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September through December, 1977

J. E. Harrar

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GENERAL CHEMISTRY DIVISION QUARTERLY REPORT

Analytical Research and Development for the Nuclear Explosive Programs

An Atomic Emission Source for Multielement Analysis

Responsible Personnel: R. I. Bystroff and L. R. Layman*

Brief Description: Glow discharge vaporization from tungsten wires coated with electrodeposited samples has been studied with atomic absorption spectrophotometry. The glow discharge, a deposition cell, and a microwave cavity have been combined into a single source device for vaporization studies by atomic emission.

Status: The method of electrodepositing samples on 0.25-mm-diameter tungsten wire was discussed in a previous report.¹ The Beenakker microwave cavity² is now in operation, and we have confirmed the ease of ionizing argon, neon, and helium. Deposits of calcium and strontium were vaporized in an atmospheric argon glow discharge atomizer³ using the configuration in Fig. 1 and the vaporized atoms were detected by atomic absorption spectrophotometry. The trace in Fig. 2 reveals that the vaporization rate is subject to large but relatively slow excursions that decrease in amplitude as the vaporization approaches completion. The arc column of the discharge wanders over the electrode surface with a similar frequency. This suggests that the vaporization takes place at one spot on the surface until that area is nearly clean and then the arc wanders to better sources of secondary electron emission. The integrated areas under the absorbance curve are linear with the known amounts deposited.

In contrast to strontium, the calcium signal exhibits tailing. This is attributed to the similar work functions of CaO (4.32) and tungsten (4.38). Strontium, with a much lower work function (2.24) centers the discharge current to the sample more effectively. The sputtering rates are estimated to be $0.2 \mu\text{g} \cdot \text{s}^{-1} \cdot \text{A}^{-1}$. At the 1100-to-1700°C operating temperature range of the

* Pacific Lutheran University, Tacoma, Washington.

1. General Chemistry Division Quarterly Report, July through September, 1977, Lawrence Livermore Laboratory, Rept. UCTD-15644-77-3 (1977), p. 1.
2. C. I. M. Beenakker, Spectrochim. Acta **31B**, 483 (1976).
3. L. R. Layman and G. N. Hieftje, Anal. Chem. **47**, 194 (1975).

Fig. 1. Sheathed wire configuration for glow discharge vaporization studies.

Fig. 2. Atomic absorption spectrum of strontium obtained downstream from a microarc discharge.

wire, thermal vaporization is not significant and tailing of calcium is eliminated at higher temperatures (2200°C).

The fact that the argon plasma can extend outside the cavity makes possible the configuration shown in Fig. 3. Solution is introduced into an electrodeposition cell (lower part of figure), in which a moving wire cathode becomes coated by the sample deposit. The deposit is carried continuously up to the discharge region, where it is vaporized and blown into the microwave-induced plasma cavity. The coupling of the microwave-induced cavity to the glow discharge electrodes on either side of the cavity helps to stabilize the plasma. This device and the sheathed cathode configuration (Fig. 1) have been constructed and are now being tested. In addition, we have adapted the PDP-8/c FOC103 system⁴ to obtain emission-time profiles of sample volatilization.

⁴. General Chemistry Division Quarterly Report, January through March, 1973, Lawrence Livermore Laboratory, Rept. UCID-15644-73-1 (1973), p. 41.

Fig. 3. Electrodeposition sampling device for continuous or discrete sample analysis by a microwave-induced plasma excitation source.

Excited State Chemistry of Metal-Oxidant Reactions

Responsible Personnel: M. A. Revelli, D. C. Johnson,* and B. W. Wallin*

Brief Description: We have extended our metal-oxidant reaction studies to include the $\text{Mg} + \text{N}_2\text{O}$ system. Using the apparatus and techniques developed in our barium studies, we can similarly produce metastable magnesium atoms to investigate directly the role of $\text{Mg}(^3\text{P})$ leading to MgO chemiluminescence.

Status: Bernard and Slafer⁵ report strong chemiluminescent MgO bands which appear to result from the reaction

However, this is but one step in a chain reaction that includes CO as a reactant. Unlike the BaO chemiluminescence spectrum that shows no change as a function of $\text{Ba}(^3\text{D})$ concentration, the $\text{MgO } B^3\Sigma - X^1\Sigma$ emission appears to depend upon the concentration of magnesium metastables.

We have recorded weak visible chemiluminescence from the reaction of atomic magnesium vapor with nitrous oxide. Upon completion of minor oven modifications, the previously described experimental system⁺⁶ will be used to directly produce the $\text{Mg}(^3\text{P})$ metastable reactants and simultaneously search for enhanced MgO chemiluminescence.

Magnesium metastables, produced when ground state $\text{Mg}(^1\text{S})$ is flowed through a low voltage potential, will populate the $\text{Mg}(^3\text{P}_{0,1,2}^0)$ levels located at 21850 cm^{-1} , 21870 cm^{-1} , and 21911 cm^{-1} , respectively. This $\text{Mg}(^3\text{P}^0)$ concentration can be measured either from the emission intensity of the spin-forbidden $^3\text{P}_1 - ^1\text{S}$ transition at 457.1 nm or from the triplet-triplet transition intensities using laser-induced atomic fluorescence techniques. A Coumarin 30 dye laser will be used to pump $\text{Mg}(^3\text{P})$ atoms to the ^3S level at 41197 cm^{-1} .

*Research Engineering Division, LLL.

⁺See pg. 15, Ref. 1.

5. D. J. Benard and W. D. Slafer, J. Chem. Phys. **66**, 1017 (1977).

6. General Chemistry Division Quarterly Report, January through March, 1977, Lawrence Livermore Laboratory, Rept. UCI-15644-77-1 (1977), p. 19.

Excited State Chemistry of Strontium

Responsible Personnel: E. F. Worden, J. A. Paisner,* and J. G. Conway†

Brief Description: We have observed the production of Sr_2^+ by the associative ionization reaction of high Rydberg states of strontium with other strontium atoms in a high density beam. The Sr_2^+ also is produced by the reaction of two $5s5p\ ^1P_1$ strontium atoms (21698 cm^{-1}). The excited states of strontium were produced by stepwise laser excitation using our laser photoionization spectroscopy apparatus. This equipment includes a quadrupole mass spectrometer for ion product confirmation.

Status: The production of dimer ions by associative ionization has been known for the noble gases and for the alkali metal atoms. However, although this process has been assumed to occur in the alkaline earth elements, no product identification has been performed.⁷ Using our laser photoionization spectroscopy apparatus with a quadrupole mass spectrometer,^{8,9} we have established the production of Sr^+ by the reactions

Reaction (1) was observed by increasing the oven temperature in the apparatus so that the beam density became high enough for atomic collisions and the production of Sr_2^+ detected as mass 176. In the equation, $\text{Sr}(5sn\ell)$ indicates Rydberg levels where ℓ is an s, p, or d electron. These Rydberg levels are populated by the stepwise laser excitations:

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†Lawrence Berkeley Laboratory.

7. A. Fontijn, Pure Appl. Chem. **39**, 287 (1974).
8. General Chemistry Division Quarterly Report, October through December, 1976, Lawrence Livermore Laboratory, Rept. UCID-15644-76-4 (1977), p. 22.
9. L. R. Carlson, J. A. Paisner, E. F. Worden, S. A. Johnson, C. A. May, and R. W. Solarz, J. Opt. Soc. Amer. **66**, 846 (1976).

and

or

We have found that for the s series, reaction (1) occurs down to $n = 8$ (41052 cm^{-1}), which is 4880 cm^{-1} below the strontium or Sr_2 ionization potential of 45932 cm^{-1} . Thus, the implied Sr_2^+ bond energy is greater than 0.61 eV. This is in agreement with the predicted binding energy for Ca_2^+ of about 0.75 eV¹⁰ and the lower limit for Ba_2^+ of 0.76 eV.⁷ The binding energies of the alkali dimers are between 0.79 and 0.70 eV.⁷

Although associative ionization was observed for all Rydberg levels with $n \geq 8$, it was not observed for the $4d^2 \ ^3P_2$, 3P_1 , or 3P_0 levels of strontium that occur near $n = 12$. Scans of the region near the 3P_2 and 3P_1 levels are shown in Fig. 4. Although a strong Sr^+ signal appears from both these levels, no Sr_2^+ signal is present. Because the reaction is energetically possible, the lack of signal must be attributed to the exceptionally small cross section of these levels for reaction (1).

The excited state/excited state associative ionization reaction, reaction (2), also is present at high strontium beam densities. An Sr_2^+ signal is obtained with one laser at 460.7 nm populating the 1P_1 level at 21698 cm^{-1} . Two strontium atoms in this level have sufficient energy (43396 cm^{-1}) for the reaction. The signal from this reaction appears as a background signal in the lower scan in Fig. 4. The dips in the Sr_2^+ signal at the 3P_1 , 3P_2 , and 3D resonances are caused by a depletion of the 1P_1 level population by the

10. K. Z. Lu, Chemistry Division, Argonne National Laboratory, private communication (1977).

Fig. 4. Scans at mass 88 (Sr^+) and mass 176 (Sr_2^+) showing production of Sr_2^+ by the $5snd \ ^1D_2$ and $5sns \ ^1S_0$ Rydberg levels but not by the $4d^2 \ ^3P_2$ and 3P_1 levels. Dips in the Sr_2^+ signal at the $4d^2 \ ^3P_1$ and 3P_2 energies are caused by a reduction in the background signal from reaction (2).

process

For higher members ($n \geq 16$) of the $5snd\ ^1D_2$ series, we have observed a spectral line reversal in the molecular ion signal. This dip in the center of the resonance line shape (see Fig. 4, middle scan) increases dramatically with laser intensity, as well as with strontium number density. A simple kinetic model involving an avalanche of electrons initiated by photoionization, reaction (6),

and sustained by electron impact ionization, reaction (7),

qualitatively reproduces this phenomena. Excited Rydberg states are electron-impact-ionized by reaction (7) before they can associatively ionize by reaction (1).

The effect of reducing the intensity of laser No. 2 is shown in the top scan in Fig. 4. The "reversal" is removed because the effects of reactions (6) and (7) are minimal. A similar scan is obtained at reduced strontium beam density; the bottom scan in Fig. 5 is the Sr^+ signal to lower strontium beam density.

Fig. 5. Scans of Sr^+ and Sr_2^+ signal vs energy. Excitation scheme is shown at right. The lower scan is the Sr^+ signal at low Sr density in the beam: the upper scans are Sr_2^+ signals without and with a neutral density filter in laser beam No. 2. The ion signal shows a reversal for some peaks in the center scan (see text for explanation).

Photoelectrochemistry

Responsible Personnel: J. H. Richardson, S. M. George,^{*} S. P. Perone,[†]
B. W. Wallin,^{**} and J. E. Harrar

Brief Description: Data on the dependence of photoemission-related currents on laser characteristics have been compiled and examined. We have designed and built a preliminary optics assembly for obtaining spectroscopic information in the vicinity of an electrode in solution. A number of candidate organic compounds to scavenge photoejected electrons and then fluoresce have been identified and we have begun the initial survey of these compounds.

Status: Data previously obtained describing the dependence of photoemission-related currents on laser characteristics has been compiled and published.¹¹ Experiments with low-peak-power cw lasers and well-known electron scavengers yielded the anticipated dependence of photoemission current on wavelength, power, and electrode potential. However, higher powers obtained with a pulsed laser gave rise to anomalous results; the observed photorelated current did not show a linear dependence on power. These results were attributed to thermal effects and nonlinear processes (e.g., two-photon effects and electron-electron annihilation-reactions). This nonlinear dependence on laser power for electron scavenging by nitrate ion at two different potentials is evident (see Fig. 6).

The results from a variety of transition metal cations are even more complicated. In no case were definitive data obtained to illustrate the scavenging of photoejected electrons. Usually, we saw photorelated current associated with the polarographic reduction wave that did not depend on whether

^{*}Summer employee, currently at University of California, Berkeley.

[†]Consultant, Purdue University, Lafayette, Indiana.

^{**}Research Engineering Division, LLL.

11. J. H. Richardson, S. M. George, J. E. Harrar, and S. P. Perone, Laser Induced Photoelectrochemistry: Dependence of Photoemission Related Currents on Laser Characteristics, Lawrence Livermore Laboratory, Rept. UCRL-80402 (1977).

Fig. 6. Relative transient photorelated current ($\% S/S_0$) vs relative pulsed laser intensity (I/I_0), where $\lambda = 520$ nm, for 3 mM NaNO_3 in 0.1 M KCl: (●) $E = -1.8$ V, (○) $E = -1.2$ V.

or not the photon energy was sufficient to eject electrons. For example, Fig. 7 illustrates the photorelated current obtained by irradiating the electrode in a solution of CuCl_2 ; the expected threshold for photoemission is -1.2 V vs SCE (saturated calomel electrode). The photorelated current seen with the transition metal cations has an even more pronounced nonlinear dependence on peak power intensity (Fig. 8).

We have assembled the optics for viewing the region in the vicinity of the electrode. A microscope objective and eyepiece are used; magnifications up to $\times 200$ can be selected. Subsequent optics collimate the image before it passes through a monochromator and is focused onto a photomultiplier tube.

We have obtained a number of organic compounds that appear to be good candidates to scavenge electrons and then fluoresce. The following requirements are suspected to be important:

- The compound must have a polarographic reduction wave between -0.5 and -1.6 V vs SCE.
- The reduction must be reversible and yet have a window so that the reduction product is not immediately reoxidized.
- The compound must be strongly absorbing, with the absorption wavelength (and hence the photoemission threshold) just before the reduction wave.

Spectrally, the reduction product must fluoresce differently than the initial species, but this requirement cannot be ascertained in advance. A survey of these likely scavengers has begun.

Fig. 7. Boxcar-averaged photorelated current for chopped cw laser. The ac coupled, synchronously detected laser output power is 2 W for 3 mM CuCl_2 in 0.1 M KCl, with $\lambda = 514.5$ nm and the same vertical sensitivity as in Fig. 6: (a) without Triton X-100, (b) with Triton X-100.

Fig. 8. Relative photorelated current ($\% S/S_0$) vs relative pulsed laser intensity (I/I_0), where $\lambda = 520$ nm, for 10 mM CuCl_2 in 0.1 M KCl: ($\bullet$) $E = -1.8$ V, ($\circ$) $E = -1.35$ V, ($\square$) $E = -0.9$ V.

Determination of Trace Amounts of Noble Gases in NTS Samples

Responsible Personnel: J. C. Newton

Brief Description: We have rebuilt the apparatus for determining trace amounts of noble gases in air samples from NTS prompt diagnostic experiments. Previous methods are being improved and preliminary analyses have been made.

Status: The determination of trace noble gases in samples from Nevada Test Site (NTS) experiments has been described.¹² In addition to determining the total amounts of He, Ne, Ar, Kr, and Xe, we now need isotope ratios with an accuracy of 1% at the 0.1-to-1000-ppm level. The three steps for analyzing the NTS samples are:

- Determining the percentage of noble gases in the original sample with a titanium sublimation pump (TSP).
- Concentrating the noble gases from about 800 cm³ (STP) of sample gas by gettering the active gases with hot calcium.
- Analyzing the concentrated sample by mass spectrometry.

To obtain the required analytical improvements, we had to rebuild the apparatus. A vacuum system, including the TSP and Barocel pressure transducer, was constructed and is now in use. An English transfer pump and a Toepler pump were added to this vacuum line. A new oven to heat the calcium-containing bulbs and sample gas was also completed.

Ensemble-averaging is being used to improve the signal-to-noise values for determining the isotope ratios. The CEC 21-103C mass spectrometer is scanned and data are acquired under the control of a DEC LSI-11 microcomputer which uses a BASIC program with assembly language patches. We found it necessary to determine and subtract background values for each mass plot. Xenon isotope ratios with respect to mass 132 were measured in pure xenon at pressures similar to concentrated air for masses 129, 130, 131, 134, and 136 to an accuracy of 2% or less.* All xenon isotopes are below the 0.1-ppm level in unconcentrated air.

*Accuracy is defined as the experimental value minus the literature value divided by the literature value $\times 100$.

12. J. C. Newton, F. B. Stephens and R. K. Stump, Determination of Trace Noble Gases in Air and Natural Gas, Lawrence Livermore Laboratory, Rept. UCRL-74695 (1973).

Work is continuing with solid phase samples prepared from concentrated air. The precision and accuracy of this technique will be determined for normal (atmospheric) air samples and appropriate concentration techniques will be evaluated.

Potentiometric Microdetermination of Pentaerythritol Tetranitrate (PETN)
in PETN-Containing Composites

Responsible Personnel: W. Selig and G. L. Crossman

Brief Description: Microamounts of the explosive PETN were determined in the composites LX-08, LX-13, and ETX-8003 by a titrimetric method based on the reduction of the nitrate group with iron(II) ion in concentrated sulfuric acid.

Status: A method is required for determining microamounts of the explosive PETN in PETN-containing composites with the compositions given in Table 1. Extraction-gravimetric techniques have been used to determine PETN in such composites.¹³⁻¹⁵ Photometric methods, based on the violet color formed when iron(II) salts are added to nitrates in the presence of sulfuric acid, are

Table 1. Composition of three PETN-containing composites.

Ingredient	Composition, wt %		
	LX-08	LX-13 and ETX-8003	LX-02-1
PETN	63.7	80	73.5
Silicone rubber	34.3	20	-
Cab-O-Sil	2.0	-	2.6
Butyl rubber	--	-	17.6
Acetyltributyl citrate	--	-	6.9

13. W. Selig, Some Analytical Methods for Explosives and Explosive Simulants, Lawrence Livermore Laboratory, Rept. UCRL-7873 (1964), p. 20.
14. W. Selig, Some Analytical Methods for Explosives - Part II, Lawrence Livermore Laboratory, Rept. UCRL-7873, Part II (1965), p. 55.
15. W. Selig, Some Analytical Methods for Explosives and Explosive Simulants - Part IV, Lawrence Livermore Laboratory, Rept. UCRL-7873, Part IV (1973), p. 35.

also available for PETN.^{16,17} We have reviewed and modified these methods¹⁸ and a photometric method is now in use at Mason & Hanger - Silas Mason Co., Amarillo, Texas,¹⁹ for composition analyses of PETN in cured LX-13. The molar absorbance of PETN in this method is fairly low - about 900. For this reason, as well as for the inherent inaccuracies in photometric methods, we hesitate to recommend such a method for the quality control of a major ingredient such as PETN.

However, the redox reaction used in these photometric methods,

can be used advantageously in the titrimetric analysis of PETN. In our work, we used a titrant of approximately 0.01 N Iron(II) ammonium sulfate solution in 1:1 sulfuric acid. Sample sizes ranged from 2 to 5 mg. A Sargent Model D recording titrator with a platinum/mercury(II) sulfate electrode system was used to monitor the electromotive force (emf) in the titrations. None of the other ingredients in the PETN-containing composites interfered. The titration medium was concentrated sulfuric acid. Absolute standard deviations, in percent PETN, ranged from 0.32 to 0.67 for four replicates. The details of this work have been published in an LLL report.²⁰

16. M. A. Laccetti, S. Semel, and M. Roth, Anal. Chem. **31**, 1049 (1959).
17. G. Norwitz and M. Galan, Microchem. J. **14**, 71 (1969).
18. W. Selig, Some Analytical Methods for Explosives - Part V, Lawrence Livermore Laboratory, Rept. UCRL-7873, Part V (1976), p. 20.
19. Composition of Semi-Micro Samples of Cured LX-13, Mason & Hanger - Silas Mason Co., Amarillo, Texas, Rept. Index No. 7-9953.1 (May 11, 1976).
20. W. Selig and G. L. Crossman, Potentiometric Microdetermination of Pentaerythritol Tetranitrate (PETN) in PETN-Containing Composites, Lawrence Livermore Laboratory, Rept. UCID-17679 (1977).

An NMR Method for Determining NH_4^+ in TATB

by J. A. G. Reinebeck and J. E. McGrath, *Chemical Corps, Fort Monmouth, New Jersey*

Responsible Personnel: J. A. G. Reinebeck

Brief Description: A method has been developed for determining NH_4^+ in 1,3,5-trinitro-2,4,6-trinitrobenzene (TATB). Nuclear magnetic resonance (NMR) is used for the analyses.

Status: During the production of TATB, impurities are introduced in small amounts with ammonia. Although the impurity is not critical, a knowledge of the ammonia ion content of TATB is desirable to assess their quality. Previously, this was done with a colorimetric method only, because it involved an extraction. There were considerable variations in the accuracy of the technique.

During a study of the decomposition of TATB by concentrated sulfuric acid, we noted that NH_4^+ ions attributable to the NH_4^+ ion occurred in the proton NMR spectrum obtained. Spectroscopic methods applied to the analytical procedure described below.

The NMR action of nuclei is determined by the ratio of peak area and the concentration of the resonating nucleus of interest. In this case the protons of NH_4^+ are determined by the NMR spectrum of a sample is obtained, peak areas are determined, and the results are compared with the peak areas determined for standard samples.

A weighed amount (0.10 to 0.15 g) of sample dissolved in a known volume of concentrated sulfuric acid (11.0 ml) and the resulting solution is transferred to a 5-mm precision bore NMR tube. A scan of the NH_4^+ region of the spectrum is made. A typical spectrum is shown in Fig. 9a.

Standard samples for comparison are prepared by dissolving weighed amounts of ammonium sulfate in known volumes of concentrated sulfuric acid. Aliquots of 1 cm³ are sealed in 5-mm precision NMR tubes to provide permanent standards. The NMR spectrum of a standard is obtained as shown in Fig. 9b.

In Fig. 9, the NH_4^+ spectrum consists of the well-known 1:1:1 triplets. This pattern results from nuclear spin-spin coupling between the protons and the nitrogen nucleus ($J = 54.1 \text{ Hz}$). This effect is observable because in concentrated sulfuric acid, the nitrogen nucleus (nuclei) have a sufficiently long lifetime. The peak labeled c of Fig. 9b is associated with the amino protons of TATB molecules.

Fig. 9. Proton NMR scan for NH_4^+ region for solutions containing (a) 0.12 g TATB/ $\text{cm}^3 \text{H}_2\text{SO}_4$, (b) 2.1×10^{-3} g $(\text{NH}_4)_2\text{SO}_4/\text{cm}^3 \text{H}_2\text{SO}_4$. Scan covers the region 200 to 400 Hz upfield from the sulfuric acid solvent peak.

Signal-averaging methods were used to improve the signal-to-noise ratio and to accumulate and store data in digital form, simplifying the integrations. Areas to be compared were obtained by summing the three areas for the NH_4^+ triplet. The expression that gives the weight percent of ammonium ion in a sample is

$$\% \text{NH}_4^+ = C_{\text{std}} \times \frac{\text{Area (standard)}}{\text{Area (unknown)}} \times \frac{(V + \rho W)}{W} \times 100$$

Here, C_{std} is the concentration of NH_4^+ in the standard (g/cm^3), V is the volume of H_2SO_4 used (cm^3), W is the weight of TATB taken (g), and ρ is the density of TATB (1.938 g/cm^3).

The results of three analyses are listed in Table 2 and compared to an indirect determination of the NH_4^+ based on the inorganic chloride ion analysis. Agreement is within the experimental error.

Table 2. The NH_4^+ content of TATB as determined by the NMR method and as inferred from a chloride ion determination.

TATB Lot No.	NH_4^+ content (wt%)	
	NMR	Calculated from Cl^- determination
B-387	0.13	0.12
B-457	0.23	0.26
B-437	0.015	0.01

Absorption Spectra of TATB in the Visible Spectral Range

Responsible Personnel: W. Selig

Brief Description: Spectral data for 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) were determined in the visible range in several solvents of relatively low dielectric power: hexamethylphosphortri- amide, ethylenediamine, and tetra- ethyl- guanidine.

Status: We have previously reported the photometric determination of TATB in dimethylsulfoxide (DMSO).²¹ The molar absorptance, ϵ , in this solvent ranged from 2.80×10^4 to 2.84×10^4 . The wavelength of maximum absorption, λ_{max} , was at 435 nm. Several solvents possess higher solvent power for TATB than DMSO,²² including hexamethylphosphortri- amide (HMPT), ethylenediamine (EDA), and 1,1,3,3-tetramethylguanidine (TMG). Therefore we also determined ϵ and λ_{max} of TATB in these solvents. The data are summarized in Table 3. TATB Lot B-457 was used throughout this work.

In the fairly alkaline solvents, EDA and TMG, TATB possesses two absorption peaks. The peak near 420 nm may be caused by partial amination of an amino hydrogen. In none of the solvents examined does ϵ surpass that found in DMSO. These solvents therefore do not afford any advantage over DMSO except that TATB is more soluble in these solvents; in addition, there are some considerable disadvantages including the high toxicity of HMPT and the hygroscopicity of the basic solvents EDA and TMG.

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21. W. Selig, The Photometric Determination of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) in Dimethylsulfoxide (DMSO), Lawrence Livermore Laboratory, Rept. UCID-17542 (1977).
 22. W. Selig, How to Estimate the Solubility of an Insoluble Compound - TA.B, Lawrence Livermore Laboratory, Rept. UCID-17412, Rev. 1 (1977).

Table 3. Spectral data of TATB in several solvents (Ref. 21).

Solvent	λ_{max} , nm	Absorbance, 10^{-4} c	Standard deviation, 10^{-4} c
DMSO	355	2.80	0.004
HMPPT, sample 1	350	2.46	0.024
HMPPT, sample 2	350	2.44	0.015
HMPPT, pooled value	--	2.45	0.024
EDA	410	1.98	0.042
	365	1.82	0.052
TMC	422	1.29	0.042
	355	1.69	0.041

Spectrophotometric Determination of Some Bifunctional Polynitroaromatic

Compounds With Ethylenediamine

Responsible Personnel: W. Selig

Brief Description: Several bifunctional polynitroaromatic compounds were determined spectrophotometrically after reaction with ethylenediamine in dimethylsulfoxide. In addition to two or more nitro groups, the compounds contained one or more amino, methoxyl, hydroxyl, carboxyl, or chloride groups. Spectral data were determined for all compounds examined, most of which are of ordnance interest.

Spectra: The work described here resulted from our attempts to enhance the sensitivity of a previously described photometric method²¹ for the explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). Several reagents specific for polynitroaromatic compounds were investigated. The most promising method was that of Glover and Kayser²³ who determined several polynitroaromatic compounds after reaction with ethylenediamine (EDA). To our knowledge, this method has not been applied to nitroaromatic compounds containing additional functional groups. Although we failed to achieve an increase in sensitivity for TATB, we have successfully increased sensitivity for its precursor, 1,3,5-trichloro-2,4,6-trinitrobenzene, for some impurities produced in TATB manufacture, and for other bifunctional polynitroaromatic compounds of ordnance interest which previously have not been determined photometrically.

Details are given in a manuscript²⁴ which has been submitted to Mikrochim. Acta.

23. D. J. Glover and E. G. Kayser, Anal. Chem. **40**, 2055 (1968).

24. W. Selig, The Spectrophotometric Determination of Some Bifunctional Polynitroaromatic Compounds with Ethylenediamine, Lawrence Livermore Laboratory, Preprint UCRL-80092, (1977).

Nonaqueous Titration of Benzotrifuroxan (BTF)

Responsible Personnel: W. Selig

Brief Description: The explosive benzotrifuroxan has been titrated potentiometrically with tetrabutylammonium hydroxide in various solvents. Its equivalent weight is solvent-dependent. With the solvent N,N-dimethylformamide, we obtained the best titration curves and the lowest standard deviation of end points.

Status: Benzotrifuroxan (BTF) is an explosive of particular interest because it contains no hydrogen. Bailey and Case^{25,26} have studied the synthesis of BTF and have prepared several complexes of BTF with aromatic compounds that act as electron donors.

We previously described the preparation and properties of some stable adducts of BTF formed mostly with nonaromatic organic compounds.²⁷ No analytical methods were found in the literature for the furoxan moiety or for BTF. Preliminary experiments revealed the weakly acidic properties of BTF.¹⁸ The equivalent weight of BTF, however, varied with the solvent used. Therefore, we studied the effects of the following solvents: methanol, acetonitrile, N,N-dimethylformamide (DMF), acetone, dimethylsulfoxide (DMSO), pyridine, and 1,1,3,3-tetramethylguanidine (TMG). The titrant in each case was tetrabutylammonium hydroxide (Bu₄NOH).

In methanol, no titration curve was obtained. In acetonitrile, the potentiometric break near the endpoint was only 50 mV, too small to be analytically useful. The other solvents yielded potentiometric breaks that varied from 150 to 300 mV. In acetone and TMG, two breaks were observed. The quality of the potentiometric breaks was best in DMF and DMSO, the solvents that yielded the steepest titration curves. The standard deviations of the end points were smallest in DMF and pyridine. Therefore, for quantitative determination of BTF, the solvent of choice is DMF. In this solvent, the equivalent weight of BTF is 151.3, corresponding to 1.67 equivalents per mole.

25. A. S. Bailey and J. R. Case, Tetrahedron **3**, 113 (1958).

26. A. S. Bailey, J. Chem. Soc. **1960**, 4710.

27. W. Selig, Adducts of Benzotrifuroxan, Lawrence Livermore Laboratory, Rept. UCID-17450 (1977).

The details of this study are given in UCRL-79565 which has been accepted for publication in Fresenius' Zeitschrift für Analytische Chemie.²⁸

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28. W. Selig, The Nonaqueous Titration of Benzotrifuroxan (BTF), Lawrence Livermore Laboratory, Preprint UCRL-79565, (1977).

Nonaqueous Titrimetry Using Bis(1,5-dimethyl-2-phenyl-3-pyrazolone)

Perchlorate as a Standard

Responsible Personnel: W. Selig

Brief Description: We investigated the standardization of solutions of perchloric acid in glacial acetic acid and tetrabutylammonium hydroxide (TBAH) with antipyrine perchlorate.

Status: Busev, et al.,²⁹ recently suggested the use of bis(1,5-dimethyl-2-phenyl-3-pyrazolone)perchlorate as a primary standard for nonaqueous titrations. This compound is commonly known as antipyrine perchlorate. It is particularly attractive because it can be used for the standardization of both acids and bases and has a high equivalent weight. Also, this compound is considerably more soluble in 1,1,3,3-tetramethylguanidine (TMG) than the commonly used standard benzoic acid.

Busev, et al.,²⁹ and Mukherji³⁰ state that antipyrine perchlorate can be titrated as a monoacidic base with perchloric acid solutions, and as a monobasic acid with basic titrants. However, we have found that the titration curves of antipyrine perchlorate vs TBAH in all but very basic solvents, such as TMG, are complex. Care must be taken to titrate to the second potentiometric break for the correct standardization of bases. The solvents of choice for titrations with antipyrine perchlorate are methanol and pyridine in which the largest potentiometric breaks and the smallest standard deviations are obtained. Satisfactory results are also obtained in acetonitrile and TMG.

The details of this study are given in a manuscript³¹ which has been accepted for publication in Fresenius' Zeitschrift für Analytische Chemie.

29. A. I. Busev, V. K. Akimov, and I. A. Emelyanova, Zh. Anal. Khim. 23, 616 (1968).

30. A. K. Mukherji, Anal. Chim. Acta. 77, 331 (1975).

31. W. Selig, On the Use of Bis(1,5-dimethyl-2-phenyl-3-pyrazolone)Perchlorate as a Standard for Nonaqueous Titrations, Lawrence Livermore Laboratory, Preprint UCRL-79678 (1977).

Solvent Purification and Electrode Optimization for Nonaqueous Titrimetry

Responsible Personnel: W. Selig

Brief Description: For our research program on nonaqueous titrimetry, we first studied methods of solvent purification. For the neutral or near-neutral solvents, N,N-dimethylformamide (DMF), dimethylsulfoxide (DMSO), pyridine, and hexamethylphosphortriamide (HMPT), best results were obtained by treating the solvents with a mixture of a strong acid cation exchanger and a strong basic anion exchanger. For the basic solvent, 1,1,3,3-tetramethylguanidine (TMG), best results were obtained by treatment with molecular sieves. Second, we have optimized the electrode system for measuring and recording the electromotive force during a titration. Best results were obtained with a glass/ceramic-fiber calomel electrode salt bridge filled with a saturated solution of tetramethylammonium chloride (Me_4NCl) in methanol, and with two platinum electrodes polarized by a constant current of 1 μA .

Status:

Solvent purification

We plan to develop nonaqueous titrimetric methods on the semimicro- and microscale and thus our first concern is the purification of the solvents. Three methods were considered: vacuum distillation, treatment with ion-exchange resins, and treatment with molecular sieves. The vacuum-distillation method was soon discarded as too time-consuming.

Ion-exchange treatment proved satisfactory for neutral or near-neutral solvents such as DMF, DMSO, and pyridine. At first, we adopted the method of Moskalyk, *et al.*,³² and purified DMF by treatment with an anion exchanger in the hydroxyl form (Dowex 1-X10). The blanks were reduced to 0.005 mmol tetramethylammonium hydroxide (Bu_4NOH) per 50 cm^3 of solvent. Solvents were purified in batches of 500 to 1000 cm^3 .

32. R. E. Moskalyk, L. G. Chatten, and M. Pernarowski, *J. Pharm. Sci.* **50**, 179 (1961).

For DMF, further improvement was achieved with the mixed resin bed method of Ferrari and Heider.³³ The resin was Fisher Scientific Co., Rexyn 309, a mixture of strong acid cation exchanger in the hydrogen form (RSO_3H^+) and a strong base anion exchanger in the hydroxyl form ($\text{R}_4\text{N}^+\text{OH}^-$). This treatment also was effective for HMPT which had yielded high blanks (>0.005 mmol Bu_4NOH) when treated with an anion exchange resin only. With the mixed resin bed treatment, the blank for HMPT was reduced to <0.0025 mmol $\text{Bu}_4\text{NOH}/50\text{-cm}^3$ of solvent. The mixed resin bed treatment has the additional advantage that the resin is relatively cheap compared to Dowex-X10 and thus can be discarded; in addition, after treatment (stirring at least 12 h), the resin rapidly settles and the solvent can be decanted rather than filtered as required with Dowex 1-X10.

Treatment with molecular sieves, Type 4A 10-30 mesh, proved most effective for purifying the basic solvent TMG. After treatment, the fines do not need to be removed by filtration. The blanks were <0.01 mmol $\text{Bu}_4\text{NOH}/50\text{ cm}^3$. This is better than the 0.02 mmol obtained for this solvent by Williams and Lautenschlager³⁴ after distillation from Ascarite. Treatment with ion exchange resins did not prove effective for TMG.

Electrode Systems

For nonaqueous titrations, the glass electrode is the most widely used indicator electrode.³⁵ The fiber-type calomel electrode can be used as reference electrode. However, the fiber can easily become plugged and cause erratic electromotive-force (emf) readings. A sleeve-type calomel reference electrode provides a good interface between electrode and test solution, but may permit excessive flow of electrolyte solution from the electrode into the solution to be titrated. A porous plug ceramic junction is a good compromise between these two types and was our preference.

Sharper and larger potentiometric breaks were obtained by Cundiff and Markunas³⁶ when the aqueous electrolyte of the calomel reference electrode was replaced by a saturated solution of KCl in methanol. Subsequently, Harlow³⁷

33. H. J. Ferrari and J. G. Heider, Microchem. J. **7**, 194 (1963).

34. T. R. Williams and M. Lautenschlager, Talanta, **10**, 804 (1963).

35. J. S. Fritz, Acid-Base Titrations in Nonaqueous Solvents, (Allyn and Bacon, Boston, 1973), pp. 60-64.

36. R. H. Cundiff and P. C. Markunas, Anal. Chem. **28**, 792 (1956).

37. G. A. Harlow, Anal. Chem. **34**, 148 (1962).

found that potassium salts reduce the potentiometric range of acids. A large potassium ion effect also has been observed for TMO.³⁴

We have, therefore, compared several electrode systems for the standardization of Bu_4NOH vs benzoic acid in DMSO. In all experiments, the rate of titrant addition was constant. Aliquots of 10 cm^3 containing $\sim 0.1\text{ mmol}$ of benzoic acid in DMSO were diluted to 50 cm^3 with DMSO and titrated vs $\sim 0.05\text{ N}$ Bu_4NOH under a nitrogen blanket. Data on the characteristics of the titration with various electrode systems are presented in Table 4.

Malmstadt and Vassallo³⁸ have examined a number of electrode systems with automatic derivative titrations of acids in acetone. They recommend a platinum/graphite electrode combination. Although the absolute potential differences are not necessarily reproducible, they claim that the electrode materials respond rapidly and provide sharp changes at the equivalence point. This approach seems to afford a simpler method of potentiometric titrations in nonaqueous media because it eliminates the salt bridge problem. We tried a graphite rod as well as a pyrolytic graphite electrode in combination with a platinum indicator electrode. However, both combinations yielded much poorer titration curves than the various combinations listed in Table 4: the curves were noisier, potential breaks were not nearly as sharp, and the electrode combinations had a memory effect.

The method of Shain and Svoboda,³⁹ however, yielded satisfactory results. These workers used two platinum electrodes, polarized by a constant current of $1\text{ }\mu\text{A}$, for the titration of acids in acetone vs Bu_4NOH . As shown in Fig. 10, the difference in potential of the electrodes reaches a maximum at the equivalence point. The results obtained by this method also are included in Table 4. Obviously, because the titration curve is not the conventional S-shaped curve but rather is a derivative type, the emf range is not significant. If a computer is used to control the titration, the polarized Pt/Pt system is faster because the titration can be stopped after the maximum emf is reached, whereas in the conventional S-shaped titration curve, sufficient data points past the end point are required to determine the inflection point. However, for feasibility studies of titrations, the conventional system should be used first.

38. H. V. Malmstadt and D. A. Vassallo, Anal. Chem. **31**, 862 (1959).

39. I. Shain and G. R. Svoboda, Anal. Chem. **31**, 1857 (1959).

Fig. 10. Titration of 0.1 mmol benzoic acid in DMSO with 0.5 N Bu_4NOH : a Pt/Pt electrode pair was polarized with 0.1 μA .

Table 4. Summary of comparison of electrodes and filling solutions (Bu_4NOH standardized vs benzoic acid/DMSO).

Reference electrode junction (manufacturer)	Salt bridge	Relative standard deviation, %	Number of replicates	95% confidence limits, %	emf break, mV	Remarks
Sleeve	KCl/methanol	1.07	5	1.33	225	reproducible emf
Ceramic fiber (Radiometer)	KCl/methanol	0.29	5	0.29	225	reproducible emf
Ceramic fiber (Beckman)	KCl/methanol	0.61	7	0.56	400-270	emf decreases, fiber clogged?
Sleeve	Me_4NCl /methanol	1.49	8	1.25	485-425	emf decreases slightly
Ceramic fiber (Radiometer)	Me_4NCl /methanol	0.37	7	0.34	160	reproducible emf
Ceramic fiber (Beckman)	Me_4NCl /methanol	0.35	8	0.29	160	reproducible emf
Platinum, polarized by +1 μA	None	0.27	6	0.28	not important	faster, simpler procedure

Based on the results presented in Table 4, our preferred electrode systems are the glass/ceramic-fiber calomel electrode in which the salt bridge was a saturated solution of tetramethylammonium chloride in methanol, or the two platinum electrodes polarized by a current of 1 mA.

Composition and Source of an Acicular Crystalline Contamination Found
on Laser Amplifier Disks

Responsible Personnel: R. G. Meisenheimer

Brief Description: A persistent contamination problem arose in the large laser fusion systems at LLNL. Large numbers of small, colorless acicular crystals appeared on the surface of the neodymium-doped laser amplifier disks. Results from several modern surface analytical instrumental methods indicate that this material is most probably lithium nitrate and that the source of the lithium is the glass itself.

History: In the very large laser systems at LLNL (Argus, Shiva, Shiva-Nova), amplifier rods have been replaced with an array of elliptical disks mounted at Brewster's angle to minimize reflection. Under the high power levels of these devices (up to 4 J/cm^2 at 1 ns of laser power; up to 20 J/cm^2 from neodymium-doped quartz flashlamps at 600 ns), it is imperative that all of the glass surfaces remain scrupulously clean. All units therefore are cleaned, assembled, and operated under clean-room conditions. In spite of these precautions, a persistent problem arose as a large number of small, colorless acicular crystals accumulated on the surfaces of the neodymium-doped laser amplifier disks. Because it is very important that this contamination be controlled, measurements of the composition of the crystals were undertaken to determine their source.

The disks, designated Nd Type ED-2, were formulated by the Owens Illinois Glass Co., and have the following general composition:

$\text{SiO}_2 = 69.0 \text{ mol\%}$

$\text{Li}_2\text{O} = 27.5 \text{ mol\%}$

$\text{Nd}_2\text{O}_3 = 0.5 \text{ mol\%}$

The remainder of the glass is made up of Ca, Al, and K oxides.

A surface with this needle-shaped contaminant is shown in Fig. 11a, an optical micrograph taken at 50x. These needle-shaped crystals also are somewhat deliquescent; when they are left exposed to the atmosphere for periods ranging from a few to many hours (depending upon the humidity), they transform

Fig. 11. Optical micrograph of contaminant crystals on glass surface at 50× (a) and of contaminant crystals after exposure to atmosphere at 300× (b).

to linear arrays of liquid droplets. This effect is illustrated in Fig. 11b, an optical micrograph taken at 300x. The fact that these crystals are deliquescent required that the analytical determinations, as well as storage and transport of the samples, take place in dry atmospheres.

It was deemed desirable to examine this surface contaminant by modern surface analytical instruments; however, these disks are quite large (up to 200 x 300 mm for Shiva) and this size cannot be accepted by most commercial surface analytical instruments. Therefore, we obtained a few 1-cm neodymium-doped glass cubes from Owens Illinois. These are small enough to fit into most of the surface analytical instruments. These glass cubes had been stored for about 2 y in a clean environment and showed a high concentration of the acicular crystals.

The first measurements were made with an ion microprobe mass spectrometer (IMMA). One of the cubes was mounted in the specimen chamber of the IMMA and an $^{16}\text{O}^-$ beam was rastered over the surface. (Using an $^{16}\text{O}^-$ beam, it is frequently possible to examine insulating surfaces without causing serious charging problems). The sputter ion current was determined as a function of m/q , the mass of the sputtered ion divided by its charge. This gives a mass spectrum of the surface atoms. One spectrum, shown in Fig. 12, discloses the presence of H, Li, C, Na, Al, Si, K, and Ca at this point.

The acicular crystals were then examined for particular elements. This was done by rastering the beam over the surface and making element maps (see Figs. 13-15). An optical micrograph of the area examined and a lithium elemental map clearly demonstrating the presence of lithium in the crystals are shown in Fig. 13. All of the other elements showed a depletion in the crystal areas. The crystals hide some of the substrate from the beam, decreasing the intensity of the signal for these elements, indicating that they are in or on the glass, not in the crystals. Several other areas were similarly mapped and the same effect observed.

There are a number of elements that are relatively insensitive to oxygen sputtering, and of course oxygen itself cannot be determined. The sample was therefore coated with a 20-nm thick layer of gold, sputtered with a $^{40}\text{Ar}^+$ beam, and a mass spectrum obtained. When this spectrum was completely analyzed, the additional information of interest was the presence of a nitrogen peak. An ^{14}N map was then made (see Fig. 14). Figure 14 reveals that the nitrogen signal is due to the crystal.

Fig. 12. Sputter ion mass spectrum of contaminated glass surface ($^{16}\text{O}^-$ beam, $320 \times 400 \mu\text{m}$ raster).

Fig. 13. Optical micrograph (a) of sample in IMMA and lithium distribution of sample area (b) shown in (a).

Fig. 14. Optical micrograph (a) of sample in IMMA and nitrogen distribution of sample area (b) shown in (a).

Fig. 15. Laser Raman spectra of uncontaminated glass surface (a) and of crystal contaminant on glass surface (b): ordinate = intensity, abscissa = frequency in cm^{-1} .

These EEM measurements thus demonstrate the presence of nitrogen and nitrogen in the crystals being studied. (With the $^{40}\text{Ar}^+$ beam, the oxygen signal was so large that no variations in intensity could be seen and no oxygen distribution data were obtained.)

One further set of measurements was made to obtain some chemical information concerning the sample. A second glass cube was examined in a laser microprobe analyzer. With this instrument, two Raman spectra were recorded, one of the substrate and the other on a crystal. (The Raman work was done in collaboration with F. Milanovich.) These spectra are shown in Fig. 10. The substrate obviously shows through with the addition of a sharp Raman resonance at 1280 cm^{-1} , characteristic of the NO_3 moiety.

On the basis of these measurements, it can reasonably be concluded that these crystals are probably lithium nitrate. There is an ample source of lithium since these glasses contain a significant concentration of this element. The lithium atoms apparently migrate to the surface and react with their surroundings. Although the driving force for this migration and the detailed chemistry have not been unravelled, we do know that lithium metal will react with nitrogen to form lithium nitride and with oxygen to form lithium oxide. Compounds such as lithium nitrate might also form in the presence of air, moisture, and other components of the glass.

Two possible ways of alleviating this problem have been suggested. One is to treat the amplifier disks in some way to decrease the lithium concentrations near the surface of the glass. A long treatment with hot water might do this. The other is to formulate an acceptable glass without lithium as one of the components.

Examination of the Interior Surfaces of a Vapor-Phase Laser Tube

Responsible Personnel: J. W. Fischer, D. D. McCoy, and R. G. Meischaemer

Brief Description: The interior walls of a vapor-phase quartz laser tube were examined to characterize deposits contained on these surfaces. The results indicated that the deposits were composed of an aluminum compound with numerous inclusions of carbon.

Status: We have examined the interior walls of an aluminum chloride/neodymium chloride, vapor-phase quartz laser tube. These surfaces were analyzed by optical microscopy, scanning electron microscopy (SEM), and electron microprobe spectroscopy (EMP) to determine the morphology and composition of optically undesirable formations on the interior surfaces of the windows and to determine the composition of black spots distributed on the interior surface of the tube itself.

A section of a window selected for analysis was exposed to boiling distilled water for several hours to remove any residual salts that deposited on the window surface as the tube was cooled from the high temperature required for vapor-phase formation.

Optical photomicrographs of a selected region of this window section are given in Fig. 16, and Fig. 17 presents SEM photomicrographs at successively higher magnifications of the window region shown in Fig. 16. SEM photomicrographs at higher magnifications of another region of the window are shown in Fig. 18; the location of this region can easily be determined by examining Fig. 17b.

In Fig. 19, we provide electron microprobe target current images of the same region of the window as shown in Fig. 16 and 17. Figure 20 shows EMP silicon K α and aluminum K α x-ray images of the same region of the window as shown in Fig. 19.

The optical and SEM images, Figs. 16-18, reveal that the interior window surface contains a variety of optically perturbing formations. Figure 17d and 17e indicate that the source of the ray pattern observed prominently in Figs. 16 and 17a-c may be a deposit material, some of which has spalled away in selected areas.

The EMP silicon K α x-ray image in Fig. 20 demonstrates that the residual material remaining on the window is relatively thin, probably less than 1 μ m,

Fig. 16. Optical photomicrographs of window surface at 62 $\times$ and at 180 $\times$ (a, b).

2

Fig. 17. Scanning electron photomicrograph of Fig. 18 window surface at 140 $\times$, 490 $\times$, 1400 $\times$, 3500 $\times$, and 10500 $\times$ (a-e respectively).

3

Fig. 18. Scanning electron photomicrograph of window surface at 1400 $\times$ and 7000 $\times$ (a, b).

Fig. 19. ENP target current images of window surface at 200 $\times$ and 500 $\times$ (a, b).

Fig. 20. EMP silicon (a) and aluminum (b) $K\alpha$ x-ray images of window surface at 500 $\times$.

because the silicon signal, which arises from the quartz, is substantial. (The sampling depth of the EMP is generally considered to be approximately 1 μm .) Comparison of Figs. 20a and 20b shows that the region of low silicon signal corresponds to that of high aluminum signal. It thus appears that the material comprising the deposits on the window surface is an aluminum compound, probably aluminum oxide, because no chlorine was detected during EMP analysis.

In addition, the interior surface of the tube itself was littered with numerous small black spots visible to the unaided eye. These were analyzed in the EMP and were found to be composed primarily of carbon. Figure 21 gives the EMP target current images of one of these spots: an EMP carbon K α x-ray image of this same black spot is shown in Fig. 21c. These carbon-rich black deposits probably resulted from organic contaminants present in the tube that were pyrolyzed during the high temperature required for vapor-phase formation.

Fig. 21. EMP target current images of black spot at 100 $\times$ (a), 200 $\times$ (b), and carbon K α x-ray image at 200 $\times$ (c).

Analysis of Corroded Aluminum Surfaces

Responsible Personnel: J. W. Fischer, D. D. McCoy, and R. G. Meisenheimer

Brief Description: We examined a corroded aluminum detonator cup and found that hydrochloric acid, resulting from the aqueous hydrolysis of residual ammonium chloride in the system, was the cause of the corrosion. An experiment that eliminated other possible sources of corrosive agents substantiated this hypothesis.

Status: A badly corroded detonator cup, composed of type 3003 aluminum alloy, was examined in an attempt to determine the cause of the extensive corrosion. The cup, which had contained the explosive 1,3,5-triamino-2,4,6-trinitrobenzene (TATB), was examined by optical microscopy, scanning electron microscopy (SEM), and electron microprobe spectroscopy (EMP), to characterize the corroded surface and hopefully to reveal the causes of the observed disintegration of the alloy.

An optical photomicrograph of a section of the corroded aluminum alloy detonator cup that originally contained a drilled hole is shown in Fig. 22. This photograph reveals that a substantial portion of the cup (at the circumference of the hole) has been completely consumed by the corrosion. Various regions in Fig. 22 are identified with plus signs and numbers as reference locations for other analytical techniques.

The region identified as +3 in Fig. 22 was further examined in the scanning electron microscope. The resulting SEM photomicrographs are shown in Figs. 22b and 23. The necessity of examining the sample by EMP precluded the deposition of a metallic layer on the corroded surface to enhance the quality of the SEM images.) The section of the corroded surface identified as region 1 in Fig. 22a is easily identifiable in Fig. 22b and is shown in successively higher magnifications in Fig. 23.

The same region of the corroded detonator cup then was examined in the electron microprobe to establish elemental composition. The EMP chlorine K α , carbon K α , and oxygen K α x-ray images of the same region of the detonator cup shown in Figs. 23 and 24a are given in Figs. 24b-d. The image in Fig. 24b shows a strong concentration of chlorine on the edge of the corroded area nearest the periphery of the hole. The image in Fig. 24c shows a strong concentration of carbon adjacent to the region of high chlorine concentration and the image in Fig. 24d shows a high concentration of oxygen over the entire

Fig. 22. Optical photomicrograph of corroded area of detonator cup at 12 $\times$ (a) and scanning electron photomicrograph of corroded area of detonator cup at 21 $\times$ (b).

Fig. 23. Scanning electron photomicrograph of detonator cup corrosion at 70 $\times$, 140 $\times$, and 490 $\times$ (a, b, c).

Fig. 24. EMP target current image (a) and EMP chlorine (b), carbon (c), and oxygen (d) $K\alpha$ x-ray images of detonator cup corrosion at 100%.

region examined, including the areas of high chlorine and carbon concentrations. Additionally the oxygen concentration in the corroded region is substantially higher than that in the uncorroded alloy. The region of high carbon concentration probably results from residual TATB or its decomposition products.

We hypothesized that the high concentration of chlorine adjacent to the area destroyed by the corrosion was due to the metal chloride salts that resulted from attack by dilute hydrochloric acid, which in turn could be produced by the aqueous hydrolysis of the ammonium chloride impurity known to exist in the TATB formulations. (The detonator cup had been exposed to an environment of high humidity.)

To test this hypothesis, a pellet of the TATB formulation and a quantity of water were placed on a plate of 3003 aluminum alloy. This test (performed by J. Humphrey) was expected to eliminate possible sources of a corrosive species other than the TATB. The plate showed definite signs of corrosion and was examined by the techniques discussed above. An optical photomicrograph of the alloy plate upon which the TATB and the water was placed is shown in Fig. 25. The location of the TATB pellet is indicated by the large white spot in the lower center of the photograph. Also in Fig. 25b we show an optical photomicrograph of a prominent corrosion pit in the aluminum surface as indicated in Fig. 25a by the number "8" and the associated arrow. Analysis of this spot by x-ray photoelectron spectroscopy (ESCA) revealed the presence of a substantial quantity of partially decomposed TATB from two well-resolved N 1s lines. The N 1s spectrum of this region is shown in Fig. 26. The lines shown are characteristic of compounds containing nitrogen atoms in two different chemical environments such as in TATB. However for pure TATB, the lines would be of nearly equal intensity.

Figure 27 presents the scanning electron photomicrographs at successively higher magnifications of the corrosion pit shown in Fig. 25b. Because secondary electron emission and light reflecting characteristics are not necessarily comparable on a given surface, simultaneous identification of the same location in the optical and SEM photomicrographs may not be readily attainable. (Again, we must note that analytical requirements prevented the deposition of metal on the sample to improve SEM photomicrograph quality.) A comparison of Figs. 23c and 27e illustrates the obvious similarity between the corroded surfaces of the detonator cup and the test sample.

Fig. 25. Optical photomicrographs of aluminum alloy/TATB test specimen at 1.9 $\times$ and 65 $\times$ (a, b).

Fig. 26. N 1s photoelectron line spectrum of white region in Fig. 25.

Fig. 27. Scanning electron photomicrographs of aluminum alloy/TATB corrosion pit at 35x, 70x, 140x, 280x, and 490x (a-e, respectively).

2

The EMP target current images of the region of the corrosion pit shown in the SEM photomicrographs (Fig. 27) are presented in Fig. 28. The same identifying structures can be easily found in the EMP target current images and the SEM photomicrographs. Closer scrutiny of Figs. 27c and 27d reveals that the bright deposit visible in the upper left corner of Fig. 27c is not present in Fig. 28a nor in Figs. 28b and 28c. This material apparently became dislodged between analysis on the SEM and EMP. Thus a portion of the region shown in Fig. 28 is not visible in the SEM photomicrographs as it was covered by this deposit.

Figure 28d is an EMP chlorine $K\alpha$ x-ray image of the same region shown in the EMP target current image (Fig. 28c). The high concentration of chlorine in the structure of the corrosion pit in the aluminum alloy is apparent. In fact, the only substantial difference in composition between the region of the corrosion pit shown in Fig. 28c and the unperturbed aluminum alloy surface was the presence of chlorine in the corrosion pit. This is shown graphically in the Fig. 29 EMP energy dispersive x-ray spectra of the corrosion pit area shown in Fig. 28c and an area of the uncorroded aluminum surface, respectively. In Fig. 29a a strong chlorine $K\alpha$ line that is nonexistent in Fig. 29b can be seen.

Thus we conclude that the hypothesis of corrosion of the aluminum alloy by hydrochloric acid resulting from the aqueous hydrolysis of ammonium chloride present in the TATB is correct. This contention was further verified when a similar test utilizing an aluminum alloy plate and specially prepared TATB that contained no residual ammonium chloride was conducted (by J. Humphrey); no corrosion of the alloy surface was observed.

Fig. 28. EMP target current images of aluminum alloy/TATB corrosion pit at 200 $\times$, 500 $\times$, and 1000 $\times$ (a, b, c), and EMP chlorine K α x-ray image of aluminum alloy/TATB corrosion pit at 1000 $\times$ (d).

Fig. 29. EMP energy dispersive spectra of aluminum alloy/TATB corrosion pit (a) and of uncorroded aluminum alloy (b).

Color Display for the Electron Microprobe

Responsible Personnel: D. D. McCoy and R. G. Meisenheimer

Brief Description: A prototype energy dispersive spectrometer (EDS) pulse height selector was built to interface x-ray signals from the electron microprobe EDS to the 8080 microprocessor used in the color display system.

Status: The color display system for the electron microprobe^{40,41} is able to display signals from four x-ray detectors simultaneously. There are two basic types of x-ray detectors used in the electron microprobe: wavelength dispersive detectors and energy dispersive detectors. Wavelength dispersive spectrometry (WDS) detects characteristic x-ray lines according to wavelength and a proportional gas detector is used to collect the selected x-ray photons. Signals are collected from only one x-ray line at a time. Energy dispersive spectrometry (EDS) uses a Si(Li) semiconductor detector to select the characteristic x-ray line according to the energy of the x-ray photon. The energy of the x-ray photon is converted to a voltage pulse, the magnitude of which is proportional to the energy of the x-ray photon. EDS collects all of the x-ray signals simultaneously.

When making x-ray images on a cathode ray tube, WDS offers a much higher output count rate for producing the image, but suffers from a loss of counts when the electron beam resides at the edges of low magnification, wide-sweep scans (x-ray optical defocusing). EDS has a much lower output count rate but does not suffer a loss of counts with beam position.

In previous reports,^{40,41} we described a display mode that gives a topographical image from various signals (e.g., target current, secondary electrons). The image is colored according to the characteristic x-ray signals resulting from the elements present in the sample. Several spectrometers, placed in different positions around the circumference of the sample, must be used in WDS. With a sample exhibiting topographical variations, it is possible for one of the spectrometers to be shaded from the x-ray emission area on the sample and, because the color of the image depends on the elemental composition

40. General Chemistry Division Quarterly Report, April through June 1976, Lawrence Livermore Laboratory, Rept. UCID-15644-76-2 (1976), p. 4.

41. General Chemistry Division Quarterly Report, April through June 1977, Lawrence Livermore Laboratory, Rept. UCID-15644-77-2 (1977), p. 12.

of the sample, this could result in the generation of an erroneous color. This problem is overcome by using EDS. All of the x-ray spectra are collected with one detector, eliminating the chance for erroneous color due to shading.

A prototype EDS pulse height selector has been built to interface x-ray signals from the electron microprobe EDS to the 8080 microprocessor CPU used in the color display system. The EDS pulse height selector will enable us to select counts from a chosen x-ray energy by placing a voltage window around the selected peak (pulse height) and allowing the 8080 CPU to receive only those pulses occurring within the window. The pulse height selector has been designed so that up to four x-ray signals can be selected for display.

The EDS pulse height selector is operated in the same manner as an x-ray single channel analyzer. A window is formed by two voltage thresholds: a lower threshold rejecting pulse heights below a selected voltage level and an upper threshold rejecting pulse heights above a selected level. Only pulse heights between the lower and upper selected levels are accepted.

The x-ray spectra obtained from EDS normally are viewed on the cathode-ray tube (CRT) of an x-ray pulse height analyzer (PHA). The EDS pulse height selector is designed to "gate" the PHA to accept only those pulse heights falling within the selected windows. This provides a visual method for setting the voltage thresholds for selecting desired x-ray signals.

A digital, X-Y sweep-driver is now being built to drive the color deflection amplifier and the sweep driver system in the microprobe. When this is completed, the 8080 CPU-to-color CRT interface will be completed. The next step will be to interface the microprobe single-channel analyzers to the x-ray counters. When this is finished, all of the accessory parts will be connected and we will begin testing the color display system.

Current Status of the ECLIPSE Automation System

Responsible Personnel: W. G. Boyle, H. S. Ames,^{*} G. W. Barton,
V. C. Barton,^{*} R. W. Crawford, R. M. Downey,^{*}
L. Taber,^{*} J. A. Wade,[†] and R. K. Yamauchi[†]

Brief Description: Changes in the current status of the C/300 ECLIPSE computer system^{**} and its peripherals, on-line instruments, and terminals are described.

Status: A system program called SOFTWARE SWITCHBOARD, written by R. Yamauchi, allows the full complement of 32 terminals to be connected to the multiplexor without sacrificing core memory to overhead.

A system operating procedure manual has been written by H. Ames and currently is being reviewed and revised. This manual will cover all operating procedures so that a well-defined system can be maintained. A standard procedure for starting the BASIC operating system is now in use.

An additional 64K words of memory and a second ALM-16 multiplexor have been installed. Fifteen lines are now operational on one of the ALM-16 multiplexors (see Fig. 30).

An improved analog bay has been installed and a new Data General CRT background terminal is in use. The terminal connectors have been standardized. The floppy disk drive has been installed and the software is being debugged. This system should be completed shortly.

The project to remove the CEC103 mass spectrometer from the PDP-7 computer and connect it to the ECLIPSE via an LSI-11 microcomputer is well underway. Most of the hardware is on hand and an LSI-11 unit is online to the CEC103. Writing the software for the LSI-11, however, may be time consuming and may not be fully completed and debugged until after the originally scheduled completion date of August 1978. As soon as the hardware for the CEC103 conversion project is connected and debugged, the other instruments specified for online operation will be brought up without waiting for the CEC103 project to be completed.

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^{**}See pg. 14, Ref. 41.

A BASIC Computer Program for Graphite Furnace Atomic

Absorption Spectrophotometry

Responsible Personnel: W. G. Boyle

Brief Description: A BASIC computer program is being written for the ECLIPSE time-shared system that will allow the use of the method of additions for both manual and automatic sampling methods with the graphite furnace atomic absorption spectrophotometer.

Status: The method of additions compares the unknown sample itself with a set of standards, consisting of unknown samples with known concentrations of added analyte (commonly known as spikes). A calibration curve is constructed by measuring the optical absorbance of these spiked samples and then plotting the absorbance vs concentration. When this curve is extrapolated to zero absorbance it yields the concentration of the original unknown. Such a procedure compensates in part for interelement effects that sometimes occur during the analytical procedure used to measure the optical absorbance of the analyte. This effect is particularly evident in graphite furnace atomic absorption (AA) techniques.

We have written a program adding the method of additions to the repertoire of BASIC programs for the graphite furnace AA, originally developed for the Environmental Protection Agency.⁴² We have attempted to make the new program compatible with the original standard calibration type programs: it will chain to the same data-taking routines. Some of the features of the method of additions program are described below. Note that a replicate measurement in this method is a repeat of a single measurement, whereas a repeated sample means that all of the spikes are run again with or without replicate measurements.

In the manual method (without use of the sampler), the following procedure is used:

- (1) Enter the sample identification code.
- (2) Enter the number of spikes.
- (3) Enter the concentration of each spike.

42. R. I. Bystroff, W. G. Boyle Jr., and G. W. Barton, Jr., Atomic Absorption Instrument Functional Description, Lawrence Livermore Laboratory, Rept. UCRL-52065 (1976).

- (4) Analyze the spike by typing the appropriate command to the command-line interpreter. For example, "S3/2" means this will be the second injection of spike number 3.
- (5) When finished, type "c" for a first-degree linear least squares fit and extrapolation to zero. This also automatically places the answer in a sample file and clears the standard file for more spiked samples.
- (6) By typing "MS," another run of the same sample may be initiated or a new sample may be identified. The information on spikes is then entered as before and another run is initiated.

Most of the options for deleting measurements and obtaining new averages are still available. For example, S1/D deletes the second measurement of spike 1. The U (unknown) commands also are available but merely give an answer for the sample involved. For example "U2/3" gives the third answer found for sample number two; and it also reports the average for all three answers. "U3/P" gives the average concentration found for the third sample. Sample results can be used completely but individual results cannot usually be deleted.

The automatic method using the AS-1 sampler uses these same commands; however in this case, they are generated by the program from information entered at the beginning of the analysis session (see Fig. 31). Thus, all sample identification codes, replicates, and multiple sample runs must be entered before the analysis is started. To make this easier, the program is divided into two routines labeled regular and irregular. For a regular routine, it is assumed that all of the spikes are going to be of equal number and concentration, and each sample will be run the same number of times. Thus spike concentration need only be entered once at the beginning of a session. For the irregular case, spike concentrations and sample repeats must be entered for each sample. (Replicates are set on the sampler itself and are the same for the entire run.) A sample wheel pattern is generated after this preliminary information is entered. This gives the operator a map so he can load the spiked samples in the proper order (Fig. 32). When all samples have been run, the program reverts to the manual mode.

Before this program is fully complete, we need to add a statistical routine and a report writing routine.

Fig. 31. Automatic sampling data entry scheme for the method of additions procedure on the graphite furnace atomic absorption spectrophotometer.

GRAPHITE FURNACE

***** SAMPLE WHEEL PATTERN *****

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POSITION		I.D.	SPIKE

1	B	BLANK	
2	S 1 /1	ONEIT	0
3	S 2 /1	ONEIT	25
4	S 3 /1	ONEIT	50
5	B	BLANK	
6	S 1 /1	ONEIT	0
7	S 2 /1	ONEIT	25
8	S 3 /1	ONEIT	50
9	B	BLANK	
10	S 1 /1	SECONDIT	0
11	S 2 /1	SECONDIT	25
12	B	BLANK	
13	S 1 /1	THIRDIT	0
14	S 2 /1	THIRDIT	25
15	S 3 /1	THIRDIT	50
16	B	BLANK	
17	S 1 /1	FOURTHIT	0
18	S 2 /1	FOURTHIT	50
19	B	BLANK	
20	S 1 /1	FOURTHIT	0
21	S 2 /1	FOURTHIT	50

Fig. 32. Sample wheel loading map.

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Microprocessor-Controlled Diluter

Responsible Personnel: W. G. Wells and J. M. Rowner^{*}

Brief Description: A microprocessor-controlled diluter based on two syringe burets and two and three-way solenoid-operated valves is described.

Status: The microprocessor-controlled diluter, based on a concept originally tested with the BBP-5/A minicomputer, has been constructed and tested. The diluter consists of two Hettich syringe burets and an MCS-80 microprocessor. Filling, rinsing, and delivering solutions and diluent are controlled by three-way and two-way solenoid valves operated by compressed air through microprocessor-controlled solenoids.

The main computer program is written in BASIC language developed for the MCS-80. Call to read and interpret instructions and operate the valves. The program is written so that the diluter can dilute the same sample or standard several times or can be quickly rinsed for a new sample or standard.

The general layout of the hardware is illustrated in Fig. 34. Three output ports are required, one for each buret to control the valve control functions. Output to the buret control is the filling, speed, and number of steps advanced. One input port is used to inform the program of the status of the burets while they are being reset.

A 10-cm³ buret with a valve-controlled drainage inlet contains the solution to be diluted and a 50-cm³ buret contains the diluent. The program has provisions to refill either one or both burets and for continuous delivery of solution if the dilution instructions call for more solution than the volume of the burets. The maximum range for a solution to be diluted in the single refill mode, that is, not refilling either buret, is about 1 to 100 (0.5 cm³ diluted to 50 cm³).

Each buret delivers or refills its entire volume in about 1 min. About 30 s are used for program prefilling, so a full-range dilution takes about 2.5 min for a complete cycle. Dilutions above this range take 2 min for each full volume delivered.

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[†]See pg. 36, Ref. 8.

Fig. 33. Diagram of the microprocessor-controlled dilutor: solid lines denote input ports, dashed lines denote output ports.

Precision over the entire range of the curve is a function of Δx and depends on the validity of the calibration factor obtained from the calibration process, but is approximately 0.1% for $\Delta x = 0.001$ cm. It also requires that the percent of volume addition be applicable to the solution and subject used in the calibration.

A paper describing this research was presented at the fourth annual International of Analytical Chemistry and Instrumentation (IACMA) meeting, November 7-11, 1977, in Detroit, Michigan.

PE283: A Computer Program to Simulate the Control of
the Perkin-Elmer Model 283 Infrared Spectrophotometer

Responsible Personnel: K. B. Samlorn

Brief Description: PE283 is a FORTRAN computer program that will enable us to test through simulation the methods used to control the Perkin-Elmer Model 283 Infrared spectrometer. The program will have all the data manipulation features that Perkin-Elmer supplies with its computerized Infrared spectrometer systems.

Status: The Perkin-Elmer Model 283 Infrared spectrophotometer contains a microprocessor for digital control of its operation that is able to communicate with an external computer through an interfacing accessory for both data acquisition and replotting on the instrument recorder. The Model 283 was obtained without the external computer, but with attachment to the General Chemistry Division ECLIPSE computer,* such data processing as ensemble averaging, differencing of spectra, smoothing, background flattening, expansion, and peak finding, will be available directly. A code called PE283 is being developed from the FORTRAN listing of the Perkin-Elmer code so that the same instrument User's Manual will apply. The structure of the code will allow easy translation into the BASIC language used on the ECLIPSE. The code PE283 will be tested on the CDC 7600s by simulating the data acquisition and replotting. The sections involving communication with the teletype have been debugged. The program is now being edited to reduce the number of variables and to eliminate excess coding.

* See pg. 14, Ref. 41.

Analytical Research and Development for the Energy Programs

^a χ^2 = 1.03, df = 1, p = .31. ^b χ^2 = 1.03, df = 1, p = .31. ^c χ^2 = 1.03, df = 1, p = .31. ^d χ^2 = 1.03, df = 1, p = .31. ^e χ^2 = 1.03, df = 1, p = .31. ^f χ^2 = 1.03, df = 1, p = .31. ^g χ^2 = 1.03, df = 1, p = .31. ^h χ^2 = 1.03, df = 1, p = .31. ⁱ χ^2 = 1.03, df = 1, p = .31. ^j χ^2 = 1.03, df = 1, p = .31. ^k χ^2 = 1.03, df = 1, p = .31. ^l χ^2 = 1.03, df = 1, p = .31. ^m χ^2 = 1.03, df = 1, p = .31. ⁿ χ^2 = 1.03, df = 1, p = .31. ^o χ^2 = 1.03, df = 1, p = .31. ^p χ^2 = 1.03, df = 1, p = .31. ^q χ^2 = 1.03, df = 1, p = .31. ^r χ^2 = 1.03, df = 1, p = .31. ^s χ^2 = 1.03, df = 1, p = .31. ^t χ^2 = 1.03, df = 1, p = .31. ^u χ^2 = 1.03, df = 1, p = .31. ^v χ^2 = 1.03, df = 1, p = .31. ^w χ^2 = 1.03, df = 1, p = .31. ^x χ^2 = 1.03, df = 1, p = .31. ^y χ^2 = 1.03, df = 1, p = .31. ^z χ^2 = 1.03, df = 1, p = .31.

[illegible]

We have presented a variety of analytical instrumentation for the desired identification and quantitation of the various compounds. All of the equipment used on Retort-1, the last recent experiment, was new, was supplied with the chromatographic column and was descending on the scale, being measured. The chromatographs were calibrated the day before the experiment and verified the morning of the experiment. During the course of the experiment, 13 gas streams were analyzed chromatographically. The individual monitors were calibrated before the experiment and checked at about the mid-point of the experiment. These instruments are connected directly to a computer for data logging.

Although a variety of problems is always present in any individual retort experiment, this latest equipment has functioned well, providing some very valuable data.

1. *Staphylococcus aureus* (ATCC 12228) (Control strain)

2. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl
 3. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl
 4. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

5. *Staphylococcus aureus*

6. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl
 7. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

8. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl
 9. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

10. *Staphylococcus aureus*

11. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

12. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

13. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

14. *Staphylococcus aureus*

15. *Staphylococcus aureus* (ATCC 12228) (Control strain) 100 µl

Dependence of Mercury in Coal and Coal Ash

Dependence on Sample Size: 0.10 g.

Applied Description: A study of the effect of sample size on the results of analyzing coal ash for mercury was conducted. The results of this study indicate better recovery of the mercury.

Abstract: Many methods have been published for determining mercury in coal ash (1-10). However, when we applied these methods to coal ash samples, we found that they either were too time consuming or gave poor results.

The use of H_2O_2 alone was found to destroy coal matter and convert it to the Analytical Methods Committee (11) and U.S. Bureau of Mines (12) hydrogen peroxide to oxidize coal (13). When this method was applied to National Bureau of Standards standard reference material GSP-1000, Trace Mercury in Coal, we found 0.14 ± 0.01 ppm. By flame photometry, the flame certified mercury content, obtained by neutron activation analysis, was 0.13 ppm (14), and atomic absorption spectrophotometry showed 0.13 ppm (15). (J. Murphy used the same NBS coal to verify his method.)

When this method was used to analyze National Bureau of Standards RM 1602, Trace Elements in Coal, and NBS Fly ash, low and erratic results were obtained. We attempted to improve the recovery of mercury by modifying the oxidation procedure. We surmised that either the coal was incompletely oxidized or the mercury was lost during the oxidation. Because we did not think that mercury could be lost in the presence of peroxide at about 100°C, we added 1 cm³ of concentrated nitric acid to the sulfuric acid-hydrogen peroxide solution toward the end of the digestion. With this addition, we found 0.12 ±

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43. T. C. Rains and O. Menis, JAOAC **55**, 1339 (1972).
 44. J. V. O'Gorman, N. H. Suhr, and P. L. Walker, Appl. Spectrosc. **26**, 44 (1972).
 45. M. D. Schlesinger and H. Schultz, U.S. Bureau of Mines, Rept. 7609 (1972).
 46. M. L. Kokot, Mineral Sci. Eng. **6**, 236 (1974).
 47. J. W. Wimberly, Anal. Chim. Acta **76**, 337 (1975).
 48. Analytical Methods Committee, Analyst **92**, 403 (1967).
 49. J. Murphy, At. Absorption Newsletter **14**, 151 (1975).

Determination of Carbonate Minerals in Oil Shales

Responsible Personnel: R. Lim and L. J. Gregory

Brief Description: In an attempt to improve our results, the method for determining carbonate minerals in oil shale was modified.

Status: We have been estimating the carbonate mineral in oil shale by the method described in a previous report.⁵⁰ This method is very similar to the one proposed by Young, Smith, and Robb.⁵¹ However, the method generally gives results that indicate a greater quantity of cations than the associated carbon dioxide liberated from the carbonates.*

In an attempt to find a method to extract more accurately only the carbonate minerals, we decided to use acetic acid for extracting dolomite, calcite, and ferroan. The newly proposed method is as follows:

- Malcolite is extracted with water at room temperature.
- Dolomite is then extracted from the residue with 10% acetic acid at about 90°C. Other minerals are extracted but not determined in this fraction.
- A separate sample of oil shale is taken and extracted with 7.5% acetic acid overnight at room temperature for the determination of dolomite, calcite, and ferroan.
- The Ca, Mg, and Fe in this fraction are determined by atomic absorption spectrophotometry. Other minerals are also extracted but not determined in this fraction.

The carbon dioxide content is determined by the method outlined in Ref. 50 to check the agreement with the cations found above. Calculations for the carbonate minerals are completed using the method and assumptions presented by Young, Smith, and Robb.⁵¹

*See pg. 49, Ref. 6.

50. R. Lim, L. J. Gregory, K. L. Leach, and S. B. Deutscher, Determination of Carbonate Minerals in Oil Shales, Lawrence Livermore Laboratory, Rept. UCID-17616 (1977).
51. N. B. Young, J. W. Smith, and W. A. Robb, Determination of Carbonate Minerals of Green River Formation Oil Shales, Piceance Creek Basin, U.S. Bureau of Mines, Rept. 8008 (1975).

Lab Master Batch (3-4)-1 raw oil shale was analyzed for carbonate minerals by the method described in Ref. 50 and by the newly proposed method using 7.5% acetic acid. The results are presented in Table 6.

The values for total carbon dioxide computed from the quantities of minerals found were 23.3% for the Ref. 50 method and 22.3% for our new method. The agreement with the actual amount found (the total evolved CO_2) is better for the newly proposed method.

Shales with high oil content are not easily wetted by water or dilute acids at room temperature. N. Young of the Laramie Energy Research Center has suggested that we treat the oil shales with absolute methanol first, followed by the addition of the extracting solution. This solved the wetting problem very nicely. However, when the oil shales were extracted with 7.5% acetic acid following the methanol treatment, we obtained low and erratic results. To investigate this problem, residues of oil shales were extracted with 7.5% acetic acid, with and without pretreatment with methanol, and then examined by x-ray diffraction (G. E. Smith, Metals and Ceramics Division). Smith found that appreciable amounts of dolomite remained in the residues pretreated with methanol, whereas little if any dolomite remained in the residue not treated with methanol. Our explanation for this behavior is that acetic acid is only slightly ionized in water and the presence of methanol might reduce the ionization further. Thus extractions with acetic acid in the presence of methanol are incomplete. However, when the extraction with acetic acid was conducted overnight with stirring, the wetting problem was not observed. Therefore, we eliminated the need for pretreatment with methanol by extracting overnight with the dilute acetic acid.

Table 6. Carbonate minerals determined in Lab Master Batch (3-4)-I raw oil shale by two methods.

Mineral	Quantity found, %	
	Ref. 50	New method
Nahecolite:		
NaHCO_3	0.40	0.40
KHCO_3	0.05	0.05
Dawsonite:		
$\text{NaAl}(\text{OH})_2\text{CO}_3$	3.5	3.5
Dolomite:		
	31.0	27.4
	$[(\text{Mg}_{0.72}\text{Fe}_{0.28})\text{Ca}(\text{CO}_3)_2]$	$[(\text{Mg}_{0.75}\text{Fe}_{0.25})\text{Ca}(\text{CO}_3)_2]$
Calcite:		
CaCO_3	16.9	17.9
Water Soluble		
CO_2	0.87	0.87
Acid Soluble		
CO_2	21.4	21.4
Total Evolved		
CO_2	22.27	22.27

Effects of Organic Additives on the Formation of Solids
from Geothermal Brines

Responsible Personnel: J. L. Harrar, C. H. Otto, Jr., L. E. Lorensen,^{*}
S. B. Deutscher, and G. E. Tardiff[†]

Brief Description: A number of organic compounds (mostly surfactants) are being tested with the hope of finding a material that will significantly decrease the rate of formation of solids from hypersaline geothermal brine.

Status: An important technical problem hindering the effective use of geothermal brines from the Salton Sea area is the rapid precipitation of solids when the brine is cooled. These solids are composed primarily of silica with some iron oxides and lesser amounts of heavy metal sulfides. Acidifying the brine to pH 4 delays precipitation and controls scaling of plant surfaces; however, the acidity increases corrosion rates. Even if acidification is used to control scaling, there still remains the problem of the neutralization of the acid by the CaCO_3 present in the reinjection well. Once the acid is neutralized, the silica precipitates and plugs the well passages.

We are actively seeking a method of brine treatment that will inhibit the formation of solids (primarily silica), even when the spent brine comes in contact with the CaCO_3 in the reinjection well. Presently, we are testing organic additives to stabilize the colloidal silica. A large number of such compounds have been selected for their known surface activity and, as field-testing time permits, they are being screened to test their effectiveness in reducing the rate of solids precipitation. For our initial screening, each compound is being added at a concentration of 50 ppm to the geothermal-plant effluent brine ($\sim 100^\circ\text{C}$). The rates of solids formation and silica disappearance from solution are measured as described previously^{**} by bottling the brine and incubating it at 85°C .

These experiments have been conducted concurrently with corrosion tests under varying conditions of brine pH and while the brine chemistry itself has

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^{**}See p. 33 of Ref. 1.

changed; for example, the silica levels have varied from approximately 450 to 600 mg/kg. Thus to rate the potency of each surfactant we calculate an improvement factor, IF, as

$$IF = \frac{\% \text{ SiO}_2 \text{ retained in solution with surfactant}}{\% \text{ SiO}_2 \text{ retained in solution without surfactant}},$$

where for a given incubation time,

$$\% \text{ SiO}_2 \text{ retained} = \frac{\text{concentration of SiO}_2 \text{ in solution}}{\text{initial concentration of SiO}_2 \text{ in solution}}.$$

As in previous work, the SiO_2 in solution is that not retained by a 5- μm porous glass filter (as determined in the filtrate by atomic absorption spectrophotometry).

A summary of the results for substances tested to date is given in Table 7. The quantity of solids precipitated from the brine parallels and varies inversely with the calculated silica-retention improvement factor; thus the solids data are not shown. However, the silica measurement data are the more reliable because filter plugging sometimes prevents accurate solids measurement. The quantities of solids precipitated vary from ~300 to ~500 mg/kg for the brines initially containing ~450 to 600 mg/kg SiO_2 , respectively. Table 8 lists the brand and chemical names of the additives tested.

From this initial screening, it is clear that the Natrosols, which are hydroxyethylcelluloses, are quite effectively keep the silica in solution at all pHs. Their effectiveness at pH 5.7 was mitigated by the fact that the silica particles had grown too large before the brine was mixed with surfactant. On the basis of these results obtained in bench testing, we also conducted two experiments adding Natrosol in the plant at high temperature, using the unacidified brine at pH 6.0.

The results were inconclusive: in the first experiment, solids formation and scaling were markedly inhibited; in the second experiment, the Natrosol had no effect. This discrepancy may be due to a difference in age of the two stock solutions used. Further experiments of this type will be conducted to resolve this question. Although not presented here, data on the levels of solid formation vs time in the presence of additives reveal that no additive postpones silica precipitation indefinitely; they merely postpone precipitation. A 24-h delay in precipitation will be sufficient if the quantity of

Table 7. Effect of organic substances on the precipitation of silica from hypersaline geothermal brine at an 80°C incubation temperature (see Table 8 for names of additives).

Brine pH	Initial SiO ₂ , mg/kg	Incubation time, h	Additive No.	SiO ₂ retained, %	Improvement factor
5.70	380	18	None	51	—
			2	51	1.00
			3	51	1.00
			4	65	1.33
			5	65	1.33
			7	55	1.14
5.15	552	4	None	51	—
			4	99	2.60
			10	88	2.42
			11	67	1.03
			15	67	1.76
			16	39	1.03
4.09	473	22	None	54	—
			2	Solution clear but not filterable	—
			3	53	0.98
			4	99	1.83
			5	98	1.81
			7	Immediate precipitate	—
			8	43	0.80
			9	48	0.89
3.09	473	240	H ₂ O (20 wt%)	93	1.72
			None	40	—
			5	83	2.08
			8	40	1.00
			9	40	1.00

Table 8. Additives tested for their effect on precipitation of silica from hypersaline geothermal brine.

Additive No.	Manufacturer	Brand name	Chemical name
2	American Cyanamid	Cyanamer P-250	Polyacrylamide
3	DuPont	NaCMC S-75H	Carboxymethylcellulose
4	Hercules	Natrosol 250L	Hydroxyethylcellulose
5	Hercules	Natrosol 250LR	Hydroxyethylcellulose with glyoxal group
7	Goodrich	Carbopol 941	Acrylic acid copolymer
8	Union Carbide	A1100	γ -Aminopropyltriethoxysilane
9	Union Carbide	Z6070	Methyltrimethoxysilane
10	Goodrich-Goodrite	K732	Polyacrylic acid
11	Goodrich-Goodrite	K748	Sodium polyacrylate
15	Rohm & Haas	Triton X-100	Phenoxypolyethoxyethanol
16	American Cyanamid	Cyanamer P-35	Polyacrylamide-anionic

solids of particle size $>1\text{ }\mu\text{m}$ is less than 2 ppm, especially if this criterion can be met even after a pH rise to 5.7 when the brine comes in contact with CaCO_3 in the reinjection well.

Additional compounds will be tested in the near future. Although the addition of surface-active agents to the brine to prevent solids formation ultimately may not be economical for generating geothermal power, the initial promise of a few of these compounds opens some interesting possibilities for solids control. It may prove to be worthwhile to use the additives in combination with the previously proven approaches of acidification and dilution of the brine.* If all of these techniques fail to produce injectable brine, solids removal coupled to mineral recovery may yet be the best solution to this precipitation problem.

* See p. 33 of Ref. 1.

Special Projects

Experimental Demonstration of the Effects of Turbulence and/or Electric

Fields on the Coagulation Processes of Aerosols

Responsible Personnel: N. M. Fulk, E. B. Huss, and J. E. Lane^{*}

Brief Description: The chemiluminescent reaction of Fe^{2+} and luminol is being studied for the measurement of real-time coagulation processes and the rates of formation of aerosols. Using 80- μm -o.d. droplets of water containing 1.7×10^{-12} g of Fe^{2+} interacting with a luminol solution, our present sensitivity is about 2 to 4×10^{-14} g of Fe^{2+} per event. However, we think this sensitivity can be improved.

Status: During December 1977, we made a successful run using the Fe^{2+} chemiluminescent system. Droplets of Fe^{2+} solution of about 80 μm o.d. were dropped onto the surface of a luminol solution. The droplet volume was about $2.7 \times 10^{-7} \text{ cm}^3$ and contained about 2×10^{-12} g of Fe^{2+} . The Fe^{2+} solution was prepared from $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ dissolved in double-distilled water that had been flushed with argon for over 8 h. The pH of the solution was 6.1. The stock solution was $5 \times 10^{-3} \text{ M}$ luminol in 0.1 M borate buffer adjusted to a pH of 11. Just before the run, 40 μm^3 of 80% H_2O_2 was added to 50 cm^3 of the luminol solution.

When the droplet interacted with the luminol surface, it gave a clear signal on the RCA 4522 photomultiplier (PM) tube using the "dc string" at 2.2 kV. The signal-to-noise ratio was between 6 and 7. The pulse rise time was about 0.3 to $0.5 \times 10^{-3} \text{ s}$ and the pulse width was about 2.5 to $3.6 \times 10^{-3} \text{ s}$. The pulses corresponded to the kick-out frequency and the time resolution should easily be about $2 \times 10^{-3} \text{ s}$, even for our crude configuration. The present sensitivity appears to be about 2 to 4×10^{-13} g of Fe^{2+} per event. This corresponds to an equivalent "dry" particle of about 0.3 μm o.d. of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$. This level of sensitivity probably can be improved.

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[†]See p. 38 of Ref. 1.

A block diagram of the droplet generator, droplet switchout, and strobe set-up for producing, selecting, and observing the droplets is shown in Fig. 34. A schematic diagram of the photomultiplier system is given in Fig. 35. In Fig. 36, we show a typical chemiluminescent reaction pulse when a 80- μ m-o.d. droplet containing 2×10^{-2} g Fe^{2+} strikes the surface of a luminol solution. A number of these pulses were recorded assuring us that the rise and fall rates were characteristic and repeatable. Figure 37 shows the light-pulse spacing relative to that of the TTL signal which switches out the Fe^{2+} -containing droplet.

Fig. 34. Diagram of the droplet generator.

Fig. 35. Diagram of the photomultiplier system.

Fig. 36. Photomultiplier signal for the light pulse from a 80- μ m-o.d. droplet containing 2×10^{-12} g Fe^{2+} . The vertical sensitivity is 250 mV/division and the horizontal sensitivity is 1 ms/division.

Fig. 37. The light pulse signal (left) and the TTL signal (right) that switches out the Fe^{2+} -containing droplet. The vertical sensitivity is 250 mV/division and the horizontal sensitivity is 5 ms/division.

Testing of a New Gas Chromatograph/Mass Spectrometer

Responsible Personnel: C. J. Morris

Brief Description: A Hewlett-Packard gas chromatograph-mass spectrometer (GC/MS) has been installed and tested in Building 362 for the Environmental Sciences Division. This instrument is capable of qualitative and quantitative analysis of a wide variety of complex mixtures. Generally, the samples best suited for GC/MS analysis are complex organic mixtures; however, gaseous or low-vapor-pressure solid organic material often can be analyzed with special techniques. This instrument is now fully operational and samples are being analyzed routinely.

Status: The following is a brief description of this new instrument:

- Gas Chromatograph. The GC used in this system is a Hewlett-Packard (HP) Model 5840A. Variable effluent splitters allow simultaneous GC/MS detection. This GC is equipped for either packed column or split/splitless capillary column separation. Normal GC detection is accomplished with a flame ionization detector; however, a thermal conductivity detector is also available for nonorganic analysis.
- Mass Spectrometer. The hyperbolic quadrupole MS includes a dual electron impact chemical ionization (EI/CI) source. The mass range of this MS is 10 to 1000 amu with a maximum scan rate of 925 amu/s.
- GC/MS Interface. This interface allows four modes of sample introduction into the MS:
 - (1) Sample introduction from the packaged column into the EI source with the jet separator.
 - (2) Direct sample introduction from the packed column into the CI source.
 - (3) Direct sample introduction from the capillary column into either the EI or CI source.
 - (4) Use of the direct outlet probe for solid or "other" sample introduction.

- Data System. This system includes the HP Model 21 MX-E computer and the HP Model 7905A 5-megabyte dual disk drive. The software system provides an extensive list of data acquisition and data reduction programs.

After a two-month testing period, we conclude that this instrument meets the required specifications for complex mixture analysis and trace analysis (its sensitivity is 1 ng in the EI mode and 50 pg in the CI mode). Figure 38 shows a typical capillary run produced from an ocean oil seepage sample.

The main operational problem involves the library search software. We are presently improving this software and current plans call for an Improved Library (30,000 spectra edited by Wiley, Inc.), coupled to an Improved Library search software program based on the McLafferty system. In addition, a new 5-megabyte (HP Model 7920A) disk drive is now available which will greatly speed the data reduction and offer an Improved data-match capability.

Fig. 38. Typical capillary runs produced from an ocean oil seepage sample using the new gas chromatograph/mass spectrometer. We have tested this instrument thoroughly and conclude that it meets the required specifications for trace and complex mixture analysis.

Microwave Spectrometer Multiple-Gas Analyzer

Responsible Personnel: L. W. Hrubesh, R. L. Morrison, A. S. Maddux,^{*}
J. N. Nielsen,^{*} and D. C. Johnson[†]

Brief Description: Work on the microwave-spectrometer multiple gas analyzer for National Institute for Occupational Safety and Health (NIOSH) is nearing completion.^{**}

Status: Development of the prototype multigas analyzer for NIOSH is nearly completed. The instrument has been fabricated in its final packaged configuration and currently is being tested and calibrated. Specifications for size and weight have been met (the instrument is packaged in a 27.2 x 48.3 x 43.2 cm deep enclosure and weighs 14.5 kg). The instrument can operate on either ac voltage or by battery. Ten compounds, selectable by pushbuttons at the front panel, can be monitored. Additional compounds can be added to the instrument's capability with slight adjustments. The instrument can measure concentrations at one-fifth the threshold limit values for each of the compounds, and has a general detection range for all compounds from 0 to 1000 ppm.

A minor problem has been observed when SO₂ apparently adsorbs onto the inlet and cell walls. Signals from SO₂ then persist for several minutes after the standard has been replaced by a zero air sample. This problem was experienced formerly with monitors for water vapor and ammonia and heating the inlet of these monitors considerably reduced the adsorption. However, because the multigas instrument is designed for minimum power consumption, we chose to accept the longer response time for SO₂ and not provide a heated inlet.

We expect to deliver the instrument to NIOSH before March 1978. The instrument then will be thoroughly tested by the engineering branch of NIOSH. As a result of this development, this microwave technique may be established as a standard analytical technique for industrial hygienists by NIOSH, at least for some vapors of current interest.

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^{**}see p. 40 of Ref. 1.

Data Management, Analysis, and Reporting

Support for the NURE:HSSR Project

Responsible Personnel: S. L. Grotch, B. F. Holder, B. S. Cumm,^{*} and J. D. Attebery⁺

Brief Description: We are providing support to the LLL's hydrogeochemical stream-sediment reconnaissance (HSSR) effort for the National Uranium Resource Evaluation (NURE). Seven Western states are being surveyed to provide relevant geochemical data that will enable improved estimates and evaluations of U.S. uranium resources. During the last quarter, computer programs were written to generate the hard copy data tables, microfiche tables, histograms, and map overlays required in the project's data release reports. In addition, data flow and management procedures were developed and standardized. Several computer programs were written to aid the interpretation of the geochemical data.

Status: A primary role of the General Chemistry Division for NURE is directing the "Information Management and Reporting." This task is concerned principally with:

- Producing all of the computer generated maps, hard copy, and microfiche data tables, and coordinating the activities leading to the reporting of geochemical data.
- Maintaining computer data bases of all relevant geological and analytical data.
- Developing the software and collaborating in the geostatistical interpretation of the data.

During the last quarter, our attention was focused on developing the techniques and procedures required for the computer generation of the NURE raw data reports. We anticipate that approximately one raw data report per week will be produced throughout the life of the project. In addition to textual material, each report will contain computer-generated items, including:

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- Full scale map overlays (at least four per report) that indicate precisely the sample site locations and the measured radionuclide concentrations for sediments and waters.
- Tabulations of analytical data (data as bar charts and as grid profiles).
- Uranium histograms showing the distribution of uranium concentration observed for the area covered by the report.

The computer software for generating these outputs is largely completed. LLL software was vital to the production of our first raw data report on the Lake Valley, Nevada, pilot study (labeled as report PCID-1764-9).

For data base management of the large amount of hydrogeochemical data, we have used the LLL Master Control Program (run by R. L. Gans of the Computations Division). These data bases contain essentially all the geological site data as well as the analytical results produced by the neutron activation systems, emission spectrometer, and Technicon AutoAnalyzer. Procedures have been developed to enter these site data into the data bases. In addition to providing a single centralized source of data for the project, Master Control also facilitates the automatic generation of the extensive raw data tables required in the NERE reports. Protocols for automatically providing these tables are largely complete.

A number of computer programs were developed during the past quarter to aid in the interpretation of the NERE geochemical data. The procedure for data analysis begins by using the computer data bases on the CDC 7600 that contain all relevant site and analytical results. These data are stored with Master Control. From these data, a Fortran-readable "project file" is formed. This "project file" serves as the input for our analysis programs.

Because the LLL time-sharing system provides for a high degree of user interaction, our programs have been structured to take advantage of this capability. In most cases, the programs query the user for the data inputs required and provide real-time graphical and textual display of output data. Two of the more frequently used computer programs developed follow:

- (1) A program that will produce a "scatter plot" such as that shown in Fig. 39. The user may plot any combination of stored variables of the form

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$$X_1^{a_1} X_2^{a_2} X_3^{a_3} X_4^{a_4} X_5^{a_5},$$

against any combination

$$Y_1^{b_1} Y_2^{b_2} Y_3^{b_3} Y_4^{b_4} Y_5^{b_5},$$

either on a log-log, semi-log, or linear scale. The chemical variables, X_i and Y_i , and the coefficients, a_i and b_i are entered by the user in real time. With this generalized format, it is a simple matter for the user to plot, for example, U/Th vs Mo^{2+} as a log-log plot (Fig. 39). Each data point is represented on the plot by an asterik with a site number printed beside the point.

- (2) To more readily determine relationships between chemical variables, the cross correlations between all pairs of analytical results are calculated and presented as a series of tables. For each element (in alphabetical order), the correlations between that element and all other elements are given. The list is then sorted by decreasing absolute magnitude of the correlation coefficients and the ten highest values are given. Finally, for all pairs of elements examined, the ten highest absolute cross correlations are tabulated. Estimates also are presented for the confidence limits appropriate to each coefficient.

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R. Bastasz C.A. Colmenares	Electron Induced Luminescence as a Technique for Studying the Absorption of Oxygen and the Oxidation of Thorium	UCRL-79763, July, 1977.
C.A. Colmenares	An Overview of Surface Related Problems in the Nuclear Energy Field	UCID-17491, May, 1977.
T.T. Coburn* R.E. Bozak J.E. Clarkson J.H. Campbell	Oil Shale Retorting: Part 3, A Correlation of Shale Oil 1-Alkene/n-Alkane Ratios with Yield	UCRL-52256, Part 3, August, 1977.
L.P. Rigdon C.J. Moody* J.W. Frazer**	Determination of Residual Chlorine in Water Using Computer Automation and the Orion Residual Chlorine Electrode	UCRL-80006, (Preprint), August, 1977.

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Presentations

E.F. Worden*	Accurate Ionization Potentials of Lanthanide Atoms by Laser Spectroscopy	Optical Society of America Annual Meeting, Toronto, Canada, October, 1977.
R.W. Solarz [†]		
J.A. Paisner [†]		
J.G. Conway**		
E.F. Worden	Laser Spectroscopy of Atoms	Monthly Meeting of the Northern Section of the Society for Applied Spectroscopy, Livermore, CA, May 1977.
E.F. Worden	Stepwise Laser Photoionization of Lanthanides	Gordon Conference on Atomic Physics, Brewster Academy, Wolfeboro, NH, July, 1977.
R.W. Solarz*, [†]	Multiphoton Spectroscopy of Heavy Elements	International Conference on Multiphoton Processes, Rochester, NY, June, 1977.
J.A. Paisner [†]		
E.F. Worden		
J.A. Paisner*, [†]	Identification of Rydberg States in the Atomic Lanthanides and Actinides	International Conference on Laser Spectroscopy, Jackson Hole, WY, July, 1977.
R.W. Solarz [†]		
E.F. Worden		
J.W. Frazer	Functional Schematics in the Automation Project Scheme	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March, 1977.
R.F. Morris*		

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Presentations (Continued)

W.F. Morris*	Application of the Systematic Approach to Laboratory Automation	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March, 1977.
W.G. Boyle*	A Microprocessor Controlled Dual Beam Automatic Dilutor	FACSS Meeting, Detroit, MI, November, 1977.
L.D. Breshears*		
G.M. Hieftje*,**	New Method for the Determination of Luminescence Lifetimes Using Laser Mode Noise as a Multifrequency Modulated Excitation Source	American Chemical Society Meeting, New Orleans, LA, March, 1977.
J.M. Ramsey**		
G.R. Haugen		
G.M. Hieftje**	New Method for the Measurement of Subnanosecond Photodetector Response Times	FACSS Meeting, Detroit, MI, November, 1977.
G.R. Haugen		
J.M. Ramsey*,**		
R.L. Bystroff*	Atomization Studies in an Atmospheric Pressure Glow Discharge	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March, 1977.
L.R. Layman**		
G.M. Hieftje**		
G.R. Haugen	Analytical Applications of Correlation Analysis and Measurement of Fluorescent Lifetimes with Mode Noise	University of Edinburgh and Heriot Watt University, Edinburgh, Scotland, September, 1977.
G.R. Haugen	Analytical Utility of Nanosecond Fluorimetry	University of Strathclyde, University of Stirling, University of Glasgow, Scotland, September, 1977.

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Presentations (Continued)

G.R. Haugen*	Analytical Utility of Nanosecond Fluorimetry	Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March, 1977.
F. Lytle*		
L.W. Hrubesh	Fast Qualitative Gas Mixture Analysis with an Automated Microwave Spectrometer	FACSS Meeting, Detroit, MI, November, 1977.
R.G. Gutmacher*	Accountability Methods for Plutonium and Uranium - The NRC Manuals	Conference on Analytical Chemistry In Energy Technology, Gallatinburg, TN, October, 1977.
F.B. Stephens		
G.W. Barton, Jr.	The EPA Water Quality Laboratory Automation Project	Alcoa Laboratories, Alcoa Center, PA, February, 1977.
G.W. Barton, Jr.	Automatic Real-Time Process Control	LRDA Division of Coal Conversion, Washington, D.C., February, 1977.
R.G. Meisenheimer*	Grain Boundary Concentration Mapping by the CORAD Technique	Joint Meeting of the Northern and Southern California Societies for Electron Microscopy and Microbeam Analysis, San Francisco, CA, February, 1977.
D.D. McCoy		
R.G. Meisenheimer	A Comparison of Bulk and Surface Analysis of Metal	FACSS Meeting, Detroit, MI, November, 1977.
J.W. Fischer*	Smelter Aerosol	
D.J. Eatough**		
N.F. Mangelsen**		
M.W. Hill**		

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Presentations (Continued)

P.G. Meisenheimer	ESCA Studies of Aging, Decomposition and Compatibility of TATB	Los Alamos TATB Meeting, Los Alamos Scientific Laboratory, Los Alamos, NM, May, 1977.
R.G. Meisenheimer J.W. Fischer D.J. Eatough*,† T. Major† J. Reder† M. Hill† N.F. Mangelsen† N.L. Eatough† L.H. Hansen†	The Formation and Stability of Sulfite Species in Aerosols	International Symposium on Sulfur in the Atmosphere, Dubrovnik, Yugoslavia, September, 1977.
R.G. Meisenheimer J.W. Fischer R.M. Izatt† D.J. Eatough*,† M.L. Lee† T. Major† B.E. Richter† L.H. Hansen†	The Formation of Inorganic and Organic S(IV) Species in Aerosols	Joint Conference on Sensing of Environmental Pollutants: American Chemical Society, New Orleans, LA, November, 1977.
R.L. Ward	Ethene from Algae	Meeting of Santa Clara Section, American Chemical Society, Palo Alto, CA, March, 1977.
R.L. Ward	Methane from Algae Grown in Desert Regions of California Using Available Ground Waters	Energy Farms Workshop of the Energy Resource Conservation and Development Commission, Sacramento, CA, July, 1977.

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Presentations (Continued)

H. Timourian*, ⁺ R.L. Ward T.W. Jeffries**	Growth of Filamentous Blue-Green Algae at High Temperature: A Source of Biomass for Renewable Fuels	IX International Seaweed Symposium, Santa Barbara, CA, August, 1977.
W. Selig	How to Estimate the Solubility of an Insoluble Compound - TATB	Los Alamos TATB Meeting, Los Alamos Scientific Laboratory, Los Alamos, NM, May, 1977.
		Propellant Characterization Working Groups Meeting, USAF Academy, Colorado Springs, CO, June, 1977.
J.L. Harrar	State of the Art of Electrochemical Studies in Geothermal Environments	Panel Discussion at Meeting of National Association of Corrosion Engineers, San Francisco, CA, March, 1977.
J.H. Hill* C.H. Otto	Sampling and Characterization of Suspended Solids in Brine from Magmamax No. 1 Well	Workshop on Sampling and Analysis of Geothermal Effluents, Las Vegas, February, 1977.
J.H. Hill* C.H. Otto C.J. Morris	Solids Control for High Salinity Geothermal Brines	Geothermal Resources Council Meeting, San Diego, CA, May, 1977.
J.E. Harrar* R.D. McCright ⁺⁺ A. Goldberg ⁺⁺⁺	Materials Evaluation for Geothermal Applications: Plant Materials	Geothermal Resources Council Meeting, San Diego, CA, May, 1977.

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⁺⁺⁺Metals and Ceramics Division, LLL.

Presentations (Continued)

K. Lewis*,†	Evaluation of Automated System	Conference on Analytical
D.L. Colwell*	for Determination of Uranium	Chemistry in Energy
C.C. Goldbeck*		Technology, Gatlinburg,
G.L. Barrar		TN, October, 1977.
J.H. Richardson	Lasers in Chemical Analysis	Chemistry Department
		Seminar, Stanislaus
		State College, Turlock,
		CA, April, 1977.
		Seminar, University of
		California at Davis,
		Davis, CA, May, 1977.
J.H. Richardson*	Sub-part-per-trillion	American Chemical
M.C. Ando**	Detection by Laser Induced	Meeting, New Orleans,
D.C. Johnson*†	Molecular Fluorescence	LA, March, 1977.
B.A. Kallin*††		
J.H. Richardson	Light Isotope Ratio Measurements	Meeting of American
R.K. Stump*	with a Computer Controlled	Society for Mass
J.D. Breshears***	Pulsed Ion Cyclotron Resonance	Spectrometry,
S.T. Helver, Jr.*†††	Spectrometer	Washington, D.C., June,
		1977.
S.B. Deutscher	Diffusion Constants and	American Nuclear Society
S.M. Alire*,f	Solubilities of Hydrogen and	Meeting, New York, NY,
S.A. Steward,f	Deuterium in Lithium Oxide	June, 1977.
R.C. Garza*	Air-Water Synthesis of Ammonia	International Conference
R.H. Hickman,*	In Order to Remove Petrochemicals	on Alternative Energy
J.F. Shan,f	as the Hydrogen Source	Sources, Miami, Florida,
S.A. Steward,f		December, 1977.
P.C. Souers,f		

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***Electronic Engineering Department, LLL.

†††Consultant, University of California at Irvine.

fChemical Engineering Division, LLL.

Presentations (Continued)

C.A. Colmenares	Plutonium Hydride Air Reactions	US-UK Stocktake Meeting, Albuquerque Operations Office, Department of Energy, July, 1977.
H. Golopel	Compatibility Tests on Unstressed Coated Kevlar Strands	ERDA Compatibility Meeting, Mound Laboratory, October, 1977.
H. Golopel	A New Booster Explosive	JOROG-9 Meeting, Los Alamos Scientific Laboratory, May, 1977.
H. Golopel	XTN-8003 Aging Studies	JOROG-9 Meeting, Los Alamos Scientific Laboratory, May, 1977.
B. Kenton* H. Loider	Relationship between Weight Loss, Evolved Gases, and Change in Nitrocellulose Concentration in PBX-9404	ERDA Compatibility Meeting, Mound Laboratory, October, 1977.
C.A. Colmenares* D. McKenzie J. Magistad*	K-58 Lifetime Estimates from Surveillance Data	ERDA Compatibility Meeting, Mound Laboratory, October, 1977.
R. Bastasz C.A. Colmenares	Auger Study of Surface Carbon and Oxygen on Thorium Following Ion Bombardment	Annual Symposium and Vacuum Equipment Exhibit, Boston, MA, November, 1977.
C.A. Colmenares	An Overview of Surface Related Problems in the Nuclear Energy Field	ERDA Workshop, Lawrence Berkeley Laboratory, March, 1977.
J.A. Happe* C.A. Colmenares T. McCreary	Corrosion and ESCA Studies of Uranium after Exposure to an RF Discharge	SUBKOG-12, St., Petersburg, FL, February, 1977. JOWOG-12 Meeting, Los Alamos Scientific Laboratory, May, 1977.
C.A. Colmenares	Testing of Aluminum-Stainless Steel Solid State Bonds for Long Term Compatibility	JOROG-12 Meeting, Los Alamos Scientific Laboratory, May, 1977.

*Speaker.

†Consultant.

Presentations (Continued)

R. Bastasz*	Electron-Induced Luminescence as	STROG-12 Technical
G.A. Colmenares	a Technique for Studying the	Exchange Meeting, St.
G.A. Somorjai†	Absorption of Oxygen and the	Petersburg, FL,
R.L. Smith**	oxidation of Thorium	February, 1977.
		JORG-12 Meeting, Los
		Alamos Scientific
		Laboratory, May, 1977.
		American Chemical
		Society Meeting, New
		Orleans, LA, March,
		1977.
G.A. Colmenares	Review of Gas-Metal Interactions	JORG-12 Meeting, Los
		Alamos Scientific
		Laboratory, May, 1977.
H. Lelder	PBX-9404	Briefing Meeting,
		Aero-Chem Laboratory,
		March, 1977.
J.W. Frazer*,††	Experimental Techniques for	Conference on
L.P. Rigdon	System Characterization and	Analytical Chemistry
G.L. Pomernacki***	Development of Control	and Applied
T.A. Brubaker†††	Algorithms	Spectroscopy, Cleveland,
		OH, March, 1977.
J.W. Frazer*,††	Rapid Characterization of	Gordon Research
L.P. Rigdon	Enzyme Kinetic Parameters by	Conference on Analytical
	Computer Automation	Chemistry, New Hampton,
		NH, August, 1977.

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††Chemistry and Materials Science Department, LLL.

***Electronics Engineering Department, LLL.

†††Colorado State University, Fort Collins, Colorado.

Presentations (Continued)

J.W. Frazer*, [†] L.P. Rigdon	Computer Graphic Techniques Improve Ion Selective Electrode Utilization	Conference on Analytical Chemistry and Applied Spectroscopy, Cleveland, OH, March, 1977.
W. Siekhaus	Modulated Molecular Beam Spectroscopy for Reaction Kinetic Studies	Seminar, Department of Physics, University of Kuwait, Kuwait, March, 1977.
W. Siekhaus	Molecular Beam Study of H ₂ -D ₂ Exchange	Seminar, Institute für Grenzflächen Forschung, Jülich, Germany, March, 1977.

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