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Determination of Trace Level Iodine in Biological and Botanical Reference Materials by Isotope Dilution Mass Spectrometry

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A method has been developed for the determination of trace level iodine in biological and botanical materials. The method consists of spiking a sample with ^{129}I , equilibration of the spike with the natural iodine, wet ashing under carefully controlled conditions, and separation of the iodine by co-precipitation with silver chloride. Measurement of the $^{129}\text{I}/^{127}\text{I}$ ratio is accomplished by negative thermal ionization mass spectrometry using LaB_6 for ionization en-

hancement. The application of the method to the certification of trace iodine in two Standard Reference Materials is described.

Key words: biological material; botanical material; iodine; mass spectrometry; Standard Reference Materials; trace analysis.

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1. Introduction

Iodine has been known to be necessary to human nutrition since the 19th century [1]. Endemic goiter in man was shown to be due to the lack of iodine in the food and water supply of affected regions. The addition of iodine to salt, iodized salt, has become a widely recognized factor in the control of iodine deficiency.

The Food and Nutrition Board, National Academy of Science—National Research Council has established a recommended daily allowance (RDA) of 150 μg of iodine. This is the basis for the U.S. RDA published by the Food and Drug Administration for nutritional labeling of foods (Fed. Reg., March 14, 1973). Most foods contain less than 1 $\mu\text{g/g}$ of iodine, and considerable uncertainty exists for values of iodine determined in foods [2]. Heckman [3] published the results of an interlaboratory study of iodine in foods using neutron activation analysis and Ce-As-I colorimetry. The study

showed wide discrepancies in analytical results. Mean relative standard deviations for all laboratories were almost 80%, with differences of over 300% reported between laboratories. In the worst case, reported results differed by over two orders of magnitude. The study recommended that either the chemical method be refined or a new method be developed. Dybczynski et al. [4] have reported a “round-robin” analysis of a milk powder reference material which showed iodine concentrations ranging from 0.05 to 3.6 $\mu\text{g/g}$.

Until recently, none of the botanical or biological Standard Reference Materials (SRMs) issued by the National Institute of Standards and Technology were certified for iodine concentrations. A number of these SRMs contained an “information only” value provided by neutron activation analysis. However, in the absence of a second reliable analytical technique, iodine concentrations could

not be certified. In view of this need for an accurate method for trace level measurements of iodine in these materials, it was decided to develop a method of analysis based on isotope dilution mass spectrometry (IDMS). Isotope dilution mass spectrometry has been used extensively at the National Institute of Standards and Technology for the certification of trace element concentrations in Standard Reference Materials. It is regarded as a "definitive method", that is, a method for which systematic errors have been thoroughly evaluated and accounted for to provide an essentially bias free and hence accurate result.

The quantity of an element present in a material is determined by IDMS from the change produced in its isotopic composition by the addition of a known amount of a pure isotope of the element of interest. After equilibration of the element in the material with the added separated isotope of the element, followed by chemical separation, the altered isotopic composition of the element is measured by thermal ionization mass spectrometry. The concentration of the element can then be calculated from a knowledge of the sample weight and natural isotopic composition, and the weight, concentration, and isotopic composition of the added separated isotope. Although it can be used for the accurate determination of element concentrations ranging from parts-per-billion (ng/g) to percent levels, IDMS has found its greatest applicability in the certification of trace level concentrations ($\mu\text{g/g}$ -ng/g). It is the most accurate of the trace analysis techniques, mainly because separations need not be quantitative since only isotope ratios and not quantities are measured. For most elements, the lower limit of analysis is determined by the level of contamination or "blank."

The development of an IDMS method for iodine presented several problems: 1) since natural iodine is a mononuclidic element (100% ^{127}I), a radioactive isotope with a long half-life would have to be used as the spike isotope; 2) a method for the isotopic equilibration of the spike isotope with the natural iodine in the material, without loss of iodine before equilibration, would have to be developed; 3) a method to separate the equilibrated iodine in a form suitable for mass spectrometric analysis would be required; and 4) a mass spectrometric analytical procedure capable of providing high precision measurements on ng quantities of iodine required development.

This paper describes the development of such an IDMS method for trace iodine in botanical and biological materials, and the application of the

method to the certification of iodine in botanical and biological Standard Reference Materials. This work was first reported in outline form in a 1982 report of the National Bureau of Standards [5] and is presented here in detail. Heumann and Schindlmeier [6] have published an IDMS method for the determination of iodine by negative thermal ionization mass spectrometry. These investigators used ^{129}I as the spike isotope for iodine in table salt and pure inorganic chemicals. The chemical separation of the iodide ion was carried out by anion-exchange chromatography, however this method of separation could not be applied to wet ashed organic materials in a high acidity solution. Since the completion of the work described in this paper, Schindlmeier and Heumann [7] have published the determination of trace iodine in food by IDMS. Their method for decomposition of the organic matrix by wet-ashing and their mass spectrometric procedure are considerably different than those described in this paper.

In 1985 the Community Bureau of Reference (BCR) of the Commission of the European Communities certified two milk powder samples (CRMs 150 and 151) for iodine. Various activation analysis techniques, IDMS, the catalytic Ce-As-I method, gas chromatography, and pulse voltammetry were included in the certification of these materials [8].

2. Experimental Section

Chemistry: Iodine-129 was selected as the spike isotope. It is a β -emitter with a half-life of 1.6×10^7 years [9]. The material used was SRM 4949A, Iodine-129 Radioactivity Standard. A solution of this material was prepared in a Teflon bottle and made alkaline by the addition of sodium carbonate. The solution, calibrated against high-purity potassium iodide (E. Merck,¹ Darmstadt, FRG), contained $0.078209 \pm 0.00011 \mu\text{mol/g}$ (1 s) of iodine. The relative isotopic composition of the iodine in this spike solution was $^{127}\text{I} = 13.90\%$ and $^{129}\text{I} = 86.10\%$.

The equilibration of the spike isotope and natural ^{127}I was studied using radioactive ^{125}I as the tracer isotope. This isotope has a half-life of 60.1 days [9].

¹Certain commercial equipment, instrumentation, or materials are identified in this paper to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Sufficient spike isotope was added to each sample studied so that 3000 counts over background were observed in a 200 s time period. The τ -ray counting was done utilizing a 7.6×7.6 cm NaI (Tl) crystal and associated electronics. Various methods of oxidizing iodide to iodate and wet-ashing the organic matrix were investigated. It was necessary only to equilibrate the spike and natural isotopes without loss of iodine; losses after equilibration will not affect the accuracy of the analysis. Studies with ^{125}I tracers and SRM 1572, Citrus Leaves, showed that fuming nitric acid solubilized the sample while retaining iodide as iodate. Wet-ashing could be effected by heating overnight on a hot-plate and then with additional heating after adding perchloric acid. Slow loss of iodine occurs at this step, but will not affect the accuracy of the results, since the spike and natural iodine are equilibrated. Co-precipitation of iodide (after reduction from iodate to iodide) was investigated using the ^{125}I tracer. These experiments showed that the iodide could be co-precipitated with chloride as AgCl-AgI with 70–85% recovery of iodide.

Mass spectrometry: Several techniques and variations have been reported in the literature for negative thermal ionization of iodine. The two major approaches are multiple filament ionization using rhenium or tungsten filaments [6,7], and cataphoretic deposition of lanthanum hexaboride [10,11] to improve the sensitivity of the measurements by lowering the work function of the ionizing filament. The above references are representative of efforts in this area, and provide cross references to other published work. Each approach has advantages and disadvantages depending on the particular application. Lanthanum hexaboride coated ionizing filaments provide very high ionization efficiency and elemental sensitivity, however the deposition procedure is difficult and time consuming, and the precision of the measurements is extremely dependent upon the reproducibility of the physical characteristics of the LaB₆ coatings. Uncoated filaments are more amenable to routine analyses but require several micrograms of iodine to obtain sufficient signal intensity.

The use of low work function filaments, using LaB₆ to obtain the required high sensitivity for measuring ultra-trace amounts of ^{129}I in the environment, has been extensively studied and reported in the literature [10,12]. Typically the $^{127}\text{I}/^{129}\text{I}$ ratio in such materials is greater than 10^6 , thus sensitivity to a small number of ^{129}I atoms is of far greater importance than the precision of the measurements. With isotope dilution mass spectrometry, using a

^{129}I spike, the amount of ^{129}I can be adjusted to optimize the measurement of the $^{127}\text{I}/^{129}\text{I}$ ratio. Thus the reproducibility (inter and intra-analysis precision) becomes the limiting factor in the measurement of an isotopic ratio.

3. Procedure

Approximately 1 g of dried and accurately weighed biological or botanical material was transferred to a 250 mL Teflon-FEP screw capped bottle. The sample was spiked with the ^{129}I spike solution (about 0.02 μmol ^{129}I for samples in the 1–3 $\mu\text{g/g}$ range) and 23 g (15 mL) of fuming nitric acid (90% HNO₃, ACS Reagent Grade) were added. The bottle was capped and allowed to stand for 1 h at room temperature. The cap was then removed and a small cover glass was placed over the top of the bottle. The bottle and contents were heated at low temperature (60 °C) for approximately 1 h. The heat was then increased (75 °C) and the sample was digested overnight. The solution was allowed to cool to room temperature and 5 mL of perchloric acid (72%, ACS Reagent Grade) were added. The bottle was again covered and heated for 2 h on the hot plate at a temperature of approximately 75 °C. The cover was then removed to allow fumes of nitric oxide to escape. The solution was allowed to cool, diluted with approximately 10 mL of high purity water and transferred to a 40 mL Pyrex glass centrifuge tube. The solution was mixed and allowed to stand until it was again at room temperature. To remove any insoluble matter produced by the reactions, the tube was centrifuged at 2000 rpm for 10 min. The centrifugate was drawn off from the precipitate using a polypropylene syringe equipped with a platinum needle, and transferred to another centrifuge tube. Five mL of hydrazine sulfate solution (2 g hydrazine sulfate/100 mL, ACS reagent grade) were added and the solution was allowed to stand for 2 h. One mL of 0.01 mol/L HCl and 1 mL of 0.005 mol/L AgNO₃ were added and the tube was allowed to stand overnight in the dark. The tube was then centrifuged at 2000 rpm for 10 min and the centrifugate was drawn off from the co-precipitated AgCl-AgI using a polypropylene syringe and platinum needle. The precipitate was washed with a few mL of high purity water, and the tube was again centrifuged at 2000 rpm for 10 min. The liquid was withdrawn from the tube using the syringe and the platinum needle.

The precipitate was then dissolved in 200 μL of an ammonium cyanide reagent solution and diluted to approximately 10 mL with high purity water. (The ammonium cyanide reagent solution was prepared by passing 50 mL of a solution containing 1 g of KCN through an acid cleaned cation exchange column and collecting the eluant containing dilute HCN in 40 mL of 2 mol/L NH₄OH. The column was washed with 10 mL of high purity water such that the final solution contained approximately 4 mg CN⁻/mL in 1 mol/L NH₄OH.) Ten mL of 2.5 mol/L HNO₃ were added to re-precipitate AgCl-AgI. The tube and its contents were allowed to stand for a minimum of 2 h and then centrifuged for 10 min at 2000 rpm. The solution was drawn off the precipitate using the syringe and needle. The precipitate was washed with 0.5 mL of 0.5 mol/L NH₄OH and allowed to stand for a few minutes. The tube was again centrifuged at 2000 rpm for 2 min and the solution was withdrawn with the syringe and needle. The precipitate was dissolved in a sufficient amount of the ammonium cyanide reagent solution to produce a solution containing approximately 10 μg I/mL. This solution was transferred to a capped 1 mL centrifuge tube for mass spectrometric analysis.

The cataphoretic deposition of LaB₆ onto rhenium filaments generally followed the procedure described by Favreau [13,14] with modifications suggested by Delmore [10,11]. The LaB₆ (obtained from CERAC, Inc., Milwaukee, WI, lot #11610-A-1) was specified by the manufacturer for use in producing thermionic coatings on rhenium. Prior to use, the LaB₆ (~325 mesh) was ground to a finer mesh size in an agate mortar, repeatedly washed with ethanol (ACS reagent grade), agitated in an ultrasonic cleaner, and then centrifuged. The ethanol was decanted and discarded before repeating the washing process. Although the LaB₆ appeared to be quite clean, as received, the ethanol wash was a precaution to remove any boric oxide, as suggested by Favreau [13]. The washed LaB₆ was dried in a vacuum oven and stored in a vacuum desiccator over magnesium perchlorate. The solutions used for cataphoretic deposition were prepared by mixing approximately 100 mg of LaB₆ with 10 mL of anhydrous spectroscopic grade methyl alcohol. Unlike several other reported methods, no electrolyte was added to the solutions. These solutions, if kept sealed from the atmosphere when not in use, were effective for 2 to 3 weeks.

The cataphoretic deposition apparatus (fig. 1) consisted of a 15 mL borosilicate glass beaker fitted with a Teflon stopper. Gold plated connectors

were installed in the bottom of the stopper to hold the ionizing filament in an inverted position in the beaker. One connector was attached to a wire extending through the stopper for electrical connection to a dc power supply. A second wire through the stopper was spot welded to a platinum foil anode ($1 \times 1 \times 0.0076$ cm). A rhenium filament, previously degassed in a vacuum and under a potential field for 1 h at a current of 4.5 A through the filament, was placed in the connectors on the bottom of the Teflon stopper. The platinum anode was aligned with the filament such that it was parallel to, and approximately 1 mm from the filament. A sufficient quantity of the LaB₆-methyl alcohol solution was added to the beaker to submerge the filament to a depth of 1 mm. Cataphoretic deposition of LaB₆ onto the rhenium filament was accomplished by applying a dc voltage sufficient to draw a current of 2.5 mA. This required a voltage of 60–100 V dc and was critically dependent on the spacing between the platinum anode and the filament cathode. The time of deposition ranged from 5–10 min and was based on visual judgment of the thickness of the LaB₆ coating on the filament.

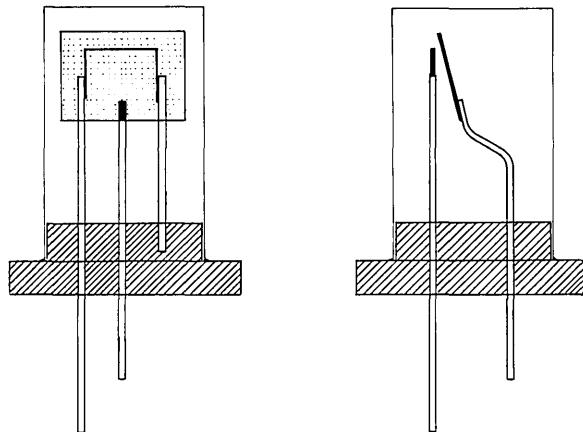


Figure 1. Cataphoretic deposition apparatus.

Delmore [11] has extensively studied the ionization efficiency and precision attainable with different types of LaB₆ coatings (thick porous, thin porous and smooth dense coatings). Our work has confirmed Delmore's investigations by showing that the porous LaB₆ coatings provide maximum signal intensity, but the smooth dense coatings produce greater inter and intra-analysis precision at the expense of ionization efficiency. Since the materials discussed in this paper contained sufficient total iodine (sample + spike), precision rather than

sensitivity was the major concern. The LaB₆ deposition procedure described here was designed to produce a smooth dense LaB₆ coating for optimization of the accuracy and precision of the measurements. The low work function of LaB₆ is easily poisoned by such gases as oxygen, hydrogen, water vapor, and carbon dioxide [15,16]. Details of the poisoning mechanism have been described by Gallagher [16]. Re-activation of the LaB₆ coated filaments was accomplished by step-wise heating in a high vacuum (1×10^{-7} Torr) at 1200, 1300, and 1400 °C for 5 min at each temperature.

Approximately 5 μL (50 ng I) of the sample solution was placed on each of two previously degassed rhenium sample filaments and evaporated to dryness using a heat lamp and a current of 1 A through the filaments for 5 min. The current through the filaments was then increased until the sample deposit melted on the filament (approximately 600 °C). The two sample filaments and the LaB₆-coated ionizing filament were then loaded into the source of the mass spectrometer. Since the LaB₆ was re-exposed to atmospheric gases for a few minutes while being loaded into the mass spectrometer source, a short reactivation of the LaB₆ was required. After the source had been evacuated to a pressure of 2×10^{-7} Torr the LaB₆ was reactivated at 1400 °C for 5 min, followed by reducing the ionizing filament temperature to 1000 °C. Both sample filaments were then heated with a current of 0.25 A (time = 0 min). At 5 min into the analysis, the sample filament currents were increased to 0.50 A and at 10 min were increased to produce a total iodine ion current at the collector of 6×10^{-11} A. Ten minutes were allowed for baseline measurements and stabilization of the ion current before data collection. A stable but slightly decaying iodine signal could be maintained for several hours.

Samples for isotope dilution analysis were spiked to give approximately identical ¹²⁷I/¹²⁹I ratios, to minimize the effect of memory from previous samples. When analyzing samples of significantly different isotopic composition, it was necessary to clean the ion source before analysis. The effects of iodine memory in the source region must be carefully monitored to ensure accuracy.

4. Results and Discussion

Table 1 shows the results for the IDMS determinations of iodine in SRM 1572, Citrus Leaves. Samples were taken from six different bottles and dried for 2 h at 85 °C before the iodine was deter-

mined as described in the procedure section. The determinations were run in two sets, A and B. Two samples, 4-A and 6-A, were lost during chemical preparation and are therefore not reported. Two samples, 3-1 and 5-1, were analysed without drying and corrected to dry weight by drying separate samples. Eight "blanks" for set A averaged 45 ± 10 ng I and three "blanks" for set B averaged 38 ± 3 ng I. Pooling the results for the two sets produced a value of 1.835 ± 0.008 μg/g (1 s, n = 12) for the concentration of iodine in SRM 1572. The results of different nuclear activation analysis techniques at NIST for the determination of iodine are in good agreement with this value, though they are less precise. Analyses by instrumental photon activation analysis (IPAA), instrumental epithermal neutron activation analysis, and thermal neutron activation analysis with radiochemical separation (RNAA) found an average iodine concentration of 1.91 ± 0.34 μg/g (2 s) for this material.

Table 1: Concentration of iodine in SRM 1572, Citrus Leaves

Sample No.	Bottle No.	Concentration, μg/g
1-A	C-1	1.845
2-A	C-3	1.838
3-A	C-5	1.839
5-A	C-7	1.844
3-1*	C-5	1.826
5-1*	C-7	1.850
1-B	C-1	1.842
2-B	C-3	1.822
3-B	C-5	1.831
4-B	C-6	1.826
5-B	C-7	1.830
6-B	C-10	1.831
Average =		1.835
s = ±		0.008

Samples analyzed as received. Corrected to dry weight by drying separate samples.

Table 2 shows the results for the IDMS determination of iodine in SRM 1549, Non-Fat Milk Powder. Samples were taken from six different bottles and dried for 48 h in a vacuum at room temperature before the iodine was determined as described above. The average concentration found for iodine in SRM 1549 was 3.376 ± 0.005 μg/g (1 s, n = 6). The blank correction for these determinations averaged 45 ± 13 ng/g. The uncertainty in the blank correction calculates to $\pm 0.4\%$ of the iodine concentration in the milk powder and is probably the principal cause of uncertainty in these determinations. The results of the determination of iodine in this material by instrumental photon activation

analysis and instrumental neutron activation analysis are again in good agreement with the IDMS value, however the uncertainty is much greater for the nuclear methods. Analyses by IPAA found an average iodine concentration of $3.40 \pm 0.46 \mu\text{g/g}$ (2 s), while INAA obtained an average value of $3.21 \pm 0.77 \mu\text{g/g}$ (2 s).

Table 2. Concentration of iodine in SRM 1549, Powdered Milk

Sample No.	Bottle No.	Concentration, $\mu\text{g/g}$
1	9-2	3.371
2	3-1	3.378
3	9-1	3.375
4	6-1	3.384
5	12-1	3.378
6	5-1	3.372
Average =		3.376
$s = \pm 0.005$		

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The Spectrum of Doubly Ionized Tungsten (W III)

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The spectrum of doubly ionized tungsten (W III) was produced in a sliding-spark discharge and recorded photographically on the NIST 10.7-m normal-incidence vacuum spectrograph in the 600–2680 Å spectral region. The analysis has led to the establishment of 71 levels of the interacting $5d^4$, $5d^3 6s$ and $5d^2 6s^2$ even configurations and 164 levels of the interacting $5d^3 6p$ and $5d^2 6s 6p$ odd ones. A total of 2636 lines have been classified as transitions between the 235 experimentally determined levels. Com-

parison between the observed levels and those calculated from matrix diagonalizations with least-squares fitted parameters shows an rms deviation of $\pm 87 \text{ cm}^{-1}$ for the even configurations and $\pm 450 \text{ cm}^{-1}$ for the odd ones.

Key words: energy levels; parameters; spectra; tungsten; wavelengths.

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1. Introduction

There are almost no experimental data on spectra or energy level analyses of ions that are isoionic or isoelectronic with W III. Of all the third spectra of the $5d$ -group, only Lu III [1] with one $5d$ electron and Au III [2] with nine $5d$ electrons have been studied. The isoelectronic Ta II has been analyzed [3] and a study of the $(5d + 6s)^k$ configurations in the second spectra [4] was done. However, no systematic studies of electronic configurations for the third spectra of this group of elements have been reported.

This is the first analysis of the spectrum of doubly-ionized tungsten (W III) to be published. It is a four-electron spectrum and belongs to the third transition group of elements with $5d$, $6s$, and $6p$ electrons in the lowest configurations. The even configurations discussed below are $5d^4$, $5d^3 6s$ and

$5d^2 6s^2$, and the odd configurations are $5d^3 6p$ and $5d^2 6s 6p$. The ground term is the 3D of the $5d^4$ configuration. It is the only term of this configuration that does not overlap with the next even configuration, $5d^3 6s$. The overlap of the configurations causes very strong configuration interaction (CI), especially between the odd ones. The level eigenvectors include different terms and configurations and produce a large number of transitions. Thus, W III is quite a complex spectrum.

2. Observations

The spectra were photographed in the region 600–2680 Å with the National Institute of Standards and Technology (NIST) 10.7-m normal-

incidence vacuum spectrograph equipped with a 1200-grooves/mm grating and having a plate factor of 0.77 Å/mm. A sliding-spark light source with a quartz spacer was used. Peak currents of approximately 50, 200, and 500 A gave excellent separation of W II, W III, and W IV lines. In order to maintain the discharge, it was necessary to introduce helium at approximately 20 Torr. A water-cooled copper hollow-cathode containing small pieces of germanium and silicon was operated at 500 mA with helium at 2 Torr to produce spectral lines of Cu, Ge, and Si at different ionization stages [5] which were used as reference lines. Part of one of the plates is presented in figure 1. Some of the spectrograms were measured at NIST and the remainder at the Instituto de Optica. The estimated uncertainty in the measurements is ± 0.005 Å.

Approximately 3700 lines were identified as belonging to W III, over 1000 lines to W IV [they were the basis of the report entitled "Analysis of the Fourth Spectrum of Tungsten (W IV)"] [6], and about 3500 lines to W II [7]. The analysis of W III has allowed us to classify 2636 lines (73% of the observed lines) as transitions between 71 even levels and 164 odd levels. The unclassified lines in the shorter wavelength region probably correspond to transitions of the $5d^3 7p$ and $5d^3 5f$ electron configurations, and the longer wavelength unclassified lines are probably $5d^3 7s$ and $5d^3 6d$ transitions.

Table 1 includes all of the W III classified spectral lines, giving for each of them: wavelength (expressed in air above 2000 Å), intensity, wavenumber, difference between the observed wavelength and the wavelength obtained from the final level values, and classification. The classification

includes the integer portion of the energy level value and the J value for each of the two levels. Table 2 contains the wavelength, intensity and wavenumber for each of 953 unclassified lines identified as W III. We have omitted lines with intensities estimated at "1".

3. Analysis

In order to give some idea of the complexity of the electronic structure and the number and the type of levels in the LS -coupling scheme, the predicted quintets, triplets, and singlets for the above mentioned configurations are presented in table 3. One should be aware that the coupling is far from pure LS . Most of the experimentally determined levels are characterized by a large number of observed transitions. This indicated a strong mixing between different terms and configurations which was later confirmed by the theoretical calculations.

The first goal of the analysis was the determination of the levels corresponding to the 5D ground term of the $5d^4$ lowest configuration. Then the energy levels of the other configurations could be established relative to the ground state (${}^5D_0 = 0.00$ cm $^{-1}$). The $5d^4 {}^5D$ ground term is the only one that does not overlap the next even configuration, and it is one of the few terms whose designation in LS -coupling is possible. The observed transitions to the even levels with predominantly quintet characteristics, $5d^4 {}^5D$ and $5d^3 {}^4F 6s {}^5F$, assisted in the determination of the $5d^3 {}^4F 6p {}^5G$ term and the 5G_6 (97039.60 cm $^{-1}$) and 5G_5 (89630.99 cm $^{-1}$) of the $5d^2 6s 6p$ configuration. The rest of the levels have no good LS -coupling names.

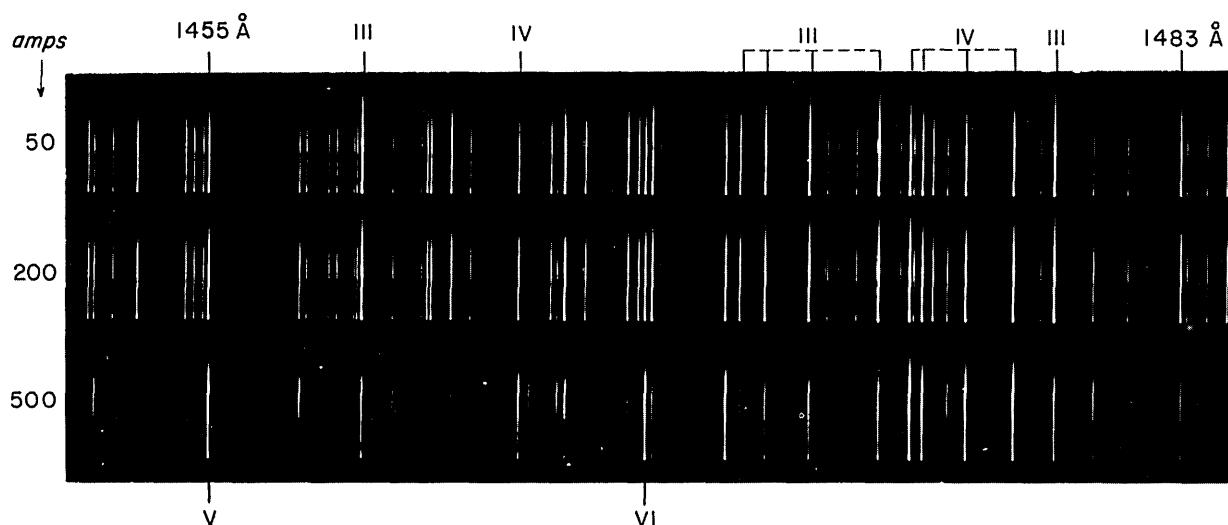


Figure 1. Tungsten spectra.

The energy range of these configurations is shown in figure 2. Tables 4 and 5 give the relevant information about the even and odd levels, respectively. The uncertainties of the optimized energy-level values are generally less than $\pm 0.10 \text{ cm}^{-1}$ and no greater than $\pm 0.20 \text{ cm}^{-1}$. Included for each level in table 4 are the configuration and term (whenever possible), J value, level value, uncertainty, number of observed transitions to or from the level, difference between the observed and calculated energy level, and leading eigenvector percentages in LS coupling. Percentages less than 5% have been omitted. Table 5 differs from table 4 in that the first two columns (configuration and term) have been omitted. Only the three first leading percentages, when they are larger than 5%, have been included.

The present situation in the energy-level analysis of W III is shown in table 6. It gives a résumé of the total number of observed and predicted levels, by J value, for the even and odd groups of configurations.

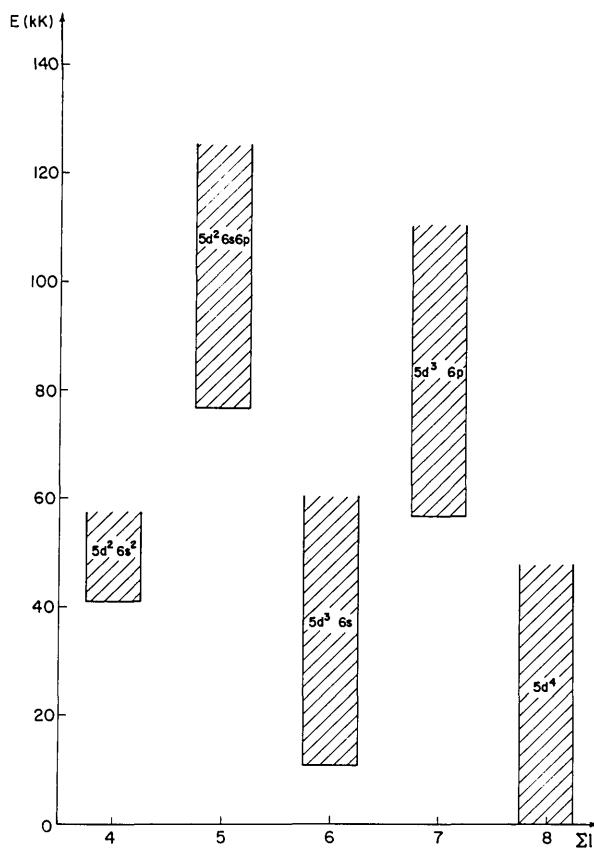


Figure 2. Main configurations of W III.

4. Theoretical Calculations

The low excitation stages of W III correspond to configurations with $5d$, $6s$, and $6p$ electrons, giving rise to large numbers of levels. Calculations for several even and odd configurations were carried out using Cowan's Hartree-Fock program that includes relativistic corrections (HFR) [8]. When the analysis had provided a reasonable number of experimentally derived levels (more than 60%) we were able to try the parametric calculations (least-squares fitting). Several coupling schemes were considered for the even and odd level systems. The average purities obtained in the most representative schemes are:

	LS	JJ
Even	53%	51%
Odd	36%	35%

indicating that no coupling scheme is appropriate to name the levels. Nevertheless, parametric calculations were performed with the use of the LS -coupling scheme for both even and odd configurations. As expected, CI plays an important role for the structure of this spectrum.

4.1 Even Configurations

The $5d^4$ and $5d^3 6s$ configurations overlap over a wide energy range and, as a consequence, their levels interact very strongly. We first set up one Hamiltonian matrix for these two configurations, including the corresponding CI parameter. The fitting was not at all satisfactory, the mean deviation being greater than $\pm 300 \text{ cm}^{-1}$. Because of the unsatisfactory results and with the knowledge that the lowest levels of the next even configuration, $5d^2 6s^2$, appear at about 40000 cm^{-1} overlapping the highest levels of $5d^3 6s$, a Hamiltonian matrix including all three even configurations was used. A least-squares fit (LSF), including all of the known 71 even levels resulted in a mean deviation of $\pm 87 \text{ cm}^{-1}$ between the observed and calculated values. The resulting LSF parameter values are presented in table 7, in which we also include the HFR values and the LSF/HFR ratios. The β parameter of $5d^2 6s^2$ was fixed at zero because the levels that help to determine its value are not known.

The resulting LS -percentage compositions of the levels are listed in table 4. More than half of these even levels have been designated in the LS -coupling scheme. The remainder have compositions which do not allow us to make any assignments of term or configuration.

4.2 Odd Configurations

For the odd configurations, the situation is considerably more complicated. Most of the levels of $5d^3 6p$ and $5d^2 6s 6p$ are so mixed that there is no way of naming the levels. This is especially true for the intermediate and low J -valued levels. The matrix for the two configurations included, of course, the corresponding CI parameters. Many attempts were made in order to get a reasonable fit of the parameter values which could provide moderate differences between the observed and calculated energy levels. Although we have used the 164 experimentally determined levels (more than 80% of those predicted for the two odd configurations), the fitting has been almost impossible. This was especially true for the $G^3(dp)$ parameters. They were, therefore, fixed at their respective HFR values for the final LSF. Table 8 contains the resulting LSF parameter values, those obtained from the HFR calculations, and the LSF/HFR ratios.

The LS -percentage compositions of the levels have been included in table 5. As can be observed for most of the levels, the leading percentages are less than 30, and there are no meaningful configuration assignments. For this reason, we have designated the levels by the energy value expressed in units of cm^{-1} .

A mean deviation of $\pm 450 \text{ cm}^{-1}$ between the observed and calculated levels was obtained. Some calculated levels differ from the observed ones by about 1000 cm^{-1} . We included them in the LSF because they are real energy levels; the large number of observed transitions and the small level uncertainties confirm this.

The question arises whether there are any other odd configurations, e.g., $5d 6s^2 6p$, $5d^3 7p$ and/or $5d^3 5f$, interacting with the two that we have identified. A study and discussion of the structure of the spectra of the third transition group, especially of configurations involving $5d$, $6s$, and $6p$ electrons, by theoreticians would be very helpful for future studies of spectra of the Pt group.

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Table 2. Unclassified lines attributed to W III—Continued

Wavelength (Å)	Int.	Wavenumber (cm ⁻¹)	Wavelength (Å)	Int.	Wavenumber (cm ⁻¹)	Wavelength (Å)	Int.	Wavenumber (cm ⁻¹)
2092.631	2h	47771.54	2184.174	2h	45769.57	2384.822	10	41919.06
2094.758	100b	47723.04	2187.282	80b	45704.54	2385.198	5h	41912.46
2095.601	10	47703.85	2187.457	2	45700.88	2389.791	2	41831.91
2096.915	2	47673.96	2189.301	2h	45662.40	2390.378	40	41821.64
2105.763	20	47473.67	2189.742	2	45653.20	2390.882	5	41812.82
2106.137	5	47465.24	2203.149	10	45375.41	2406.102	10H	41548.35
2107.929	10h	47424.89	2207.922	2h	45277.33	2409.463	20H	41490.40
2109.494	2h	47389.71	2213.065	5b	45172.12	2410.423	5	41473.88
2111.380	10	47347.39	2213.697	20	45159.23	2419.355	20	41320.77
2114.890	2	47268.81	2214.239	2	45148.17	2420.502	5	41301.19
2116.133	2h	47241.05	2215.252	2	45127.53	2421.010	10	41292.53
2116.335	5h	47236.54	2215.346	5	45125.61	2424.668	2h	41230.23
2124.984	40h	47044.31	2218.163	5b	45068.31	2446.390	40	40864.17
2128.825	2h	46959.44	2222.584	5	44978.67	2462.021	5h	40604.75
2129.737	20h	46939.33	2224.193	80b	44946.14	2475.589	10h	40382.22
2137.183	5h	46775.81	2226.783	30	44893.87	2478.567	2h	40333.71
2139.310	200	46729.31	2227.330	2	44882.84	2480.002	50	40310.37
2140.027	2H	46713.65	2228.909	2	44851.05	2491.577	2h	40123.11
2144.613	30	46613.77	2231.953	2	44789.89	2492.934	30	40101.28
2146.370	10H	46575.62	2235.357	30	44721.69	2499.230	5H	40000.26
2146.672	2	46569.07	2239.775	20	44633.48	2546.285	2	39261.11
2151.596	20	46462.51	2247.686	5	44476.40	2551.358	2b	39183.05
2152.540	2	46442.13	2249.348	5h	44443.54	2552.349	5	39167.84
2153.072	2	46430.66	2249.896	100	44432.72	2557.930	2	39082.38
2155.250	2h	46383.74	2251.924	2h	44392.71	2594.231	30H	38535.54
2156.426	30	46358.45	2257.221	2h	44288.54	2615.448	20	38222.95
2156.942	2h	46347.36	2267.592	2	44086.01	2616.328	2h	38210.10
2161.868	2h	46241.77	2273.173	10h	43977.78	2620.204	20	38153.58
2162.916	30h	46219.36	2283.338	30	43782.01	2626.244	2h	38065.83
2164.479	10	46185.99	2283.979	5	43769.73	2632.206	2h	37979.62
2169.375	20h	46081.77	2284.612	5	43757.60	2634.654	10h	37944.33
2169.947	20	46069.62	2287.760	5	43697.40	2647.711	5	37757.22
2170.234	30h	46063.53	2298.648	5	43490.43	2658.824	20	37599.42
2171.543	2b	46035.76	2307.661	5	43320.59			
2171.764	2	46031.08	2318.892	30	43110.79			
2178.906	2b	45880.22	2322.621	2	43041.58			
2180.942	5	45837.39	2323.114	20	43032.45			
2181.869	20h	45817.92	2343.473	10b	42658.64			
2182.086	10b	45813.36	2343.501	20b	42658.13			
2183.783	2	45777.76	2352.863	10	42488.41			

^a The symbols represent: b=blended; h=hazy; H=very hazy.

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Table 3. Predicted terms in *LS*-coupling scheme for the low configurations of W III

Even configurations: $5d^4$, $5d^3 6s$, $5d^2 6s^2$											
d^4						$d^3()s$			$d^2 s^2$		
3P	5D	3D	3F	3G	3H	4F	5F	3F	3P	3F	1S
3P			3F			4P	5P	3P			1D
1S	1D	F	1G		1I	2G	3G	1G			3F
1S	1D		1G			2D	3D	1D			1G
						2P	3P	1P			
						2H	3H	1H			
						2F	3F	1F			
						2D	3D	1D			

Odd configurations: $5d^3 6p$, $5d^2 6s 6p$					
Terms			Terms		
$d^3()p$			$d^2()sp()$		
4F	$^5(DFG)$	$^3(DFG)$	3F	3P	$^5(DFG)$
4P	$^5(SPD)$	$^3(SPD)$	3F	1P	$^3(DFG)$
2G	$^3(FGH)$	$^1(FGH)$	3P	3P	$^5(SPD)$
2D	$^3(PDF)$	$^1(PDF)$	3P	1P	$^3(SPD)$
2P	$^3(SPD)$	$^1(SPD)$	1G	3P	$^3(FGH)$
2H	$^3(GHI)$	$^1(GHI)$	1G	1P	$^1(FGH)$
2F	$^3(DFG)$	$^1(DFG)$	1D	3P	$^3(PDF)$
2D	$^3(PDF)$	$^1(PDF)$	1D	1P	$^1(PDF)$
			1S	3P	3P
			1S	1P	1P

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Table 4. Observed even levels of W III ($5d^4$, $5d^3(6s)$, $5d^2 6s^2$)—Continued

Configuration	Term	J	Obs. level (cm $^{-1}$)	Unc.	No.	O-C	Leading percentages		
							55	$(^2P)^3P$	21 3P_2
$5d^3(^2P)6s$	3P	0	29512.01	.04	17	31.	55 $(^2P)^3P$	21 3P_2	10 ${}^3P^*$
		2	29800.86	.03	59	25.	28 $(^4P)^5P$	23 3P_1	15 $(^2P)^3P$
		1	29855.75	.03	33	39.	33 $(^2P)^3P$	20 $(^4P)^5P$	13 3P_2
		4	30507.27	.03	52	-180.	35 $(^2G)^3G$	21 1G_1	18 $(^2G)^1G$
		5	31211.76	.03	33	-53.	42 $(^2H)^3H$	30 $(^2G)^3G$	12 3G
		3	31821.76	.02	58	71.	35 $(^2G)^3G$	34 $(^4F)^3F$	10 3F_1
		1	31838.58	.03	32	74.	23 $(^2P)^1P$	22 $(^2D_2)^3D$	16 3D
		4	33631.43	.02	53	114.	27 $(^2H)^3H$	23 3F_1	22 $(^4F)^F$
		2	33972.34	.03	52	-48.	17 3F_2	17 $(^2D_2)^3D$	14 3F_1
$5d^3(^2H)6s$	3H	6	35429.01	.04	17	-99.	97 $(^2H)^3H$		
		3	36226.46	.03	56	-92.	22 3F_2	19 3F_1	19 $(^2D_2)^3D$
		2	36353.31	.03	44	0.	16 3F_2	15 ${}^3F^*$	13 $(^2D_2)^3D$
		4	36467.29	.03	45	6.	28 3F_1	18 $(^2H)^3H$	15 3F_2
$5d^3(^2H)6s$	3H	5	36904.37	.03	31	65.	52 $(^2H)^3H$	38 $(^3G)^3G$	
		4	37769.78	.02	49	94.	36 $(^4F)^3F$	16 1G_1	12 $(^2G)^3G$
		1	37808.94	.03	29	-7.	33 3P_1	29 $(^2P)^3P$	16 $(^4P)^3P$
		3	39321.27	.03	48	60.	52 $(^2D_2)^3D$	11 3D	9 $(^4F)^3F$
		2	39344.94	.03	45	-28.	20 $(^2D_2)^3D$	17 $(^2P)^3P$	16 3P_1
$5d^3(^2H)6s$	1H	5	41322.55	.03	27	47.	88 $(^2H)^1H$	11 $(^2G)^3G$	
$5d^3(^2F)6s$	3F	2	41403.97	.03	39	-67.	39 $(^2F)^3F$	18 3F_1	11 ${}^3F^*$
$5d^3(^2P)6s$	1P	1	41570.01	.03	23	21.	50 $(^2P)^1P$	14 $(^2D_2)^3D$	11 3P_2
$5d^3(^2F)6s$	3F	3	42615.95	.03	40	3.	67 $(^2F)^3F$	22 3F_1	
		4	43378.25	.03	37	29.	67 $(^2F)^3F$	13 3F_1	
		2	45388.55	.03	28	18.	19 $(^2F)^3F$	17 $(^2D_2)^3D$	13 $(^2D_1)^3D$
$5d^3(^4P)6s$	3P	2	46259.17	.03	23	-64.	54 $(^4P)^3P$	20 3P_2	5 ${}^3F^*$
		4	47181.63	.03	30	-184.	34 $(^2G)^1G$	31 1G_2	22 1G_1
		2	47577.82	.03	24	-60.	28 1D_1	15 ${}^3F^*$	13 ${}^1D^*$
		1	47955.45	.04	12	-243.	44 $(^4P)^3P$	20 3P_2	18 $(^2P)^1P$
		2	50539.59	.04	20	68.	31 ${}^3F^*$	19 1D_1	15 1D_2
		3	51992.73	.03	25	-62.	43 ${}^3F^*$	21 $(^2F)^1F$	15 $(^2D_1)^3D$
		3	52568.07	.03	23	35.	39 $(^3F)^1F$	27 ${}^3F^*$	11 1F
$5d^2 6s^2$	F	4	55564.60	.06	9	29.	79 ${}^3F^*$	9 $(^2F)^3F$	8 3F_1
$5d^3(^2D_1)6s$	3D	2	56632.80	.05	14	69.	66 $(^2D_1)^3D$	20 $(^2D_2)^3D$	
		1	56732.38	.06	7	21.	65 $(^2D_1)^3D$	32 $(^2D_2)^3D$	
		3	57384.91	.04	15	15.	60 $(^2D_1)^3D$	22 $(^2F)^1F$	8 $(^2D_2)^3D$

Table 5. Observed odd levels of W III ($5d^3(^3)6p$, $5d^2 6s 6p(^1)$)

J	Obs. level (cm $^{-1}$)	Unc.	No.	O-C	Leading percentages	
					$72 (^4F)^5G$	$9 (^4F)^3F$
2	57231.04	.05	7	-432.	$72 (^4F)^5G$	$9 (^4F)^3F$
1	60195.86	.05	9	-30.	$46 (^4F)^5F$	$34 (^4F)^3D$
3	61488.36	.04	9	-183.	$83 (^4F)^5G$	$6 (^4F)^3F$
2	62821.85	.05	10	-277.	$42 (^4F)^5D$	$27 (^4F)^3D$
4	65106.05	.04	10	-124.	$70 (^4F)^5G$	$7 (^4F)^3F$
2	67111.20	.04	14	-251.	$34 (^4F)^5F$	$11 (^2P)^3D$
3	67187.37	.04	14	415.	$50 (^4F)^5F$	$17 (^4F)^3D$
0	67351.62	.10	3	-555.	$65 (^4F)^5D$	$11 (^2P)^1S$
1	67358.91	.04	15	2.	$25 (^4F)^5F$	$21 (^2P)^3D$
5	67731.94	.04	11	-268.	$36 (^4F)^5G$	$15 (^4F)^3F$
0	68838.57	.11	3	-112.	$29 (^4F)^5D$	$25 (^2P)^3P$
1	68976.80	.04	15	480.	$27 (^4F)^5D$	$14 (^4P)^3D$
4	70221.35	.03	19	309.	$33 (^4F)^5F$	$24 (^4F)^3D$
3	70681.63	.04	18	224.	$34 (^4F)^5D$	$23 (^4F)^3G$
2	70762.26	.04	15	488.	$54 (^4F)^5D$	$10 (^4F)^3F$
4	72073.75	.04	10	115.	$31 (^4F)^5D$	$15 (^4F)^3G$
1	72425.51	.06	9	963.	$44 (^4F)^5D$	$13 (^4P)^3P$
3	72881.50.	.04	16	551.	$37 (^4F)^5F$	$24 (^4F)^3G$
2	73135.83	.04	15	-1459.	$40 (^4F)^3F$	$13 (^4P)^3D$
5	73289.66	.05	9	109.	$59 (^4F)^5G$	$13 (^4F)^3F$
3	73697.35.	.03	17	-637.	$22 (^4P)^5D$	$15 (^2P)^3D$
1	73804.59	.05	11	192.	$23 (^4P)^5D$	$23 (^4F)^3D$
4	74021.35	.03	19	280.	$42 (^2G)^3H$	$34 (^4F)^3F$
2	74791.95	.04	19	-524.	$31 (^4F)^3D$	$8 (^2D2)^3F$
0	75142.73	.05	4	458.	$52 (^4P)^5D$	$30 (^2P)^1S$
6	75697.21	.06	5	678.	$79 (^4F)^5G$	$18 (^2G)^3H$
5	75800.20	.03	16	236.	$36 (^4F)^5F$	$30 (^2H)^3I$
2	76039.80	.04	18	-17.	$18 (^3F(^3P))^5G$	$16 (^4P)^3S$
3	76134.60	.03	23	-915.	$21 (^2G)^3G$	$20 (^4F)^3D$
1	76378.09	.04	19	-456.	$34 (^4P)^5D$	$25 (^2P)^3D$
2	76831.39	.04	22	404.	$21 (^4P)^5D$	$20 (^4P)^3P$
3	77071.73	.04	21	-685.	$28 (^4F)^3F$	$11 (^2G)^1F$
2	77757.00	.04	22	-932.	$35 (^3F(^3P))^5G$	$8 (^2D2)^3F$
4	77827.64	.04	15	685.	$23 (^2H)^3H$	$21 (^2G)^1G$
4	78408.35	.03	22	385.	$54 (^4F)^3G$	$14 (^4F)^3F$
0	78507.70	.06	7	203.	$43 (^2P)^3P$	$16 (^4P)^3P$
2	78786.47	.04	18	-517.	$32 (^4P)^5P$	$18 (^4P)^3D$
3	79139.81	.03	23	743.	$16 (^3F(^3P))^5D$	$14 (^2G)^3F$
						$11 (^4P)^3D$

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Table 5. Observed odd levels of W III ($5d^3(^3P)$) $6p$, $5d^2$ $6s$ $6p(^3P)$)—Continued

J	Obs. level (cm $^{-1}$)	Unc.	No.	O–C	Leading percentages		
					35	14	10
1	79216.24	.05	13	−119.	(4P) 5P	(2P) 3D	(2D2) 3D
4	79597.73	.04	19	41.	(4F) 3F	(2G) 3F	(4F) 3G
3	79699.75	.04	21	361.	(4P) 5P	(2P) 3D	(4P) 5D
5	80493.89	.04	15	−227.	(4F) 3G	(2H) 3H	(4F) 3F
3	80558.62	.04	25	247.	28 (3F) 3G	24 (4P) 5D	22 (4F) 3D
6	81013.46	.05	9	−629.	51 (2H) 3I	28 (2H) 3H	
1	81054.33	.04	15	−45.	34 (2P) 3S	27 (4P) 3P	6 (4P) 5P
2	81293.43	.04	21	207.	20 (2D2) 3D	9 (2D2) 3P	9 (4P) 5D
1	82095.43	.04	17	−486.	53 (3F) 3P 5F	17 (2P) 3P	5 (3F) 3P 3D
5	82210.83	.04	16	−171.	34 (2G) 3H	32 (2H) 3I	6 (2H) 1H
4	82502.08	.03	24	164.	55 (2G) 3G	10 (2G) 1G	7 (2G) 3H
2	82801.82	.04	20	188.	11 (3F) 3P 5F	11 (2P) 1D	9 (2F) 3F
2	82980.19	.04	21	−470.	36 (2G) 3F	17 (2P) 3D	9 (4P) 5S
4	83571.04	.04	22	−109.	65 (4P) 5D	6 (2D1) 3F	6 (3F) 3P 5G
1	83601.96	.06	13	350.	27 (2P) 1P	12 (2D2) 3P	10 (4P) 3D
3	83611.69	.05	19	−240.	32 (3F) 3P 5G	15 (2D2) 3F	10 (4P) 5D
5	83957.03	.04	14	110.	38 (3G) 3G	13 (2G) 3H	11 (2H) 3H
3	84127.03	.04	25	−369.	25 (2G) 3G	13 (4F) 3F	12 (4P) 5P
1	84389.26	.07	15	538.	29 (2P) 3P	16 (4P) 3P	11 (4P) 5D
4	84869.01	.03	24	1.	28 (2H) 3H	27 (2G) 3F	9 (2G) 3H
2	85044.18	.05	18	297.	22 (3F) 3P 5F	18 (4P) 5S	17 (2D2) 3P
4	85078.28	.05	18	77.	53 (3F) 3P 5G	11 (4P) 5D	9 (2H) 3H
5	85222.97	.05	16	200.	30 (2H) 3H	24 (4F) 3G	19 (2H) 3G
2	85527.01	.04	23	408.	21 (2G) 3F	11 (2P) 1D	9 (2D2) 3P
3	85834.94	.04	22	403.	18 (2G) 3F	17 (2H) 3G	8 (2D2) 3F
6	85965.60	.06	7	671.	37 (2H) 1I	36 (2G) 3H	15 (2H) 3H
4	86271.52	.04	24	−129.	17 (2H) 1G	15 (4F) 3F	13 (3F) 3P 5G
3	86283.75	.03	28	63.	18 (2F) 3F	9 (2F) 3G	9 (3F) 3P 5F
2	86487.10	.04	23	418.	27 (3F) 3P 5F	12 (4P) 5P	10 (2P) 3D
3	86578.41	.04	25	−567.	16 (2D2) 3D	15 (2F) 3G	11 (2D2) 1F
1	86865.05	.04	17	496.	16 (4P) 3P	13 (2D2) 1P	10 (2D2) 3D
2	86867.50	.05	21	167.	18 (2F) 3P	11 (2G) 3F	8 (4P) 3P
4	87590.69	.04	20	−23.	21 (2F) 3F	13 (2F) 3G	13 (2H) 3G
2	87621.20	.04	20	−8.	26 (4P) 3P	11 (4P) 3D	9 (3F) 3P 5D
5	87862.02	.04	18	−263.	48 (2G) 1H	27 (2H) 3G	7 (2H) 3I
3	88429.94	.04	27	608.	24 (3F) 3P 5F	12 (2G) 1F	11 (2H) 3G
3	88813.10	.04	26	418.	11 (1D) 3P 5D	9 (2D2) 3D	9 (3F) 3P 5D
0	88867.52	.13	4	−184.	54 (3F) 3P 5D	13 (1D) 3P 3P	11 (3P) 3P 5D

Table 5. Observed odd levels of W III ($5d^3(^3)6p$, $5d^2 6s 6p(^1)$)—Continued

<i>J</i>	Obs. level (cm $^{-1}$)	Unc.	No.	O-C	Leading percentages	
6	88884.95	.06	8	-353.	44 (2H) 3H	41 (2H) 3I
2	89240.38	.03	22	536.	24 (4P) 3P	13 (3P) 3F
1	89283.42	.06	15	-161.	50 (4P) 3D	15 (2D_2) 3D
3	89329.95	.04	22	22.	43 (3F) 3P 5F	12 (4P) 3D
5	89630.99	.04	15	-931.	77 (3F) 3P 5G	6 (3F) 3P 5F
4	89700.42	.06	17	350.	28 (2D_2) 3F	9 (1D) 3P 3F
1	89903.01	.07	12	111.	57 (3F) 3P 5D	7 (3F) 3P 5F
3	90097.20	.03	30	-360.	17 (2F) 3F	14 (4P) 3D
1	90492.33	.05	18	-264.	31 (2D_2) 1P	15 (4P) 3S
7	90511.29	.17	2	281.	100 (2H) 3I	7 (2D_1) 1P
5	91161.95	.05	12	-354.	32 (2H) 1H	25 (2G) 3G
2	91362.35	.05	21	23.	15 (2P) 3P	12 (2D_2) 3D
3	91763.26	.05	16	-151.	26 (2H) 3G	17 (2P) 3D
4	91776.22	.06	16	-46.	60 (3F) 3P 3F	11 (2D_2) 3F
2	91973.61	.05	17	293.	12 (3F) 3P 3F	9 (4P) 3D
0	92089.69	.09	6	-62.	37 (3F) 3P 5D	22 (2D_2) 3P
4	92117.89	.04	20	-138.	26 (2H) 1G	17 (2H) 3G
2	92358.71	.06	18	-949.	22 (3F) 3P 5D	11 (2P) 3P
1	92882.06	.08	9	154.	22 (3P) 3P 5D	19 (4P) 3S
2	93226.03	.05	20	-1092.	16 (2D_2) 1D	16 (4P) 3D
3	93358.07	.04	27	-59.	23 (2D_2) 3D	19 (4P) 3D
5	93778.68	.04	10	-95.	26 (2H) 3G	23 (2H) 1H
1	93778.68	.04	16	-713.	45 (3P) 3P 5D	9 (4P) 3S
4	93867.25	.04	27	-188.	30 (2H) 3G	13 (2G) 3F
6	93870.12	.09	7	310.	56 (2H) 1I	23 (2G) 3H
4	94347.63	.05	20	21.	27 (2F) 3G	17 (2F) 3F
3	94508.46	.05	24	-239.	20 (2F) 3D	11 (3P) 3P 5D
2	95134.61	.05	21	-404.	23 (3P) 3P 5D	9 (3F) 3P 3D
5	95137.13	.07	13	-81.	45 (3F) 3P 3F	12 (2H) 1H
1	95363.16	.06	15	-164.	18 (3F) 3P 5D	15 (2P) 1P
3	95422.00	.05	25	314.	36 (3F) 3P 5D	10 (3P) 3P 5D
1	96530.77	.07	15	551.	13 (2F) 3D	9 (3F) 3P 3D
2	96561.09	.05	21	141.	18 (2F) 3F	17 (2F) 1G
3	96630.14	.05	21	-241.	20 (2G) 1F	16 (2D_2) 1F
4	96704.93	.04	24	848.	47 (3F) 3P 5D	14 (2F) 3F
6	97039.60	.09	8	327.	95 (3F) 3F 5G	8 (3F) 1P 3F
4	97144.15	.05	21	-716.	25 (2F) 1G	22 (2H) 1G
5	97227.61	.07	15	360.	60 (2F) 3G	16 (3P) 3P 5F
						5 (3F) 1P 3G

Table 5. Observed odd levels of W III ($5d^3(^3P)$) $6p$, $5d^2$ $6s$ $6p(^3P)$)—Continued

<i>J</i>	Obs. level (cm $^{-1}$)	Unc.	No.	O-C	Leading percentages	
					24 (^2F) 3D	23 (^2F) 1F
3	97531.10	.06	18	-150.	24 (^2F) 3D	23 (^2F) 1F
2	98061.07	.05	20	-99.	17 (^3F) 3P 3D	13 (^2F) 1D
1	98188.14	.06	14	-94.	37 (^3P) 3P	19 (^4P) 3S
3	99424.24	.06	21	355.	38 (^3F) 1P 3G	10 (^3P) 3P 3D
2	99814.69	.08	17	600.	17 (^3P) 3P 3D	14 (^3P) 3P
4	100202.96	.06	19	267.	15 (^3F) 3P 3G	14 (^1G) 3P 3H
1	101307.86	.06	15	278.	22 (^1D) 3P 3D	18 (^1D) 3P 3P
3	101383.26	.06	20	873.	27 (^3F) 3P 3F	20 (^3F) 1P 3F
2	101947.18	.07	14	82.	16 (^2D1) 3F	12 (^3P) 3P 3S
1	102058.13	.09	9	-543.	25 (^2D1) 3D	14 (^2D2) 3D
3	102348.13	.06	18	-750.	33 (^3P) 3P 3D	25 (^3F) 3P 3D
2	102576.20	.06	16	135.	28 (^3P) 3P 3S	15 (^2D1) 3F
4	102826.51	.08	16	-431.	17 (^3P) 3P 3D	15 (^3F) 3P 3G
3	103127.98	.06	20	-601.	20 (^2D1) 3D	15 (^2D1) 3F
1	103272.45	.05	10	-1800.	21 (^3P) 3P 3P	16 (^3P) 3P 3S
5	104191.52	.02	10	290.	28 (^1G) 3P 3H	21 (^3F) 3P 3F
2	104287.86	.06	18	437.	30 (^3P) 3P 3P	19 (^3F) 1P 3D
2	104761.77	.07	14	519.	14 (^2D1) 3D	13 (^2D1) 3P
3	105033.31	.09	13	684.	30 (^1D) 3P 3F	21 (^1G) 3P 3G
4	105064.05	.08	14	-331.	31 (^3F) 1P 3G	15 (^1G) 3P 3G
4	105628.72	.07	16	-477.	32 (^1G) 3P 3H	23 (^3P) 3P 3D
2	105670.02	.06	17	101.	22 (^1D) 3P 3P	16 (^2D1) 3P
3	106044.97	.06	17	-79.	30 (^1D) 3P 3P	21 (^1G) 3P 3G
1	106699.96	.10	10	-860.	22 (^2D1) 3P	20 (^3F) 1P 3D
3	107269.17	.06	20	-297.	14 (^1G) 3P 3G	13 (^1D) 1P 1F
2	107611.49	.07	12	245.	16 (^3F) 1P 3D	12 (^2D1) 3F
4	107840.81	.07	15	-235.	27 (^1G) 3P 3F	23 (^3G) 3P 3G
3	108249.41	.06	16	275.	16 (^3F) 1P 3D	13 (^2D1) 3F
1	109744.12	.09	8	235.	21 (^1D) 3P 3D	14 (^2D1) 3D
4	109818.37	.07	18	54.	21 (^1G) 3P 3H	20 (^3F) 1P 3G
2	109841.13	.09	13	516.	23 (^1D) 3P 3P	18 (^1D) 3P 3D
3	109950.38	.08	16	672.	20 (^3P) 3P 3P	15 (^1D) 3P 3D
2	110863.47	.08	15	394.	15 (^1D) 3P 3D	11 (^2D1) 3D
3	111063.06	.07	18	601.	24 (^3F) 1P 3F	21 (^2D1) 1F
4	111196.15	.08	14	-241.	49 (^2D1) 3F	15 (^3F) 1P 3G
3	111610.84	.07	19	-750.	24 (^1D) 3P 3D	7 (^3F) 1P 3D
6	112353.65	.16	3	-496.	94 (^1G) 3P 3H	7 (^3P) 3P 3P

Table 5. Observed odd levels of W III ($5d^3(^1)6p$, $5d^2 6s 6p(^1)$)—Continued

J	Obs. level (cm $^{-1}$)	Unc.	No.	O-C	Leading percentages		
					28 (^2D1)^1D	21 (^2D2)^1D	15 (^2F)^1D
2	112844.05	.07	18	13.	28 (^2D1)^1D	21 (^2D2)^1D	15 (^2F)^1D
3	113709.40	.07	15	214.	15 ^3F(^1P)^3D	14 ^3P(^1P)^3D	10 (^2D1)^1F
1	113730.91	.09	12	169.	25 (^2D1)^1P	19 ^3P(^3P)^3P	11 (^2F)^3D
1	115619.98	.13	6	-67.	21 ^3P(^1P)^3D	14 ^3P(^3P)^3D	14 ^1D(^1P)^1P
3	115795.95	.08	17	826.	19 (^2D1)^3D	14 ^1D(^3P)^3D	10 ^3F(^1P)^3F
2	116620.34	.09	13	132.	33 ^1G(^3P)^3F	9 ^1D(^1P)^1D	8 ^3F(^3P)^1D
4	116735.40	.09	15	-937.	30 ^3F(^1P)^3F	17 ^3P(^3P)^1G	15 ^3F(^3P)^3F
3	116774.06	.08	13	-114.	54 ^1G(^3P)^3F	12 ^3P(^3P)^3D	9 ^1D(^1P)^1F
3	118243.40	.07	15	-687.	31 ^3F(^1P)^3D	17 ^3P(^1P)^3D	12 ^3P(^3P)^3D
2	119448.46	.09	13	401.	36 ^1G(^3P)^3F	11 ^3P(^1P)^3D	11 ^3F(^3P)^1D
5	120680.26	.12	7	51.	81 ^1G(^1P)^1H	9 ^3F(^1P)^3G	5 ^1G(^3P)^3H
4	121296.58	.15	11	-742.	66 ^1G(^1P)^1G	9 ^3F(^1P)^3F	9 ^1G(^3P)^3F
3	125865.71	.10	11	747.	40 ^3P(^1P)^3D	18 ^1G(^1P)^1F	12 ^3P(^3P)^3D

Table 6. Observed and predicted number of levels for the reported configurations of W III

Even configurations			Odd configurations		
$5d^4 + 5d^3 6s + 5d^2 6s^2$			$5d^3 6p + 5d^2 6s 6p$		
Number of levels			Number of levels		
J	Observed	Predicted	J	Observed	Predicted
0	4	9	0	6	14
1	11	12	1	27	37
2	18	21	2	38	47
3	15	15	3	41	44
4	14	15	4	29	32
5	6	6	5	15	18
6	3	3	6	7	7
			7	1	1
Total	71	81	Total	164	200

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Table 7. LSF and HF parameter values for the $5d^4$, $5d^3 6s$, and $5d^2 6s^2$ configurations of doubly ionized tungsten (W III), in cm^{-1}

Configuration	Parameter	LSF	HF	LSF/HF
$5d^4$	E_{av}	22339 (140)		
	$F^2(dd)$	43442 (371)	56483	.77
	$F^4(dd)$	28186 (315)	37195	.76
	ζ_d	2364 (19)	2575	.92
	α	13 (3)		
	β	100 (69)		
$5d^3 6s$	E_{av}	39566 (124)		
	$F^2(dd)$	45990 (485)	59115	.78
	$F^4(dd)$	29686 (391)	39110	.76
	$G^2(ds)$	16130 (125)	15055	1.07
	ζ_d	2542 (17)	2799	.91
	α	17 (4)		
$5d^2 6s^2$	E_{av}	55546 (1179)		
	$F^2(dd)$	59344 (7308)	61460	.96
	$F^4(dd)$	35759 (4070)	40862	.87
	ζ_d	2616 (61)	3024	.87
	α	275 (151)		
	β	0 Fix		
C.I.	$R^2(dd,ss)$	-18165 (307)	-17985.	1.01
	$R^2(ds,ss)$	-20965 (133)	-18305.	1.14
	$R^2(dd,ds)$	-21280 (343)	-18410.	1.15

Standard deviation is $\pm 87 \text{ cm}^{-1}$.

Table 8. LSF and HFR parameter values for the $5d^3 6p$ and $5d^2 6s 6p$ configurations of doubly ionized tungsten (W III), in cm^{-1}

Configuration	Parameter	LSF	HF	LSF/HF
$5d^3 6p$	E_{av}	89431 (420)		
	$F^2(dd)$	48290 (1500)	59619	.81
	$F^4(dd)$	27390 (1250)	39488	.69
	$F^2(dp)$	12169 (800)	21245	.57
	$G^1(dp)$	8170 (270)	8926	.92
	$G^3(dp)$	7400 Fix	7432	1.00
	ζ_d	2739 (63)	2837	.97
	ζ_p	5668 (139)	3660	1.55
	α	47 (11)		
	β	-300 Fix		
$5d^2 6s 6p$	E_{av}	115093 (436)		
	$F^2(dd)$	48563 (3700)	61866	.78
	$F^4(dd)$	27464 (3700)	41152	.67
	$F^2(dp)$	16869 (1000)	22960	.73
	$G^1(sp)$	41388 (1800)	41007	1.01
	$G^2(ds)$	13643 (976)	15090	.90
	$G^1(dp)$	10478 (478)	9240	1.13
	$G^3(dp)$	7900 Fix	7922	1.00
	ζ_d	3211 (95)	3057	1.05
	ζ_p	5678 (240)	4044	1.40
C.I.	$R^1(dp,ps)$	-3004 (392)	-22980	.13
	$R^2(dp,sp)$	-8760 (520)	-14475	.61
	$R^2(dd,ds)$	-21405 (772)	-18095	1.18

Standard deviation is $\pm 450 \text{ cm}^{-1}$.

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About the authors: Drs. Laura Iglesias, Fernando R. Rico, and Olga Garcia-Riquelme have published many papers on the spectra of the transition elements. The latter two persons have recently retired but continue to be actively involved in the analyses of spectra. Dr. M. Isabel Cabeza was a post-doctoral fellow during the course of this work and is presently employed in industry in Spain. Dr. Victor Kaufman, recently retired, has been with the Spectroscopy Group of NIST since 1960.

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Apparatus for Neutron Scattering Measurements on Sheared Fluids

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We report on the construction of an apparatus to allow neutron scattering measurements on fluids undergoing shear. The apparatus has been used with the cold neutron small-angle-neutron-scattering (SANS) spectrometer at the NIST research reactor and will be made

available to users as a permanent part of the NIST facility.

Key words: fluids; neutron scattering; rheology; SANS; shear.

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1. Introduction

It is now well established that investigations of fluids subjected to a shear are rewarding. For example, studies of the structural changes induced by shearing motions lead to a better understanding of long-range intermolecular correlations in liquids [1], and allow the investigation of the alignment and intramolecular changes of condensed phase polyatomic molecules [2], and the phase changes and thermodynamic properties of liquids out of equilibrium [3]. The relationship of theory, especially nonequilibrium computer simulation, with experiment is particularly rich in this area and the two complementary approaches have given fresh insight into the origin of non-Newtonian behavior in liquids and the basis of rheology and fluid dynamics [4].

This note is to report on the construction of an apparatus which allows neutron scattering measurements to be made on fluids undergoing shear [5]. The apparatus has been used with the small-angle-neutron-scattering (SANS) spectrometer at the NIST research reactor and will be available to users on a permanent basis. Full details on the ap-

paratus and the results of preliminary experiments will be presented in a future publication.

2. Apparatus

The apparatus consists of a Couette-type concentric cylinder sample cell coupled to a computer automated drive and thermal control system [6]. Neutrons are scattered from the fluid contained within the annular gap between the cylinders. The apparatus is shown schematically in figure 1.

The rigid aluminum frame consists of vertical rails attached to heavy plates at bottom and top. The vertical rails are commercial structural elements of the type commonly used for optical bench construction. They have a unique cross section which allows the attachment of numerous commercially available slides, carriages, clamps, etc. allowing for easy attachment of components and accessories. A work table (WT) is attached to the rails and supports the drive motor (M). The table is drilled and tapped in a regular pattern to provide

an easy method for mounting of accessories. The cell chuck (CH), mounted on the motor shaft, can accommodate cells of various sizes and has provision for precise alignment of the cell rotor (CR) axis and the motor axis. Vertical adjustment of the cell stator (CS) is accomplished with a commercial rack-and-pinion assembly (Z), which was extensively modified to improve rigidity and stability. Parallelism between the motor and stator axes is obtained by adjustment of an aligning coupling (A). Collinearity is achieved using a pair of micrometer actuated translation stages (X) and (Y). An optional torque transducer (TT) can be used to obtain rheological information about the samples.

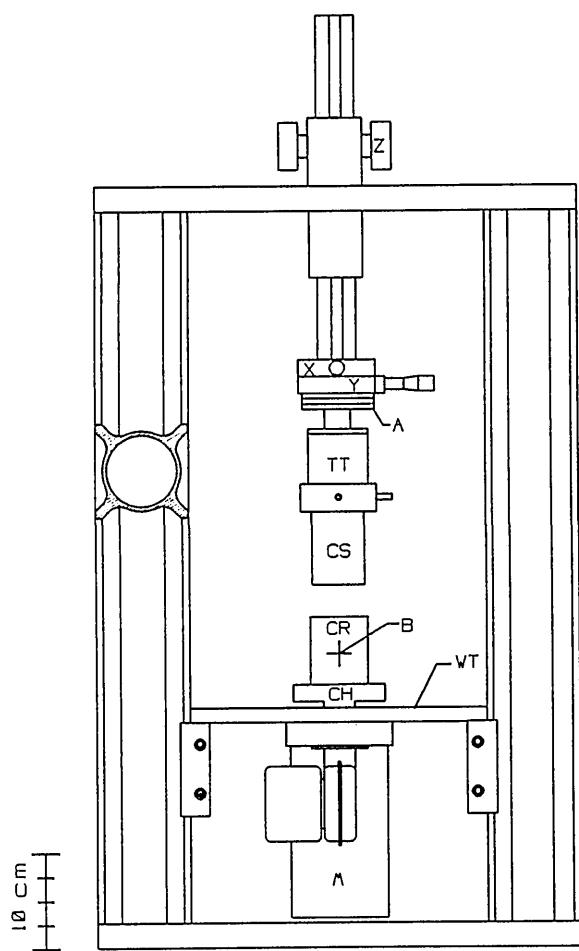


Figure 1. Schematic drawing of the shearing apparatus: M—Drive Motor, CR—Cell Rotor, CS—Cell Stator, TT—Torque Transducer, A—Alignment Coupling, X—Micrometer Adjust, Y—Micrometer Adjust, Z—Vertical Adjust, WT—Work Table, CH—Cell Chuck, B—Beam Center. See text for details.

A more detailed schematic of the cell is shown in figure 2. The cell consists of a stationary cylindrical quartz glass stator surrounded by a rotating cylindrical quartz glass rotor. Quartz exhibits low and uniform scattering at small angles and is ideal for SANS experiments. The cell used for our preliminary work has a mean diameter of about 56.5 mm and an annular gap of 0.5 mm for the samples.

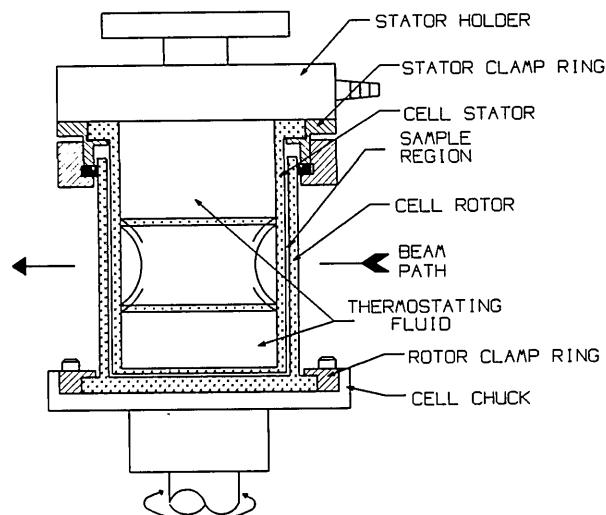


Figure 2. Detailed drawing of the shearing cell.

Thermostating fluid is circulated within the stator for temperature control. Temperatures are measured using a platinum resistance thermometer in contact with the thermostating fluid in the stator. The thermostating fluid is excluded from the neutron beam path by the cross-tube located inside the stator. The nominal operating temperature range for the apparatus is currently 245–373 K and is determined primarily by the range of the thermostating fluid bath controller. At elevated temperatures the motor can be cooled using an optional cooling fan.

The drive motor is a state-of-the-art dc brushless servo motor. These motors have permanent magnet armatures and the fields are commutated by computer controlled switching using position feedback from a shaft resolver integral with the motor shaft. This technology allows smooth, continuous rotations under programmed conditions of acceleration, velocity, torque (velocity limited), direction, position, angle, start, stop, delay, time and any sequence thereof. These capabilities allow the precise control of all rotational parameters to an accuracy of better than 0.1% over extended periods of time.

The controlling computer can be any of a number of PCs available today. Computer hardware and software are available to allow completely automatic operation of the shearing apparatus in parallel with the existing on-line data acquisition system at the NIST reactor.

A velocity-torque curve for the drive system is shown in figure 3. The viscosity and shear rate data are geometry dependent and are calculated for the cell dimensions as described. The torques at high RPMs are upper bounds based on the motor specifications and may be limited in an actual experiment because of hydrodynamic constraints peculiar to any given sample and the additional load imposed by the dynamics of the rotating elements. The apparatus is designed to accommodate other cell geometries to allow more versatility in the applicable range of shear rates and torques.

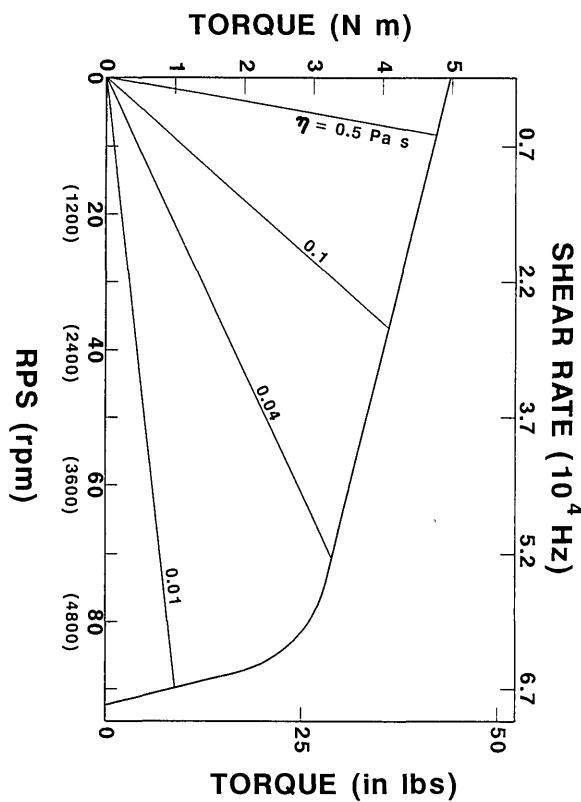


Figure 3. Plot of the torque as a function of the rotation speed and of viscosity for various viscosities. Viscosity and shear rate data are dependent on geometry and are calculated for the cell as described in the text.

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Conference Reports

ELEVENTH NATIONAL COMPUTER SECURITY CONFERENCE Baltimore, MD October 17-20, 1988

Report prepared by

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The National Computer Systems Laboratory (NCSL) and the National Computer Security Center (NCSC) of the Department of Defense co-sponsored the Eleventh National Computer Security Conference held in Baltimore, Maryland on October 17-20, 1988. More than 1600 attendees from government, industry, and academia participated in the four-day conference which provided a forum for the exchange of ideas and technology in computer security issues. The theme of the conference—"Computer Security . . . Into the Future"—reflected the growth of computer security awareness as well as parallel advances in research, vendor products, emerging areas of special interest, and planning for the future. NCSL's Irene Gilbert and NCSC's Eliot Sohmer co-chaired the program committee of the conference.

1. History of the Conference

Since the passage of the Brooks Act in 1965, the National Computer Systems Laboratory (formerly the Institute for Computer Sciences and Technology) has played a vital role in protecting the security and integrity of information in government computer systems through its Computer Security Program. Computer security standards and guidelines addressing the cost-effective protection of unclassified information have been issued since 1972. Working with a broad spectrum of organizations from government, industry, academia, and voluntary standards groups, NCSL advances the development of standards, develops test methods, transfers technology to potential users, and provides technical assistance to government and industry in computer security applications. The Computer Security Act of 1987 strengthened NCSL's role in protecting sensitive information in federal government computers.

Computer security initiatives in the Department of Defense (DoD) parallel those of NCSL. In 1978, the Assistant Secretary of Defense for Communications, Command, Control and Intelligence established a Computer Security Initiative to ensure the widespread availability of trusted ADP systems within the DoD community. In 1981, the Department created the National Computer Security Center and charged the new organization with responsibility for administering the activities of the Initiative. The Center advances the development of trusted computer systems and publishes guidelines on computer security issues. In response to the increasing importance of computer security in government and industry in recent years, the DoD

Computer Security Initiative has expanded to support basic research for the development of additional trusted systems. DoD's technology transfer program ensures that other federal agencies and the private sector benefit from advances in computer security technology.

To pursue common goals and to address mutual concerns, NCSL and NCSC joined forces in 1979 to co-sponsor the first National Computer Security Conference held at the National Bureau of Standards. Dr. Dennis Branstad, NCSL (now a NIST Fellow) and Mr. Stephen Walker, then Chairman, Computer Security Technical Consortium, organized the first seminar as an information exchange on computer security issues. The Conference has grown significantly in size and scope since its inception 11 years ago. This growth parallels the increase in security awareness in information processing systems and the greater interest in the existing and emerging technology available to protect vital information in computer systems.

2. The Eleventh National Computer Security Conference

The 1988 Conference offered participants a variety of presentations and panel discussions providing insight on the use of today's technology to protect vital information and on planning for tomorrow's needs by understanding the products and services to be available in the future. The first-day "Overture" presentations and tutorials encouraged newcomers to gain an overview of selected introductory topics such as the "Orange Book" (DoD Trusted Computer System Evaluation Criteria), trusted network interpretation, Dockmaster, and risk management activities.

The second day of the conference opened with welcoming remarks from NCSL Director James H. Burrows and NCSC Director Patrick R. Gallagher. Following the keynote address by the Honorable Tom McMillan, Democratic Representative from Maryland, a plenary session on the Computer Security Act of 1987 focused on how NIST and the National Security Agency will interact on policy, technology, and implementation of the legislation. Participants in the plenary session included James Burrows, NCSL; Patrick Gallagher, NCSC; Eliot Sohmer, NCSC; Dennis Branstad, NCSL; Jerry Rainville, NSA; Stuart Katzke, NCSL; and moderator Stephen Walker, Trusted Information Systems. Among the subjects addressed in the plenary session were the imple-

mentation activities at NIST and NSA, the Memorandum of Understanding between the two agencies, use of resources, and FY89 plans; impact of the Computer Security Act on NSDD-145; trusted system technology; cryptography; INFOSEC products; trusted network interpretation/trusted database interpretation; trusted UNIX activities; and international security standards and export control.

Following this overview, speakers from the private and public sectors addressed the major computer security issues facing government and industry today and in the future. Selected presentations are summarized below.

2.1 Models and Modeling Integrity

Several papers described security policies and formal policy models for computer systems. T. Keefe and W. Tsai of the University of Minnesota joined with M. Thuraisingham of Honeywell to present a paper describing a security model for a multilevel secure object-oriented system. The model supports a data sensitivity level classification appropriate for use in Multilevel Secure Database Management Systems (MLS/DBMS). The advantage of this model is that it allows a subject to act with the lowest clearance level necessary to accomplish a task, avoiding the over-classification of data. G. Dinolt, J. Freeman, and R. Neely of the Ford Aerospace Corporation reported on a security policy and formal policy model for an internet system. The model provides a view of the internet system as a whole, not as a collection of components, and was developed in accordance with requirements of the DoD "Orange Book." This research illustrates a way of modeling the security attributes of an internet system which has been used in the production of the formal specification of the Multinet Gateway System and in the formal verification of that specification.

Representatives from Odyssey Research Associates, Inc. presented a paper describing the Ulysses computer security modeling environment. Ulysses is a collection of tools that assist in the design and verification of secure computer systems. The design methodology supported by Ulysses uses the same principles of modularity and reusability that characterize modern programming development environments. Because of its overall system design, Ulysses has the potential to significantly reduce the time and effort needed in constructing secure models.

The next series of papers addressed the application of computer security technology to integrity issues. David D. Clark of M.I.T. outlined an evaluation criteria for integrity as defined by the Clark/Wilson model, which proposes an integrity policy based upon separation of duties, well-formed transactions, and audit trail to meet the needs of business and the non-defense sector. William R. Shockley, Gemini Computers, spoke on implementing the Clark/Wilson integrity policy using current technology. He described a methodology for converting a policy in Clark/Wilson notation into a corresponding mandatory policy expressed as a lattice of access classes with supporting identification and authentication policies. Shockley concluded that the Clark/Wilson integrity requirements can be met by existing, appropriately configured Trusted Computing Bases. Finally, Paul A. Pittelli of the Department of Defense presented a paper which defined a security policy for data integrity which is expressed in non-interference theory.

2.2 Risk Management

The risk management process enables computer users and managers to analyze information assets, threats, and vulnerabilities, to determine the measure of risk, and to select cost-effective safeguards for reducing the risks. The session on risk management was chaired by Donna Dodson of NCSL. The first speaker was Thomas W. Osgood, Manager, Security Assurance, Computer Sciences Corporation, who described a model for ADP risk analysis in the military environment typified by the Defense Communications Agency Joint Data Systems Support Center in the Pentagon. The methodology presented uses multiple metrics, a standardized threat nomenclature, and standardized reporting to meet the requirements of both a single-site, single-system environment and the more typical multiple-site, multiple-system environments of most military commands. A second paper by Martin Marietta researchers H. Mayerfeld and E. Troy described a new artificial-intelligence-based approach to standardizing and automating the risk management process, resulting in risk assessments that are more objective, uniform, and cost-effective. This approach uses a four-level abstraction hierarchy for classifying system components and assets to construct system models; risk to informational assets is determined according to the criteria of confidentiality, integrity, and availability.

Modeling security risk in networks was the subject of a talk by Howard L. Johnson, Information Intelligence Sciences, Inc., and J. Daniel Layne, Computer Technology Associates, Inc. Distributed secure systems also have distributed security policy and unequal security risk. In addressing the complex subject of risk analysis in a distributed system, Johnson and Layne's approach expands the Orange Book concept of the primary external interface as the human "user" to include all "external subjects" such as humans, host computers, networks, other components, and other systems. This risk evaluation methodology has been programmed to simulate many different system environments.

2.3 Audit and Intrusion Detection

Since no combination of technologies can prevent legitimate users from abusing their authority in a computer system, auditing utilizes automated tools to analyze the vast amount of audit data for suspicious behavior by users. The next series of talks focused on the use of audit and intrusion detection in computer security. Teresa Lunt of the SRI International Computer Science Laboratory presented a survey of the automated audit trail analysis techniques and intrusion-detection systems currently available. One particularly effective approach is a statistical user profile augmented with a rule-base that characterizes intrusions. Ms. Lunt concluded that auditing and intrusion-detection mechanisms are useful in detecting the less skilled penetrator because they increase the difficulty of penetration.

A case study on expert systems in intrusion detection was presented by Michael Sebring, Eric Shellhouse, and Mary Hanna of NCSC and R. Whitehurst of SRI International. The Multics Intrusion Detection and Alerting System (MIDAS) is the expert system which provides real-time intrusion and misuse detection for NCSC's networked mainframe Dockmaster. Using statistical profiles that characterize normal system and user behavior, one can detect system or user activity that deviates beyond certain limits. MIDAS employs this basic concept to evaluate the audited activities of more than 1200 Dockmaster users. W. Sibert of Oxford Systems presented the next paper which described the significant features of the SunOS MLS auditing mechanism and how it performs useful audit functions in large distributed systems. Although distributed systems pose difficulties in storing audit messages, Sibert concluded that the use of multiple

buffers and failure recovery algorithms makes auditing practical and efficient in a distributed system.

2.4 Applying Security Techniques

Security issues assume greater significance as distributed systems of increasing size and complexity are built. Integrating security in a large distributed system was the subject of a talk by M. Satyanarayanan of Carnegie Mellon University. "Andrew" is a distributed computing environment which eventually will encompass over 5000 workstations at that university; it addresses issues such as the many levels of abstraction spanned, the need for compatibility, and the many detailed aspects of the system that are affected. Andrew offers substantially greater security than existing distributed systems without significant loss of usability or performance.

Ann Marmor-Squires and Patricia Rougeau of TRW Federal Systems Group presented a joint paper on process models and integrated environments for trusted system development for Defense needs. They concluded that several contributing technologies, when merged, achieve a better result than components alone could produce, such as a new risk-driven process model coupled with formal methods. John McDermott of the Naval Research Laboratory offered a technique for removing a class of Trojan horses from high-order languages. This defensive technique exploits the symbiotic relationship between the source text of the legitimate compiler and the self-reproducing feature of the Trojan horse object code. The technique is appropriate for very high assurance systems where every available defensive measure is desired.

In the area of communications security, Paul Lambert of Motorola described an architectural model of the Secure Data Network System (SDNS) Key Management Protocol. The SDNS project has developed a security architecture within the Organization of International Standardization's (ISO) Open System Interconnection (OSI) computer network model. Within this architecture, the Key Management Protocol (KMP) provides a uniform mechanism for the establishment of secure communications. Lambert emphasized the security services furnished by the KMP and its relationship to the OSI reference model.

2.5 Verification

Crow, Lee, Rushby, von Henke, and Whitehurst of SRI International presented an over-

view of the Enhanced Hierarchical Development Methodology (EHDM) specification and verification system, a state-of-the-art environment designed specifically to meet the needs of security verification. Under development at SRI since 1983, EHDM incorporates many modern ideas and techniques concerning language design, specifications, and development environments in order to provide a state-of-the-art verification system. EHDM is currently used primarily in the SeaView project which combines element-level labeling with A1 assurance. Other papers in this area concerned the State Delta Verification System (SDVS) and code level verification.

2.6 Database Management Security

Unisys Defense Systems researchers James Gray and James O'Connor have developed a distributed architecture for a multilevel secure database management system. The architecture is notable in two respects: its ability to include as a factor the effect of the security class of the query in the classification of derived data, allowing tuple level labels to be safely used for mandatory access control; and its provision of reliable tuple level labeling without requiring the relational operators to be trusted. This architecture thus becomes a suitable basis for a near-term solution to multilevel database management using existing DBMS components to implement the relational operators.

2.7 Networking and Local Area Networks

As more computer systems are interconnected through networks, the need for network security standards grows. NCSL's Dennis Branstad chaired the networking session. Typical of this category of presentations was MITRE's Kimberly Kirkpatrick's talk on network security standards. In response to the need to provide security for each participant in an open system, various standards bodies are developing security-related standards within the context of the International Standards Organization/Open Systems Interconnection (ISO/OSI) reference model. Ms. Kirkpatrick summarized the security activities of the various standards groups as of May 1988, citing the structure, interactions, and work in process within each organization. She concluded that standards for security based on the ISO/OSI reference model are a fledgling area, with much work to be done before security standards reach the International Standard status.

Local area networks (LANs) are being widely used for a large number of applications. To address the vulnerability of networks such as an Ethernet to a variety of security threats, B. Herbison, Digital Equipment Corporation, reported on the Ethernet Enhanced-Security System. The system consists of Digital Ethernet Secure Network Controllers which are encryption devices and VAX Key Distribution software, which manages the controllers on an Ethernet or extended Ethernet and enforces a LAN access control policy. This system is effective in protecting against masquerading, wiretapping, and modification attacks, and, to a limited extent, some denial of service attacks.

2.8 System Security Requirements

Representative of this series of papers is one describing a secure software library for the Strategic Defense System (SDS), authored by Hadley, Hellwig, Rowe, and Vaurio of NCSC. Their presentation addressed the use and distribution of reusable software, a major challenge facing the Strategic Defense Initiative (SDI). The focus of their talk was the need and method of achieving a secure SDS software library where reusable software can be cataloged, accessed, and distributed. Other papers in this series dealt with the trusted military message processor, sensitivity labels and security profiles, and lessons learned in managing the accreditation process.

2.9 Automated Tools

Irene Gilbert of NCSL served as the session chair for automated tools. NCSL's D. Richard Kuhn presented a paper describing a suite of static analysis tools for security certification. The tools are currently being used on software for secure Electronic Funds Transfer (EFT) but could be applied to other applications. NCSL has been assisting the Department of the Treasury by developing source code analysis tools to assist in the evaluation of software used in EFT equipment. The experimental tools described in this paper are being used on relatively small Treasury systems, but the research shows promise for expanding the use of tools for application to large systems.

2.10 Security Architectures

System security is considered stronger if based upon a hardware architecture that enforces Trusted Computing Base (TCB) constraints. Unisys Corporation's Larry Ketcham described how a software-based security architecture can protect itself against programs that attempt to compromise system security. The focus is on issues involving the creation and protection of program code and the extent to which compilers are included in the TCB. Ketcham concluded that when the operating system, compilers, and hardware together are able to protect the integrity of the TCB, a multi-domain security architecture is achieved.

3. Conference Summary

"Computer Security . . . Into the Future" covered a range of broad issues and specific advanced technologies which enhance the integrity and security of automated information in government and industry today. The importance of planning for the security of tomorrow's computer systems is critical to all who understand the value of their organization's information resources.

Conference proceedings are available from conference co-chair Irene Gilbert, NCSL, A216 Technology Bldg., National Institute of Standards and Technology, Gaithersburg, MD 20899, or you may call (301) 975-3360.

News Briefs

General Developments

CME INITIATES ROUND ROBIN ON ULTRASONIC REFERENCE BLOCKS

The Center for Manufacturing Engineering (CME) organized and initiated a round robin on the measurement of aluminum ultrasonic reference blocks as part of an effort to develop an annex to an ASTM standard (E-127). As requested by ASTM, NIST, as the lead laboratory, is supplying reference blocks and calibration data for this activity. If the results of the round robin are successful, laboratories will be able to certify ultrasonic reference blocks by a block-to-block comparison method using more readily available ultrasonic instrumentation and reference blocks measured by NIST.

FIRST ELEMENTS OF ADVANCED MEASUREMENT FACILITY ARRIVE IN CME

The first components of a new Molecular Measuring Machine Facility under long-term development have been installed in CME's metrology laboratory. Arrival of the components marks the mid-point of a major program in CME to develop the world's most advanced long-scan atomic-resolution dimensional measuring machine. Housed in a new lab-control room suite, the components consist of a custom-chambered vacuum system and a parallel-processor computer system for data acquisition, environmental monitoring, and positional control. The new facility, dubbed M-Cubed, is being designed to provide the capability to repeatedly locate and measure positions of individual features of atomic dimension to accuracies of 0.1 nm anywhere within a 50×50 mm area. Requiring advances in the state of the art of each of its subsystems (e.g., interferometry to one eighth-

thousandth of a wavelength and characterization of the wear of slideways to resolutions of 0.01 nm per meter of travel), the machine at the heart of the facility is scheduled for initial assembly in December 1989 and full operation in summer 1991.

NONDESTRUCTIVE EVALUATION SENSORS FOR PROCESSING OF HIGH- T_c SUPERCONDUCTORS

Research in the Metallurgy Division has demonstrated the feasibility of using nondestructive evaluation (NDE) sensors to monitor microstructural characteristics of high- T_c superconductors during high-temperature processing. The research was applied to the $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ system. Both ultrasonic velocity and eddy current conductivity measurements were made on the material during simulated processing at high temperatures. Phase changes in the oxide and changes in oxygen concentration were readily detected and monitored in real time.

The ability to monitor the quality of high- T_c superconductors during manufacturing will enhance U.S. industry's ability to produce these technologically important materials.

NIST WORKSHOP ON CALIBRATION OF STRONTIUM-90 OPHTHALMIC APPLICATORS

Strontium-90 ophthalmic applicators are radioactive sources used in the treatment of pterygium, an eye condition that can be corrected with shallow-dose exposures of beta particles. The Ionizing Radiation Division of NIST sponsored a workshop to bring together the small community that is focussing on this measurement problem. This community consists of the industrial source manufacturer, university and hospital research laboratories, and the Nuclear Regulatory Commission.

In the United States the condition has been mainly found in people of Hispanic descent, although it afflicts people in tropical regions around the world. Surgical removal of the diseased tissue followed by treatment of the residual cells with intense beta radiation is a remarkably effective treatment. As a result of this workshop, several laboratories will use different detectors and measurement techniques to evaluate discrepancies in surface absorbed dose rate that have been found in the calibration of ophthalmic applicators. The discrepancies seem to be explainable by differences in the size of the collection electrodes of the extrapolation chambers used to measure the beta-particle radiation.

NIST ESTABLISHES NEW DATA SERVICE

NIST has established a new data service that supports the development of advanced methods of elemental and isotopic analysis by providing formatted data and application sheets to permit the routine use of RIS/RIMS in analytical chemistry. The data service relates to the analytical techniques of Resonance Ionization Spectroscopy (RIS) and Resonance Ionization Spectroscopy followed by Mass Spectrometry (RIMS). These still emerging techniques, applicable in principle to nearly all atoms, have the potential of providing unsurpassed sensitivity (single atom) and selectivity (both specific atomic number and atomic weight). They are well suited to important problems in non-destructive testing, monitoring environmental pollutants, performing trace impurity analysis, and inspecting radioactive contamination as well as many other areas.

A format for RIS/RIMS data sheets has been designed in consultation with the RIS community. Data sheets for an initial group of 10 elements (As, B, Cd, C, Ge, Au, Fe, Pb, Si, and Zn) have been prepared. These sheets list the element, its stable isotopes, isotope shifts and hyperfine structure, RIS schemes, atomic energy levels, lifetimes, oscillator strengths, laser schemes, atom sources, estimates of laser power requirements, and references. Also included are the results of calculations of excited state photoionization cross sections by Hartree-Fock techniques. Data sheets for additional elements will be prepared in the future.

CRITICAL DATA FOR REPLACEMENT REFRIGERANT

There is a concerted effort by the nation's scientific community and industry to identify possible re-

placements for chlorofluorocarbons (CFCs) that are depleting the ozone layer in the stratosphere. One candidate is R123 (1, 1-dichloro-2, 2, 2-trifluoroethane), which has a much shorter atmospheric lifetime than R11 (trichlorofluoromethane). R123 has been proposed as a replacement for R11 as a foam-blown agent. Scientists have recently determined the critical parameters of R123 that are fundamental to the development of equation-of-state models for the thermophysical properties of fluids. Knowledge of these and similar properties are essential to rapid and efficient replacement of ozone-depleting CFCs. The new critical parameters are: $T_c = 456.94\text{ K}$; $P_c = 36.74$; $p_c = 550\text{ kg/m}^3$. Prior to these measurements the critical parameters had only been estimated.

DRAG AND TORQUE CALCULATIONS DEVELOPED FOR SHUTTLE TANKS IN LOW-EARTH ORBIT

NIST scientists have collaborated on the development of a computer algorithm needed for orbit and attitude control of large external Space Shuttle tanks which may be placed in long-term, low-altitude orbits.

Present practice is to discard these tanks, which weigh more than 30 t, after they have reached 98 percent of orbital velocity at an altitude of 100 km. There are compelling economic and environmental reasons for utilizing these tanks—they might serve as holding facilities, carry experiments, or be used as building components for larger structures in space—rather than letting them burn up upon re-entry into the atmosphere.

The algorithm has been implemented for calculating the aerodynamic drag and torque on such structures under the assumptions of free molecular flow theory. They divide the structures into circular cross sections, project these according to the angle of attack, and approximate the drag profile by the convex envelope of the projection ellipses.

SHORTEST WAVELENGTH x-RAY LASER DEVELOPED

NIST scientists have designed, in collaboration with private industry, a scheme for generating coherent radiation in the x-ray region between 10 and 100 Å. Preliminary measurements on a prototype device based on this scheme have recently been made and show evidence for lasing at 42.3 Å. If so, the device would be the shortest wavelength x-ray laser and the first to reach the so-called "water window" between 24 and 43 Å. This is the wave-

length region where carbon atoms will absorb radiation but water will not. An x-ray laser in this region could be used as a probe of the structure of living cells. The cell could be observed in its original state rather than having to be frozen, sliced, or stained as is necessary for techniques such as electron microscopy. Other uses of an x-ray laser are microlithography, plasma probing, and resonance excitation of atoms.

In this scheme, the laser is prepared by first ionizing a cloud of atoms to their zinc-like state. These ions are then further photoionized, leaving them in a metastable copper-like state. Since the ion decays slowly from this state, a population inversion builds up and lasing action takes place before the state decays. The x-ray laser device being tested combines an exploding foil, made of the lasing material, plus a second foil which, when exploded, generates photoionizing radiation. The lasing material is selected according to the desired laser wavelength, e.g., silver will provide a laser at 42 Å and dysprosium at 12 Å. Calculations also indicate that the population inversion will increase with decreasing wavelength, a significant occurrence since devices would become more efficient as they are pushed to their limits.

ATOMIC CLOCK USED TO TIME TRAFFIC LIGHTS

It was recently reported in *The Wall Street Journal* that a pioneering project involving the synchronization of Los Angeles County traffic lights with time signals provided by NIST is expected to save southern Californians thousands of hours of driving time a year and sharply cut fuel use and pollution. The time signals are derived from the NIST atomic clock and broadcast from the NIST radio station WWV in Fort Collins, CO. By tapping the precision of the timekeeping device, county officials say they can improve the timing of stoplights on major roads to allow traffic to flow more smoothly at posted speeds.

NIST scientists assisted in this project by working with industry to provide additional broadcast information in the WWV time code that enhances the usefulness of unattended, WWV-based clocks in such applications. Advantages of the new system include automated time resetting after a power outage, automated adjustments for daylight saving time changes, and elimination of the need for expensive wiring to central control systems. Seattle, WA and Dayton, OH are also planning to test the system.

TWENTY DEVICES PASS MAC VALIDATION TESTS

To date, 20 devices have successfully passed the National Computer Systems Laboratory conformance tests using the message authentication code (MAC) validation system (MVS). The system was developed to assist the Department of the Treasury with a program to certify message authentication devices for electronic funds transfer (EFT). The MVS tests message authentication devices for conformance to two data authentication standards: FIPS 113, Computer Data Authentication, and ANSI X9.9-1986, Financial Institution Message Authentication (Wholesale).

The MVS uses telephone lines to perform automated testing on message authentication devices which are remote to NIST. The testing facility is implemented on a personal computer equipped with a data encryption standard (DES) encryption board. Accessing the MVS by means of a remote bulletin board, assigned identifiers, and password pairs, the user selects one or more of five authentication options (one binary authentication option and four coded character set options). All applicants must successfully complete the binary option, but the combination of coded character set options to test is left to the discretion of the applicant.

NCSL has also developed a key management validation system (KMVS) to test key management devices for conformance to ANSI X9.17, Financial Institution Key Management (Wholesale). ANSI X9.17 has numerous options which allow flexibility for various applications. A subset of these options is being considered for federal government use.

DECISION SUPPORT SOFTWARE FOR AUTOMATED MANUFACTURING INVESTMENTS

A microcomputer program, AutoMan, has been developed to support multi-attribute decisions about automated manufacturing investments. This work was done in collaboration with NIST researchers, the Navy, and private industry. AutoMan is unique in permitting users to combine quantitative and qualitative criteria in evaluating investments. Quantitative criteria may include such traditional financial measures as life-cycle cost and net present value as well as such engineering performance measures as throughput and setup time. Qualitative criteria may include flexibility and product quality.

The user first specifies the criteria and investment alternatives and then establishes weights for

be used to record, store, and process information about an organization's data and data processing resources. The new standard adopts a voluntary industry standard ANSI X3.138-1988. NIST and the American National Standards Institute (ANSI) worked together for several years to develop the technical specifications for IRDS. In addition, NIST has developed prototype software which implements the standard. For further information contact Alan Goldfine, NIST, A266 Technology Bldg., Gaithersburg, MD 20899; telephone: 301/975-3252. The FIPS publication will be available from the National Technical Information Service, Springfield, VA 22161.

WORLD'S SMALLEST PRISM MADE AT NIST
 Researchers at the NIST laboratories in Boulder, CO, have created what they believe to be the smallest optical prism ever made. The microscopic glass prism is only 5×10^{-3} in on a side—about the thickness of a heavy sheet of paper. Barely visible to the naked eye, the "microprism" may be used in micro-optics and fiber optics research and instrumentation—for example, as a test probe for making accurate measurements of the performance characteristics of optical fibers in the tight confines of an integrated optical circuit. Besides being measuring tools, microprisms might also eventually have applications as actual elements in miniaturized optical circuits. A guest scientist at NIST developed the procedure to grind the infinitesimal prism in conjunction with a NIST physicist.

PROGRAM ON HIPing OF METAL POWDERS ESTABLISHED

The hot isostatic pressing (HIPing), or consolidation of rapidly solidified metal powders into near-net, or close-to-final, shapes, may be a very reliable way to make parts out of advanced alloys such as titanium aluminide. A team of scientists and engineers from industry, universities, and government are working to develop the measurement and control tools needed to automate the HIPing process. The collaborative effort is jointly sponsored by NIST and the Defense Advanced Research Projects Agency (DARPA). For titanium aluminide alloys, rapidly solidified powders are sealed in a canister or mold and placed inside a furnace. The material is heated to approximately 1100 °C and compressed into solid shapes by hydrostatic pressures up to 200 MPa, or 30,000 psi. Under the collaborative effort, researchers are

developing sensors, process models, and an "expert" computer system to automate the entire production cycle from raw powders to finished parts. For information on the cooperative HIPing program, contact: Dr. Robert J. Schaefer, NIST, A153 Materials Bldg., Gaithersburg, MD 20899; telephone: 301/975-6162.

AGREEMENTS REACHED ON OSI IMPLEMENTATIONS

The second version of stable implementation specifications for OSI (Open Systems Interconnection) protocols has been agreed to and is now available. These agreements are based on recognized international OSI standards and were reached by vendors and users participating in the NIST Workshop for Implementors of OSI. They support the second version of the Federal Information Processing Standard for GOSIP (Government Open Systems Interconnection Profile), which is expected to be proposed later this year. The agreements are considered advanced enough for use in product and test suite development. Stable Implementation Agreements for Open Systems Interconnection Protocols, Version 2 Edition 1 (NIST SP 500-162) is available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. Order by stock no. 003-003-02921-1 for \$26 prepaid.

FIRST 200 LABORATORIES ACCREDITED FOR BULK ASBESTOS

More than 200 laboratories received the first accreditations to perform analysis for asbestos content in bulk insulation and building materials under the new National Voluntary Laboratory Accreditation Program (NVLAP) for bulk asbestos in schools. The laboratories have demonstrated their competence to analyze bulk material samples by polarized light microscopy (PLM) using test method procedures specified by the Environmental Protection Agency (EPA). Approximately 500 other laboratories are being evaluated to determine their ability to meet NVLAP requirements. The accredited laboratories have undergone an on-site assessment performed by a technical expert in optical microscopy and have demonstrated full compliance with NIST technical evaluation criteria. The laboratories also have successfully participated in the first round of proficiency testing in which they were required to determine the presence and type of asbestos in pre-characterized quality assurance

materials developed by NIST. For information on NVLAP, contact: National Voluntary Laboratory Accreditation Program, NIST, Building 411, Gaithersburg, MD 20899; telephone: 301/975-4016.

LASER-PUMPED CESIUM CLOCK UNDER DEVELOPMENT

A new atomic clock is being developed at NIST that should improve short-term stability and frequency uncertainty to about 10 times better than the present national standard. The new clock, which will be accurate to 1 s in 3 million years, is the first to use laser light instead of magnetic fields for cesium atom state selection and to use photoelectric fluorescence detectors instead of hot-wire ionization for detection. The major construction phase is complete, and researchers are currently testing subsystems of the new clock, which uses state-of-the-art laser control and vacuum systems. Other advances in laser technology, frequency control servosystems, and microwave cavity design are also incorporated. The new clock will use counter-propagating beams of cesium atoms, thus reducing errors caused by asymmetries in the device. Other features will provide more flexibility and control of microwave power, modulation parameters, magnetic C-field strength, and cavity phase shift, enabling higher accuracy operation and simpler evaluation of the clock's performance.

NIST ASKING FOR COMMENTS ON POSIX REVISION

A Federal Information Processing Standard (FIPS) for POSIX, a portable operating system interface, was approved in September 1988 as the first step toward a more open software environment for Federal agencies. POSIX defines the interface, or link, between applications and computer operating systems based on UNIX, originally developed by AT&T. The initial FIPS, which was based on an Institute of Electrical and Electronics Engineers (IEEE) draft standard, was issued to enable federal agencies to begin specifying POSIX in procurements. Now NIST is planning on revising the standard to adopt the final IEEE standard 1003.1-1988 (Portable Operating System Interface for Computer Environments). Comments on the proposed revision must be received by July 12, 1989. They should be sent to NIST, Attn: Revision of FIPS 151, B154 Technology Bldg., Gaithersburg, MD 20899. For further information, contact Roger Martin at NIST, telephone: 301/975-3295.

Standard Reference Materials

STANDARD REFERENCE MATERIAL 1588—ORGANICS IN COD LIVER OIL

Standard Reference Material (SRM) 1588, Organics in Cod Liver Oil, is now available from the NIST Office of Standard Reference Materials. It is intended primarily for use in developing and validating analytical methods for the determination of selected chlorinated pesticides, chlorinated biphenyls, and alpha-tocopherol in cod liver oil and other similar complex lipophilic matrices, and should be of particular interest to food scientists.

The Certificate of Analysis for SRM 1588 provides certified concentrations for six chlorinated pesticides, five chlorinated biphenyls, and alpha-tocopherol. The chlorinated pesticides are hexachlorobenzene, alpha-HCH, trans-chlordane, cis-chlordane, trans-nonachlor, and dieldrin. The chlorinated biphenyls, identified according to the numbering scheme in K. Ballschmiter and M. Zell, Fresenius Z. Anal. Chem. 302, 20 (1980), are PCB 101, PCB 138, PCB 153, PCB 170, and PCB 180. The nominal concentrations of the pesticides range from 50 ng/g for trans-chlordane to 209 ng/g for trans-nonachlor; and, of the PCBs, from 45 ng/g for PCB 170 to 276 ng/g for PCB 153. The nominal concentration of the alpha-tocopherol is 112 µg/g.

The certified concentrations of the pesticides and PCBs are based on analyses using independent procedures based on gas chromatography with electron capture detection and gas chromatography with mass spectrometric detection. The certified concentration of alpha-tocopherol is based on analytical determinations based on two high-performance liquid chromatography methods—one, a normal phase procedure, the other, a reversed phase procedure.

In addition to the certified concentrations, the Certificate of Analysis provides noncertified concentrations of six added polychlorodibenzo-p-dioxins and octachlorodibenzofuran. The concentrations, ranging from 0.21 ng/g for 2,3,7,8-tetrachloro-dibenzo-p-dioxin to 1 ng/g for octachlorodibenzofuran, are based on the mass of the compound added to the mass of oil. SRM 1588, Organics in Cod Liver Oil, is available for \$199 per set of five sealed vials from the Office of Standard Reference Materials, NIST, B311 Chemistry Bldg., Gaithersburg, MD 20899; telephone: 301/975-6776.

STANDARD REFERENCE MATERIAL 1598— INORGANIC CONSTITUENTS IN BOVINE SERUM

A bovine serum Standard Reference Material (SRM 1598), certified for trace elements of clinical importance, is now available from the Office of Standard Reference Materials. SRM 1598 was developed primarily for use in calibrating instrumentation and evaluating the accuracy of analytical methods for selected trace elements in blood serum, plasma, and similar biological fluids.

The Certificate of Analysis provides certified concentrations and uncertainties for 13 elements. The nominal concentrations of the elements listed in ng/g are: aluminum (3.7), cadmium (0.089), chromium (0.14), cobalt (1.24), manganese (3.78), molybdenum (11.5), and selenium (42.4); and those listed in ng/g are: copper (0.72), iron (2.55), magnesium (20.0), potassium (196), rubidium (0.17), and zinc (0.89). The concentrations are based on the agreement of results by at least two independent methods. In addition, non-certified concentrations are provided for Ca, Na, As, Cs, Pb, Hg, Ni, Tl, and V.

The serum was produced at the U.S. Department of Agriculture facilities in Beltsville, MD. The dairy cows had been inspected and found to be free of any disease or pathological conditions.

The concentrations of certain trace elements in serum change during the course of specific diseases in animals and humans. For example, low serum selenium has been associated with a number of human diseases, such as Keshan disease, increased risk for coronary heart disease, and possibly, cancer. Reliable trace element determinations in serum are also important for nutrient bioavailability studies and nutrient monitoring during parenteral feeding. Because of the similarity of human and bovine sera, SRM 1598 should be useful in validating trace element methodology and experimental data.

NEW VALUE FOR THE ATOMIC WEIGHT OF NICKEL DETERMINED

Absolute values have been obtained for the first time for the isotopic abundance ratios of a reference sample of nickel (Standard Reference Material 986) using thermal ionization mass spectrometry. Samples of known isotopic composition, prepared from nearly isotopically pure separated nickel isotopes, were used to calibrate the mass spectrometers. The resulting absolute isotopic ratios are: $^{58}\text{Ni}/^{60}\text{Ni} = 2.596061 \pm 0.000728$, $^{61}\text{Ni}/^{60}\text{Ni} = 0.043469 \pm 0.000015$, $^{62}\text{Ni}/^{60}\text{Ni} = 0.138600 \pm$

0.000045, and $^{64}\text{Ni}/^{60}\text{Ni} = 0.035295 \pm 0.000024$, which yield atom percents of $^{58}\text{Ni} = 68.076883 \pm 0.005919$, $^{60}\text{Ni} = 26.223143 \pm 0.005144$, $^{61}\text{Ni} = 1.139897 \pm 0.000433$, $^{62}\text{Ni} = 3.634529 \pm 0.001142$, and $^{64}\text{Ni} = 0.925543 \pm 0.000599$. The atomic weight calculated from this isotopic composition is 58.693351 ± 0.000147 . The indicated uncertainties are overall limits of error based on two standard deviations of the mean and allowances for the effects of known sources of possible systematic error.

The International Union of Pure and Applied Chemistry Commission on Atomic Weights and Isotopic Abundances lists the present value of the atomic weight of nickel (58.69 ± 0.01) as one of the least well known atomic weights. Nickel is also one of the few remaining elements where the atomic weight is based, at least in part, on chemical determinations made in the early 1920s. Based on this work, a value of 58.6934 ± 0.0002 could be recommended which is several orders of magnitude more precise than the presently accepted value and, most important, is now known on an absolute scale.

“STANDARD CRACK” CAN HELP FIND METAL FATIGUE

A “standard crack” recently developed at NIST can help the airline industry do a better job of testing for metal fatigue in aircraft. Eddy current testing is the method most often used to detect the cracks, normally invisible to the naked eye, that lead to failure. A difficulty of the eddy current technique is the lack of samples of well-defined “flaws” that accurately simulate fatigue cracks. These are necessary to calibrate accurately eddy current instruments and to provide base data for interpreting test results. Now engineers at NIST’s Boulder, CO, laboratories have invented a technique for producing artificial flaws of known sizes which can be used to calibrate test equipment. NIST’s Office of Standard Reference Materials in Gaithersburg, MD, will sell 3- by 2-in blocks of metal containing these standard defects. The initial offerings will be research prototypes and should be available by mid-June. Inquiries concerning the purchase of these materials should be made to the Office of Standard Reference Materials, NIST, B311 Chemistry Building, Gaithersburg, MD 20899; telephone: 301/975-6776.

MATERIAL CAN HELP PINPOINT NICOTINE EXPOSURE

Researchers studying human exposure to cigarette smoke, both active and passive exposure, need to ensure that the methods they use to track the concentration of nicotine by-products in urine samples are reliable. A new bottled reference material (RM), issued jointly by NIST and the Environmental Protection Agency, can assist laboratories in validating urine measurement methods. It is designed for determining levels of cotinine, which is the major urinary metabolite of nicotine. With the new material, laboratory personnel can test the reliability of instruments and methods by analyzing the RM the same way as a urine sample and comparing results with the ones listed for the RM. The new material is sold in a kit that includes vials of freeze-dried urine each containing cotinine at one of three levels: blank, low, and high. These quantities are typical of, respectively, nonsmokers with no exposure to cigarette smoke, nonsmokers with passive exposure to smoke, and smokers. The RM (Number 8444) costs \$148 and is available from the Office of Standard Reference Materials, NIST, B311 Chemistry Bldg., Gaithersburg, MD 20899; telephone: 301/975-6776.

NEW SRM REPORT CONTAINS MICROSHERE EXPERIMENTS

A series of microscope experiments for students is described in a NIST report on the construction, preparation, and recommended uses of Standard Reference Material (SRM) 1965, Microsphere Slide, 10- μm Polystyrene Spheres. The SRM is a microscope slide with the first commercial product made in space, the 10- μm polystyrene spheres, deposited on it. The SRM is an education tool as well as a standard to calibrate microscopes for small particle measurements. The spheres are arranged in two types of groupings. One is an "unordered" arrangement, resembling strings of beads. The other grouping is an "ordered" two-dimensional hexagonal array for use as a microlength standard and to act as a "stage" micrometer. Copies of *Description of the SRM 1965 Microsphere Slide* (SP 260-107) are available prepaid for \$3.75 from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402. Order by stock no. 003-003-02911-4. SRM 1965 is available for \$105 from the Office of Standard Reference Materials, NIST, B311 Chemistry Bldg., Gaithersburg, MD 20899; telephone: 301/975-6776.

NEW LOW-ALLOY STEEL CALIBRATION STANDARD AVAILABLE

A new standard for checking and calibrating oxygen and nitrogen analyzers in the steel industry has been developed under a cooperative program between the American Society for Testing and Materials (ASTM) and NIST. Information on the concentrations of these gases is important to the properties of steel because they contribute markedly to steel brittleness and therefore to the strength and durability of steels. Standard Reference Material (SRM) 1754, Oxygen and Nitrogen in Low-Alloy Steel, AISI 4320, is in rod form, $0.95 \times 0.95 \times 10.2$ cm ($3/8 \times 3/8 \times 4"$). The new SRM was certified through the NIST/ASTM Research Associate Program involving nine industrial laboratories. SRM 1754 is available for \$119 per unit of 1 rod from the Office of Standard Reference Materials, NIST, B311 Chemistry Bldg., Gaithersburg, MD 20899; telephone: 301/975-6776.

Standard Reference Data

NEW NIST GAS KINETICS DATABASE AVAILABLE FOR PCs

A new computerized database with an extensive compilation of information on the rates of chemical reactions important to research chemists, environmental scientists, and combustion engineers has been developed by NIST scientists. Available on a floppy disk for personal computers (PCs), it contains data on the rates of approximately 2,000 chemical reactions with more than 5,300 individual data entries. The database is an important tool for modeling combustion systems or chemical processes occurring in the atmosphere. This type of data is necessary in understanding the reactions of chemicals and their role in depleting the Earth's ozone layer. A special software option allows users to display rapidly in a single graphic all of the rate constants determined for a single chemical reaction as a function of temperature. These plots showing all of the available information are useful for revealing discrepancies in experimental results. NIST Standard Reference Database 17, Gas Kinetics, is available for \$190 from the Office of Standard Reference Data, NIST, A320 Physics Bldg., Gaithersburg, MD 20899; telephone: 301/975-2208.

MAJOR REFERENCE WORK ON ATOMIC DATA PUBLISHED

After about 10 years of detailed data evaluation and compilation work, two major volumes of atomic transition probability data have been published as Supplements 3 and 4 to Volume 17 of the *Journal of Physical and Chemical Reference Data*. The books, about 500 pages each, contain data for approximately 18,000 spectral lines of the transition metals scandium through nickel for all stages of ionization. The largest amount of data, about 5,000 transitions, is available for iron. All data have been critically selected and are listed with estimated accuracies in the range from a few percent up to 50 percent for weaker lines.

The books are a continuation of a series started at NIST with two earlier volumes on lighter elements published in 1966 and 1969. These atomic reference data are widely used by the plasma physics, astrophysics, atomic physics, and spectrochemical communities. The earlier volumes have been cited about 2,000 times each.

Calendar

August 24, 1989

28th ANNUAL TECHNICAL SYMPOSIUM—INTERFACES: SYSTEMS AND PEOPLE WORKING TOGETHER

Location: National Institute of Standards and Technology Gaithersburg, MD

No computer is an island. Increasingly, systems are being tied together to improve their value to the organizations they serve. This symposium will explore the theoretical and practical issues in interfacing systems and in enabling people to use them effectively. On the day preceding the symposium, two 1-day tutorials will be offered. The first will be a Workshop for Computer Users with Disabilities. The second tutorial will be on User Interface Design. The conference is being sponsored by the Association for Computing Machinery and NIST.

Contact: Elizabeth B. Lennon, B151 Technology Building, NIST, Gaithersburg, MD 20899, 301/975-2832.

November 20–22, 1989

REDUCING THE COST OF SPACE INFRASTRUCTURE AND OPERATIONS

Location: National Institute of Standards and Technology Gaithersburg, MD

This conference, sponsored by NIST and the Office of Space Commerce of the Department of Commerce, will assemble entrepreneurs to discuss methods of reducing the cost of commercial enterprise in low-Earth orbit. The great cost of space infrastructure and operations is presently limiting the extent of commercial participation in space

activities. Meanwhile, the private sector is being urged to make major investments in space activities while working to reduce launch fabrication and operations costs. In order to develop recommendations on future industrial activity in low-Earth orbit, this conference will consist of keynote presentations on major topical areas and a follow-up workshop in each area. A draft report on each workshop will be presented at the end of the conference.

Contact: William Stone, B168 Building Research Building, NIST, Gaithersburg, MD 20899, 301/975-6075.

February 5–8, 1990 FOURTH INTERNATIONAL SYMPOSIUM ON BIOLOGICAL AND ENVIRONMENTAL REFERENCE MATERIALS

Location: Sonesta Village Hotel, Orlando, FL

The Fourth Symposium will continue the series being held approximately every 2 years. The excellent exchange of ideas and views documented in the Proceedings of the Third Symposium, held in May 1988 at Bayreuth, Bavaria, FRG, covered a wide variety and scope of information in this area. Activities at the Fourth Symposium are expected to both broaden these discussions and to focus on more specific aspects of further research on problems and progress of projects discussed at the previous symposium. The major aim of this symposium series is to bring together efforts in the production, study, and use of these reference materials in the analytical, biological, biomedical, clinical, environmental, and nutritional communities.

Contact: Wayne R. Wolf, B311 Chemistry Building, NIST, Gaithersburg, MD 20899, 301/975-2030.