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OPTICAL ASSAY TECHNOLOGY FOR SAFEGUARDS

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Quarterly Report

July 1 - September 30, 1990

Date Transmitted: October 1990

Prepared for the Office of Safeguards and Security

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ABSTRACT

Research conducted in the Ames Laboratory Nuclear Safeguards and Security Program during the period July 1, 1990 to September 30, 1990 is reviewed; included are reprints and preprints of papers written during this quarter. The first demonstration of isotopic selectivity in Inductively Coupled Plasma - Laser Excited Atomic Fluorescence Spectroscopy (ICP-LEAFS) is reported and the application of ICP-LEAFS to U isotopic analysis is discussed. Current work in applying optical spectroscopy to the analytical determination of gas phase metal atoms is reviewed. Program administration topics are included in a separately bound Management Supplement to this report.

INTRODUCTION:

This report includes information about activities in the Ames Laboratory Nuclear Safeguards and Security Program during the period 7/1/90 to 9/30/90. The first section contains a summary of research activities, the second section contains reprints and preprints of papers submitted in this period, and the last section, issued as a Management Supplement under separate cover, contains a discussion of administrative matters pertaining to the program.

RESEARCH SUMMARY:

1. INDUCTIVELY COUPLED PLASMA - LASER EXCITED ATOMIC FLUORESCENCE SPECTROSCOPY (ICP-LEAFS) (Murray, Vera, Weeks)

Purpose:

To assess the feasibility of ICP-LEAFS for the determination of Pu and its isotopes without the need for chemical separations from matrix elements or the oxidation state adjustment of Pu prior to analysis.

Progress:

A Nd-YAG laser was used to "pump" a high-resolution tunable dye laser and generate isotopically resolved fluorescence from uranium. This observation was the first of its kind and can be contrasted with the observations of Human et al (Spectrochim. Acta **39B** (1985) 1345-1363) who stated (pg. 1360) that,

> **Our interest in uranium fluorescence was prompted by the possibility of evaluating its isotopic ratio by scanning the spectrally narrow laser beam over the atom/ion absorption profile while monitoring the resulting fluorescence signal. Disappointedly, no significant fluorescence was observed for all the lines possessing a useful isotope shift.**

We were successful because the dye laser we employed in our studies produced extremely narrow bandwidth emission that was sufficient to resolved closely spaced isotopic components. This dye laser (Pegasus Corp.) was designed to achieve narrow bandwidth emission without the use of intracavity etalons, which can complicate the tuning of dye lasers. The Pegasus Dye Laser features a small oscillator (Fig. 1) followed by a series of amplifier stages. Narrow bandwidth emission is most easily produced when the dye laser oscillator is illuminated with a "pump" laser power only slightly above the threshold for lasing. Thus only a few of the many possible longitudinal cavity modes are excited, which results in reduced bandwidth. Three amplifier stages are then used to increase the dye laser output power to the level necessary for fluorescence spectroscopy.

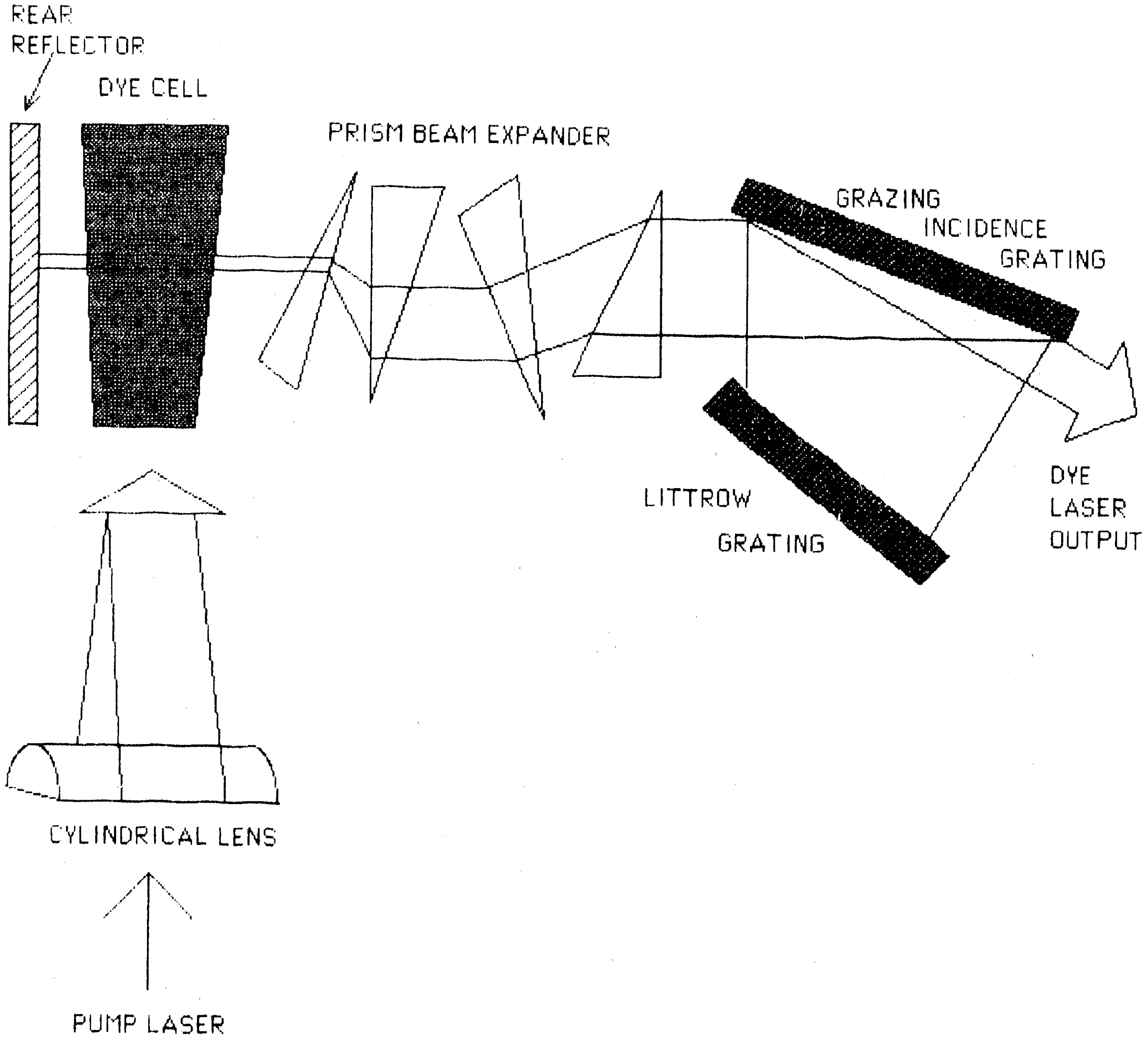

Figure 1. Oscillator section of Pegasus Dye Laser. The "pump" laser energy per pulse is reduced to ~1 mJ by a neutral density filter before being imaged onto the oscillator dye cell.

The dye laser mode structure was measured with a Fabry-Perot interferometer coupled to a photodiode array detector . Measurements were performed for both single laser pulses and multiple pulse averages. The dye laser output consists of a group of three to five prominent modes with most of the intensity in the central mode (Fig. 2) . The laser had a time-averaged bandwidth of less than 900 MHz, which is ~1.0 pm (10^{-3} nm) in the operating range of rhodamine 6G dye.

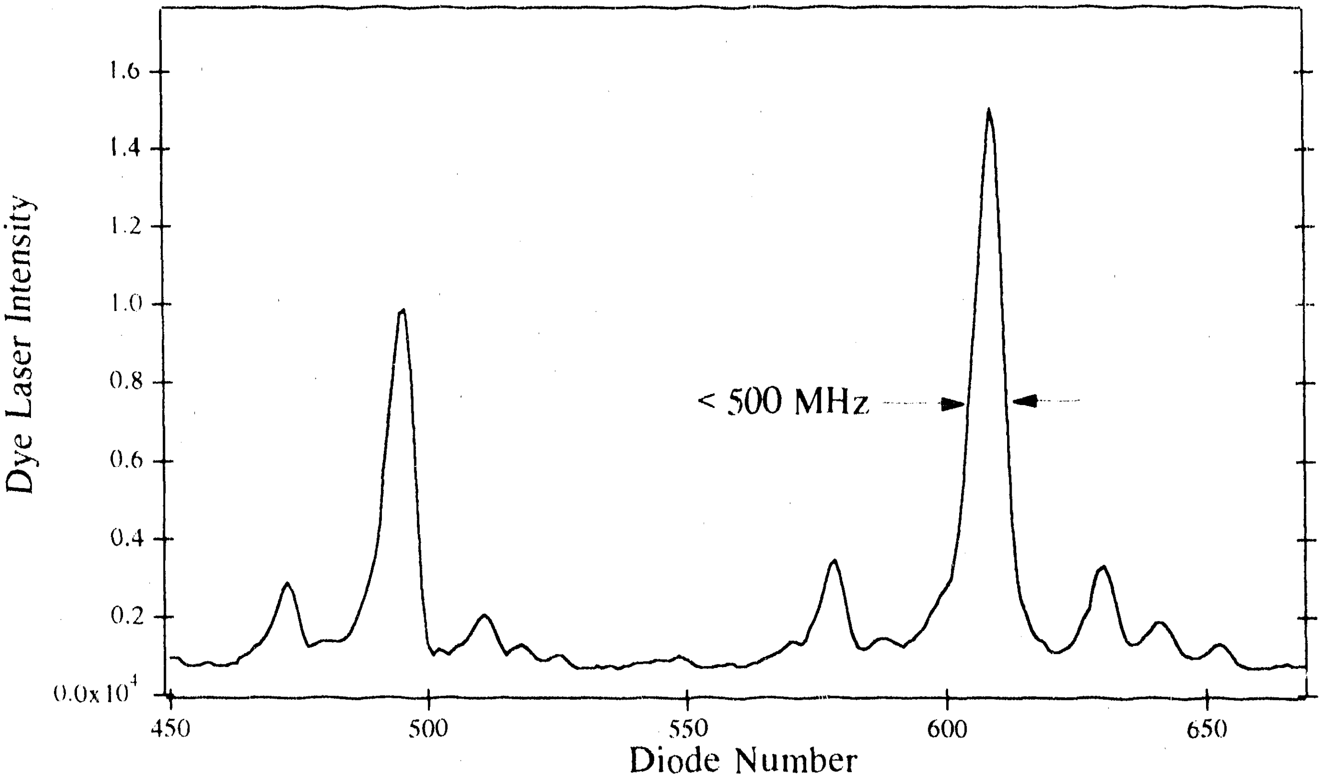

Figure 2 Mode structure of dye laser fundamental. Two measurements of the dye laser mode structure of a single laser pulse are shown.

To efficiently promote fluorescence it is generally necessary to convert the orange-red dye laser output wavelength to a wavelength in the ultraviolet region. This was accomplished using an angle-tuned second harmonic generating crystal. The bandwidth of the frequency doubled dye laser pulses could not be measured using the Fabry-Perot interferometer, but is estimated to be approximately twice that of the fundamental. With the pump laser producing about 80 millijoules per pulse, the dye laser produced about 6 millijoules per pulse for a conversion efficiency of ~7.5%.

The experimental apparatus used to observe fluorescence in an inductively coupled plasma (ICP) is shown in Fig. 3. A 0.32 meter monochromator equipped with a fast (1.5 nsec risetime), high gain, low noise photomultiplier tube was used to measure fluorescence. The fluorescence signal was first observed with a 400 MHz oscilloscope, the gate and delay settings of a gated integrator optimized and, when the optical system was deemed optimized, fluorescence spectra were collected by routing the

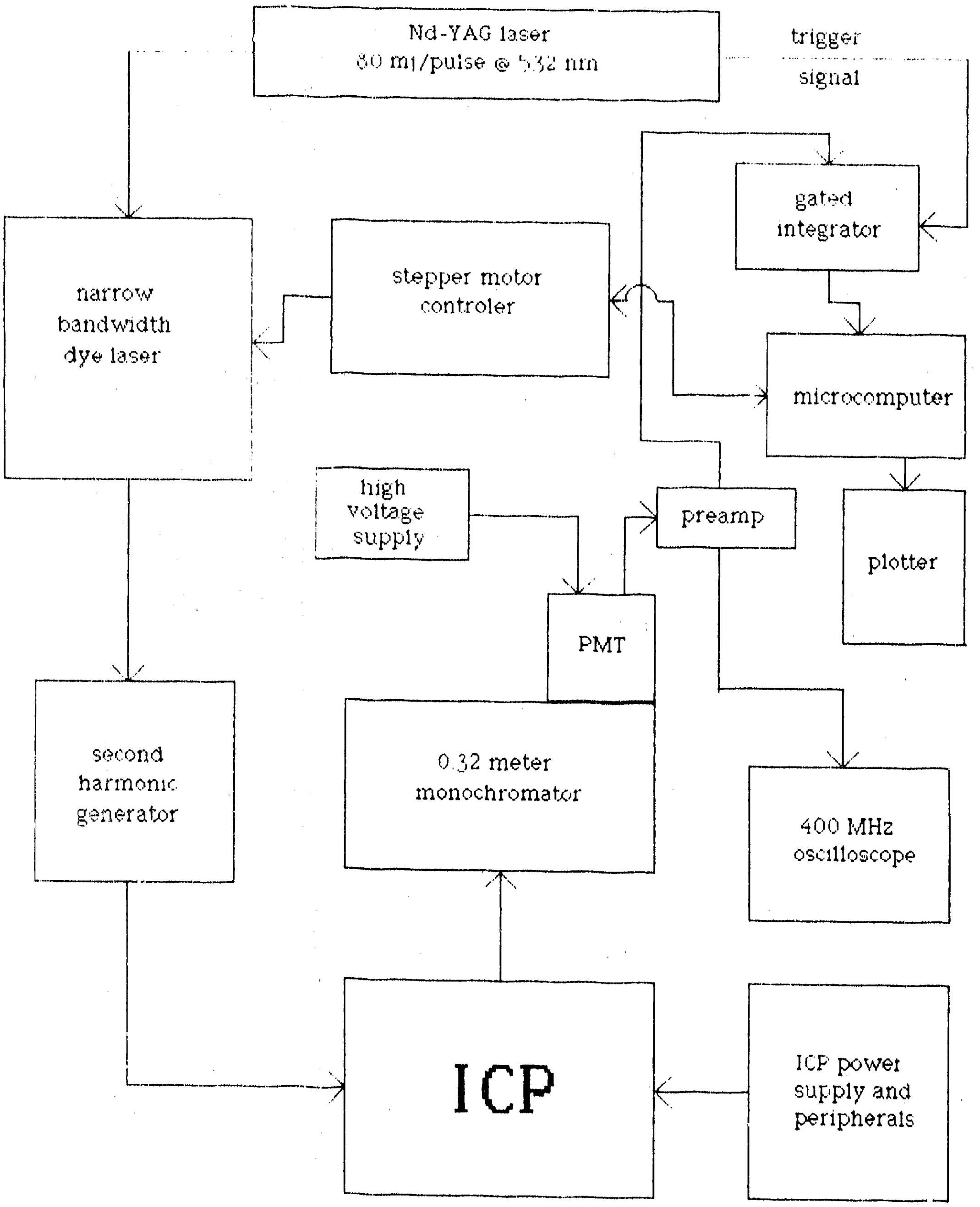

Figure 3. ICP-LEAFS experimental apparatus. The dye laser oscillator output beam is routed through three "amplifiers" before being imaged onto the second harmonic generator crystal.

photomultiplier output to a gated integrator. The fluorescence signal was then digitized and stored on a small computer. The ICP torch box was fitted with a HEPA exhaust filter to prevent the release of U particulates to the room air ducts and positioned at the end of the optical table holding the laser.

Uranium is almost totally ionized in the analytical zone of the ICP. Hence it was necessary to find an ion absorption line with a large ^{235}U - ^{238}U isotope shift relative to the dye laser linewidth (~2 pm). It was also deemed useful to work within the operating range of efficient rhodamine dyes. These considerations led us to investigate the 0 - 34886 cm^{-1} transition shown in Fig. 4.

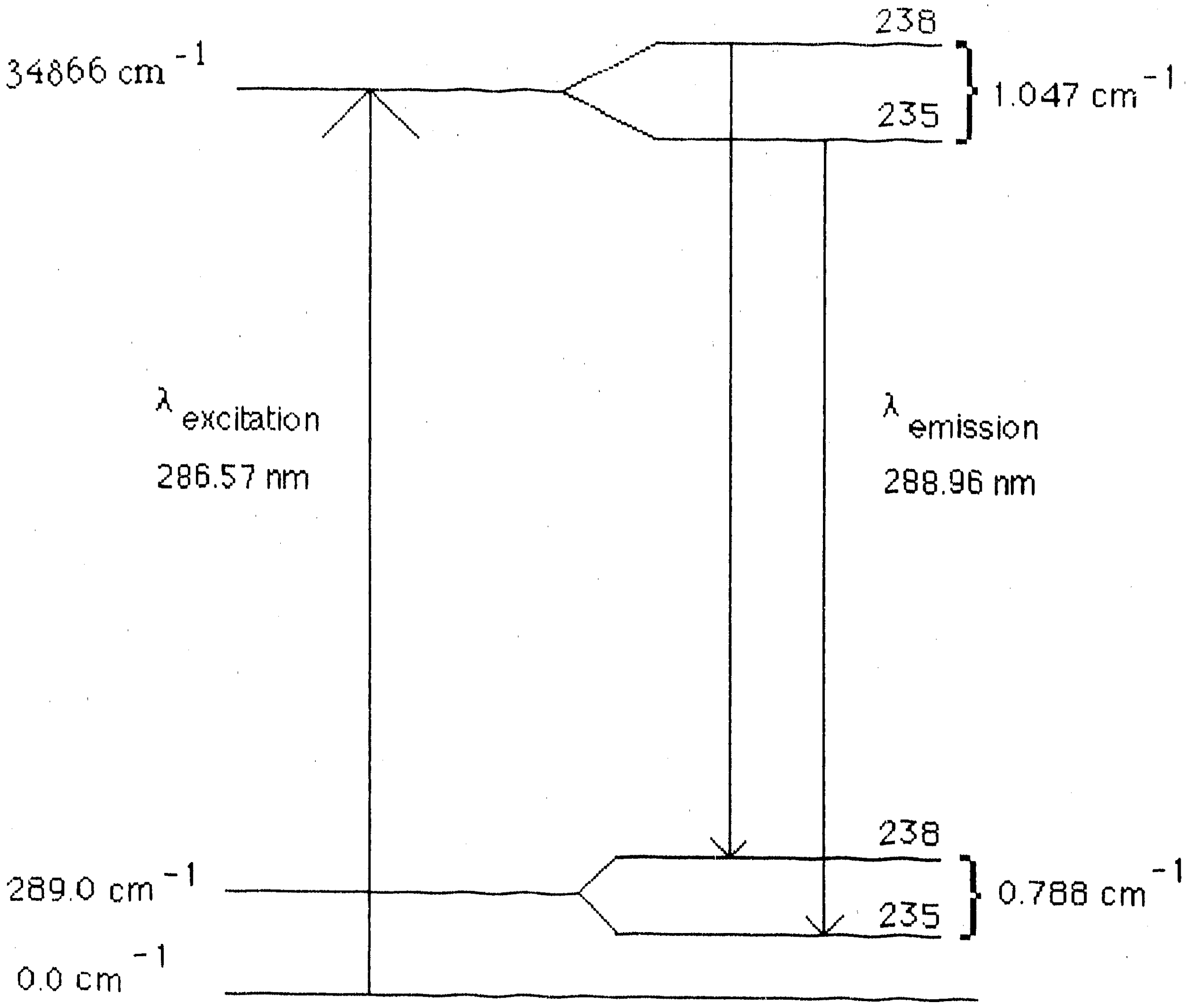

Figure 4. Energy level scheme for the U ion fluorescence transition with resolvable isotopic splitting.

Fluorescence emission, both resonant and Stokes shifted lines, corresponding to the transitions diagramed in Fig. 4 were investigated. The fluorescence spectrum shown in Fig. 5 was generated from a 1:1 mixture of ^{238}U and ^{235}U (500 ppm, each isotope) dissolved in 5% HNO_3 and introduced into the ICP. A series of 1:1 ^{235}U - ^{238}U solution of differing concentrations was examined with the lowest concentration solution (20 ppm each isotope) still easily observable. The detection limit was estimated to be 1 ppm.

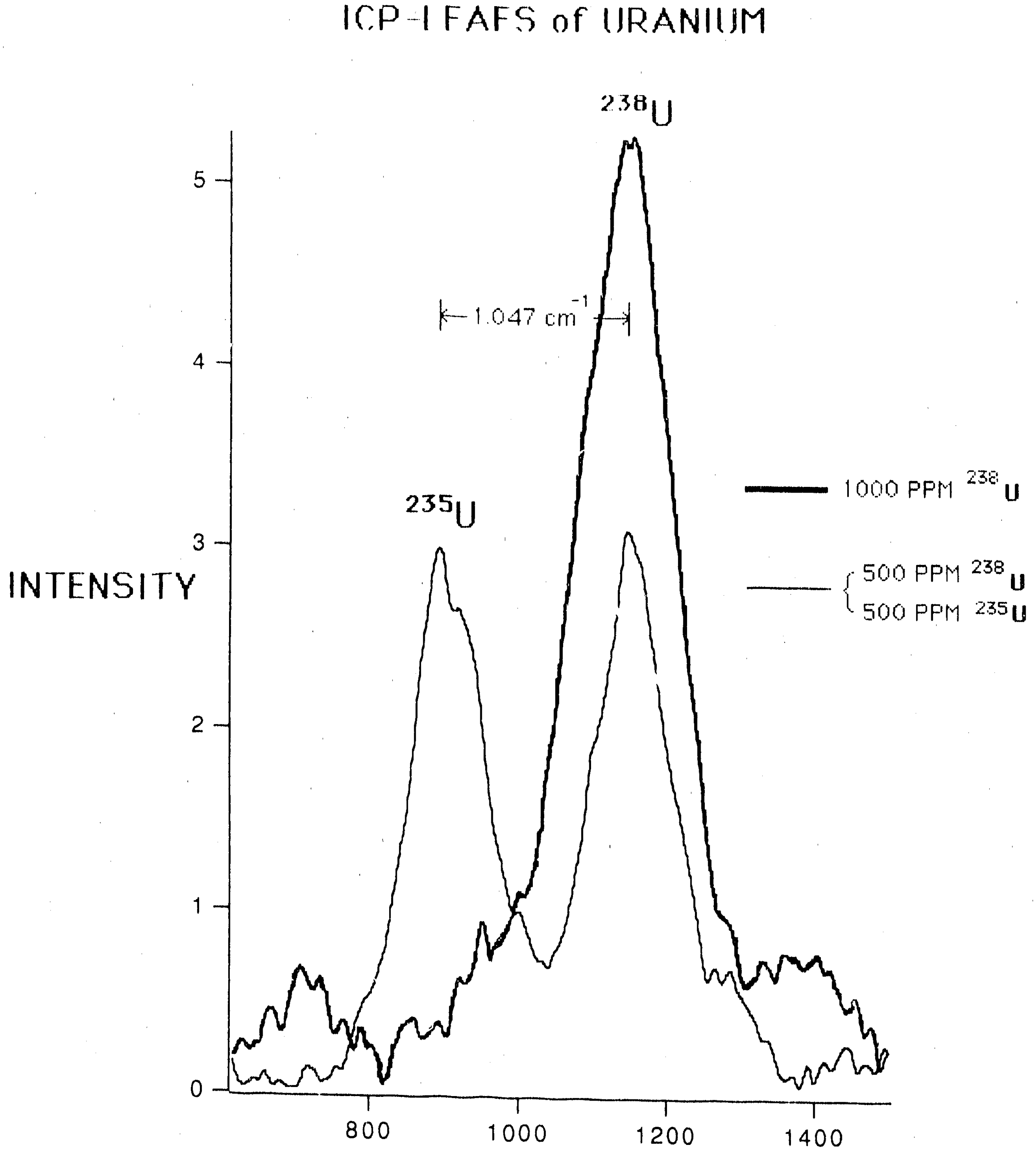

Figure 5. Resolution of ^{235}U - ^{238}U splitting in the ICP-LEAFS study of U. Fluorescence was excited by irradiating U ions in the ICP with a high-resolution laser at ~286.57 nm. Non-resonance fluorescence at ~288.96 nm was observed.

Future Studies:

Since the isotope splitting of the 286.57 nm U transition is known (1.047 cm^{-1}) and the Doppler broadening of the spectral lines is easily calculated, the bandwidth of the frequency doubled dye laser can be estimated from the FWHM of the fluorescence peaks shown in Fig. 5. This calculation yields a dye laser bandwidth of approximately 2.0 pm, confirming that the process of second harmonic generation approximately doubles the laser bandwidth. A different process for extending the wavelength range of dye lasers, Raman shifting, will be considered in future experimentation. Raman shifting produces frequencies of coherent light shifted from the fundamental laser wavelength by the frequency of a molecular vibration (or a multiple of this frequency). The conversion efficiency of this process can rival or exceed that of second harmonic generation. Raman shifting may not increase the laser bandwidth as greatly as second harmonic generation, which can lead to improved spectroscopic resolution. This would be particularly important for the extension of this work to Pu isotopic determinations since Pu isotopic shifts are usually smaller than those of U.

The relatively high detection limit for U determined from the experiments described above (Human et al measured a U detection limit of 20 ppb using another excitation/detection line pair) was due to a combination of intrinsic and instrumental factors. It is unfortunately true that to observe isotopic effects one must seek out transitions with large isotopic shifts regardless of their intrinsic strengths. However, many instrumental parameters have not been optimized (i.e., PMT gain for optimal signal to noise) and it is hoped that better detection limits will result from such efforts.

Studies of matrix interference effects on ICP-LEAFS determinations of U will be undertaken to verify that fluorescence spectroscopy is especially resistant to matrix interferences. Such studies for ICP-LEAFS of Pu by Berthoud et al are very encouraging.

We have demonstrated that ICP-LEAFS can be used for the determination of U isotopes. The full potential of the method remains to be explored. Some of the future concerns of this research will involve: 1) spatial analysis of the plasma reservoir to determine the optimal position for ICP- LEAFS monitoring, 2) the evaluation of alternate signal processing methods, such as gated photon counting, to improve detection limits, 3) a search for other U(II) fluorescence transitions and their suitability for use in isotopic determinations, 4) a systematic evaluation of the interferences in various sample matrices, and 5) a thorough experimental optimization followed by the determination of important analytical parameters.

2. AVLIS SAFEGUARDS (Lipert, Schuler, Weeks)

Purpose:

A new method for the enrichment of uranium, atomic vapor laser isotope separation (AVLIS), has been under development in the U.S. since 1973. In AVLIS, uranium feed stock is first vaporized by electron-beam heating. Then, high-resolution lasers are used to ionize only the U-235 atoms. An electric field can then be used to separate the U-235 ions from U-238 and other neutral atoms in the vapor. This approach to isotopic separation is fast compared to the gaseous diffusion process currently in use. Therefore, adequate safeguarding and on-line process control requires the continuous and rapid analysis of the composition of the feed and product streams.

In addition to being fast, the monitoring technique should be nonintrusive so that process interruptions and hazardous waste generation are minimized. This suggests that the most appropriate approach to safeguarding AVLIS is the spectroscopic analysis of the composition of the atomic vapor. This would allow the amount of materials to be tracked by monitoring the absorption or emission of light by atoms in the vapor phase. Because the absorption spectra of the various uranium isotopes are very similar, a high resolution light source, such as a high-resolution dye laser, is required. Thus, we are currently developing laser-based spectroscopic methods for the real-time monitoring of the flow of fissionable materials through the AVLIS process.

Progress:

The first stage of this project was the building of a laboratory-scale model of an AVLIS apparatus in which various spectroscopic probes (absorption, laser induced fluorescence, plasma emission) can be tested. Because work on AVLIS is classified in the U.S., we have constructed an atomic beam apparatus of our own design (see Fig. 6), guided by the general features of AVLIS that are publicly known. The apparatus consists of two chambers, separated by two slits mounted on the ends of an inner cylinder. The lower chamber houses the vaporization source and has windows for monitoring plasma emission. As in AVLIS, electron-beam heating is used for sample vaporization. The ejected atoms pass through the two slits to form a collimated effusive atomic beam in the upper chamber. This chamber has four windows that allow laser atomic absorption spectroscopy and laser induced fluorescence to be performed on the collimated atomic beam. The collimation of the atomic beam will result in a known and reproducible path length through the atomic vapor. Also, when coupled with laser irradiation at a right angle to the beam, it will reduce the Doppler broadening of spectral lines by filtering out those atoms with the largest velocity components in the direction of laser. This will make it easier to resolve isotopic and hyperfine splittings. Down stream from the last slit, material can be collected on a cold-finger trap for correlating mass flow with spectroscopic measurements.

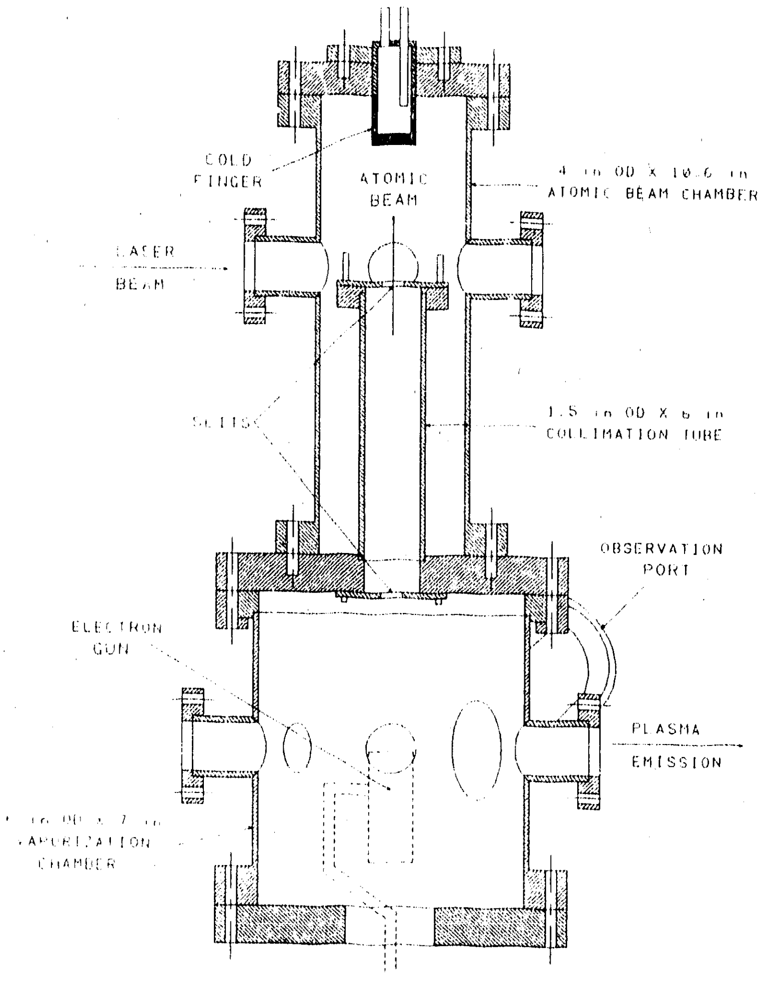

Figure 6. Atomic beam apparatus constructed for initial AVLIS experimentation.

The initial tests were run using a surrogate material, yttrium metal. Yttrium was chosen because it is relatively innocuous and has absorptions (at 594.67 and 602.51 nm) in the wavelength region where we hope to study uranium (at 591.5 nm). The ability to resolve the hyperfine splitting in these absorption bands (e.g., the Y line at 594.67 nm is split by hyperfine effects into a triplet with separations of 0.11 and 0.29 GHz) would establish the feasibility of resolving the isotopic splitting in uranium (^{235}U - ^{238}U splitting is > 5.4 GHz). In addition, although yttrium has a lower melting point than uranium, like uranium it readily forms refractory oxides that make it difficult to generate a significant vapor pressure over the metal by simply heating it in, for example, a heat pipe oven.

The yttrium samples consisted of 5-10 g buttons obtained from the Ames Laboratory Materials Preparation Center. The first series of experiments were directed toward characterizing and optimizing the atomic vapor source. A problem with the original design of the atomic beam apparatus was soon evident. Although viewports were placed in the vaporization chamber, it was not possible to see the yttrium button. Therefore, it was not possible to tell if the sample had melted or to estimate its temperature (from its color) or, assuming it was being vaporized, how much sample was left. In addition, the windows on the vaporization chamber, while not affording a view of the sample, still became heavily coated with yttrium, making them useless for spectroscopic work. Nevertheless, preliminary results show that with the electron gun running at full power, yttrium was deposited on an aluminum foil target at a rate of .3 mg/min.

These findings have resulted in the following modifications to the original apparatus.

1. A new viewport has been added to the vaporization chamber so that the heated sample can be watched.
2. Larger slits have been installed (20 mm x 3 mm vs. 10 mm x 1 mm). The larger slits will increase the mass throughput, making it easier to obtain quantitative data on the intensity of the atomic beam for material with a lower vapor pressure than yttrium.
3. Baffles have been installed to prevent the deposition of material on the windows of the vaporization chamber. The windows used for spectroscopic measurements on the collimated atomic beam should not need baffles. These modifications have just recently been completed.

Future work:

Work will continue on refining the operating parameters for the atomic beam source. Specifically, attention will be focused on the following areas:

1. Controlling the rate of sample vaporization
2. Steering the electron beam
3. Collimating the atomic beam.

The stage has been reached where spectroscopic measurements will serve as the guide in this source optimization process. Initially, we will continue to study yttrium. Because yttrium oxidizes readily, an earlier attempt in this laboratory to obtain a yttrium spectrum in a heat pipe oven was not successful. A demountable hollow cathode lamp has been constructed in which the hollow cathode material can be changed. Several hollow cathodes have been made for this lamp, including one of yttrium. With this, we will soon be able to obtain a yttrium spectrum using optogalvanic spectroscopy. This will provide a guide for spectroscopic work in the AVLIS apparatus. We expect to monitor the optogalvanic signal while measuring absorption in the AVLIS atomic beam. The optogalvanic signal will be used to lock the laser frequency on an atomic transition, which will facilitate the continuous monitoring of the atomic beam.

The knowledge acquired up to this point will guide the design and construction of a second generation AVLIS instrument for use within a glovebox enclosure. With this apparatus, experiments on uranium and plutonium will be possible.

3. MODERN DATA ACQUISITION APPARATUS

During this quarter, a commitment was made to upgrade and refine instrumental control and automation in this program. One consideration that led to the change in computational equipment was a difficulty faced in interfacing equipment to MS-DOS computers. As experimenters entered the program they were either conversant or minimally trained in instrument-computer interfacing. The minimally trained researchers were severely limited by their inability to quickly change experimental apparatus and configure new experiments to run under computer control. The scientists with programming experience often create functioning computer code that is poorly documented and is difficult to continue to use once the researcher has left the program. Obtaining the services of a professional programmer or using a commercially available product involve considerable difficulties. Professional programmers are costly and require the active collaboration of the experimenter to plan, explain, and help design the software functions. Commercially available software is almost always limited to the operation of a single device. When the software is not so limited, it is essentially a programming language and again the experimenter is forced to become a programmer.

A Macintosh IIci computer and LabVIEW 2 software (National Inst.) were obtained this quarter and will be evaluated for data acquisition. The computer was chosen because it is a relatively inexpensive machine that has an icon-based operating system, a large addressable memory (8 Megabytes), a fast clock speed (25 MHz), can perform multi-tasking, and supports the LabVIEW 2 software package. LabVIEW 2 software is an intuitive, icon-based programming environment that supports operation of multiple devices and is specifically designed for scientific applications. This software package includes comprehensive data analysis tools. An important feature of LabVIEW 2 software is that it is "self-documenting." This software utilizes icons to represent instruments and mathematical functions; the final interfacing project is represented by a "wiring" diagram. All code is generated by the computer itself.

The Macintosh-based data acquisition system is now being interfaced with laboratory instruments. Laboratory devices not currently equipped with IEEE-488 interfaces are being so equipped and an IEEE-488 controller has been installed in the computer.

4. MODIFIED HEAT PIPE OVEN FOR HIGH-TEMPERATURE SPECTROSCOPY (Wang and Weeks)

Progress:

This work was essentially completed in this quarter. A report describing this work is included in Section 2 of this report.

5. HIGH-RESOLUTION ICP-ATOMIC MULTIELEMENT EMISSION SPECTROSCOPY (Edelson)

Progress:

A report on the applicability of high-resolution ICP- atomic multielement emission spectroscopy to environmental problems was presented at the 31st Annual Meeting of the INMM in Los Angeles this July. A copy of the paper submitted for publication in the Proceedings is included in Section 2 of this report.

6. APPLICATION OF ATMOSPHERIC PRESSURE AFTERGLOW DISCHARGES TO THE ISOTOPIC DETERMINATION OF URANIUM IN UF_6 (Murray and Zamzow)

Purpose:

A difficulty associated with obtaining an accurate materials balance in the U isotope enrichment process is being addressed by the project. A small, commercially available detector, the Atmospheric Pressure Afterglow Discharge, is being evaluated for real-time measurements of UF_6

in atmospheric gases. If successful, this device can be employed as an exhaust stack monitor to accurately determine quantities of UF_6 escaping an enrichment plant in gaseous exhaust streams.

Progress:

A safety analysis of a proposed experimental trial of the Atmospheric Pressure Afterglow Detector has been completed. A manifold system has been constructed featuring a monel sampling bottle that will be used to contain a small amount of UF_6 mixed with argon. A portion of this mixture will be sent to the APAD source which will be enclosed in the glovebox currently used to house an ICP. Light emanating from the APAD will be imaged onto a high-resolution spectrometer and analyzed for both elemental and isotopic information. The initial experiments will be undertaken late in FY1990.

PREPRINTS AND REPRINTS

1. Reprint of, "HIGH-RESOLUTION INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROSCOPY APPLIED TO PROBLEMS IN NUCLEAR WASTE MANAGEMENT," by M.C. Edelson, R.K. Winge, D.E. Eckels, and J.G. Douglas. Paper submitted for publication in the Journal of the Institute for Nuclear Materials Management.

HIGH-RESOLUTION INDUCTIVELY COUPLED PLASMA - ATOMIC EMISSION SPECTROSCOPY APPLIED TO PROBLEMS IN NUCLEAR WASTE MANAGEMENT

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ABSTRACT

High-resolution Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) is a variant of the more conventional ICP-AES that is widely used for environmental monitoring. The enhanced selectivity provided by high resolution spectrometry permits application of the ICP-AES technique to more difficult measurement problems. The relevance of high-resolution capabilities to three such analytical problems are discussed herein.

1. Pu in very complex, radioactive matrices can be determined with good accuracy without the need for prior chemical separations. Isotopically resolved spectra from actinides in fuel dissolver solutions can be obtained after a simple ion-exchange step.

2. High-resolution methods permit the simultaneous determination of fission products and actinides in simulated high-level nuclear waste solutions. Such measurements can be useful for both safeguards and waste processing.

3. The ICP-AES technique, with a photodiode array detector, can be used to determine the composition of nuclear waste glasses. Such measurements can assist the glass producer as well as providing predictors of nuclear waste form performance in a repository.

INTRODUCTION

The Office of Safeguards and Security of the USDOE (OSS) has the responsibility for the materials control and accountability (MC&A) of fissionable materials throughout the USDOE complex. The "Nuclear Fuel Cycle" is fully implemented within the USDOE and there is a continuing need to develop diverse measurement tools to monitor actinides in different physical forms and in highly radioactive matrices (e.g., fuel dissolver solution and high level nuclear waste (HLW)).

This paper will discuss the applications of OSS-sponsored research in high-resolution ICP-AES to the determination of actinides. Applications to both safeguards and environmental measurements will be highlighted.

OPTICAL EMISSION SPECTROSCOPY

In contrast with radiation monitoring techniques optical emission spectrometry is applicable to both radioactive and non-radioactive materials. This is especially significant for environmental monitoring where the presence of all toxic agents must be ascertained. Many important actinide isotopes are relatively long lived (e.g., 235U, 238U, 239Pu) and, consequently, of low specific activity. Such analytes can be determined with good sensitivity by optical emission or mass spectroscopy [1-3].

Conventional ICP-AES is burdened with spectral interferences caused partly by insufficient instrumental resolution (Figure 1). High resolution ICP-AES can be used to determine individual isotopes [4-5]. Thus the powerful isotope dilution method, commonly applied to analysis by mass spectroscopy, can be utilized with optical emission spectrometry [6] to reduce analytical bias.

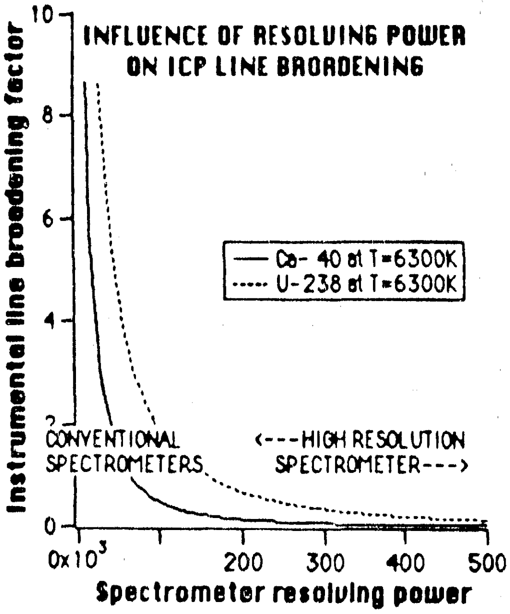

Fig 1 Influence of spectrometer resolving power on the width of ICP lines. Calculated under the assumption that line broadening is solely due to Doppler broadening and natural line shape is Gaussian. ICP temperature set equal to 6300K.

High-resolution ICP-AES has been used at Ames to measure U and Pu in simulated reprocessing solutions; recently the same methods have been tested with highly radioactive PUREX process solutions in Richland [7]. Results from this study are reproduced in Tables 1 and 2; note that the ICP-AES results for total Pu were consistant with an isotope dilution mass spectrometric (IDMS) assay of the same solution after the Pu was separated from the highly radioactive matrix. While the precision of the ICP analysis was poorer that that of the IDMS analysis, no chemical separation was required. It should also be noted that no activity need be transferred to expensive experimental apparatus when analyzing radioactive materials with high-resolution ICP-AES methods. The materials can be analyzed within hot cells or gloveboxes [8] and only expendable glassware and relatively inexpensive solution pumps need be contacted with radioactive materials; the emitted light can be conveyed to remote spectrometers by lenses or optical fibers.

TABLE 1. DETERMINATION OF TOTAL PLUTONIUM IN A PROCESS SOLUTION MATRIX[1]

Method	Plutonium (g/L)	Std. Dev.
ICP-AES[2]	1.19	0.08
IDMS	1.110	0.003

[1] Adapted from Ref. 7.

[2] Determined on process solution after dilution with nitric acid. Wavelength for Pu line used was 476.7165 nm. Six replicate analyses were performed.

NUCLEAR WASTE ANALYSIS

The USDOE has recently announced that a high priority will be accorded the environmental restoration and modernization of its facilities.

TABLE 2. PLUTONIUM ISOTOPE RATIO DETERMINATION[1]

Method	240/239Pu	Std. Dev.
ICP-AES[2]	0.068	0.009
IDMS	0.06378	0.000064

[1] Adapted from Ref. 7.

[2] ICP-AES determinations performed on anion exchange separated process solution. Isotopic ratio determined by ratioing peak heights. Pu wavelength used was 402.1463 nm. Three replicate analyses were performed.

There will be a substantial commitment of funds to demonstrating new technology that can reduce the cost of environmental remediation and a reorganization of production activities to minimize future waste generation [9]. As the USDOE goes about the task of remediating its operating facilities it will face nuclear waste assay problems of great complexity and, since USDOE wastes contain significant amounts of fissionable material, there will be a nuclear safeguards interest in the fate of these wastes.

Nuclear waste isolation is an area of great public controversy. Indeed, the government of Sweden demanded that an acceptable solution to the disposal of nuclear wastes be demonstrated as a precondition to future growth in its nuclear energy program [10]. In the United States, nuclear power growth is moribund, partially as a result of public uncertainty regarding the issue of nuclear waste disposal.

Nuclear wastes need to be analyzed chemically to determine appropriate waste treatments and stabilization techniques. These analyses are complicated by the intense radioactivity from fission products and the low concentration of long lived actinides, which become increasingly environmentally important as the waste ages and the short-lived waste components disappear [11]. Computer codes are useful guides to the waste composition, but the actual composition should be verified by laboratory analysis wherever possible.

High-resolution ICP-AES has been applied to studies of simulated nuclear wastes suggested as input material for the TRUEX process [12]. As is evident from Figs. 2 and 3, ICP-AES is sufficiently sensitive to determine actinides at expected concentrations and should be applicable without chemical pre-separations.

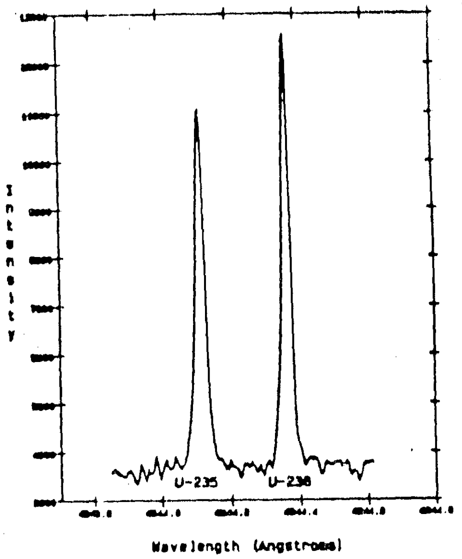

Fig. 2 Uranium in diluted simulated Pu scrap waste matrix. U-238 concentration = 14 ppm; U-235 concentration = 12.8 ppm.

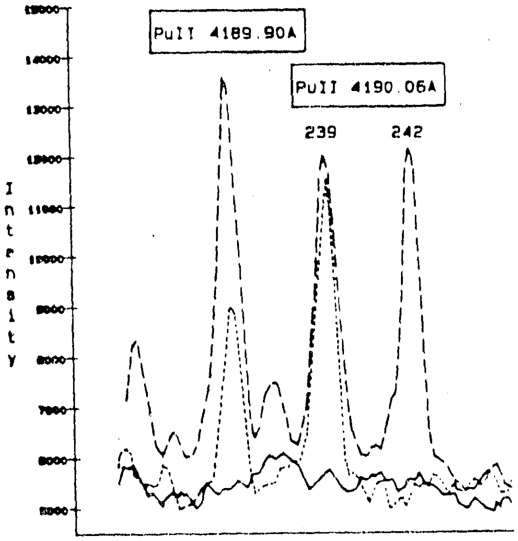

Fig 3 Plutonium in simulated Pu scrap waste matrix. Solid curve is spectrum of waste matrix; dotted curve is spectrum of waste matrix after addition of 50 ppm Pu-239; dashed curve is waste matrix spectrum after addition of Pu-239 and Pu-242. Line at 418.99 nm does not have resolvable isotopic structure whereas the line at 419.01 nm can be isotopically resolved.

The matrix tested in Figs. 2 and 3 has relatively high concentrations of actinides in a spectroscopically simple matrix. We have also applied the high-resolution ICP-AES technique to a more demanding problem: the determination of trace Np in a U and Pu-containing matrix at high U:Np ratios. Ion-exchange chromatography was used to improve method selectivity and the high-resolution ICP-AES instrumentation was used as an on-line monitor of solutions flowing out of the resin column. It was possible to construct element-selective elution curves (Fig. 4) and establish a detection limit of ~1 ppm Np (relative to U) in this line rich matrix [13].

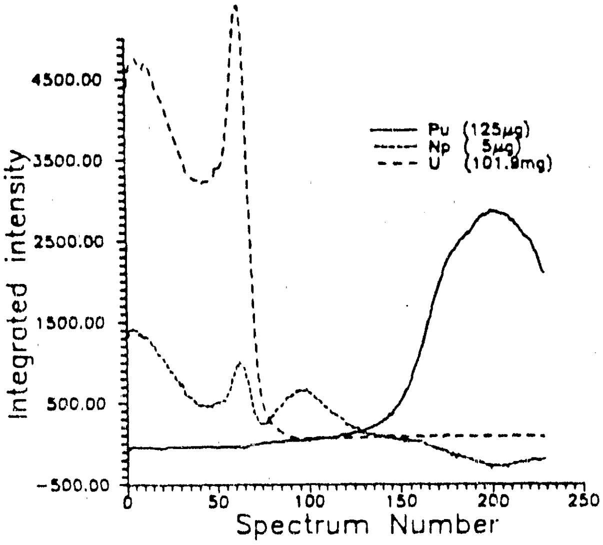

Fig 4 Chromatographic elution curve constructed with elemental concentration data from ICP-photodiode array spectrometer. Actinide data obtained simultaneously and normalized against an added internal standard.

ICP-mass spectroscopy (ICP-MS) can provide even better sensitivity than ICP-AES but, in common with all MS techniques, must "ingest" ions to measure them and therefore becomes contaminated during the assay of radioactive materials. In a climate of waste minimization it may not be wise to routinely expose expensive instrumentation to a "diet" of active fission products. (Of course, the excellent sensitivity of ICP-MS suggests that only small amounts of material will be deposited within the mass spectrometer.)

NUCLEAR WASTE GLASS ANALYSIS

The final stage of nuclear high-level waste disposal will be achieved by incorporating the liquid wastes in a stable glass matrix and burial in a nuclear waste repository. The chemical composition of the glass matrix must be closely controlled to retain the leach-resistance and waste-holding capacity originally determined in optimization studies [14]. The capability of current analytical techniques for accurately measuring the composition of nuclear waste glass candidate matrices is currently being evaluated at the Battelle Pacific Northwest Laboratory [15]. The majority of participants in this study utilize ICP-AES to determine the composition of candidate glasses. A typical glass material analyzed by working group participants is given in Table 3.

Commercial ICP instruments generally rely upon single-channel detectors, such as the photomultiplier tube (PMT), to record the emission spectrum generated by the ICP. The PMT is a very sensitive detector with applicability to the entire optical spectrum. Unfortunately, it is a non-integrating, fragile device that can only monitor one element's emission. The "direct-reading" spectrometer utilizes PMTs for multichannel detection. This device features multiple exit slits, each monitored by its own PMT detector, and provides simultaneous, multichannel information. Unfortunately, the "direct reader" is very expensive and is difficult to reconfigure once the monitoring wavelengths have been chosen.

The Spectrochemistry Group at Ames has chosen the photodiode array (PDA) for evaluation as an ICP-AES detector [16]. This detector offers true simultaneous, multichannel detection. It is compared with the PMT and other light detectors in Table 4.

TABLE 3. NOMINAL COMPOSITION OF GLASS SAMPLES DISTRIBUTED BY MCC FOR ANALYSIS

Element Oxide	Weight %
Aluminum`	3.38
Boron	10.18
Barium	0.64
Calcium	2.20
Cerium	1.17
Chromium	0.23
Cesium	0.94
Iron	4.08
Lanthanum	2.54
Lithium	2.54
Molybdenum	1.94
Sodium	9.74
Neodymium	3.72
Nickel	0.11
Phosphorus	0.59
Silicon	43.30
Strontium	0.47
Titanium	3.02
Uranium	2.08
Zinc	2.93
Zirconium	1.92

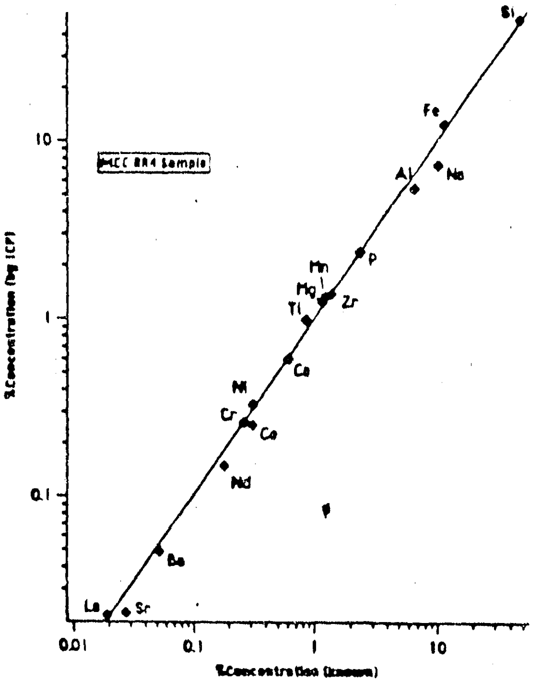

Fig 5 Results from the ICP-AES determination of the constitutents of an unknown glass sample.

We have applied the PDA to the analysis of candidate waste glasses and preliminary results have been encouraging (Fig. 5). The PDA detector holds the promise of improving the precision of ICP analysis by using multiple internal standards to compensate for instrumental drift. It can also be used to perform qualitative analyses without the need for any reference standards.

We will continue to develop an ICP spectrometer based on the PDA detector and investigate the use of Expert Systems software to improve the "user friendliness" of the device.

TABLE 4. COMPARISON OF DETECTORS FOR ICP-AES

	ADVANTAGES	DISADVANTAGES
PHOTOGRAPHIC PLATE		
	Inexpensive	Non-linear
	Simultaneous	Poor dynamic range
	Multichannel	Insensitive
PHOTOMULTIPLIER TUBE (PMT)		
	Inexpensive	Fragile
	Fast response	Single-channel
	Wide dynamic range, linear	
PHOTODIODE ARRAY (PDA)		
	Linear response	Poor UV sensitivity
	Simultaneous	Expensive
	Multichannel	Blooming
	Simple background correction	
CHARGE COUPLED DETECTORS (CCD/CID)		
	Low noise (CID)	Blooming (CCD)
	Linear response	Poor aspect ratio (CID)
	Simultaneous	
	Multichannel	Poor UV sensitivity
	Simple background correction	Expensive

CONCLUSIONS

Technology developed for safeguarding nuclear materials can be applied successfully to environmental problems. The measurement technologies that are applicable to both radioactive and non-radioactive substances, such as optical emission spectrometry and mass spectrometry, can easily be applied to many environmental analysis problems.

High-resolution ICP-AES has been successfully used to determine Pu and other actinides in very radioactive, chemically complex matrices. In contrast to IDMS, the elemental determination of Pu could be accomplished without the need for chemical separation of Pu from other solution constituents.

High-resolution ICP-AES was used to determine actinides and rare earths in simulated nuclear waste solutions and, using a diode array detector,has been used to measure the composition of candidate nuclear glass materials.

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2. Preprint of, "A HIGH TEMPERATURE OVEN FOR LASER SPECTROSCOPY," by Z-M. Wang, S. Weeks, and M.C. Edelson. Paper to be submitted for publication after clearance review.

A High Temperature Oven for Laser Spectroscopy

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ABSTRACT

A commercial heat pipe oven (HPO) was modified to extend the useful temperature range from 700°C to ~1700°C. The utility of the modified heat pipe oven as an atom source for spectroscopy is demonstrated with a laser atomic absorption study of the hyperfine splitting of Tm (m.p. 1545°C).

Index Headings: **Modified heat pipe oven; Laser atomic absorption spectroscopy; Thulium; Hyperfine splitting; Isotope shift.**

INTRODUCTION

Atomic absorption spectroscopy (AAS) has been used extensively for chemical analysis and plasma diagnostic studies [1,2]. Flames[3-7] and graphite furnaces[8-11] are most commonly used in AAS for solvent evaporation, particle dissociation, and atomization. Heat-pipe ovens (HPO) permit the study of weak absorption systems through the use of long, well-defined path lengths that are conveniently probed with laser light sources [12,13] and are the method of choice for certain AAS studies, such as determinations of absorption coefficients and high precision measurements of isotope ratios or hyperfine splitting. Long observation times due to controlled vaporization-condensation cycles that retard the loss of material by condensation in the apparatus make HPOs ideal atom sources when limited sample quantities are available, when wisdom demands use of the minimum amount of hazardous materials, or when stable confinement of reactive metal vapors is required.

A commercial HPO was recently used in this group [14] for the study of Eu isotope ratios by laser atomic absorption spectrometry (LAAS). Mixtures of ^{151}Eu and ^{153}Eu, alloyed with ytterbium, were volatilized in the HPO and the isotopically-resolved absorption at 576.5 nm measured with a high-resolution continuous wave (cw) dye laser. The extension of this study to higher melting materials was limited by the high temperature limit of the HPO working range (~700 °C), which was primarily due to the stainless steel materials used in HPO construction.

This paper describes a modification to a commercial HPO that extends the maximum working temperature of the device to ~1700 °C. This increase in the high temperature limit is achieved by using high temperature ceramics and tantalum to construct a heating zone within the commercial HPO. Results on the hyperfine splitting of thulium (Tm), a rare earth metal with a high melting point (1545 °C), are presented to demonstrate the utility of the modified HPO for LAAS studies

EXPERIMENTAL

Heat Pipe Oven Modification. The commercial HPO was recommended for use at temperatures below 700 °C [15]. To achieve higher temperatures, the HPO was modified so that the materials exposed to the highest temperatures were tantalum (m.p. 2996 °C), which was used to construct a resistive heating element, and a refractory ceramic (BTC AL), which has a maximum working temperature of 1900 °C [16].

The HPO was modified (Fig. 1) to contain two concentric ceramic tubes supported within the shell of the original HPO by two Macor insulating spacers. The spacers were attached to the tube with three axial perpendicular set screws. The inner ceramic tube was 45 cm long with a 12 mm outer diameter and an 8 mm inner diameter. This tube contained a tantalum resistive heating element fabricated from 0.25 mm diameter wire wound into a loose coil to fit the tube's inner diameter. The heating element was approximately 25 cm long and had a resistance of 10 Ω at room temperature. The outer ceramic tube, fabricated from another ceramic material (BTC ML60)[16], was 28 cm long with an outer diameter of 20 mm and an inner diameter of 15 mm. The gap between the two tubes was filled with an alumina powder to minimize heat losses from the inner tube. The effective heating region was 25cm long.

A second pair of insulating supports was used for connecting the tantalum heater wire to solid copper conductors that were soldered to two vacuum feedthroughs. These served as terminals on the flange of a high vacuum "tee". High temperatures were achieved at low currents (e.g., a current of 3 A at 160 V was sufficient to melt yttrium (m.p. 1522 °C) in the HPO). The shell of the original HPO, which included the cooling coils and the end window mounts, was used without modification. The original HPO heater was not used.

The service life of the heater element was extended by heating only at reduced pressures in an inert atmosphere, but was dependent upon the operating conditions. For temperatures in excess of 1500 °C, the heater element lifetime was ~ 10 hours. When used at temperatures below 1000 °C the lifetime exceeded 30 hours. An experienced operator could prepare and install a new heater element in about 1 hour.

The HPO temperature was monitored with a tungsten-rhenium thermocouple placed within the inner tube close to the sample. The two wires were placed in ceramic tubes for rigidity and electrical insulation and were brought out of the high temperature portion of the HPO for attachment to copper conductors. These, in turn, were connected to exterior terminals through a second high-vacuum "tee". The thermocouple was calibrated by observing the melting of pure metal foils in the modified HPO (Fig. 2).

Instrumentation. A complete list of the instrumentation and experimental apparatus is given in Table I and the experimental lay-out is depicted in Fig. 3. Atomic absorption was studied with a cw ring dye laser using rhodamine 690 dye that was pumped by all lines of a 5W Ar^+ laser. The dye laser wavelength and power were continuously monitored with an optical wavemeter (0.01 cm^{-1} precision) and a disk calorimeter.

respectively. The laser was directed down the optical axis of the modified HPO and onto the entrance slit of a low resolution monochromator. The dye laser was modulated by a mechanical chopper and power was reduced to ~2 mW with neutral density filters to avoid detector saturation . The modulated detector signal was directed to the current monitoring port of a lock-in amplifier that was phase-matched and locked to the TTL reference signal provided by the mechanical chopper. The various instrument output signals (i.e., light detector, wavemeter, power meter) were routed to a laboratory computer for storage and later analysis. Data points were collected every 1.6 seconds and the unnormalized transmission spectrum was plotted in real-time on the computer monitor. This real-time spectral display proved to be very useful in monitoring the experiment.

Procedures. The sample was loaded into a 3 cm long by 4 mm high by 5 mm wide sample boat with a pair of forceps. (The sample boat was fabricated from BTC AL.) The boat was placed in the inner ceramic tube, which was then gently rocked back and forth along its long axis until the sample boat moved to the center of tube. The ceramic tube assembly was inserted into the commercial HPO, which was then sealed. The HPO was then evacuated to ~10 mtorr, flushed with purified argon gas until the system pressure reached 500 mtorr, and then re-evacuated. This procedure was repeated five times to minimize the amount of oxygen and moisture within the system.

The tantalum heater element was out-gassed by slowly increasing the HPO temperature to 500 °C and then repeating the evacuation-Ar filling procedure discussed in the previous paragraph. This was repeated approximately 15 times during a 30 minute period. (The service life of the tantalum heater element was substantially increased by adopting this procedure to reduce tantalum oxidation.) The HPO was then brought to 500 mtorr with Ar and sealed; the heater temperature was gradually increased to heat the sample. During sample heating, the evacuation-Ar filling operation was occasionally repeated to remove moisture and oxygen liberated by additional out-gassing.

The laser wavelength was continuously scanned over a 0.4 cm^{-1} (12 GHz) spectral range containing the spectral features of interest and each scan required approximately two minutes. As the scanning was repeated the heater temperature was gradually raised until light absorption was noted.

RESULTS AND DISCUSSION

The modified HPO was used to study the absorption spectrum of three metals: thulium (m.p. 1545 °C), samarium (m.p. 1072 °C), and yttrium (m.p. 1522 °C). Thulium provided an excellent sample for LAAS. It was relatively stable to oxidation in dry air at room temperature and could be handled easily during sample loading. The sample was not cleaned to remove any surface oxides prior to placement in the HPO. Natural thulium is monoisotopic (atomic mass = 169) and has a relatively simple atomic spectrum with strong absorption systems in the region accessible to efficient rhodamine dyes. The thulium used in this study was obtained in the form of metal chips at 99.9% purity (Alfa Products).

For the Tm transition at 567.585 nm (0 - 17614 cm^{-1}), absorption was first noted at 787 °C and became experimentally useful at 810 °C (Fig.4a). The sample became totally absorbing at temperatures greater than 855 °C (Fig. 4b), where the vapor pressure of Tm $\approx 10^{-5}$ atmospheres [17]. The wavelengths of absorption maxima were determined by averaging several spectra. The two prominent lines at 17613.655 and 17613.710 cm^{-1}, and the weak line at 17613.76 cm^{-1} (Fig. 4b), resulted from hyperfine splitting [18]. The observed spectral line widths (0.036 cm^{-1}), which were in excellent agreement with calculated Doppler widths [19] of 0.032 cm^{-1}, prevented the clear resolution of the weak hyperfine multiplet.

The spectral data obtained from Fig. 4 were sufficient to determine the hyperfine splitting of the Tm ground state. The transition at 567.585 nm connects the ground state ($4f^{13}6s^2\ ^2F_{7/2}$) to the excited state at 17614 cm^{-1} ($4f^{13}6s6p\ (7/2,1)_{9/2}$) [20]. Tm has a nuclear spin of 1/2 [21], thus each state is a doublet; the total angular momentum quantum numbers (F) of the ground state are 3 and 4, whereas the F numbers for the excited state are 4 and 5. The operative absorption selection rules suggest that the observed transition should have three components, as was observed in Fig. 4. The measured wavenumber differences were 0.055, 0.050, and 0.105 cm^{-1} and resulted in six possible hyperfine level structures, outlined in Fig. 5. Comparison of the measured intensities with those tabulated in Ref. 22 immediately identified the correct level structure reproduced in Fig. 6. Both the ground and excited states are inverted and the ground state splitting is 0.05 cm^{-1}.

A similar analysis applied to the 597.128 nm (0 - 16742 cm^{-1}) transition revealed that the transition should be split into four components as is shown in Fig. 7. This transition (gf = 0.0061) is weaker than the transition at 567.585 nm (gf = 0.027) and thus it was necessary to increase the HPO temperature to 900 °C to observe the two weakest hyperfine components. The corresponding level structure is shown in Fig. 8.

The samarium absorption at 565.986 nm had partially resolved, but complex, isotopic structure that was difficult to interpret and the yttrium sample, although completely melted in the modified HPO, did not yield an absorption spectrum. This is thought to be due to the formation of a tenacious oxide layer on the yttrium melt that "crusts" on the surface and prevents the release of the metal atom vapor. Similiar behavior has been noted for uranium. The production of yttrium atoms is primarily by the dissociation of YO at temperatures at or above 2100 °C [23].

CONCLUSIONS

The structural modifications described in this article permit the application of HPO-techniques to materials melting as high as 1700 °C. Modest sample sizes produce ample vapor densities that persist for extended experiments (e.g., Tm was studied for up to 1 hour using a single 50 mg sample). The modified HPO is well adapted for laser spectroscopic studies.

The modified HPO is useful for laser atomic absorption spectroscopy studies of high melting materials, but high resolution spectroscopic studies using this device are limited by the extensive Doppler broadening that accompanies high temperature volatilization. Doppler-free spectroscopic techniques could be used to gain additional resolution , if required. Another limitation of the modified HPO is sample oxidation resulting from incomplete oxygen removal from the device and filler gases. We expect that sample oxidation can be reduced by restricting sample handling and preparation to inert environments.

ACKNOWLEDGMENTS

The authors thank Dr. Kevin Carney (AtoChem Inc.) for assistance in setting up the laser spectroscopic apparatus and writing the data acquisition software used in this work; Mr. Edward DeKalb (Ames Laboratory) for general technical assistance; Mr. Jerry Hand, for design assistance with the thermocouple and heater support structures; Mr. A.P. D'Silva (Ames Laboratory), for the use of the gas purification system; Dr. John C. Travis (National Institute of Standards Technology) for helpful discussions regarding the atomic hyperfine levels.

This work was funded by the Office of Safeguards and Security of the U.S. Department of Energy.

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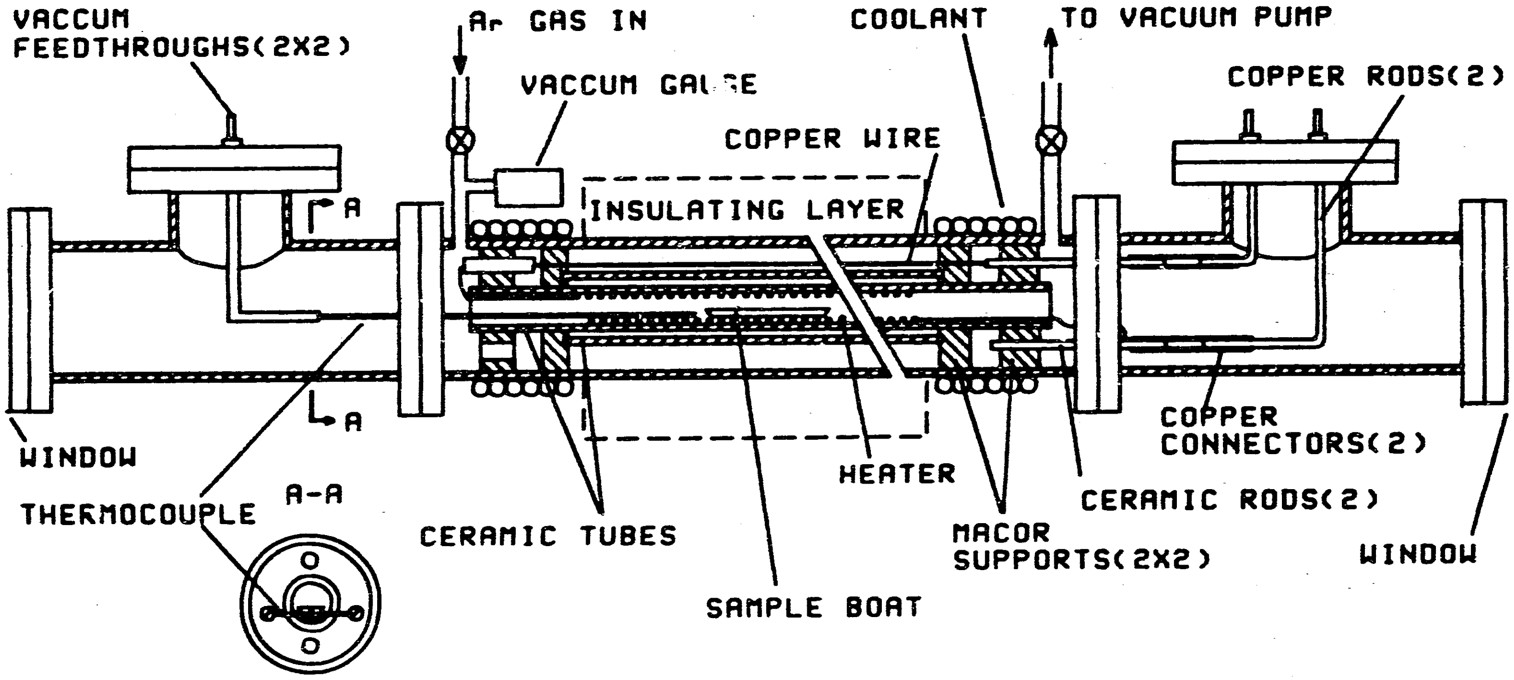
TABLE I. Experimental apparatus and operating conditions

Laser system	
Argon laser	Innova 90-5, output power: 5W (all lines)
Ring dye laser	CR699-21, output power: 190 mW at 567.585 nm; 140 mW at 597.128 nm scan range: 12 GHz; line width: < 20 MHz Coherent Laser Co., Palo Alto, CA
Dye	Rhodamine 590/ethylene glycol+methanol Exciton Chemical Co., Dayton, OH
Optical table	Type XL-A(2) and Type XL-B(1) with NRC pneumatic isolation mounts, Newport Corp., Fountain Valley, CA
Modified HPO	based on Model HP-801 heat pipe oven, Comstock, Oak Ridge, TN; maximum operating temperature: 1700°C
Gas purification system	Semigas Systems Inc., San Jose, CA
Optical detection system	
Photomultiplier tube	R758, Hamamatsu Corp., Middlesex, NJ
Monochromator	Model 82-410, focal length: 0.25 m; grating: 1180 g/mm; slits: 0.25 mm; Jarrell-Ash Co., Waltham, MA
Data acquisition system	
Wavemeter	WA-20, Burleigh Instr. Inc., Fishers, NY
Power meter	Model 365, Scientech Inc., Boulder, CO
Lock-in amplifier	Model SR-510, Stanford Research Systems, Inc., Sunnyvale, CA
Mechanical chopper	Model 350CD, Scitec Instruments Ltd., Boston Electronics Corp., Brookline, MA
Data acqusition computer	Hewlett-Packard Vectra, Sunnyvale, CA

FIGURE CAPTIONS

Fig. 1	Modified heat pipe oven. The total length of the oven is 90 cm.
Fig. 2	Thermocouple calibration curve.
Fig. 3	Experimental diagram for high resolution laser atomic absorption. The symbols denote: HVPS: high-voltage power supply; P: photomultiplier tube, MC: monochromator, MHPO: modified heat pipe oven, L1: argon ion laser, L2: ring dye laser, M: mirror, C: mechanical light chopper, F: neutral density filter, PM: power meter, ---: optical path, and ___: electrical connections.
Fig. 4	Transmission spectra of Tm at 567.585 nm and (a) 810 °C and (b) 855 °C. The dye laser scan range was 12 GHz from 17613.45 cm^{-1} to 17613.85 cm^{-1}. The peaks are due to hyperfine effects.
Fig. 5	The six possible hyperfine splitting level diagrams of Tm based on the spectra shown in Fig. 4.
Fig. 6	Hyperfine energy level diagram of Tm line at 567.585 nm showing the hyperfine structure for the three spectral lines observed in Fig. 4.
Fig. 7	Transmission spectra of Tm line at 597.128 nm and (a) 840 °C and (b) 900 °C. The dye laser scan range was 12 GHz form 16742.00 cm^{-1} to 16742.40 cm^{-1} . The four peaks are due to hyperfine effects.
Fig. 8	Hyperfine energy level diagram of Tm line at 597.128 nm showing the hyperfine structure for the four spectral lines observed in Fig. 7.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COPPER RODS(2)
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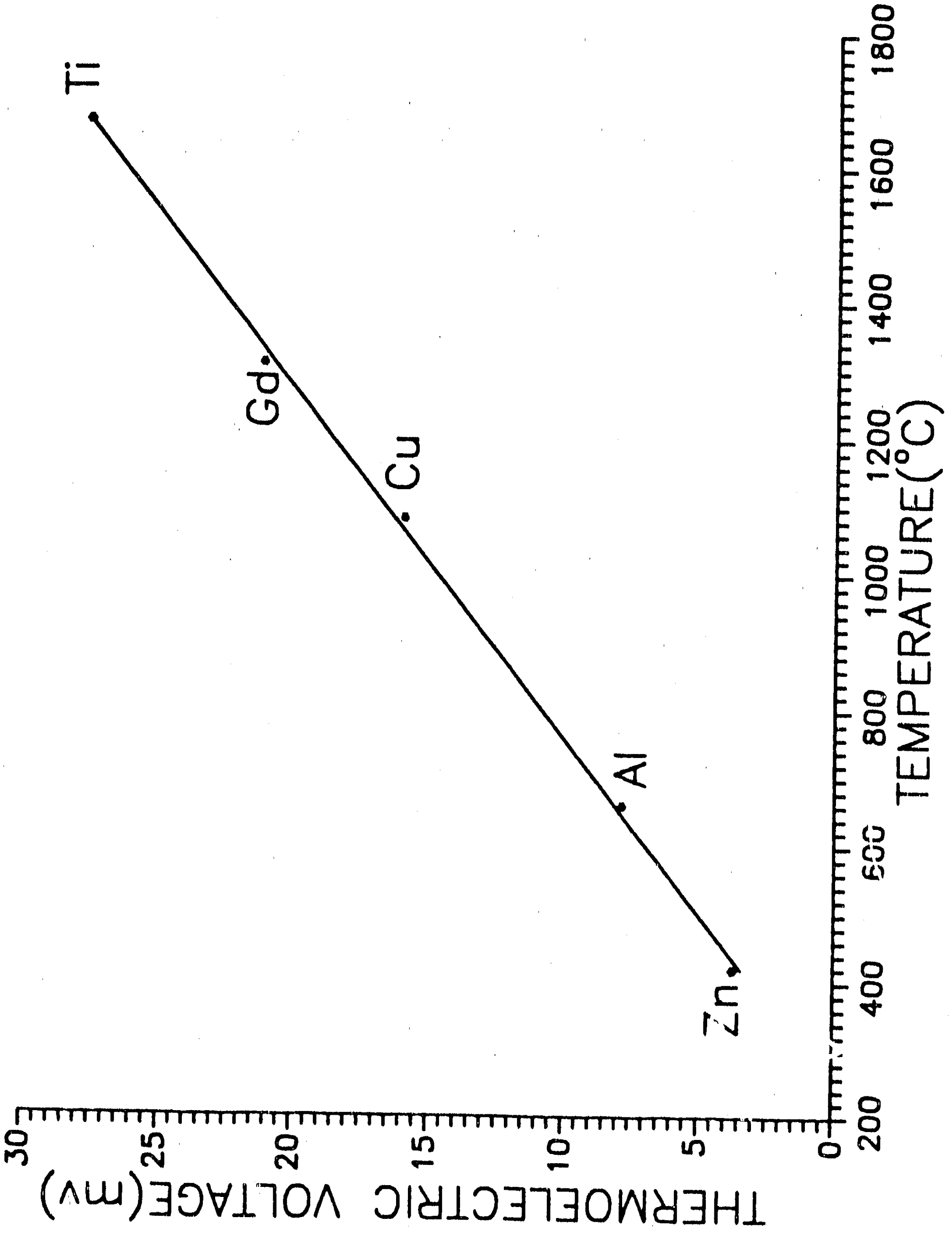
INSULATING LAYER
A
A
WINDOW
A-A
THERMOCOUPLE
CERAMIC TUBES
SAMPLE BOAT
HEATER
MACOR SUPPORTS(2X2)
CERAMIC RODS(2)
COPPER CONNECTORS(2)
WINDOW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Gd
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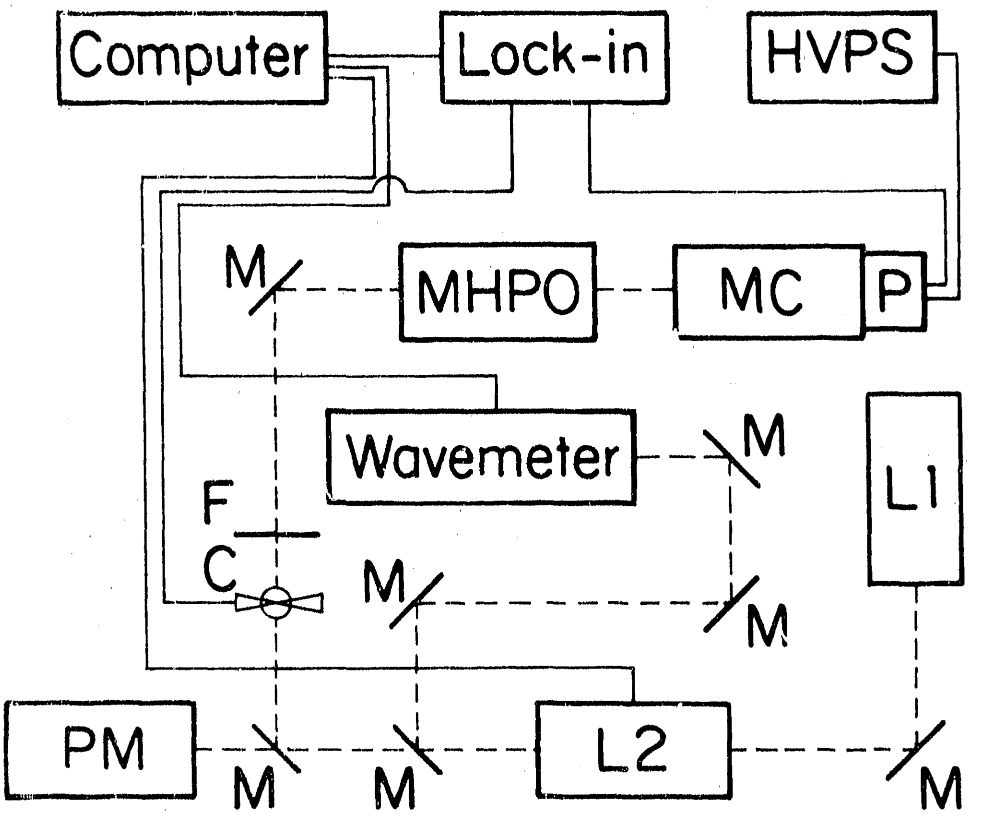
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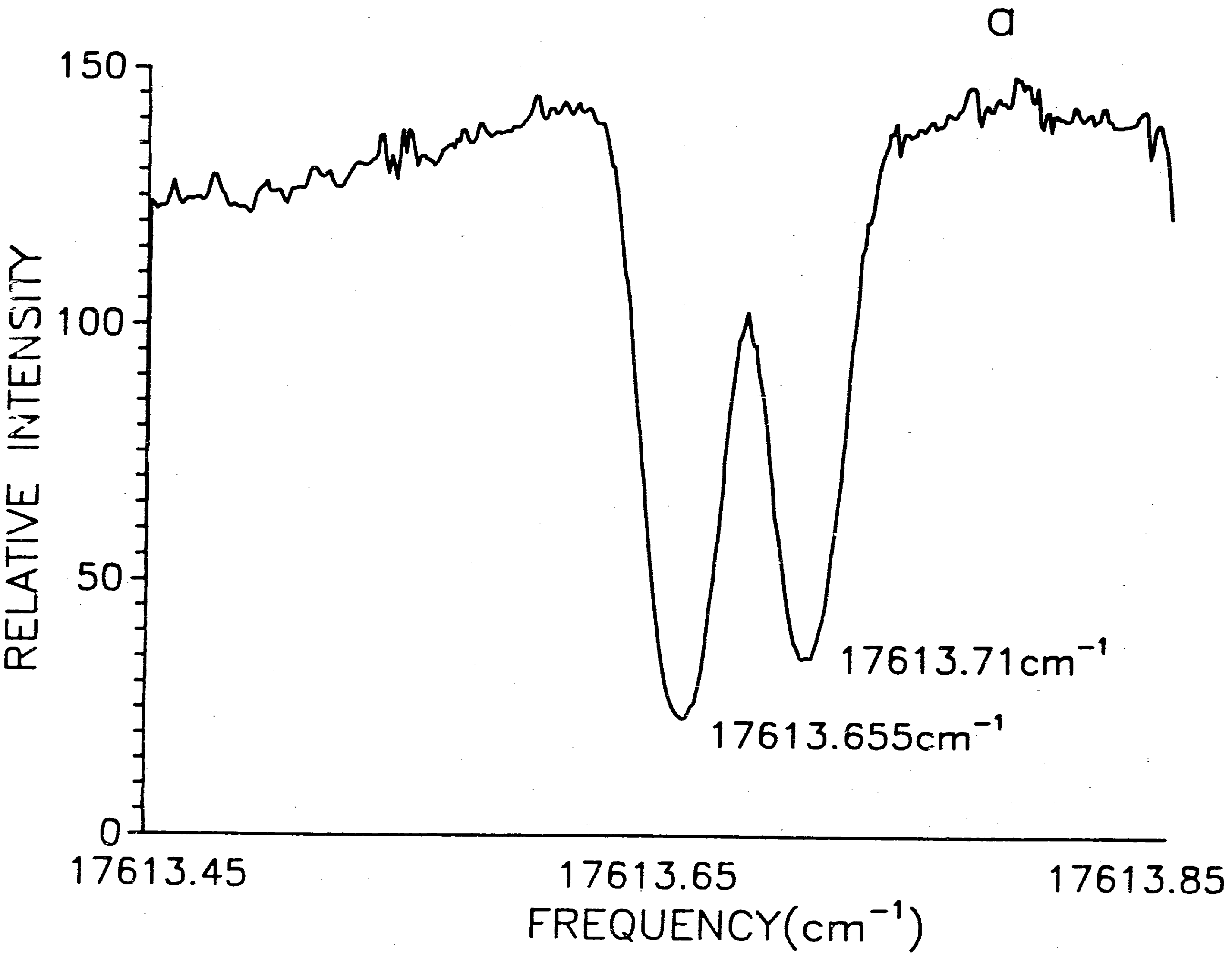
a
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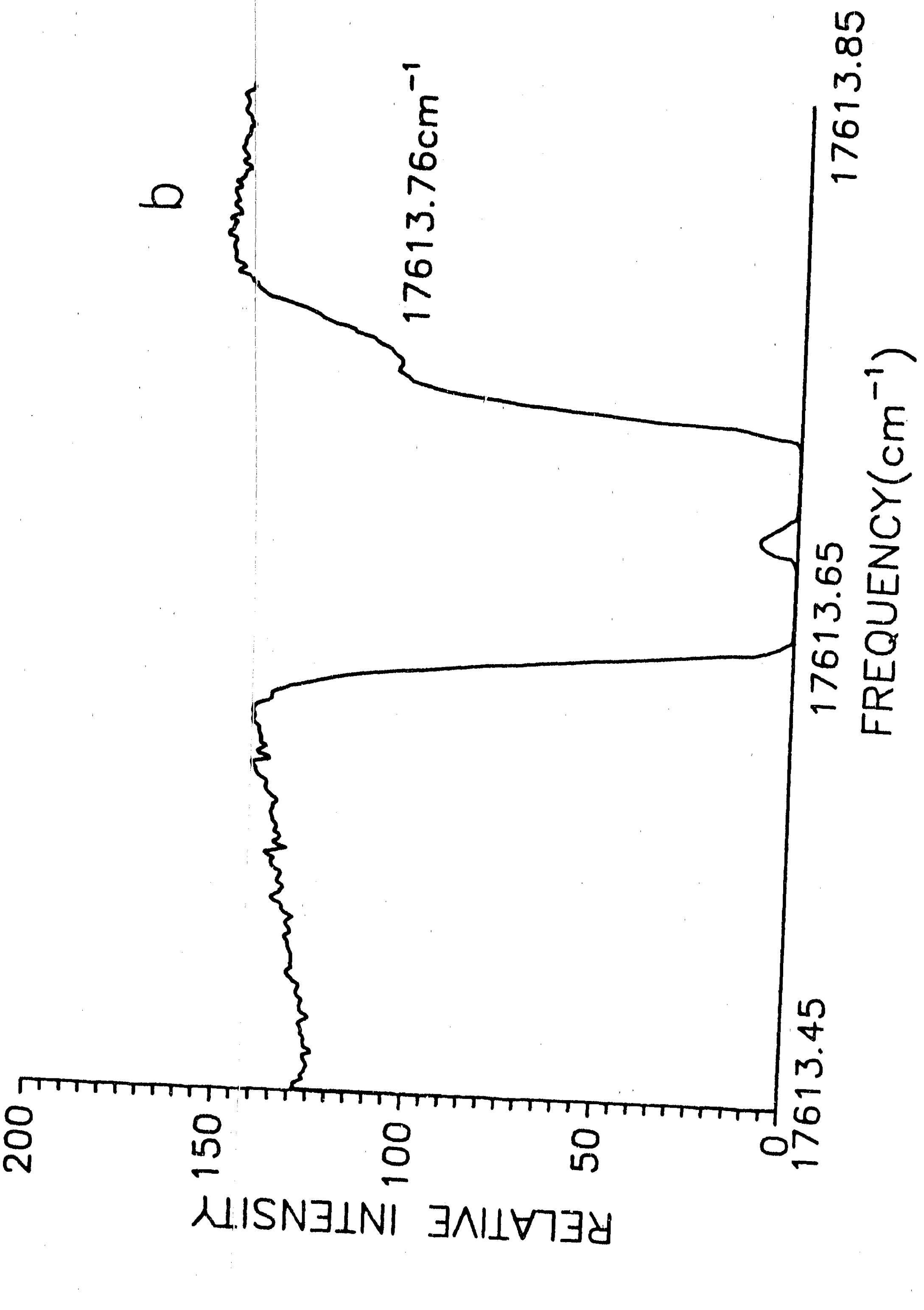
17613.45
17613.65
17613.85
FREQUENCY(cm^{-1})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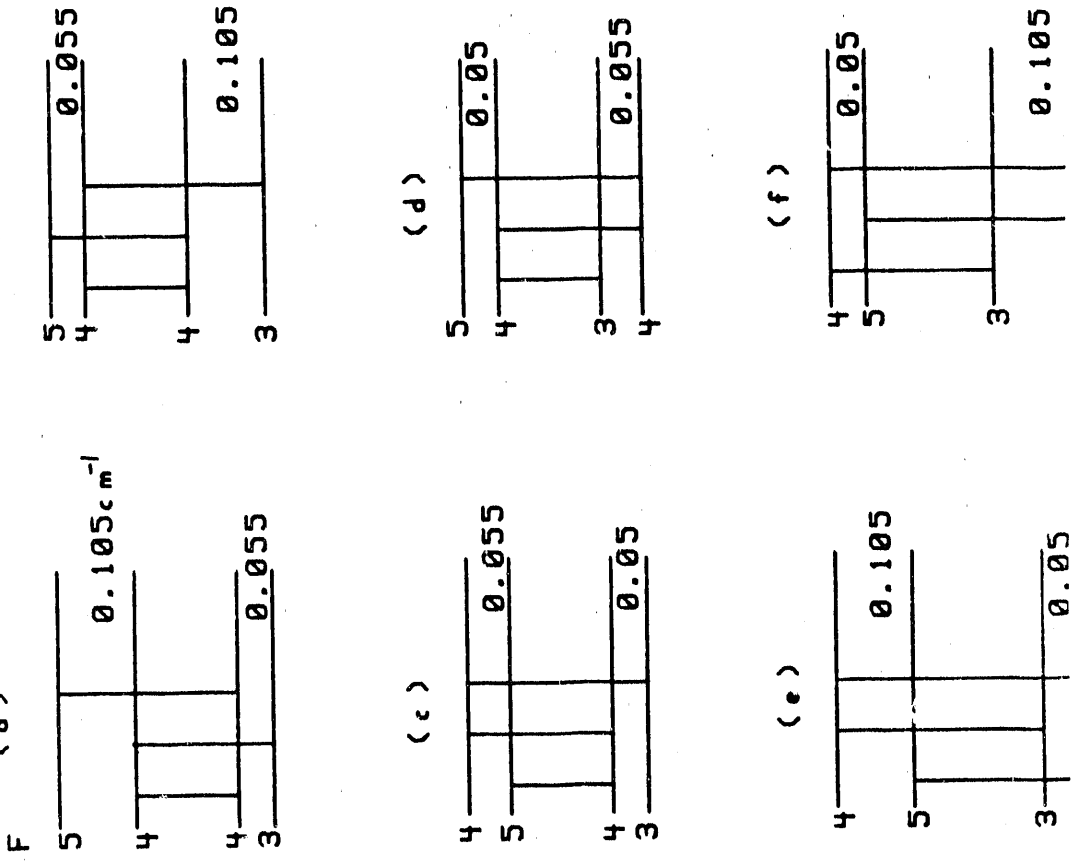
17613.85
FREQUENCY(cm^{-1})


(a)
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(b)
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(c)
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5
4
3
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0.05
(d)
5
4
3
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(f)
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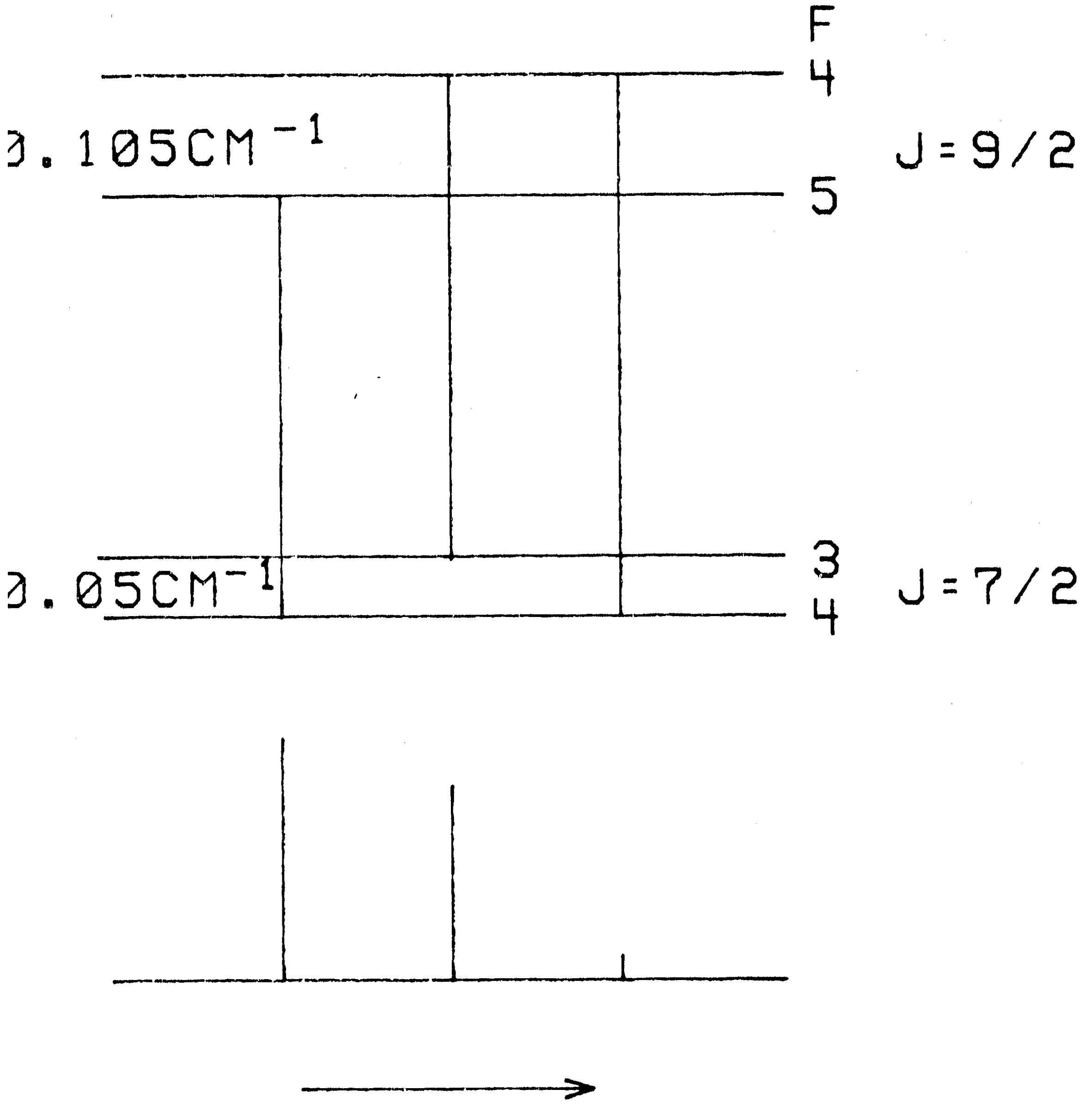
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3
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J=7/2
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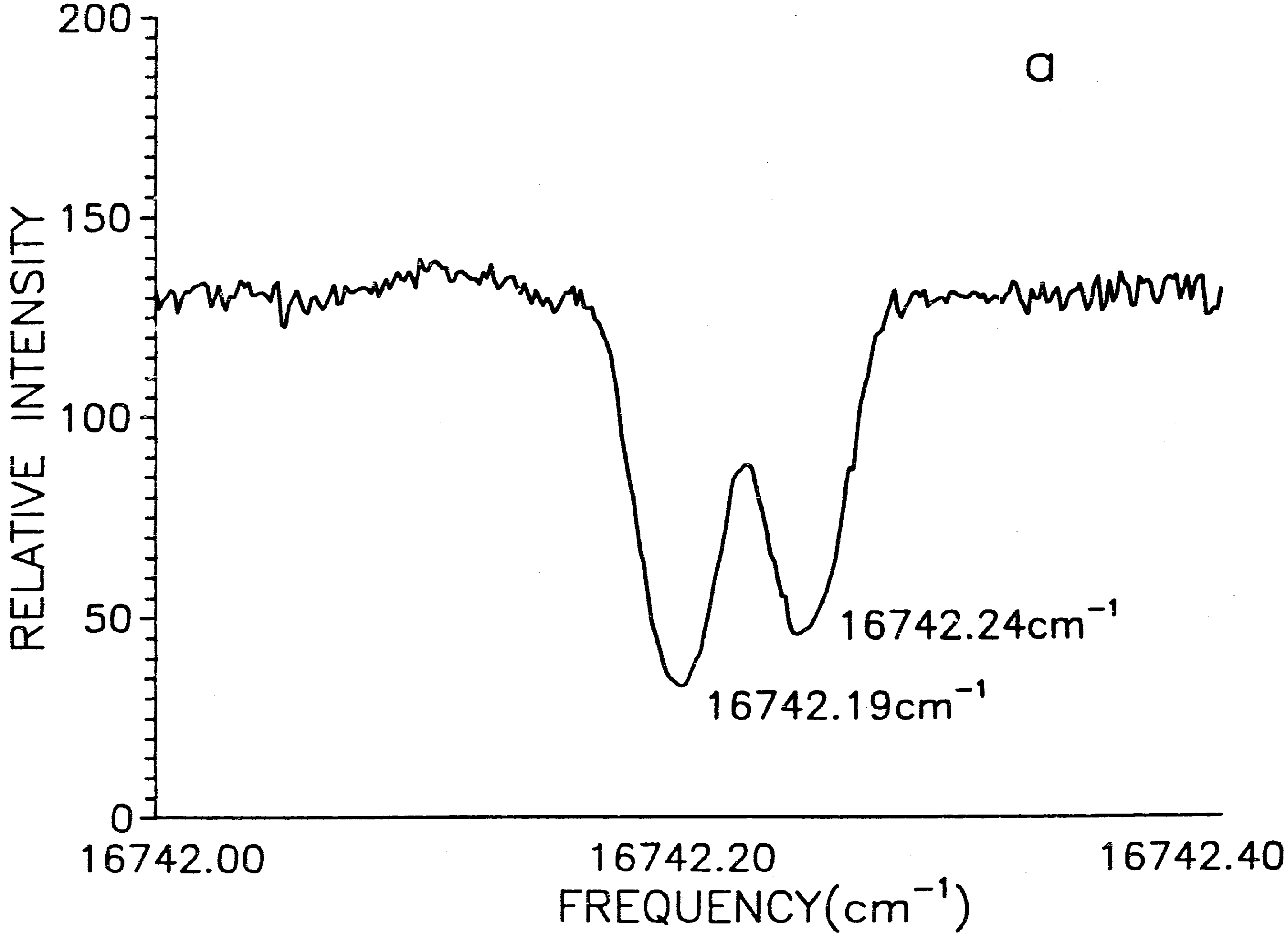
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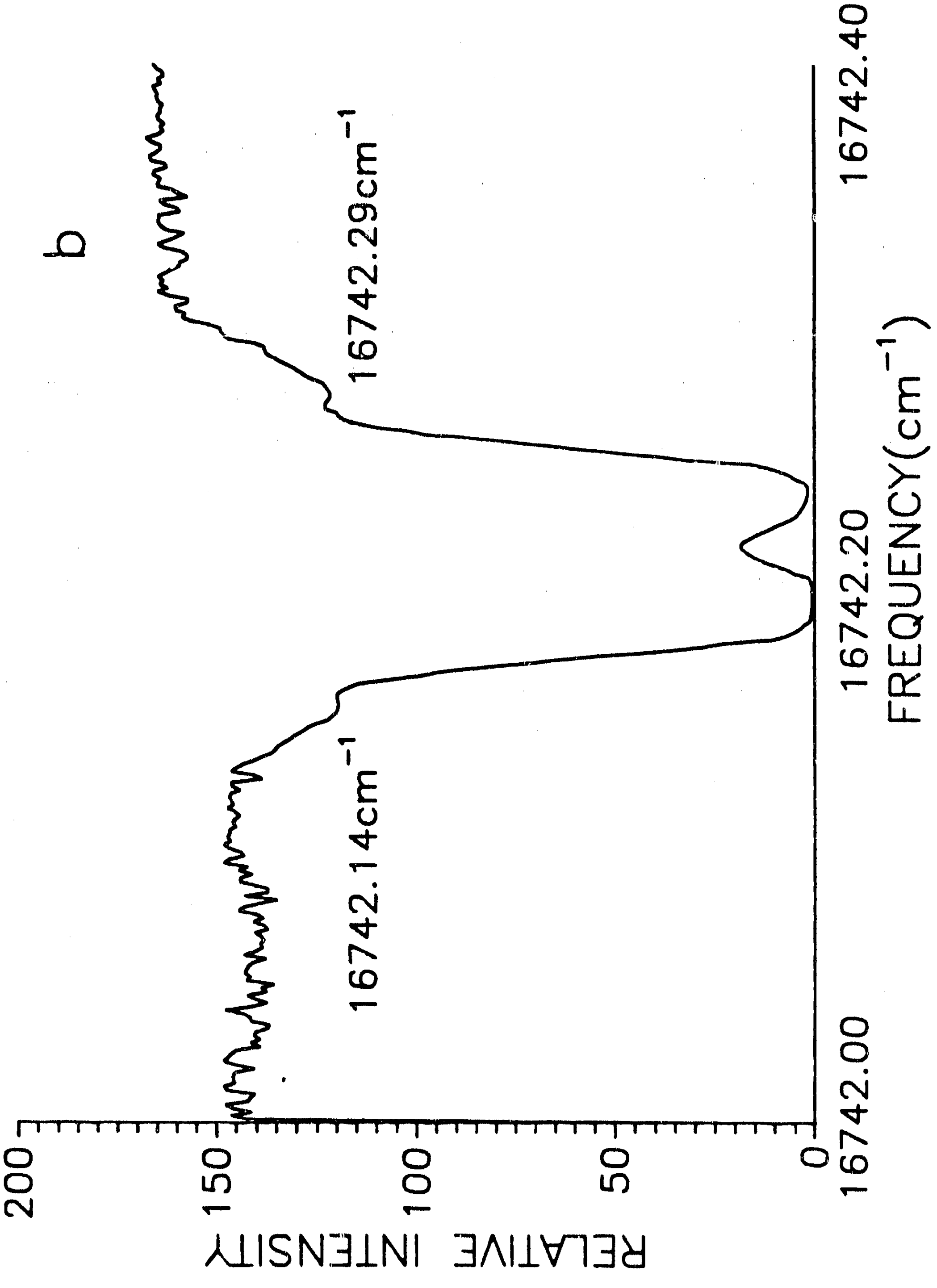
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16742.29cm^{-1}
RELATIVE INTENSITY
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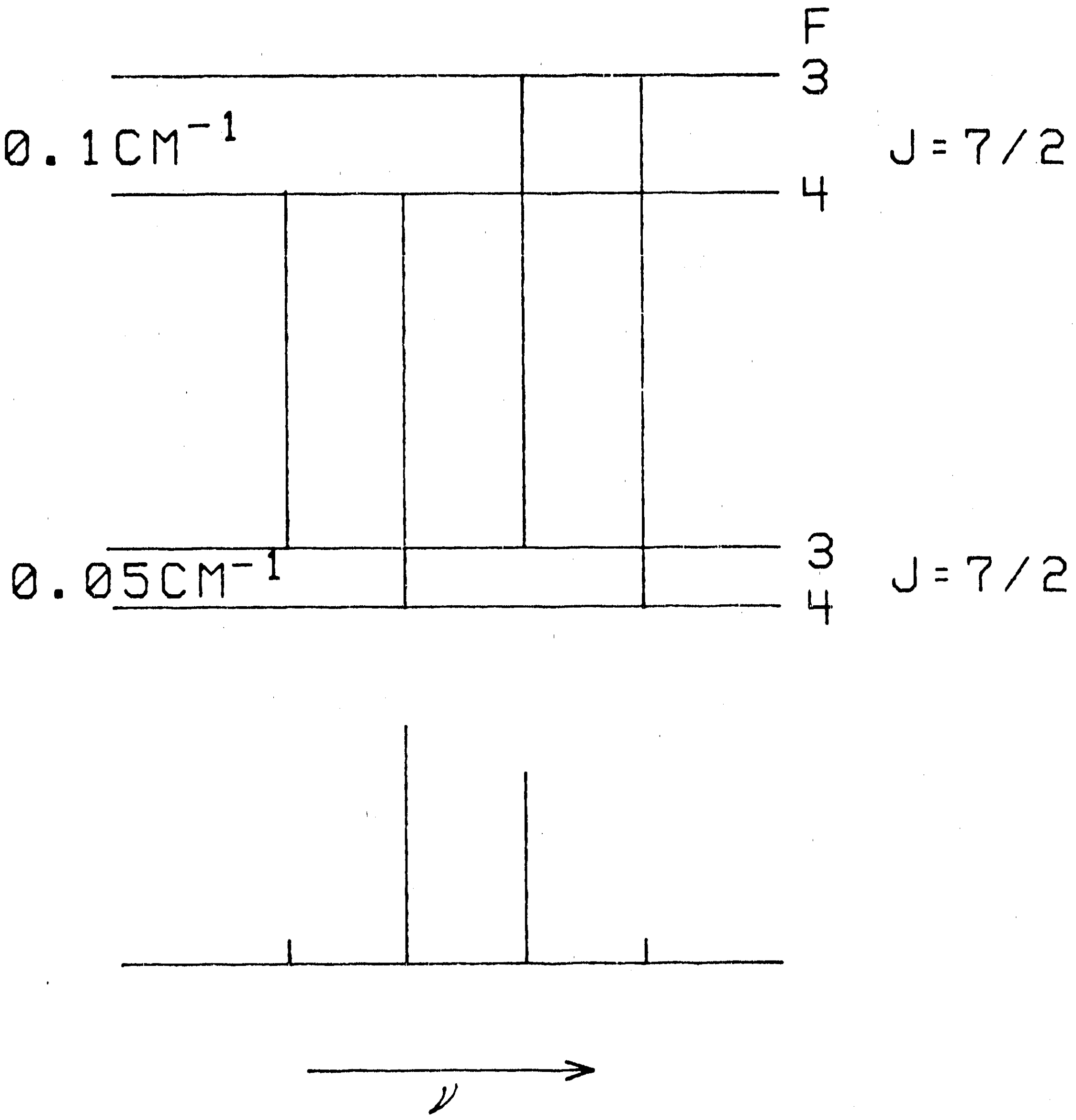
16742.40
FREQUENCY(cm^{-1})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J=7/2
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