collected by the shaped electric fields produced by the Collector Wheel at -12.5 kV and focused to a 1.5 mm dia spot on the wheel, a significant improvement over the previous design, where only 50 to 75% (depending on tuning) of the transmitted ions were collected. This was caused by the very large angular dispersion of the ions exiting the quadrupole mass filter. Design of the new collector was guided by ion trajectory simulations, shown at the right, in which >90% of all ions exiting within a 65^0 half-angle cone at the edge of the exit collimator are implanted within a 1.5 mm dia spot in the collector. If the exiting cone half-angle is reduced to 50^0, a more realistic upper limit, no ions are lost. Two of the 12 collector positions on the wheel are apertures, behind which either a faraday cup or an electron multiplier can be positioned, thereby permitting monitoring of quadrupole performance under conditions identical to the implants.

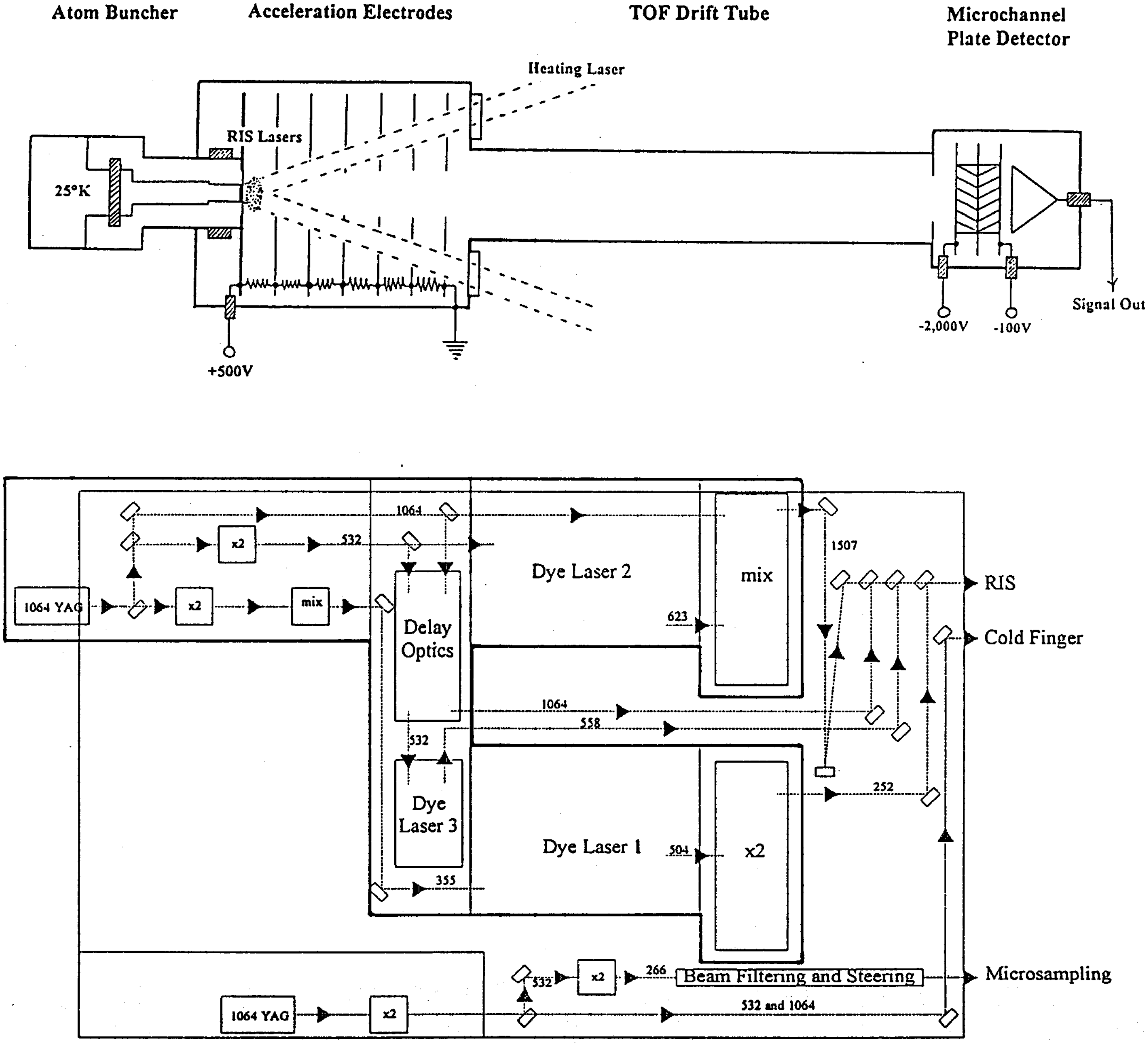


Figure 9. Ultra-sensitive "RIS-TOF" RIMS system at IRIM dedicated to heavy noble gas analyses. (Upper) As in the previous step, the enriched Kr sample is released into the static time-of-flight mass spectrometer by flash-evaporation of the collector Al using a single laser pulse. Due to the small ionization volume and low laser duty cycle, an "Atom Buncher" concentrator is used to reduce the detection time. This consists of a 3 mm dia spot at 25 K at the end of a probe in the ionization region that is laser flash-heated to ~1,000 K a few μs before ionization to release the ~1% of the sample that condenses on it between pulses. Combined with the near-100% ionization efficiency of the RIS process, this results in counting 90% of the Kr atoms in the system in less than 10 min. (Lower) Almost all components of the new Kr RIS laser system (outlined by the darker line in the figure) are mounted on six very heavy aluminum sub-assemblies that are bolted together, resulting in a single rigid unit. Combined with the factor of two higher output at the required wavelengths, these measures result in stable operation and reliable, routine ionization of krypton.

Activities Since Inception and Current Status

The Institute for Rare Isotope Measurements (IRIM) was founded at the University of Tennessee in 1993 to provide the facilities and exploit applications in the earth and planetary sciences using ultra-sensitive isotopic and elemental analyses based on resonance ionization mass spectrometry (RIMS). After operating for a year on seed money provided by The University of Tennessee, the Scripps Institution of Oceanography, and the Environmental Sciences Division of Oak Ridge National Laboratory, a linked, multi-year program was funded in 1994 by NSF and DOE to develop the methodology for Kr-81 and Kr-85 analyses and apply them to the geosciences. The following year an Innovative Research Program grant was awarded by NASA to extend the capabilities to krypton and xenon isotope measurements from micron-sized samples in the planetary sciences. The NASA funding was a very important complement to the NSF and DOE grants, as it permitted significant improvements to the RIMS system, while the NSF and DOE funding was focused primarily in solving the many problems unique to the very challenging Kr-81 and Kr-85 analytical problem. More recently, funding has been received from the Tennessee Water Resources Research Center (TNWRRC) and the American Water Works Association Research Foundation (AWWARF) to address some of the remaining issues, and to start applying this technique to Kr-85 measurements of hydrogeologic samples.

Although the science goals of the funded projects listed above were distinct, the equipment needs during this first stage in IRIM's development consumed (as anticipated) a major portion of the effort and resources. There was significant overlap in the equipment needs between all of the projects, none of which could have carried the burden alone. Therefore, the funding for the equipment development in the projects complemented each other, all working together towards the common goal of enabling Kr-81, Kr-85, and, Kr and Xe isotopic abundance measurements in the earth and planetary sciences. As we describe below the status of each distinct system at IRIM, the major sponsor of each of these systems will be identified, realizing that some aspects of the effort may have been sponsored in part by others.

Summarizing, the objectives of the original DOE and NSF sponsored programs were:

1. To assure the continuity of RIMS-based ^{81}Kr and ^{85}Kr measurements by purchasing the Noble Gas Lab technology and equipment from Atom Sciences, Inc.
2. To identify shortcomings of the system, design and implement modifications to overcome these, and to design and implement improvements to enable "routine" measurements in the earth and planetary sciences of ^{81}Kr and ^{85}Kr, and of Kr and Xe isotopic abundances.
3. To initiate collaborative research in the earth and planetary sciences, both at the University of Tennessee, and at other institutions.

1. Assure continuity of RIMS-based ^{81}Kr and ^{85}Kr measurements:

In the original proposal, the PI had negotiated a \$187,000 (~10% of the cost) lease-purchase agreement with Atom Sciences, Inc. for the "Noble Gas Lab" equipment and technology. A \$25,000 down payment in March 1994, permitted IRIM to move the equipment to the University of Tennessee on April 15, 1994. The balance was to be paid in three annual installments of \$54,000 each out of the pending NSF grant application, otherwise, the equipment was to be returned after a year. In November of that same year, the University decided to advance IRIM the anticipated equipment funds for the second and third years of the NSF grant so that the "Noble Gas Lab" could be purchased outright, receiving immediate free and clear title for it. Because of the accelerated payment schedule, the PI was able to negotiate a \$22,000 reduction in purchase price. Title to the equipment went to the University on November 30, 1994.

2. Identify shortcomings, design and implement improvements:

Technological developments were centered on the following two research disciplines.

(A) Hydrogeology: -- Kr-85 measurements, providing a much-needed environmental tracer to improve young aquifer recharge and contaminant intrusion studies; later to be expanded to include Kr-81, which is appropriate for older aquifers.

(B) Planetary Sciences: -- Micron-scale spatially resolved measurements of krypton (and later xenon) isotopes in extra-terrestrial materials.

(A) The following distinct steps and equipment are necessary for Kr-85 and Kr-81 analyses in hydrogeologic samples; the requirements, status, and primary sponsors are listed below:

1. Groundwater Sampling System (Figure 4.) -- is capable of collecting and storing 20 liter water samples with no loss of dissolved gases or contamination from atmospheric air; sampling rate is adjustable to minimize mixing from different aquifer regions. Sponsor: TNWRRC

Status: Designed, constructed, developed protocols and field-tested.

- *meets design criteria*
- *has been used for sampling at Sturgeon Falls, Canada (Sept '97), the Great Artesian Aquifer, Australia (Jan '98), and the Memphis Aquifer, Tennessee (Nov '00)*
- *can be deployed with 2-day's notice, 30 20-l water and 48 gas containers are on-hand*
- *100% operational*

2. Water-Air Separation System (Figure 5.) -- has high efficiency (>95%) and no detectable contamination from atmospheric air; is capable of operating from single 20-liter sampling bottles, or with a continuous feed. (The latter at somewhat lower efficiency.)

Sponsors: TNWRRC & DOE

Status: Designed, constructed, developed operating protocols and completed testing.

- *meets design criteria*
- *numerous test samples run; used in routine manner to process Sturgeon Falls samples*
- *100% operational*

3. Air-Krypton Separation System (Figure 6.) -- is capable of handling 10 mℓ to 10 ℓ air samples with high efficiency (>95%) and >90% Kr purity in processed samples.
Sponsors: TNWRRC & DOE

Status: Significantly modified and improved existing system, developed operating protocols and completed testing.

- *meets design criteria*
- *numerous test samples run; used in routine manner to process Sturgeon Falls samples*
- *100% operational*

Note: The krypton recovery efficiency of systems 2. and 3. combined is ~92%, the Kr purity >96%. A very conservative upper limit to memory and contamination from atmospheric krypton is <<0.02%. One sample can be processed through systems 2. and 3. in 8 hours

4. First Isotopic Enrichment System (Figure 7.) -- consists of a plasma ion source and velocity filter capable of reducing interfering isotopes by 10^5 while collecting 50% of the desired isotope of a 1 microliter Kr sample in 10 hours. Sponsors: NSF & DOE

Status: Extensively modified and rebuilt improving reliability, stability, quantitation and minimum sample size. Developed operating protocols and completed testing.

- *meets design criteria*
- *numerous test samples run on a routine basis*
- *more than 40 samples can be enriched before routine ion source maintenance*
- *suite of calibrated Kr-85 samples, ranging from zero to twice ambient was enriched*
- *enrichment results are predictable, with no unaccounted losses or background*
- *minimum water sample reduced to 10 l, additional factor of 3 reduction possible*
- *100% operational*

5. Second Isotopic Enrichment System (Figure 8.) -- consists of an electron impact ionizer and quadrupole mass filter capable of reducing interfering isotopes by 10^3 to 10^4 while collecting 50% of the desired isotope in 45 minutes. Sponsors: DOE & NSF

Status: Completely redesigned ion collector, ion multiplier and enriched isotope collector. Added gas calibration pipette and pole heaters. Developed operating protocols and completed testing.

- *does not meet design criteria,(as anticipated) but functions at reduced performance*
- *ion collector, faraday cup and multiplier results are congruent, leading in better quantitation*
- *throughput was increased by a factor of 2.5, reducing background and processing time*
- *losses were reduced by a factor of more than 2, resulting in better sample utilization and significant reduction of memory effects*
- *100% operational*

Note: This system was to be replaced by a sector magnet system with much better enrichment factor, quantitation, efficiency and lower memory, but funding for the new system was not granted. The quadrupole system, while limiting accuracy of the Kr-85 (or Kr-81) isotopic abundance measurement to ~15%, is functional and routinely usable.

6. RIS-TOF Mass Spectrometer (Figure 9.) -- uses a cold finger for "atom bunching" and resonance ionization to achieve sensitivity down to 100 atoms. When fully operational, 90% of the atoms in a sample can be counted in less than 10 minutes. Sponsors: NASA, DOE & NSF

Status: Major up-grades completed only on Dec '99. New, more reliable and powerful laser system, 20X higher time-resolution data acquisition system, gas calibration pipette, and improved vacuum system was designed and installed.

- *meets almost all design criteria*
- *generation of the critical VUV photons is routine*
- *high-resolution TOF mass spectra obtainable on a routine basis* (Figure 10.)
- *sensitivity is as good, or higher, than before, i.e., ~10X more sensitive than conventional noble gas mass spectrometers*
- *laser system improvements have made maximum sensitivity routinely possible, rather than a "tour-de-force" effort*
- *not yet fully operational; needs a chance to prove itself*

Work remaining:

-- background is high; possibly due to remaining ultra-small leaks; may require replacement of all metal gaskets -- larger leaks found earlier (~10^{-10} cm^3 s^{-1}) were due to CuO flakes on knife edges.

-- problems with VUV windows and UHV valves -- functional, but will need replacing soon.

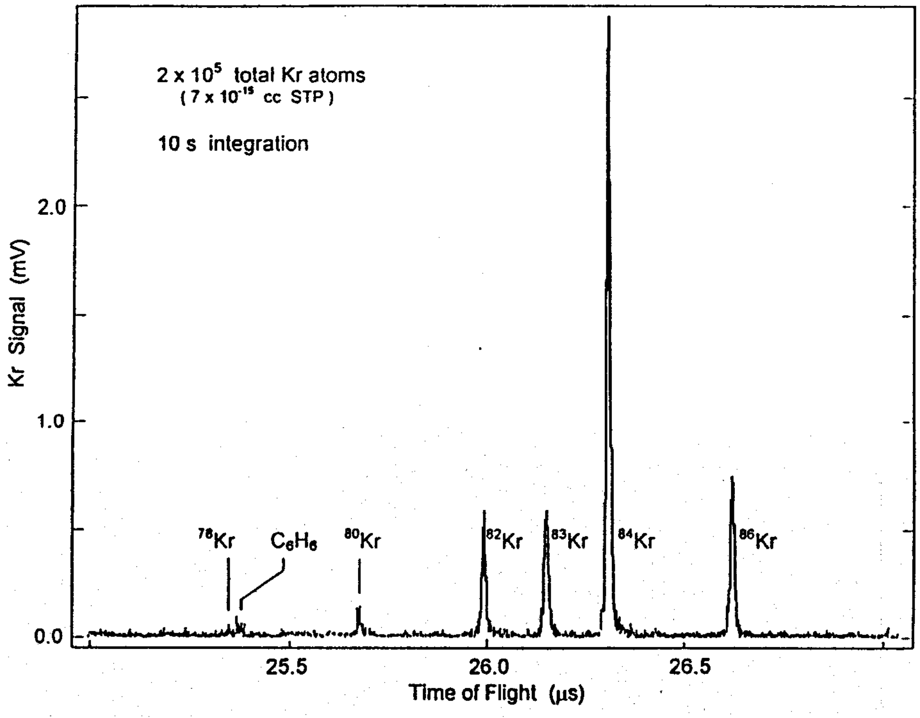


Figure 10. RIS-TOF mass spectrum recorded with the RIMS system at IRIM. Note that the mass resolution is 1200, almost a factor of two better than what had been achieved earlier, which is sufficient to resolve ^{78}Kr from C_6H_6, separated by only 0.2 amu. Although these data were recorded for only 100 laser pulses, (10 s) ^{80}Kr and ^{78}Kr are clearly detectable with only about 4,500 and 700 atoms, respectively, in the system. These results imply that operation with typical recording times, (~6,000 laser pulses for 10 min.) will result in quantitative measurements of samples containing less than 1,000 atoms of the desired isotope.

Note: Due to delays in completion of the Science and Engineering Building on the main UT campus, IRIM at first received only 1/3 of its allotted space. Work on the two enrichment systems, and design of modifications to the TOF mass spectrometer was possible. Preparations for the sampling at Sturgeon Falls, Ontario had to be done in the halls and parking lot. Due to the severe crowding, it was too dangerous to operate the laser systems. Delivery of the new laser system *could only occur after January 1998*, when space finally became available for safe, routine operation. Also, only then was there sufficient space to pursue water degassing and krypton separation development.

(B) The following systems are needed for spatially resolved krypton and xenon isotopic measurements of extraterrestrial samples:

1. UV Laser Micro-Sampling System -- delivery system for quadrupled Nd:YAG (266 nm) laser pulses that can focus to <5 μm on the sample, and rastered in X, Y and Z with 2 μm resolution. System also has a collinear optical viewing system to identify regions of interest on the sample that are to be degassed by pulsed laser heating. Sponsor: NASA

Status: System has been designed, built, and tested.

- *meets design criteria*
- *complete degassing in 1 to 3 laser pulses demonstrated on Kr-implanted silicon*
- *degassing spatial resolution better than accuracy of test implants, ~10 micrometers*
- *100% operational*

2. RIS-TOF Mass Spectrometer -- (same system as described in 6., above.)

3. Xe RIS Laser System -- will permit simultaneous analyses of Kr and Xe isotopes in the same sample at the identical location. Sponsor: NASA

Status: Conceptual system design completed. Nd:YAG pump laser and two dye lasers are in place on optical table

- *to be implemented later at very little additional equipment cost*

Status of Sample Analyses:

- Twenty three groundwater samples have been collected from 14 locations at Sturgeon Falls, Canada for Kr-85 analysis. The site chosen is in a recharge area at the flow divide, is simple hydrogeologically and well-characterized. Additional samples have been collected for tritium analysis (by Waterloo) for comparison. Data from this site will verify the Kr-85 method.
- Groundwater samples have been collected (by Bern) from four locations in the Great Artesian Aquifer, Australia for Kr-81 analysis and comparison to the Cyclotron AMS data.
- Samples from five production wells of the Memphis Light, Gas and Water Utility have been collected for Kr-85 analysis and comparison with $^3H/^3He$ analyses.
- Eight Sturgeon Falls samples have been processed through step 3.
- Sixteen Kr-85 standards have been processed through step 5.
- Four Millbillillie meteorite chips and seven Bjurbole chondrules are loaded in the UV laser micro-sampling chamber ready for RIS-TOF Kr isotope analysis.

3. Initiate collaborative research in the earth and planetary sciences

Collaborations, some with joint funding to the collaborating institutions, have been established in the following fields.

Hydrogeology:

The University of Tennessee, Knoxville, Tennessee

L.D. McKay, *Department of Geological Sciences,* dedicated a significant fraction of his research effort in developing applications of Kr-85 in hydrogeology. He is a strong advocate of the importance of this isotope, has been a Co-Investigator on numerous projects, and has initiated many of IRIM's collaborations. Co-directed graduate student W. Dong, who prepared for Kr-85 in groundwater flow and recharge studies.

R. Yoder, *Agricultural. & Biosystems Engineering,* on recharge evaluation using Kr-85. (with McKay, Dec'00 DOE proposal)

Physics Institute, The University of Bern, Bern Switzerland

H.H. Loosli and B.E. Lehmann, use of Kr-81 to age-date old water; samples have already been collected by Bern and shipped to IRIM for analysis. They have both come to IRIM at different times, and the PI has visited their laboratory in Bern

Waterloo Centre for Groundwater Research, The University of Waterloo, Ontario, Canada

J.A. Cherry and W.D. Robertson, calibration of first Kr-85 measurements and comparison with tritium. Robertson traveled with us to their field site in Northern Ontario, from which we have collected water samples. Cherry visited IRIM earlier to establish collaboration.

Ground Water Institute, The University of Memphis, Tennessee

R.W. Gentry, J.L. Anderson and D. Larsen, Several major projects are in process with researchers at the University of Memphis Ground Water Institute. These are on use of Kr-85 to determine recharge and pollution intrusion to the Memphis aquifer. The PI and Co-PI (McKay) have made numerous visits to Memphis for collaboration and sample collection. Gentry has visited IRIM frequently and will spend several weeks during Summer'01 using the facilities. We are joint PIs and Co-PIs on several proposals and funded projects.

Mines and Energy Resources, Adelaide, South Australia

A. Love, Kr-81 from Great Artesian Aquifer, samples already received by IRIM.

Isotope Geochemistry/ETH, Zurich, Switzerland

R. Wieler and H. Baur, development of ion source for noble gas isotope enrichment. Wieler spent several days at IRIM to familiarize himself with the enrichment process.

Department of Geology and Geophysics, University of Utah, Salt Lake City, Utah

D.K. Solomon, Co-PI on project with Memphis, comparison of Kr-85 with T/He-3.

GEUS, Danish Geological Survey, Copenhagen, Denmark

K. Hinsby, discussions in process to utilize Kr-85 to assess fertilizer and pesticide intrusion into shallow aquifers. PI was invited to present paper at Groundwater Quality conference in Denmark by GEUS.

Extraterrestrial Studies:

Department of Geological; Sciences, The University of Tennessee, Knoxville, Tennessee

H.Y. McSween, Co-Investigator on NASA Innovation Research Program, which funded development of planetary science capabilities, and is co-director of Ph.D. graduate student K. Ocker-Stone, who is investigating chondrule pre-compaction exposure and evolution of Martian atmosphere.

Physics Institute, The University of Bern, Bern Switzerland

O. Eugster, study of exposure and formation ages of selected meteorites using Kr and Xe isotopes, some samples are already on-hand at IRIM. Has come to IRIM and provided background data on samples. The PI has visited his facilities in Bern.

Department of Earth Sciences, The University of Manchester, United Kingdom

J.D. Gilmour, studies of Kr and Xe from evolved meteorites. Gilmour returned to Manchester in October'00 after a fifteen-month sabbatical at IRIM. He is an Adjunct Assistant Professor at UT and is co-directing PhD student Ocker-Stone's thesis, who will collect Xe data for thesis using Manchester facilities. Gilmour is Co-PI with Thonnard on a NASA proposal to continue the collaboration.

McDonnell Center for Space Sciences, Washington University, St. Louis, Missouri

C.M. Hohenberg, K. Khem and A. Meshik, development of planetary fly-by mission volatiles collector. Noble gases from meteorites and pre-solar grains. RIMS applications to planetary sciences. The PI and the St. Louis group have spent time at each other's institutions to collaborate and use each other's facilities. St. Louis sub-contracted IRIM to assist in the collector design and testing. Hohenberg plans to spend a six-month sabbatical at IRIM.

Enrico Fermi Institute, The University of Chicago, Illinois

R.S. Lewis, pre-solar grains, will supply separated grains for Kr and Xe isotopic analysis.

Bibliography

R.V. Ambartzumian and V.S. Letokhov, Selective Two-Step Photoionization of Atoms by Laser Radiation, Appl. Optics 11, 354 (1972).

P. Collon, D. Cole, B. Davis, M. Fauerbach, R. Harkerwicz, W. Kutschera, D.J. Morrissey, R.C. Pardo, M. Paul, B.M. Sherrill and M. Steiner, Measurement of the Long-lived Radionucleide ^{81}Kr in Pre-nuclear and Present-day Atmospheric Krypton, Radiochim. Acta 85, 13 (1999).

P. Collon, W. Kutschera, H.H. Loosli, B.E. Lehmann, R. Purtschert, A. Love, L. Sampson, D. Anthony, D. Cole, B. Davis, D.J. Morrissey, B.M. Sherrill, M. Steiner, R.C. Pardo and M. Paul, ^{81}Kr in the Great Artesian Basin, Australia: A New Method for Dating Very Old Groundwaters, Earth Planet Sci. Lett. 182, 103 (2000).

H. Craig, T.E. Cerling, R.D. Willis, W.A. Davis, G. Joyner and N. Thonnard, Krypton 81 in Antarctic Ice: First Measurement of a Krypton Age on Ancient Ice. EOS 71, 1825 (1990).

B. Ekwurzel, P. Schlosser, W.M. Smethie, Jr., L.N. Plummer, E. Busenberg, R.L. Michel, R. Weppernig and M. Stute, Dating of Shallow Groundwater: Comparison of the Transient Tracers H-3/He-3, Chlorofluorcarbons and Kr-85, Water Resource Res.30(6), 1693 (1994).

K. Fröhlich, M. Ivanovich, M.J. Hendry, J.N. Andrews, S.N. Davis, R.J. Drimmie, J.Fabryka-Martin, T. Florkowski, P. Fritz, B. Lehmann, H.H. Loosli and E. Nolte, Application of Isotopic Methods to Dating of Very Old Groundwaters: Milk River Aquifer, Alberta, Canada, Applied Geochemistry 6, 465 (1991).

G.S. Hurst, M.G. Payne, M.H. Nayfeh, J.P. Judish and E.B. Wagner, Saturated Two-Photon Resonance Ionization of He(2^1S), Phys. Rev. Lett. 35, 82 (1975).

G.S. Hurst, M.H. Nayfeh and J.P. Young, A Demonstration of One-Atom Detection, Appl. Phys. Lett. 30, 229 (1977).

G.S. Hurst, M.G. Payne, S.D. Kramer, C.H. Chen, R.C. Phillips, S.L. Allman, G.D. Alton, J.W.T. Dabbs, R.D. Willis and B.E. Lehmann, Method for Counting Noble Gas Atoms with Isotopic Selectivity, Rep. Prog. Phys. 48, 1333 (1985).

B.E. Lehmann, H. Oeschger, H.H. Loosli, G.S. Hurst, S.L. Allman, C.H. Chen, S.D. Cramer, R.D. Willis and N. Thonnard, Counting ^{81}Kr Atoms for Analysis of Groundwater, J. Geophys Res. 90(B13), 11547 (1985)

B.E. Lehmann, H.H. Loosli, D. Rauber, N. Thonnard and R.D. Willis, ^{81}Kr and ^{85}Kr in Groundwater, Milk River Aquifer, Alberta, Canada, Applied Geochemistry 6, 419 (1991).

B.E. Lehmann, S.N. Davis and J.T. Fabryka-Martin, Atmospheric and Subsurface Sources of Stable and Radioactive Nuclides used for Groundwater Age Dating, Water Resour. Res. 29(7), 2027 (1993).

M. McMaster, T. Svensson, A. Rossi and I. Callow, An Appraisal of Three Atmospheric Tracers in Hydrogeological Regimes, unpublished report, Univrsity of Waterloo, Canada (1995).

M.G. Payne, G.S. Hurst, M.H. Nayfeh, J.P. Judish, C.H. Chen, E.B. Wagner and J.P. Young, Kinetics of He(2^1S) Using Resonance Ionization Spectroscopy, Phys. Rev. Lett. 1154, 82 (1975).

M.G. Payne, L. Deng and N. Thonnard, Applications of Resonance Ionization Mass Spectrometry, Rev. Sci. Instrum., 65, 2433, (1994).

K. Rozanski and T. Florkowski, Krypton-85 Dating of Groundwater, Isotope Hydrology 2, 949 (1979).

W.M. Smethie, Jr., D.K. Solomon, S.L. Schiff and G.D. Mathieu, Tracing Groundwater Flow in the Borden Aquifer using Krypton-85, J. Hydrol. 130, 279 (1992).

N. Thonnard, R.D. Willis, M.C. Wright, W.A. Davis and B.E. Lehmann "Resonance Ionization Spectroscopy (RIS) and the Detection of ^{81}Kr," Nucl. Instr. Meth. Phys. Res., B29, 398, 1987.

N. Thonnard, M.C. Wright, W.A. Davis and R.D. Willis, The Second-Generation RIS-TOF Noble Gas Detector: Detection Limits Below 100 Atoms in Less Than 5 Minutes, Inst. Phys. Conf. Series 128, 27 (1992).

N. Thonnard and B.E. Lehmann, The Institute for Rare Isotope Measurements, AIP Conf. Proc. 329, 335, (1995).

R.D. Willis, N. Thonnard and M.C. Wright, Counting ^{81}Kr Atoms in Groundwater Using RIS-TOF, Inst.Phys. Conf. Ser.94, 213 (1989).

Participants with Significant Roles in Project

Dr. Norbert Thonnard

Dr. Thonnard provided overall project and budget management, and supervised all aspects of the research. Having lead the development of Resonance Ionization Spectroscopy (RIS)-based methods for the analysis of rare krypton (81 and 85) isotopes before joining the University of Tennessee to form the Institute for Rare Isotope Measurements (IRIM), he continued to lead the conceptualization of new instrumentation, and improvements to the existing systems required to meet the analytical needs.

Dr. Larry D. McKay

Dr. McKay, an Associate Professor in Geological Sciences at the University of Tennessee and holder of the Jones Professorship in Hydrogeology, provided supervision of all aspects related to hydrogeology in this project. He conceived the experiments necessary to demonstrate the capabilities of Kr-85 as a new tracer, and played a major role in the design of sampling protocols, analysis of data and preparation of reports and manuscripts. Dr. McKay was also instrumental in bringing many collaborators in his field to the project, and developing enthusiasm for the use of this new tool.

Charles F. Joyner

Senior Technician. May, 1996 through June 2000. Funded by NSF, DOE, NASA and USGS. Before joining IRIM, Mr. Joyner worked for 8 years at Atom Sciences, (and with the P.I. from 1988 to 1993) the research company where the RIS-based 85Kr analysis technique was first developed. Was fully familiar with the Kr-85 analysis technique and performed a large fraction of the laboratory measurements. Also trained all new students and employees in the use of the analysis equipment, was responsible for the day-to-day laboratory operations, and the maintenance and repairs of all equipment. His expertise in electronics, vacuum systems and laser systems contributed significantly to the implementation of the system modifications.

Katherine D. Ocker Stone

Graduate Research Assistant. Supported principally by NASA.

Michael Mobley

Graduate Research Assistant. Supported by DOE.

Adam Berryhill

Student Assistant, and later, full-time Research Assistant.. Supported by NSF and NASA..

Weiquan Dong
Graduate Research Assistant. Supported by TNWRRC.

Christopher Stone
Student Assistant, and later, full-time Research Assistant. Supported by NSF.

Dennis Cumbie
Research Associate. January 1997 through August 1997. A Masters graduate from the hydrogeology program at the University of Tennessee. Was responsible for the development and construction of the in-well sampling hardware, collection hardware and containers, and water degassing system.

Allan Ewing
Research Assistant. February 1995 through August 1995. A Master's graduate from physics at the University of Tennessee, assisted in the re-assembly of the optics for the resonance ionization laser system.

Artur Kolodziejski
Graduate Research Assistant. Supported by DOE.

Karla Kubler
Graduate Research Assistant. Supported by DOE.

Scott Legg
Student Assistant. Supported by NASA

Educational Activities

Since the beginning of NSF (9/1/94) and DOE (12/1/94) funding in support of the development of the Institute for Rare Isotope Measurements, a total of thirteen students, six undergraduate, and six graduate, participated in a very significant (>>160 hours during their involvement) manner in the activities at IRIM. As IRIM's thrust by necessity is very equipment intensive, it provides students a unique opportunity to become familiar with a wide variety of instrumentation and experimental techniques. And, as the analytical capabilities being developed at IRIM have open new research possibilities, participants gain experience at this "burning edge," and have to work harder (especially graduate students) to understand how their research will fit in with the present state of knowledge. The interdisciplinary nature of IRIM's mission provides students with a very wide range practical and conceptual experiences.

Graduate Students:

Ali Passian, (Physics) June 1994 through September 1994, worked temporarily at IRIM during his first summer at UT. He was to consider alternative schemes for large isotopic selectivity based on collinear beam excitation, and did a very thorough literature search and developed a very good understanding of the advantages and limitations (resulting in my reduced interest) of the technique. In addition to learning about new experimental developments in a field he was unaware of, he developed some practical electronic skills by assembling and testing an ultra-stable current and temperature controller for the tunable diode lasers that would have been used.

Artur Kolodziejski, (Geology) May 1995 through December 1995, who was simultaneously working as a mining engineer for the State Government assessing pollution due to mine run-off, had a working appreciation of how a new tracer could be valuable to his profession. Before having to return to Poland due to a family emergency, he investigated various strategies for numerical modeling Kr-85 transport in the sub-surface, and participated in evaluation of the first groundwater sampling site

. Michael Mobley, (Physics) October 1995 through August 1997, designed a new sample collector, ion current monitor, and EM detector for the second isotopic enrichment step. Ran extensive ion trajectory computer simulations using SIMION to optimize the new design, achieving a factor of 2X to 3X improvement in all relevant parameters. In addition to becoming proficient with a very complex software package, he had to truly understand electrostatics and forces on charged particles to properly set-up the simulations. He also prepared engineering drawings of the new components, and saw them through fabrication in the machine shop.

Katherine Ocker-Stone, (Geology) May 1996 through present, arrived at IRIM with practical knowledge of conventional static noble gas mass spectrometry. Being interested in RIMS applications to planetary, science and embarking on research projects as diverse as determining chondrule exposure ages and evolution of the Martian atmosphere, has had to learn a very significant body of knowledge that was also new to the PI. Her learning experience was very much enhanced by the participation of very knowledgeable collaborators IRIM has attracted. The 15-month sabbatical at IRIM of Dr. Jamie Gilmour of the University of Manchester, and frequent contacts with Dr. Otto Eugster from the University of Bern have resulted in her developing a very good understanding of the field. In addition, she has developed a very broad base of laboratory and design skills, as much of the apparatus did not exist when she arrived. Was responsible for the design and assembly of all of the additions to the RIS-TOF system. Developed proficiency in all aspects of operation and adjustment of the laser and TOF MS systems.

Karla Kubler, (Geology) January 1997 through June 1997, mostly modified an existing software package for mass spectrometer control for the first isotopic enrichment step while completing her M.S. thesis (on another topic.) She not only had to teach herself PASCAL, but also had to learn the principles of the mass spectrometer, data collection strategies to reduce systematic errors, and the unique requirements imposed by IRIM's applications.

Weiquan Dong, (Geology) August 1998 through August 2000, came to IRIM with a background in geochemistry and practical experience almost exclusively in wet chemistry. He was interested in applications of Kr-85 in hydrogeology, a field in which he had no formal training or experience. With the guidance of Co-PI McKay, and very diligent study and library research on his own, developed a very good understanding of the subject. With guidance from the PI, he gained an understanding of the physics of the technology, and designed and optimized the first two steps in the Kr-85 analysis process for groundwater.

Undergraduate Students:

Adam Berryhill, Student Assistant, April 1994 through April 1996 and full-time Research Assistant after graduation through September 1996, participated in disassembly, moving, and reinstallation of the equipment at the University of Tennessee. Assisted in setting up the IRIM facility, and developed a wide range of technical skills, ranging from all aspects of vacuum system maintenance, mass spectrometer operation, mechanical component design and fabrication, and, electrical and electronic system assembly.

Chris Stone, Student Assistant, November 1994 through December 1994 and full-time Research Assistant after graduation through May 1995,. assisted in assembly of the first enrichment system and became competent in operation and maintenance of the vacuum and electronic systems.

The skills developed at IRIM by both of the above students were directly responsible for very well-paying and challenging employment received in high-tech industry.

Scott Legg, Student Assistant, September 1998 through December 1998, designed printed circuit board lay-out, specified and procured components, assembled, and tested a high voltage power supply and Marks Generator for a pulsed-laser system.

Science Alliance Summer Undergraduate Research Fellows Program:

This is a graduate school recruitment program for promising undergraduate science students. A stipend is provided to these students by the Science Alliance, who are then assigned for a 10 week period during the summer to a particular research program. During the past eight years, five students were assigned to IRIM, and with the exception of Mobley, they all worked with the PI on various aspects of developing a method to collect and preserve for return to earth volatile components from the coma in a comet fly-by space mission. At IRIM, all of the students designed and constructed some aspect of the apparatus, made trapping efficiency measurements, and gave a 15-minute presentation of their work at the end of the summer. The students were:

Michael Mobley, Summer 1994	(later became UT Physics Graduate Student)
Andy Glenn, Summer 1996	(later became UT Physics Graduate Student)
Steve Kadlec, Summer 1997	
Randy Lillard, Summer 1998	
Josh Hayes, Summer 1999	

Opportunities for Training and Personnel Development

Just as the interdisciplinary nature of IRIM's research gives participants the opportunity of learning about current problems in a wide variety of scientific fields, so is the diversity of instrumentation, most of it designed and constructed at IRIM, an opportunity for team members to learn new experimental techniques, an appreciation and understanding of a wide variety of laboratory skills.

Starting with the water sampling equipment, and progressing through all the systems to the final laser-based TOF mass spectrometer, knowledge from many disciplines is required. Students have had to learn how to design, assemble and maintain vacuum hardware and laser-based optical systems, operate machine tools, (lathe, drill press, etc.) use drafting software to prepare machine-shop ready drawings, and electronic test equipment (oscilloscopes, meters) to trouble-shoot the many interconnected systems. They have had to develop the patience required to tune-up and operate four different mass spectrometer systems, the self-control to think before acting, and discipline to make changes in a systematic fashion and to record what was done. They have also been required to develop good safety habits as many aspects of the work could be rather dangerous. Not all students have learned all skills, but the group is small and each individual has become competent in many areas.

As an example, lets focus on Ms. Ocker-Stone, who is interested in obtaining spatially-resolved (micrometer-scale) and calibrated krypton and xenon isotopic analyses of extraterrestrial material. With assistance from the PI, a new RIS laser system had to be specified, designed and installed, a calibration gas pipette with 10^8 dilution capability was designed and assembled, and a UV microprobing gas extraction and viewing system had to be made. In addition, she also learned to tune and maintain two pulsed Nd:YAG lasers and three dye lasers.

Although most of the equipment has been completed, many upgrades and capability expansions are in the works, offering future participants, be they undergraduate, graduate, post-doctoral, or visiting collaborator many new practical experiences.

Overall Research Results

The activities pursued in this project were designed to enable analytical measurements at sensitivity levels (few hundred atom detection limit) not possible before, and to evaluate potential applications of this new capability.

1. Facilities have been set up to permit reliable Kr-81 and Kr-85 analyses from practical-sized samples. The analytical process is complex, requiring six distinct steps utilizing one-of-a-kind equipment that is not commercially available. The development, based on an earlier "proof-of-principle" system, has resulted in reliable operation of each of the six steps, and an understanding of all issues related to reproducibility and calibration. No automation or cosmetic issues were addressed, so the system still looks rough, but it is now feasible to process a suite of 24, or more, samples in a semi-routine manner without adjustment of major system parameters or extensive maintenance. Samples have been processed through all steps without any difficulties, and the intermediate results look completely normal. Although everything is working, and the required sensitivity is there, it has not been possible to report a final result from a "real sample" that has been through all processing steps at this time. An extremely small leak has developed in the instrument of the last (and most sensitive) step, thereby masking the analyte signal with a large atmospheric krypton background. This is not a fundamental problem because earlier operation of this same instrument resulted in a factor of 200X to 500X lower background. Results should be forthcoming as soon as this problem is resolved.

2. The necessary hardware has been developed and deployed to apply the analytical sensitivity of the instrument of the last step to spatially resolved Kr (followed by later Xe) isotopic measurements with micron-level resolution on extraterrestrial samples. A laser microprobing system and accurate gas calibration system was designed and installed. Tests were performed with artificially generated samples, verifying degassing efficiency and spatial resolution. All test are positive, but results from extraterrestrial samples await correction of the background problem discussed above.

3. The response to the availability of these new analytical capabilities from researchers, both in the fields of hydrogeology, and in planetary sciences, has been very positive. Active collaborations have established with some of the top research groups in their respective fields. Joint exploratory research proposals have been submitted (and some funded) to start

investigations that would not have been possible earlier. Samples have been collected and shipped to us, and several researchers have spent time at our facilities to work with us in our laboratory. Sufficient space is available to accommodate these collaborators without compromising our own activities.

Recommendations for follow-on research are:

(1) Foremost, repair the leak (or other cause of background) so that analysis of partially processed samples in the pipeline can be completed. These results should be sufficient to convince the community that these analyses are indeed feasible.

(2) Implement several modest improvements, identified late in the course of this project, that will enhance reproducibility and quantitation, and reduce the sample size to a minimum of 3 liters of water.

(3) Operate the system for approximately one year, analyzing 50 to 75 environmental samples, and a similar number of planetary samples. This should identify any remaining "weak links" in the process.

(4) Implement simultaneous Kr and Xe operation for planetary samples.

(5) Implement the remaining improvements identified in (3) above.

(6) Secure funding for operating expenses so that the facility can start serving a wider community by becoming a "user facility."

Research Output

Refereed publications and extended abstracts:

M.G. Payne, L. Deng, and N. Thonnard, "Applications of Resonance Ionization Mass Spectrometry," (Invited Review), Rev. Sci. Instrum., 65, 2433-2459, 1994.

N. Thonnard and B.L. Lehmann, "The Institute for Rare Isotope Measurements: An Inter-Disciplinary Facility for RIS-Based Applications," AIP Conf. Proc., 329, 335-338, 1995.

N. Thonnard, "Resonance Ionization: Potential Application of Few-Atom Detection Techniques to Inter-Planetary Dust Particle and 'Stardust' Studies," Lun. Planet. Sci. 26, 1411-1412, 1995.

N. Thonnard, "Resonance Ionization of Heavy Noble Gases: The Potential of Krypton and Xenon Measurements from Single Presolar Grains," Meteoritics 30, 588, 1995.

C. Hohenberg, N. Thonnard, K. Kehm, A. Meshik, A. Berryhill and A. Glenn, "Active Capture of Low-Energy Volatiles: Bringing Back Gases from a Cometary Encounter," Lun. Planet. Sci. 28, 581-582, 1997.

K. Ocker and N. Thonnard, "The Path to Krypton and Xenon Isotope Measurements from Few-Micron Sized Samples; I. A Low-Blank Gas Extraction System," Lun. Planet. Sci. 28, 1037-1038, 1997.

N. Thonnard, L.D. McKay, D.H. Cumbie and C.F. Joyner, "Status of Laser-Based Krypton-85 Analysis Development for Dating of Young Groundwater," GSA Abstracts with Programs, 29, No. 6, A-78, 1997.

C.M. Hohenberg, N. Thonnard, K. Kehm, A.P. Meshik, A. Berryhill and A. Glenn, "Active Capture of Volatiles: Implications for Planetary and Atmospheric Xenon," Meteorit. Planet. Sci. 33, A69, 1998.

K. Ocker and N. Thonnard, "The Path to Krypton and Xenon Isotope Measurements from Few-Micron Sized Samples; II. Pulsed UV Laser Microprobing." Lun. Planet. Sci. 30, Abstract #1622, LPI, Houston (CD-ROM), 1999.

K.D. Ocker, N. Thonnard, J.D. Gilmour and C.F. Joyner, "The Path to Krypton and Xenon Isotope Measurements from Few-Micron Sized Samples; III. Kr calibration and First Application of the RIS-TOF System," Lun. Planet. Sci. 31, #2012 (CD-ROM), 2000.

K.D. Ocker, N. Thonnard and C.F. Joyner, "Versatile Sample Viewing System with Large Magnification Range," Rev. Sci. Instrum.,31, 581-582, 2000.

One-Time Publications and Books

N. Thonnard, "Rare Noble Gas Isotope Measurements Using Laser-Based Resonance Ionization," in *Abstracts of Eighth International Conference on Geochemistry, Cosmochronology, and Isotope Geology*, M.A. Lanphere, G.B. Dalrymple and B.D. Turin, eds., US. Geo. Surv. Circ. 1107, p322, 1994.

N. Thonnard and L.D. McKay, "Emerging New Ultra-Sensitive Analytical Techniques using Resonance Ionization: Applications in Groundwater Dating and Other Trace Analyses," in *ATV 1997 - Committee on Groundwater Pollution*, publ. by the Danish Academy of Technical Sciences, p135, Copenhagen 1997.

W. Dong, C.F. Joyner and N. Thonnard, "Low-Blank and Efficient Groundwater Sampling and Gas Separation for Krypton-85 and Krypton-81 Analyses." (Abstract) in *South Central GSA Section Meeting 2000,* The Geological Society of America, Boulder, 2000.

J.D. Gilmour, J.A. Whitby, G. Turner, K.D. Ocker, C.F. Joyner and N. Thonnard, "Isotopic Analysis of Xenon and Krypton by Resonance Ionization Mass Spectrometry," (Abstract) in *Geosciences 2000 Conference*, The University of Manchester, Manchester, 2000.

Equipment and Facility Developmed

A complete laboratory has been set-up to enable detection of Kr-81 and Kr-85, rare (part in 10^{18}) constituents of the atmosphere, to provide new tracers and age-dating tools for use in atmospheric, hydrogeologic, oceanographic and polar research.

Six distinct systems were either developed or significantly modified and enhanced consisting of:

(1) a controlled groundwater sampling and storage system that eliminates the possibility of contamination from modern air

(2) a water degassing system with >95% dissolved gas recovery

(3) a separation system with >95% krypton retention and >90% purity

(4) a static mass spectrometer that can process several μl of krypton, collect >50% of the desired isotope and reduce undesirable (major) isotopes by a factor of 10^5

(5) a static mass spectrometer optimized for 10^{-13} to 10^{-11} cc samples that can collect>50% of the sample reduce interfering isotopes by $>10^4$

(6) a static time-of-flight mass spectrometer with resonance ionization and pulsed cryogenic sample concentration having a 100 ^{85}Kr atom 3? detection limit

System (6) above is also applicable to planetary science research with modifications permitting resolved krypton and xenon isotopic analyses of extraterrestrial material containing a few thousand analyte atoms. The krypton system is in the testing phase, with xenon capabilities to follow within a few years.

Presentations

Invited Presentations:

Norbert Thonnard
Laser-Based Resonance Ionization: An Emerging Analytical Technique to Guide and Monitor the Environmental Impact of Energy Production in the Next Century.
Symposium on Energy and the Environment in the Next Century
44th Annual Meeting, Southeastern Section, Geological Society of America
April 6-7, 1995, Knoxville, Tennessee

Norbert Thonnard and Larry D. McKay
Development of ^{81}Kr and ^{85}Kr for use as Groundwater Tracers.
Second Topical Research Symposium, Geosciences Research Program, Office of Basic Energy Sciences, U.S. Department of Energy
January 29-30, 1996, Oak Ridge, Tennessee

Norbert Thonnard and Larry D. McKay
Emerging New Ultra-Sensitive Analytical Techniques using Resonance Ionization: Applications in Groundwater Dating and Other Trace Analyses.
ATV Committee on Groundwater Pollution, Danish Academy of Technical Sciences
April 23, 1997, Lyngby, Denmark

Other presentations:

At National and International Meetings

Norbert Thonnard and Harmon Craig (poster)
Fifth International Symposium on Antarctic Glaciology
September 5-11, 1993, Cambridge, England.

Norbert Thonnard
Eighth International Conference on Geochronology, Cosmochronology and Isotope Geology
June 5-11, 1994, Berkeley, California.

Norbert Thonnard and Bernhard Lehmann (poster)
Seventh International Symposium on Resonance Ionization Spectroscopy and Its Applications
July 3-8, 1994, Bernkastel-Kues, Germany.

Norbert Thonnard (poster)
Twenty-Sixth Lunar and Planetary Science Conference
March 13-17, 1995, Houston, Texas.

Norbert Thonnard (poster)
58th Annual Meeting of the Meteoritical Society
September 11-15, 1995, Washington, D.C.

Charles Hohenberg, Norbert Thonnard, Karl Kehm, Alex Meshik, Adam Berryhill and A. Glenn
Twenty-Eighth Lunar and Planetary Science Conference
March 17-21, 1997, Houston, Texas

Norbert Thonnard, Larry McKay, Dennis Cumbie and Chuck Joyner
1997 Geological Society of America Annual Meeting
October 20-23, 1997, Salt Lake City, Utah

Norbert Thonnard, Charles F. Joyner, Weiquan Dong and Larry D. McKay,
51st National Groundwater Association Annual Meeting
December 3-6, 1999, Nashville, Tennessee

Colloquia (by Thonnard)

Department of Geological Sciences, The University of Tennessee
October 14, 1993, Knoxville, Tennessee

Department of Physics and Astronomy, The University of Tennessee
November 30, 1993, Knoxville, Tennessee

ORNL/UTK Atomic Physics Group
February 3, 1994, Oak Ridge, Tennessee

McDonnell Center for Space Sciences, Washington University
February 9, 1995, St. Louis, Missouri

Department of Geological Sciences, WCGR, University of Waterloo
October 16, 1996, Waterloo, Ontario

Department of Geology, The University of Memphis
December 11, 1998, Memphis, Tennessee

Outreach Activities

Presentations to community-based organizations and general-interest lectures:

Lecture linking atomic spectroscopy and astronomy,
Advanced Physics Class
May 1994, Bell County High School, Kentucky

Practical applications of atomic physics and resonance ionization,
Society of Physics Students
October 1994, Eastern Kentucky University, Richmond, Kentucky

Lecture on application of physics techniques to analytical problems,
Combined Physics and Advanced Biology Class,
December 1994, Bell County High School, Kentucky

Tour of IRIM facilities and discussion of using physics on environmental problems and ultra-sensitive analyses,
Russian Exchange Students at Oak Ridge High School,
March, 1995, Knoxville, Tennessee

Tour of IRIM facilities and discussion of using physics on environmental problems,
Physics Class from Bell County High School
May 1995, Knoxville, Tennessee

Lecture on the interplay between applied physics and basic physics from an atomic physics perspective,
Science Alliance Summer Undergraduate Research Fellow Lecture Program
Department of Physics and Astronomy, The University of Tennessee
July 1998, Knoxville, Tennessee

Contributions to Society

Within Discipline:

One objective of this research was to develop and implement laboratory facilities enabling practical utilization of two promising radioactive isotopes of the noble gas krypton, Kr-81 and Kr-85, which provide a means of determining how long a sample has been isolated from the earth's atmosphere. Because noble gases do not interact chemically with their surroundings, these isotopes have the potential of providing more accurate assessment of important environmental issues related to protection and management of groundwater resources. The low concentration of these isotopes in the environment, which makes them very difficult, or nearly impossible to measure, resulted in little utilization of their advantageous properties until now. The development of analytical methods based on selective and efficient laser ionization of only the targeted element, (krypton, in this case) has made analyses for these isotopes in environmental samples feasible.*

Initially, krypton-85 will primarily be a research tool until its applicability and limitations have been tested in a variety of hydrogeologic settings. First "practical" applications will be in the Memphis Sand aquifer, a sedimentary aquifer in the northern part of the Lower Mississippi Embayment. One study could be to determine the rate of recharge to the Memphis Sand aquifer; another to determine the dynamics of mixing between the shallow, unconfined (and potentially polluted) aquifer with the deeper, confined aquifer through "windows" in the confining layer. A study has been proposed to determine the potential of agricultural pollution influx to the shallow aquifers that are the primary source of water in Denmark. The results from Kr-85 analyses could complement the results from other tracer measurements, and most likely, soon start providing less ambiguous results in the above studies.

In the 20 thousand to 1 million year time regime, Kr-81 could become one of the most important age-dating tools based on environmental tracers. The need for Kr-81 is becoming more urgent as experience with other promising age-dating techniques, such as CL-36, He-4 and U-234/U-238, have been problematical in certain environments. Other applications of reliable tracers in hydrogeology would be to assess the sustainability of older aquifers.

For example, one would like to understand the origins of waters in the Fort Pillow aquifer, a confined aquifer underlying the Memphis Sand aquifer. Water from the Fort Pillow aquifer is of high quality, and starting to be exploited in a few regions of the Memphis Metropolitan area, although little is known about its sustainability. Combining Kr-81 with Kr-85 measurements could give valuable insight. For example, any Kr-85 signal would be proof that some modern (<40 years) water is entering the aquifer, but a sub-modern Kr-81 concentration indicates that a fraction of the water has an average residence time >20 thousand years

**Note:* The process for these measurements is complex, and utilizes six distinct pieces of equipment, all of which have been completed and tested, and operate correctly. At this time, however, we are not able to report final results on environmental samples, which have been collected and processed successfully through all steps except for the last one. A technical problem (perhaps a small leak) has developed which raised the background, thereby preventing completion of the analyses. We anticipate rectifying this problem shortly, and will provide the results of the completed analyses in a supplement report. The discussions in this, and in the following sections, assumes that the problem has been corrected, which we fully expect to happen soon.

Other Disciplines:

Another major application of the technology being implemented for Kr (and later also Xe) isotopic measurements is in the field of planetary sciences. Some of the most un-altered materials in the Solar System are refractory (high temperature) grains that can be found in carbonaceous meteorites. These are believed to be the most primitive, and preserve samples from the dying stars that supplied the raw materials that formed our Solar System. But these are only a few micrometers in diameter, and may contain at most only a few thousand atoms of the heavy noble gases Kr and Xe. Changes in Kr and Xe isotope ratios can provide valuable insight to the nucleosynthesis history of the materials that formed our Solar System, and the thermal and aqueous evolution of pre-planetary and planetary bodies. Measurements of these type of samples would only require the last step of the processing system described earlier.

Human Resources Development:

As discussed more thoroughly in the main body of this report, twelve students worked on various phases of the development of this facility. The diversity of the instrumentation that was required to assemble the multi-step system discussed earlier has provided a broad experience base to the them. This has provided students not only with the opportunity of developing new practical skills, but also, as the capabilities of this facility attracts collaborators working on problems that could not be solved before, build a better understanding of current leading-edge problems in the fields of hydrogeology and planetary sciences.

Resources for Research and Education:

Also mentioned earlier, the facilities developed here are unique and provide new analytical capabilities. Once the utility of these analyses becomes accepted, they could become the prototype for several others as demand increases.

Beyond Science and Engineering:

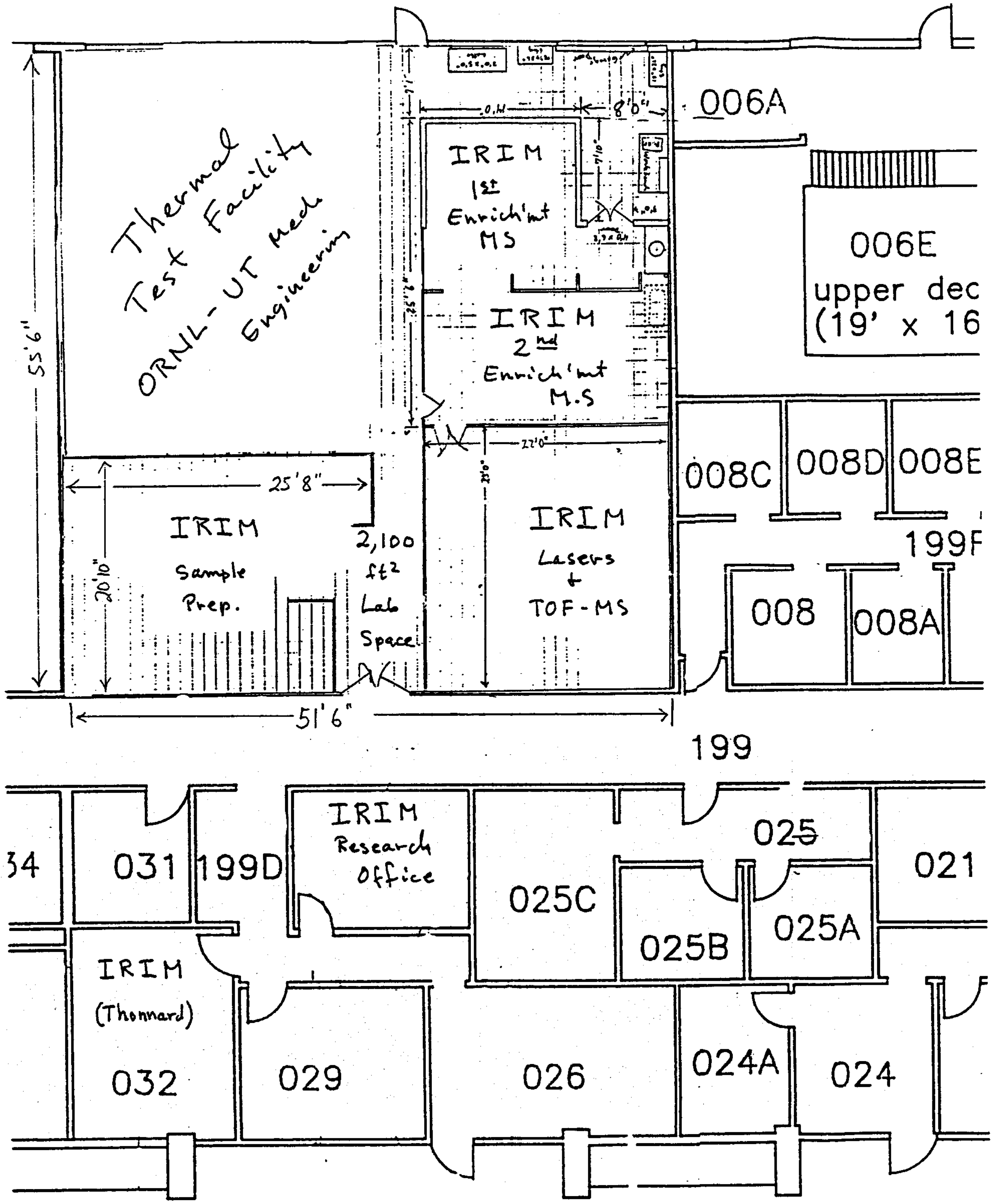
Although the facilities developed here serve the needs and expand the capabilities for research in the geologic and planetary sciences, many of the applications will help resolve and/or develop a better understanding to a variety of issues in resource utilization and in environmental assessment, contributing to the overall well-being of society.

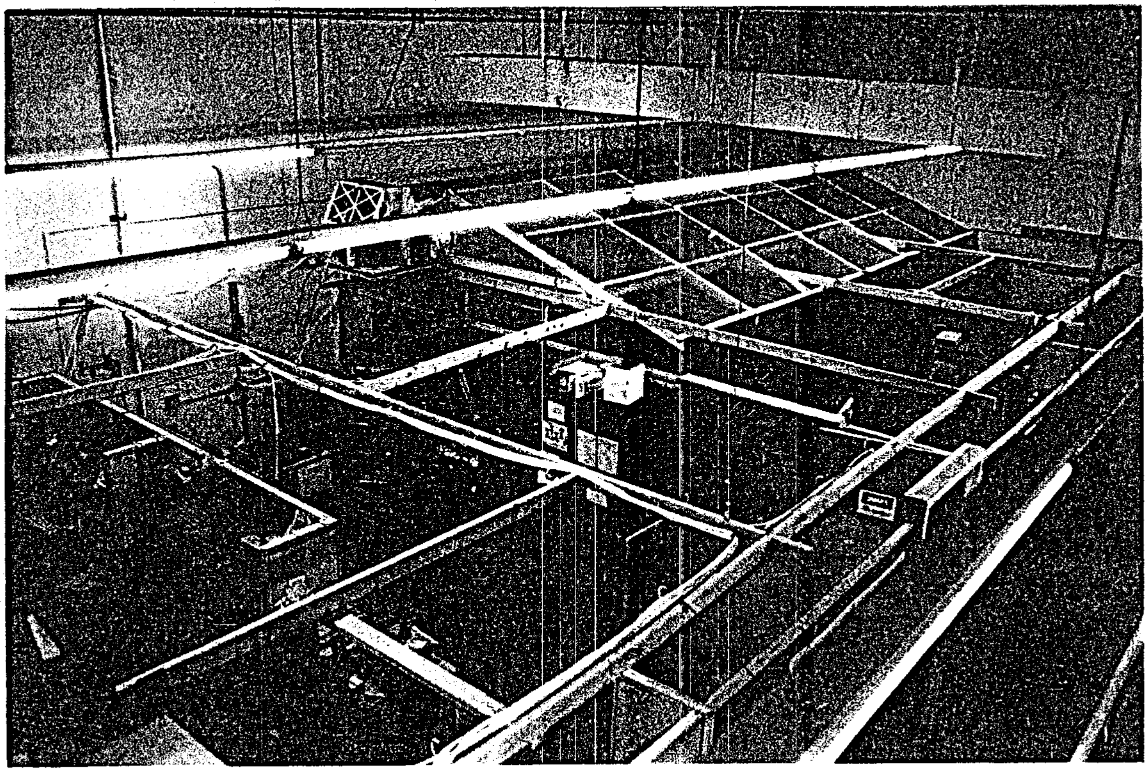
For example, the Department of Energy and related national laboratories could use Kr-85 in contaminant fate and transport studies at sites such as Savannah River or Oak Ridge, and the US Geological Survey in their ongoing research on hydrology of aquifer systems. In the long term, krypton-85 measurements may become a widely used investigative tool for researchers and practitioners working on a variety of topics, including assessing aquifer or basin yields, and examining the integrity of clay-rich confining layers below contaminated sites.

Kr-81 could help resolve some of the issues being debated about DOE's Yucca Mountain long-term radioactive waste repository. Although the disposal site being developed is very high above the saturated zone, some investigators believe the water table occasionally rises to the disposal chamber level. But if Kr-81 measurements of water in the saturated zone result in a very long average residence time, one could conclude that any run-off from the repository would be "locally confined," and therefore not a pathway for wide-spread dispersal. Kr-81 would not suffer from the uncertainties in Cl-36 age-determinations introduced by high salinity and/or high uranium content of the formation.

Finally, Kr-81 could be used to determine the age of polar ice cores that are older than approximately 80,000 years. At great depths, ice becomes plastic and the usual annual variations in dust layers become smeared and can no longer be counted to provide a reliable age. Ancient polar ice contains dissolved gases from the earth's atmosphere, dust from various parts of the world, and seeds and pollen grains. These all are invaluable historical records of atmospheric composition, air circulation patterns, temperature, rainfall, and many more parameters about the status of the earth's climate during the past one million years. With the mounting evidence of the rapid changes that have occurred in our climate over the past one hundred years, it would be extremely valuable to have historical data to calibrate climate change model calculations

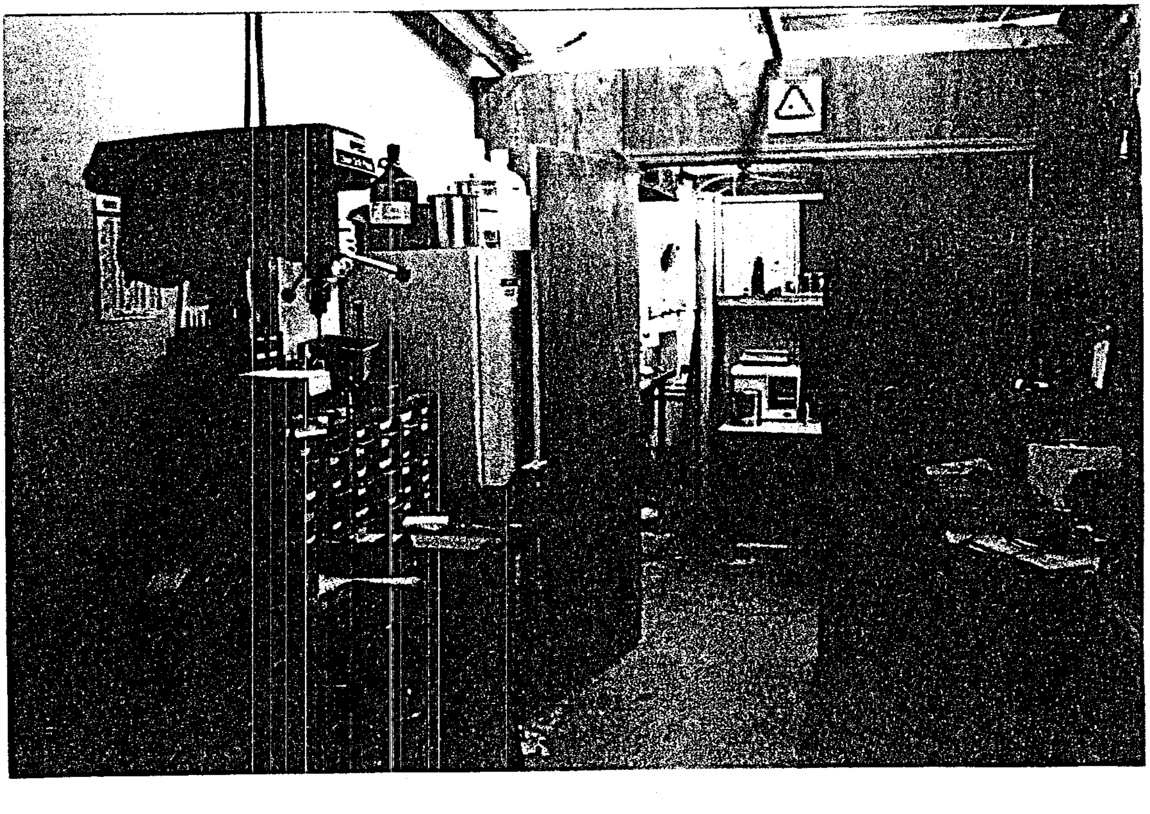
The University of Tennessee
Pellissippi Research Facility
10521 Research Drive, Knoxville, TN 37932

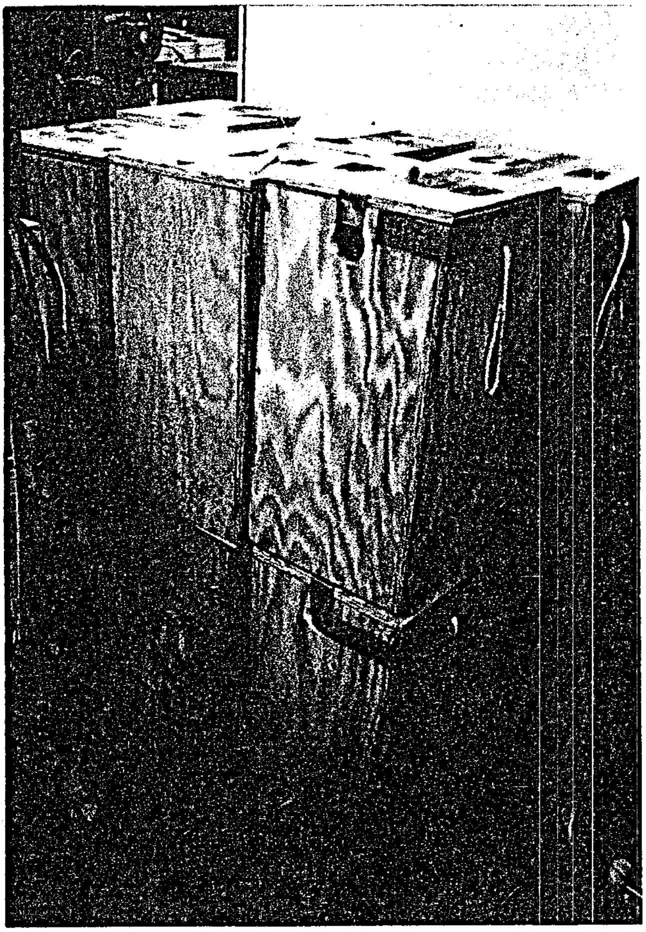




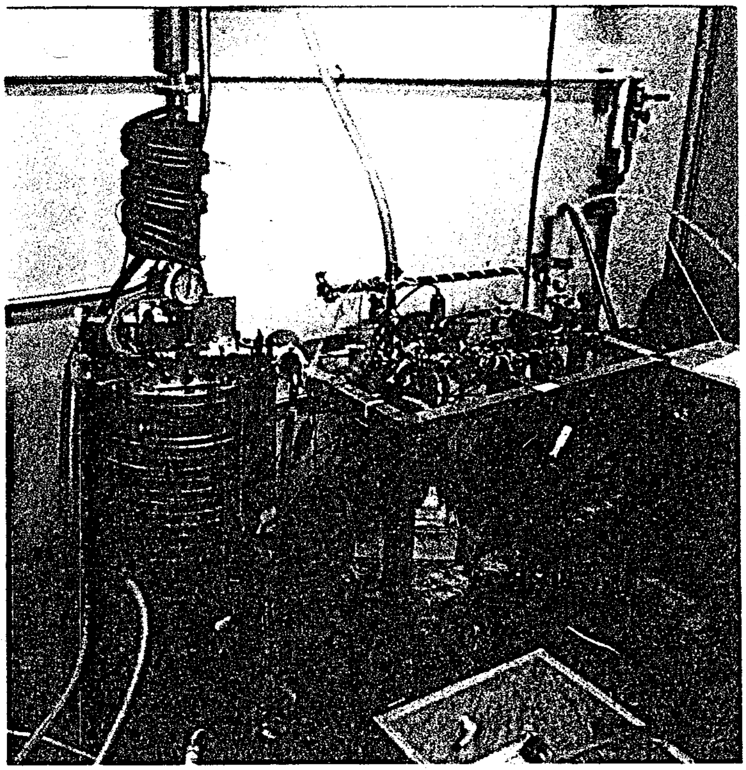
IRIM facilities, looking at electronics work area, 2nd enrichment system and laser/TOF MS lab. The latter is enclosed and under positive pressure with two stages of filtration to reduce dust on optics.

Shop area with chemical storage cabinet.

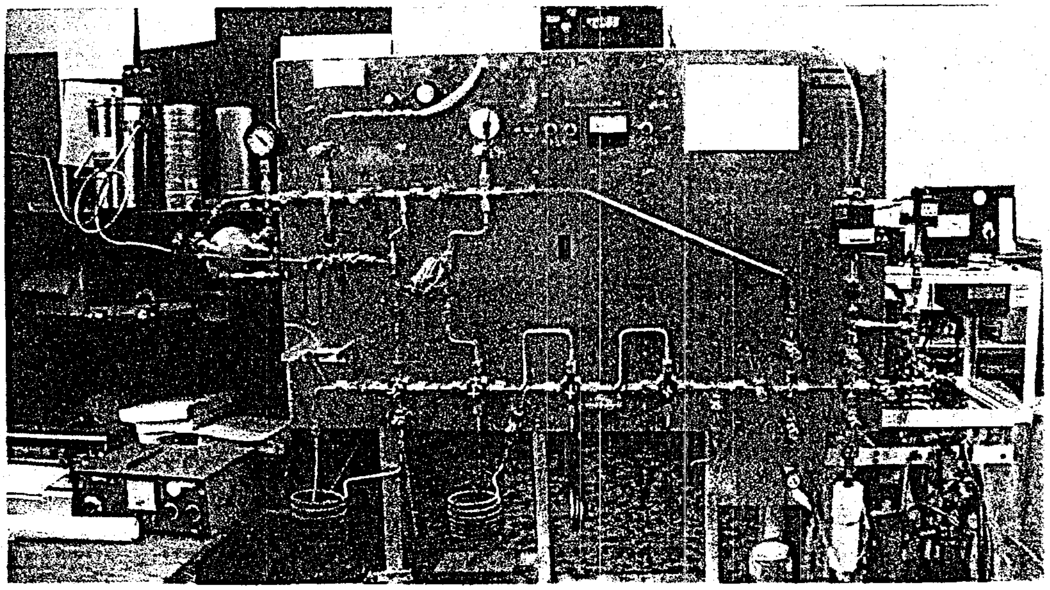




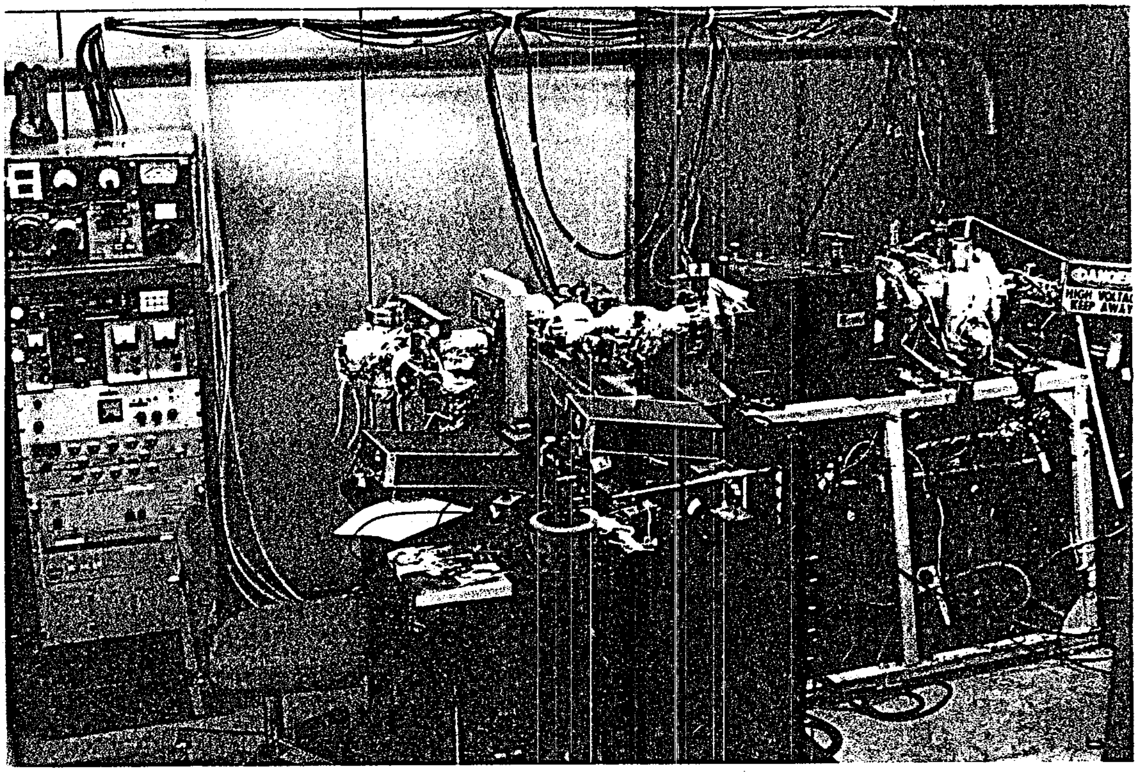
Twelve of thirty water sampling bottles in shipping crates awaiting analysis. They consist of 20 *l* vacuum-tight glass bottles with appropriate fittings for contamination-free sampling.



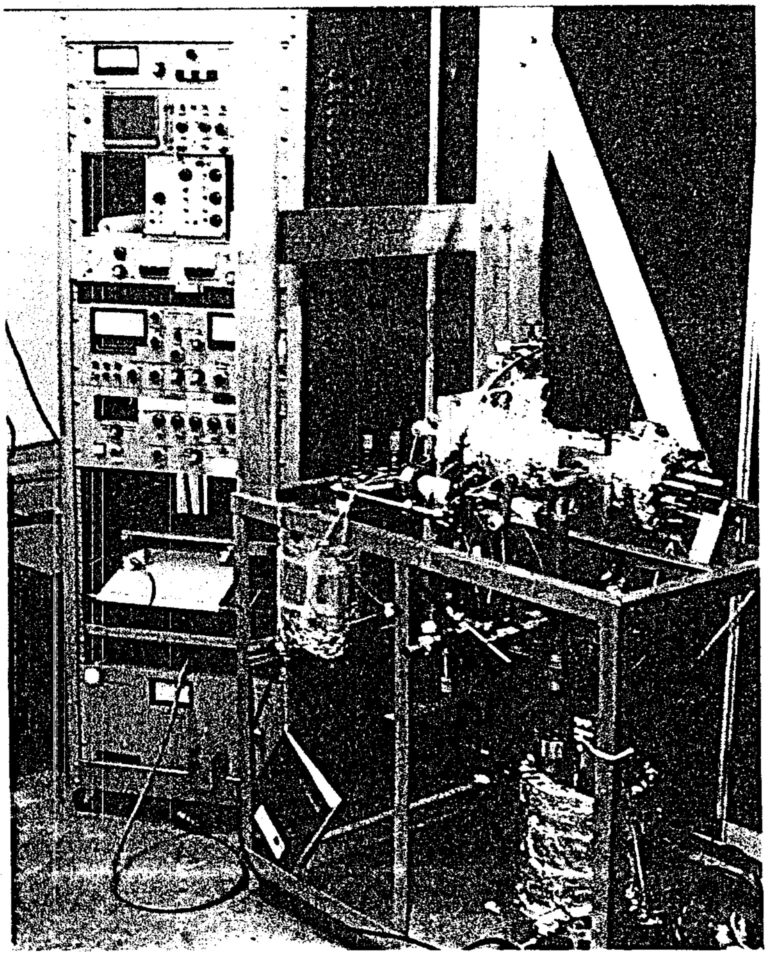
Water degassing system undergoing tests. The samples are sprayed into evacuated, large stainless steel reservoir. More than 98% of dissolved gases are recovered from sample.



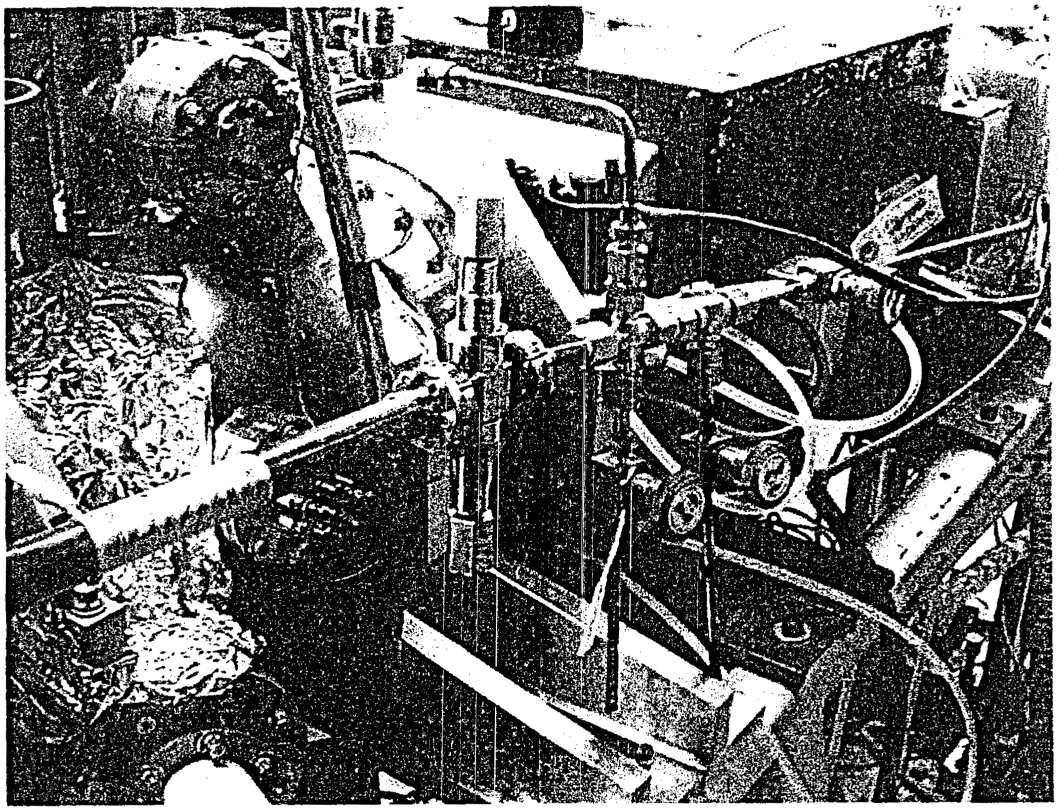
Kr-air separator. Typical samples contain 300 to 500 cc of air, which yield a few milliliter of krypton at an efficiency greater than 98%.



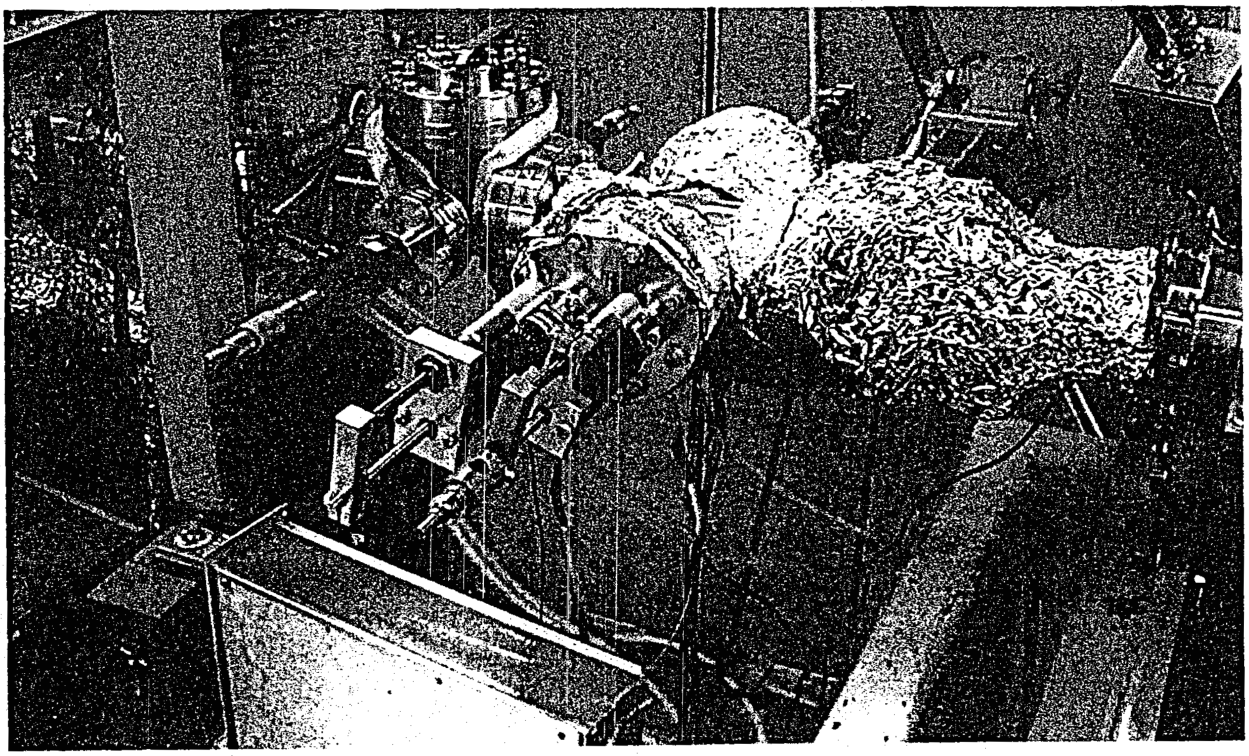
First isotope enrichment mass spectrometer . Interfering isotopes are reduced by 5 orders of magnitude while 50% of the desired isotope is recovered.



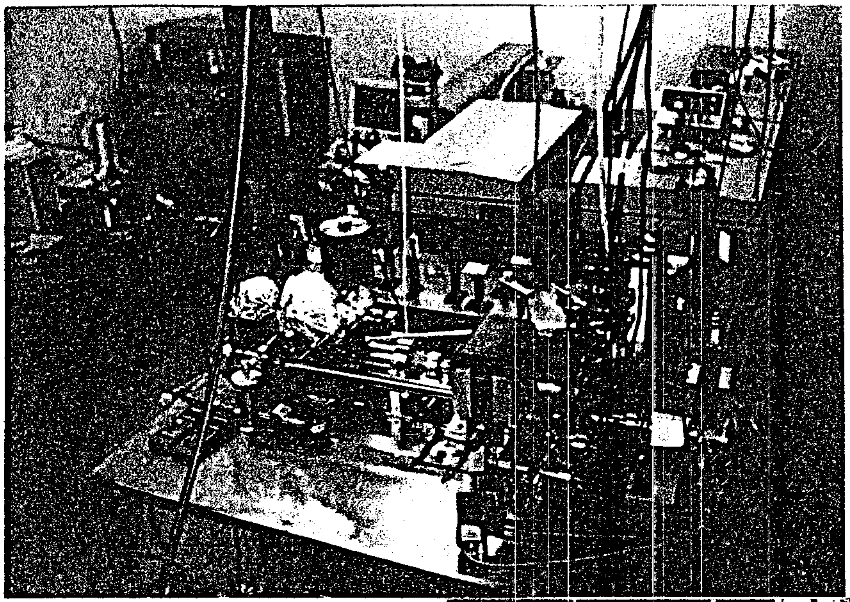
Second isotopic enrichment mass spectrometer. Forty to fifty percent of the desired isotope is recovered, while interfering isotopes are reduced by 3 to 4 orders of magnitude.



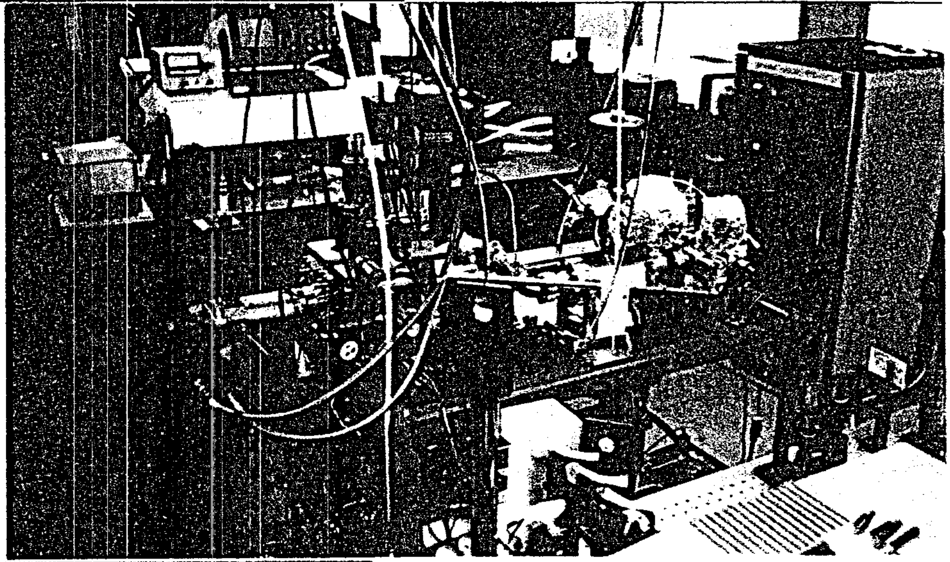
Gas inlet system to first Enrichment system. Shown is the calibration pipette (cross valve arrangement) one sample and two Kr-85 standards.



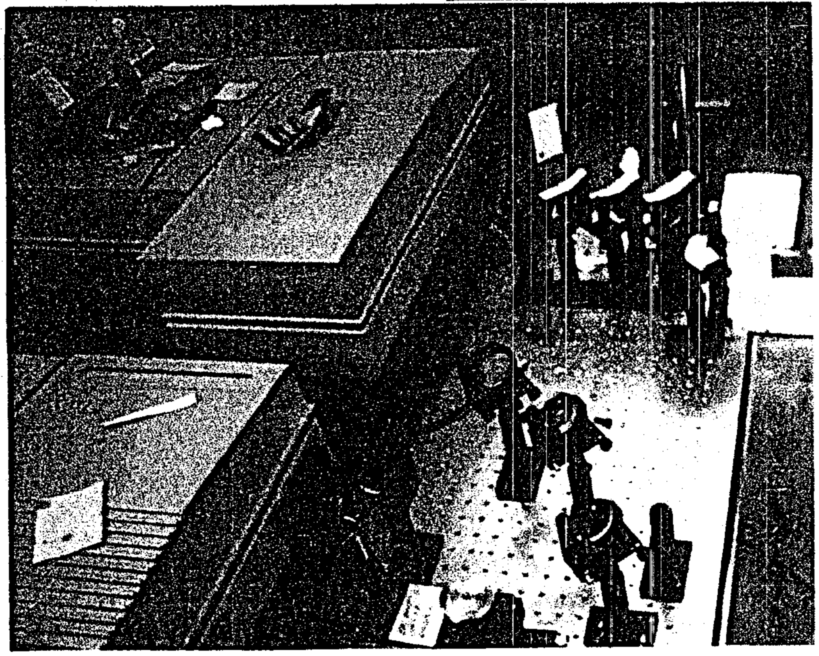
Positioning micrometer feed-throughs for the defining slit, wire beam stabilization system, and the Faraday cup that continuously monitors the reference beam current (from left).



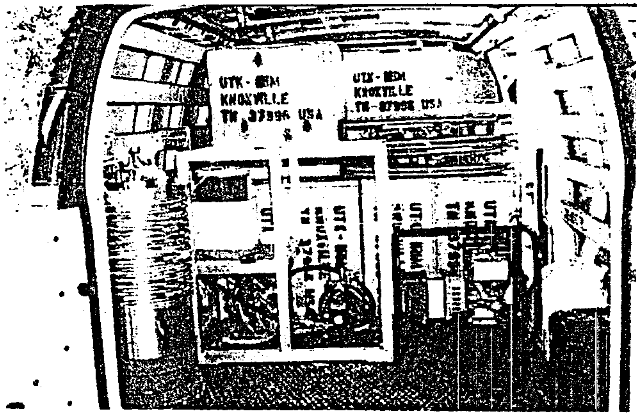
Krypton resonance ionization laser system and time-of-flight mass spectrometer. A detection limit of 100 ^{85}Kr atoms was shown earlier.



View in opposite direction showing TOF MS and xenon resonance ionization laser system.

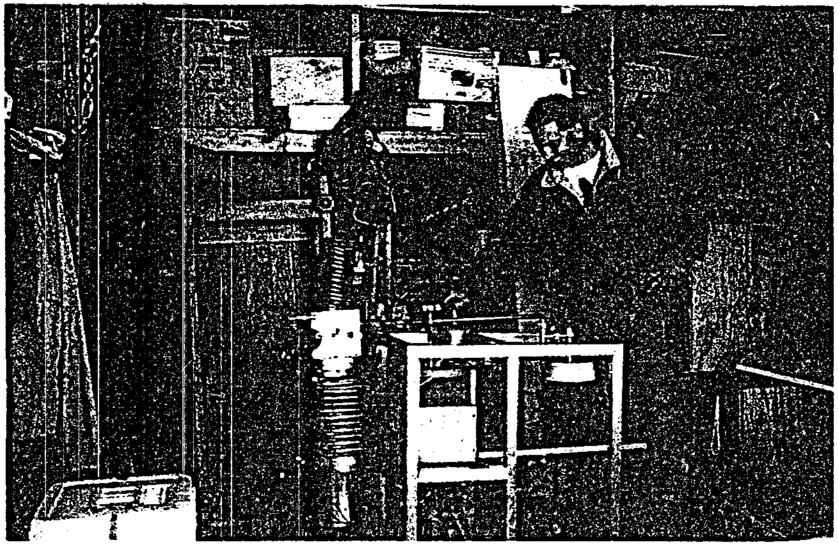


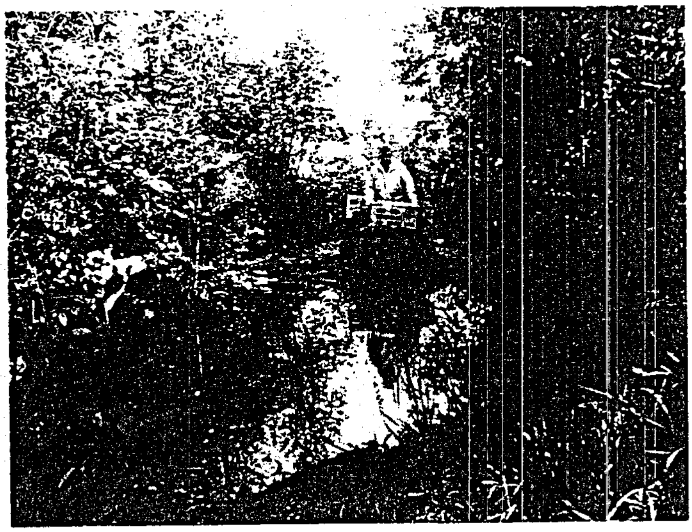
Details of beam combing optics.



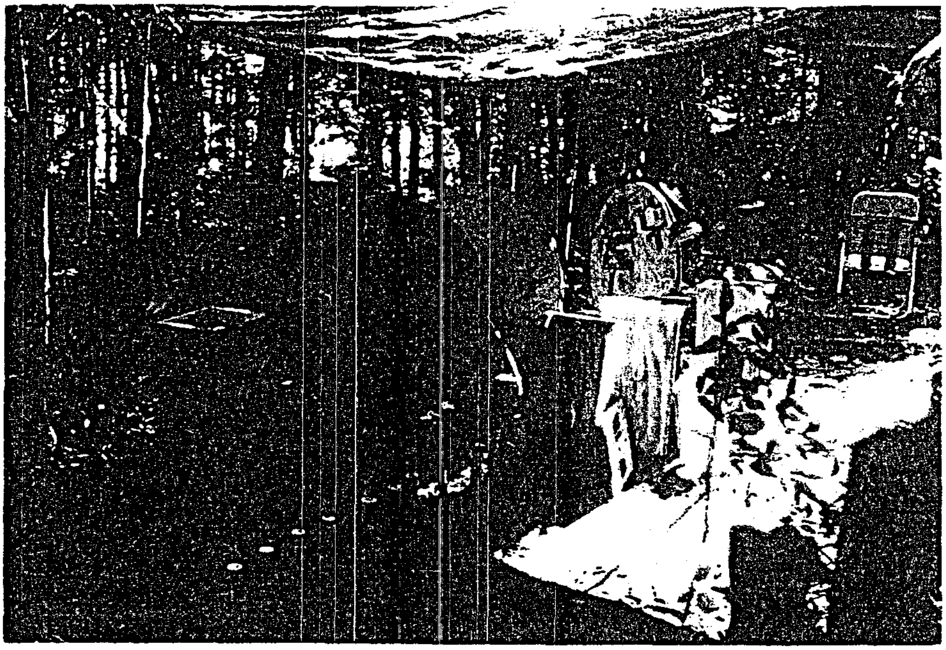
Almost ready to roll --- van being loaded for 995 mile trip to the Sturgeon Falls, Ontario site of the University of Waterloo Centre for Groundwater Research. Visible here of the 3,000 pound load are crates with gas storage cylinders, water sampling bottles, sampling/packer reels, portable generator, and the water degassing system.

"Base Camp" at the Lincoln Motel in Sturgeon Falls. Set-up of water degassing system in a storage shed.

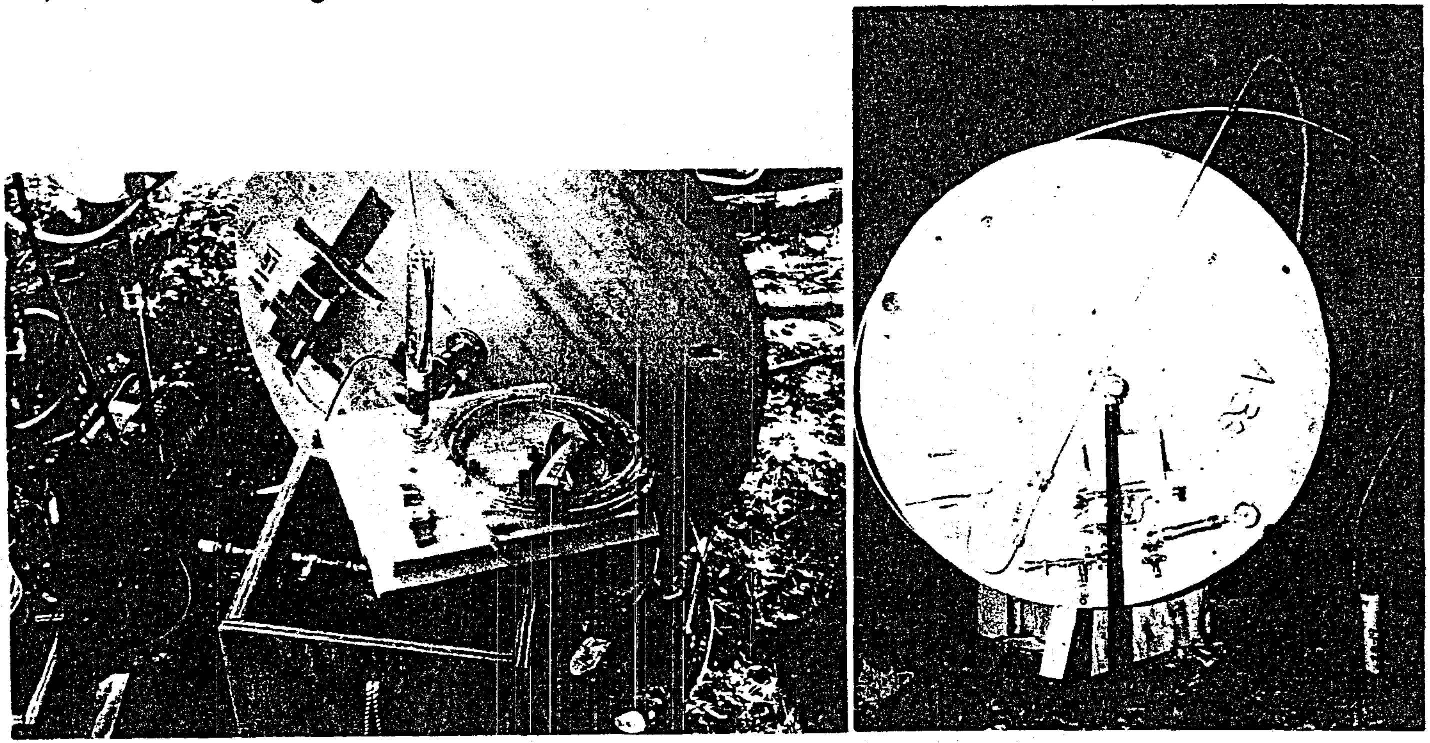




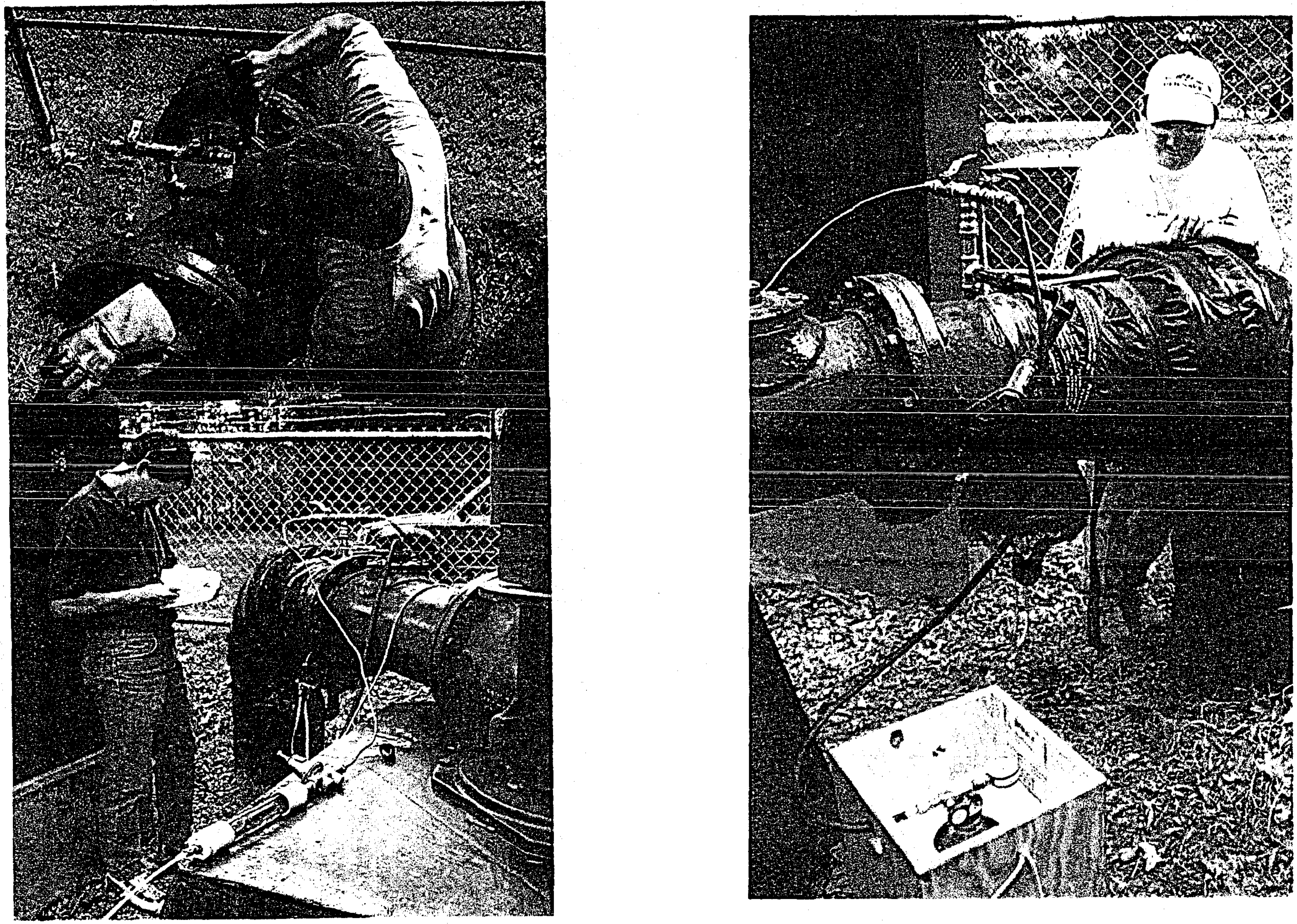
Transporting water sampling bottles to the flow-divide piezometer nest of the WCGR field site. The low permeability of the silty sand aquifer can be clearly seen from the high water table -- it had not rained for more than a week. We very much appreciated the ATV!



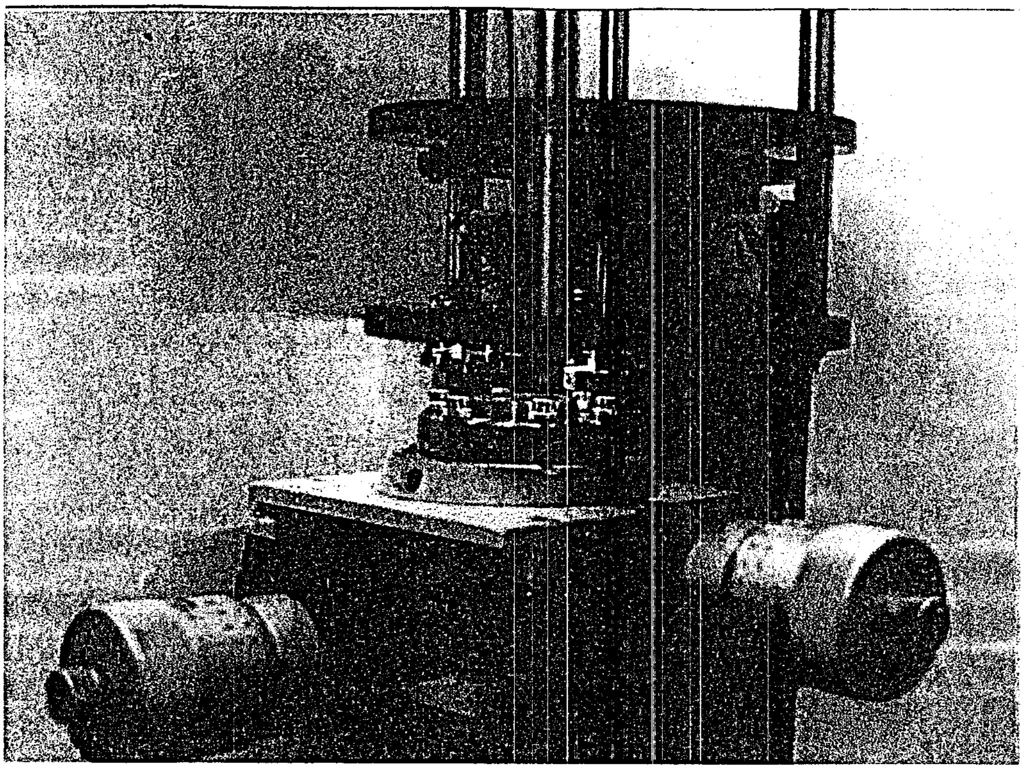
Site "28" at the flow-divide line with twenty-two piezometers ranging from 0.6 m to 21.0 m screen depth. Four depths are being sampled at this time. The wooden crates contain the evacuated 20 l glass water bottles; the wooden reels carry samplers consisting of packers for 0.38", 0.6" and 1.0" I.D. piezometers connected to 15 or 30 meter 5/16" TFE liners enclosing a 1/8" Cu sample tube and three 1/16" Nylon tubes for packer inflation and pressure monitoring.



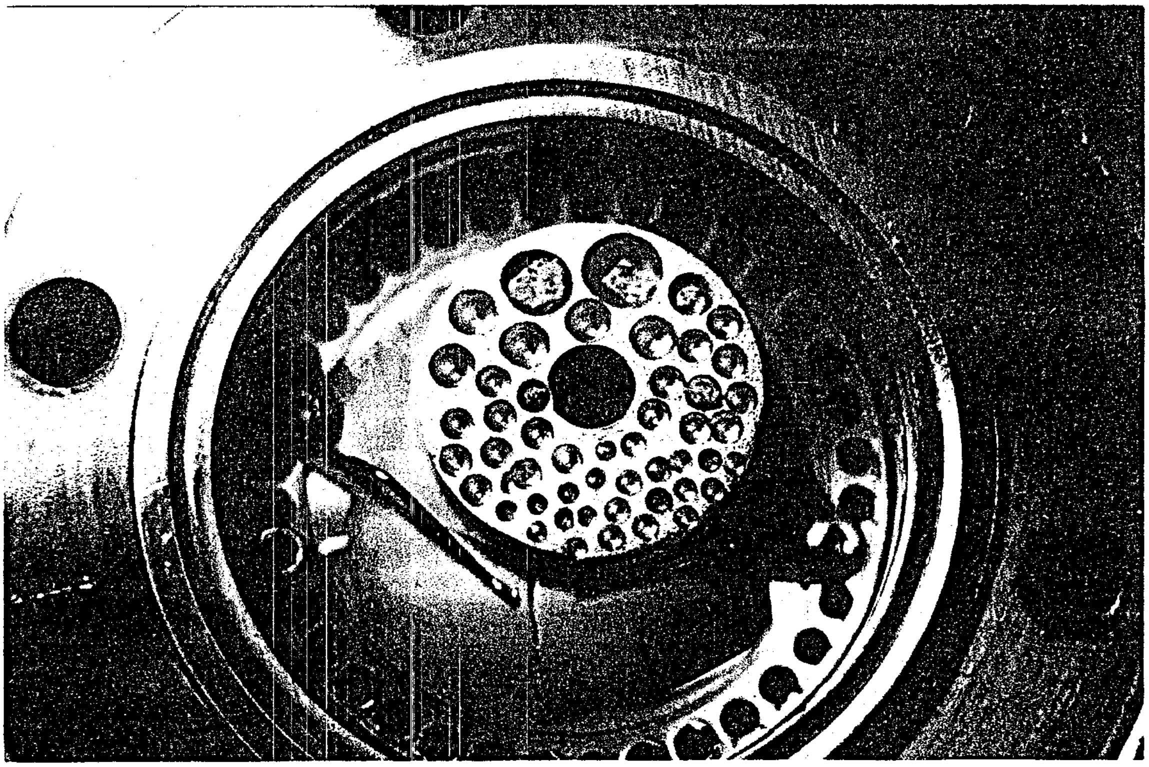
Calibrating sampling rate for each sampler/packer set using needle valve on manifold connected to 20 l sample bottle. (left) After completion of Kr-85 sampling, a few 3/8" Cu tubes were filled and pinched-off for later CFC and tritium/He-3 analysis. (right)



Sampling from a production well of MGL&W in the Memphis Sand Aquifer. Installing valve assembly for repeated sampling of the same well, (upper left) collecting dissolved gases in diffusion sampler for He-3 analysis, (lower left) and collecting 20 liters of water for Kr-85 analysis (right).



Micro-sample chamber in manipulator. The bottom portion of the viewing system is shown.



View inside the micro-sample chamber. The copper piece holds 12 micro-sized samples that are to be analyzed.