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GENERAL CHEMISTRY DIVISION QUARTERLY REPORT

ANALYTICAL RESEARCH AND DEVELOPMENT FOR THE
NUCLEAR EXPLOSIVES PROGRAMS

Hyphenated Instruments Development

Responsible Personnel: R. W. Crawford, T. B. Hirschfeld, C. M. Wong, R. H. Sanborn, and R. G. Meisenheimer.

Brief Description: Modern analytical instruments are fast, precise, and employ the power of computers, but often the results from a single instrument are ambiguous. We are attempting to wed several instruments in real time to increase the reliability of analysis. Initial experiments will test gas chromatography (GC) as an input to fast-Fourier-transform infrared (FTIR) and mass spectrometry, either in series or parallel.

Status: Advances in instrumentation and the incorporation of powerful computers have created some remarkable analytical tools. One of the most powerful instruments in the realm of organic qualitative and quantitative analysis is the computerized gas chromatograph-mass spectrometer (GC-MS).¹ This instrument combines the outstanding separatory properties of the capillary chromatographic column with the fast and sensitive fingerprinting capability of the mass spectrometer. The computer allows rapid data accumulation, e.g., a scan from 40 to 400 atomic mass units (AMU) with three data readings at each 1/8 of an AMU in only one second. The computer also makes it possible to store large amounts of data, rapidly access it, and then search large libraries of known compounds to match the unknown spectra.

However, the GC-MS system has some problems in unequivocally identifying unknowns using the computer library search. One of the problems is due to inaccuracies or large differences in instrument characteristics that cause real differences between spectra from known compounds. Most library spectra

1. General Chemistry Division Quarterly Report, July through September 1979, Lawrence Livermore Laboratory, Livermore, CA, UCID-15644-79-3 (1979), p. 29.

are taken on magnetic instruments, which produce different cracking patterns than do the quadrupole instruments in GC-MS systems. Instrument manufacturers are attempting to reduce this problem by using computer software that adjusts the relative peak intensities from different instrument types to match a theoretical "standard instrument."

A second problem involves the Probability-Based Search (PBS) algorithm used for searching libraries. This algorithm, developed by McLafferty and co-workers,² can use either condensed or full library spectra for searching. The condensed search is most frequently used, since it significantly reduces the searching time. For example, to search all compounds between the molecular weights of 113 and 156, a condensed search takes 50 seconds whereas a full search takes 660 seconds. The condensed spectra in the library consist of 10 peaks chosen for both the uniqueness of a particular mass and the intensity. Unfortunately, the condensed spectra of the library are compared to the full spectra of the unknown sample. The following example illustrates the problems that arise with this approach and the need for an improved algorithm to increase the reliability for the condensed search routine.

A mixture of 10 pure normal alkanes, C-6 through C-16, was injected into the GC-MS. The spectrum for each pure alkane was obtained by manual selection of peak centers and corrected for solvent or column bleed. For each spectrum, the computer used the PBS algorithm to search the library spectra to come up with the best matches (a maximum of 10). Table 1 gives an example of the results--the computer matching for C-10, n-decane.

As can be seen, the results are discouraging: the true identity of the compound used is listed as the eighth and ninth choices, while the first two choices are branched C-8 alkanes. Figure 1 shows the condensed library spectra of the first choice (2,5-dimethylhexane) and the eighth choice (n-decane) vs the injected n-decane. By visual inspection, it is obvious that the library spectrum of n-decane matches much more closely than the library spectrum of 2,5-dimethylhexane picked by the computer.

A better, but somewhat more time-consuming, approach is to first find the 10 best fits using the condensed spectra, and then repeat the search using the full spectra of only these 10 compounds. Table 2 shows an example of this approach, again using n-decane as the unknown. As can be seen, this approach

2. F. W. McLafferty, R. H. Herlet and R. D. Villwoeck, Org. Mass Spectry. 9, 690 (1974).

TABLE 1. Results of probability-based computer search of library spectra to match the spectrum of n-decane, when condensed spectra are searched.

Compound	Confidence
	Index
2,5-Dimethylhexane	.9796
3,3-Dimethylhexane	.9780
2,2,3,3-Tetramethylpentane	.9775
3-Methyl-2-Propylpentanol	.9751
n-Pentyl Bromide	.9726
3-Bromopentane	.9706
2-Bromopentane	.9703
n-Decane (source 1)	.8791
n-Decane (source 2)	.8708

gives only two library spectra that really match the full unknown spectra, and both of them are n-decane.

Another problem faced by GC-MS is differentiation between isomers. Figure 2 shows the mass spectra of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene; they are essentially identical. Since isomeric information can be critical, especially in toxicological studies, data other than mass spectra are needed.

A possible solution to this problem is to add the information of infrared spectrometry (IR). Infrared spectra are quite specific in separating and

TABLE 2. Results of probability-based computer search of library spectra to match the spectrum of n-decane, when condensed spectra are searched to find the 10 best fits and then the full spectra of those 10 are searched.

Compound	Confidence
	Index
n-Decane (source 1)	.8480
n-Decane (source 2)	.6964

FIG. 1. Comparison of the unknown spectrum (n-decane) with the GC-MS condensed library spectra of the first choice of the library search (2,5-dimethylhexane) and the eighth choice (n-decane).

FIG. 2. Example of the mass spectra of two isomers, showing the lack of differentiation.

identifying isomeric compounds. Figure 3 shows the library IR spectra of 1,2,4-trimethylbenzene and 1,3,5-trimethylbenzene; the differences are obvious, especially at 1600, 1500, 840, 800, and 690 wavenumbers.

On the other hand, IR spectrometry has great difficulty in differentiating between long-chain hydrocarbons that differ by only one carbon, whereas the mass spectrometer can easily make this distinction since each of these hydrocarbons have molecular ions of useful intensity. To illustrate this, Fig. 4 shows the gas-phase IR spectra of the C-15 and C-16 normal alkanes. The very slight difference in intensity at 2970 and 2860 wavenumbers would be useful only under ideal conditions; although different, liquid-phase spectra of these same compounds are no more differentiated than gas-phase spectra. Thus, MS and IR are naturally complementary techniques; moreover, the availability of FTIR opens totally new possibilities for combining these instruments. With the addition of a cryogenic detector and a 2-ml-volume, light-pipe gas cell to the Digilab FTIR instrument, we can scan and record an entire spectrum with 8 cm^{-1} in 0.5 sec.

The initial experiments will involve connecting the output of the GC in the GC-MS to the FTIR instrument and then back to the MS, so that peaks can be detected by both methods. This eliminates the possibility of losing peak sequence in complex GC runs, which would occur if separate GC-MS and GC-IR runs were made. Since the FTIR technique is 10 times less sensitive than the MS (10-ng vs 1-ng sample size), larger-capacity GC columns have to be used to increase sample volume. We have acquired both a Support Coated Open Tubular (SCOT) column and a wide-bore (0.32 mm vs the normal 0.2 mm) Wall Coated Open Tubular (WCOT) column, which will increase sample volume by two to four times.

The GC oven has been modified to take gases in and out through needle valves and heated lines. These lines will be connected to the light pipe in the FTIR instrument. If peak-spreading occurs in the light pipe and the series connection does not work, parallel operation will be tested using a splitter at the end of the GC column.

Primary accomplishments for this initial quarter were the design of initial experiments, ordering of equipment and supplies, installation and testing of the GC-IR attachment, and training of personnel on the major instruments.

FIG. 3. Example of the infrared spectra of two isomers, showing the marked differentiation.

FIG. 4. Example of the infrared spectra of adjacent members of a homologous series, showing the lack of differentiation.

Improved Inlet for Quantitative Mass Spectrometry

Responsible Personnel: R. W. Crawford, C. M. Wong, and K. B. Raut*

Brief Description: We are doing experiments to test an apparatus for the on-line cryogenic (-196°C) separation of gases at the inlet of a mass spectrometer. This technique will be eventually applied to the CEC Model 21-103C mass spectrometer to improve the quantitative analysis of complex mixtures.

Status: The previous experiments that showed promise for this cryogenic technique were done on a quadrupole mass spectrometer.³ Recent experiments were done on the time-of-flight (TOF) mass spectrometer that was used for on-line analysis in the underground coal-gasification field test (Hoe Creek No. 3). The two main advantages of using this spectrometer were its compatibility with an available computer system (a portable LSI-11 system designed for the UTI Corporation quadrupole mass spectrometer) and its proven analytical performance. The inlet of this instrument is a continuous-flow type, which eliminates the changes in partial pressure with time that are characteristic of reservoir inlets. This allowed us to simplify the experiments.

The technique used is as follows. After calibration with pure gases, a gas mixture is analyzed and its spectrum is recorded in the normal fashion. A liquid-nitrogen (-196°C) trap is then placed between the gold leak and the mass spectrometer. A second spectrum, which consists of gases that are not condensed at -196°C (H_2 , N_2 , O_2 , Ar, Co, and CH_4), is recorded. The computer then takes the difference between the first and second spectra and records it as the condensibles (CO_2 , C_2H_6 , C_3H_8 , C_4H_{10}). Each spectrum is calculated separately. The calculated partial pressures of the noncondensable and condensable fractions are then summed and normalized.

Table 3 shows the results of five replicate runs for the determination of nitrogen. The analyzed gas mixture contained 1.00% N_2 , 0.99% Ar, 27.77% CO_2 , 24.56% CO, 41.00% H_2 , 5.05% CH_4 , 0.31% C_2H_6 , 0.12% C_3H_8 , and 0.10% n- C_4H_{10} .

* Summer Institute professor, Savannah (Georgia) State College.

3. General Chemistry Division Quarterly Report, April through June 1979, Lawrence Livermore Laboratory, Livermore, CA, UCID-15644-79-2 (1979), p. 6.

TABLE 3. Results of the determination of nitrogen in gas mixtures by mass spectrometry using the cryogenic inlet system. Known value = 1.00% N₂, determined as mean of 12 runs using the CEC 21-103C mass spectrometer. (See text for other gas constituents.)

Normal technique		Cryogenic trap technique	
Run number	N ₂ found, %	Run number	N ₂ found, %
1	0.35	1	0.66
2	0.69	2	0.87
3	0.75	3	0.90
4	0.86	4	1.00
5	<u>0.50</u>	5	<u>0.97</u>
Mean	0.63	Mean	0.88
Standard deviation	0.20	Standard deviation	0.12
Bias	-0.37	Bias	-0.12

This mixture was used because it is typical of the complex samples received from fossil-fuel programs.

The results of these analyses are encouraging. The precision of the nitrogen determination using the new technique is almost twice as good as that of the normal analysis, and the accuracy is a factor of three better. Results for the other constituents are not shown, since they are quite similar by both methods. Nitrogen is more accurately determined by this method because it is present in low concentrations, and because it is subject to interference by the CO₂ and higher hydrocarbons.

We will perform more experiments with various mixtures to prove the method further. A special shuttle-valve system will then be tested so that the analysis can be made on a peak-by-peak basis. In this mode, each particular mass would be read first for the entire mixture, and then for noncondensibles only. Each peak in the spectrum would be read in sequence; this would allow the method to be adapted to reservoir-inlet systems.

Analyses of Fluorocarbon FC-86 with the
Gas Chromatograph-Mass Spectrometer

Responsible Personnel: J. C. Newton and R. W. Crawford

Brief Description: The components of a sample of a fluorocarbon mixture produced commercially were identified by gas chromatography-mass spectrometry.

Status: Gas chromatography-mass spectrometry (GC-MS) is proving to be useful in numerous studies in the General Chemistry Division.¹ Recently a sample of the fluorocarbon FC-86, which was stated to be principally perfluorohexane, was submitted for analysis. It was of particular interest to know if the sample contained any reactive impurities. A Porasil-packed chromatographic column was used to separate the sample and the chromatographic effluent was analyzed by the mass spectrometer. Because the liquid boils at 56-58°C, it was necessary to cool the syringe with dry ice before drawing the liquid sample into the syringe. Good separation of the impurities was obtained. The column was temperature-programmed from 150 to 190°C at a rate of 3°C/minute.

Figure 5 shows the total number of ions (recorded by the mass spectrometer as the peaks were eluted from the gas chromatograph) plotted against time. The identification of the peaks is shown in Table 4. Peak 7 was attenuated by turning the high voltage on the multiplier down while the peak was off scale. Thus perfluoroheptane appears to be present in a larger concentration than perfluorohexane. The last two peaks could not be identified because of the absence of molecular ion peaks. However, they are probably higher homologs of the perfluorocarbons eluted at earlier times.

The component in peak 5 is of particular interest because it contains mass peaks at 135, 147, and 197. This can be explained by including an oxygen atom in the fragments to identify the peaks as $C_2F_5O^+$, $C_3F_5O^+$, and $C_4F_7O^+$, respectively. To establish the reactivity of this compound, infrared analyses were performed (by R. Sanborn), and it was found that the component was not an aldehyde, ketone, or carboxylic acid. Peak 5 is thought to be an ether, a common impurity in fluoroalkanes.

FIG. 5. GC-MS plot of the total ions, mass 69, and mass 135 for fluorocarbon FC-86.

Table 4. Compounds identified in the GC-MS spectrum of Fig. 5.

Peak	Retention time	Compound	Formula
1	6.7	Perfluoropentane	C_5F_{12}
2	7.4	Dialkylperfluoro ether	-
3	8.4	Perfluorocyclohexane	C_6F_{12}
4	9.9	Perfluorohexane	C_6F_{14}
5	10.7	Dialkylperfluoro ether	$C_6F_{14}O$
6	12.0	Perfluorocycloheptane	C_7F_{14}
7	13.4	Perfluoroheptane	C_7F_{16}
8	15.2	-	-
9	17.5	-	-

There is some supporting evidence that peak 5 is an ether. Because peak 5 appears just after the perfluorohexane peak, it likely has a similar boiling point. Perfluorohexane boils at $56^{\circ}C$, which suggests that peak 5 is due to perfluorinated dipropyl ether, $C_3F_7OC_3F_7$. However, from the data in Fig. 5, the compound appears to be ethyl butyl perfluoro ether or methyl pentyl perfluoro ether. The boiling points of these compounds are not available but can be expected, by comparison to the homologous hydrocarbons, to be similar to that of $C_3F_7OC_3F_7$.

Further work will include analyzing the available pure components of this mixture.

Far-Infrared Laser Development

Responsible Personnel: W. A. Bookless,* C. G. Stevens, L. W. Hrubesh, and D. C. Johnson[†]

Brief Description: The development of the far-infrared (FIR) laser progressed in three areas. First, it was found that short pulses (~5 ns) are necessary for optimal energy output, so we obtained a pulsed nitrogen-pumped dye laser for the system. Second, various other methods were used to increase the output power of the FIR laser by a factor of 50. Third, we designed and tested a wavelength-measurement device, using microwaves to simulate the FIR laser output.

Status: Work proceeded satisfactorily on the development of the tunable far-infrared (FIR) laser,** in three specific areas:

1) In experiments with various pumped-laser sources we found that a short pulse is essential to the super-fluorescent process being used to generate FIR radiation. Experiments indicate that a pulse length in the nanosecond regime is necessary to achieve efficient power output. To facilitate this we obtained a pulsed nitrogen-pumped dye laser from the LIS Group of Y-Division on long-term loan. This will increase our beam time and thus speed progress.

2) Through various alterations in working pressure, temperature, and optical configurations, we increased the power output of the laser by a factor of 50. This is significant, because we can now do spectroscopy on the lasing levels by observing effects on the FIR power output with short (1-sec) time constants. We have done scans of the UV pump beam through the 13p absorption state of the potassium and observed the FIR output shown in Fig. 6. Figure 6a shows this scan observed with a Golay detector. Figures 6b and c show the same scan with a liquid-helium-cooled, gallium-doped germanium bolometer. By using the GaGe bolometer we realized an improvement in signal-to-noise ratio by a factor of 8 in addition to the signal gain of 50.

* Associated Western Universities research fellow, University of Wyoming.

[†] Mechanical Engineering Dept., LLL.

**See Ref. 3, p. 9.

FIG. 6. FIR emission from the $13p$ state of potassium, following excitation from the $4s$ state by a pulsed frequency-doubled nitrogen-pumped dye laser (wavelength = 292.75 nm). The traces show the FIR output intensity vs the wavelength of the pumped laser as the pumped laser is scanned through the $4s$ - $13p$ absorption. The detector output was synchronized with the pulsed UV laser by a lock-in amplifier with a 1-second time constant. a) Detected with a Golay cell; signal-to-noise ratio (S/N) = 5.6. b) Detected with a gallium-doped germanium bolometer (4K); S/N = 10, bias = 1.3 V. c) Detected with a gallium-doped germanium bolometer (4K); S/N = 40, bias = 1.45 V.

3) We designed a modified Fabry-Perot interferometer to measure the wavelength of the FIR and tested the design with microwaves that simulate the FIR. Initial tests indicate that the resolution is sufficient to determine which of the possible lasing levels are actually involved in the stimulated emission.

Photoelectrochemistry

Responsible Personnel: J. H. Richardson, S. B. Deutscher, S. P. Perone,* and J. E. Harrar

Brief Description: Coulostatic laser-flash irradiation of n-type TiO_2 semiconductor electrodes permitted measurements of transient photopotential excursions with 10-ns time resolution. The dependence of this transient photopotential on the initial electrode potential, the laser intensity, and the nature and concentration of electrolyte was characterized. The initial photopotential appears to be related to the transient expansion of the space-charge layer that is due to rapid photo-induced charge injection; this is analogous to the double-layer expansion seen in classical electrochemical studies. The subsequent photopotential decay appears to follow a time dependence similar to that predicted for double-layer relaxation.

Status: A manuscript describing the results and suggesting our interpretation based on space-charge relaxation is nearly complete. Experiments were done with four different n-type TiO_2 semiconductor electrodes. The electrodes were characterized by their Mott-Schottky plots and by cyclic voltammetry; the resistance and capacitance of the electrodes varied by an order of magnitude, and the doping density by two orders of magnitude.

The electrochemical cell was modified from that used previously.[†] A cylindrical platinum-gauze electrode was used as the fourth electrode (the quasi-reference electrode), for monitoring the rapid photopotential transients. A hemi-cylindrical platinum-gauze electrode of the same area was used as the counter-electrode. These electrodes were oriented concentrically to the semiconductor electrode. The laser system, timing circuitry, and electronic measurement apparatus were identical to those described previously.[†]

* Department of Chemistry, Purdue University, Lafayette, Indiana.

[†] See Ref. 1, p. 23.

The electrolyte used was usually aqueous 1M KNO_3 . Similar results were obtained with 1M KCl or $0.5\text{M K}_2\text{SO}_4$. The long-time response was similar in 0.01M KNO_3 , indicating that the decay of the photopotential transient was not due to double-layer relaxation. However, the short-time response (risetime) was considerably slowed in this solution, indicating that the higher solution resistance increased the measurement time constant.

The response of the various electrodes to irradiation were characterized with both cw irradiation (by measuring the photocurrent) and pulsed irradiation (by measuring the photocurrent and photopotential). It is significant that much faster transients could be observed in the photopotential (coulostatic) mode than in the photocurrent mode (10 ns vs 100 μs), even under circumstances where no net charge transfer took place. Table 5 summarizes the results obtained for the four n-type TiO_2 semiconductor electrodes.

The most interesting observation is the decay of the initial photopotential to a final value (represented by $\Delta E_{\text{Final}}/\Delta E_{\text{Max}}$ in Table 5). There are three possible explanations. The first is that the decay is due to a dark back-reaction of photo-oxidation products produced by the flash. Such a mechanism would be more significant as the electrode potential approached the flat-band potential, as indeed was observed (Table 5). However, the rate is electrolyte independent, although the possible role of the solvent needs to be clarified. The second explanation is electron-hole recombination. This process generally occurs much faster at the doping densities used than observed here, although there are no previous measurements of this rate at an electrode/electrolyte interface (band-bending would tend to decrease the rate of recombination by increasing the spatial separation of electrons and holes).

The third explanation is that there is a transient nonequilibrium expansion of the space-charge region in the semiconductor, followed by a relaxation back to its equilibrium dimensions, with an associated overshoot and decay of the photopotential. Such a relaxation effect has been observed with coulostatic electrical charge injection at a mercury/dilute electrolyte interface.⁴ In that case the transient response was described in terms of an initial over-expansion of the Helmholtz layer (interfacial double layer) followed by a relaxation back to an equilibrium thickness, with corresponding changes in the measured double-layer potential--very similar in nature and

4. S. W. Feldberg, J. Phys. Chem. **74**, 87 (1970).

TABLE 5. Summary of n-type TiO_2 semiconductor electrode characteristics and results (in 1M KNO_3).

	Electrode			
	A	B	C	D
Area (cm^2)	0.11	0.14	0.20	0.21
Resistance (Ω)	330	29	38	86
Capacitance at 1.0 V vs SCE (μF)	0.14	2.2	1.8	1.8
Doping density (cm^{-3})	1.6×10^{18}	3.0×10^{20}	1.4×10^{20}	1.5×10^{20}
Flat band potential (V vs SCE)	-0.4	-0.75	-0.53	-0.80
Threshold potential (V vs SCE)				
cw photocurrent	-1.1	-1.1	-0.88	-0.93
pulsed photocurrent	-0.55	-	-0.50	-0.50
pulsed photopotential	-1.3	-1.3	-0.90	-1.1
Risetime (ns)				
near flatband	12	10	12	12
1.5 V vs SCE	12	10	15	12
Time to final value (ms)				
near flatband	1	0.05	0.18	0.15
1.5 V vs SCE	20	2.2	1	1
$\Delta E_{\text{Final}}/\Delta E_{\text{Max}}$				
near flatband	0.10	0.18	0.13	0.20
1.5 V vs SCE	0.15	0.76	0.56	0.41

time dependence to that observed here. This explanation was further substantiated by comparing the observed time dependence to the theoretically predicted time dependence. Holes and electrons can be substituted for cations and anions in this theory, with corresponding changes in mobilities and concentrations. The semiconductor's depletion layer replaces the solution's Helmholtz double-layer thickness, and the flat band potential replaces the potential of zero charge. The modified theory predicts a time^{-2/3} dependence of the photopotential, and as shown in Fig. 7, this was observed near the flat band potential and at long times.

These studies provide a foundation for further investigations of the transient behavior of other semiconductor photoelectrodes and other photoelectrolysis processes. It should now be possible to study the dynamics of redox stabilized photoelectrodes as well as dye-sensitized photoelectrolysis on a previously inaccessible time scale.

FIG. 7. Photopotential vs time^{-2/3} for n-type TiO₂ electrode (electrode D, -0.5 V vs SCE, 1.0M KNO₃, laser power ≈ 28 kW).

Contamination Studies for the Weapons Development Program

Responsible Personnel: S. B. Deutscher, E. T. Mones,* and R. J. Morgan*

Brief Description: The long-term durability of Kevlar 49 fibers (in the form of epoxy strands and multilayer composites) under stress is currently under study.⁵ The behavior of the major contaminant, Na_2SO_4 , at the interface of the fiber and the epoxy matrix is a major concern. Analyses of the fibers and water used to wash the fibers showed that Na_2SO_4 is present on the surface of as well as incorporated in the fiber, and that the occluded Na_2SO_4 can diffuse out of the fiber.

Status: The processing of Kevlar 49 by DuPont involves H_2SO_4 treatment followed by a NaOH wash. There is concern that residual SO_4^{2-} and Na^+ ions are affecting the fiber's failure processes and its durability in long-term weapons applications. Three samples of different fiber batches, two consisting of four filaments and the other of one filament, and the water used to wash them were analyzed for their Na_2SO_4 content.

Samples varying from 1 to 3 g were placed in HNO_3 -washed 400-ml beakers, covered with deionized H_2O , and allowed to sit with occasional stirring for three periods of time: 6 h, 11 days, and 15 days. At the end of the allotted time the fibers were separated by filtration and washed. The filtrate was evaporated to a specific volume and analyzed. The fiber samples were allowed to air-dry for several days, weighed, and then combusted in a platinum-lined Parr bomb under oxygen. The combustion products were absorbed in a KOH solution, which was then diluted to volume. Sodium analyses were performed using atomic absorption spectrophotometry. Sulfate was determined by a potentiometric titration with a lead ion-selective electrode and a titrant of lead perchlorate.⁶ Ash weights were obtained by placing the fiber in a

* Organic Materials Division.

5. R. J. Morgan, E. T. Mones, W. J. Steele, and S. B. Deutscher, The Durability of Kevlar 49 Fibers, Lawrence Livermore Laboratory, Livermore, CA, UCRL-83599 (1979).

6. W. Selig, Mikrochim. Acta(Wein) 1970, 168.

platinum crucible and heating for 8 h at 700°C in an oxygen atmosphere. In addition, a multi-element analysis of the solutions was done by ICP spectrometry.

The results of the ICP analysis are given in Table 6. The results of the wet chemical analyses of the three samples of Kevlar (treated and untreated) and of the water used to wash the fibers are shown in Table 7.

The results indicate that Na_2SO_4 is indeed present both on the surface of the fiber and between the fibrils, and that the occluded Na_2SO_4 can diffuse out of the fiber. Further spectroscopic work is being done (by x-ray diffraction, scanning electron microscopy, and Fourier-transform infrared spectroscopy), to determine whether the impurities can diffuse through the epoxy, affecting the integrity of the composite.

TABLE 6. Composition of Kevlar 49 and wash waters as determined by ICP spectrometry (concentration in mg/kg).

Element ^b	Sample ^a				
	Fibers washed at 6 h		Wash waters from fibers washed at 15 days		
	A	C	A	B	C
Na	1563	1251	283	299	349
Si	24	19	53	10	39
P	174	nd ^c	44	nd	nd
B	0.5	1	4	23	36
K	10	6	65	6	nd
Ca	2	3	0.2	2	14
Fe	2	1	1	0.3	0.3
Al	1	1	nd	nd	nd
Mg	1	1	0.1	0.5	2
Li	0.5	0.4	nd	nd	nd
Zn	0.1	0.02	0.1	1	2
Cu	0.2	0.04	0.2	0.1	0.1
Ti	0.05	nd	nd	nd	nd
Mn	0.006	nd	nd	nd	0.1

^aSamples A and B were 4-filament fibers; sample C was a 1-filament fiber.

^bNot detected in any sample:

As <0.6	Pb <0.2
Cd <0.01	Se <0.3
Co <0.02	Sr <0.026
Mo <0.01	U <0.64
Ni <0.01	V <0.03
	Zr <0.01

^cNot detected.

TABLE 7. Analysis of Kevlar-49 fibers and wash waters (concentrations in mg/kg).

Sample ^a	Untreated fibers			Fibers washed at 6 h			Wash waters from fibers washed at:					
							6 h		11 days		15 days	
	Na ⁺	SO ₄ ²⁻	Ash	Na ⁺	SO ₄ ²⁻	Ash	Na ⁺	SO ₄ ²⁻	Na ⁺	SO ₄ ²⁻	Na ⁺	SO ₄ ²⁻
A	3850	5930	12,270	3000	5240	10,500	140	590	270	410	270	450
B	3810	6090	12,160	3000	5480	10,900	140	240	220	390	300	-
C	2770	5930	9310	2300	3190	7210	280	330	270	380	300	-

^aSamples A and B were 4-filament fibers; sample C was a 1-filament fiber.

Potentiometric Study of Some Anions with Quaternary Ammonium Halides

Responsible Personnel: W. Selig

*Will be
published
(see end)*

Brief Description: Quaternary ammonium halides were evaluated for the potentiometric titration of small amounts of large inorganic and organic anions. Emf's were monitored with liquid-membrane ion-selective indicator electrodes (ISE's) and a double-junction reference electrode. The same titrants and electrode systems were also used for the determination of ionic surfactants and soaps. In addition, various anions were determined using solid-state ISE's as endpoint sensors.

Status: We previously reported several new titrants for the precipitation titration of perchlorate and fluoroborate.^{7,8} The titrants were hexadecylpyridinium chloride (CPC), hexadecyltrimethylammonium chloride (CETAC), and benzyldimethyltetradecylammonium chloride (BDTAC). CETAC and CPC yielded the highest precision and largest potentiometric breaks. CPC has been used in further work with a large number of inorganic and organic anions. Emf's were monitored with a fluoroborate ISE and a double-junction reference electrode. The perchlorate, nitrate, and calcium ISE's also respond to the various anions and can also be used for emf monitoring.

Sharp endpoint breaks were obtained for permanganate, hexafluoroarsenate, hexafluorophosphate, persulfate, hexachloroplatinate, tetrachloroaurate, tetrachlorothallate(III), and other inorganic anions. Titratable organic anions are nitroform, phenylborates, benzenesulfonates, 2,4,6-trinitro-compounds, and some sulfonphthaleins. Because the liquid-membrane electrodes function only in an aqueous medium, the method is limited to organic anions.

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7. W. Selig, A New Titrant for Perchlorate: Cetyltrimethylammonium Bromide, Lawrence Livermore Laboratory, Livermore, CA, UCRL-82719 (1979).
 8. W. Selig, New Titrants for Perchlorate and Fluoroborate, Lawrence Livermore Laboratory, Livermore, CA, UCRL-83153 (1979).

The details of this work are presented in two reports that have been accepted for publication in Mikrochim. Acta.^{9,10}

The same titrants and ISE's were also used to determine various anionic surfactants and soaps. This obviates the need for preparing the special liquid-membrane or other electrodes used heretofore in the potentiometric titration of surfactants and soaps. We recommend electrophoresis-grade sodium dodecylsulfate for the standardization of the quaternary ammonium halide titrants. The reverse titration of cationic surfactants with standard sodium dodecylsulfate is similarly feasible. Details are presented in a report that has been submitted for publication in Zeitschrift für Analytische Chemie.¹¹

We have found that several solid-state ISE's also respond to many of the previously investigated inorganic and organic anions.^{9,10} This obviates the limitation of operating in a strictly aqueous medium. The largest endpoint breaks were obtained with the iodide and cyanide electrodes. In most cases the titration curves had shapes similar to those obtained in the nonaqueous titration of weak organic acids^{12,13} using two platinum electrodes polarized by a constant current. They have the shape of an inverted V, with a more or less sharp peak after a steep rise in potential, followed by a decline in emf. It is therefore possible to calculate the endpoints by either of two methods: 1) the usual calculation of the maximum change in emf vs titrant increment, or 2) the point of maximum emf as was done by Shain and Svoboda.¹²

Some inorganic anions thus titratable are perrhenate, persulfate, ferricyanide, hexafluorophosphate, and hexachloroplatinate. Examples of titratable organic anions are nitroform, tetraphenylborate, cyanotriphenylborate, picrate, long-chain sulfates and sulfonates, and some soaps. The reverse titration of quaternary ammonium halides vs sodium dodecylsulfate is

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9. W. Selig, A Potentiometric Study of Some Anions with Cetyltrimethylammonium Bromide. I. Inorganic Anions, Lawrence Livermore Laboratory, Livermore, CA, UCRL-83037 (1979).
 10. W. Selig, A Potentiometric Study of Some Anions with Quaternary Ammonium Halides. II. Organic Anions. Lawrence Livermore Laboratory, Livermore, CA, UCRL-83344 (1979).
 11. W. Selig, The Potentiometric Titration of Surfactants and Soaps Using Ion-Selective Electrodes, Lawrence Livermore Laboratory, Livermore, CA, UCRL-83495 (1979).
 12. I. Shain and G. R. Svoboda, Anal. Chem. **31**, 1857 (1959).
 13. W. Selig, Microchem. J. **24**, 73 (1979).

also feasible. In addition, some titrations can be carried out in a partially nonaqueous medium.

Details are given in a report that has been accepted for publication in Microchemical Journal.¹⁴

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14. W. Selig, Microtitration of Various Anions with Quaternary Ammonium Halides Using Solid-State Electrodes, Lawrence Livermore Laboratory, Livermore, CA, UCRL-83613 (1979).

ANALYTICAL RESEARCH AND DEVELOPMENT FOR THE ENERGY PROGRAMS

Automated, Portable, On-Line Mass Spectrometer for the
Oil-Shale Program

Responsible Personnel: R. G. Bedford and F. Danielli*

Brief Description: Control of a commercial quadrupole spectrometer used to analyze gases from oil-shale retorting experiments^{15,16} was converted from a D-112 (PDP-8-type) computer to a DEC LSI-11 system. The LSI-11 that controls the mass spectrometer will be part of a network that includes a Tektronix model 4051 graphics system to be shared with another LSI-11 used for data acquisition from gas chromatographs.

Status: The D-112 computer that has been used to control the oil-shale quadrupole mass spectrometer and high-temperature drop calorimeter is being retired from service and has been replaced with LSI-11 microprocessor systems. The system that controls the mass spectrometer includes the following hardware: LSI-11 microprocessor with 32K words of MOS memory, Teletype model 43 terminal, Data Systems DSD 440 dual double-density floppy disk, Western Dynex DD 6222 10-Mbyte disk with one fixed and one removable cartridge (top loading), GPIB interface for Tektronix 4051 system, ADAC 12-bit A/D converter data-acquisition board, 16-bit D/A converter (DRV-11 parallel interface), and a Doric 2301 data logger (DLV-11 serial interface). The 12-bit A/D converter will be replaced later by a 14-bit A/D converter.

New software was provided to operate the system. Programs were adapted from the time-of-flight mass spectrometer used for the Hoe Creek No. 3 underground coal-gasification field experiment last summer.[†] Four routines are used: mass scale calibration, background measurement, spectral calibration of pure gas standards, and data acquisition/data reduction.

* Electronics Engineering Department, LLL.

† See Ref. 1, p. 46.

15. General Chemistry Division Quarterly Report, January through March 1977, Lawrence Livermore Laboratory, Livermore, CA, UCID-15644-77-1 (1977), p. 46.

16. General Chemistry Division Quarterly Report, April through June, 1977, Lawrence Livermore Laboratory, Livermore, CA, UCID-15644-77-2 (1977), p. 39.

Results from the first three routines are saved in disk files on the system device and read back by the data acquisition/reduction program.

The Doric data logger is programmed by the operator to scan the thermocouples or other voltage sources at the desired rate (maximum 1 scan per minute). Mass spectrometer data acquisition is triggered by the Doric scans. The data acquisition routine records the Doric data and the mass spectrum in a disk file and then determines gas composition in real time using a stepwise linear regression. The calculated spectrum is written in the file with the experimental data and the composition in a separate file. Data for each scan is saved in a separate file in ASCII code, and identified by scan number for convenient access by the 4051. Doric data and compositions are typed on the console as they are obtained if desired.

The program can scan up to 60 masses and include 20 compounds in the regression. The time required for a complete scan and computation for a typical spectrum of 22 masses with 6 compounds in the regression is less than 10 seconds. The program occupies about 18K words in memory and is currently being used with the RT-11 single-job monitor because it is too large to use in the foreground of the foreground/background monitor. At the present time data cannot be processed with the Tektronix 4051 during the time it is being accumulated. We intend to either adapt the program to the foreground/background monitor or write a subroutine to provide communication with the 4051 between scans.

Field Tests of Organic Additives for the Control
of Scaling of Hypersaline Geothermal Brine

Responsible Personnel: J. E. Harrar, F. E. Locke,* L. E. Lorensen,[†] C. H. Otto, Jr., S. B. Deutscher, W. P. Frey,** E. O. Snell,** and R. Lim

Brief Description: Several compounds were found that significantly retard the formation of the siliceous scales from the brines of the Salton Sea Geothermal Field. The best overall performance was exhibited by a polyethylene imine of molecular weight ~1800 (Corcat P-18, Cordova Chemical Company).

Status: For the final test series of this project, a new group of 19 compounds was selected from the classes previously established to have high activity as silica-precipitation inhibitors. In this group were the following:

- A series of quaternary ammonium compounds (obtained from Armak) to be compared especially with Ethoquad 18/25, which was evaluated previously.^{††}

- A series of polyethylene imines (obtained from Cordova Chemical Company), some having different molecular weights and some having certain other functional groups.

- Three polyaminoethylene hydrochloride salts (obtained from Dynapol, Inc.) including the PAE HCl tested previously.^{††}

- A group of miscellaneous quaternary ammonium and polyamine-type compounds having certain features not previously examined.

These compounds were first evaluated by means of our "standard" precipitation test,¹⁷ in which the additive is injected into the brine-treatment test system at 220°C, samples of effluent brine are collected at 105°C, and then the kinetics of silica precipitation are observed at 90°C.

* Mechanical Engineering Department, LLL.

† Organic Materials Division, LLL.

**Metals and Ceramics Division, LLL.

††See Ref. 3, p. 30.

17. J. H. Hill, J. E. Harrar, C. H. Otto, Jr., S. B. Deutscher, H. E. Crampton, R. G. Grogan, and V. H. Hendricks, Apparatus and Techniques for the Study of Precipitation of Solids and Silica from Hypersaline Geothermal Brine, Lawrence Livermore Laboratory, Livermore, CA, UCRL-52799 (1979).

The most promising of these compounds were then subjected to 40-h scaling tests to determine their effectiveness in retarding the scales formed at 220, 125, and 90°C. In addition to single compounds shown to be good inhibitors in the precipitation test, we conducted several scaling tests of combinations of compounds with complementary functions which, it was hoped, would lead to significant retardation of scale.

The best compounds found are listed in Table 8, and the best of these appears to be Corcat P-18. It reduced the scales at 125 and 90°C by factors of 4 and 18 respectively, and it also has activity as a corrosion inhibitor. PAE·HCl was not quite as good at these temperatures, but it also reduced the scale at 220°C by a factor of 2-3. The results obtained this time for Ethoquad 18/25 were mixed; it reduced the scale at 90°C again, but not at 125°C, possibly because the concentration used (35 ppm) was too high. A fourth compound, Mirapol A-15 (a Mirapol Chemical Company polydiquaternary compound), which structurally has all of the characteristics that we now know are prerequisites for antiscalant activity, also appeared promising but could not be evaluated thoroughly.

A detailed report of these most recent experiments was prepared.¹⁸ Because both Corcat P-18 and PAE·HCl are not produced commercially in large quantities, they are rather expensive. Thus in the near term the most cost-effective additive formulation would probably be a mixture of one of these silica-precipitation inhibitors and a small amount of hydrochloric acid. We found that an amount of acid insufficient to lower the brine pH significantly not only augmented, but enhanced, the retardation effect of the silica inhibitor. We are also recommending a third ingredient--a phosphonate crystalline-scale inhibitor--which also appears to enhance the overall activity of the antiscalant mixture even though it does not directly affect the silica.¹⁹

18. J. E. Harrar, F. E. Locke, C. H. Otto, Jr., L. E. Lorensen, W. P. Frey, and E. O. Snell, On-Line Tests of Organic Additives for the Inhibition of the Precipitation of Silica from Hypersaline Brine. IV. Final Tests of Candidate Additives, Lawrence Livermore Laboratory, Livermore, CA, UCID-18536 (1980).

19. J. E. Harrar, F. E. Locke, C. H. Otto, Jr., L. E. Lorensen, S. B. Deutscher, W. P. Frey, and R. Lim, Trans. Geothermal Resources Council, **3** 295 (1979).

TABLE 8. Three compounds that inhibit silica scaling from geothermal brine.

Structure	Chemical name	Trade name
$ \begin{array}{c} \text{---CH}_2\text{CH}_2\text{NH} \quad \text{CH}_2\text{CH}_2\text{NH} \\ \quad \quad \\ \text{CH}_2\text{CH}_2\text{N} \\ \\ \text{CH}_2\text{CH}_2\text{NH}_2 \end{array} $	<p>Polyethylene imine mol wt $\approx$ 1800</p>	<p>Corcat P-18 (Cordova Chemical Co.)</p>
$ \left[\begin{array}{c} (\text{CH}_2\text{CH}_2\text{O})_x\text{---H} \\ \\ \text{CH}_3(\text{CH}_2)_{17}\text{---N---CH}_3 \\ \\ (\text{CH}_2\text{CH}_2\text{O})_y\text{---H} \end{array} \right]^+ \text{Cl}^- $ <p>$x + y = 15$</p>	<p>Methyl polyoxyethylene (15) octadecylammonium chloride</p>	<p>Ethoquad 18/25 (Armak Chemical) or Q-18-15 (Tomah Products)</p>
$ \begin{array}{c} \text{---}(\text{CH}_2\text{CH}_2)_n \\ \\ \text{NH}_2 \cdot \text{HCl} \end{array} $ <p>or</p> $ \begin{array}{c} \text{---}(\text{CH}_2\text{CH}_2)_n \\ \\ \text{NH}_3^+ \text{Cl}^- \end{array} $	<p>Poly (aminoethylene, HCl salt) mol wt $\approx$ 120,000</p>	<p>PAE·HCl (Dynapol, Inc.)</p>

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