Lawrence Livermore Laboratory

GENERAL CHEMISTRY DIVISION QUARTERLY REPORT
October through December 1976

Scientific Editor: J. E. Harrar.

General Editor: H. L. Lentzner

March 9, 1977

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Prepared for U.S. Energy Research & Development Administration under contract No. W-7405-Eng-48.

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GENERAL CHEMISTRY DIVISION QUARTERLY REPORT

Analytical Research and Development for the Whitney Program

ANALYTICAL METHODOLOGY AND MEASUREMENTS

Determination of Imperfections on the Surface of a Laser Spatial-Filter Lens

Responsible Personnel: J. W. Fischer and R. G. Meisenheimer

Brief Description: A laser spatial-filter lens was examined by x-ray photoelectron spectroscopy and scanning electron microscopy to determine the nature of imperfections on the surface of the lens. It appears that the surface imperfections arise from delamination of the surface coatings on the lens.

Status: We examined a 22.5-cm-diameter spatial-filter lens, which was used in the laser fusion energy program, to determine the nature and origin of imperfections on its surface. The imperfections were visible to the unaided eye and appeared as discolored regions on the lens surface. Several portions of the lens containing the imperfections, as well as several segments in which no abnormalities appeared, were examined by both x-ray photoelectron spectroscopy (ESCA) and scanning electron microscopy (SEM).

X-ray photoelectron spectroscopy showed only one substantive difference between the normal and abnormal areas of the spatial filter. Titanium was found on the lens surface in the area containing the imperfections, while the pristine regions contained no observable titanium. However, silicon was observed on samples from both of these regions.

Portions of the lens from both the normal and imperfect regions were then examined in the scanning electron microscope and several photomicrographs taken. The photomicrographs from the normal areas revealed a uniformly clean and smooth surface. Photomicrographs from the imperfect areas are shown in Fig. 1.

Examination of the photomicrographs clearly indicates that the imperfections observed on the surface of the lens are regions in which the multiple coatings are damaged. This observation is substantiated by the ESCA data, in which titanium was observed only in the damaged regions with silicon being found in both damaged and undamaged areas. The spatial filter is known to be coated with alternating layers of SiO_2 and TiO_2 ; the outer layer is

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700 X

3000 X

10 000 X

Fig. 1. Scanning electron photomicrographs of imperfections on a laser spatial-filter lens.

SiO₂. It appears that the multiple coating on the spatial-filter delaminated during use. This resulted in the removal of the outer layer of SiO₂ and exposure of underlying layers of TiO₂.

From the examination of the area circled in Fig. 1, it appears that three layers of coating have been removed, exposing the fourth layer, which should be composed of TiO₂. Since the 10,000 X photomicrograph was taken at an angle of about 70 deg to the lens surface, and because the thickness of one apparent layer, as measured directly on Fig. 1, is ~1 mm, the calculated thickness of a layer of coating is given approximately by the following equation:

$$\begin{aligned}\text{Thickness of one layer} &= (1 \text{ mm} \times 10^{-4}) \cot (90-70 \text{ deg}) \\ &= 2.7 \times 10^{-4} \text{ mm (2700 \AA)}.\end{aligned}$$

This calculated result for the approximate thickness of a single layer of coating, as determined from the scanning electron photomicrograph, is in reasonable agreement with the known value of 2.5×10^{-4} mm.

These facts support the hypothesis that three successive layers of coating were removed from the lens surface during the damage process. We theorize that there was inadequate bonding, perhaps due to a contaminant, between the third and fourth layers. This resulted in decohesion at this interface.

LEED Investigation of the (533) Face of Thorium

Responsible Personnel: R. Bastasz,* C. A. Colmenares, G. A. Somorjai,[†] and R. L. Smith**

Brief Description: We have prepared an ultrapure surface of thorium, which consists of an ordered array of atomic steps and terraces. This specimen is being used to evaluate the reactivity of atoms having low coordination that are present at thorium surfaces. Oxidation and other corrosion reactions are of particular interest.

Status: As part of a continuing program to study the surface chemistry of the actinide metals, we recently began a study of the properties of a single crystal of thorium metal having a stepped surface. A high purity, single crystal of thorium^{††} was oriented and polished so as to expose its (533) crystal face, which is composed of a repeating series of atomic steps and terraces. This surface is designated Th(S)-[4(111)×(100)] to indicate that it contains terraces of (111) orientation 4 atomic rows in average width and a step of (100) orientation 1 atomic layer in height (see Fig. 2).

Crystals with this type of surface topography are of interest because the atomic steps on metals surfaces are often the active sites for corrosion and catalysis reactions.¹ If, in the case of thorium, atomic steps affect the reactivity of the metal, then the crystal surface we have prepared will be unusually reactive, due to the high density of steps along its (533) face.

From our previous study of the (100) and (111) thorium crystal faces, both of which lack atomic steps, we obtained baseline data.^{2,3} By comparing

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^{††}Supplied by F. A. Schmidt, Ames Laboratories, ERDA, Ames, Iowa.

1. G. A. Somorjai and D. W. Blakeley, Nature **258**, 580 (1975).
2. General Chemistry Division Quarterly Report, October through December, 1975, Lawrence Livermore Laboratory, Rept. UCID-15644-75-4 (1976), p. 34.
3. R. J. Bastasz, C. A. Colmenares, R. L. Smith, and G. A. Somorjai, A LEED and AES Study of the Structure, Debye Temperature, and Oxidation of the (111) Crystal Face of Thorium, Lawrence Livermore Laboratory, Rept. UCRL-78772 Preprint (1976).

this set of data with data obtained from the (533) surface, we will be able to gauge the influence of surface irregularities upon the chemistry of thorium metal.

Two analysis methods are being used to gather data about the surface properties of the thorium crystal. Auger electron spectroscopy (AES) identifies the elements that compose a surface layer and can measure submonolayer amounts of an element on the surface. It is used to monitor the precise composition of the thorium crystal surface. Low-energy electron diffraction (LEED) provides information about the geometric arrangement of atoms at the surface. LEED allows us to ascertain the structure of adsorbed overlayers during reactions on the thorium surface, as well as to verify that steps are present on the thorium (533) surface.

Initial work on the (533) crystal surface has shown that it is stable to at least 800°C. A LEED pattern recorded after annealing the crystal to this temperature shows a (111)-like array of diffraction beams split into doublets (see Fig. 3). This type of pattern is a general characteristic for all stable stepped surfaces.⁴

Auger data indicate that carbon, oxygen, and chlorine are prevalent at the crystal surface in addition to thorium. We have endeavored to reduce these contaminants by repeated ion bombardment at elevated temperatures and temperature cycling, so that we have a clean thorium surface. This procedure has been successful in eliminating chlorine from the surface and reducing substantially the amount of carbon and oxygen. We expect to further reduce the contaminants to less than 10% of a monolayer.

A well characterized, clean surface is required for experiments to measure the intrinsic reactivity of the thorium surface and to evaluate the effectiveness of low coordination thorium atoms in catalyzing corrosion and oxidation reactions. We will next expose the crystal to gas-phase oxygen and other reactive gases in order to monitor chemical changes occurring on the thorium surface.

4. G. A. Somorjai, Surface Science Lectures Vol. 1 (International Atomic Energy Agency, Vienna, 1975), p. 173.

Fig. 2. Surface atom arrangement of thorium (533) surface.

Fig. 3. LEED pattern from thorium (533) surface following ion bombardment and annealing. Incident beam energy = 45 eV.

Oxidation of Uranium in Oxygen-Nitrogen Gas Mixtures

Responsible Personnel: C. A. Colmenares, D. R. McKenzie, and T. G. McCreary

Brief Description: The oxidation of depleted uranium (D-38) was studied between 393 and 450 K in oxygen-nitrogen gas mixtures. The oxygen pressure was varied from 6 to 42 kPa in the gas mixture (total pressure 101 kPa), in order to determine the pressure dependence of this oxidation.

Status: Since uranium is rapidly oxidized by oxygen and water vapor, an understanding of the uranium oxidation reaction is essential to make better use of the metal in its various nuclear applications.

The apparatus we used to measure the oxidation of uranium consists of a heated test chamber capable of holding six samples in the flowing test gas, and an analytical balance (see Ref. 5 for complete description).

We used a sample of depleted uranium (D-38), which contained ~500 ppm metallic impurities, including 150 ppm Fe, 60 ppm C, 45 ppm Mn, and <100 ppm Zn. The test coupons were polished on 600-grit emery paper, ultrasonically cleaned for 10 min in trichloroethylene, and ultrasonically cleaned again in absolute alcohol before testing.

The uranium-oxygen reaction was followed gravimetrically, and the results were plotted as sample weight gain (Δw) in mg per unit sample area (A) in cm^2 vs the elapsed time in hours (t). All curves were fitted to an equation of the form

$$(\Delta w/A) = kt^n + C$$

using a nonlinear least-squares computer code, where k, n, and C are constants. For the 16 samples, the average value of the constant n was 0.805. Refitting the data for the 16 samples with n fixed at 0.805, the maximum value of the constant C was 0.2 mg/cm^2 . Since each run was continued until $(\Delta w/A)$ reached 8 mg/cm^2 , the value of C was relatively small in all cases.

The activation energy and pressure dependence of this rate constant, k, were calculated using small sample statistics.⁶ We found that the rate

5. C. A. Colmenares, D. R. McKenzie, and T. E. Shell, J. Phys. E. **6**, 1121 (1973).

6. General Chemistry Division Quarterly Report, January through March 1974, Lawrence Livermore Laboratory, Rept. UCID-15644-74-1 (1974), p. 30.

constant k was independent of oxygen pressure in the range of 6.26 to 41.6 kPa (total pressure 101 kPa). The activation energy for the reaction was 70.97 ± 2.41 kJ/mol (16.96 ± 0.58 kcal/mol*), for the temperature range of 393 to 450 K. Figure 4 shows the log k versus reciprocal temperature plot for the 16 samples. This least-squares fit is expressed as:

$$\log k = 7.470 - \frac{3709 \pm 1.26}{T} \text{ (95\% confidence).}$$

*The error is given by the 95% confidence interval.

Fig. 4. Rate constant for the reaction of oxygen and uranium (D-38) versus temperature.

Use of Polarized X-Rays to Improve Detection Limits in Energy Dispersive
X-Ray Fluorescence Analysis

Responsible Personnel: R. W. Ryon

Brief Description: Polarized x rays have been shown to be a superior and practical excitation source for measuring trace elements by energy dispersive x-ray fluorescence. In our study, polarized x rays were obtained by the scatter method. Improved detection limits were obtained by using a close-coupled system, which was optimized to give high counting rates.⁷

A more intense polarized x-ray source is now being designed. The new source will feature a cylindrical boron carbide scatterer and use the design parameters determined in the first phase of this project. Detection limits are expected to be 3 to 10 times lower (depending on the particular element) than can be obtained with the best secondary emission excitors.

Status: The geometry of the system used in this study is schematically shown in Fig. 5. The x-rays from the source are first scattered by a suitable material, such as boron carbide. Those rays that travel along the y-axis are polarized with the electric vector being perpendicular to the y-z plane. If the beam is scattered a second time (by the specimen), and is observed along the x-axis perpendicular to the y-z plane, a minimum of source radiation will be detected. In the ideal case of highly collimated beams and thin scatterers, only the fluorescent x-rays from the specimen will be detected. With unpolarized excitation, scattered source radiation is the overwhelming contributor to the limited count rate of the system, and to the spectral background.⁸

The primary source of radiation used in our experiments was an unfiltered molybdenum anode x-ray tube, typically operated at 45 kV and 40 mA.

7. "Polarized Radiation Produced by Scatter for Energy Dispersive X-Ray Fluorescence Trace Analysis," in Advances in X-Ray Analysis, Vol. 20 (Plenum Press, New York, 1977) pp. 565-574; Lawrence Livermore Laboratory Rept. UCRL-78063 Rev. 1 Preprint (1976).
8. General Chemistry Division Quarterly Report, January-March, 1976, Lawrence Livermore Laboratory, Rept. UCID-15644-76-1 (1976), p. 6.

Fig. 5. Schematic drawing of the system used to measure trace elements by energy dispersive x-ray fluorescence. The x rays were polarized by scattering a collimated primary beam with a boron carbide scatterer. After scattering twice, the intensity measured along the x axis is much less than that measured along the z axis.

Multiple scatter within the polarizer and specimen sets an ultimate limit on the background reduction obtainable, when a highly polarized source is used. We set out to determine whether this phenomenon would excessively restrict the achievable background reduction by measuring polarization as a function of specimen and polarizer thicknesses.

We found from these studies that the polarization is limited to about 96% for thin (filter membrane) specimens, and to about 92% for bulk specimens. However, conventional x-ray tubes cannot be operated with enough power to maintain high counting rates, when using the collimation required to obtain high polarization. Therefore, it is tube power rather than multiple scatter that is the limitation when a flat polarizing scatterer is used.

Similar results are observed when the polarizer thickness is considered. The detection limits for elements potassium through strontium are not greatly influenced by the thickness of the boron carbide polarizer, particularly when the polarizer is more than about 3 mm thick. As with specimen thickness, the polarizer thickness does not place any practical limit on the achievable polarization with the experimental conditions used here.

The second major question that needed an answer was whether or not the intensity of the polarized source would be so low, due to the inherent geometric requirements and polarizer efficiency, that the method would be impractical. It can be shown theoretically that, when power is the limitation, the lowest detection limits will be obtained by opening up the collimators to obtain the maximum counting rate.⁷

The experimentally determined effect of system collimation of the relative detection limits is demonstrated in Fig. 6. The relative improvement in detection limits increases as the collimators are opened (less polarization), until the maximum counting rate is approached. With the system used in these experiments, the maximum count rate is about 20 000 counts/s. This rate is reached when the collimators are opened to give about 85% polarization.

To address the question of the usefulness of the polarized source in analysis, we tested the efficacy of the polarized source in comparison with other possible x-ray excitation methods. The experimental conditions were held constant, except for changing the source and adjusting its intensity to give the same overall counting rate in each case. The results for NBS Standard Orchard Leaves are shown in Fig. 7. The boron carbide polarizer gave detection limits that were lower than those obtained by other means, except

Fig. 6. Measured detection limits, relative to those obtained with an unpolarized source, as a function of the system collimation. As the solid angles of the collimators are increased, the count rate increases until the system maximum of about 20 000 counts/s is obtained at about 85% polarization. Specimen: 0.63 g/cm² NBS orchard leaves. Polarizer: 1.3-mm boron carbide.

Fig. 7. Comparison of $K\alpha$ detection limits for NBS orchard leaves. The source was a 45-kV molybdenum x-ray tube with the current adjusted to 40% instrument dead time. The boron carbide scatterer gave 85% polarization.

for a limited region of crossover with the nearly monochromatic yttrium secondary. The detection limits for the elements between potassium and strontium in a thick specimen of orchard leaves were about 2 to 4.5 times lower than those obtained with direct excitation, and about <1 to 3 times lower than those obtained with the yttrium secondary.

Any further reduction of detection limits will require a more intense source of polarized x rays. It is not practical to increase the primary source intensity very much above that used in our experiments. The intensity limitation may be overcome by using a more efficient geometry. Only a very small fraction of the total output of the primary x-ray source is intercepted by the flat scatterer used here. The intercepted fraction can be increased by using a curved polarizing scatterer.⁹

The desired geometry may be described as follows. Any triangle which is inscribed within a circle and whose hypotenuse is a diameter line is a right triangle. If the polarizing scatterer corresponds to a portion of the circle, and the x-ray source and specimen are located at the intersections of the circle with a diameter line, every point on the polarizer will scatter x-rays from the source to the specimen at $90 \pm \omega$ degrees. The angular divergence ω (and therefore the polarization) is determined by the sizes of the source and specimen in the same manner as when a flat scatterer is used. The intensity of the polarized x rays reaching the specimen can be 10 to 15 times greater than previously obtained.

The geometric requirements for an x-ray source which incorporates a cylindrical scatterer have been determined. Ed Russell (Mechanical Engineering), Joe Summers (Mechanical Engineering), and Ralph Kalibjian (Electronics Engineering) are presently designing such a device.

9. R. H. Howell, W. L. Pickles, and J. L. Cate, X-Ray Fluorescence Experiments with Polarized X-Rays, Lawrence Livermore Laboratory, Rept. UCRL-75623 (1974).

Laser-Induced Molecular Fluorescence

Responsible Personnel: J. H. Richardson, B. W. Wallin,* D. C. Johnson,* and M. E. Ando[†]

Brief Description: The detection of biochemicals and polycyclic aromatic hydrocarbons in concentrations less than 1 part per trillion (ppt) has been achieved by laser-induced molecular fluorescence (LIMF). We are starting work on the detection of explosives and biochemical compounds and comparisons of instrumentation.

Status: The LIMF research** as a major project of the Lasers for Chemical Analysis portion of Chemistry Program is nearing completion. The initial objective was to develop and evaluate LIMF as an analytical technique. In the first phase of our work we studied an ideal chromophore using visible excitation. This phase was completed,¹⁰ with riboflavin being detected quantitatively in concentrations of less than 1 ppt.

The goal of the second phase of the study was to extend the excitation range into the uv region, thereby increasing the number and classes of compounds that could be detected. We have just completed this phase with the quantitative analysis of polycyclic aromatic hydrocarbons in the sub-part-per-trillion range.¹¹

Table 1 summarizes the results to date. Considering the volume of solution actually sampled, the minimum detectabilities correspond to $\sim 10^7$ molecules. Many of the plots of fluorescence intensity vs concentration are linear for over six orders of magnitude, limited by self-absorption or solubility at the more concentrated end. The time resolution capabilities of the boxcar integrator that was used permitted significant improvements in sensitivity for fluoranthene and pyrene. Finally, because analog detection is used, all data can be acquired in a couple of minutes.

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[†] Summer employee.

**See page 1 of Ref. 8.

10. J. H. Richardson, B. W. Wallin, D. C. Johnson, and L. W. Hrubesh, Anal. Chem. Acta **86**, 263 (1976).

11. J. H. Richardson and M. E. Ando, Sub-Part-Per-Trillion Detection of Polycyclic Aromatic Hydrocarbons by Laser Induced Molecular Fluorescence, Lawrence Livermore Laboratory, Rept. UCRL-78982, preprint (1977).

The third and final phase of the study will be to apply LIMF to detection of explosives and molecules of biochemical interest. Most explosives would be better candidates for photoacoustic spectroscopy, although fluorescamine is a potential fluorescent label for explosives containing primary amines. A series of vitamins will be investigated to conclude the biochemical portion of the study.

Table 1. Absorptivities, excitation wavelengths, fluorescence wavelengths, and minimum detectabilities of various substances in water.

Molecule	Transition of interest	Excitation wavelength (λ_{ex}), nm	Absorptivity at λ_{ex} , $M^{-1}cm^{-1}$	Fluorescence wavelength (λ_{em}), nm	Minimum detectability	
					M	$\mu g/l$ (ppb)
Riboflavin	--	375.0	1.1×10^4 (a)	540	1.25×10^{-12}	0.47×10^{-3}
FAD (Flavin adenine dinucleotide)	--	267.0	3×10^4 (a)	525	5×10^{-11}	39×10^{-3}
Benzene	$1_A \rightarrow 1_{L_b}$	259.95	9×10^1 (b)	302,273	2.5×10^{-7}	19
Naphthalene	$1_A \rightarrow 1_{L_a}$	273.0	6×10^3 (c)	340,360	1×10^{-11}	1.3×10^{-3}
Anthracene	$1_A \rightarrow 1_{B_b}$	258.7	5×10^3 (c)	404	5×10^{-11}	8.9×10^{-3}
		254.0	1×10^5 (c)		$< 2.5 \times 10^{-11}$	$< 4.4 \times 10^{-3}$
Fluoranthene	$1_A \rightarrow 1_{B_b}$	287.0	4×10^4 (b)	450	5×10^{-12}	1×10^{-3}
Pyrene	$1_A \rightarrow 1_{B_b}$	273.0	6×10^4 (c)	395	2.5×10^{-12}	0.5×10^{-3}

^aWater.

^bMethanol/water.

^cMethanol.

Stark-Shift Laser Spectrometry for Chemical Analysis

Responsible Personnel: L. W. Hrubesh, D. C. Johnson,* and E. A. Rinehart†

Brief Description: We are continuing to characterize the analytical capabilities of a submillimeter-laser spectrometer.

Status: Very high sensitivity and spectrometric resolution have been obtained by others^{12,13} in the measurement of gaseous paramagnetic molecules using fixed-tuned submillimeter lasers and tunable magnetic fields. This technique, commonly called laser magnetic-resonance spectrometry (LMRS), has an electric analogy, Stark-shift laser spectrometry (SSLS).¹⁴ In addition to providing ultrahigh resolution for molecular spectroscopy, SSLS also has considerable promise as an analytical tool for gas mixtures. We have developed such a spectrometer to investigate the analytical potential of this technique.

Optically pumped waveguide lasers make possible a large number of laser source lines for Stark-shift spectrometry at submillimeter wavelengths. Many more are expected to result from continued work. Near coincidences are expected to exist between these source lines and pure rotational absorption transitions (usually in their ground vibrational state) of asymmetric polar molecules. The additional frequency offset can be made up by the application of an electric field to the gas, which frequency shifts its Stark components in proportion to some power of the applied field. A Stark-shift absorption spectrum can be obtained by detecting the laser power transmitted through a gas sample, which is simultaneously being subjected to a swept voltage. The distinct pattern of absorption lines, and in some cases, the frequency locations of select Stark lines, can be used to identify the presence of particular gases in a mixture. Quantitative information can be obtained from the absorption intensities.

The spectrometer that has been constructed is shown in Fig. 8. The CO₂-pumped far-infrared (FIR) waveguide laser is similar to that described

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† Consultant, University of Wyoming, Laramie

12. K. M. Evenson, H. P. Broida, J. S. Wells, and R. J. Mahler, Phys. Rev. Lett. **21**, 1038 (1968).

13. H. E. Radford, K. M. Evenson, and C. J. Howard, J. Chem. Phys. **15**, 3178 (1974).

14. G. Duxbury and R. G. Jones, Molec. Phys. **20**, 721 (1971).

Fig. 8. Submillimeter laser analytical spectrometer.

by Hodges and Hartwick.¹⁵ The CO₂ laser frequency is stabilized at the peak of the FIR pump transition by using a separate Stark cell and servo loop to control the CO₂ cavity length. Most of our current work is with CH₃F and CH₃OH as the submillimeter laser medium, but future work will make use of any available laser lines that can be optically pumped by the CO₂ laser. The analytical Stark cell is 50 cm long and has a plate spacing of 0.215 cm. Breakdown limits the applied voltages to less than 10 V in the pressure range from 1 to 10 Pa. Field intensities from zero to approximately 50 kV/cm can be applied to the gas in either a continuous sweep or at selected constant values. Either a Golay cell or a helium-cooled bolometer is used as a detector. The absorptions are observed as derivative spectra because slight field modulation and phase-sensitive detection are used. Although a mixture of several gases gives a very complicated spectrum, several variables can be used to help interpret the complex spectra in a real analysis. For example, different spectra for the same compound can be obtained by using different laser lines available from the optically pumped waveguide laser. Also, because the laser radiation is polarized, two distinctly different spectra are observed from a compound depending upon the orientation of the applied electric field with respect to the laser radiation electric field (these are the $\Delta M = 0$, and $\Delta M = \pm 1$ sets of Stark transitions.)

The initial Stark shift spectrum obtained with the instrument is shown in Fig. 9. This spectrum of acetone is typical of the type expected for other organic solvents with many lines and a distinct intensity pattern. We hope to improve considerably both the sensitivity and resolution of the spectrometer, then demonstrate its capability for analyzing a mixture of several organic solvents. We also expect this technique to be useful for chlorinated and fluorinated compounds as well as moderately reactive molecular species.

15. D. T. Hodges and T. S. Hartwick, Appl. Phys. Lett. **23**, 252 (1973).

Fig. 9. Stark shift spectrum of acetone at 486.1 μm .

Determination of Lanthanide Ionization
Potentials by Laser Spectroscopy

Responsible Personnel: E. F. Worden, J. G. Conway,* and G. P. Vayer[†]

Brief Description: The photoionization thresholds of the lanthanides neodymium, samarium, europium, dysprosium, and erbium have been determined using laser spectroscopy techniques. These results yielded the following ionization potentials in eV: Nd, 5.523; Sm, 5.639; Eu, 5.666; Dy, 5.936; and Er, 6.104. The values have an absolute accuracy better than ± 0.003 eV and represent the most accurate values obtained for these rare earths.

Status: The photoionization threshold of neutral atomic vapor atoms can be obtained by employing one or two pulsed dye lasers at a fixed frequency and one scanning laser. The atoms are excited in an atomic beam to a known level of the atomic system (using one or two dye lasers at the appropriate frequency or frequencies), and then scanned with another laser from frequencies below the ionization threshold to higher frequencies until the onset of photoionization is observed. Figure 10 represents the two cases schematically. The threshold is usually easily recognized, but may be more distinct for some levels of an atom than others.

The apparatus, timing techniques, and detection system have been described in detail.¹⁶⁻¹⁸ Briefly, the system consists of dye lasers (Molelectron UV 200) that are pumped by a pulsed N₂ laser (Molelectron UV 400). These are crossed with an atomic beam in a vacuum chamber at $<10^{-4}$ Pa, ($<10^{-6}$ Torr). Laser pulse widths are about 5 ns. Laser timing is controlled by a master oscillator with fixed and/or programmable delay lines between each N₂ laser. Photoions produced by the lasers are first filtered through a

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[†]Research Engineering Division, LLL.

16. General Chemistry Division Quarterly Report, July through September, 1975, Lawrence Livermore Laboratory, Rept. UCID-15644-75-3 (1975), p. 46.
17. L. R. Carlson, J. A. Paisner, E. F. Worden, S. A. Johnson, C. A. May and R. W. Solarz, J. Opt. Soc. Am., **66**, 846 (1976).
18. R. W. Solarz, C. A. May, L. R. Carlson, E. F. Worden, S. A. Johnson, J. A. Paisner and L. J. Radziemski, Phys. Rev. A **14** 1129 (1976).

Fig. 10. Excitation sequences for determining the photoionization threshold in atoms with two (a) or three (b) lasers. The time scale represents the delay of about 20 ns between pulsed lasers 1 and 2 (a and b) and 2 and 3 (b). λ_2 (a) and λ_3 (b) are the frequencies of the scanning lasers while other lasers are fixed at frequencies of known transitions.

quadrupole mass spectrometer to get rid of undesired ions and then detected by a channeltron detector.

Typical photoionization threshold scans for neodymium are shown in Figs. 11 and 12. In Fig. 12, 492.453-nm dye-laser radiation was used to populate the $20\ 300.84\text{ cm}^{-1}$ level of neodymium. The observed threshold is at 412.41 nm, and when the wavenumber of this radiation is added to the level wavenumber, one obtains $44\ 541.6\text{ cm}^{-1}$ or 5.523 eV as the ionization potential of neodymium. The peak before the threshold is marked $2\lambda_2$ and is caused by the absorption of two photons of λ_2 by ground-state neodymium atoms to produce ions. Figure 13 shows a scan in which λ_1 at 463.424 nm excites the $21\ 572.61\text{ cm}^{-1}$ level of neodymium and λ_2 is scanned to detect the limit of 435.25 nm. This limit yields the same ionization potential. A number of peaks appear before the limit in this scan. Some are $2\lambda_2$ peaks from ground state absorption, but most are peaks caused by transitions from the $21\ 572\text{ cm}^{-1}$ level to levels just below the limit that absorb another λ_2 photon to ionize. These are $\lambda_1 + 2\lambda_2$ peaks and represent levels with energies just below the ionization energy. These peaks are generally much weaker than the strong autoionization peaks observed above the photoionization threshold. The autoionization peaks appear above a continuous photoionization background so that the ion signal does not go to zero between peaks. The strength of the peaks and the underlying background allow identification of the photoionization threshold. While most autoionization levels so far observed for actinides and lanthanides are quite sharp,^{16,18} many are broad and serve as further identification of autoionization peaks.

If tunable lasers with energy ranges exceeding the ionization potential were available, the data could be obtained with one laser. Presently it is more convenient to employ two or three tunable dye lasers.

Scans similar to those for neodymium have been obtained for samarium, europium, dysprosium, and erbium. The photoionization thresholds obtained for these elements are given in Table 2 along with values determined by other techniques. Agreement is within the quoted limits for all values except for neodymium where our value is higher than the spectroscopic value. The spectroscopic value involves extrapolation and interpolation techniques applied to limited data. We believe our values are the best for neodymium and the other lanthanides. We plan to investigate some of the remaining lanthanides and also report on the observation of Rydberg series, which will permit a more accurate determination of ionization potentials.

Fig. 11. Typical photoionization threshold scan for neodymium. In this scan 492.453 nm radiation was used to populate the 20300.84 cm^{-1} level in atomic Nd, λ_2 scanned. Wavelength standard scans shown at the top are obtained by setting a monochromator at precise thorium wavelengths and recording on the second pen of a two pen recorder the response of the monochromator photomultiplier to a portion of the scan laser output focused into the monochromator. See Ref. 17. The photoionization threshold is observed at 5.523 eV.

Fig. 12. Photoionization scan in which 463.424 nm radiation was used to populate the 21572.61 cm^{-1} level. Again the threshold was observed at 5.523 eV.

Table 2. First ionization potentials of some rare earths.

Element	Laser photoionization value ^a , eV	Spectroscopic value ^b , eV	Surface ionization value ^c , eV	Electron impact value ^d , eV
Nd	5.523(3)	5.489(20)	5.49(5)	5.49(10)
Sm	5.639(3)	5.631(20)	5.61(5)	5.58(10)
Eu	5.666(3)	5.666(7)	5.64(5)	5.68(10)
Dy	5.936(3)	5.927(8)	5.82(5)	5.90(10)
Er	6.104(3)	6.101(20)	5.95(3)	5.93(10)

^aThis work; numbers in parentheses indicate the estimated uncertainty in the last digit quoted.

^bW. C. Martin, L. Hagan, J. Reader and J. Sugar, J. Phys. Chem. Ref. Data **3**, 771 (1974).

^cG. R. Hertel, J. Chem. Phys. **48**, 2053 (1968).

^dR. J. Ackerman, E. G. Rauk and R. J. Thorn, J. Chem. Phys. **65**, 1027 (1976).

Ion-Selective Electrodes for Direct Measurement of Chloride

Responsible Personnel: W. Selig

Brief Description: The Ionel chloride ion-selective electrode (ISE) and the Orion model 94-17A chloride ISE were tested over the range of 10^{-6} to 10^{-2} M by direct emf measurement.

Status: The Orion chloride ISE has been commercially available for several years and is used in many laboratories. It is based on a membrane of silver sulfide/silver chloride. The Ionel Co. has developed a new chloride ISE based on a membrane of mercuric sulfide/mercurous chloride. The theoretical limits of detection of these membranes are defined by the solubility of the more soluble component. At 25°C the K_{sp} for AgCl is 1.56×10^{-10} while that of Hg_2Cl_2 is 2×10^{-18} . One would therefore expect the Ionel chloride ISE to be considerably more sensitive than the Orion chloride ISE. Indeed, the Ionel ISE is more sensitive over the range of 10^{-4} to 10^{-6} M. However, its response in this region is non-Nernstian. Even in the region from 10^{-4} to 10^{-2} M its response is less than Nernstian as shown in Table 3.

Table 3. Response of Ionel and Orion chloride ion-selective electrodes.

Concentration decade, M	Response, mV	
	Orion	Ionel
$10^{-6} - 10^{-5}$	8.8	25.5
$10^{-5} - 10^{-4}$	39.5	45.5
$10^{-4} - 10^{-3}$	57	47.5
$10^{-3} - 10^{-2}$	57	49.5

A calibration curve for both electrodes is shown in Fig. 13. Emf readings were taken after stirring for 10 min; the measurements were made in order of increasing concentrations. One cm^3 of 1 M nitric acid was added to 50 cm^3 of the solution to adjust its pH and ionic strength.

Several potentiometric titrations of chloride with silver nitrate were also made with both electrodes. The shape of the curves and the magnitudes of the endpoint breaks were the same.

Fig. 13. Response of chloride ion-selective electrodes.

We conclude that the Ionel chloride ISE is useful for the direct measurement of chloride concentration over the range of 10^{-4} to 10^{-6} M.

Analysis of Explosive Composites

Responsible Personnel: G. L. Crossman

Brief Description: Methods were developed for the analysis of explosive composites containing TATB,* HMX,[†] and Estane** or Kel-F^{††} binder. They are based on sequential extraction techniques.

Status: The analysis of explosive composites RX-26-AD, -AE, -AF, -AG and -AJ was required by Organic Materials Division. These materials contain the explosives TATB and HMX; Estane is the plastic binder for the first four materials while the last one has a Kel-F binder.

The Estane in the Estane-containing composites was extracted with 1,2-dichloroethane. HMX and TATB are insoluble in this solvent. The HMX in the residue was then extracted with acetone, leaving only TATB. Table 4 shows the results, which are given as the mean of duplicate analyses. The results obtained for synthetic mixtures are shown in Table 5. The high values for Estane and the low values for HMX can be explained by the presence of a small amount of dichloroethane-soluble RDX*** present as an impurity in the HMX. These results can be improved by using 1,2-dichloroethane saturated with RDX to remove the Estane.

Kel-F was extracted by digestion in concentrated nitric acid. On a separate sample the TATB was determined by extracting HMX and Kel-F with acetone. These results are shown in Table 6.

*1,3,5-Triamino-2,4,6-trinitrobenzene

[†]1,3,5,7-Tetranitro-1,3,5,7-tetrazacyclooctane

**Polyurethane elastomer

^{††}Copolymer of vinylidene fluoride and chlorotrifluoroethylene.

***1,3,5-Trinitro-1,3,5-triazacyclohexane

Table 4. Extraction-gravimetric analysis of composites containing TATB, HMX, and Estane.

Composite	Component, wt% (mean)		
	Estane	TATB*	HMX
RX-26-AD	4.46	19.34	76.20
RX-26-AE	3.74	38.53	57.73
RX-26-AF	4.26	46.30	49.44
RX-26-AG-1	4.31	61.16	34.53
RX-26-AG-2	3.79	61.90	34.31
RX-26-AG-2	3.82	61.60	34.58
RX-26-AG	5.56	57.39	37.05

*Calculated by difference.

Table 5. Recovery of ingredients in synthetic mixtures of TATB, HMX, and Estane.

Ingredient	Amt. taken, %	Amt. recovered, %	Difference, %
Estane 5702 F-1	3.97	4.17	+0.20
	4.23	4.40	+0.17
TATB, B-360	45.77	45.85	+0.08
	35.88	36.01	+0.13
	20.99	20.94	-0.05
HMX, A958	50.26	49.98	-0.28
	59.90	59.59	-0.31
	74.99	74.63	-0.36

Table 6. Analysis of a composite containing HMX, TATB, and Kel-F.

Sample	Kel-F, %	TATB, %	HMX, % ^a
RX-26-AJ	7.00	54.74	38.26

^aCalculated by difference.

Measurement of HF Produced by LX-09 Explosive

Responsible Personnel: R. W. Crawford, K. Ernst, J. W. Fischer, and A. J. Pane

Brief Description: Because there has been some circumstantial evidence that hydrogen fluoride can be released from LX-09 explosive,* and the release of HF into a weapon system could have serious consequences, a set of experiments are underway to test for HF production from this explosive.

Status: As reported previously,** evidence of the evolution of fluorine was found in thorium tabs exposed to heated LX-09. Two additional experiments have been performed and a third is in progress to verify these results.

In the current experiments, a gold and a thorium tab are mounted in the side arm of an apparatus in such a way that the LX-09 can be heated while the tabs remain near room temperature. In the initial experiment, the apparatus was constructed of stainless steel. It was evacuated and filled to 100 kPa (1 atm) with helium. The LX-09 was then kept at 120°C for three days. The surfaces of both the gold and thorium tabs were examined by ESCA both before and after the experiment. The results are shown in Table 7. The units are arbitrary peak heights and are useful only for calculating ratios within a given experiment. The results show that reactive fluorine compounds are formed because absorbed fluorine is found in equal concentrations on both surfaces.

A second, identical experiment was performed in Pyrex glass instead of stainless steel. This was done to eliminate the possibility of fluorine-containing compounds being decomposed by the stainless steel to form reactive fluorine species. The results of this experiment (Table 7) indicate that this may be a contributing factor. In addition, the locations of the fluorine bands on the gold and thorium samples were determined precisely by ESCA and found to be different for the two metals. The location of the fluorine peak on the gold sample was typical of that found for fluorine in a fluorocarbon. The position of the fluorine peak on the thorium sample was that of ionic fluorine.

*HMX, 2,2-dinitropropyl acrylate, bis(2-fluoro-2,2-dinitroethyl) formal.

**See page 23 of Ref. 2.

Table 7. Results of ESCA analysis of specimens exposed to LX-09.

	F on Au	F on Th	Ratio
<u>Stainless steel apparatus</u>			
Pre-exposure	Not detected	5	-
Post-exposure	2.4	22	7
Post-exposure; surface etched 10 nm	3.5	43	11
<u>Glass apparatus</u>			
Pre-exposure	Not detected	Not detected	-
Post-exposure	0.5	2.5	5

A third experiment, which is identical to the second except that pure bis(2-fluoro-2,2-dinitroethyl) formal (FEFO) is being used instead of LX-09, is almost complete. This experiment will show whether or not FEFO can react on the surface of the thorium to form an ionic fluorine. If this proves to be the case, a new apparatus may be built that will eliminate the chance of FEFO reaching the thorium and gold surfaces.

AUTOMATION AND INSTRUMENTATION

Installation of ECLIPSE Computer System and Water Quality

Laboratory Automation Projects

Responsible Personnel: G. W. Barton, H. S. Ames,* W. G. Boyle, R. I. Bystroff, R. W. Crawford, J. R. Elliott,* E. R. Fisher,* K. A. Gertz,* V. H. Hendricks,* A. M. Kray,* M. D. Maples,* W. F. Morris, E. S. Peck, L. P. Rigdon, and L. Taber*

Brief Description: A Data General ECLIPSE C/300 computer system has been placed in operation to aid our analysis effort, which supports Whitney programs and a variety of other LLL projects. We developed the hardware and software for this system in the course of automation projects for the Environmental Protection Agency (EPA) and the U.S. Geological Survey (USGS). Automation systems have been installed and are operating in three EPA laboratories. Progress on the automation of the other laboratories continues in various stages of development, and new features and improvements in the standard automation package have been implemented.

Status: The General Chemistry Division has installed a Data General ECLIPSE C/300 computer system in building 222. By incorporating this type of system, we will be able to take advantage of the software and hardware that were developed for automation of the EPA laboratories.** The system will aid General Chemistry's analytical services supporting the A, B, and W programs, the fossil fuel and geothermal energy efforts, the National Uranium Resource Evaluation, and a variety of other programs. The LLL ECLIPSE C/300 system will handle on-line analytical instrument data acquisition tasks and sample-data management for all samples submitted to General Chemistry from log-in of the samples through generation of the analysis reports. To date, the atomic absorption spectrophotometer programs have been interfaced and are operating. A Technicon AutoAnalyzer is currently being brought on line and data management software is being developed.

*Electronics Engineering Department, LLL.

**See page 4 of Ref. 2.

Thus far, automated systems have been installed and are operating in three EPA laboratories: the Environmental Monitoring and Support Laboratory and the Municipal Environmental Research Laboratory, both in Cincinnati, Ohio, and the Region V Laboratory in Chicago, Illinois. First-draft "Feasibility Studies" have been completed for the EPA Region IV, Region VII, and National Enforcement Investigation Center Laboratories located respectively in Athens, Georgia; Kansas City, Missouri; and Denver, Colorado. Work for the EPA Region III Laboratory, Annapolis, Maryland, has advanced to the specifications stage and a feasibility study will begin in February, 1977 for the EPA Region II Laboratory, Edison, New Jersey.

The USGS automation project includes laboratories in Denver, Colorado, and Atlanta, Georgia, and has advanced to the design stage. The "Feasibility Study" was completed in January, 1976, and approved by the Department of Interior in June, 1976. "Purchase-Order Bid Specifications" have been prepared, and a notice of their availability has been published in the Commerce Business Daily. The first-draft "Functional Description" of the USGS laboratory and "Definition of the Project" have been completed, and the "System Conceptual Design" will be completed in January, 1977.

New features have been added to the EPA instrument automation software specifically for the Technicon AutoAnalyzer and the atomic absorption spectrophotometer programs. Improvements in the Technicon AutoAnalyzer programs include the capability to enter the identities of greater numbers of samples, standards, and quality controls with better efficiency. This is accomplished by providing the capability to enter blocks and multiple patterns of data. Real-time data acquisition has also been improved by allowing the BASIC-language program to detect and control the interval within which the peak signal is measured. Software has also been included to handle operation of the Technicon AutoAnalyzer I.

The atomic absorption spectrophotometer (AAS) software is applicable to both flame and graphite-furnace modes of operation. The software now makes use of "chaining" techniques so that less core space is used while the AAS programs are running on the computer system. New options in the graphite-furnace-mode AAS software include peak integration and integration preceded by peak curve fitting. Additional quality control features have been added to allow the introduction of more check standards, spikes, and duplicate unknowns in the semi-automatic and random-sequential AAS flame mode programs.

Computer-Controlled Burets

Responsible Personnel: W. G. Boyle and J. D. Breshears*

Brief Description: The previously described¹⁹ 50-cm³ computer-controlled buret has been calibrated and both the 10-cm³ and 50-cm³ burets have been tested. A microprocessor-controlled dilutor is being developed.

Status: The 50-cm³ computer-controlled buret has been calibrated. The calibrations for this buret and the new calibrations for the 10-cm³ buret²⁰ were entered into the FOCAL program and the delivery of specific volumes checked (see Table 8).

A microprocessor-controlled dilutor is being developed. This work is based on the information obtained during operation of these burets under the control of the PDP-8/e minicomputer. Hopefully this will result in a prototype bench-top dilutor.

*Electronics Engineering Department, LLL.

19. General Chemistry Division Quarterly Report, April through June 1973,
Lawrence Livermore Laboratory, Rept. UCID-15644-73-2 (1973), p. 2.

20. General Chemistry Division Quarterly Report, July through September, 1976,
Lawrence Livermore Laboratory, Rept. UCID-15644-76-3 (1976), p. 1.

Table 8. Calibrations of computer-controlled burets.

Volume requested, cm ³	Volume found, cm ³
<u>10-cm³ buret</u>	
1	1.0010
1	1.0014
3	3.0014
3	3.0006
6	6.0013
6	6.0010
9	8.9970
9	8.9966
<u>50-cm³ buret</u>	
10	9.9973
10	10.0025
20	20.0208
20	20.0247
30	30.0147
40	40.0176
48	48.0051

Automation of the Hewlett-Packard Model
5950A ESCA Spectrometer

Responsible Personnel: J. W. Fischer, R. M. Downey,* and R. G. Meisenheimer

Brief Description: The microprocessor system required to automate the sample handling system of the Hewlett-Packard model 5950A ESCA spectrometer²¹ has been constructed, installed, and interfaced to the spectrometer. Development of the software package is currently underway.

Status: We have completed the microprocessor system required for automation of the Hewlett-Packard model 5950A ESCA spectrometer. The system has been interfaced to the spectrometer sample-handling system as well as to the Hewlett-Packard model 2100A minicomputer used to automate the spectrometer scanning and data-taking functions. The minicomputer was modified to permit the Intel model 8080 microprocessor to directly control execution of the machine language program in the minicomputer via the switch register.

The minicomputer will communicate with the microprocessor through a 14-bit word transferred to the microprocessor through a relay register card previously installed in the minicomputer. The modifications and additions maintain complete compatibility with the machine-language software package supplied by Hewlett-Packard for the minicomputer and even enhance its effectiveness.

The microprocessor system was designed and constructed to provide maximum flexibility. Included are eight sense switches for on-line interaction with software execution. In addition, there is an eight-bit LED display register to indicate program status so that the operator may set the sense switches or input data. A 16-function key pad was also incorporated into the system for the inputting of data and other interaction functions. In addition, a seven-digit decimal display register was installed for information output such as the echoing of data input through the keypad.

Software for this system is now undergoing development with the flow charts being essentially complete.

*Electronics Engineering Department, LLL.

21. General Chemistry Division Quarterly Report, April through June, 1976,
Lawrence Livermore Laboratory, Rept. UCID-15644-76-2, p. 6.

Special Projects for the Energy Program

Formation of Solids from Geothermal Brine

Responsible Personnel: J. H. Hill, C. H. Otto, and C. J. Morris

Brief Description: The rate of formation of suspended solid material from geothermal brine has been measured as a function of the pH of the brine. Acidification of the brine inhibits the formation of suspended solids, but solids do not readily dissolve in acid after they precipitate.

Status: The quantities and rates of precipitation of solids from expanded (reduced in temperature and pressure) geothermal brine must be known if we are to design a geothermal power system. Suspended solids cause erosion and plugging of plant components and may cause problems in the reinjection of the spent brine.

The rate of production of suspended solids in Magmamax No. 1 brine was determined as a function of pH during acidification experiments conducted at the LLL Field Test Facility in October and November, 1976. In these experiments, the high temperature (220°C), high pressure (1.73 MPa, 250 psi) brine was separated from the steam, acidified, and expanded through nozzles in the brine modification apparatus. Samples were taken from elbows in the exhaust system about 40 cm downstream from the nozzles. The temperature of the brine at the sampling point was about 95°C. All samples were transferred to a constant temperature bath at 85°C immediately after they were taken and their pH was measured. To determine the rate of solids production, the samples were removed from the constant temperature bath at timed intervals and immediately filtered through glass frits having a nominal porosity of 4 to 5.5 μm . The solids were then washed with distilled water, dried at 110°C, and weighed.

Initial experiments were conducted over intervals of 24 h with samples ranging in pH from 1.6 to 5.8. Results are shown in Fig. 14. These data indicate that the formation of suspended solids from Magmamax No. 1 brine in this pH range is essentially complete in 4 h or less. They also indicate that acidification of the brine to a pH <4.6 greatly inhibits the production of suspended solids. The amount of solids produced at a pH <4.6 is less than

*See page 37 of Ref. 20.

Fig. 14. Rate of precipitation of solids at 85°C in separated Magmamax #1 brine.

one-tenth the amount produced in unmodified brine (pH 5.8). These results were confirmed by additional experiments conducted over shorter time intervals.

The quantity of suspended solids produced as a function of pH in a 4-h time interval is shown in Fig. 15. This figure emphasizes the marked decrease in solids formation as the brine is acidified to a pH <4.6. Over 400 ppm of solids precipitated from unmodified brine (pH >5.8); however, acidification of the brine to a pH <4.6 reduced solids production to <30 ppm.

The effect of acidification on the redissolving of precipitated solids was also investigated. In this experiment, a 19-liter sample of brine was taken from Magmamax No. 1 well and allowed to cool to ambient temperature. Aliquots of the brine, together with its suspended solids, were then treated with acid at various temperatures and for varying periods of time. The unmodified brine contained 580 ppm of suspended solids. The experiments showed that less than one-third of the solids redissolved when the brine was acidified with 1.0 M HCl and 0.1 M HNO₃.

In conclusion, the acidification of hot Magmamax No. 1 brine to a pH <4.6 inhibits the formation of suspended solids and seems to be a promising technique for the control of solids production. However, the solids do not redissolve readily after they precipitate even in 1.0 M HCl and 0.1 M HNO₃. Therefore, it does not seem practical to try to remove solids from cold brine by redissolving them with acid.

Fig. 15. Solid precipitation as a function of pH in separated brine at 85°C in 4 h.

Electrochemical Corrosion Tests in Geothermal Brines

Responsible Personnel: J. E. Harrar, A. Goldberg,* and R. D. McCright*

Brief Description: The corrosion rates of alloys that are candidates for use in a geothermal power plant are being measured in hypersaline geothermal brine by the linear polarization resistance technique. The effect of scaling is also being studied. On-line measurements of the pH and redox potential (E_h) of the brine, and the corrosion potentials of the test materials are also being obtained. All measurements are being carried out in the field at the LLL Geothermal Test Facility.

Status: Various programs are presently underway to test and select corrosion-resistant materials for use in a geothermal power plant that could be operated with the high-salinity geothermal brine of the Imperial Valley of California. The effects and control of scaling, and analytical characterization of the brine are also subjects of investigation.[†] We have initiated a project to use electrochemical techniques to provide additional information for these programs.

The first field tests in the electrochemical project were conducted in October and November using brine from Magmamax No. 1 well. The measurements were made in the separated, effluent brine, i.e., brine that has been reduced to atmospheric pressure, $\sim 100^\circ\text{C}$, and separated from the steam. The brine is low in total sulfide because most of the H_2S is flashed with the steam. The properties of both unmodified (pH ~ 5.5) and acidified (pH < 4.5) brine were studied. The main objectives of this investigation were (a) to determine the feasibility of the linear polarization-resistance (LPR) technique²² for measuring corrosion rates in the geothermal brine, (b) to use the LPR technique to rapidly compare the corrosion resistance of a number of candidate alloys, (c) to ascertain the effects of scaling on corrosion rates, and (d) to determine the feasibility and usefulness of the on-line measurement of pH, solution redox potential (E_h), and corrosion potentials of the test materials.

*Metals and Ceramics Division, LLL.

[†]See p. 37 of Ref. 20 and previous article of this report.

22. F. Mansfeld, in Advances in Corrosion Science and Technology, M. G. Fontana and R. W. Staehle, Eds. (Plenum Press, New York, 1976), Vol. 6.

Figure 16 is a schematic diagram of the apparatus and instrumentation used to measure the corrosion and brine parameters. The test cell, through which the brine flowed continuously, was fabricated from polycarbonate plastic. Corrosion rates were measured by means of a Petrolite Instruments Company M-103 corrosion-rate instrument and a probe assembly with interchangeable electrodes. These electrodes are fabricated from the test material. The E_h and the corrosion potentials of the corroding specimens were measured vs the SCE by means of a digital voltmeter. As shown in Fig. 16, the components for measuring the other parameters are fairly conventional, but they were required to operate in the field and in the cell at $\sim 100^\circ\text{C}$.

An example of the data obtained by the corrosion-rate measurement is shown in Fig. 17. For some materials, corrosion rates are reproducible to only $\pm 30\%$, and sometimes it takes a few days to reach steady-state, but in general the technique appears to be quite valid and useful. High, medium, and low corrosion-rate materials can easily be distinguished. The LPR technique produces information much more rapidly than weight loss methods; we were able to test 17 materials in 6 working days. Measurement of the corrosion potentials is also valuable; these data are useful in indicating galvanic and pitting-type corrosion phenomena, and can be correlated with material behavior indicated by the LPR measurements.

The LPR technique was also used to monitor the effect of pH on corrosion rates. The data are only preliminary, but it appears that pretreatment of the metal with low temperature, unmodified brine provides a significant degree of protection against corrosion in the acidified brine. Under these conditions a silica-rich scale is laid down on the surface of the metal.²³ This scale retards corrosion and is not completely dissolved upon acidification of the brine.

Measurements of the pH and E_h of the brine also have been quite useful in characterizing the brine itself and in providing experience with the problems that will be encountered when these parameters are monitored in more sophisticated facilities. We found that both measurements (pH with a glass combination electrode, and E_h with a platinum electrode) were reliable as long as the pH of the brine was less than ~ 4.6 . Above that value, scaling rendered

23. L. B. Owen, Precipitation of Amorphous Silica from High-Temperature, Hypersaline Geothermal Brines, Lawrence Livermore Laboratory Rept. UCRL-51866 (1975).

Fig. 16. System for measuring corrosion parameters and brine characteristics.

Fig. 17. Corrosion rates of a mild steel and a high chromium alloy in modified effluent brine (100°C and pH 2.1-4.5).

the electrodes inoperative. In an operating plant, good control of the pH at lower values, short exposure times, and/or periodic cleaning of the electrodes will be required. Because there is less scaling, a higher temperature exposure would also be beneficial.

Further work will include measurements in "remixed" effluent brine (brine remixed with the steam), additional scaling studies, longer-term tests, and tests in brine with its redox potential modified to prevent scaling. Extensive field studies are mandatory for this work because the complexity of the composition of the brine* and its instability when drawn from the well make it impossible to simulate accurately in the laboratory.

*See p. 37 of Ref. 20.

Identifying Carbonate Minerals in Oil Shales

Responsible Personnel: R. Lim, L. J. Gregory, K. L. Leach, and S. Deutscher

Brief Description: A method proposed by Young, Smith, and Robb²⁴ of the U.S. Bureau of Mines for determining the carbonate minerals in oil shales has been investigated. It has been applied to the Anvil Points oil shales of the LLL program and those of the Colorado Green River Formation. We have compared our results with those obtained by acid-evolution of carbon dioxide.

Status: A complete material characterization is essential for calculations in the LLL Oil Shale Program. Carbonate minerals constitute a major fraction of the oil shale. It is necessary to quantitatively determine each carbonate constituent because each mineral has a different thermal activity at different temperatures. Carbonate minerals found in oil shale are nahcolite (NaCO_3), dawsonite [$\text{NaAl}(\text{OH})_2\text{CO}_3$], dolomite [$(\text{Mg}_{1-x}\text{Fe}_x)\text{Ca}(\text{CO}_3)_2$], calcite (CaCO_3), and ferroan [$(\text{Mg}_{1-x}\text{Fe}_x)\text{CO}_3$]. Direct determination of these minerals is complicated because there are iron and magnesium cations in two of the minerals.

Young, Smith, and Robb²⁴ reported a method for the determination of carbonate minerals in Green River Formation oil shale. Their method is based on successive leaching of the sample with water and acid. The water extracts sodium from nahcolite. The acid treatment extracts sodium from dawsonite, and calcium, magnesium, and iron from dolomite, calcite, and ferroan. The cations are determined individually by atomic absorption and flame emission spectrophotometry. The quantities of the respective carbonate minerals can be calculated from this information.

We have used this method to analyze oil-shale samples from the Anvil Points mine in Colorado. We compared these results with values for the total carbonate determined by acid evolution of CO_2 (see Table 9). Water-soluble carbonates were leached and determined separately. In most cases the quantities of minerals calculated from the cation values were higher than found by acid evolution of CO_2 .

24. N. B. Young, J. W. Smith, and W. A. Robb, Determination of Carbonate Minerals of Green River Formation Oil Shales, Piceance Creek Basin, Colorado, U.S. Bureau of Mines Rept. 8008 (1975).

Table 9. Carbon dioxide calculated from acid leach cation values and measured by acid evolution. LLL oil-shale samples.

Sample	Carbon dioxide calculated from cation values, wt%	Carbon dioxide determined by acid evolution, wt%	Ratio of cation CO ₂ to acid CO ₂
T-3	27.02	23.76	1.137
T-4	22.36	18.62	1.201
T-5	11.07	12.32	0.899
T-6	27.35	23.41	1.168

Because we thought that our oil shale samples might be significantly different from the Green River oil shale, samples of the latter were obtained from the U.S. Bureau of Mines in Laramie and were analyzed by the same procedures. In this work we determined amounts of CO₂ evolved on water treatment, CO₂ evolved on acid treatment of the water soluble portion of the oil shale, and CO₂ evolved on acid treatment of the water insoluble portion of the oil shale. Cations were determined in both the water-soluble and water-insoluble portions by atomic absorption spectrophotometry.

The amounts of cations tend to be somewhat higher than those reported by the USBM investigators.²⁴ Good agreement for all samples was found only for magnesium. The greatest discrepancy (a factor of two) between the two laboratories was for the amount of sodium in one of the samples. This sample was found to contain high levels of chloride, which suggested the presence of halite (NaCl). Therefore, a correction was applied in the calculation of the associated CO₂ value for this sample. But we have not corrected all of our cation results for possible interference by non-carbonate minerals.

In an attempt to better understand these differences, we also performed a series of acid extractions with 6 M HCl at temperatures of 90 and 70°C (15 min. each). These conditions more closely duplicated those used by the USBM. We determined calcium by atomic absorption in these acid extractions because it showed the largest discrepancy and its accurate determination was of greatest importance to the LLL program. To assure ourselves that all calcium had been extracted, all samples were extracted a second time with 6 M HCl at the appropriate temperature, and the extract analyzed for calcium.

No significant amounts of calcium were found in the second extractions. On the basis of these results we conclude that:

- Increasing the acid concentration results in a more complete calcium extraction.
- With 6 M HCl, the extraction is virtually complete in 15 min and independent of the extraction temperature in the range of 70 to 90°C.
- Even when we use a nearly identical extraction procedure (6 M HCl for 15 min at 90°C), we find more calcium than USBM.

We cannot readily account for our higher extraction efficiency since we used virtually the same USBM procedure, including sample preparation and particle size. Our direct determination of total CO₂ in the Green River oil shale samples agrees well with the Laramie results. As expected, our results for CO₂ calculated from the cation values tend to be somewhat higher than Laramie's calculated results. We are continuing this work to resolve the discrepancy between our results and those of the USBM.

Numerical Studies of Combustion Processes

Responsible Personnel: J. R. Creighton

Brief Description: An analytic model of the induction period in methane combustion has been developed from a detailed chemical kinetics model. From this analytic model a two-reaction, four-chemical-species model of methane combustion was developed for use in two-dimensional combustion codes.

Status: The overall goal of our program is to develop computer codes to model combustion processes, especially for the internal combustion engine, but also for flames, flow reactors, shock tubes, and other significant combustion devices.* We are responsible for furnishing detailed chemical kinetic schemes for various fuels and simplified kinetics models for the combustion of these fuels.

The kinetics of methane combustion have been emphasized because methane appears to be the practical fuel with the simplest kinetics. Previously,¹⁰ we described a detailed chemical kinetics scheme for methane combustion that agreed rather well with experiment. (Much of the comparison with experiment was done by C. K. Westbrook of T-Division, LLL.) In the past quarter, the kinetics of formaldehyde pyrolysis and combustion was studied to refine the methane combustion model. However, the major accomplishment was the completion of a simple analytic model²⁵ of the kinetics of methane combustion. This model involves seven elementary reactions, and can accurately predict the induction period of methane oxidation in shock tubes. This model has been further simplified to a two-reaction, four-chemical-species model for use in large combustion codes.

This model can be solved to give the induction time for methane combustion. The chemical equations will also give a reasonable representation of the energy release during combustion, but the rapidly changing temperature and major species concentrations cause the rate equations to become highly

*See p. 30 of Ref. 21.

25. John R. Creighton, Investigation of the Relationship Between Quasi-global and Detailed Kinetics Mechanisms for the Combustion of Methane, Lawrence Livermore Laboratory, Rept. UCRL-78424 (1976); presented at the 1976 Fall Meeting of the Eastern Section of the Combustion Institute.

nonlinear so that they cannot be solved analytically. A two-reaction, four-chemical-species, simplified model has been obtained from the analytic model. This simplified model is required for two- and three-dimensional combustion codes when one cannot afford the computer time to solve a detailed chemical kinetics scheme. The two reactions are

where F is the fuel, O the oxidizer, R a radical, and P the products. These reactions can describe any chain reaction involving oxidation, provided the numerical coefficients for the oxidizer are properly adjusted. These are not elementary reactions, so the reaction rates may be complicated functions of the species concentrations. The rate for the first reaction has contributions from the dissociation of methane and combustion, which is proportional to the radical density. The reaction cannot begin until the temperature becomes high enough to promote significant dissociation. Once some radicals are available, branching chain reaction leads to combustion; however, at low temperature this is exceedingly slow. In methane combustion the destruction of one radical in the second reaction leads to creation of more than one additional radical. This can be handled by making the combustion rate in the first reaction a multiple of the rate of the second reaction. This model combines the desirable features of the single Arrhenius reaction-rate model and the autocatalytic model. The rates and rate constants can be correlated with the rate constants of a detailed kinetics model. A complete reaction can be calculated with this model about 20 times faster than with a detailed kinetics model.

The oxidation mechanism for CO was studied with the hope that an analytic model could be developed for it. We found that there are a number of radical reactions that make the rate equations nonlinear so no analytic model was obtained.

Studies of the pyrolysis of formaldehyde indicated some differences between calculation and experiment, which could not be resolved. This could indicate an incorrect kinetic mechanism in the calculation, or problems in experimental technique. Experiments currently under way at Princeton

University may help resolve this discrepancy. The pyrolysis of formaldehyde is not an important part of the methane combustion mechanism, although the oxidation of formaldehyde is. Calculations of the combustion of formaldehyde agree with experiment.

Biosolar Production of Fuels from Algae

Responsible Personnel: B. J. Berger,* T. W. Jeffries,[†] P. H. Moulthrop,**
H. Timourian,[†] and R. L. Ward

Brief Description: During the past year we have evaluated the idea of producing biofuels using photosynthesis. Blue-green algae are of great interest for this purpose because of their high photosynthetic efficiency. Under appropriate conditions, these algae can be induced to split water to form H₂ and O₂ using solar energy as their primary energy source. The exhausted algae can then be converted to CH₄ and CO₂ by anaerobic digestion. Based on our evaluation, we think that a long-range study of such a process for producing renewable fuels would be appropriate, and the potential of biofuels as an alternative to fossil and nuclear fuels should be determined.

Status: This is a new program established as a result of our studies under the auspices of the Energy and Resource Planning Group of LLL. Specific objectives of this group are 1) to develop an understanding of national and international needs for research and development in energy and other resource areas of civil concern, 2) to propose specific research and development projects for LLL to fill those needs, and 3) to respond to ERDA requirements for assessment studies. The context of the group's work is to assess technological issues and opportunities within the broader framework of the social and economic impacts of new technologies on the nation. Because of the existing laboratory capabilities, we decided to examine biological processes that could be useful in energy production, storage, and conservation. Our studies in this area deal with the possible production of biofuels based on photosynthesis, nature's oldest solar conversion process.

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Microscopic blue-green algae are a potential source of such fuels. The familiar scum observed on stagnant ponds is a mixed population of green and blue-green algae. The blue-green algae are of particular interest because of their ability to use atmospheric nitrogen for growth. The production rate of biomass per unit area by this group can exceed that of any other known plant. Blue-green algae can be grown on sewage or other nutrient sources, and the biomass subsequently converted into methane gas by a fermentation process. Fixed nitrogen can be produced as a byproduct of the fuel-conversion step. Alternatively, in an inert atmosphere of argon, the algae can be induced to split water through biophotolysis to form O_2 and H_2 .

Biofuels are the only significant, long-term, renewable source of organic fuels. They include fuels obtained from the conversion of waste materials, plants grown specifically for use as fuel, and hydrogen gas produced by biological processes. The reclamation of organic wastes is a growing, albeit small, source of energy. Prospects for renewable biofuel production depend on capital and operating costs for biomass production, on competition with agricultural crops for land and water resources, and on the photosynthetic efficiency that can be achieved.

We are interested in blue-green algae for their potential contribution to renewable biofuel resources because of their high photosynthetic efficiencies, their ability to use water resources unacceptable to agricultural crops (e.g., saline ground and surface waters), and their potential for being used in advanced solar bioconversion systems.²⁶

We have suggested a system (see Fig. 18) for integrating methane production from algae biomass with hydrogen production by biophotolysis. In this scheme, algae biomass would be grown on inorganic nutrients derived from sewage or process recycling. Carbon dioxide would be obtained from biological- or industrial-waste sources. The algae biomass could be harvested by a combination of microscreening and autoflocculation processes and subsequently passed into the bioconverter stage. Under appropriate conditions, the algae would be induced to split water to form H_2 and O_2 gases. The exhausted cells would then be transferred to an anaerobic digester

26. T. W. Jeffries, P. H. Moulthrop, H. Timourian, R. L. Ward and B. Berger, Biosolar Production of Fuels from Algae, Lawrence Livermore Laboratory Rept. UCRL-52177 (1976).

Fig. 18. Biosolar production of fuels from algae.

where the remaining biomass would be converted to CH_4 and CO_2 . Fixed nitrogen would be recovered from the effluent digester sludge.

Several technically difficult steps would have to be solved, however, for this integrated process to be practical. Productivity must be high enough to justify the costs of pond construction. Also, the microalgae harvest methods must be efficient and inexpensive enough to keep the total cost of algae biomass to a minimum. At present, this is believed possible if filamentous cells can be maintained in culture. Finally, although the hydrogen-producing reaction has been demonstrated by several laboratories, its conversion efficiency must be markedly improved. Organic fuels derived from biomass will not be economically competitive with fossil fuels for several decades, but as the fossil fuels are depleted, biomass fuels will become essential. Production of biomass from algae may be one of the most efficient ways to provide such fuels. And inasmuch as there are major technological problems to be overcome in achieving an economical algae production method, it is probably not too soon to begin a serious R&D effort in this field.

1976 PUBLICATIONS AND PRESENTATIONS OF THE GENERAL CHEMISTRY DIVISION

Journal Publications

G. W. Barton, Jr.	Systems Evaluation	<i>ASTM Stand. News</i> <u>4(5)</u> , 19 (1976)
G. W. Barton, Jr.	Reflections on the "Forms of Sounds"	<i>Amer. J. Phys.</i> <u>44</u> , 593 (1976)
J. H. Richardson B. W. Wallin* D. C. Johnson* L. W. Hrubesh	Sub-Part-Per-Trillion Detection of Riboflavin by Laser Induced Fluorescence	<i>Anal. Chim. ACTA</i> <u>86</u> , 263 (1976)
E. A. Rinehart [†] J. H. Richardson D. C. Johnson* L. W. Hrubesh	Experimental Evidence of Laser-Induced Separations in Bulk Gas Mixtures	<i>Appl. Phys. Lett.</i> <u>28</u> , 131 (1976)
H. F. Schaefer III** C. F. Bender ^{††} J. H. Richardson	A Peroxy Isomer of Nitrogen Dioxide	<i>J. Phys. Chem.</i> <u>80</u> , 2035 (1976)
W. Selig	Lower Limits of the Potentiometric Microtitration of Chloride with Silver Ions	<i>Microchem. J.</i> <u>21</u> , 291 (1976)
W. Selig	Determination of Microgram Amounts of Orthophosphate Using Ion-Selective Electrodes	<i>Mikrochim. Acta</i> 1976 II, 9
W. Selig	Semimicro Determination of Hydroxy and Amino Compounds Using Pyromellitic Dianhydride	<i>Microchem. J.</i> <u>21</u> , 92 (1976)
R. G. Meisenheimer	Some 14 MeV Neutron Sputtering Characteristics of a Polycrystalline Niobium Sample	<i>J. Nucl. Mater.</i> <u>63</u> , 429 (1976)
R. G. Meisenheimer J. W. Fisher S. J. Rehfeld [‡]	Thallium in Human Erythrocyte Membranes: An X-Ray Photoelectron Spectroscopy Study	<i>Biochem. Biophys. Res. Commun.</i> <u>68</u> , 994 (1976)
L. W. Hrubesh R. F. Curl ^{§§}	Microwave Spectrum of NO ₂ in the $v_2=1$ State	<i>J. Mol. Spectry.</i> <u>61</u> , 144 (1976)

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Journal Publications (Continued)

R. W. Gaver*	Quantitation of Manganese (II)	<i>J. Environmental Sci. and Health</i> <u>A2(12)</u>
F. P. Milanovich†	Ion Binding to Dissolved	(1976)
R. L. Ward	Yellow Organic Substances of Natural Waters by Electron Spin Resonance	
J. A. Fee**	Evidence for a Coordination	<i>Biochem. Biophys. Res. Commun.</i> <u>71</u> , 427
R. L. Ward	Position Available to Solute Molecules on One of the Metals at the Active Center of Reduced Bovine Superoxide Dismutase	(1976)
E. F. Worden	The Emission Spectrum of Curium	<i>Atomic Data and Nuclear Data Tables</i> <u>18</u> , 459 (1976)
E. K. Hulet††		
R. G. Gutmacher		
J. G. Conway‡		
L. R. Carlson	Radiative Lifetimes, Absorption	<i>J. Opt. Soc. Am.</i> <u>66</u> , 846 (1976)
J. A. Paisner‡‡	Cross Sections, and the Observation of New High-Lying Odd Levels of ²³⁸ U Using Multistep Laser Photoionization	
E. F. Worden		
S. A. Johnson ^u		
C. A. May ^{uu}		
R. W. Solarz‡‡		
R. W. Solarz‡‡	Detection of Rydberg States in Atomic Uranium Using Line Resolved Stepwise Laser Photoionization	<i>Phys. Rev.</i> <u>A14</u> , 1129 (1976)
C. A. May ^{uu}		
L. R. Carlson		
E. F. Worden		
S. A. Johnson ^u		
J. A. Paisner‡‡		
L. J. Radziemski ^d		
E. F. Worden	Energy Levels of the First Spectrum of Curium, Cm I	<i>J. Opt. Soc. Am.</i> <u>66</u> , 109 (1976)
J. G. Conway‡		

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Journal Publications (Continued)

J. E. Harrar	An Automated Sample-Processing	<i>J. Inst. Nucl. Mat.</i>
W. G. Boyle	and Titration System for the	<i>Man.</i> <u>5(3)</u> , 199 (1976)
J. D. Breshears*	Determination of Uranium	
C. L. Pomernacki*		
H. R. Brand		
A. M. Kray*		
R. J. Sherry [†]		
J. A. Pastrone [†]		
J. E. Harrar	Computer-Controlled Instrumen-	<i>Chem. Instrum.</i> <u>7</u> , 229
C. L. Pomernacki*	tation for Automated Controlled- (1976)	
	Current Coulometry, Potentiometry,	
	and Galvanostatic Measurements	

Miscellaneous Publications

G. W. Barton, Jr.	Sample Management Programs	Office of Research
H. S. Ames*	for the Laboratory Automation	and Development
	Minicomputer	Automatic Data Pro-
		cessing Workshop
		Proceedings, No. 2,
		Environmental Protec-
		tion Agency Rept.
		EPA-600/9-76-008
		(1976) pp. 76-78.

ERDA Reports

C. A. Colmenares	Equilibrium Water Vapor	UCID-17049
L. C. McDavid [†]	Pressure and Total Moisture	February, 1976
	Content Measurements on TATB	
R. J. Bastasz	A LEED and AES Study of the	UCRL-78772 (Preprint)
C. A. Colmenares	Structural, Debye Temperature,	October, 1976
R. S. Smith [†]	and Oxidation of the (111)	
G. A. Somorjai**	Crystal Face of Thorium	
R. W. Ryon	Improved Detection Limits in	UCRL-78063 Rev. 1
	Energy Dispersive X-Ray	September, 1976
	Fluorescence Analysis, Using	
	Polarized X-Rays	
J. R. Creighton	Investigation of the Relation-	UCRL-78524 (Preprint)
	ship between Quasi-Global and	November, 1976
	Detailed Kinetics Mechanisms	
	for the Combustion of Methane	

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ERDA Reports (Continued)

W. Selig	Semimicro Determination of Hydroxy and Amino Compounds Using Pyromellitic Dianhydride	UCRL-77367 Rev. 1 April, 1976
W. Selig (ed.)	Some Analytical Methods for Explosives, Part V	UCRL-7873 Part V September, 1976
W. Selig	Lower Limits of the Potentiometric Titration of Perchlorate Using a Perchlorate Ion-Selective Electrode	UCRL-78326 (Preprint) June, 1976
T. W. Jeffries*	Biosolar Production of Fuels from Algae	UCRL-52177 November, 1976
P. H. Moulthrop†		
H. Timourian*		
R. L. Ward		
B. J. Berger**		
R. G. Meisenheimer	Some Fusion Device Materials Research at Lawrence Livermore Laboratory	UCRL-78322 (Preprint) September, 1976
R. G. Meisenheimer	A Lawrence Livermore Laboratory Contribution to the Joint Publications on the Round-Robin Neutron Sputtering Experiments	UCRL-78396 (Preprint) July, 1976
R. H. Sanborn	MO200: A Model for Evaluating Safeguards through Material Accountability for a 2000 Tonne per Year Mixed-Oxide Fuel-Rod Fabrication Plant	UCRL-77495 March, 1976
R. W. Crawford	Computer-Aided Quality Control for AutoAnalyzers	UCRL-78778 (Preprint) October, 1976
L. B. Lohring††		
H. S. Ames‡	Specification for the Development of a Spectroscopy Facility for Y-Division	UCIR-1018 May, 1976
G. R. Haugen		
R. I. Bystroff		

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ERDA Reports (Continued)

H. S. Ames*	Computer Automation of Multi-channel AutoAnalyzers	UCRL-78609 Preprint August, 1976
R. W. Crawford		
H. S. Ames*	A Feasibility Study for the Computerized Automation of the Annapolis Field Office of EPA Region III	UCRL-52052 August, 1976
G. W. Barton, Jr.		
R. I. Bystroff		
R. W. Crawford		
A. M. Kray*		
M. D. Maples*		
R. W. Crawford	Technicon AutoAnalyzers: Functional Description	UCRL-52046, April, 1976
G. W. Barton, Jr.		
R. W. Crawford	Sample File Control: Functional Description	UCRL-52047 April, 1976
H. S. Ames*		
R. W. Crawford	Total Organic Carbon Analyzer: Functional Description	UCRL-52045 April, 1976
L. P. Rigdon		
R. I. Bystroff	Atomic Absorption Instrument Functional Description	UCRL-52065 April, 1976
W. G. Boyle, Jr.		
G. W. Barton, Jr.		
W. F. Morris	Feasibility Study for Automation of the Central Laboratories, Water Resources Division, U.S. Geological Survey	UCRL-52001 January, 1976
E. S. Peck		
E. R. Fisher*		
G. W. Barton, Jr.		
H. A. Golopol	A New Booster Explosive, LX-15	UCRL-52175 December, 1976
D. B. Fields [†]		
G. L. Moody [†]		
H. G. Hammon [†]	Noble Gas Permeability of Polymer Films and Coatings	UCRL-78027, Preprint April, 1976
K. Ernst		
J. C. Newton		
G. M. Hieftje**	New Method for the Determination of Luminescence Lifetimes by Using the Beat Noise of a CW-Laser as a Multifrequency Modulated Source	UCRL-78700, Preprint October, 1976
G. R. Haugen		
J. M. Ramsey**		
L. W. Hrubesh	NH ₃ Preconcentrator/Integrator Instruction Manual	UCID-17174 June, 1976
V. C. Barton*		
C. J. Morris		
D. D. Jackson ^{††}	Possibilities for Controlling Heavy Metal Sulfides in Scale from Geothermal Brines	UCRL-51977 January, 1976
J. H. Hill		

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R. G. Bedford	The Vapor Pressure of Uranium Tetrakis (2,2,6,6-Tetramethyl heptane-3,5-dionato)	UCRL-77990, Rev. 1, Preprint December, 1976
R. W. Mar*	The Sublimation of Boron	Sandia Laboratories Report, SAND 76-8503 August, 1976
R. G. Bedford		
R. G. Bedford	The Sublimation of Bis(η^8 -1,3,5,7-cyclooctatetraene) Uranium (Uranocene)	UCRL-77947, Rev. 1 Preprint March, 1976
E. B. Huss		
J. H. Richardson	Spectroscopic Properties of Gas Phase Molecular Ions	UCRL-78209 Preprint May, 1976
J. H. Richardson	Dynamics of Variably Pulse-Pumped Dye Laser	UCRL-78398, Preprint October, 1976
L. L. Steinmetz†		
B. W. Wallin**		
J. H. Richardson	The Effect of Stress on the Fluorescence of Kevlar Fiber	UCID-17333 October, 1976
G. R. Haugen		
L. S. Penn††		
J. H. Feikert**		
R. J. Sherry**		
L. R. Carlson	Determination of Absolute Transition Probabilities Using Time Resolved Optical Pumping	UCRL-78662 Preprint November, 1976
J. A. Johnson		
E. F. Worden		
C. A. May‡		
R. W. Solarz‡‡		
J. A. Paisner‡‡		
J. W. Frazer ^u	Equivalence-Point Determinations for Automated Potentiometric Titrations Using Ion-Selective Electrodes	UCRL-78773 Preprint October, 1976
W. Selig		
L. P. Rigdon		
J. E. Harrar	Studies of Factors Affecting Uranium Determinations by Automated Coulometric Titration (New Brunswick Laboratory/Davies-Gray Method)	UCRL-52060 April, 1976
W. G. Boyle		

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ERDA Reports (Continued)

Presentations

C. A. Colmenares [†] R. J. Bastasz	Practical Aspects of Photo-electron Spectroscopy	Lecture Series, JOWOG-12B Meeting, Aldermaston, England October, 1976
C. A. Colmenares	Surface Science Research at the Lawrence Livermore Laboratory	JOWOG-12B Meeting, Aldermaston, England October, 1976
C. A. Colmenares R. H. Pritchard [†]	Accelerated Aging of Detonators at Several Temperatures	ERDA-Wide Compati- bility Meeting, Albuquerque, New Mexico, October 1976.
R. W. Ryon	Polarized Source Radiation Produced by Scatter for Energy Dispersive X-ray Fluorescence Trace Analysis	Conference on Applications of X-ray Analysis, Denver, Colorado, August 1976.
G. W. Barton, Jr.	The EPA Water Quality Laboratory Automation Project	Conference on Analytical Chemistry and Applied Spectro- scopy, Cleveland, Ohio, March, 1976.
G. W. Barton, Jr. [†] W. F. Morris W. L. Budde**	The EPA-ERDA Water Quality Laboratory Automation Project	Conference on Analytical Chemistry in Energy and Environmental Tech- nology, Gatlinburg, Tennessee, October, 1976.
W. Selig	Semimicro Determination of Hydroxy and Amino Compounds Using Pyromellitic Dianhydride	Meeting of JANNAF Propellant Character- ization Working Group, Picatinny Arsenal, Dover, New Jersey, June, 1976.

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Presentations (Continued)

R. G. Meisenheimer	Fusion Device Materials Research at the Lawrence Livermore Laboratory	American Vacuum Society Meeting, Chicago, Illinois, September, 1976.
R. G. Meisenheimer	Neutron Sputtering	Argonne National Laboratory Faculty Institute on Fusion Technology, Chicago, Illinois, August, 1976.
R. G. Meisenheimer	Measurement of CTR Wall Sputtering	Conference on Surface Studies, Los Alamos Scientific Laboratory, Los Alamos, New Mexico, March, 1976.
R. G. Meisenheimer	D-T Neutron Sputtering	International Neutron Sputtering Workshop, San Francisco, CA, February, 1976.
R. G. Meisenheimer	Some 14 MeV Neutron Sputtering Characteristics of Polycrystalline Niobium Samples	International Conference on Surface Effects in Controlled Fusion Devices, San Francisco, February, 1976.
R. G. Meisenheimer* J. W. Fischer	Sulfur Speciation by X-ray Photoelectron Spectroscopy	Conference on Analytical Chemistry in Energy and Environmental Technology. Gatlinburg, TN, October, 1976.
R. L. Morrison	Continuous Water Monitor for Oil-Shale Retort Effluent	Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, TN, October, 1976.
R. L. Morrison	Detection and Identification of Explosives	Northern California Criminalists Association Meeting, Pleasanton, CA, July, 1976.
R. H. Sanborn	MO200: A Model for Evaluating Safeguards through Material Accountability for a 2000 Tonne per Year Mixed-Oxide Fuel Rod Fabrication Plant	1976 Summer Computer Simulation Conference Washington, DC, July, 1976.

* Speaker

Presentations (Continued)

R. W. Crawford*	Computer-Aided Quality Control	Technicon International
L. B. Lobring [†]	for AutoAnalyzers	Congress, New York,
		December, 1976.
R. W. Crawford*	Computer Automating the	Conference on
H. S. Ames**	AutoAnalyzer	Analytical Chemistry
W. F. Morris		in Energy and Environ-
L. P. Rigdon		mental Technology
		Gatlinburg, TN,
		October, 1976.
H. S. Ames**	Multi-Channel, Multi-User	Conference on
R. W. Crawford*	Computer Automation for	Analytical Chemistry
W. F. Morris	Technicon AutoAnalyzers	and Applied Spectros-
L. P. Rigdon		copy, Cleveland,
		Ohio, March, 1976.
H. A. Golopel	Hexanitrostilbene (HNS) as a	Explosives Safety
	Booster Explosive	Engineering Conference
		Livermore, CA,
		May, 1976.
G. R. Haugen	Nanosecond Fluorimetry: Past,	Seminar, California
	Present, and Future	State University at
		Northridge, September,
		1976.
R. J. Bastasz*	The Mean Displacement and	Conference on Surface
C. A. Colmenares	Debye Temperature of a Thorium	Studies, Los Alamos,
R. L. Smith ^{††}	(111) Surface	New Mexico, March,
G. A. Somorjai [‡]		1976.
R. J. Bastasz*	The Structure and Chemisorption	American Chemical
C. A. Colmenares	Characteristics (CO and O ₂) of	Society Meeting, San
G. A. Somorjai [‡]	the (111) Crystal Face of	Francisco, CA,
R. L. Smith ^{††}	Thorium	August, 1976.
R. J. Bastasz	A New Surface Structure from a	Seminar, Lawrence
	Thorium (111) Crystal	Berkeley Laboratory,
		May, 1976.
R. J. Bastasz	Structure and Reactivity of	Seminar, Lawrence
	Solid Surfaces of Thorium	Berkeley Laboratory,
		November, 1976.

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Presentations (Continued)

R. L. Ward	How Biological Nitrogen Fixation and Increased Photosynthesis Efficiency Will Lead to Increased Crop Yields	California Dietetic Association Meeting, Walnut Creek, CA, November, 1976.
L. W. Hrubesh* D. C. Johnson [†] E. A. Rinehart**	Stark Shift Laser Spectroscopy at Submillimeter Wavelengths for Chemical Analysis	International Conference and Winter School on Submillimeter Waves and Their Applications, San Juan, Puerto Rico, December, 1976.
L. W. Hrubesh	Advances in Microwave Rotational Spectrometry Applied to Gaseous Pollutant Measurements	American Chemical Society Meeting, New York, April, 1976.
L. W. Hrubesh* A. S. Maddux ^{††} V. C. Barton ^{††}	Automated Gas Mixture Analysis with Microwave Rotational Spectroscopy	Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tennessee, October, 1976.
L. W. Hrubesh* J. C. Kantor [‡]	Microwave Spectrometry for Process Control Applications	Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, Ohio, March, 1976.
J. R. Creighton	Investigation of the Relationship between Quasi-Global and Detailed Kinetics Mechanisms for the Combustion of Methane	Meeting of Eastern Section of the Combustion Institute, Philadelphia, November, 1976.
J. R. Creighton	How to Present 100 Simultaneous Variables in a Computer Generated Movie	Symposium on Computer Use by Engineers, Albuquerque, New Mexico, October, 1976.
J. R. Creighton	Chemistry and Materials Science Department Resources for Combustion Calculations	Symposium on Reactive Fluid Dynamics, Livermore, CA, May, 1976.

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J. R. Creighton	Elucidation of Reaction Mechanisms by Computer Solution of Chemical Kinetics Rate Equations	American Chemical Society Meeting, San Francisco, August, 1976.
J. R. Creighton	LLL Chemistry and Materials Science Department Resources for Combustion Calculations	Meeting of the Direct-Injection Stratified-Charge Engine Cooperative Research Project, Livermore, CA, June, 1976.
E. F. Worden* L. R. Carlson S. A. Johnson [†]	Non-Uranium Actinide Spectroscopy with Lasers	Symposium on Actinide Atomic Spectra, Argonne, Illinois, May, 1976.
L. R. Carlson* E. F. Worden S. A. Johnson [†]	High Lying Levels in Atomic Uranium	Symposium on Actinide Atomic Spectra, Argonne, Illinois, May, 1976.
L. R. Carlson* E. F. Worden S. A. Johnson [†] C. A. May** R. W. Solarz ^{††} J. A. Paisner ^{††}	Radiative Lifetimes, Transition Strengths, and the Observation of New High Lying Odd Levels in Atomic Uranium	International Conference on Atomic Physics, Berkeley, CA, July, 1976.
J. A. Paisner*, ^{††} L. R. Carlson E. F. Worden S. A. Johnson [†] C. A. May** R. W. Solarz ^{††} L. J. Radziemski [‡]	Observation and Behavior of Very High Lying States in Atomic Uranium	International Conference on Atomic Physics, Berkeley, CA, July, 1976.
R. W. Solarz*, ^{††} J. A. Paisner ^{††} C. A. May** L. R. Carlson	Autoionization Phenomena, Field-Ionization Spectroscopy, Behavior of High Lying States of UI in DC Electric Fields	Symposium on Actinide Atomic Spectra, Argonne, Illinois, May, 1976.
R. W. Solarz*, ^{††} J. A. Paisner ^{††} L. R. Carlson C. A. May** S. A. Johnson [†]	Multistep Laser Spectroscopy of Atomic Uranium	American Physical Society Meeting, New York, February, 1976.

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R. W. Solarz*, [†]	Observation on New Levels for	International Conference on Quantum
J. A. Paisner [†]	Isotope Separation in Atomic	Electronics, Washington, DC, June, 1976.
L. R. Carlson	Uranium by Multistep Ionization	
E. F. Worden		
S. A. Johnson**		
C. A. May ^{††}		
L. R. Carlson	Laser Spectroscopy of Atomic Uranium. Application to Laser Isotope Separation	Seminar, Naval Research Laboratory, Washington, DC, April, 1976.
G. C. Stevens	Recent Progress on Isotope Separation at the Lawrence Livermore Laboratory	Gordon Research Conference on Isotopes, Plymouth, New Hampshire, July, 1976.
R. G. Meisenheimer	Rutherford Backscatter Apparatus	Conference on Surface Studies, Los Alamos Scientific Laboratory, Los Alamos, NM, March, 1976.
J. A. Happe*	and Some Applications at LLL	
J. H. Richardson	Lasers in Chemical Analysis	Seminar, Pennsylvania State Univ., University Park, Penn. November, 1976.
J. H. Richardson*	Sub-Part-Per-Trillion Detection of Riboflavin by Laser Induced Fluorescence	Federated Analytical Chemistry and Spectroscopy Societies Meeting, Philadelphia, November, 1976.
B. W. Wallin [‡]		
D. C. Johnson [‡]		
L. W. Hrubesh		
R. I. Bystroff*	Computerization of a Spectroscopy Facility for Laser Glass Evaluation	Conference on Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tenn., October, 1976.
G. R. Haugen		
J. H. Richardson		
J. C. Newton		
S. L. Grotch	A New Technique for Improving Mass Spectral Searching	Seminar, U.S. Army Research Laboratories, Natick, Massachusetts, December, 1976.

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Presentations (Continued)

S. L. Grotch	The Use of "Faces" to Aid in Pattern Recognition Studies	Office of Naval Research Conference on Computer-Controlled Chemical Experimentation, University of Arizona, Tucson, Arizona, November, 1976.
S. L. Grotch	Recent Research in Pattern Recognition	Office of Naval Research Conference on Computer-Controlled Chemical Experimentation, University of Washington, Seattle, May, 1976.
J. E. Harrar*	An Automated Sample Processing and Titration System for the Determination of Uranium	Institute of Nuclear Materials Management Meeting, Seattle, Wash., June, 1976.
W. G. Boyle		
J. D. Breshears [†]		
C. L. Pomernacki [†]		
H. R. Brand		
A. M. Kray [†]		
R. J. Sherry**		SALE Meeting, New Brunswick, New Jersey, June, 1976.
J. A. Pastrone		International Atomic Energy Agency, Seibersdorf, Austria, September, 1976.
		CBNM, EURATOM, Geel, Belgium, September, 1976.
		Atomic Weapons Research Establishment, Aldermaston, England, September, 1976.
		Atomic Energy Research Establishment, Harwell, England, September, 1976.
J. E. Harrar	Electrochemical Corrosion Studies	Geothermal Review Meeting, Livermore, CA, December, 1976.

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J. H. Hill	Chemistry and Suspended Solids	Geothermal Review Meeting, Livermore, CA, December, 1976.
J. H. Hill*	Sampling a Two-Phase Geothermal	Conference on
C. J. Morris	Brine Flow for Chemical Analysis	Analytical Chemistry in Energy and Environmental Technology, Gatlinburg, Tenn., October, 1976.

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Available from
National Technical Information Service
U.S. Department of Commerce
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