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THE FOURTH ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANTS VOLUME II

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			Hydroxylammonium Nitrate TEAN Production
			Triethanolammonium Nitrate Combustion Stability

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

This report contains the abstracts and viewgraphs of the papers presented at the BRL's Fourth Annual Conference on HAN-Based Liquid Propellants. Conference Papers include the following:

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Diamond Anvil-FTIR Studies of HAN and dHAN to 40 Kbar

R.A. Fifer & M.A. Davies*

US Army Ballistic Research Laboratory
Aberdeen Proving Ground, MD 21005

***National Research Council Assoc, 1987-88**

4th LP structure & Properties Conference, BRL, Aug 30-31, 1988

REASONS FOR STUDYING THE VIBRATIONAL SPECTROSCOPY OF HAN AND LIQUID PROPELLANTS

A. To obtain qualitative and quantitative information about the **structure and bonding** in the liquids as a function of concentration, tempeature, and pressure.
- -correlation with physical properties
- -"calibration" of theoretical models

B. To determine the **"phase diagrams"** of the liquids. Concentration, temperature, pressure regimes for formation of:
- -glasses
- -solid solutions
- -crystalline phases
  - e.g., crystalline HAN
    - crystalline TEAN
    - crystalline HAN-hydrates
- -phase separations
- -decomposition

8/30/88 LP10

RELEVANT PREVIOUS STUDIES

A. **R.A. Fifer, 21st JANNAF Comb. Mtn., CPIA 412(2), 539(1984)**

measured: FTIR spectra of aqueous HAN and dueterated HAN (dHAN) as a function of concentration (9 - 17 M) and temperature (-170 to +70 C)

observed:

- -band shifts due to effect of concentration and temperature on intermolecular bonds in the liquid
- -formation and ir spectra of glasses (below -60 C)
- -formation of two polymorphs of anhydrous crystalline HAN (see 23rd JANNAF Comb. Mtn., 1986)

B. **C.A. VanDijk & R.G. Priest, Combustion & Flame 57, 15 (1984)**

measured: Raman spectra of 11 M HAN as a function of pressure (2 - 10 Kbar, 30 - 150 Kpsi) and temperature (20 - 120 C)

observed:

- -reaction (decomposition) above 5 Kbar and 70 C.
- -reaction apparently slower at high pressure than at 1 atm.
- -reaction accompanied by formation of new bands at 1288 and 2225 cm^{-1} due to solid N_2O.

(No band shifts for HA+, N-, or H_2O reported, but "..OH stretch peaks in the 3100-3200 cm^{-1} region appear to be broadened in the pressurized case.")

Concentration and Temperature Dependence of of Low Frequency Band Positions

CONCENTRATION DEPENDENT BANDS AT 35°C

SHIFT FOR 9.5 → 17 M HAN/dHAN, cm^{-1}

1519/1164	−10/−20	ν_3 or ν_6 , NH_3^+/ND_3^+ DEF.
1190/886	−15	ν_8 , NH_3^+/ND_3^+ ROCK
721	+6	ν_4 , NO_3^- BEND
823	−4	ν_2 , NO_3^- BEND

TEMPERATURE DEPENDENT BANDS FOR 9.5 OR 12 M HAN/dHAN

SHIFT FOR +35 → −60 C, cm^{-1}

1190/886	+6	ν_8 , NH_3^+/ND_3^+ ROCK
721	+5	ν_4 , NO_3^- BEND

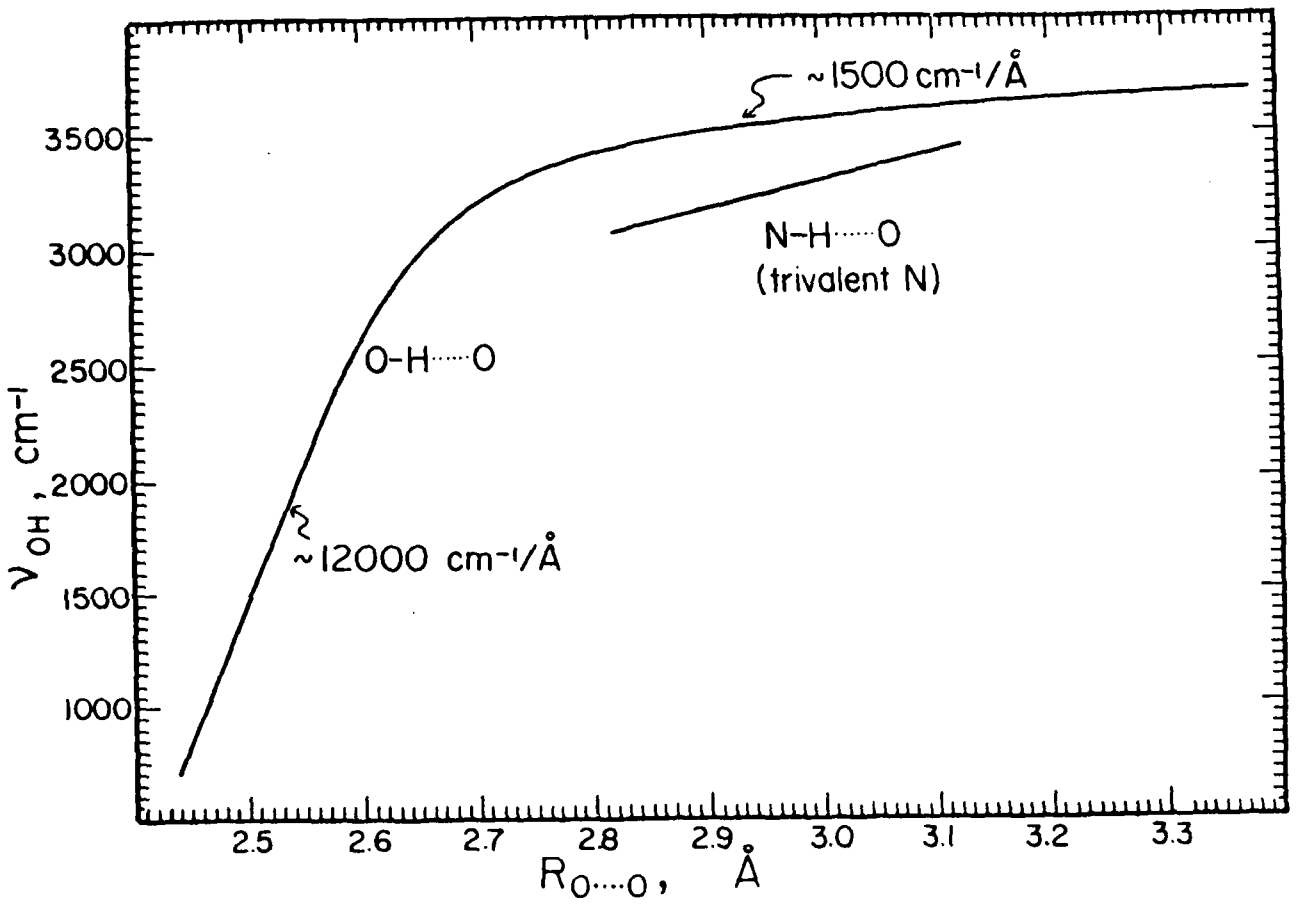
BANDS INDEPENDENT OF CONCENTRATION AND TEMPERATURE

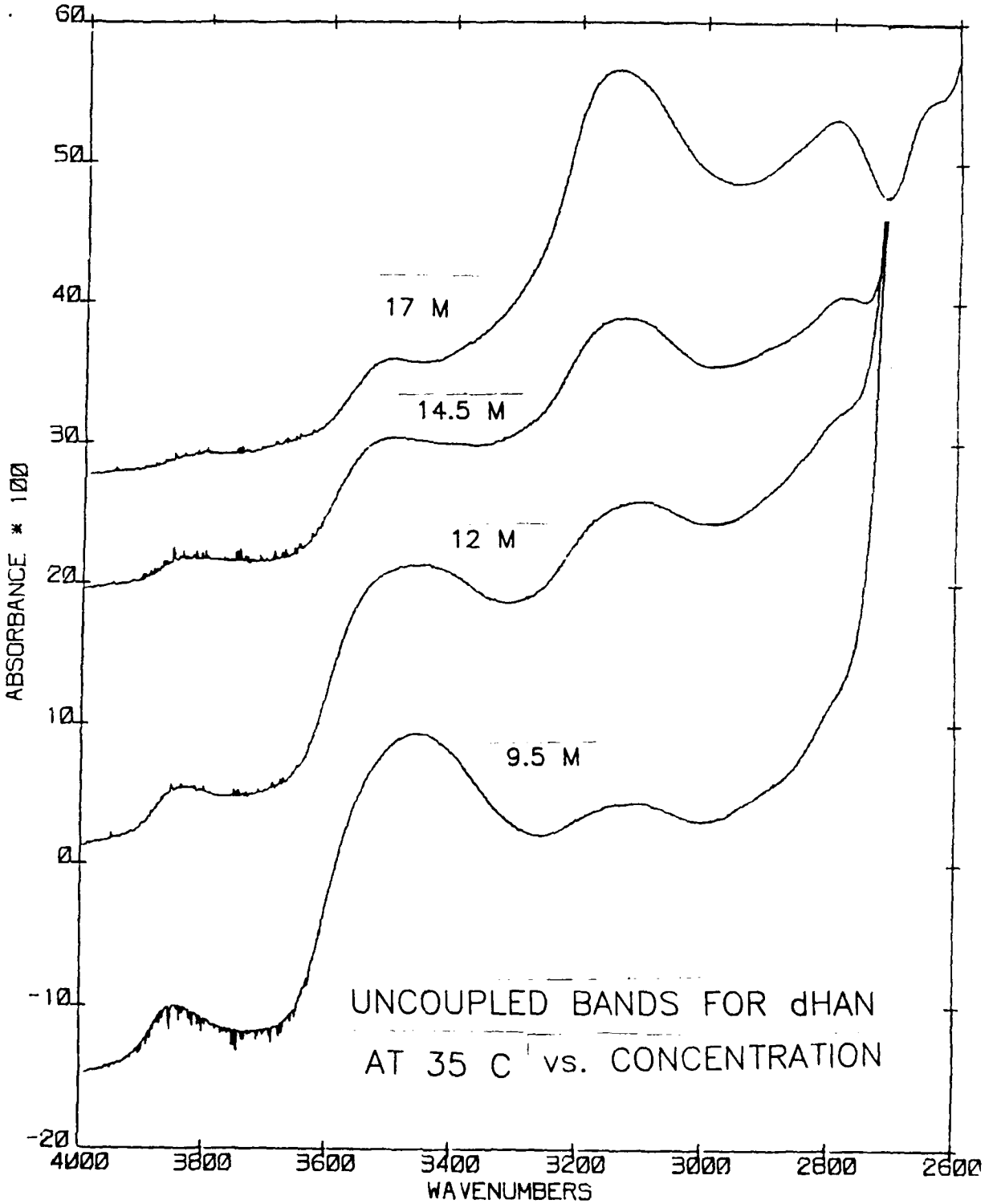
1007/990	ν_4, N−OH/N−OD STRETCH
1045	ν_1 , NO_3^- SYM. STRETCH
1764	ν_1 $+\nu_4$, NO_3^-, BEND + STRETCH

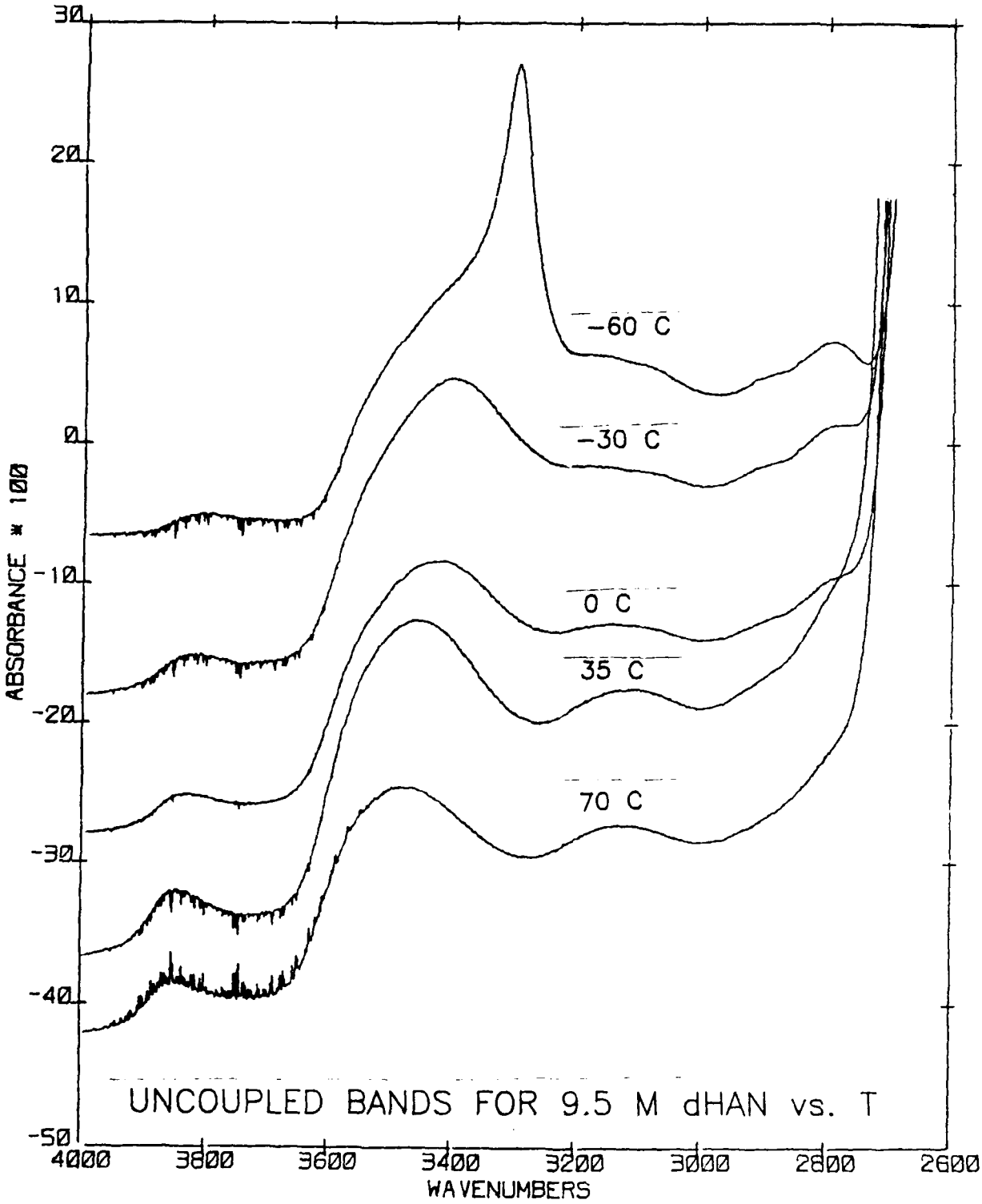
Isotopic Uncoupling Spectroscopy

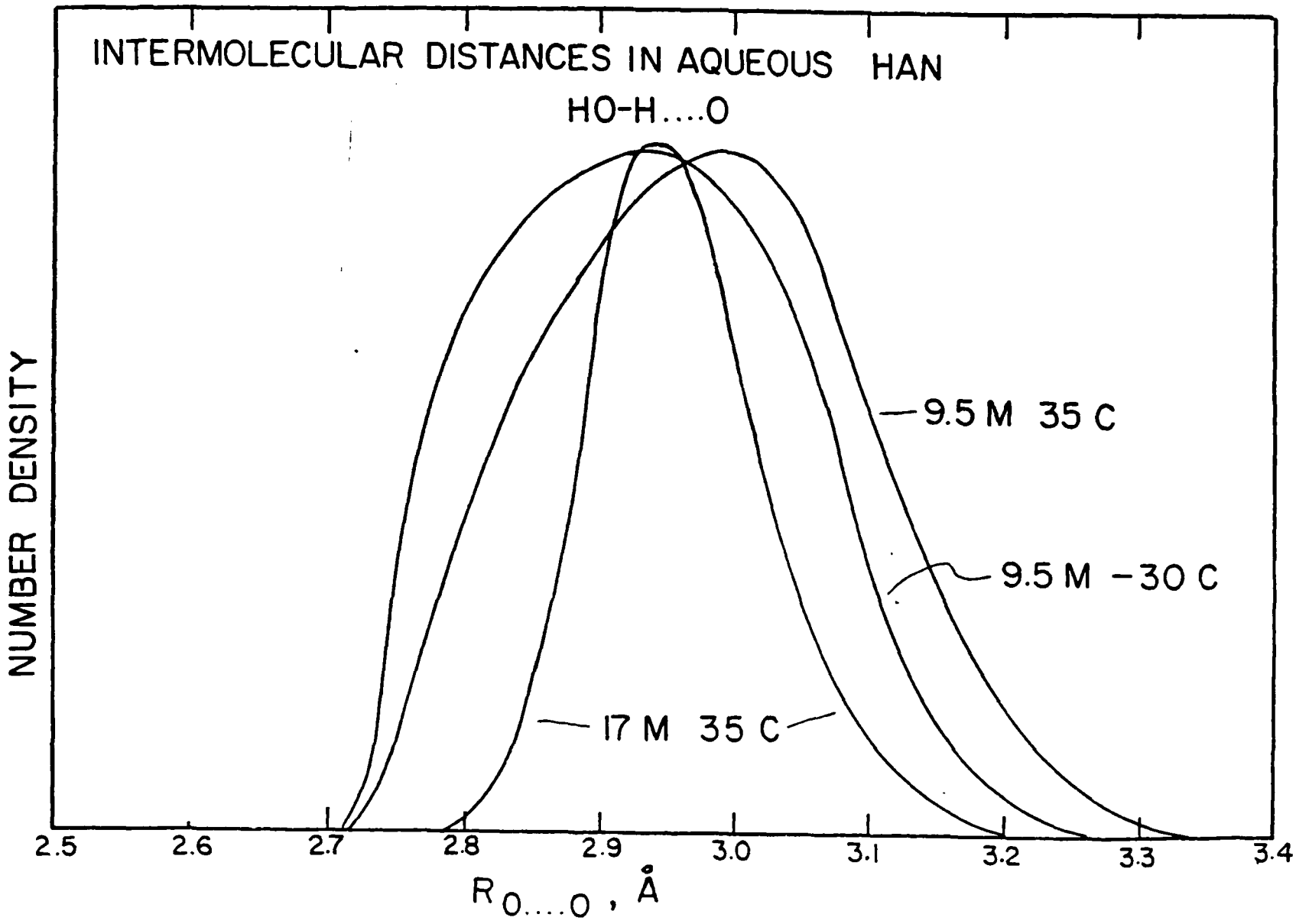
uncoupled vibration	species measured
$HO-H$	$DO-H$ in dHAN
$H_3\overset{+}{N}O-H$	$D_3\overset{+}{N}O-H$ in dHAN
$\begin{array}{c} H \\ \vert \\ HO\overset{+}{N}-H \\ \vert \\ H \end{array}$	$\begin{array}{c} D \\ DO\overset{+}{N}-H \\ D \end{array}$ in dHAN

where $dHAN \equiv D_3\overset{+}{N}OD + NO_3^- + D_2O$
(97% D, 3% H)


~1500 cm⁻¹/Å
N-H·····O
(trivalent N)
O-H·····O
~12000 cm⁻¹/Å
3500
3000
2500
2000
1500
1000
ν OH , cm⁻¹
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
R O····O , Å


60
50
40
30
20
10
0
-10
-20
ABSORBANCE * 100
17 M
14.5 M
12 M
9.5 M
UNCOUPLED BANDS FOR dHAN
AT 35 C vs. CONCENTRATION
4000
3800
3600
3400
3200
3000
2800
2600
WAVENUMBERS


30
20
10
0
-10
-20
-30
-40
-50
ABSORBANCE * 100
-60 C
-30 C
0 C
35 C
70 C
UNCOUPLED BANDS FOR 9.5 M dHAN vs. T
4000
3800
3600
3400
3200
3000
2800
2600
WAVENUMBERS


INTERMOLECULAR DISTANCES IN AQUEOUS HAN
HO-H....O
NUMBER DENSITY
9.5 M 35 C
9.5 M -30 C
17 M 35 C
2.5
2.6
2.7
2.8
2.9
3.0
3.1
3.2
3.3
3.4
R O....O , Å

RELATED DEVELOPMENT: RECENTLY COMPLETED SBIR PROJECT

TITLE: HIGH PRESSURE EQUIPMENT FOR OPTICAL LIQUID PROPELLANT STUDIES

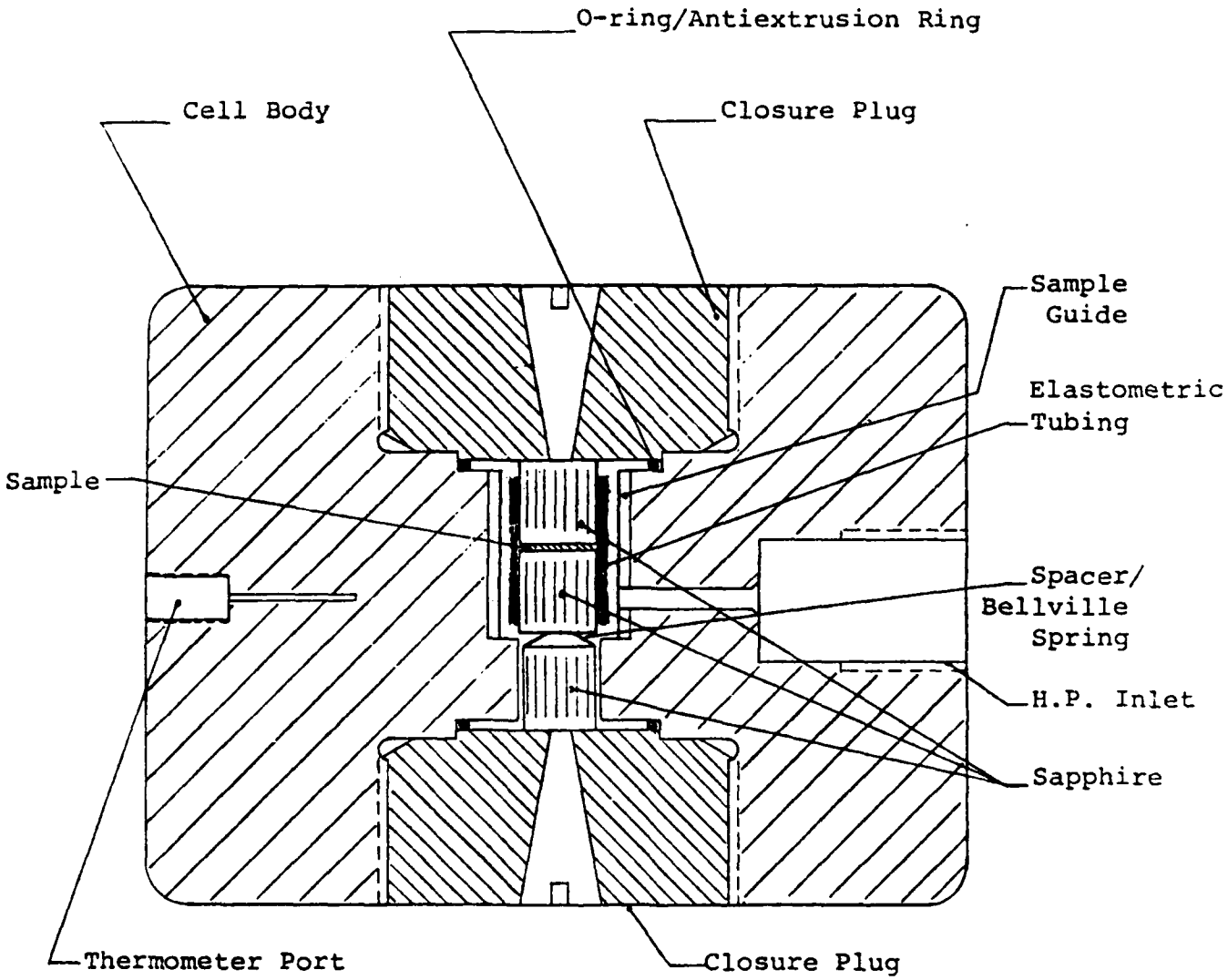
INSTITUTION: KLD Associates, Inc.
Huntington Station, NY

PI: Dr. David S. Mahler

ACCOMPLISHMENTS:

-Successfully designed, constructed & tested an intensifier-driven optical cell meeting the following specifications:

- -Maximum pressure: 1379 MPa (200 Kpsi)
- -Temperature Range: -60 to +60 C
- -Sample size: < 50 microliters
- -Compatible with optical microscopes and uv/vis/ir spectrometers



Overall Dimensions: 2.5" D x 1.875" L

Sapphires: .250" x .250"

Closure Plug: 1.125" D x 0.5" L

Figure 1. High Pressure Microscope Cell

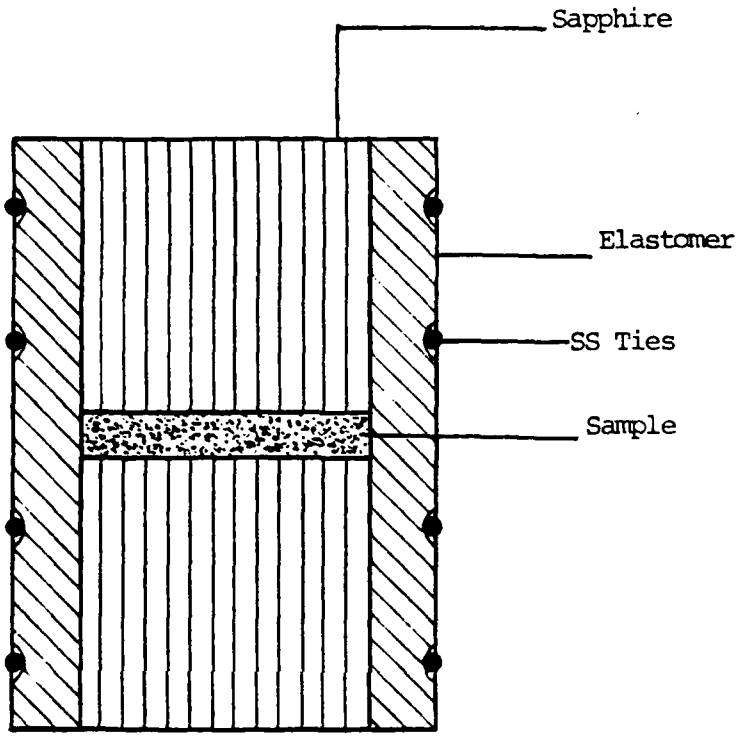
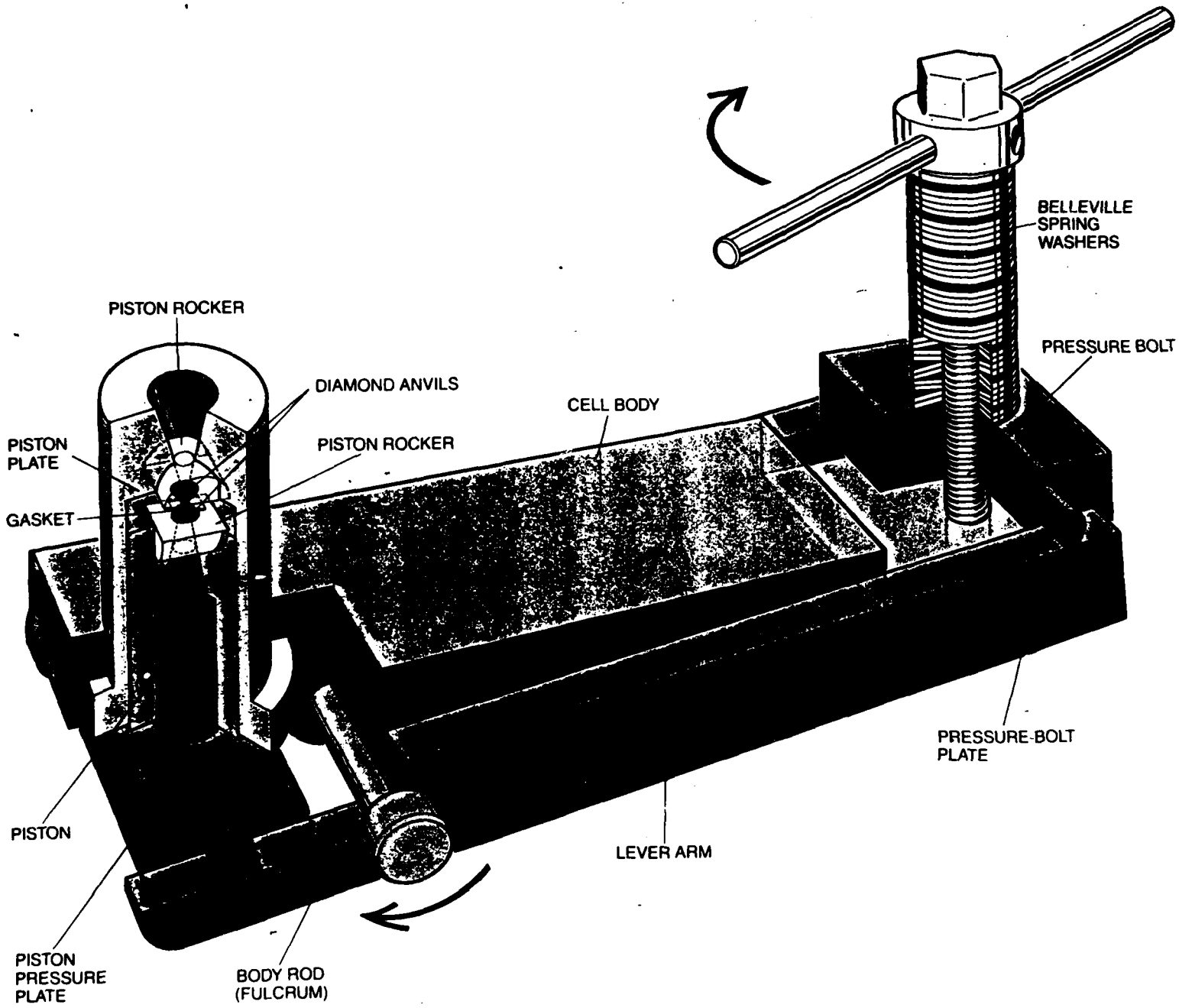


Figure 3. Sample Holder



THRUST MECHANISM of the diamond-anvil cell developed at the Na-

ADVANTAGES/DISADVANTAGES OF DIAMOND ANVIL CELLS COMPARED TO INTENSIFIER-DRIVEN OPTICAL CELLS

Advantages:

- -simplicity of operation
- -small (~20 cm, "palm size"); no large or complicate equipment
- -small sample volumes (~1 microliter)
- -very high pressures (up to 2,000,000 atm [30,000,000 psi])
- -temperature control simple
- -low cost ($2-5K for 50-100 Kbar cell)

Disadvantages:

- -pressure measurement not straightforward or direct
- -small aperatures (e.g., 250 microns) make good S/N difficult with FTIR
- -sample/gasket preparation requires microscope and a steady hand!

8/30/88 LP4

ADVANTAGES/DISADVANTAGES OF FTIR COMPARED TO RAMAN FOR DIAMOND ANVIL CELL MEASUREMENTS

Advantages:

- -speed of data acquisition
  - -all wavelengths collected simultaneously
  - -no entrance/exit slits to define resolution
- -no sample fluorescence*
- -no diamond fluorescence*
- -negligible sample heating
- -lower cost: FTIR prices dropped 70% in 5 years

Disadvantages:

- -need beam condenser or infrared microscope accessory for reasonable cell transmission
- -need smaller cell pathlengths (e.g., 10 microns); more difficult to prepare/mount

---

*New near-ir FT-Raman technique also eliminates fluorescence.

8/30/88 LP5

PROBLEMS WITH RUBY FLUORESCENCE TECHNIQUE FOR PRESSURE DETERMINATION IN INFRARED STUDIES

- For small (e.g., 10 micron) pathlengths, hard to get good signal from single small (<10 micron) particle.
- Laser must be attenuated to prevent heating/decomposition of thermally sensitive samples.
- Complicated & expensive: requires laser (e.g., Ar+) and scanning visible spectrometer,

DISADVANTAGES OF (INFRARED-ABSORBING) INTERNAL CALIBRANT FOR INFRARED STUDIES:

- Potential spectral interferences (e.g., coincidence of HAN and calibrant lines).

8/30/88 LP6

Quartz Internal Pressure Calibrant Technique for High Pressure Infrared Spectroscopy*

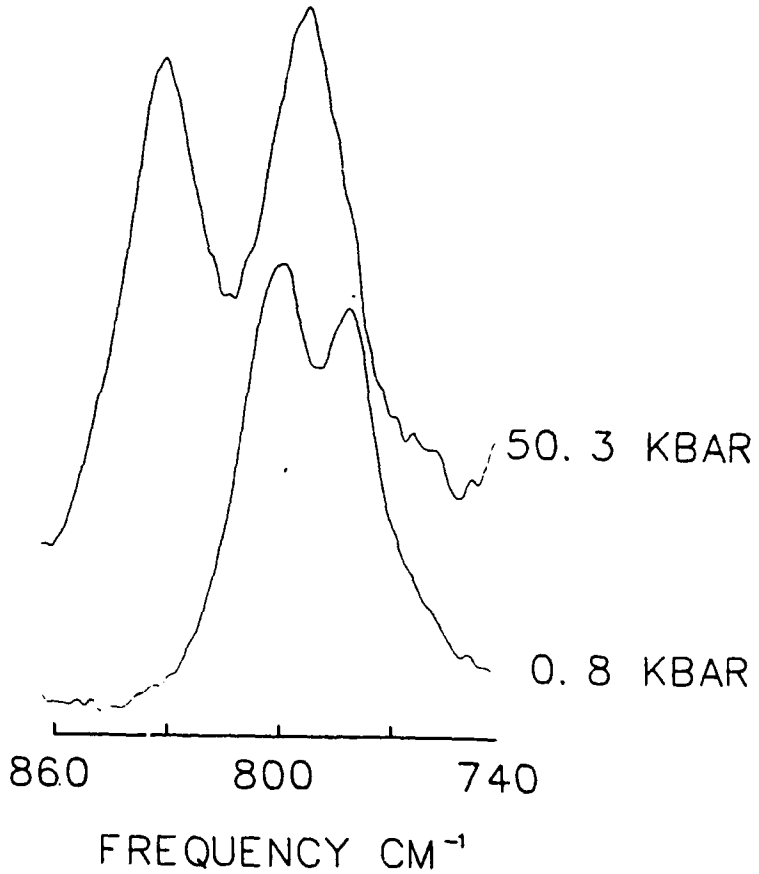


FIG. 2. Representative infrared spectra of crystalline quartz in the frequency region 740–860 cm^{-1} at two pressures.

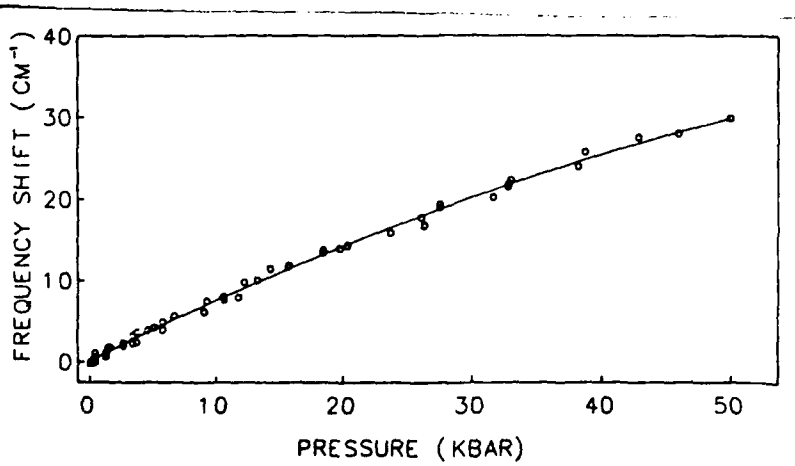


FIG. 3. Pressure dependence of the frequency of the 801 cm^{-1} band of crystalline quartz.

* P.T.T. Wong, D.J. Moffatt, and F.L. Baudais, Applied Spectroscopy 39(4), 733 (1985)

CURRENT STATUS (after 1 year)

A. Techniques Developed:

1. Sample preparation & assay
   - -preparation of anhydrous HAN and dHAN
   - -preparation of aqueous HAN and dHAN; determination of molarity & density
2. Gasket preparation and filling
   - -selection of gasket material
     - thin
     - medium-hard to achieve desired pressures without excessive extrusion
     - compatible with HAN and LP's
   - -allignment of gasket on diamonds
   - -filling to avoid leaks, H/D exchange, etc.
3. Optics, detector, cell/FTIR allignment
   - -small area MCT detector
   - -beam condenser
   - -accurate allignemt of DAC (constructed positioning device)
   - -optimal allignment of FTIR optics
4. Quartz internal calibrant
   - -determination of best particle size, amount
   - -effect of crystallinity & grinding on spectrum

B. Preliminary results obtained (room T, P=0-40 Kbar):

1. 13 M HAN
2. 8.32 M dHAN
3. 12.74 M dHAN

EXPERIMENTAL

FTIR: Mattson Sirius 100 with small area MCT detector and beam condensing optics
4 cm^{-1} resolution
400 scans coadded

DAC: High Pressure Diamond Optics, Inc. (Tucson, AZ)
0.6mm diamond faces

Gaskets: Tantalum, 25 micron initial thickness
250 micron (initial) aperature

Pressure Calibrant: 5 micron silica (Pennsylvania Sand Co.)

Samples:
- -prepared from anhydrous (crystalline) HAN & H_2O or dHAN & D_2O
- -HAN concentration determined by titration[a]
- -densities measured by ultrasound[b]

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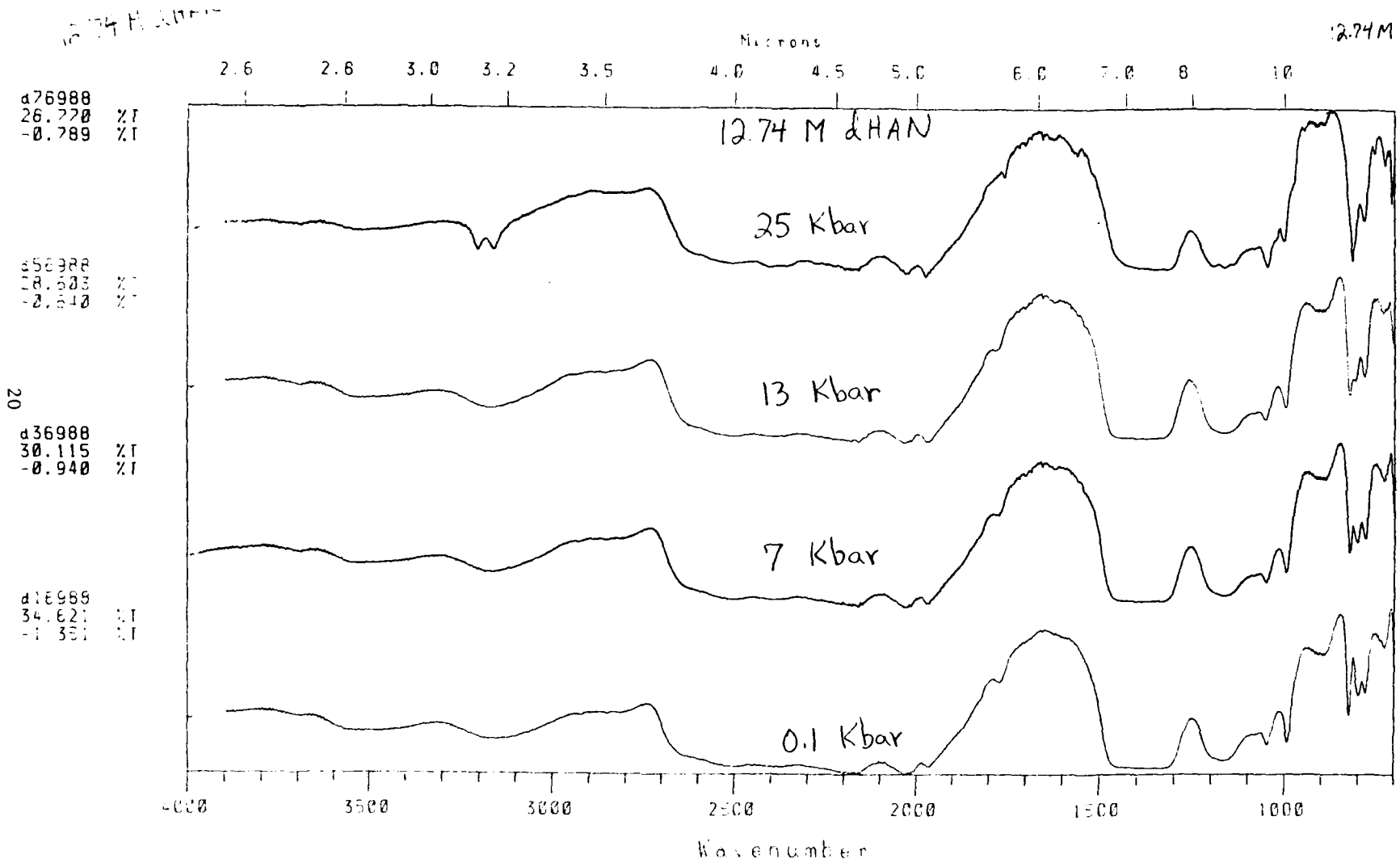
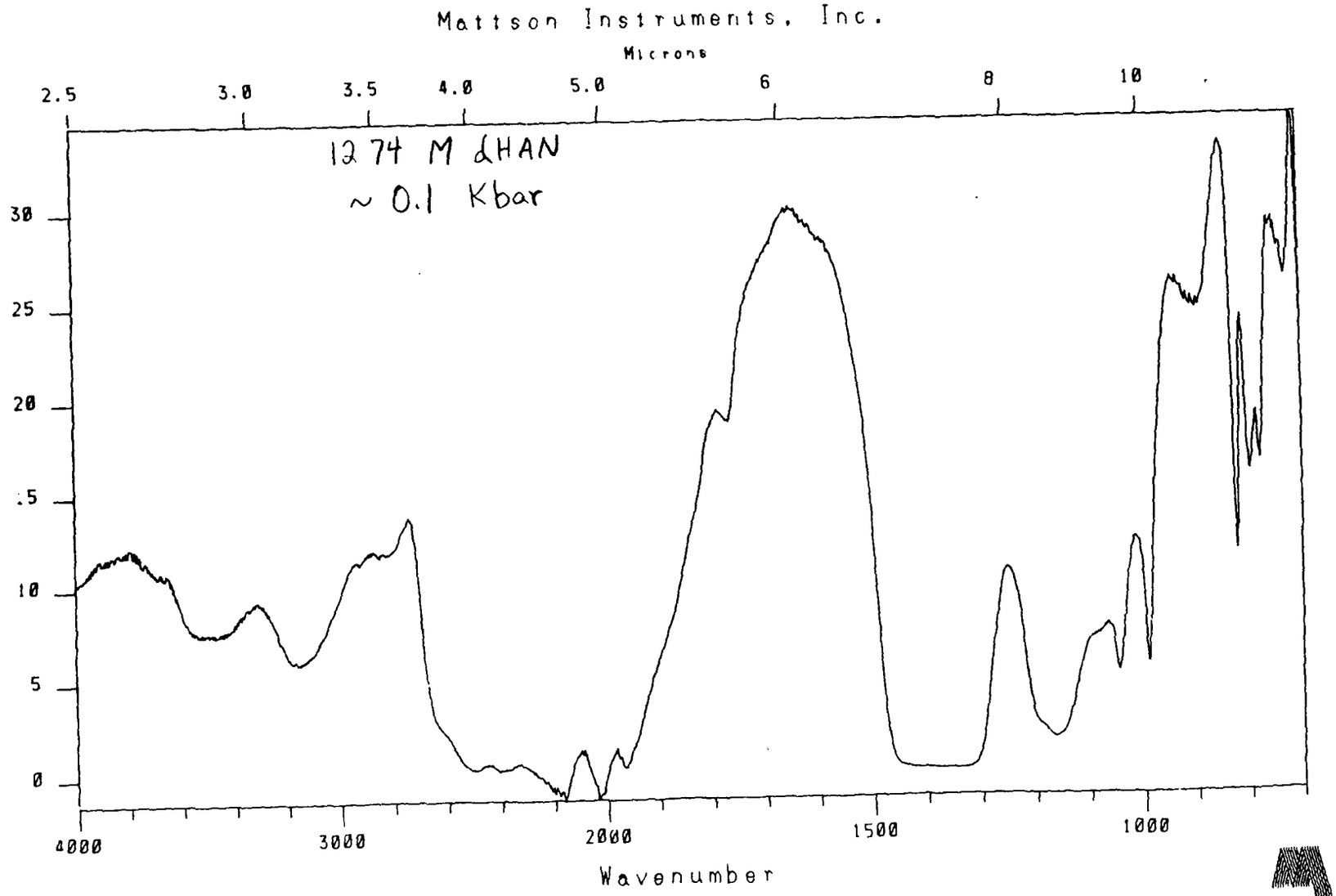
[a]performed by M. Decker
[b]forthcoming BRL report by R. Sasse et. al will describe density-concentration relationships for HAN and dHAN

8/30/88 LP7


12.74 M
Microns
2.6
2.8
3.0
3.2
3.5
4.0
4.5
5.0
6.0
7.0
8
10
d76988
26.770 %T
-0.789 %T
12.74 M dHAN
25 Kbar
13 Kbar
d36988
30.115 %T
-0.940 %T
7 Kbar
0.1 Kbar
3500
3000
2000
1000
Wavenumber

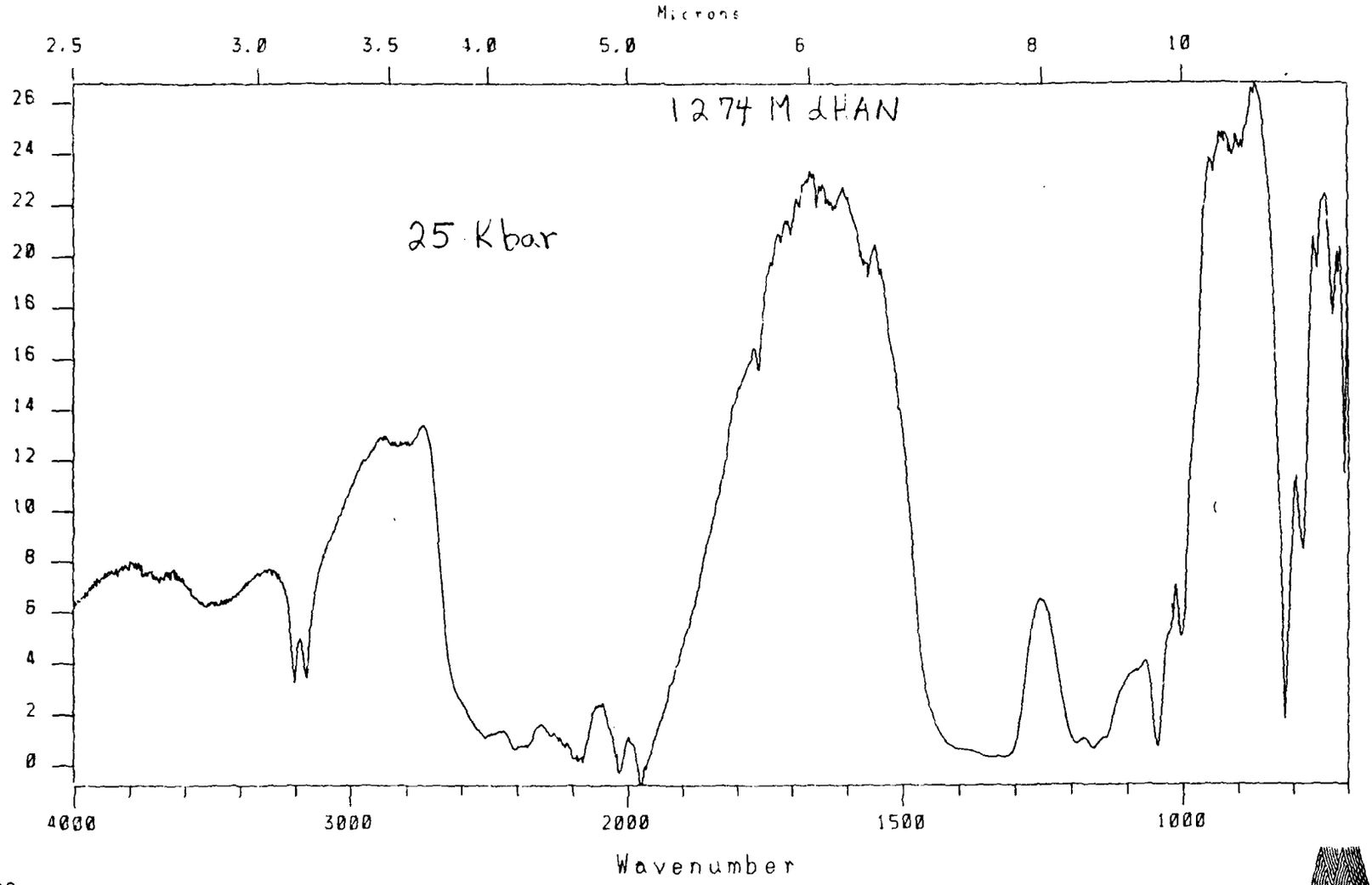
12.74 M #4



d16988.ras

Mattson Instruments, Inc.

12.74 M # 10



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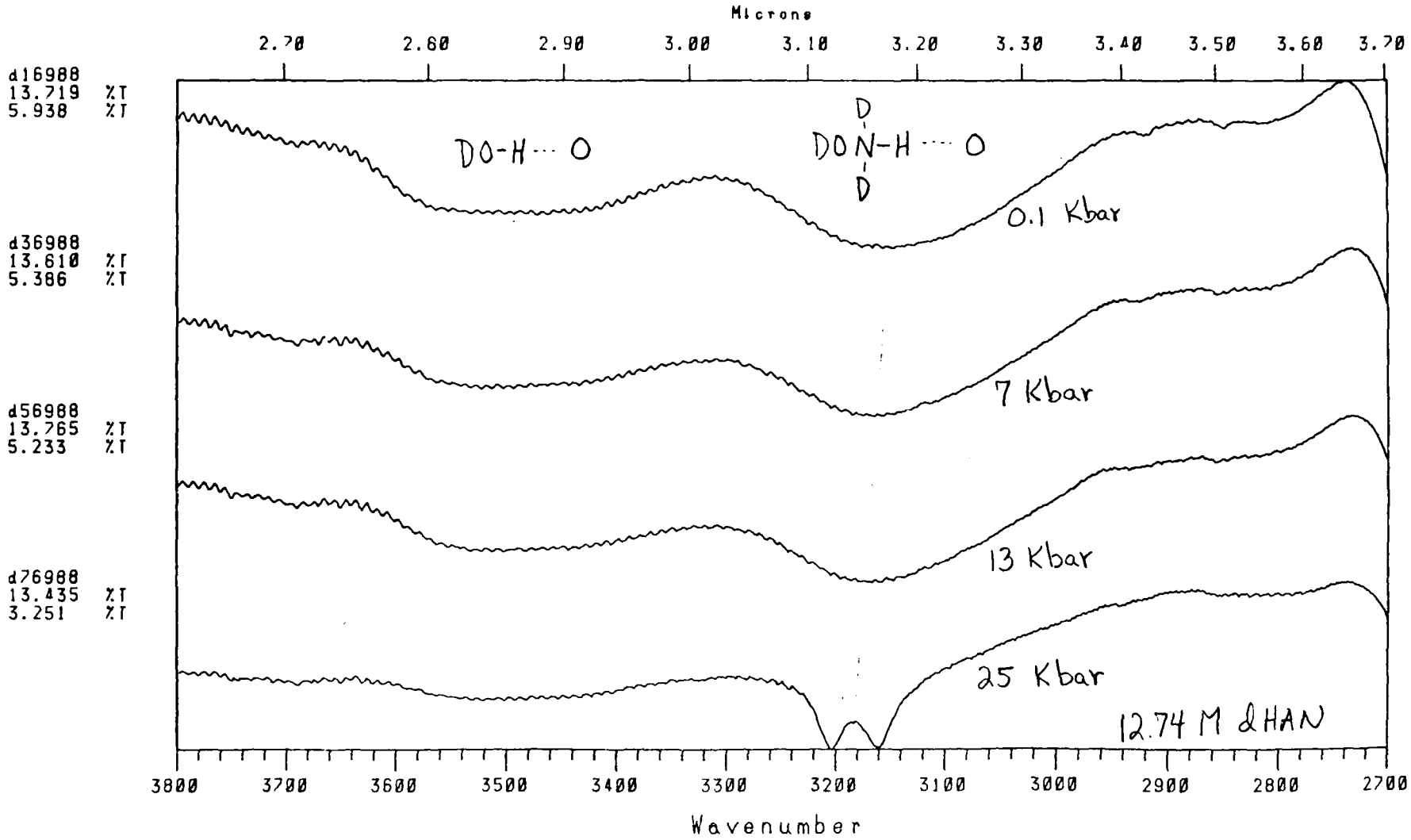
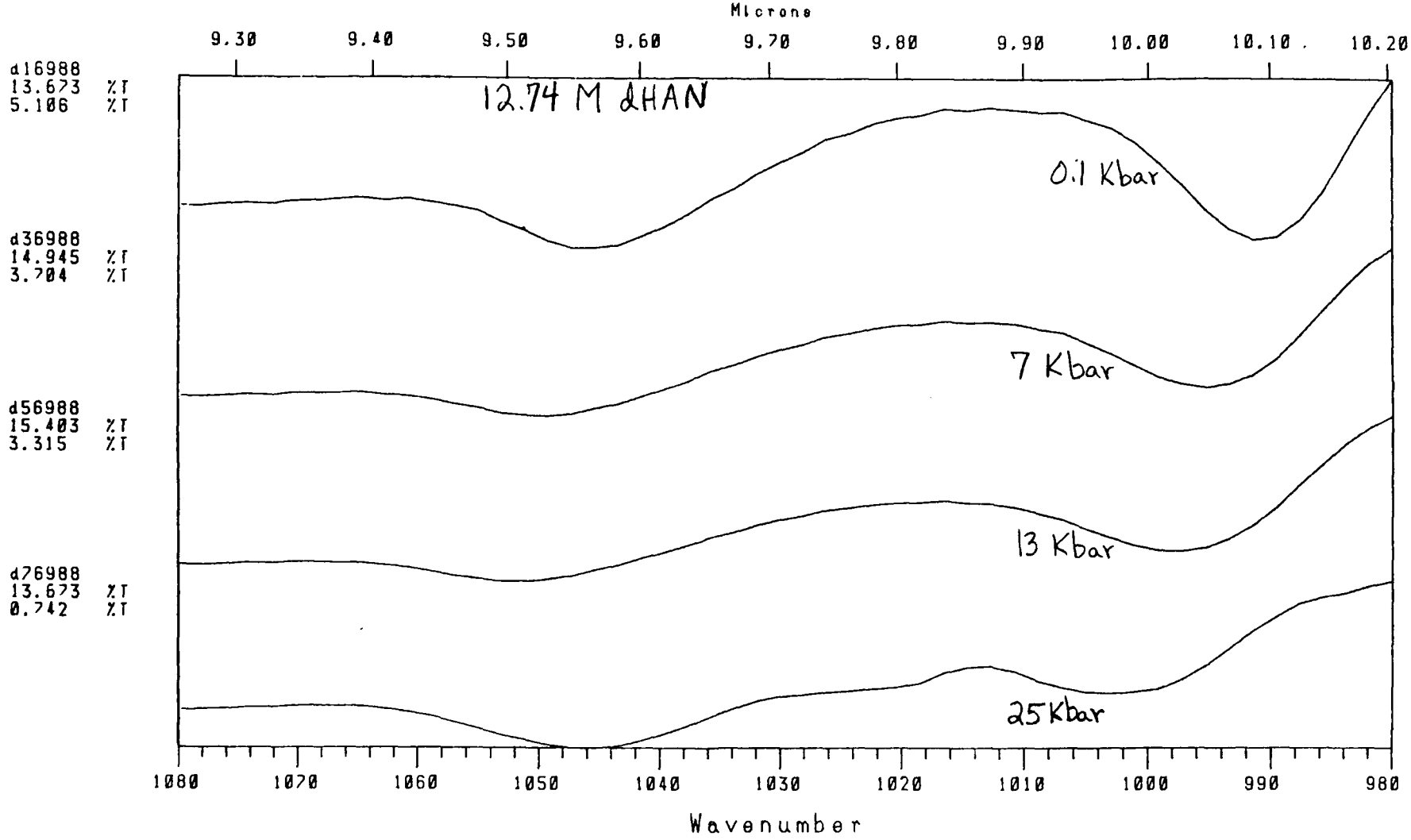
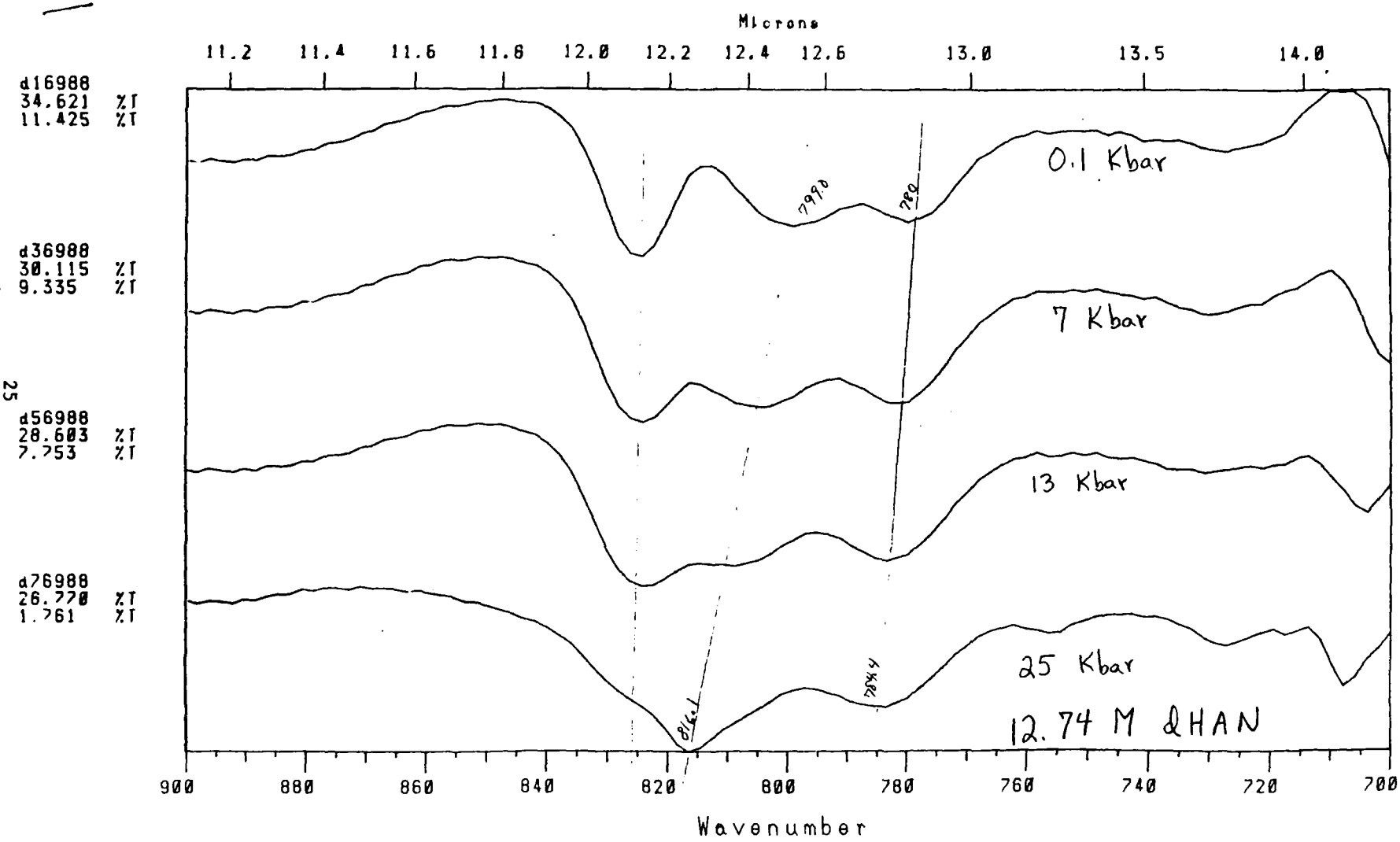
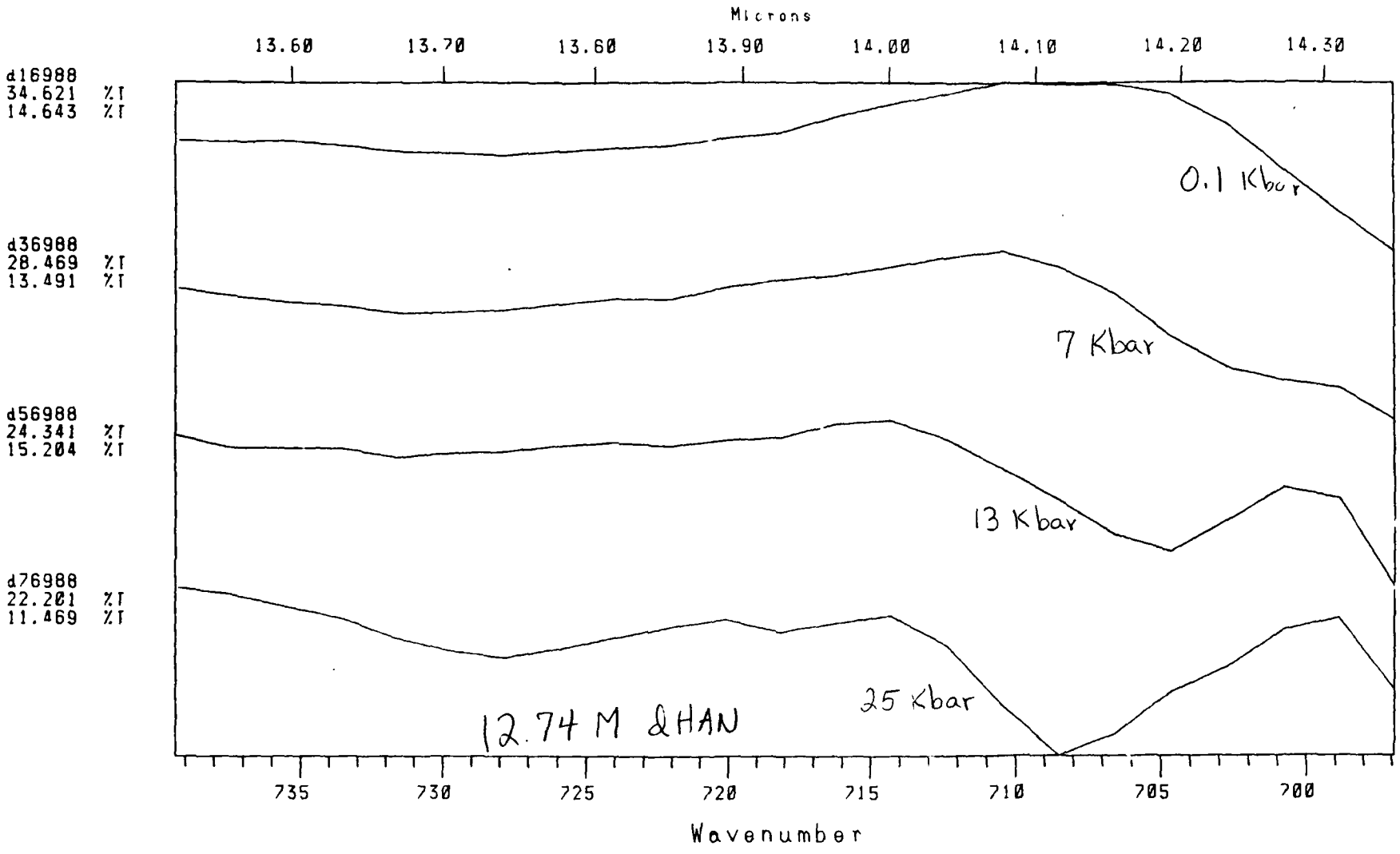

Microns
2.70
2.60
2.90
3.00
3.10
3.20
3.30
3.40
3.50
3.60
3.70
d16988
13.719 %T
5.938 %T
d36988
13.610 %T
5.386 %T
d56988
13.765 %T
5.233 %T
d76988
13.435 %T
3.251 %T
DO-H ··· O
D
DO N-H ··· O
D
0.1 Kbar
7 Kbar
13 Kbar
25 Kbar
12.74 M d HAN
3800
3700
3600
3500
3400
3300
3200
3100
3000
2900
2800
2700
Wavenumber


Microns
9.30
9.40
9.50
9.60
9.70
9.80
9.90
10.00
10.10
10.20
d16988
13.673 %T
5.106 %T
d36988
14.945 %T
3.704 %T
d56988
15.403 %T
3.315 %T
d76988
13.673 %T
0.742 %T
12.74 M DHAN
0.1 Kbar
7 Kbar
13 Kbar
25 Kbar
1080
1070
1060
1050
1040
1030
1020
1010
1000
990
980
Wavenumber


Microns
11.2
11.4
11.6
11.8
12.0
12.2
12.4
12.6
13.0
13.5
14.0
d16988
34.621 %T
11.425 %T
d36988
30.115 %T
9.335 %T
d56988
28.603 %T
7.753 %T
d76988
26.770 %T
1.761 %T
0.1 Kbar
7 Kbar
13 Kbar
25 Kbar
12.74 M QHAN
799.0
789
784.4
900
880
860
840
820
800
780
760
740
720
700
Wavenumber


Microns
13.60
13.70
13.80
13.90
14.00
14.10
14.20
14.30
d16988
34.621 %T
14.643 %T
0.1 Kbar
d36988
28.469 %T
13.491 %T
7 Kbar
d56988
24.341 %T
15.204 %T
13 Kbar
d76988
22.201 %T
11.469 %T
25 Kbar
12.74 M &HAN
735
730
725
720
715
710
705
700
Wavenumber

FUTURE WORK

- other solutions, smaller pressure increments
- determine if HAN can serve as own pressure calibrant
- experiments at sub- & super-ambient T's
    - effect of concentration, pressure & temperature on structure/bonding
    - phase transformations:
        (phase separation, glasses, hydrates, etc.)
    - onset of decomposition
- experiments with liquid propellant formulations!

8/30/88 LP9

INFRARED SPECTROSCOPY OF ACOUSTICALLY LEVITATED DROPLETS

Thomas B. Brill and James T. Cronin

University of Delaware
Department of Chemistry
Newark, DE 19716
(302) 451-6079

The stationary suspension of a liquid droplet or a solid particle in air on the nodes of a monochromatic sound wave (acoustic levitation) was investigated as a non-intrusive sampling technique for IR studies of particles and liquid droplets. A 22 KHz acoustic levitator was constructed for use in an external optical bench assembled from the beam condenser mirrors of a micro-sampling device. This permitted the focal point of the IR beam to be positioned at various points in and around the droplet or particle. IR spectra of 1-3 mm diameter droplets of LP1845, oil droplets, bubbles and solid particles have been recorded. Some of the spectra are non-routine in appearance. Variables, such as the phase and composition of the sample, the particle size, and the beam position all can profoundly influence the appearance of the spectrum. A combination of reflection and absorption of radiation occurs, the balance of which can be shifted by the above mentioned variables. Semi-empirical modeling of the optical features for this unusual sample state is currently being attempted.

I. SPECTROSCOPIC CHARACTERIZATION OF THE THERMOLYSIS OF LGP1845

II. FTIR STUDIES OF ACOUSTICALLY LEVITATED DROPLETS

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Department of Chemistry
University of Delaware
Newark, DE 19716

Support: DAAG20-84-K-0198

Outline

1. Rapid-Scan FTIR/Thermal Profiling
   a) Description
   b) Typical results of a multicomponent propellant
   c) Conclusions

2. Acoustic Levitation
   a) Description
   b) Design considerations
   c) Typical results
   d) Conclusions

Little is known about the molecular processes when condensed phases thermally decompose at high rates

We sought:

* Simulation ignition/combustion conditions

* Real–time characterization of gases evolved from the condensed phase at high heating rates

* Simultaneous measurement of heat changes in the condensed phase

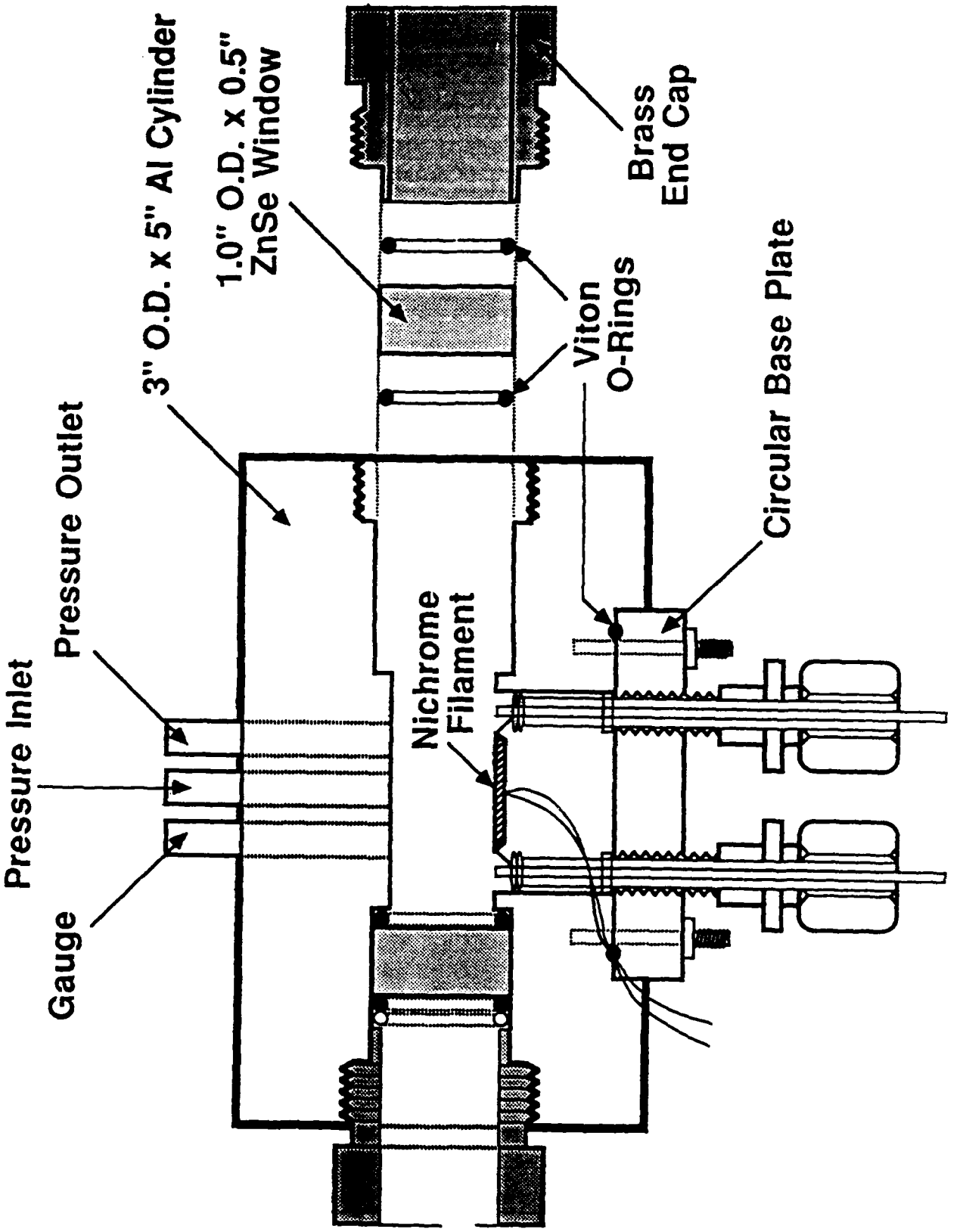
Infrared Studies of Thermolysis

Requirements;

- Fast heating rate
- Elevated pressures
- In situ, real-time analysis of products

Methods;

- Resistance heating: $dT/dt=50-800\ K/sec^{-1}$
- Pressure: 1-1000 PSI Ar (static)
- Rapid-scan infrared spectroscopy : 80 scans sec^{-1}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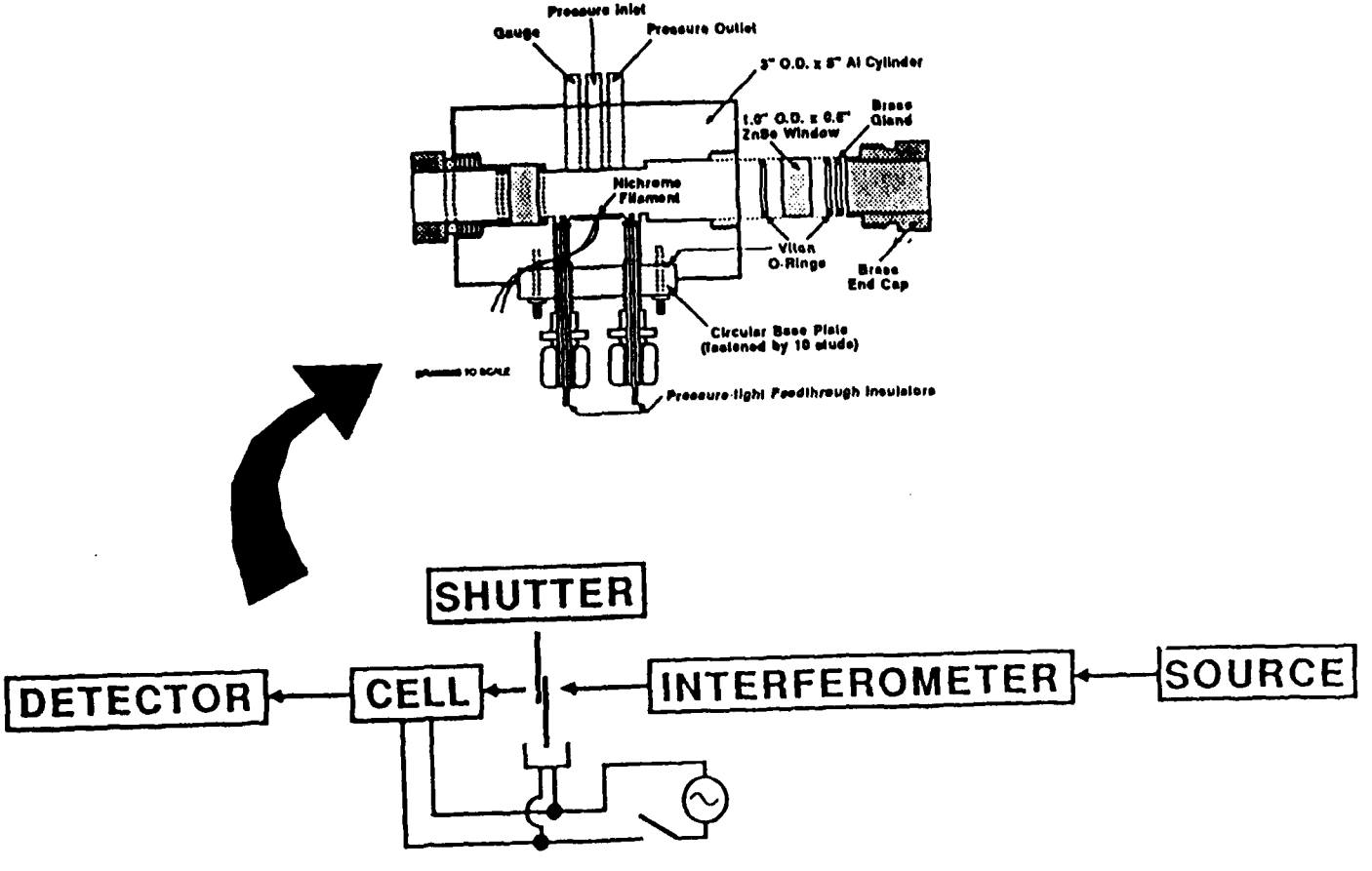
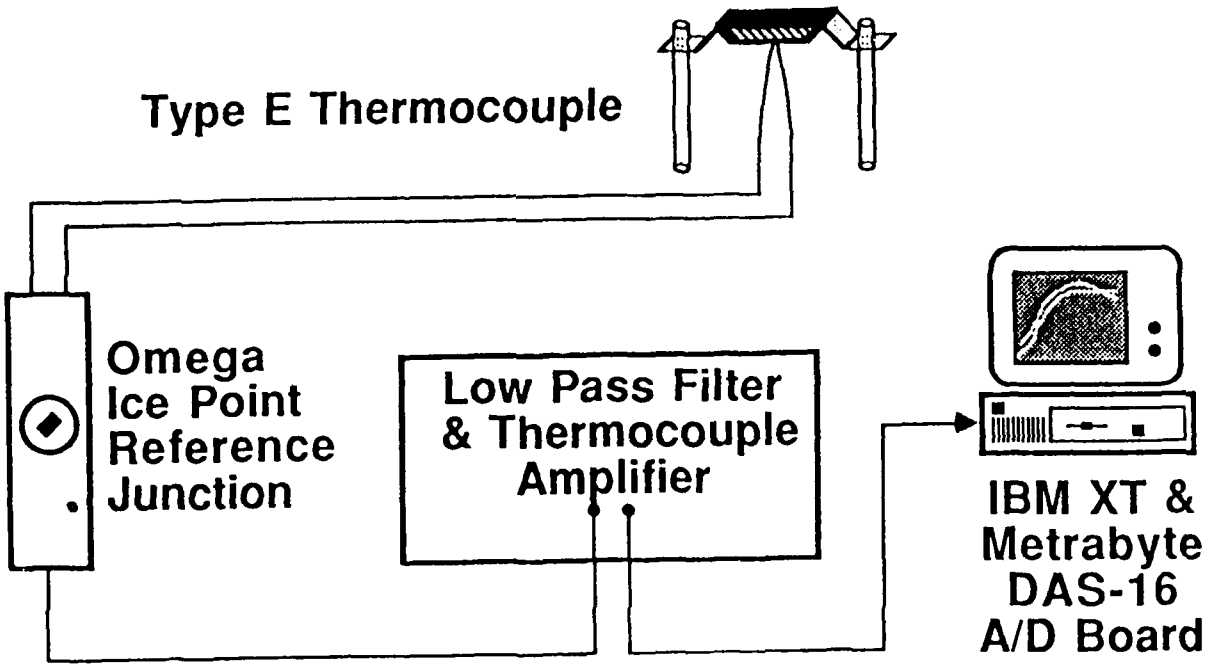
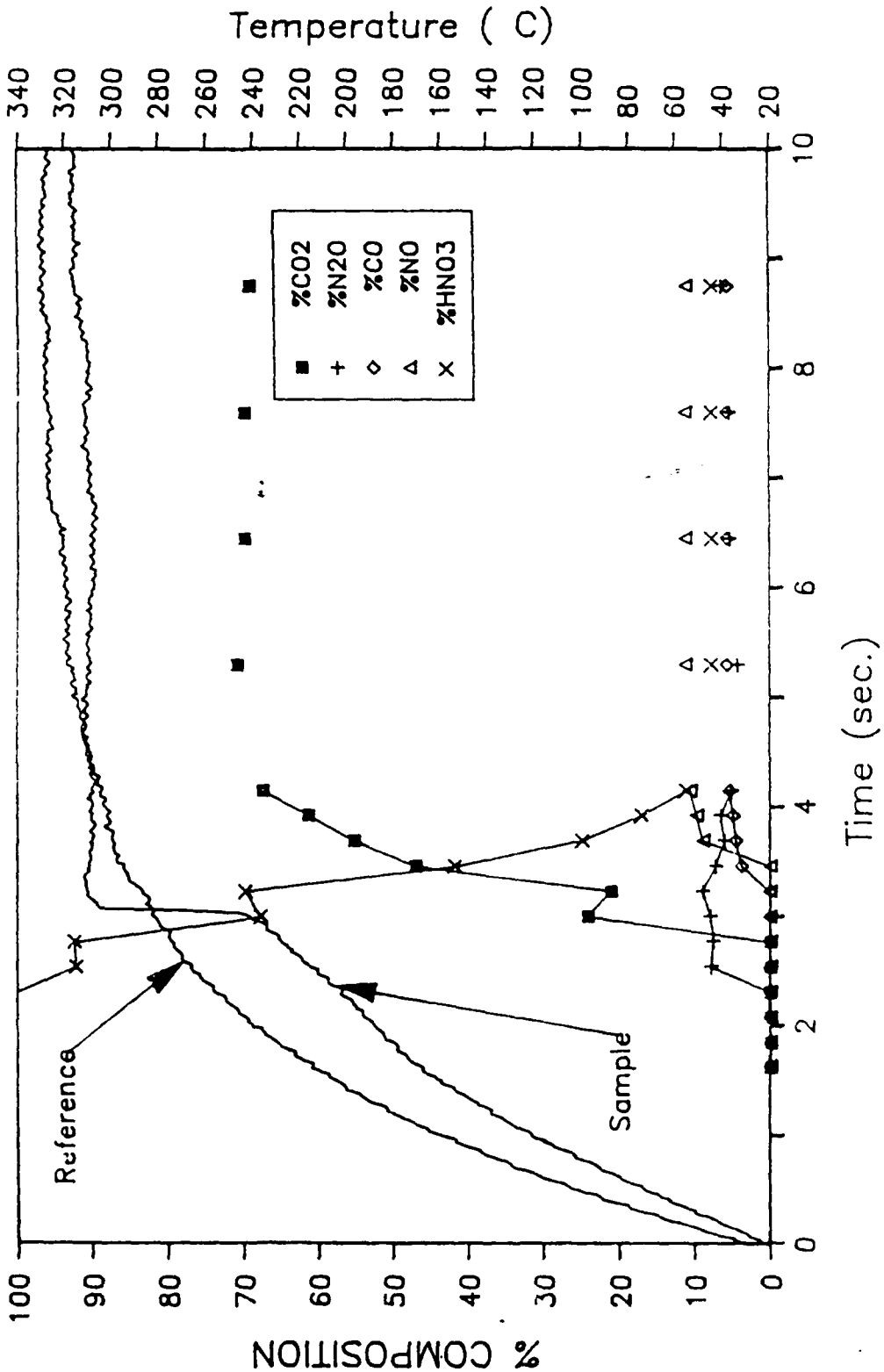
Gauge
Pressure Outlet
3" O.D. x 5" Al Cylinder
1.0" O.D. x 0.5"
ZnSe Window
Nichrome
Filament
Viton
O-Rings
Brass
End Cap
Circular Base Plate


Pressure Inlet
Gauge
Pressure Outlet
3" O.D. x 5" Al Cylinder
1.0" O.D. x 0.5" ZnSe Window
Brass Gland
Nichrome Filament
Viton O-Rings
Brass End Cap
Circular Base Plate (fastened by 10 studs)
Pressure-tight Feedthrough Insulators
SHUTTER
DETECTOR
CELL
INTERFEROMETER
SOURCE

Thermal Analysis Cell




Temperature (C)
340
320
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
%CO2
%N2O
%CO
%NO
%HNO3
Reference
Sample
100
90
80
70
60
50
40
30
20
10
0
% COMPOSITION
0
2
4
6
8
10
Time (sec.)

Conclusions

* Four major events which vary in length with pressure and heating rate

  1) Endothermic evaporation of water which concentrates sample.

  2) Endothermic decomposition of HAN, proton transfer from NH_3OH^+ to NO_3^-, to yield $HNO_3(g)$. In the 160–170 C range.

  3) Partial decomposition of TEAN, marked by small quantities of HCN and NO. In the 240–250 C range.

  4) Combustion of sample, marked by vigorous exotherm.

Facts on Levitation

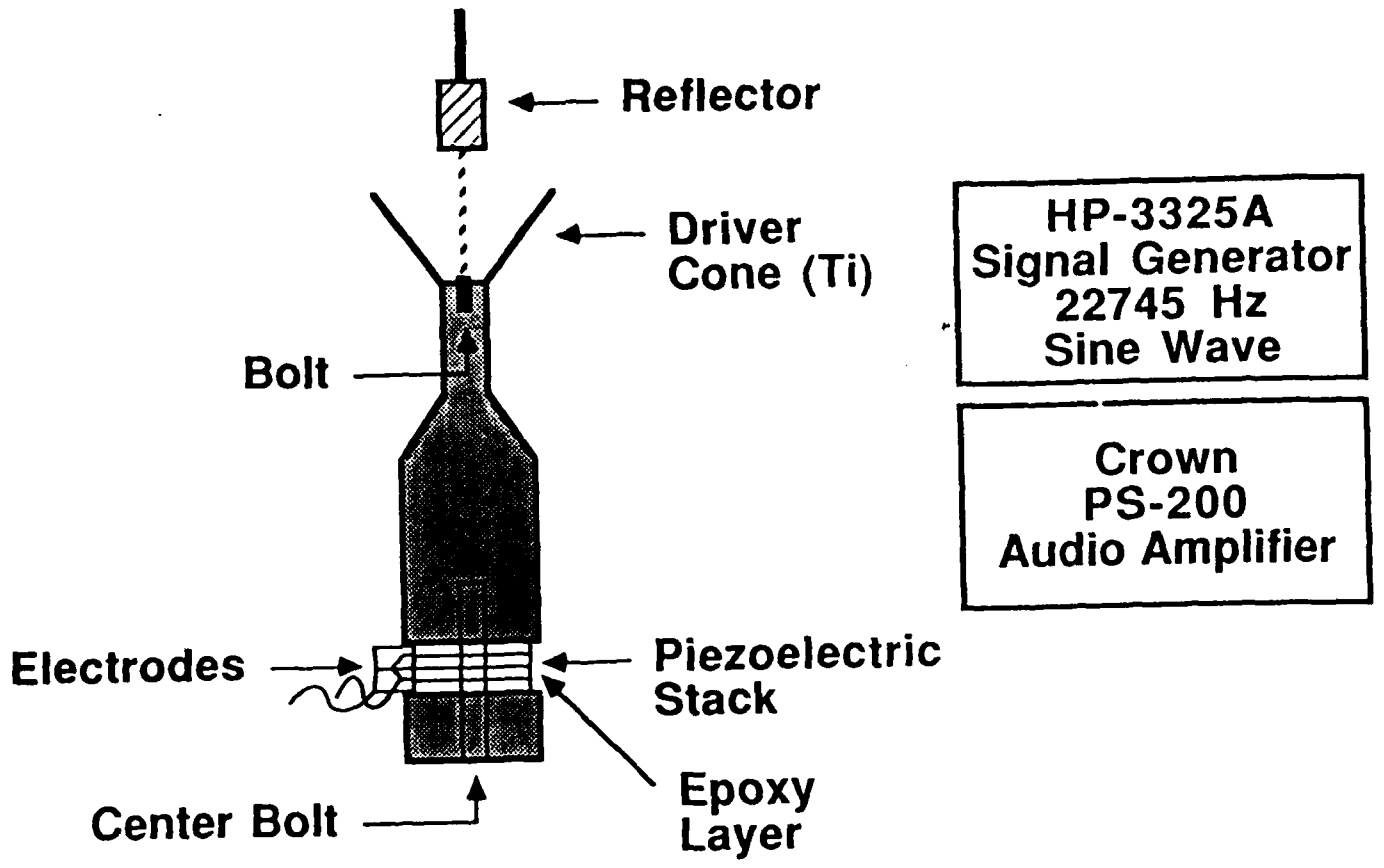
* Various types; Aerodynamic, Electrostatic, Optical and and Acoustic Levitation.

* Important uses include; forming spherical objects and and containerless processing/positioning.

* Advancement in droplet studies, unobtrusive sampling.

Acoustic Levitation Objectives

* Demonstrate feasibility of acoustic levitation as an unobtrusive FTIR sampling technique.
* Investigate parameters associated with unobtrusive sampling.
* Attempt to record levitated FTIR spectra.
* Attempt FTIR spectra of decomposing levitated samples.


Reflector
Driver
Cone (Ti)
Bolt
Electrodes
Piezoelectric
Stack
Epoxy
Layer
Center Bolt
HP-3325A
Signal Generator
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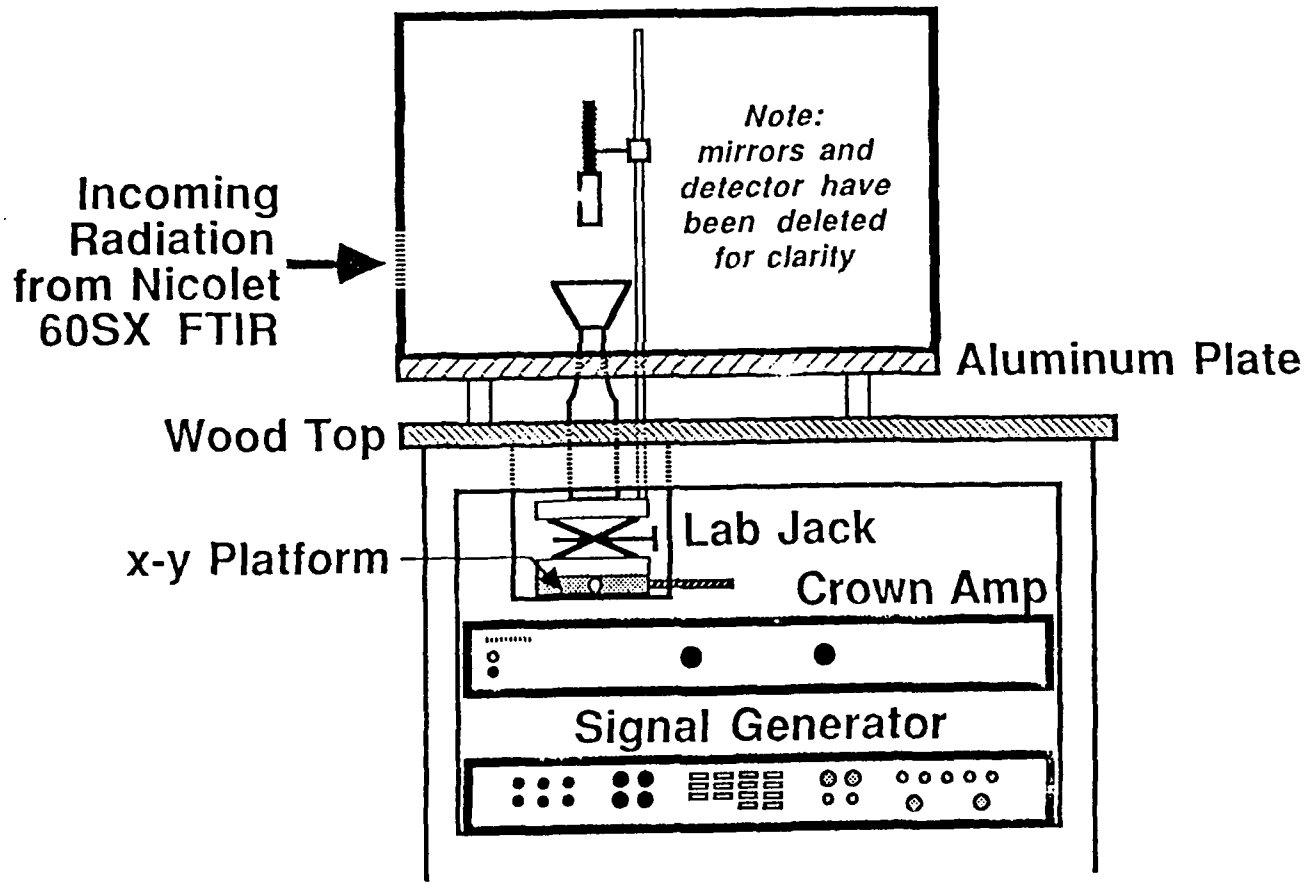
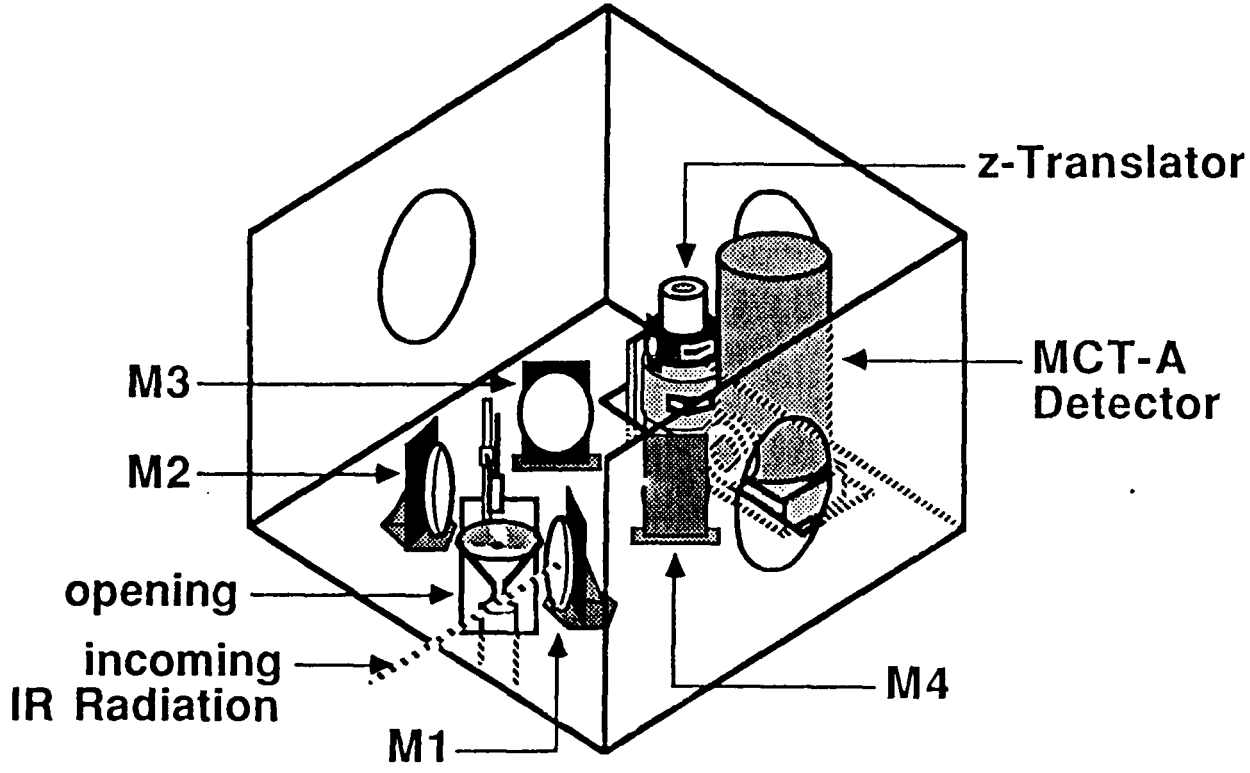
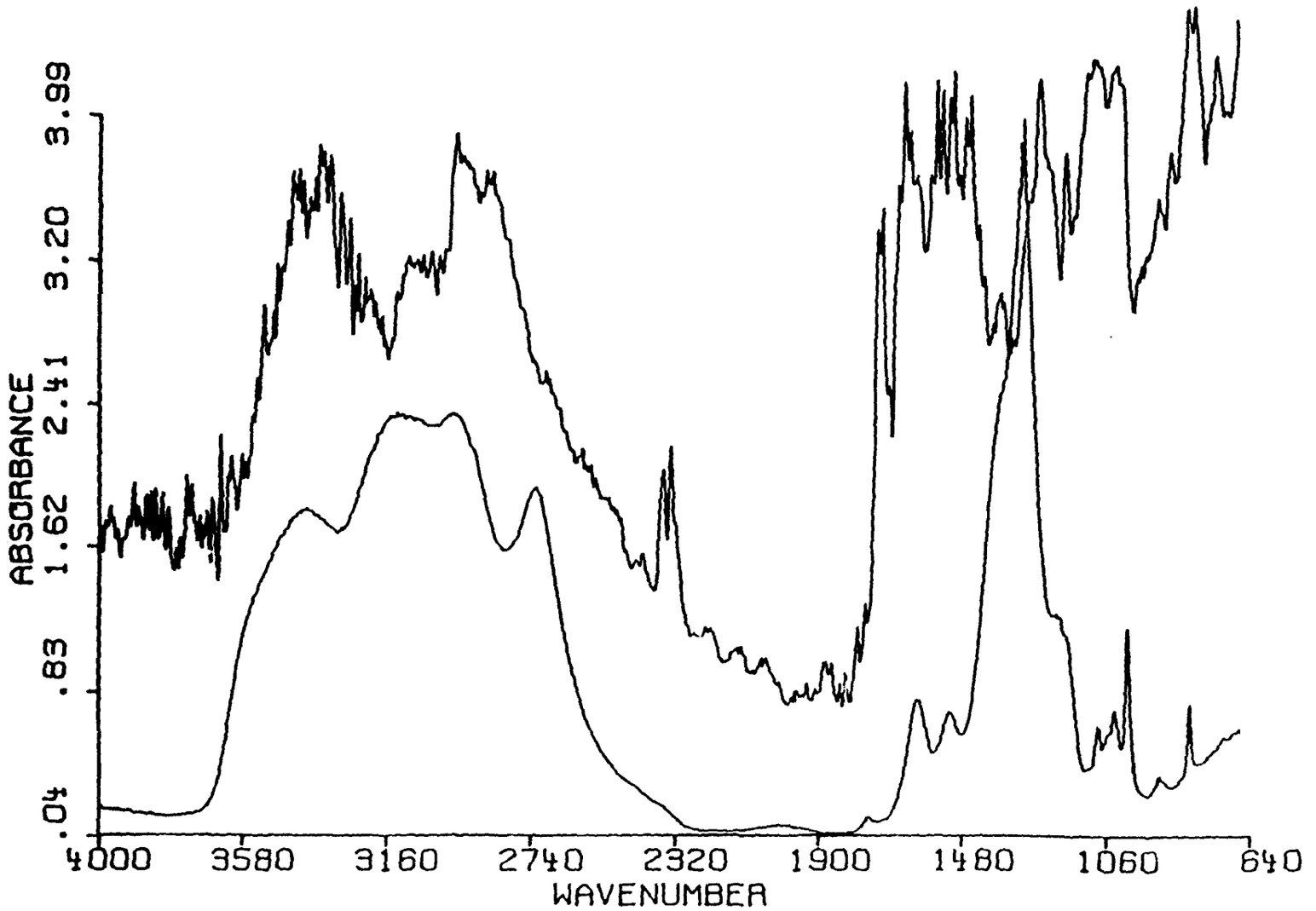
Sine Wave
Crown
PS-200
Audio Amplifier


Incoming
Radiation
from Nicolet
60SX FTIR
Note:
mirrors and
detector have
been deleted
for clarity
Aluminum Plate
Wood Top
x-y Platform
Lab Jack
Crown Amp
Signal Generator


z-Translator
MCT-A
Detector
M3
M2
opening
incoming
IR Radiation
M1
M4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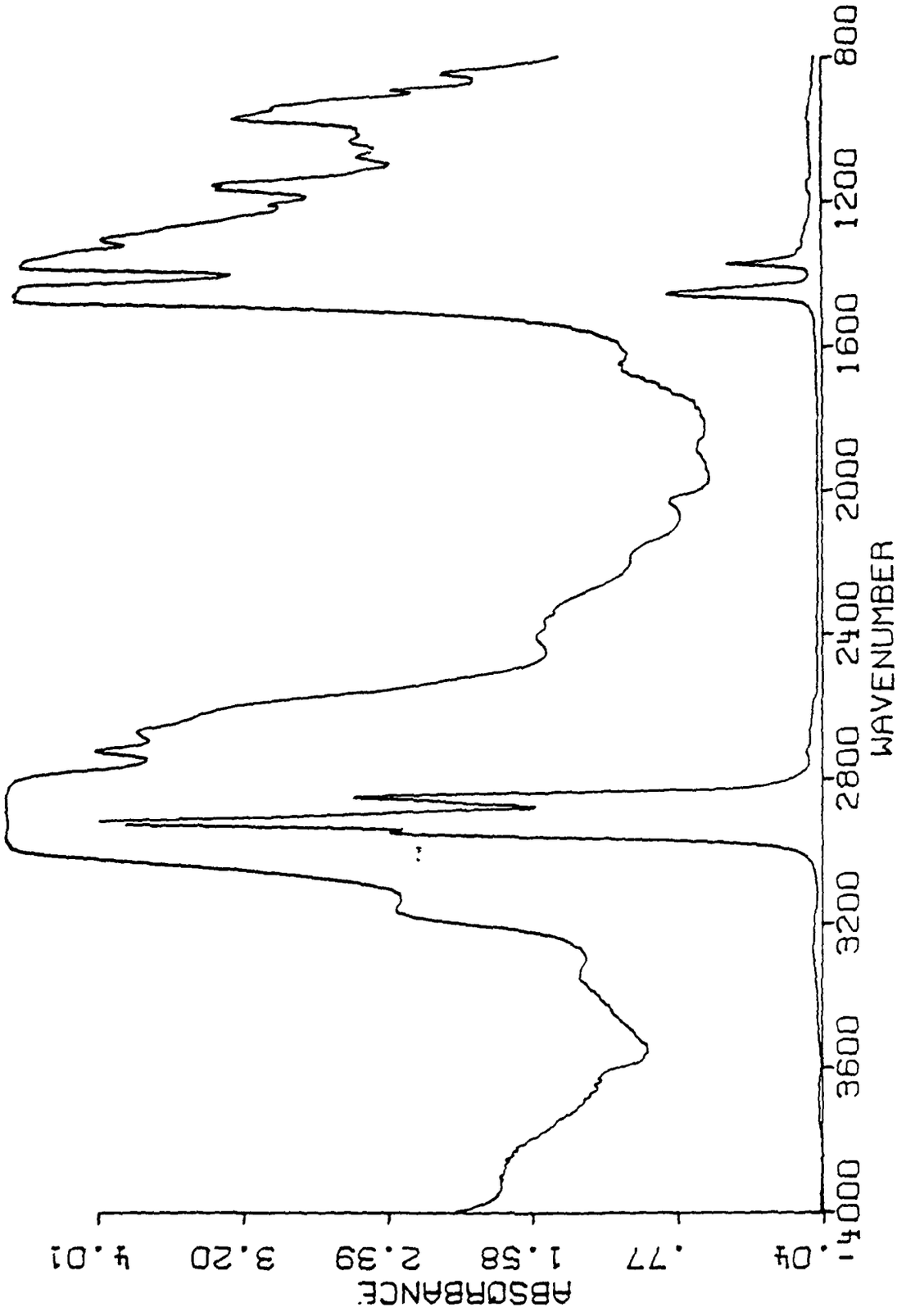
.04
.83
1.62
2.41
3.20
3.99
4000
3580
3160
2740
2320
1900
1480
1060
640
WAVENUMBER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WAVENUMBER
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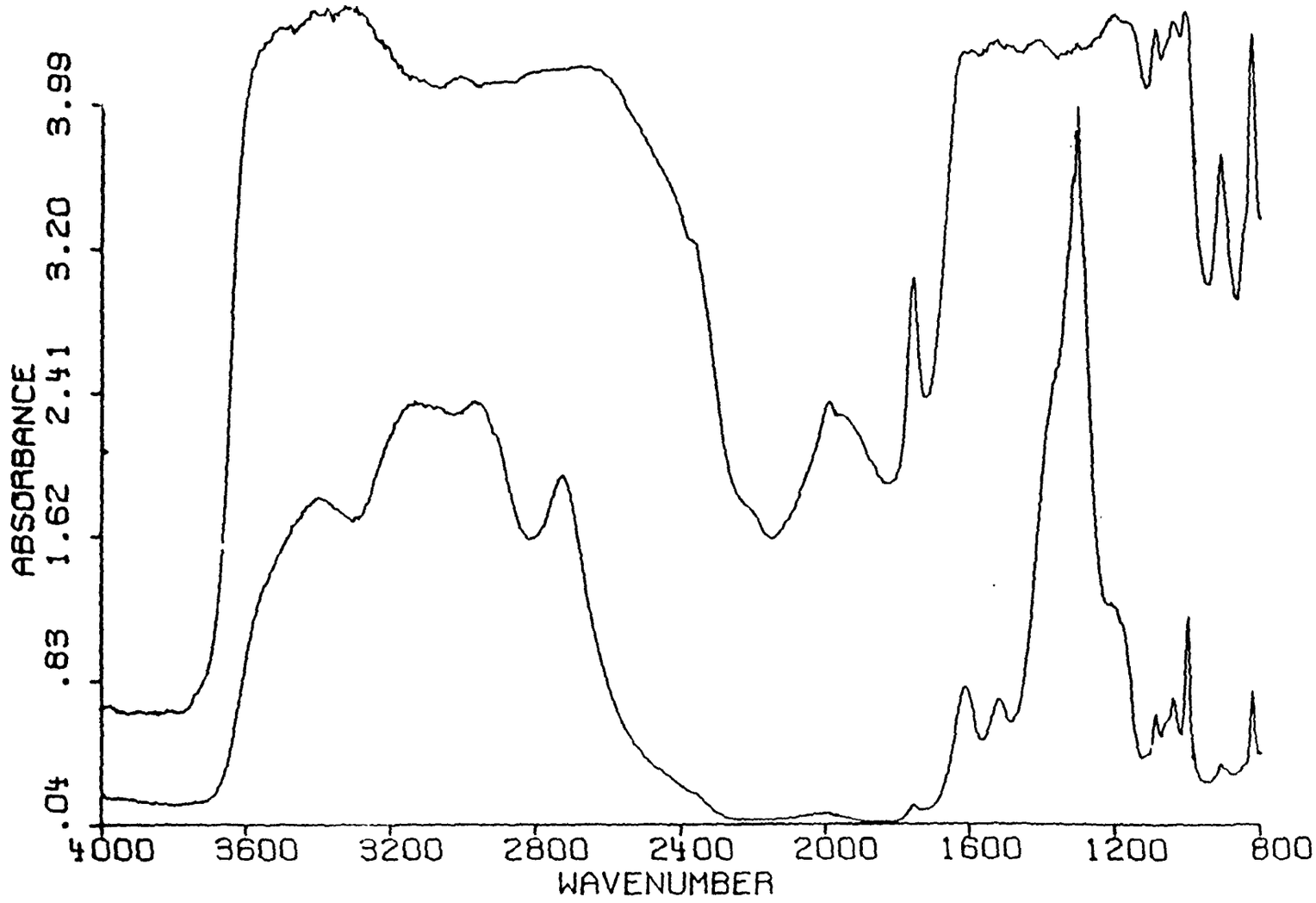
2800
2400
2000
1600
1200
800


ABSORBANCE
.04
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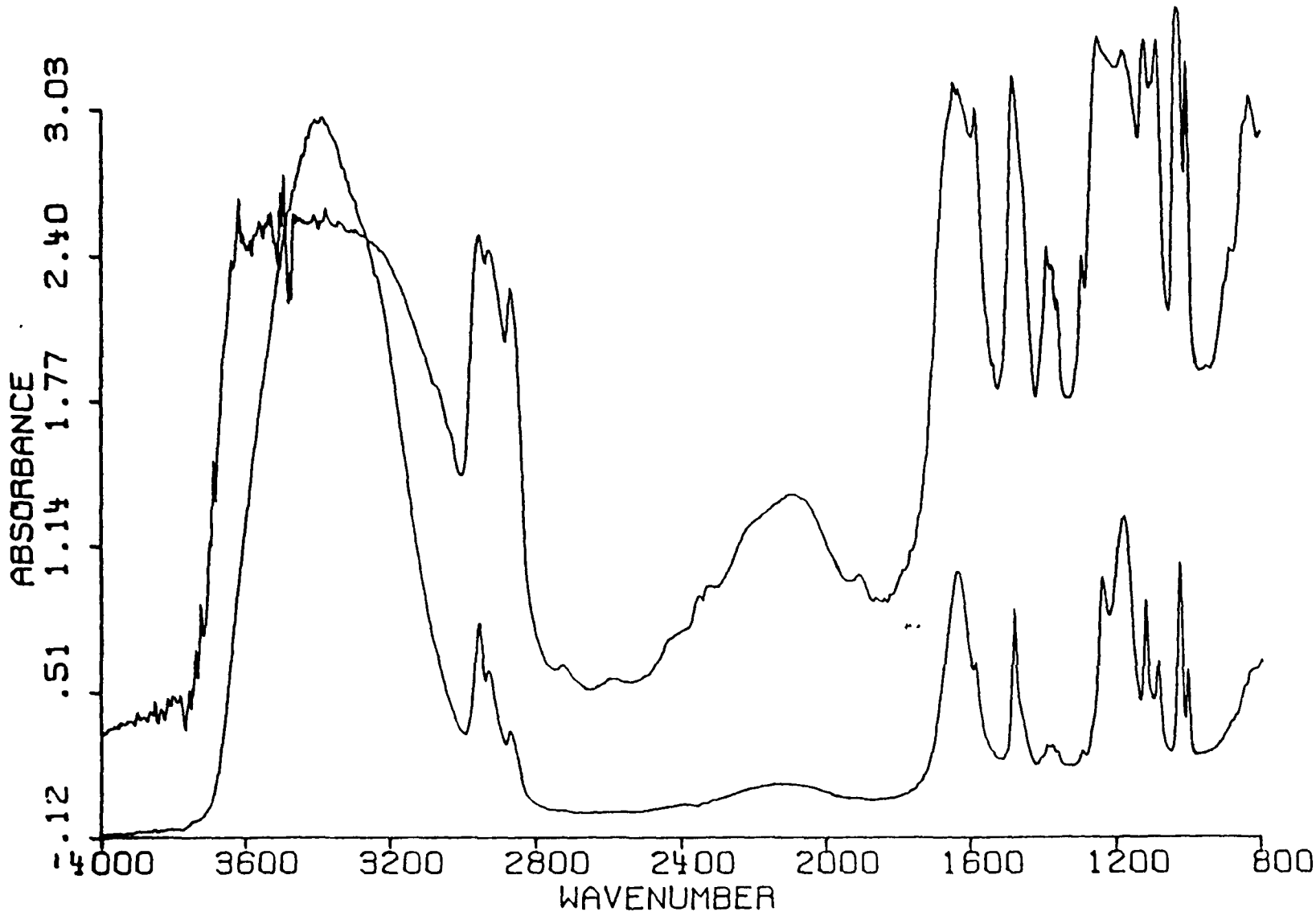
WAVENUMBER


ABSORBANCE
-.12
.51
1.14
1.77
2.40
3.03
4000
3600
3200
2800
2400
2000
1600
1200
800
WAVENUMBER

Conclusions

a) Collection of FTIR spectra of levitated samples is feasible.

b) Complex procedure with many variables:

* Stability of the sample
* Position of sample in the infrared beam
* Size and nature of the sample
* Complicated spectra

c) Emission techniques should yield higher quality spectra.

Laser-Induced Shape Distortion & Breakdown

in

Single NH_4NO_3 Water Droplets

BRL
August 31, 1988

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David H. Leach

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New Haven, CT 06520-2157
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4th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT STRUCTURE AND PROPERTIES
US ARMY BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MD
30 AUG - 1 SEP 88

Title of Paper Laser-Induced Shape Distortion and Breakdown in Single NH_4NO_3 Water Droplets

Presentation Time Request 30 **(min)**

Type of Paper: X **Progress;** ____ **Summary;** ____ **State-of-art;** ____ **Other**

Speaker's Name Richard K. Chang **Phone Number** (203) 432-4272

Affiliation/address Yale University
Applied Physics
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Co-author(s) name(s) David H. Leach, Jia-biao Zheng, and Jian-Zhi Zhang

ABSTRACT (Use reverse side if necessary)

Nonlinear optical spectra from a single water droplet containing nitrate ions can potentially provide information on the droplet species, size, and shape. However, the droplet may be significantly perturbed by the high-energy and/or high-intensity laser pulse needed for such optical diagnostics. It is, therefore, important to understand the laser-induced shape distortion forces and the laser-induced breakdown (LIB) mechanisms when the incident laser fluences and/or irradiance exceed certain values.

The high-energy laser pulse can exert a large electrostrictive force on the droplet and cause shape distortions of large amplitude. Such distortions may provide a means to determine in situ the surface tension of the droplets. We have recorded shadowgraphs of laser-induced shape distortions by a high-energy (~20 mJ intercepted by the droplet) but low-intensity laser pulse.

LIB occurs when a high-intensity but low-energy laser pulse is incident on a transparent droplet. When the incident laser irradiance is below 1 GW/cm^2, the integrity of a 5 M NH_4NO_3 water droplet is left intact, and the emission spectra, which are confined within the droplet rim, consist of multiorder stimulated Raman scattering (SRS) peaks of the NO_3^- ions. Above 1 GW/cm^2, the emission spectra within the droplet consist of the SRS peaks as well as a broad continuum, which is indicative that LIB has occurred within the droplet. We have been using spatially resolved plasma emission spectroscopic techniques to investigate physical mechanisms associated with LIB caused by high-intensity laser irradiation of a transparent droplet. At the 10 GW/cm^2 level, the emission spectra are devoid of SRS peaks and consist of only the broad plasma continuum and the discrete plasma peaks, e.g., from singly ionized nitrogen [N(II)] and neutral hydrogen of the Balmer series H_α. Using a spatially and temporally resolved technique, we have been able to determine the plasma propagation velocity of the detonation wave that travels from the droplet illuminated face toward the laser.

We gratefully acknowledge the partial support of this research by the U.S. Army Research Office (Contract No. DAAL03-87-K-0076).

OBJECTIVE

Nonlinear optical spectroscopy to determine species and their concentrations within droplets.

SUMMARY OF PROGRESS

1. Stimulated Raman scattering (SRS) spectrum

2. Time development of SRS

3. Quenching of SRS by laser-induced breakdown

4. Laser-induced breakdown plasma emission
   (spatial and temporal development)

5. Droplet shape distortion due to electrostriction

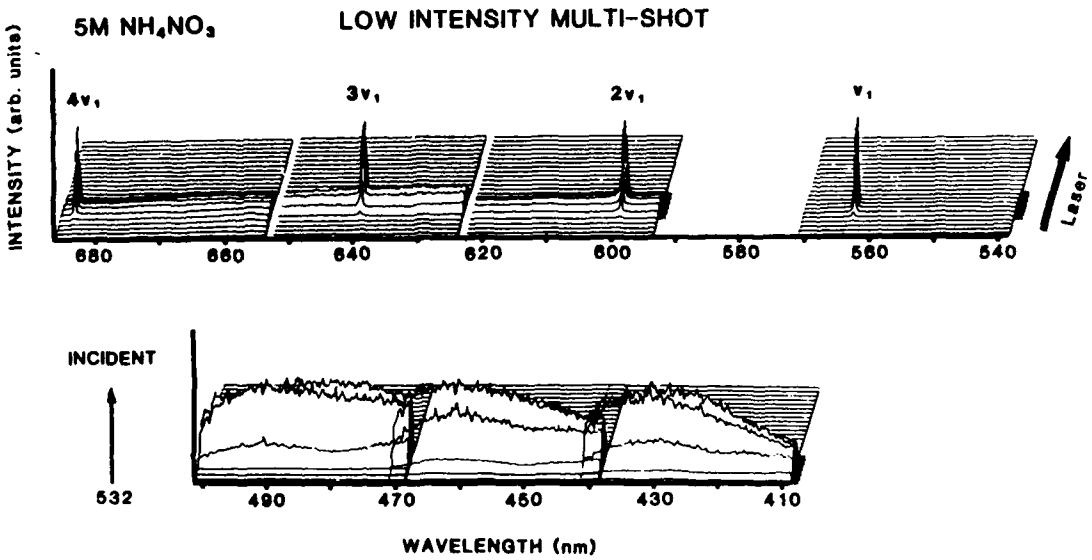

Fig. 1. Spatially resolved emission spectra from 5 M NH_4NO_3 water droplets that were irradiated with a 532 nm laser pulse with irradiance of 1.4 GW/cm^2. The horizontal axis corresponds to wavelengths dispersed by the spectrograph. The vertical axis in the plane corresponds to distance along the laser beam direction (indicated by the arrow), which is aligned parallel to the vertical slit of the spectrograph. The shaded bar along this vertical axis defines the droplet along its principal diameter. The third axis out of the plane corresponds to the intensity (detected by a vidicon camera placed at the exit plane of the spectrograph) at various wavelengths and at various locations along the slit. The displayed spectra in each wavelength segment resulted from the integration of ≈50 laser shots. The intensity peaks of the first four orders of the stimulated Raman scattering are all confined within the droplet and are labeled υ_1, $2\upsilon_1$, $3\upsilon_1$, and $4\upsilon_1$, where υ_1 denotes the symmetric stretching mode of the NO_3^- ions. The broad plasma continuum is noted to be confined within the droplet and to increase toward shorter wavelengths. The origin of the plasma continuum is ascribed to LIB within the droplet.

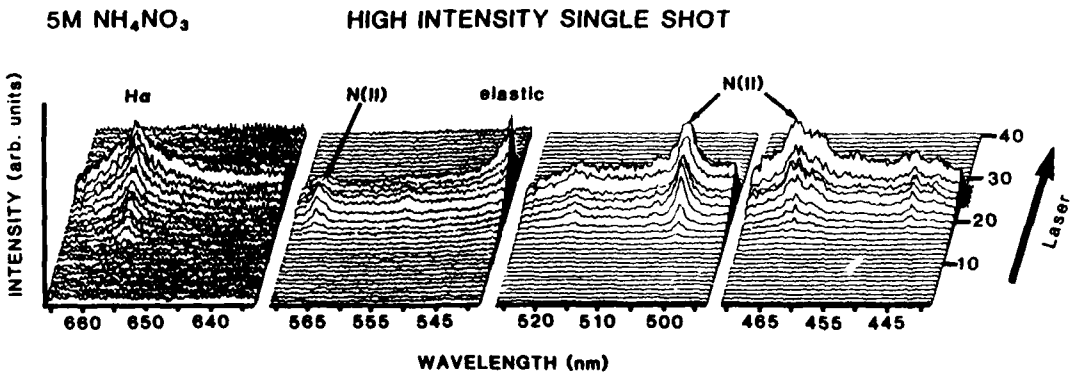

Fig. 2. Same as Fig. 1, except the input laser irradiance is increased to 9.6 GW/cm^2. The four stimulated Raman peaks are no longer detectable. LIB is responsible for the broad plasma continuum and the discrete plasma peaks. The broad plasma continuum is no longer confined within the droplet but is extended to the region behind the droplet illuminated face. The discrete plasma peaks are assigned to the emission of hydrogen (the Balmer line of H_α) from water and to the emission of singly ionized nitrogen [N(II)] from air and NO_3^- ions.

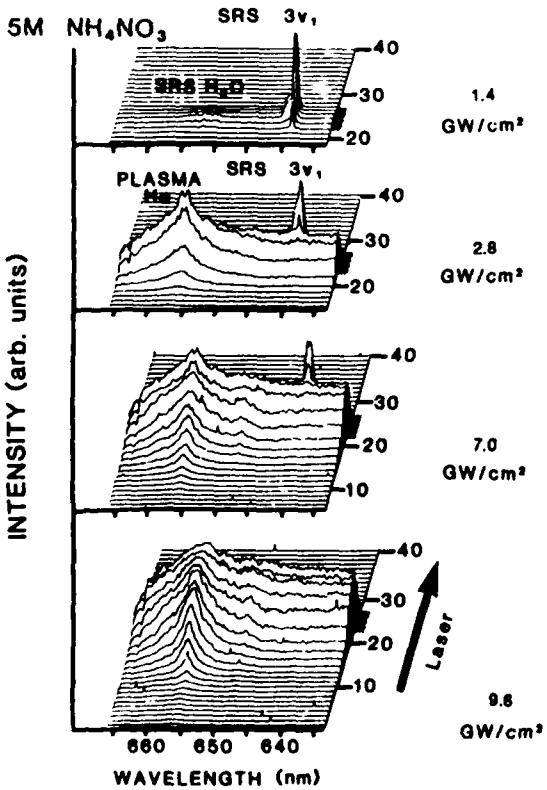

Fig. 3. Spatially resolved emission spectra within a 635 to 665 nm wavelength range at four different irradiances. At 1.4 GW/cm^2 the spectra consist of only the SRS peaks associated with the stretching mode of NO_3^- ($3\upsilon_1$) and the OH stretching mode of water. At 2.8 GW/cm^2, the $3\upsilon_1$ SRS peak is still detectable while the SRS peak of water is overwhelmed by the plasma continuum and the H_α emission peak. At 7 and 9.6 GW/cm^2, the plasma continuum and the H_α emission peak extend further behind the droplet illuminated face. At 9.6 GW/cm^2, SRS is quenched by the absorption associated with the plasma produced by the LIB.

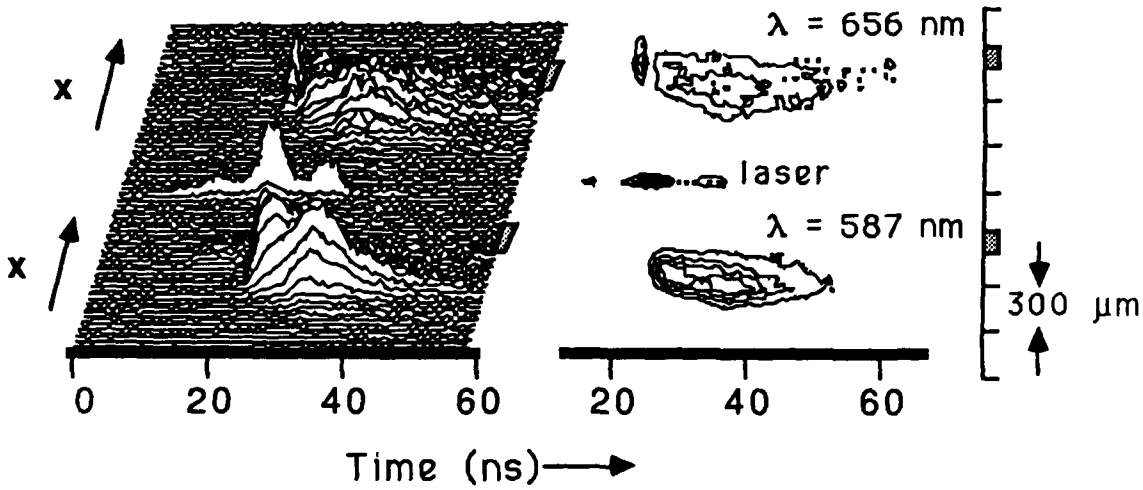

Fig. 4. Temporally and spatially resolved plasma emission spectra from 1 M NH_4NO_3 water droplets irradiated with a 532 nm laser pulse at ≈7 GW/cm^2. The droplet and the plasma plumes were imaged onto the slit of a streak camera that was swept at 5 nsec/mm. The horizontal axis corresponds to time in nanoseconds. The vertical axis in the plane corresponds to distance along the slit (denoted as x), with the top half detecting the emission at λ = 656 nm (chosen for the hydrogen Balmer line of H_α), the bottom half detecting the emission at λ = 587 nm (chosen to be within the broad plasma continuum), and the central part detecting the laser emission at λ = 532 nm. The laser direction is along the x axis, and the region spanned by the droplet illuminated face and shadow face are indicated. The plasma emission intensity as a function of time and distance along the slit is plotted out of the plane (see curves on the left). The nominal 20 nsec Q-switched laser pulse actually consists of three pulses. The equal intensity contours as a function of time and distance along the slit are also shown (see curves on the right). Note that there is no detectable plasma expulsion from the droplet shadow face. All the plasma expulsion occurs from the droplet illuminated face in the form of an optical detonation wave (when the laser pulse is on) and in the form of a shock wave (when the laser pulse is off). For the detonation wave, the propagation velocity of the H_α emission, starting from the droplet illuminated face and traveling toward the laser, is ≈25 km/sec. The corresponding propagation velocity of the continuum emission is ≈15 km/sec.

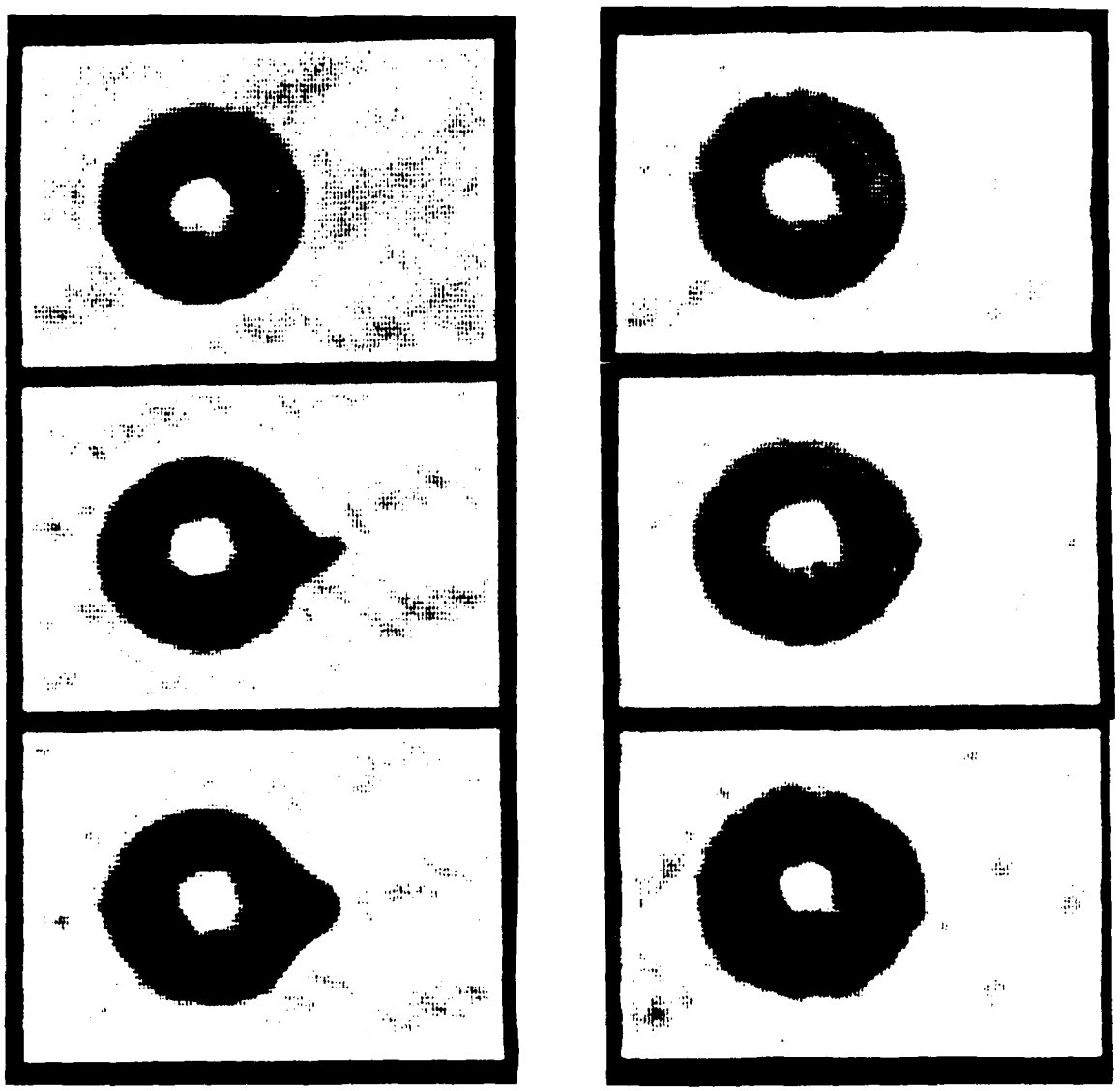

Fig. 5. Shadowgraphs of a droplet at various delay times Δt after a droplet has been irradiated by a long pulsed dye laser (λ = 620 nm, 400 ns pulse duration) which is propagating from the left to the right. The left-hand column corresponds to a CCl_4 droplet ($a \approx 50$ µm) and the right-hand column corresponds to a 1 M NH_4NO_3 water droplet ($a \approx 50$ µm). The dye laser beam has 80 mJ focused to a spot diameter of 200 µm. Thus the laser energy intercepted by the CCL_4 or 1 M NH_4NO_3 water droplet is 20 mJ. The Δt for the three successive frames along the column are 0, 2, and 4 µsec, respectively. The observed bulge at the droplet shadow face is caused by the electrostrictive force exerted by the internal laser intensity (the lens effect of the illuminated face). The electrostrictive force opposes the surface tension force. The surface tension of CCL_4 is 27 dynes/cm and that of pure water is 71 dynes/cm. The surface tension of a 1 M NH_4NO_3 water droplet is larger than that of a pure water droplet. Consequently, a pronounced bulge is observed for the CCL_4 droplet (left-hand column) while only a small bulge is observed for the 1 M NH_4NO_3 water droplet (right-hand column).

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30 AUG - 1 SEP 88

Title of Paper Droplet Combustion and Thermal Decomposition Behavior of Liquid Propellants

Presentation Time Request 30 **(min)**

Type of Paper: X **Progress;** ____ **Summary;** ____ **State-of-art;** ____ **Other**

Speaker's Name To be decided **Phone Number** (916) 752-8928

Affiliation/address Department of Mechanical Engineering
University of California, Davis CA 95616

Co-author(s) name(s) C. K. Law, S. C. Deevi, D. L. Zhu, C. Call

ABSTRACT (Use reverse side if necessary)

To understand the fundamental chemical reactions and thermal behavior of HAN-based liquid propellants, it is imperative that an in-depth study be carried out on the individual ingredients of the propellant. Such an understanding is crucial to evaluate the potential chemical reactions controlling the combustion and microexplosion behavior of droplets of liquid propellants.

To gain an insight into the combustion phenomena of liquid propellants, the combustion behavior of freely falling liquid propellant droplets was investigated in a high temperature, elevated pressure environment. Influences of ambient pressure, ambient temperature, initial propellant water concentration, and initial droplet size on the combustion rate and state of microexplosion have been systematically investigated using a high pressure droplet chamber and a strobe back-lighted video imaging technique. With increasing pressure and temperature, the droplet gasification rate increased while the state of microexplosion advanced to the very early stages in the droplet lifetime. Droplet sampling was carried out prior to the microexplosion to determine the physical and chemical changes prior to the microexplosion.

The energetic ingredients of liquid propellant, HAN and TEAN were subjected to thermal treatment in a controlled manner in an inert atmosphere from atmospheric to 1000 psi. Thermal decomposition of HAN occurred much more vigorously at a lower temperature than TEAN without leaving any residue after the thermal treatment. Thermal decomposition of TEAN was observed to be complex, with several oxidation reactions during the decomposition process. Both at atmospheric and high pressures, TEAN solid exhibited a phase transition from solid to liquid corresponding to a heat of fusion of about 130J/g. The major decomposition of TEAN occurred in the liquid state with the net heat of reaction being exothermic in the pressure range investigated. Even during the onset of the decomposition process, TEAN was discolored and appeared like a black, viscous liquid. During the process of decomposition, vigorous bubbling was observed and ultimately shiny black needles were left behind. The decomposition process both at atmospheric and high pressures was interrupted and the liquid phase decomposition products were subjected to a variety of chemical analysis techniques. Our results conclusively suggest that TEAN is dissociated to triethanolamine and nitric acid, and proton transfer is the first step in the dissociation followed by decomposition.

DROPLET COMBUSTION AND THERMAL DECOMPOSITION BEHAVIOR OF LIQUID PROPELLANTS

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DEPARTMENT OF MECHANICAL ENGINEERING
UNIVERSITY OF CALIFORNIA, DAVIS

SPONSORED BY:

ARMY RESEARCH OFFICE
(TECHNICAL MONITOR: DR. DAVID MANN)

ACKNOWLEDGEMENT

Dr. V. R. Pai Verneker
Martin Marietta Laboratories
Baltimore, MD.

OUTLINE OF PRESENTATION

1. PROPERTIES OF PROPELLANTS

2. OBJECTIVE

3. EXPERIMENTAL METHODOLOGY

4. RESULTS

   A. GASIFICATION HISTORY

   B. MICROEXPLOSION

   C. THERMAL DECOMPOSITION BEHAVIOR

5. CONCLUDING REMARKS

1. PROPERTIES OF PROPELLANTS

A. CHEMICAL STRUCTURES

1. HYDROXYL AMMOMIUM NITRATE (HAN)

$$NH_3OH^+ NO_3^-$$

2. TRIETHANOL AMMONIUM NITRATE (TEAN)

$$(C_2H_4OH)_3NH^+ NO_3^-$$

B. COMPOSITION OF LP1845

$$7\ NH_3OHNO_3 + (C_2H_4OH)_3NHNO_3 + 10\ H_2O =$$

$$32\ H_2O + 6\ CO_2 + 8\ N_2$$

CONCENTRATION BY WEIGHT :

63.2% HAN

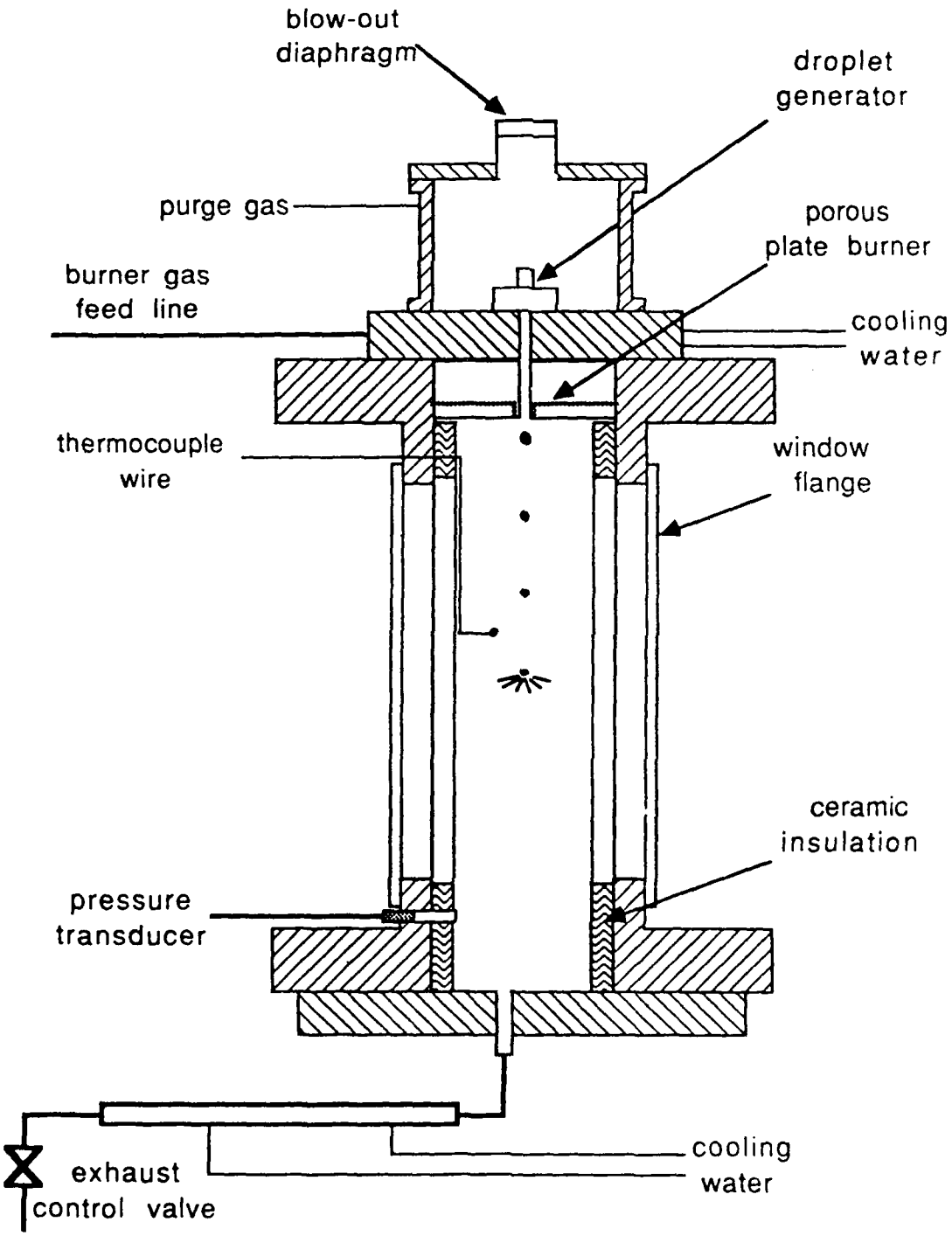
20.0% TEAN

16.8% WATER

C. ADIABATIC FLAME TEMPERATURE

$T_{ad} = 2285$ K

3. COMBUSTION CHAMBER



2. OBJECTIVE

A. EXPERIMENTALLY DETERMINE:

1. GASIFICATION RATES
2. MICROEXPLOSION DIAMETERS

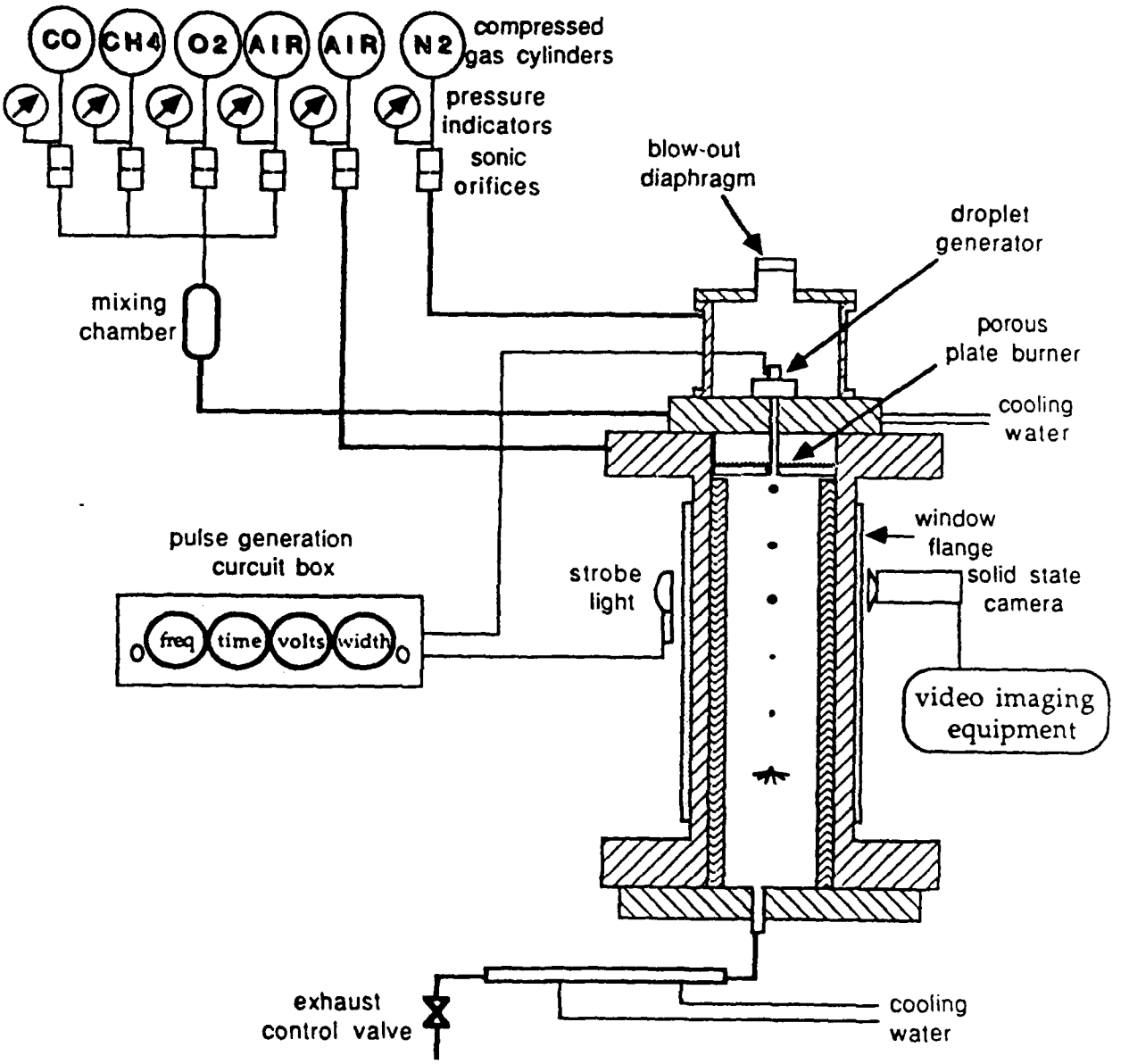
AS A FUNCTION OF THE EXPERIMENTAL PARAMETERS:

1. AMBIENT PRESSURE
2. AMBIENT TEMPERATURE
3. INITIAL DROPLET SIZE
4. LP WATER CONTENT

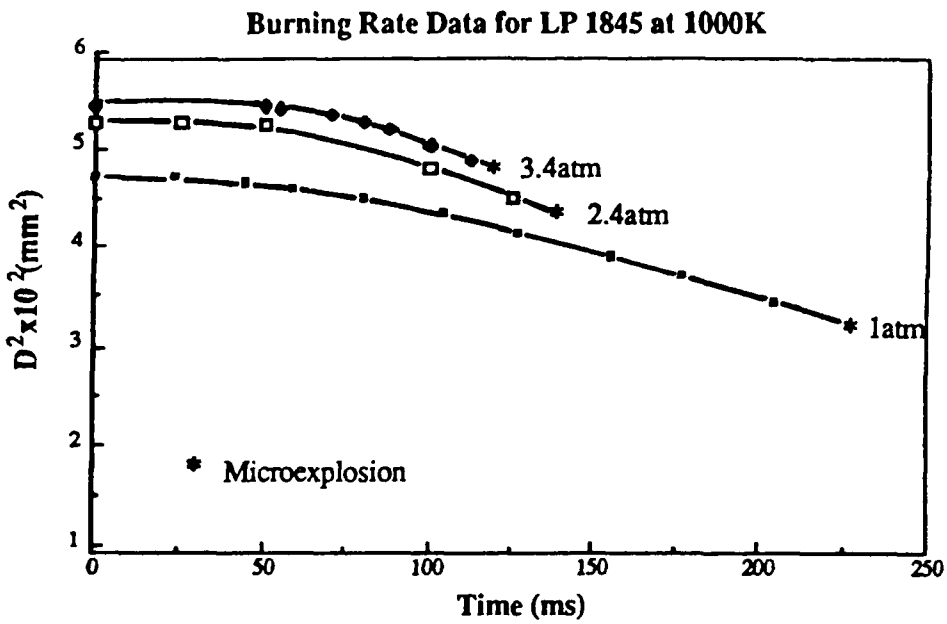
B. AMBIENT PRESSURE IS OF PARTICULAR INTEREST:

1. HIGH PRESSURE WITHIN GUN CHAMBER
2. INCREASING PRESSURE INCREASES DROPLET TEMPERATURE, AND THUS LIQUID-PHASE REACTION RATES

ELEVATED PRESSURE DROPLET COMBUSTION APPARATUS



4. RESULTS: GASIFICATION RATES



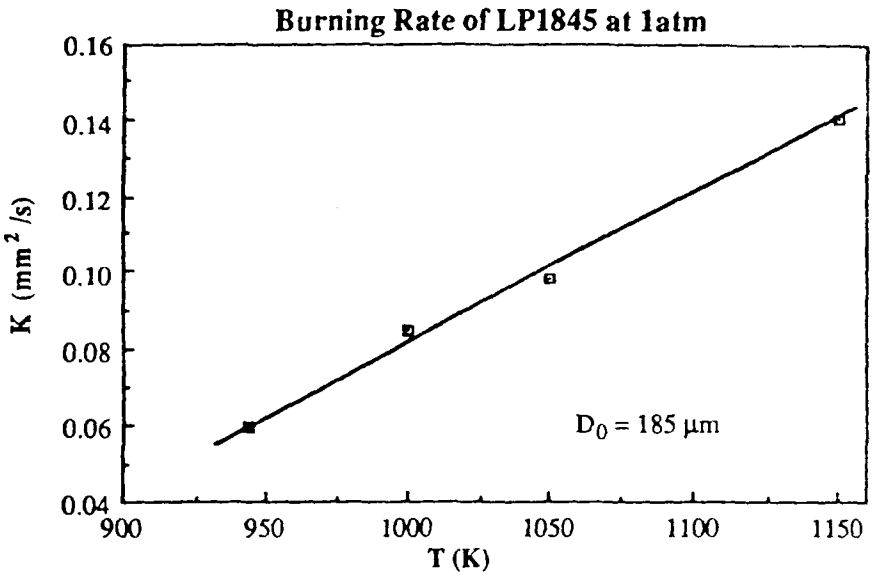
A. CLASSICAL DROPLET GASIFICATION THEORY PREDICTS LINEAR D^2 VS. TIME BEHAVIOR

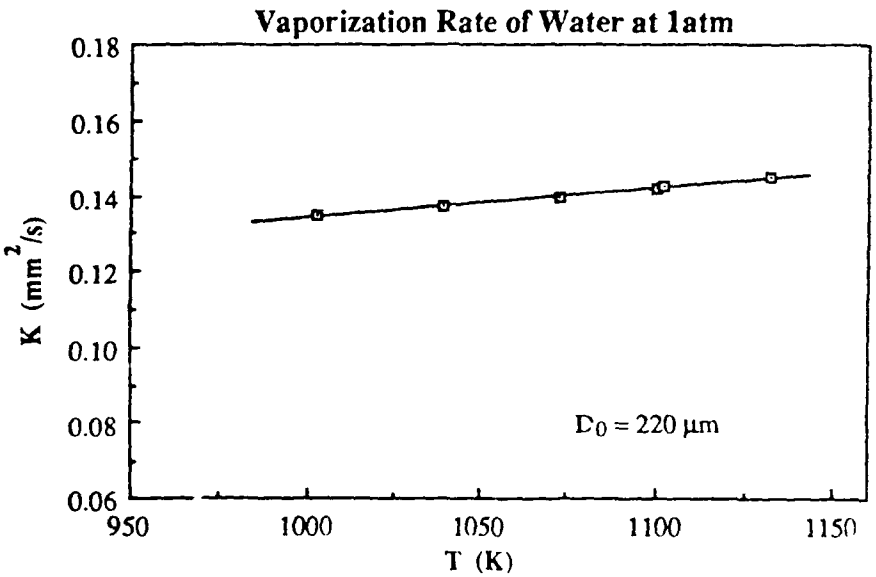
B. QUALITATIVE OBSERVATIONS

1. SLIGHTLY NON-LINEAR GASIFICATION RATE
2. DROPLETS MICROEXPLODE
3. NO "FLAME" OBSERVED

C. GASIFICATION OR BURNING RATE CONSTANT DEFINED AS NEGITIVE SLOPE OF (APPROXIMATELY) LINEAR SEGMENT

4. Gasification Rates

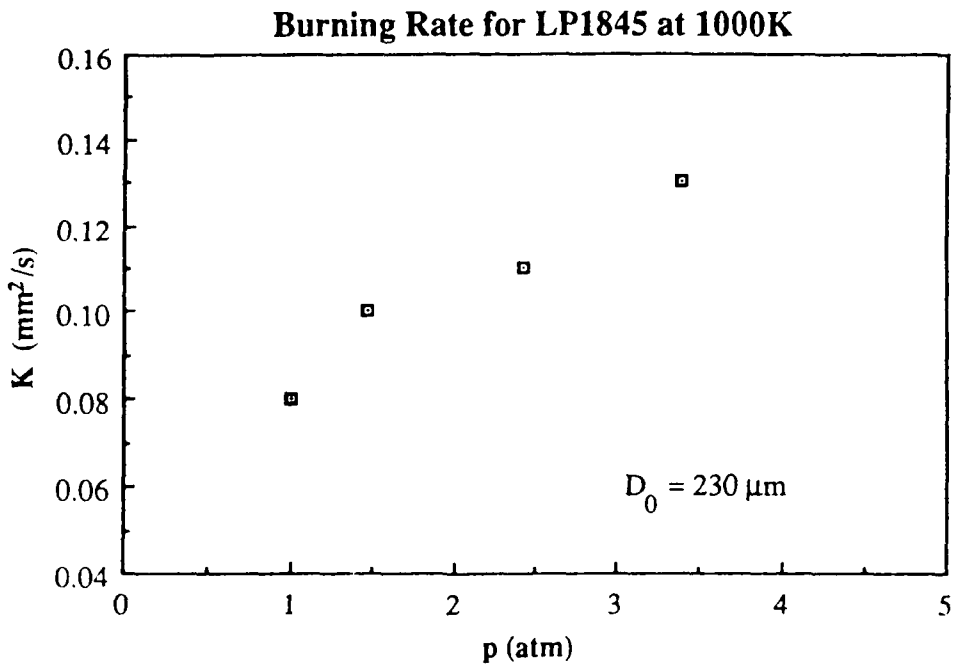




A. BURNING RATE INCREASES WITH AMBIENT TEMPERATURE

B. GREATER DRIVING FORCE FOR HEAT TRANSFER

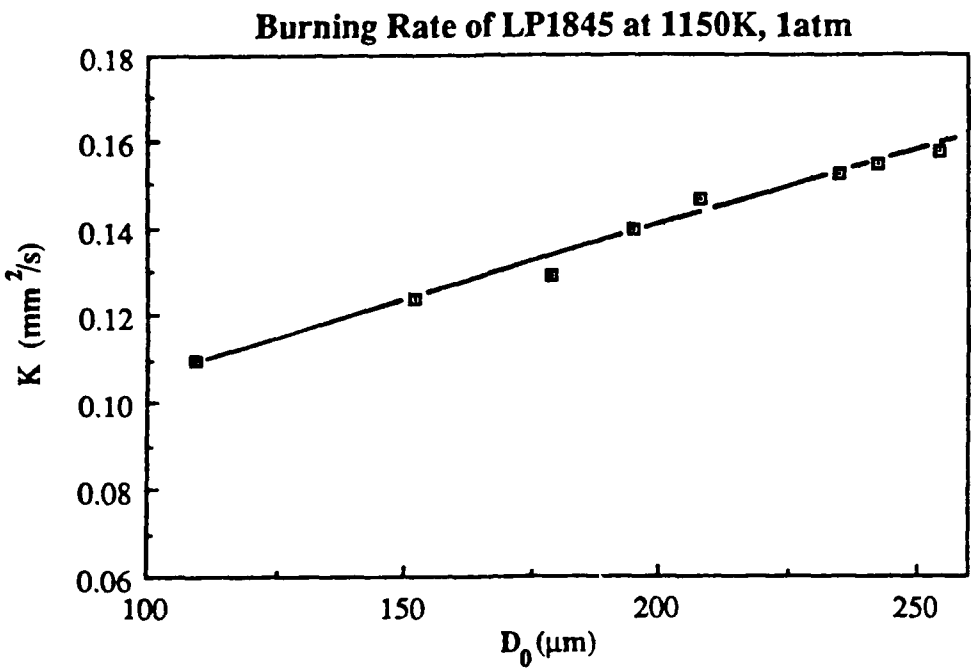
C. INCREASE IN K FOR PURE WATER IS WEAKER



BURNING RATE INCREASES WITH PRESSURE DUE TO :

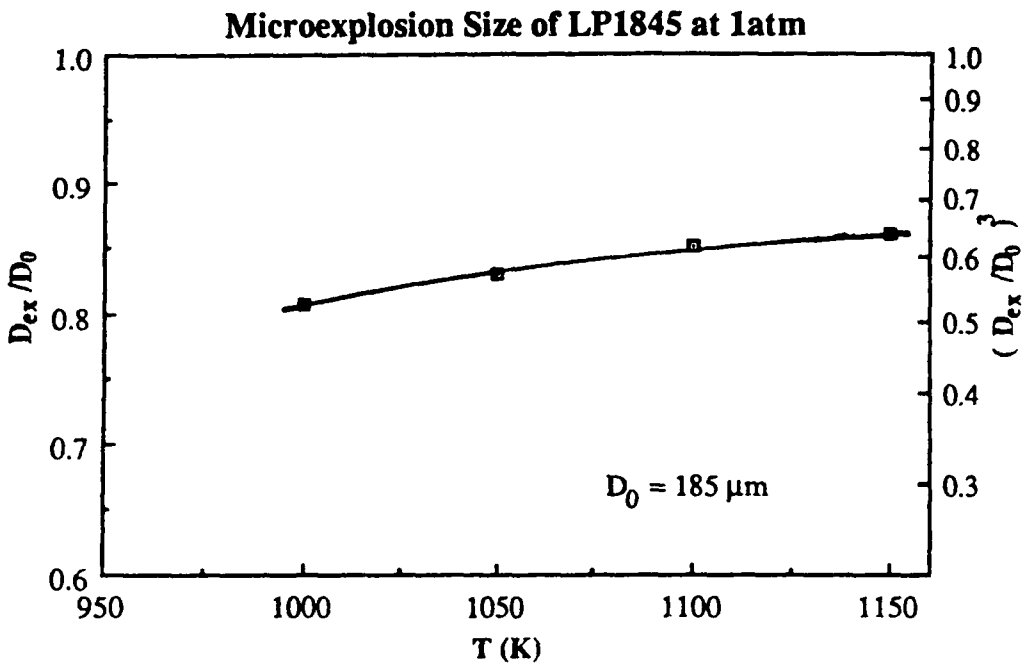
1. BOILING POINT RISES WITH PRESSURE.

2. CHEMICAL REACTIVITY INCREASES WITH INCREASING PRESSURE.



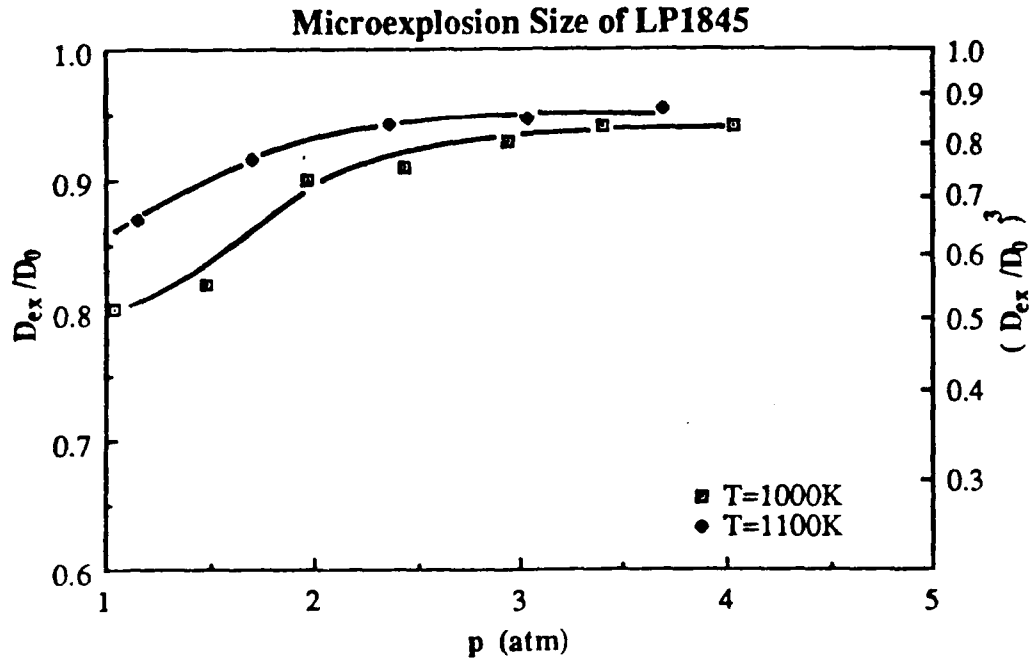
A. HEAT GENERATION DUE TO CHEMICAL REACTION IS A VOLUMETRIC EFFECT.

B. SINCE HEAT EXPENDITURE THROUGH VAPORIZATION IS A SURFACE EFFECT, K SHOULD DEPEND ON D_0.



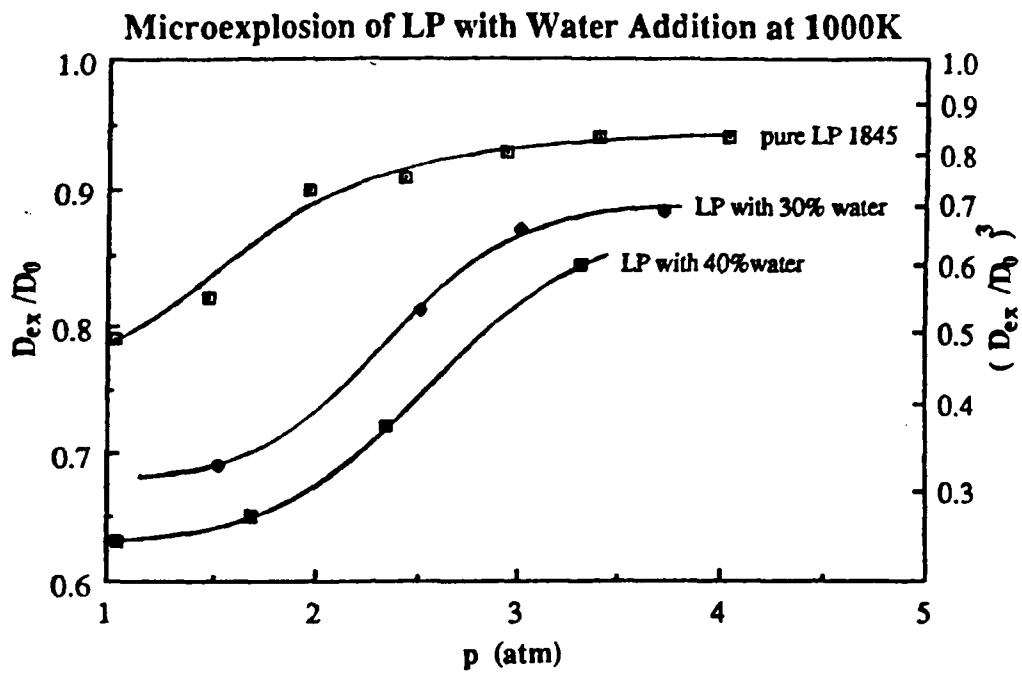
A. THE MICROEXPLOSION DIAMETER IS NORMALIZED BY THE INITIAL DIAMETER.

B. DIAMETER AT MICROEXPLOSION INCREASES WITH AMBIENT TEMPERATURE.



A. MICROEXPLOSION IS ADVANCED WITH INCREASING PRESSURE.

B. LOWER AMBIENT TEMPERATURE DELAYS DROPLET MICROEXPLOSION



A. AS LP WATER CONTENT IS INCREASED, BOILING POINT IS LOWERED.

B. CHEMICAL REACTIVITY IS DECREASED.

C. MORE WATER NEEDS TO BE DEPLETED FOR THE SALT TO BE SUFFICIENTLY CONCENTRATED TO INDUCE MICROEXPLOSION.

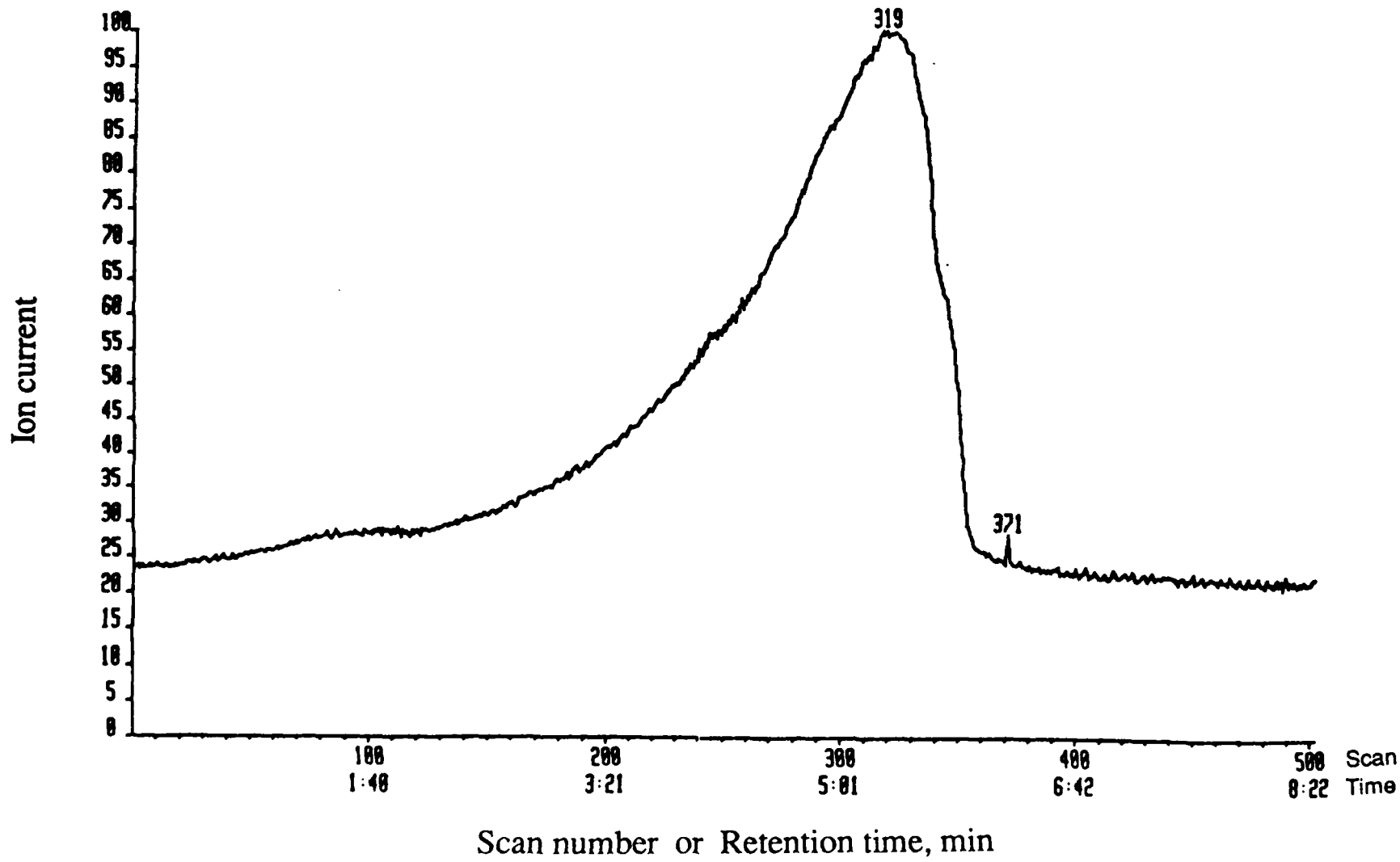
D. MICROEXPLOSION IS DELAYED.

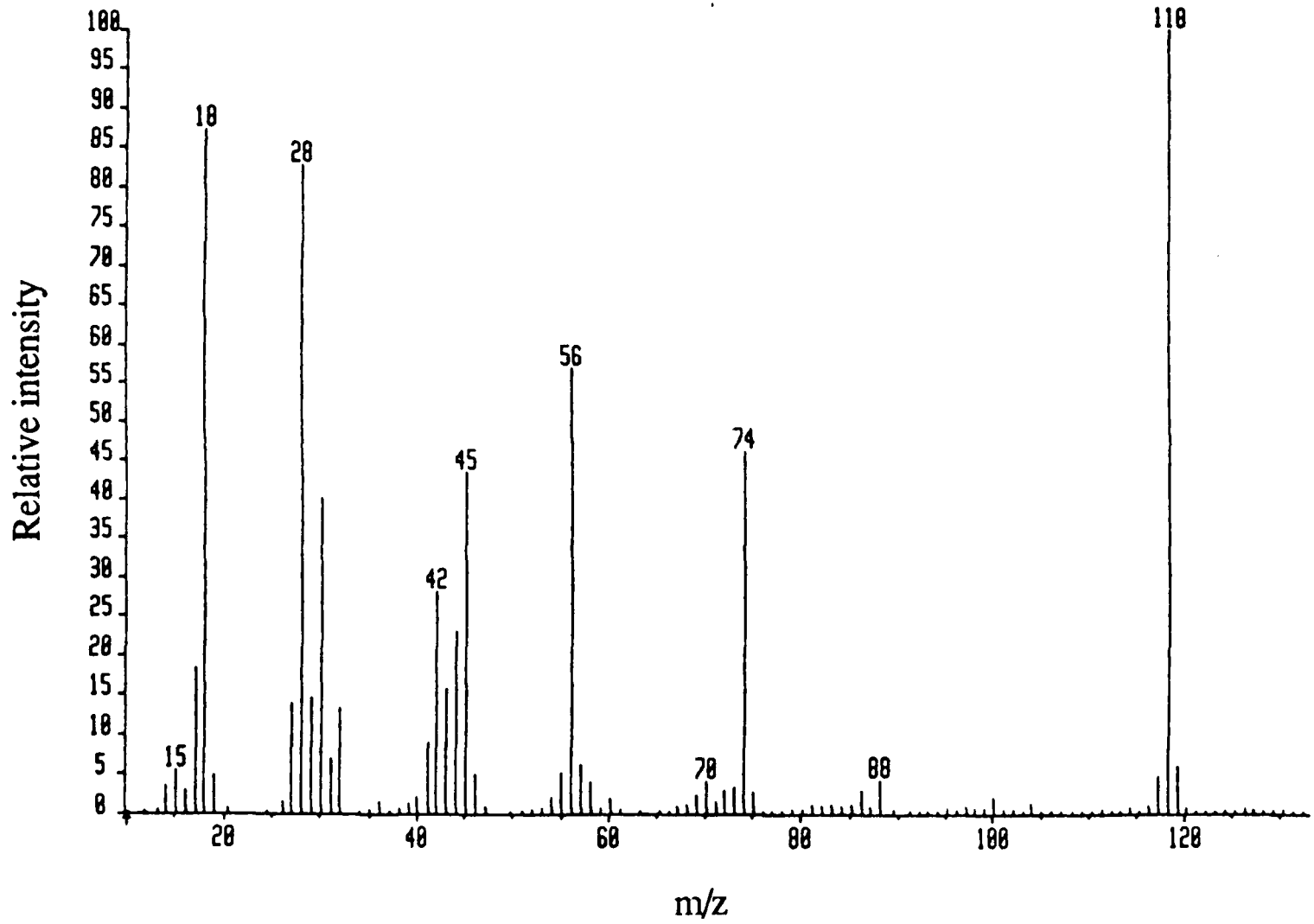
POSSIBLE CAUSES OF MICROEXPLOSION:

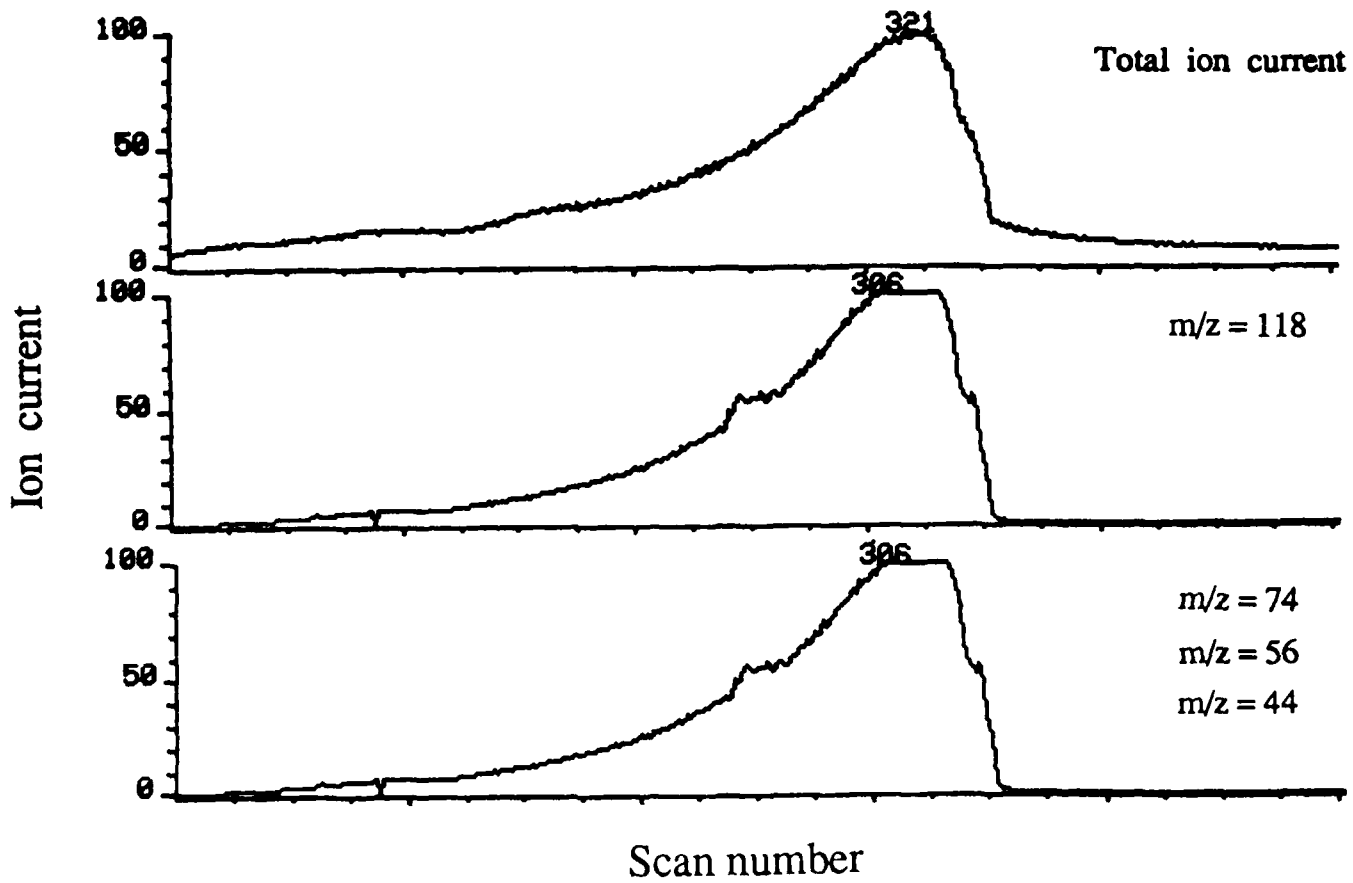
A. GAS EVOLUTION FROM LIQUID-PHASE REACTION.

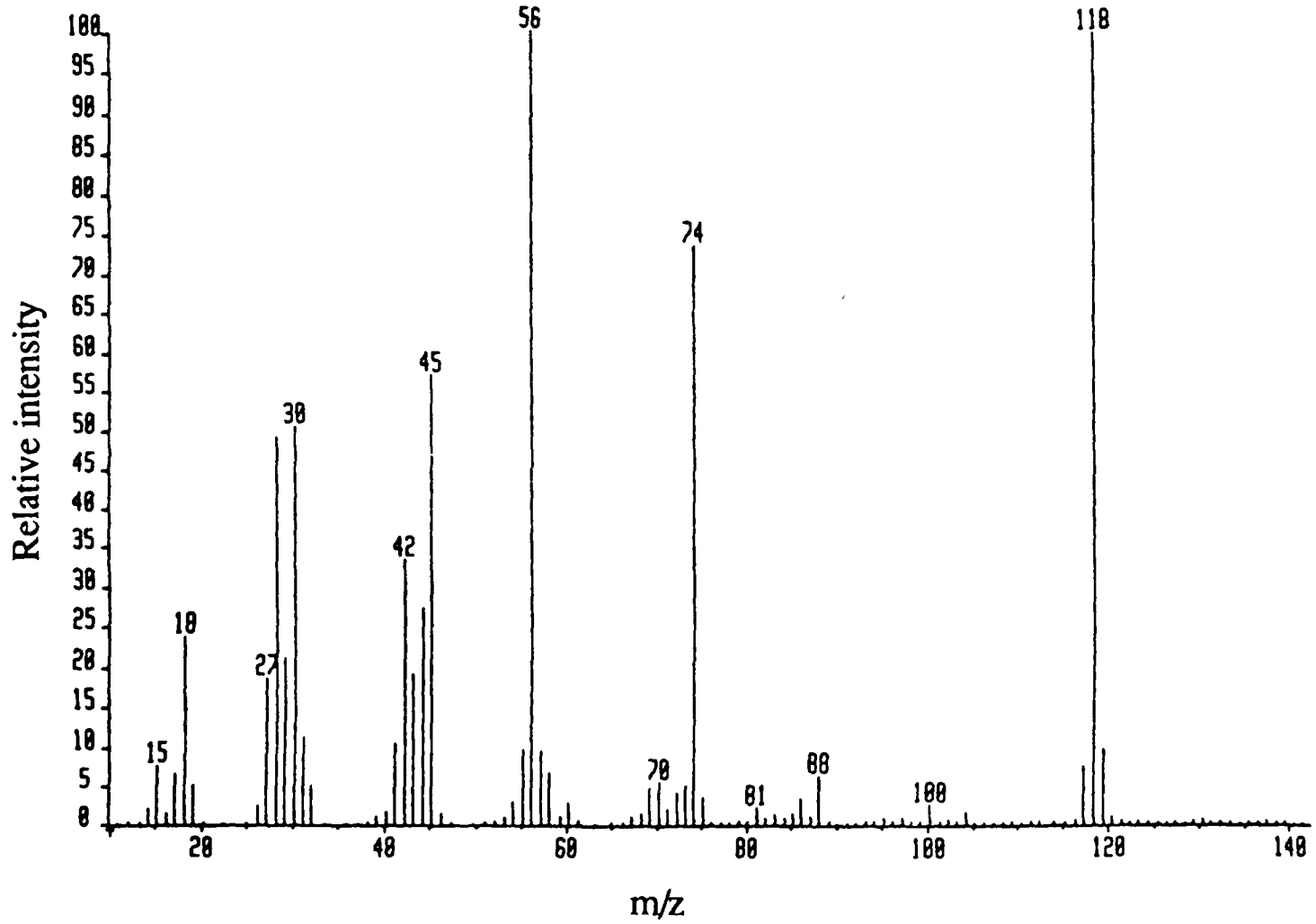
B. INTERNAL HEATING FROM CHEMICAL REACTION PAST THE LIMIT OF SUPERHEAT.

C. INTENSIFIED SURFACE REACTION DUE TO THE HIGH SALT CONCENTRATION (AT SURFACE).


Ion current
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
319
371
100
1:40
200
3:21
300
5:01
400
6:42
500
8:22
Scan
Time
Scan number or Retention time, min


Relative intensity
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
18
28
42
45
56
74
15
70
88
110
20
40
60
80
100
120
m/z

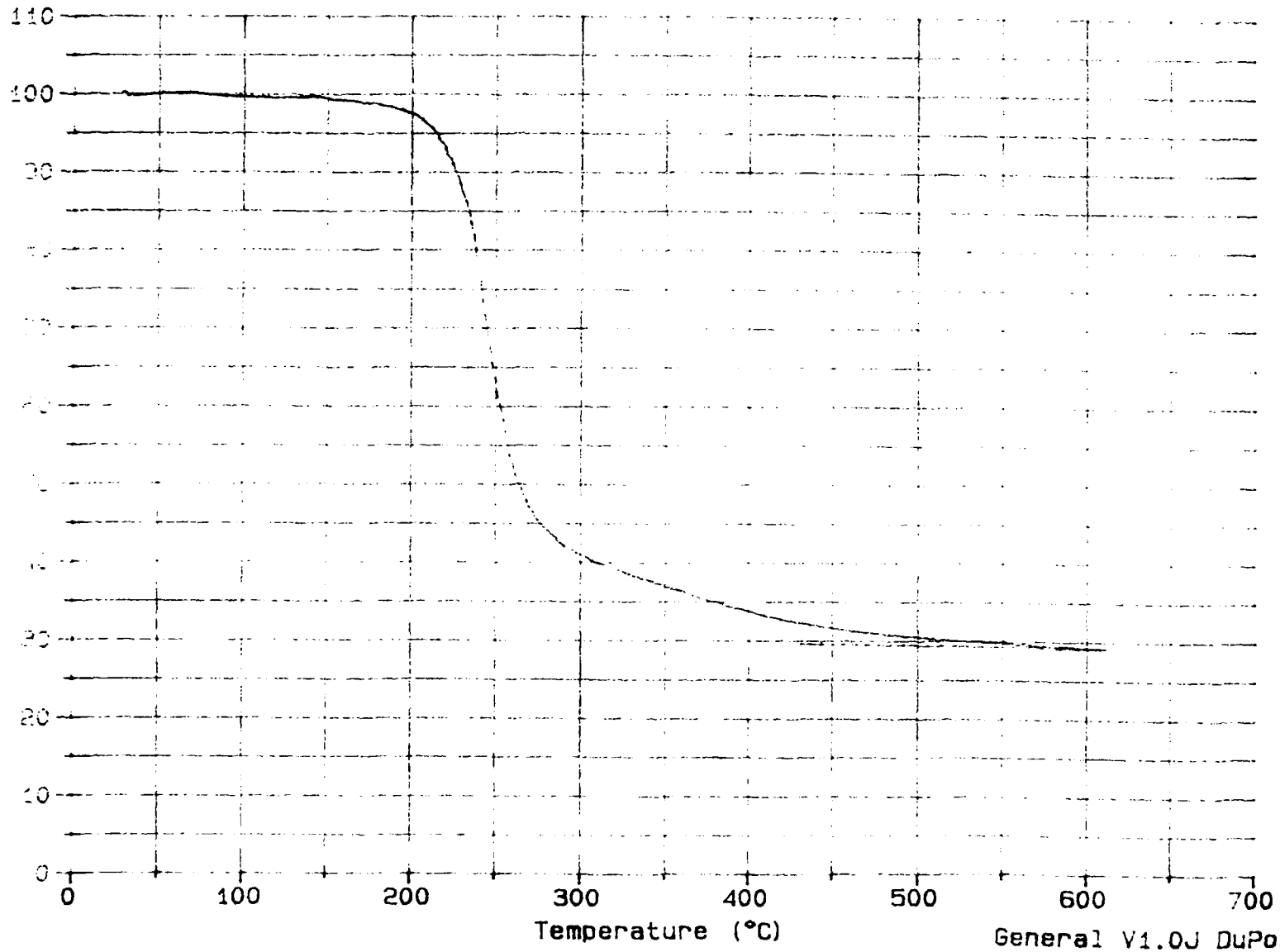

100
50
0
321
Total ion current
100
50
0
306
m/z = 118
100
50
0
306
m/z = 74
m/z = 56
m/z = 44
Ion current
Scan number


Relative intensity
m/z
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
20
40
60
80
100
120
140
15
18
27
30
42
45
56
70
74
81
88
100
118

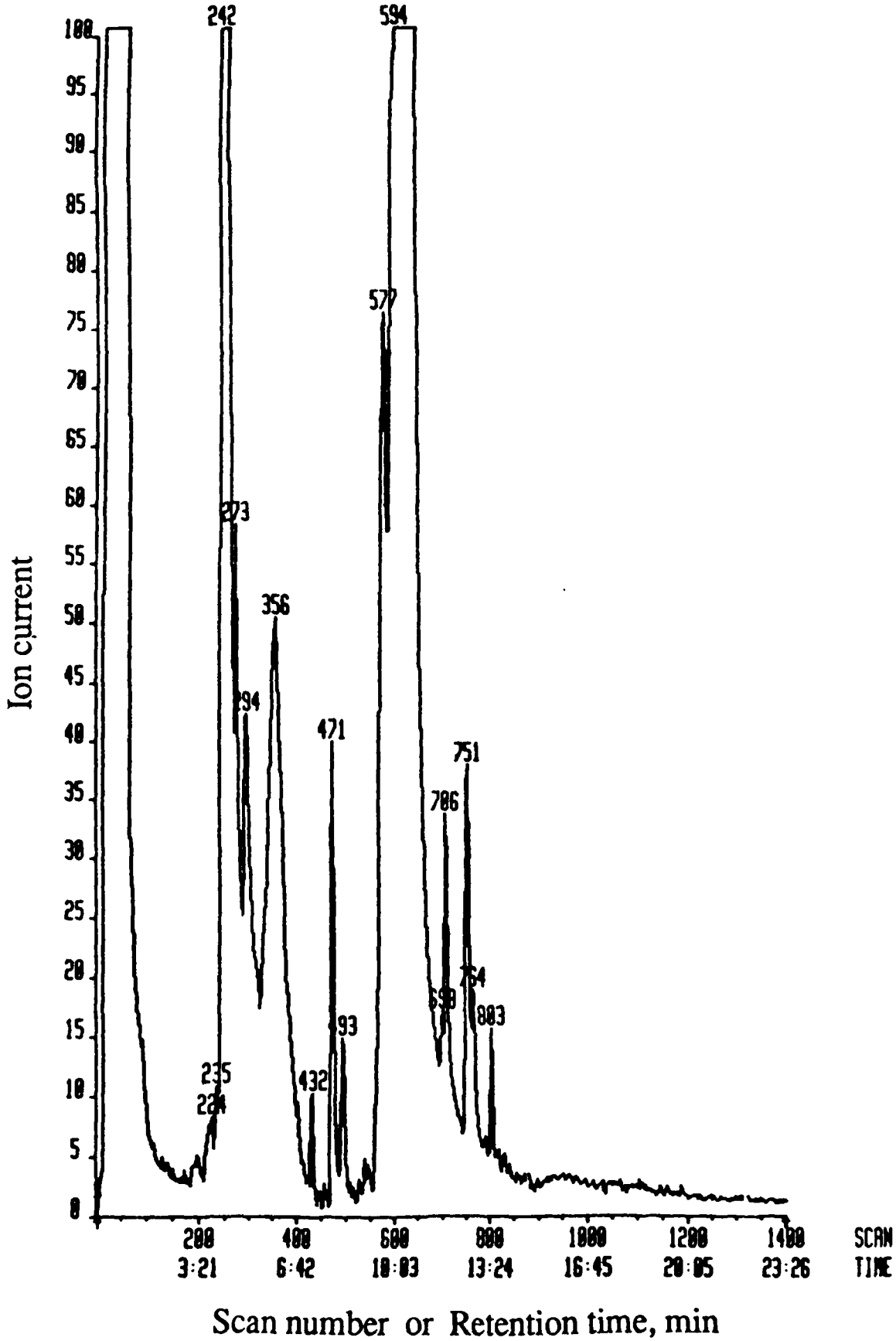
Sample: TEAN IN ARGON
Size: 11.40 mg
Method: PROP
Comment: RAMP 10°C/MIN TO 600°C

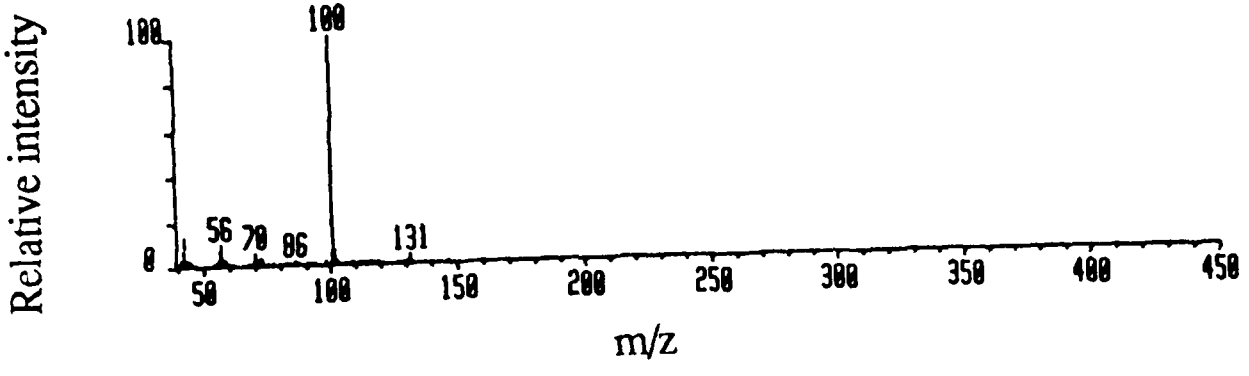
TGA

File: LP.03
Operator: DEEVI
Run date: 03/07/87 16:48



General V1.0J DuPont 9900


Ion current
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
242
594
577
273
356
294
471
751
706
754
883
93
235
224
432
200
3:21
400
6:42
600
10:03
800
13:24
1000
16:45
1200
20:05
1400
23:26
SCAN
TIME
Scan number or Retention time, min

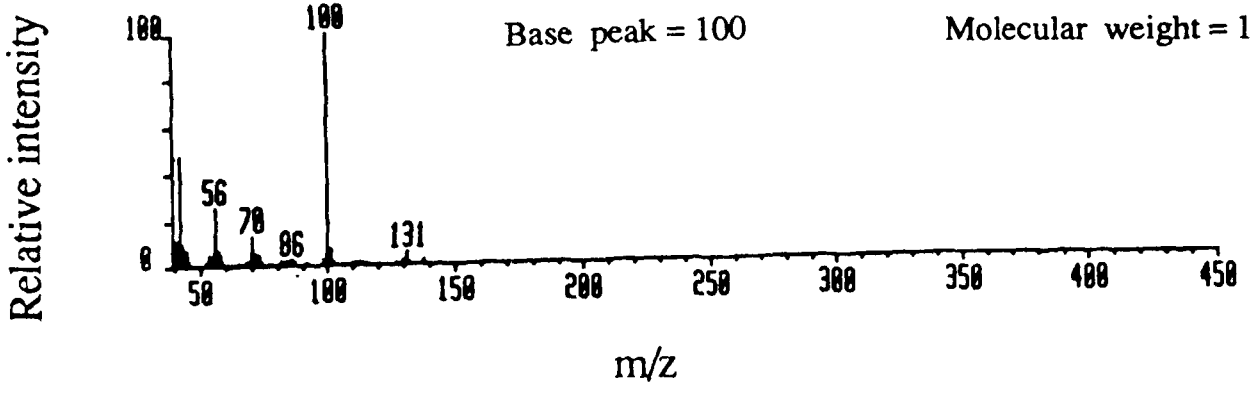


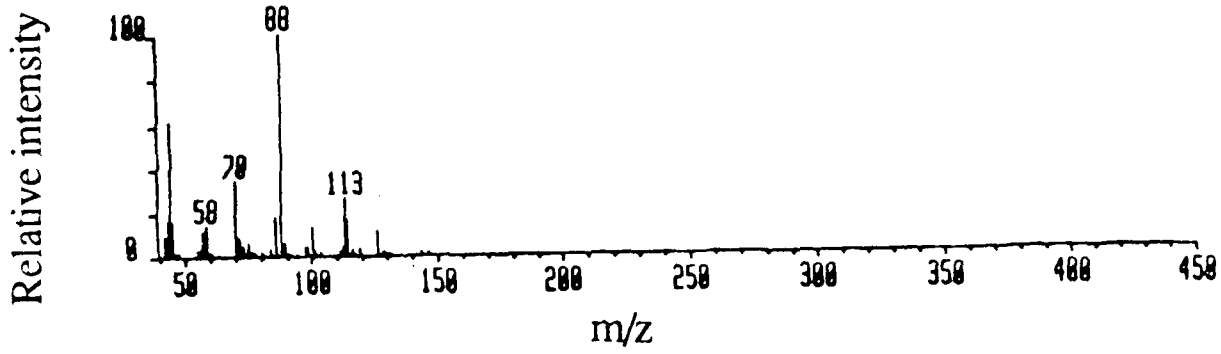
4 - Morpholine ethanol

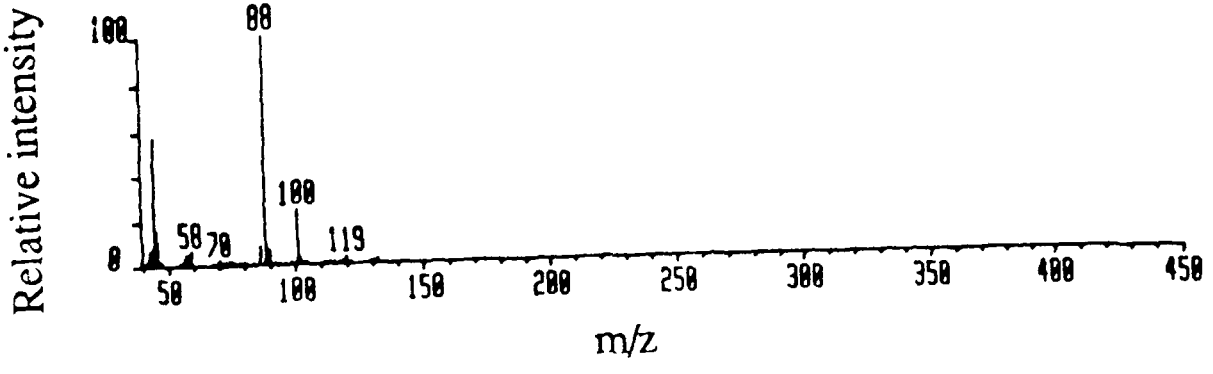
Base peak = 100

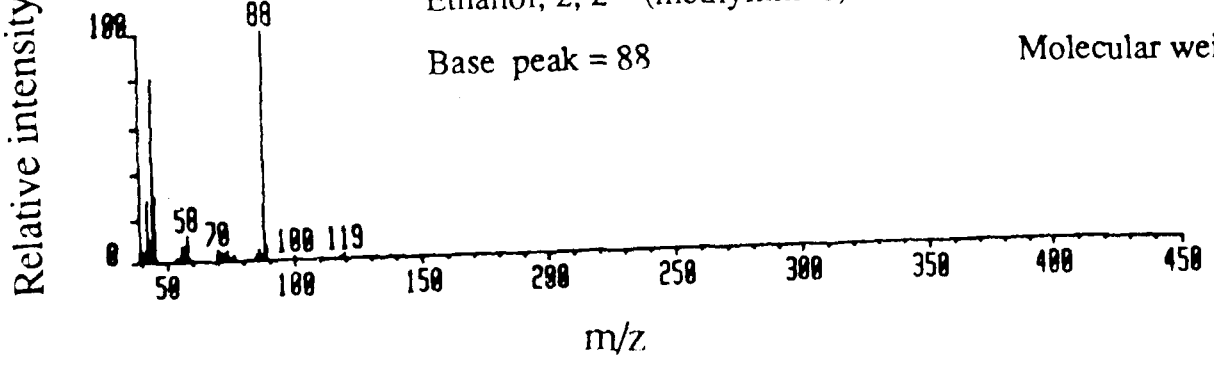
Molecular formula = $C_6H_{13}NO_2$

Molecular weight = 131




Relative intensity
100
0
88
70
58
113
50
100
150
200
250
300
350
400
450
m/z



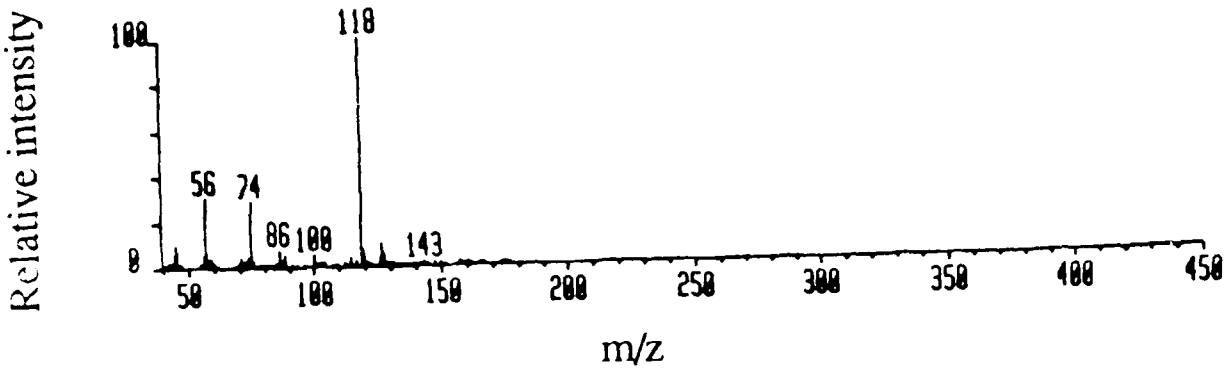


Ethanol, 2, 2' - (methylimino) bis -

Base peak = 88

Molecular formula = $C_5H_{13}NO_2$

Molecular weight = 119

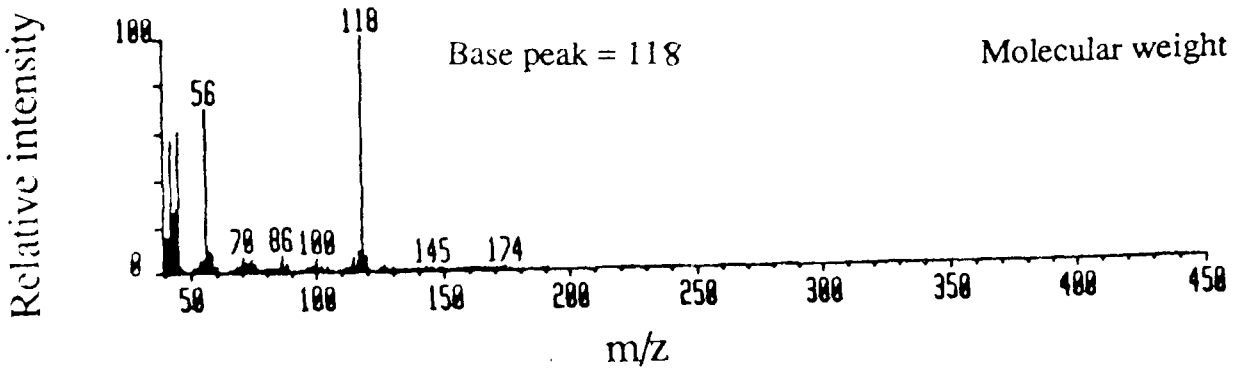


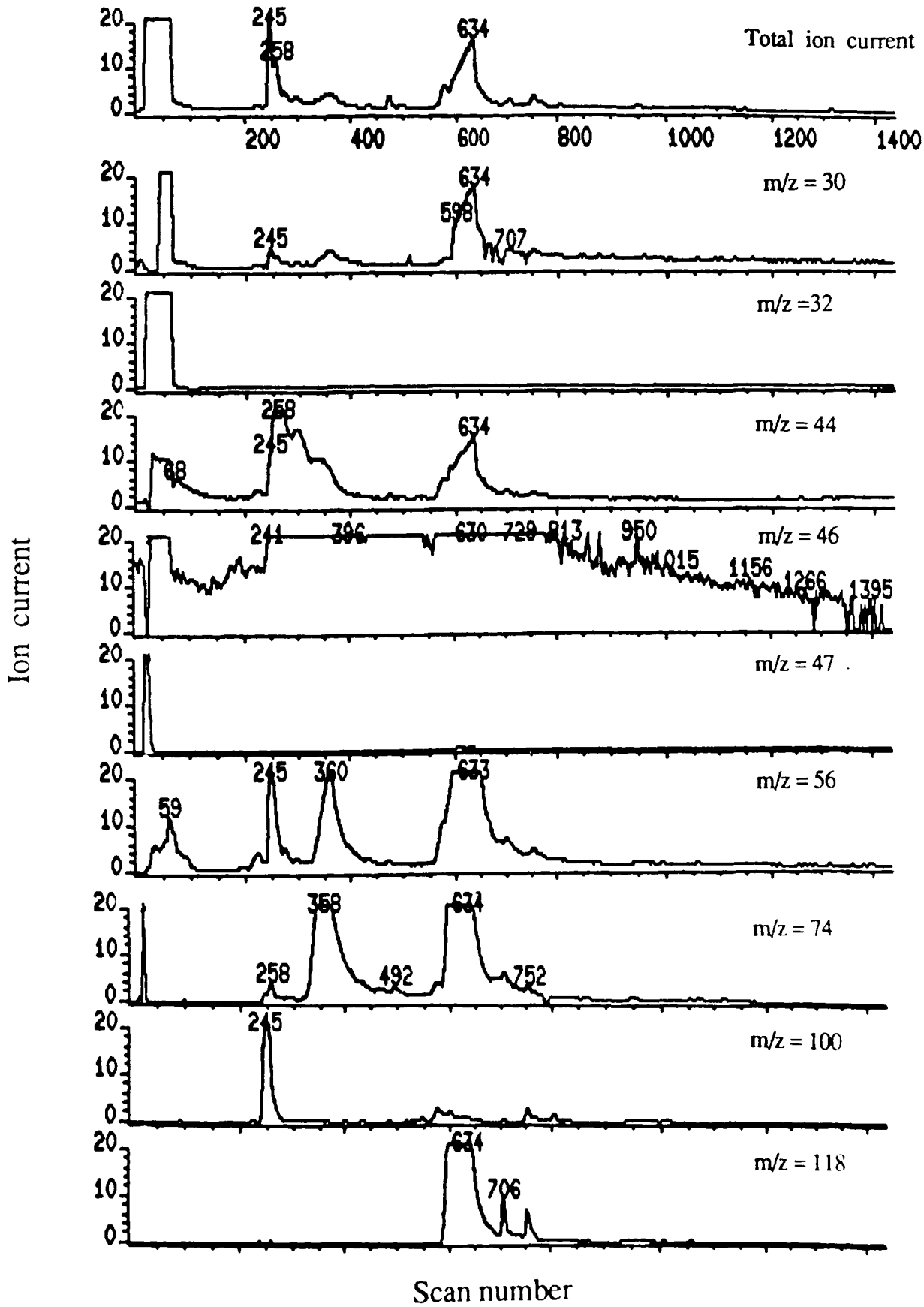
Ethanol 2, 2', 2" - nitrilotris -

Base peak = 118

Molecular formula = $C_6H_{15}NO_3$

Molecular weight = 149




Total ion current
m/z = 30
m/z =32
m/z = 44
m/z = 46
m/z = 47
m/z = 56
m/z = 74
m/z = 100
m/z = 118
Ion current
Scan number

5. CONCLUDING REMARKS

A. BURNING RATE AND MICROEXPLOSION SIZE INCREASE WITH

1. INCREASE OF AMBIENT PRESSURE
2. INCREASE OF AMBIENT TEMPERATURE

B. LIQUID PHASE REACTIONS CAN BE IMPORTANT

C. EXTENSION OF PRESENT UNDERSTANDING TO ULTRA-HIGH PRESSURE COMBUSTION REQUIRES FURTHER STUDY.

RAMAN SPECTROSCOPY OF NITRATE SALT SOLUTIONS UP TO 500°C AND 35MPA

Thomas B. Brill and Peter D. Spohn

University of Delaware
Department of Chemistry
Newark, DE 19716
(302) 451-6079

By using a cell described in earlier LP conferences, the Raman spectra of $Ca(NO_3)_2$, $Zn(NO_3)_2$, $NaNO_3$, and $LiNO_3$ solutions in water were recorded up to 500°C and 35MPa. Because of the increased linewidths at high temperature, the interpretation of the spectral changes is non-trivial. Multicomponent analysis using a simplex routine combined with Fourier transformation to establish the number of species present appears to give the most reliable curve resolution. Density measurements at high pressure and temperature were also useful in interpreting the spectral changes witnessed. The behavior of the ion-water and ion-ion interactions can be established from these studies.

CHARACTERIZATION OF AQUEOUS NITRATE SALT SOLUTIONS AT ELEVATED TEMPERATURES AND PRESSURES USING RAMAN AND INFRARED SPECTROSCOPY

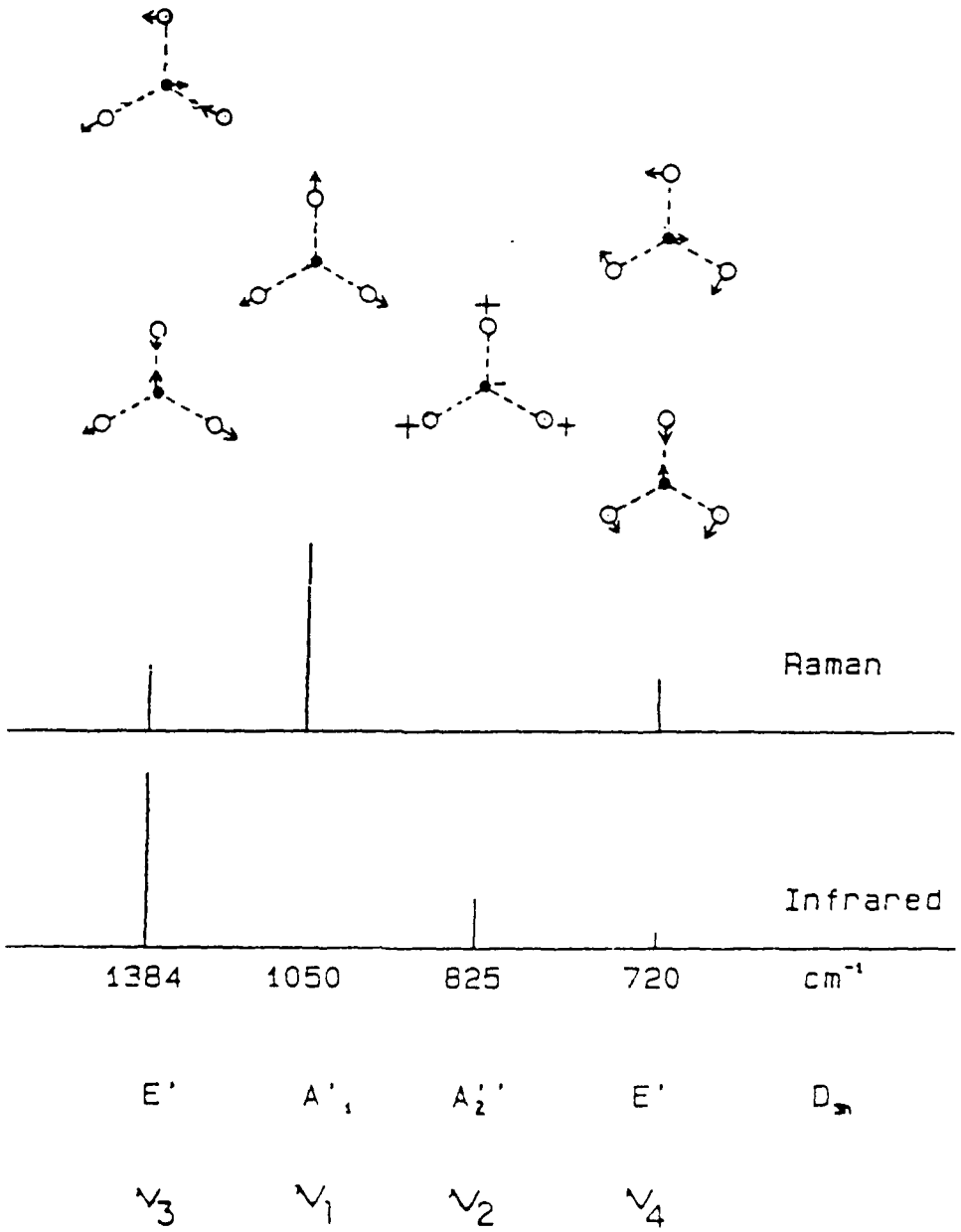
P. D. Spohn

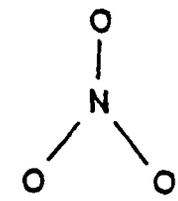
OBJECTIVES:

1) Gain an understanding of how the nitrate ion is incorporated into the coordination sphere of cations in aqueous solutions at elevated temperatures.

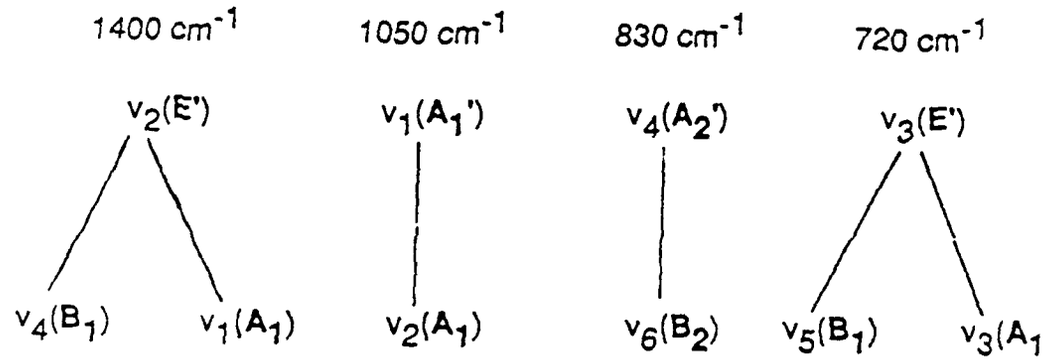
2) Determine the changes in the nature of the anion with different cations as temperature is varied.

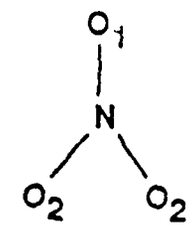
3) Determine the number, nature, and relative concentrations of nitrate species present at elevated temperatures.


Raman
Infrared
1384
1050
825
720
cm⁻¹
E'
A'₁
A''₂
E'
D₃ₕ
ν3
ν1
ν2
ν4

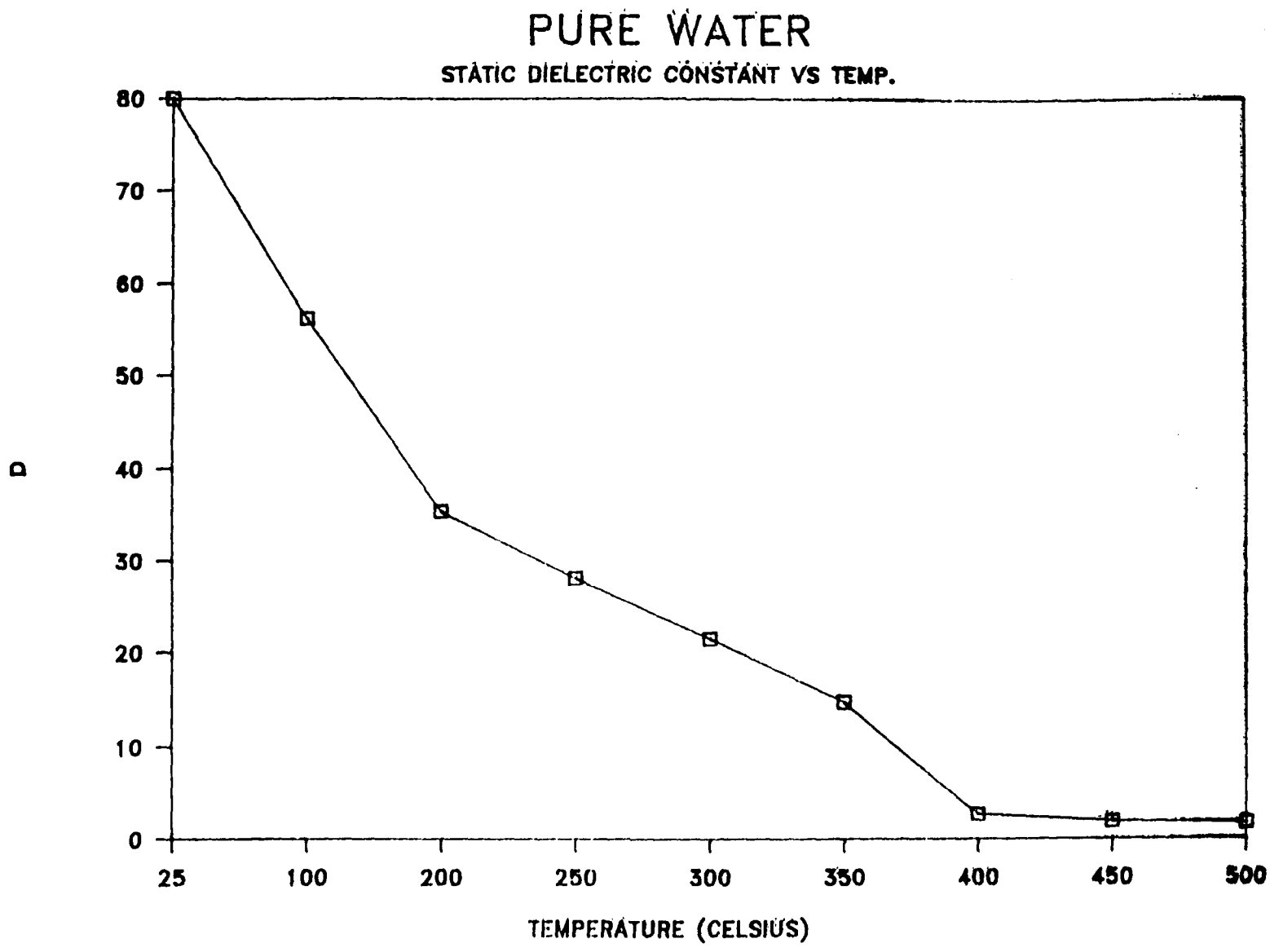

O
N
O
O

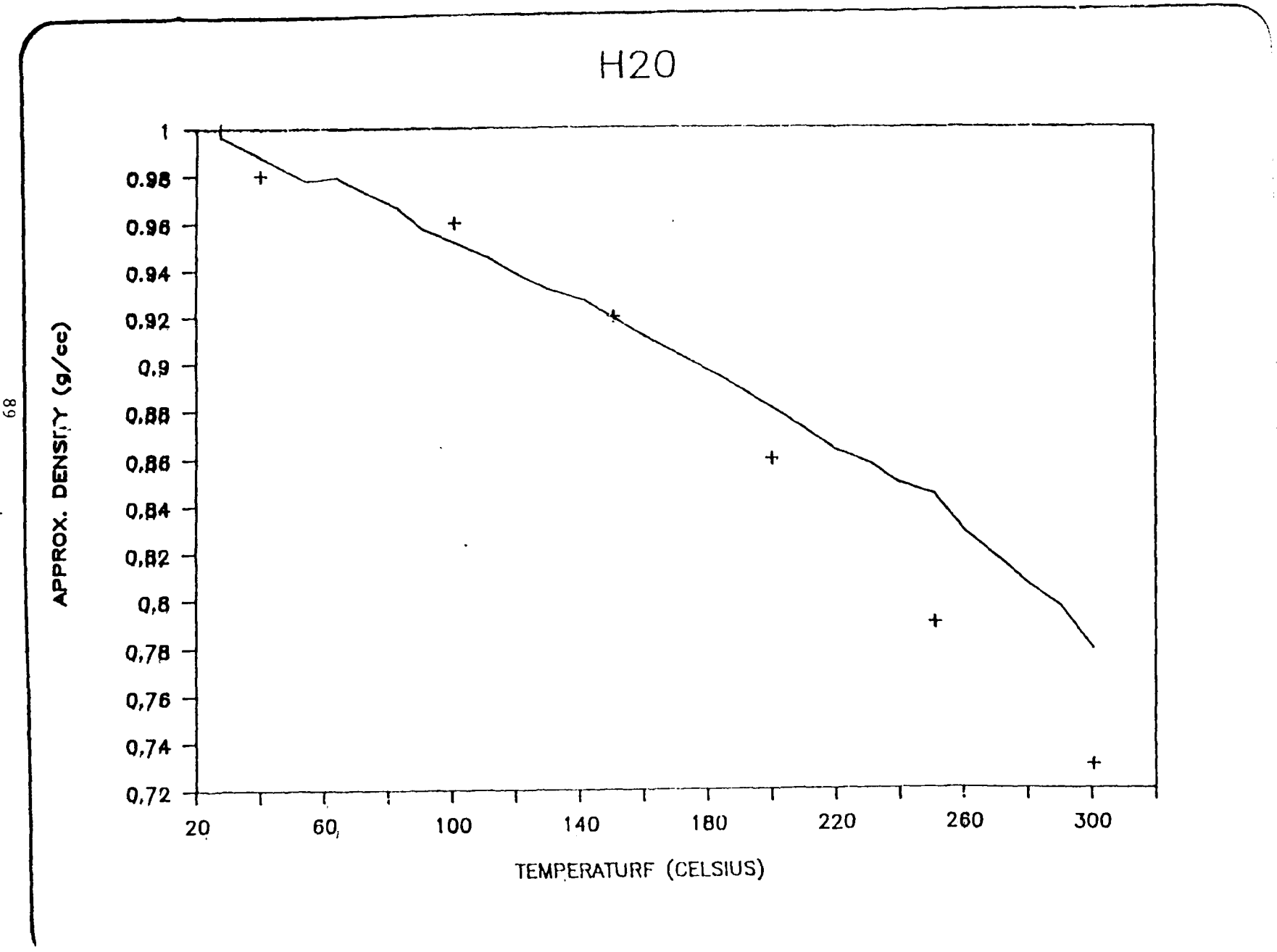
(D_{3h})

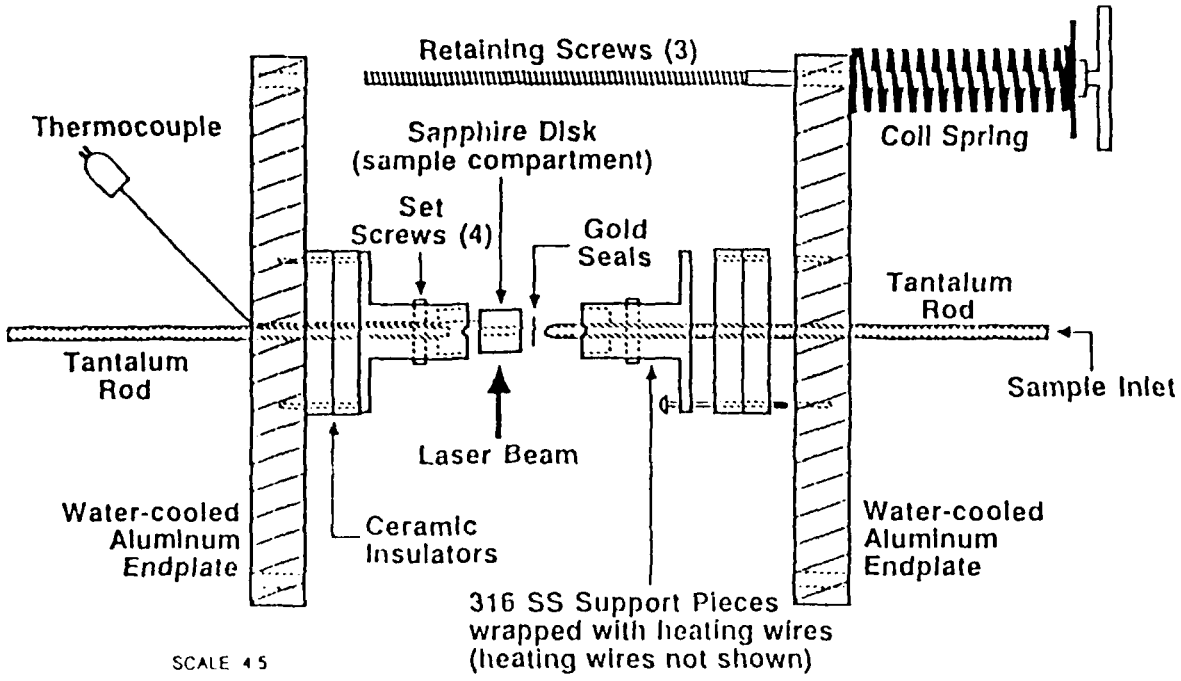

1400 cm-1
1050 cm-1
830 cm-1
720 cm-1
v2(E')
v1(A1')
v4(A2')
v3(E')
v4(B1)
v1(A1)
v2(A1)
v6(B2)
v5(B1)
v3(A1)

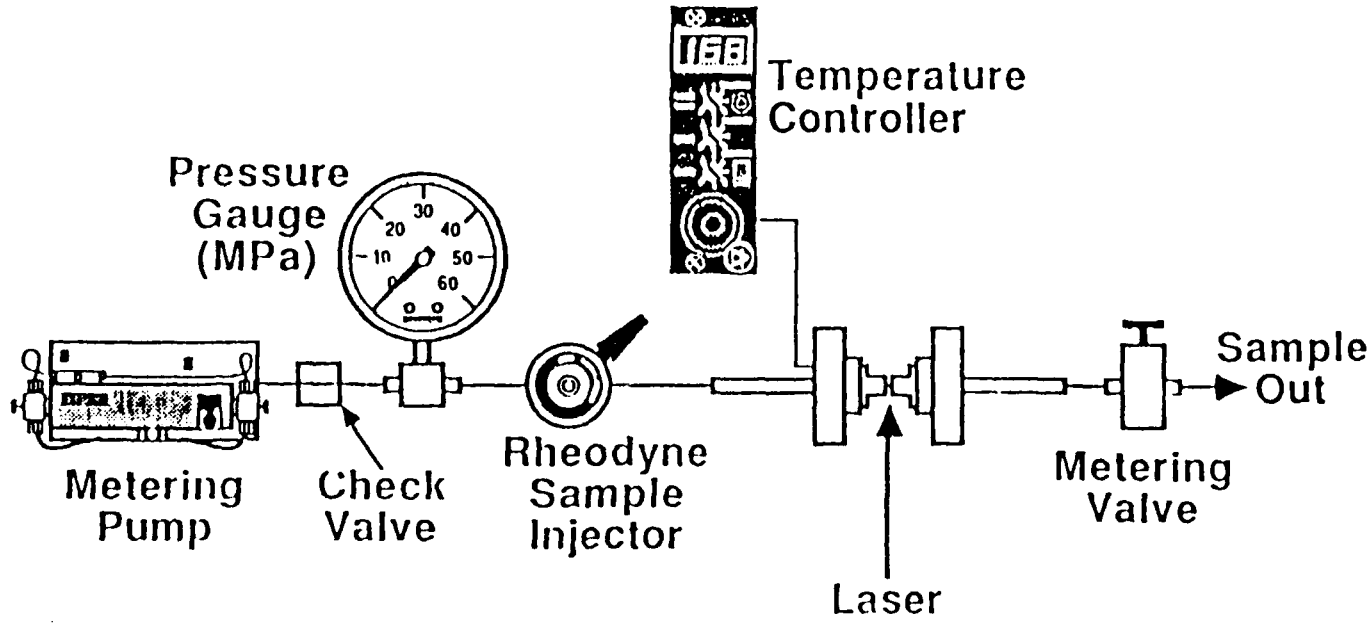

O1
N
O2
O2

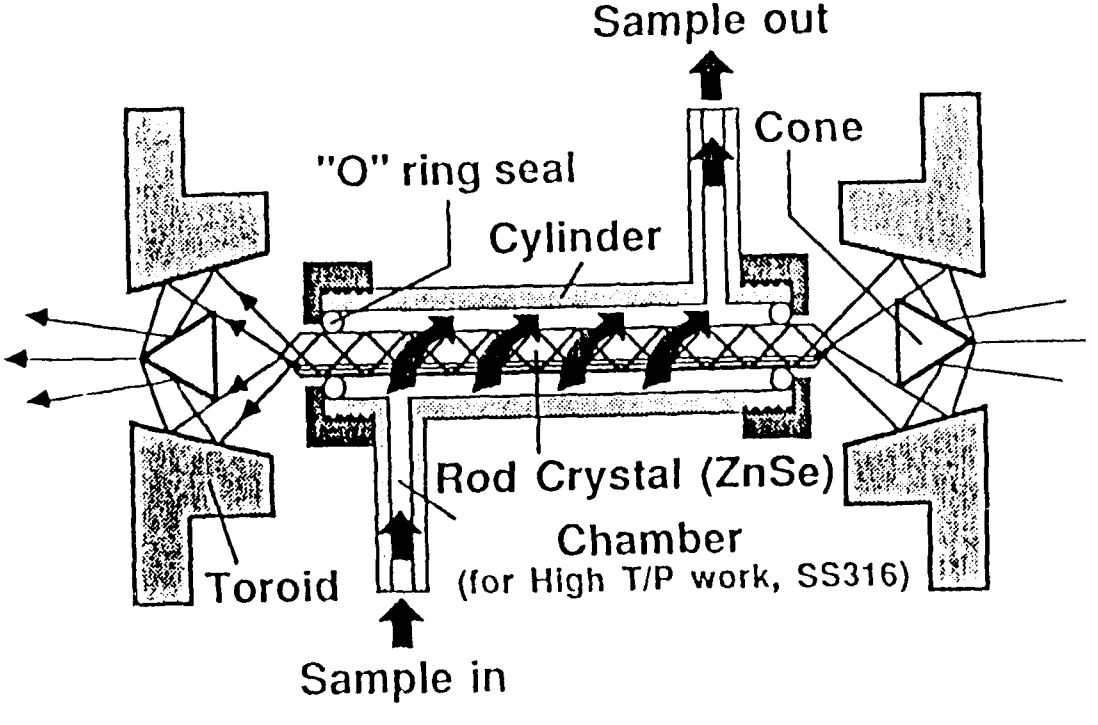
(C_{2v})

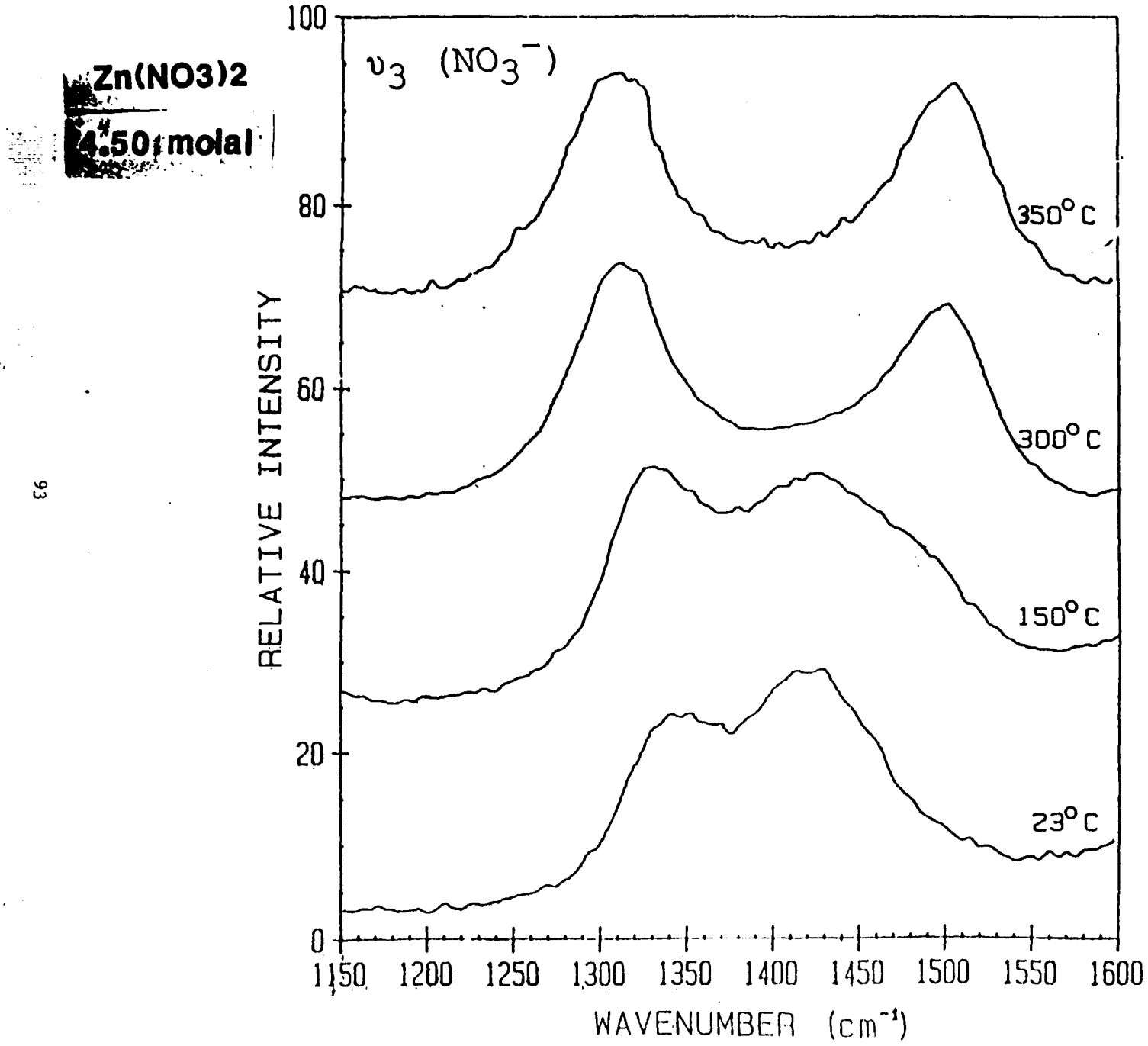

PURE WATER
STATIC DIELECTRIC CONSTANT VS TEMP.
D
80
70
60
50
40
30
20
10
0
25
100
200
250
300
350
400
450
500
TEMPERATURE (CELSIUS)

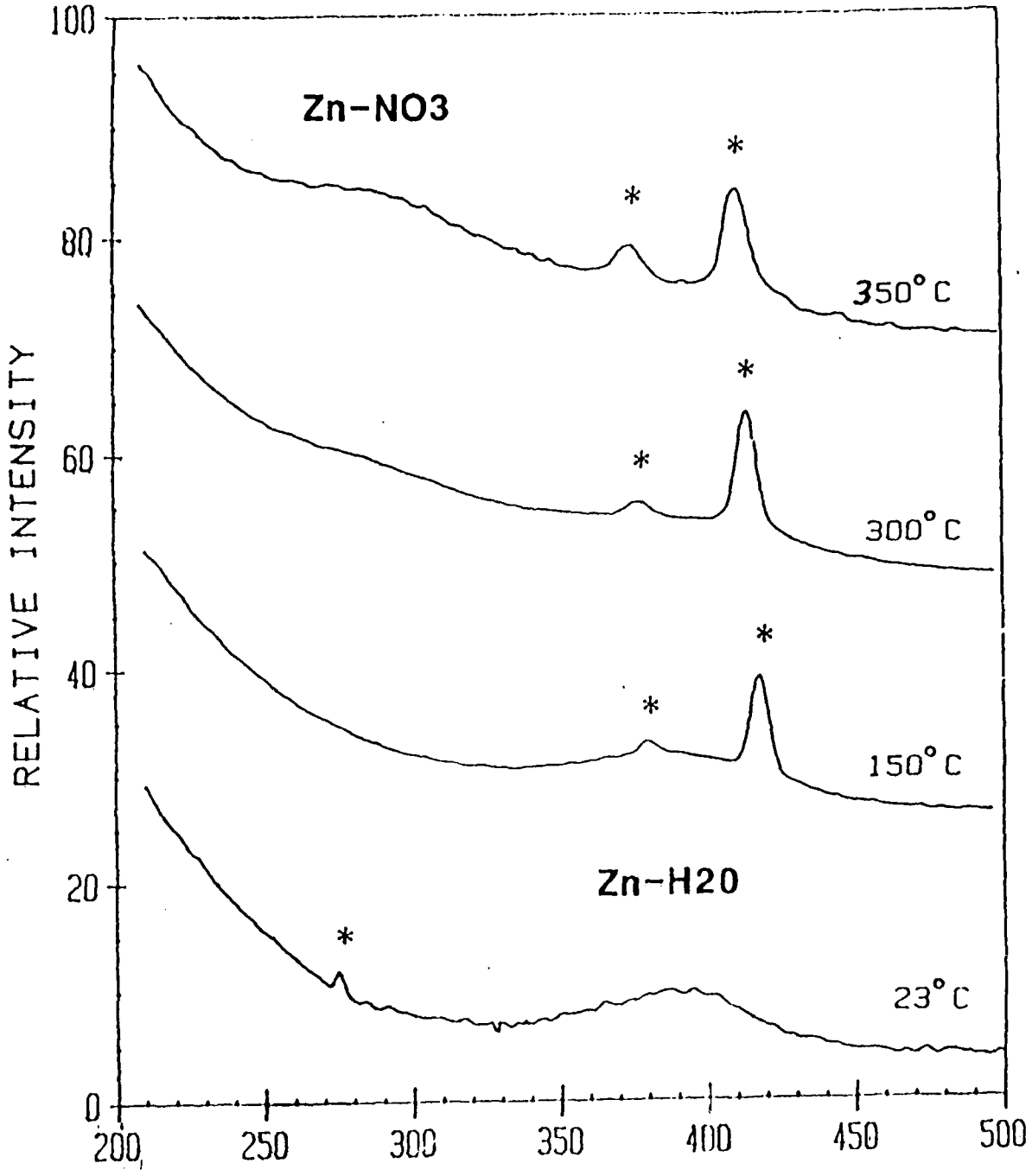

H20
APPROX. DENSITY (g/cc)
1
0.98
0.96
0.94
0.92
0.9
0.88
0.86
0.84
0.82
0.8
0.78
0.76
0.74
0.72
20
60
100
140
180
220
260
300
TEMPERATURE (CELSIUS)

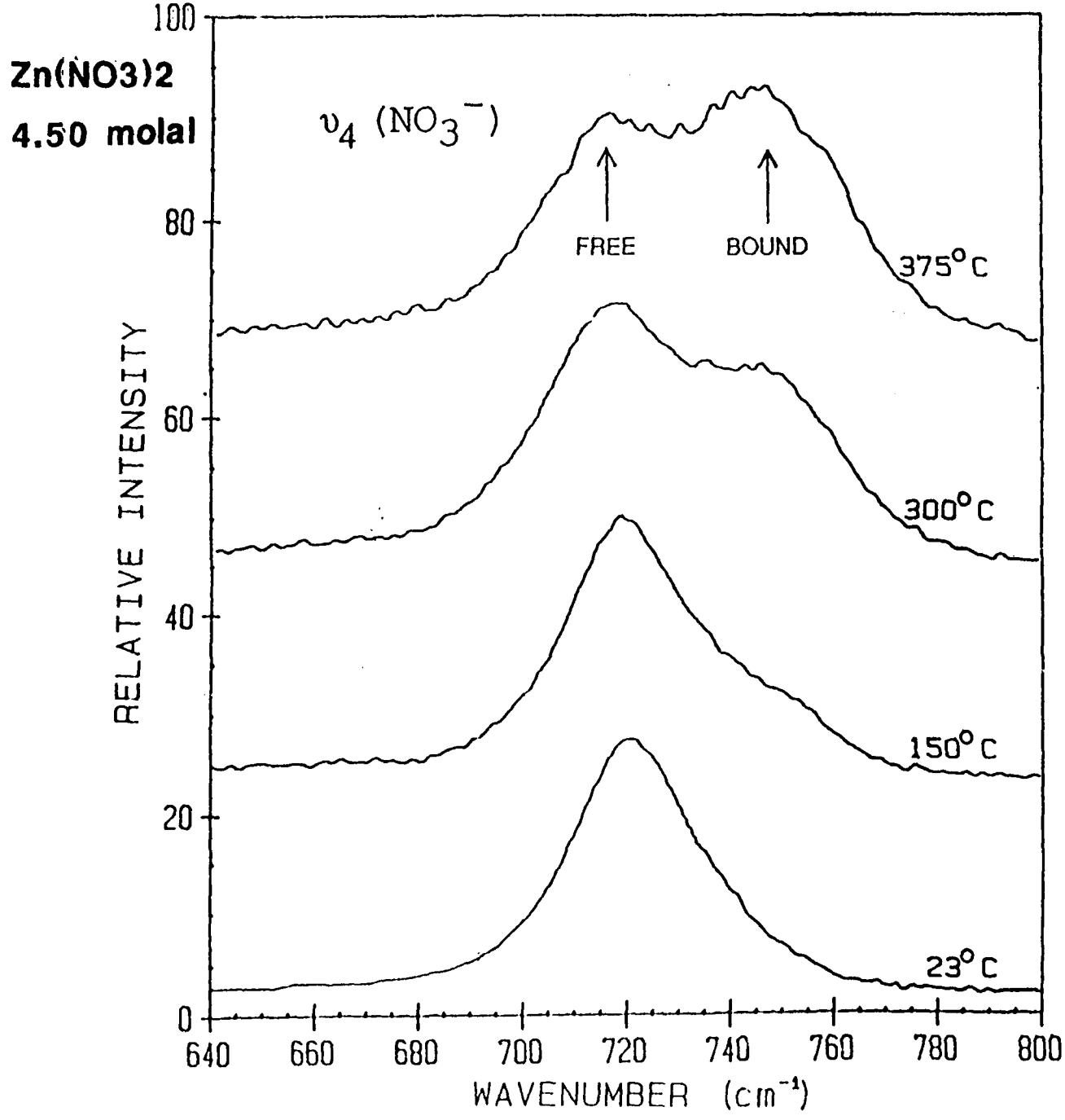

Retaining Screws (3)
Thermocouple
Sapphire Disk
(sample compartment)
Coil Spring
Set
Screws (4)
Gold
Seals
Tantalum
Rod
Tantalum
Rod
Sample Inlet
Laser Beam
Water-cooled
Aluminum
Endplate
Ceramic
Insulators
Water-cooled
Aluminum
Endplate
316 SS Support Pieces
wrapped with heating wires
(heating wires not shown)
SCALE 4 5

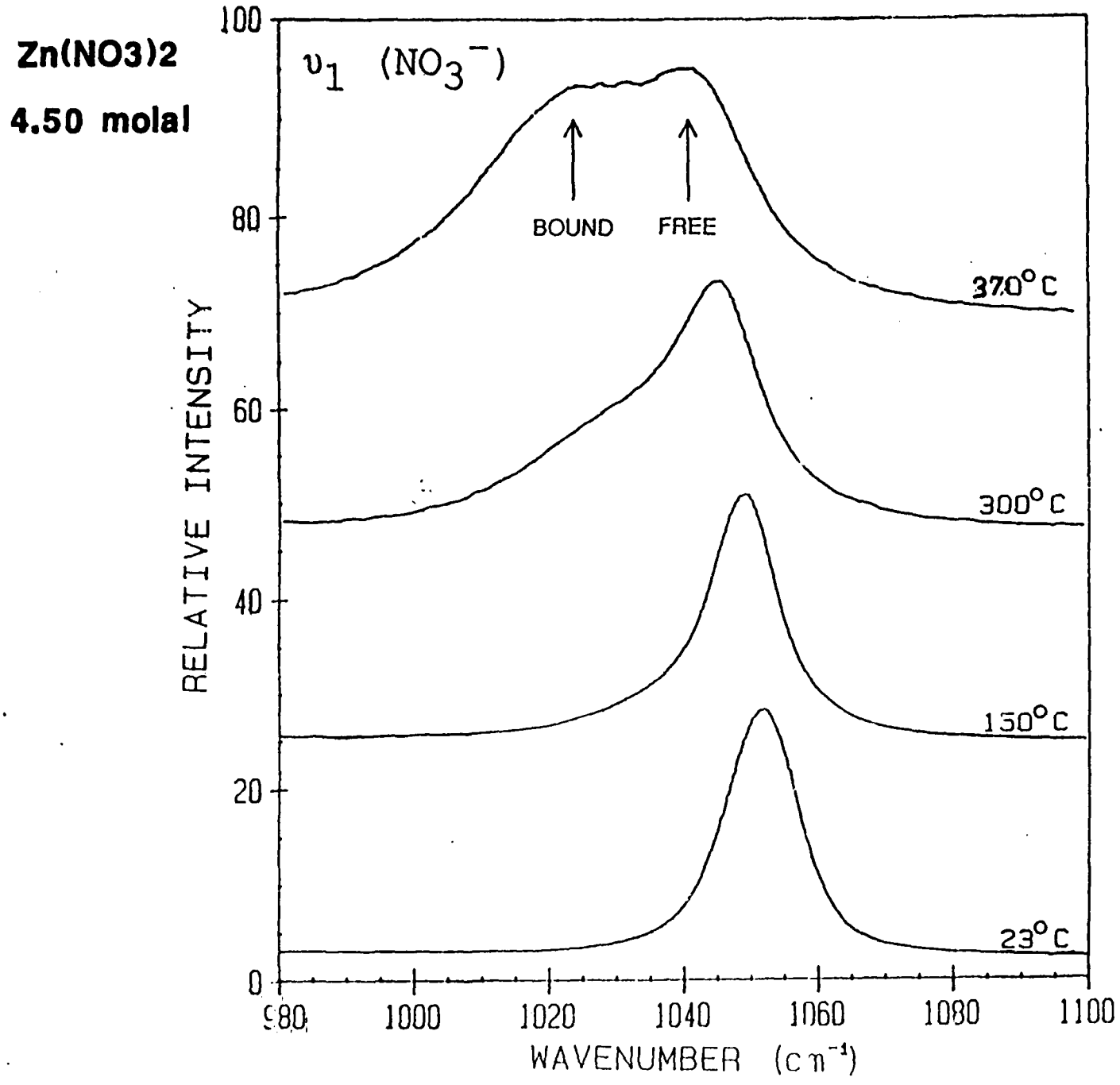

Temperature
Controller
Pressure
Gauge
(MPa)
Sample
Out
Metering
Pump
Check
Valve
Rheodyne
Sample
Injector
Metering
Valve
Laser

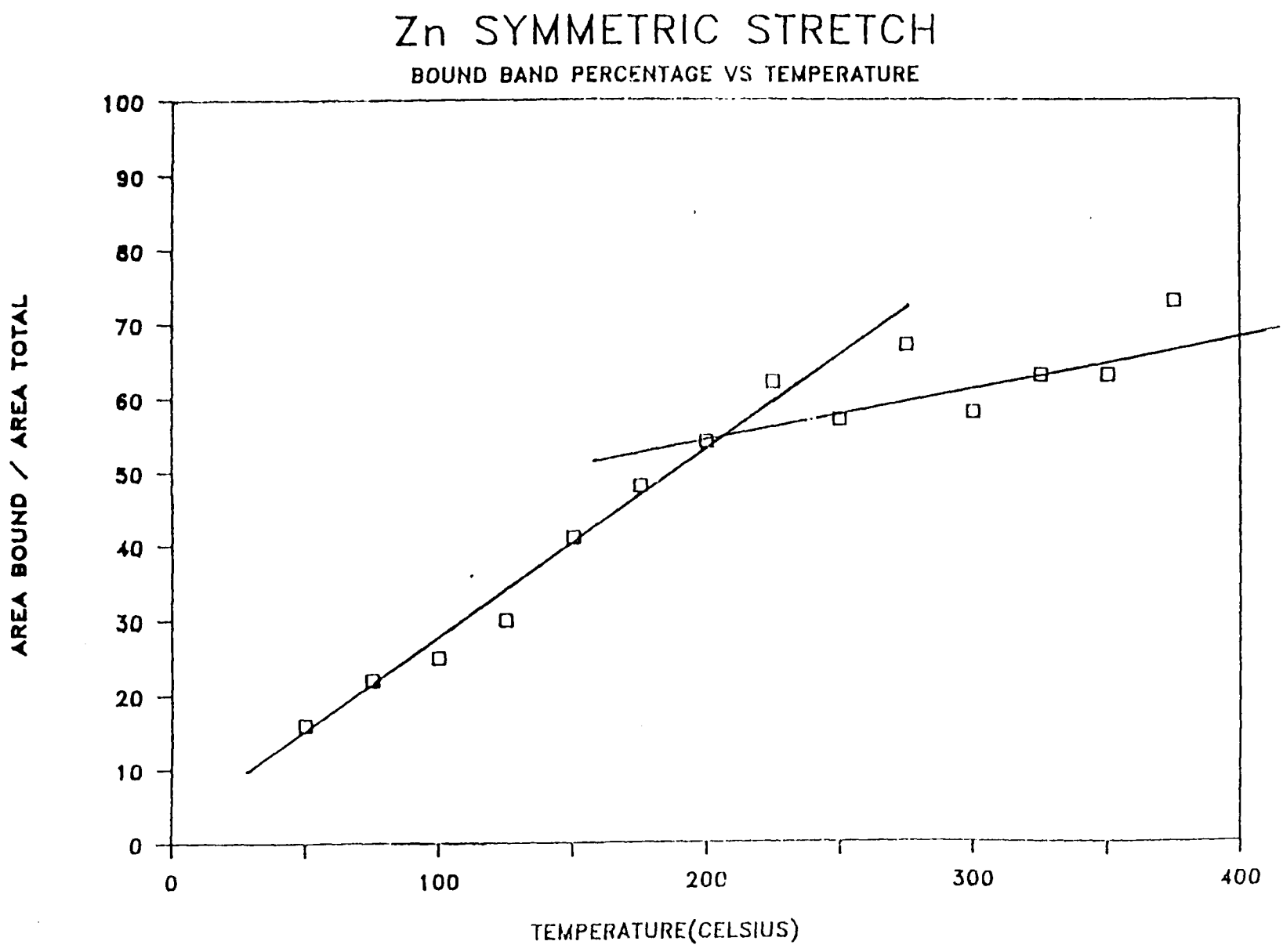

Sample out
Cone
"O" ring seal
Cylinder
Rod Crystal (ZnSe)
Chamber
(for High T/P work, SS316)
Toroid
Sample in

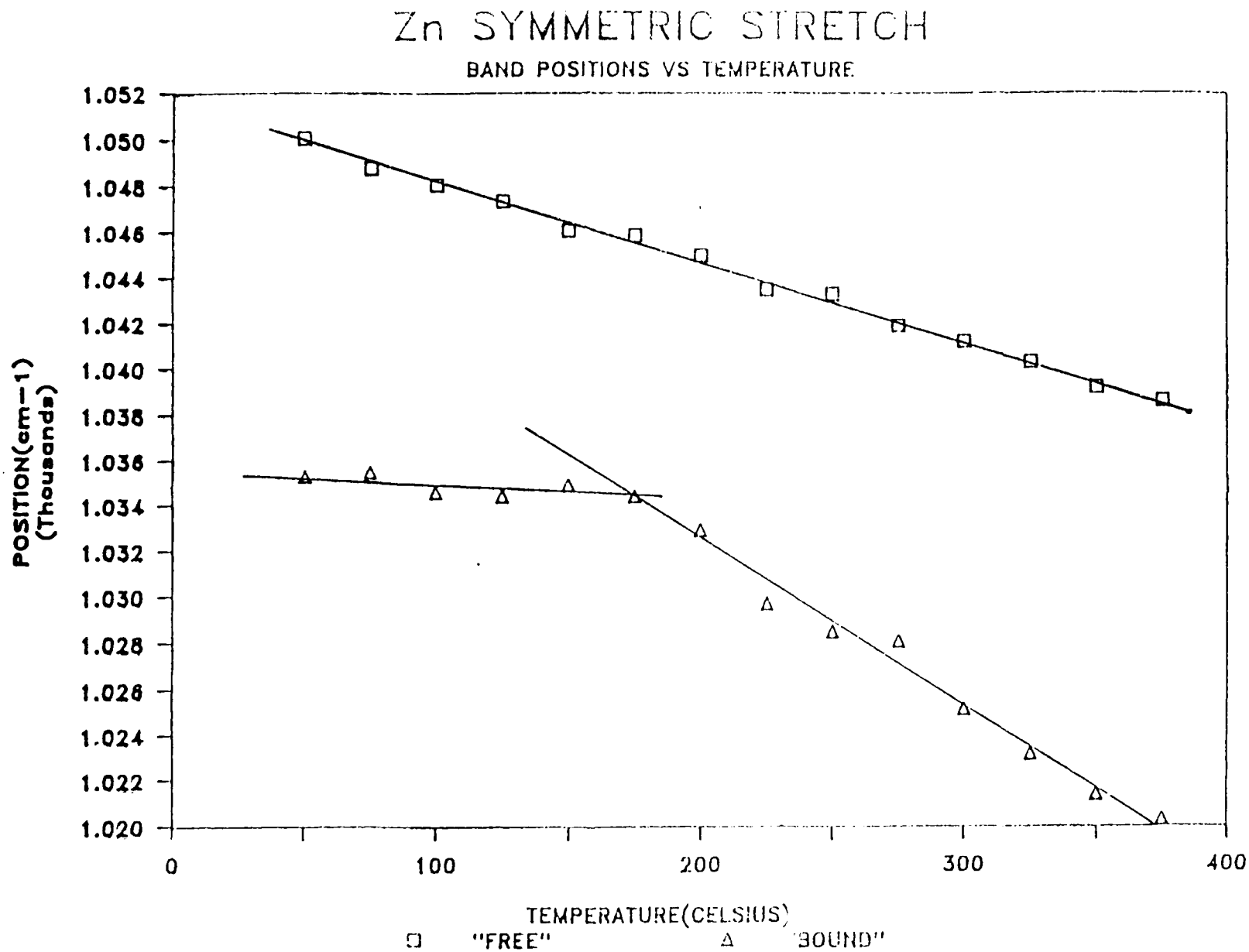

Zn(NO3)2
4.50 molal
υ_3 (NO_3^-)
350° C
300° C
150° C
23° C
RELATIVE INTENSITY
0
20
40
60
80
100
1150
1200
1250
1300
1350
1400
1450
1500
1550
1600
WAVENUMBER (cm^{-1})

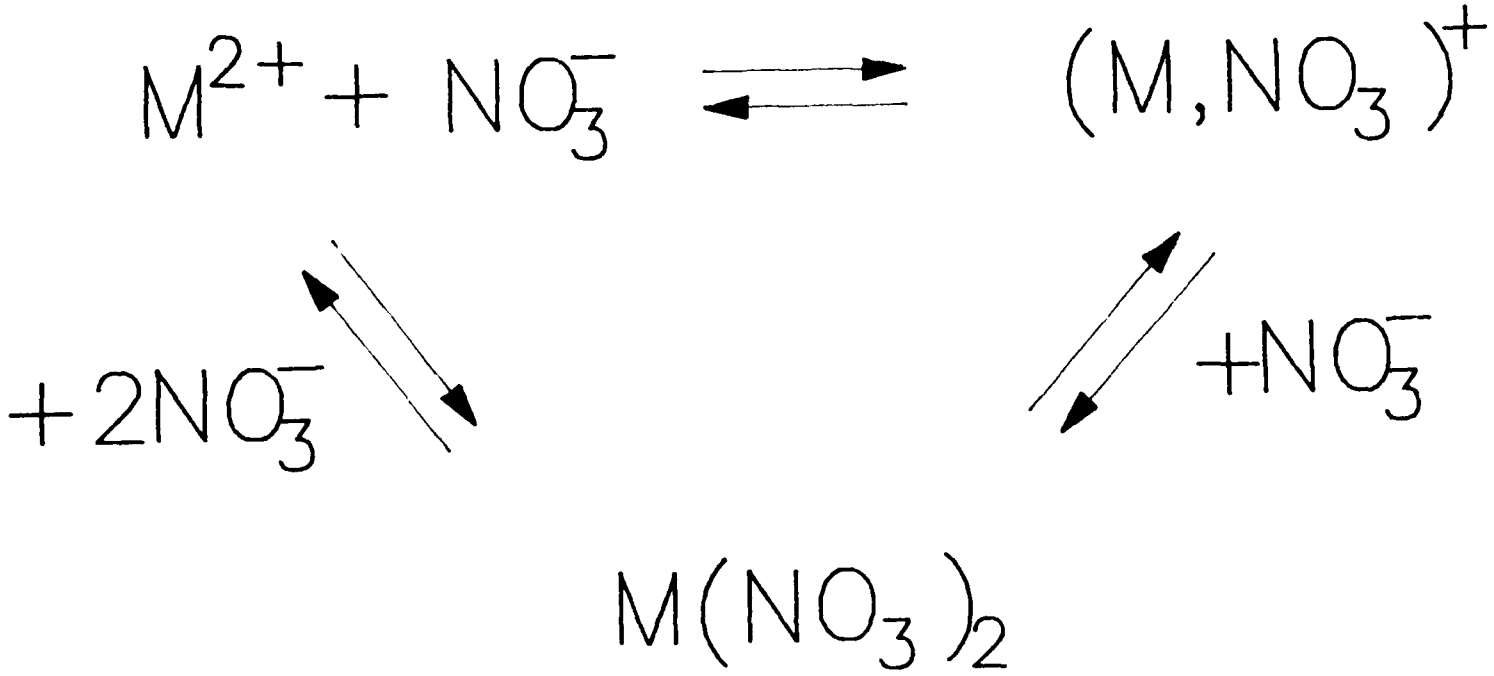

Zn-NO3
Zn-H20
350° C
300° C
150° C
23° C
RELATIVE INTENSITY
100
80
60
40
20
0
200
250
300
350
400
450
500


Zn(NO3)2
4.50 molal
υ_4 (NO_3^-)
FREE
BOUND
375° C
300° C
150° C
23° C
RELATIVE INTENSITY
WAVENUMBER (cm^{-1})
0
20
40
60
80
100
640
660
680
700
720
740
760
780
800


Zn(NO3)2
4.50 molal
υ_1 (NO_3^-)
BOUND
FREE
370° C
300° C
150° C
23° C
RELATIVE INTENSITY
0
20
40
60
80
100
980
1000
1020
1040
1060
1080
1100
WAVENUMBER (cm^{-1})


Zn SYMMETRIC STRETCH
BOUND BAND PERCENTAGE VS TEMPERATURE
AREA BOUND / AREA TOTAL
100
90
80
70
60
50
40
30
20
10
0
0
100
200
300
400
TEMPERATURE(CELSIUS)

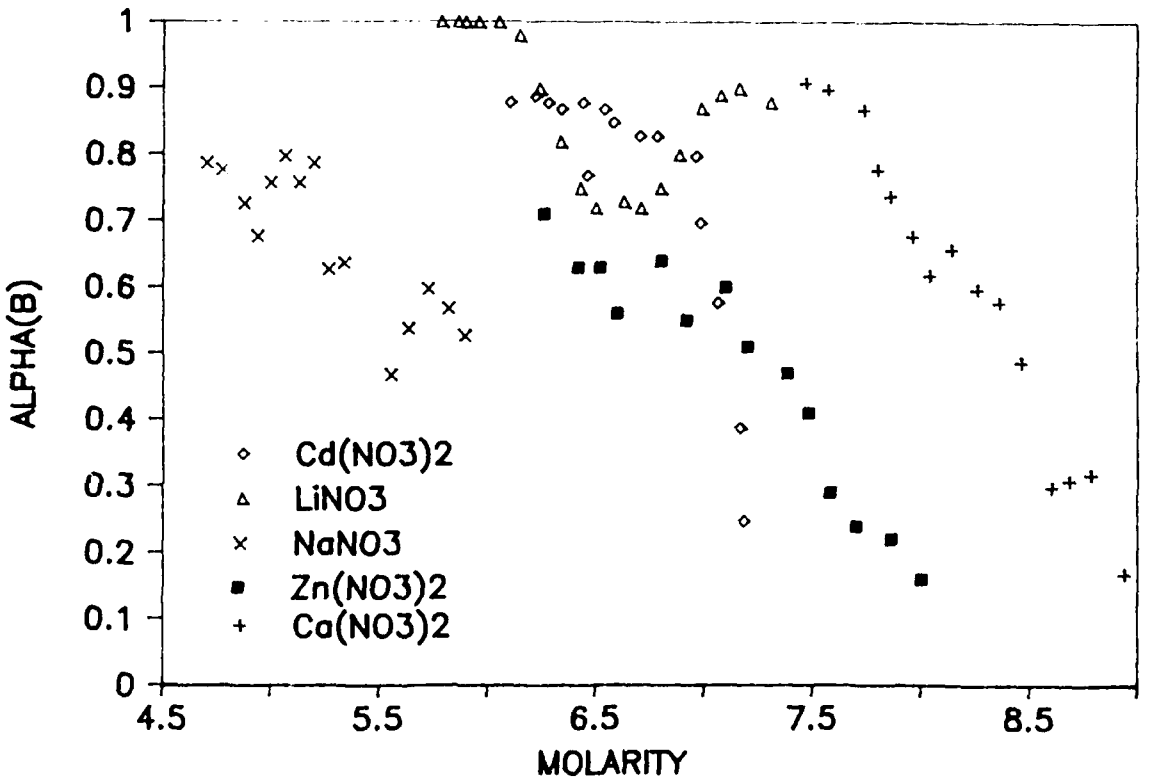

Zn SYMMETRIC STRETCH
BAND POSITIONS VS TEMPERATURE
POSITION(cm-1)
(Thousands)
1.052
1.050
1.048
1.046
1.044
1.042
1.040
1.038
1.036
1.034
1.032
1.030
1.028
1.026
1.024
1.022
1.020
0
100
200
300
400
TEMPERATURE(CELSIUS)
"FREE"
"BOUND"


$M^{2+} + NO_3^-$
$(M,NO_3)^+$
$+2NO_3^-$
$+NO_3^-$
$M(NO_3)_2$

$$I_T = I_A + I_B = C_A + C_B$$

$$\mathrm{ALPHA(B)} = 1 - I_B/I_T$$

$$2.303 \log Qm = -\frac{\Delta H}{RT} + \frac{\Delta S}{R}$$


ALPHA(B)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
4.5
5.5
6.5
7.5
8.5
MOLARITY
Cd(NO3)2
LiNO3
NaNO3
Zn(NO3)2
Ca(NO3)2

Model Possibilities

Model 1) Simple equilibrium:

$$Zn^{2+} + NO_3^- \leftrightharpoons ZnNO_3^+$$

$$Q_m = \alpha_B / (m(1-2\alpha_B)(1-\alpha_B))$$

$$\alpha_B = I_B / I_{tot}$$

Model 2) A simple equilibrium which takes the effects of water into account:

$$Zn(H_2O)_6^{2+} + NO_3^- \leftrightharpoons Zn(H_2O)NO_3^+ + H_2O$$

$$m(H_2O) = 55.51 - 6m(Zn(H_2O)_6^{2+}) - 5m(Zn(H_2O)NO_3^+)$$

Model 3) Simple two site model:

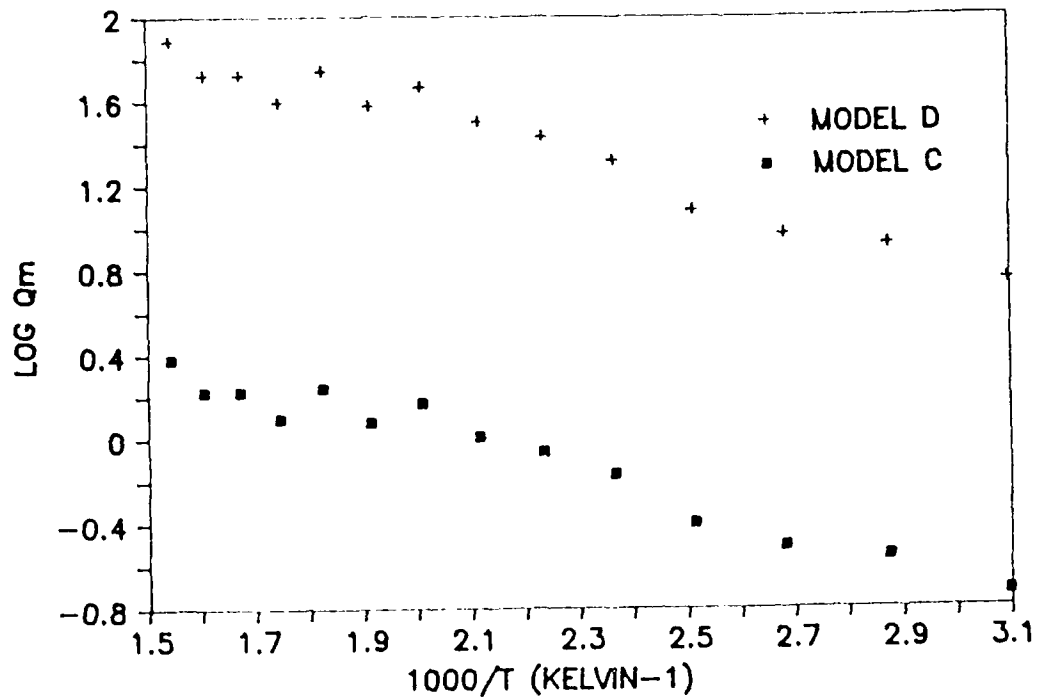
$$NO_3^-(\text{free}) \rightleftharpoons NO_3^-(\text{bound})$$

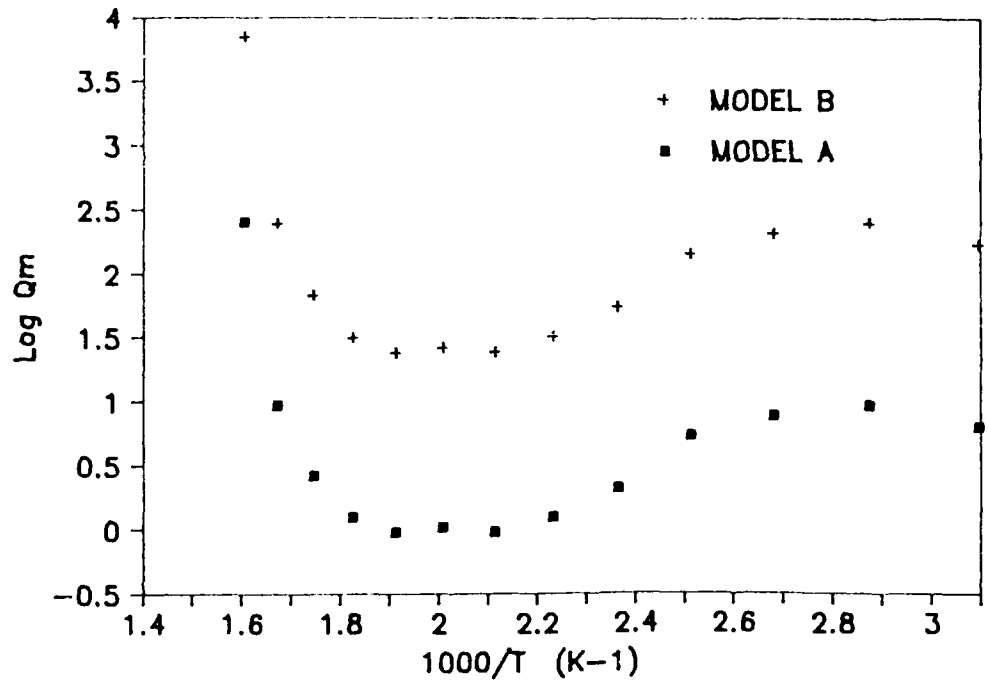
$$Q_m = I_B / I_F$$

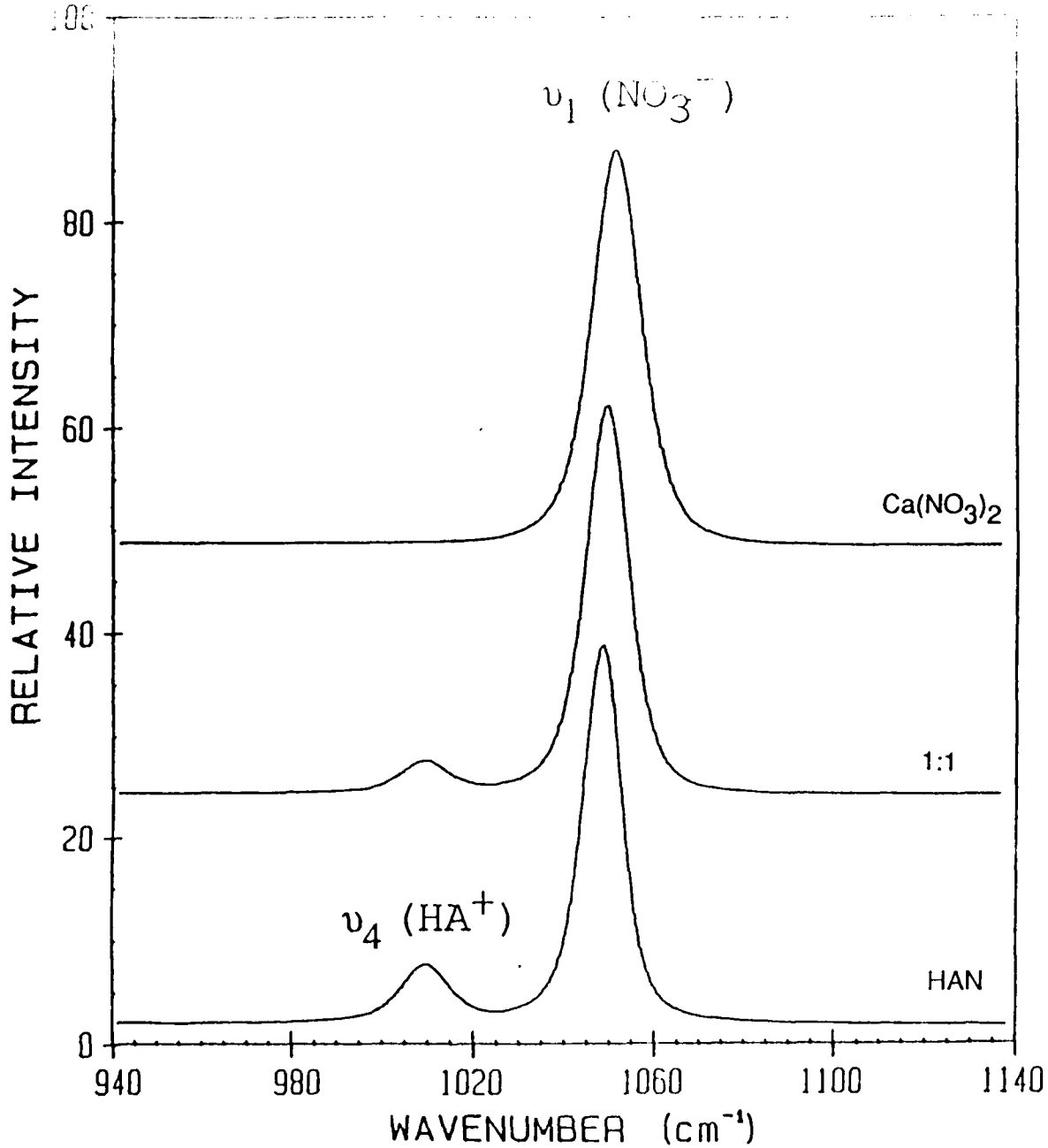
Model 4) Two site model that includes water solvent:

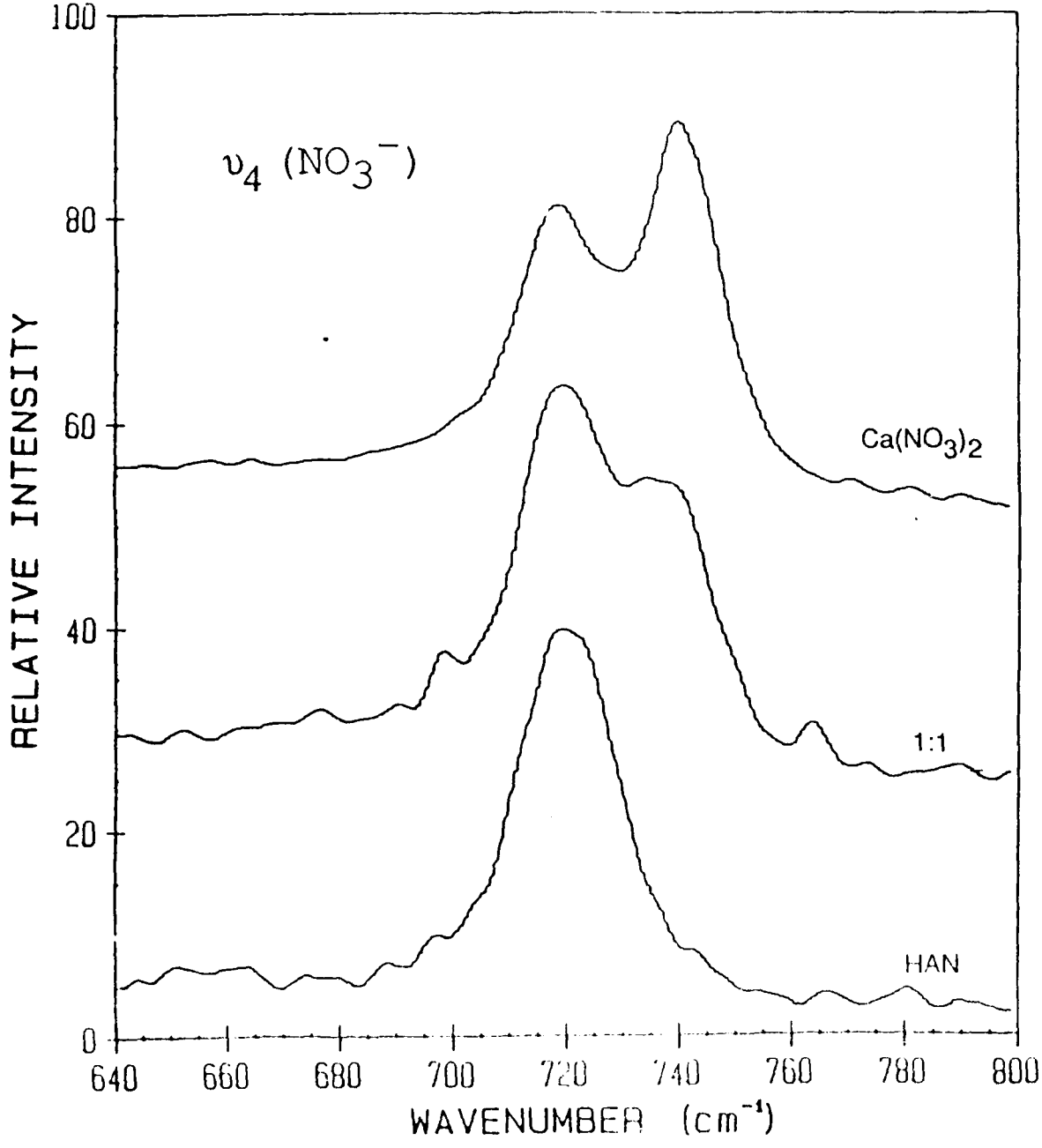
$$\underset{\text{outer sphere}}{Zn^{2+}(H_2O)_6NO_3^-} \rightleftharpoons \underset{\text{inner sphere}}{Zn(H_2O)NO_3^+} + H_2O$$

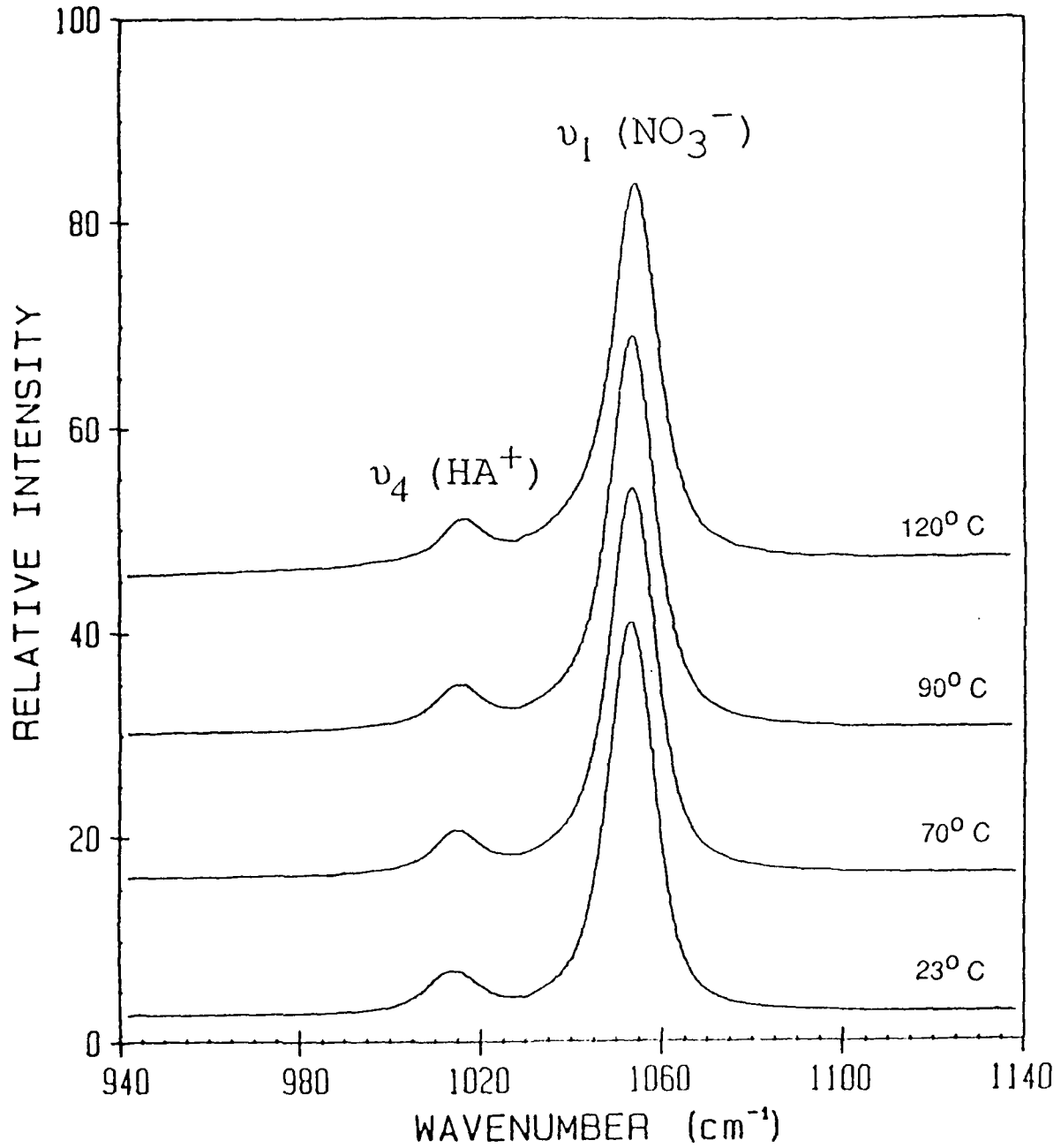
$$Q_m = I_B \cdot m(H_2O) / I_F$$


2
1.6
1.2
0.8
0.4
0
−0.4
−0.8
LOG Qm
1.5
1.7
1.9
2.1
2.3
2.5
2.7
2.9
3.1
1000/T (KELVIN−1)
MODEL D
MODEL C


MODEL B
MODEL A
Log Qm
1000/T (K-1)
4
3.5
3
2.5
2
1.5
1
0.5
0
-0.5
1.4
1.6
1.8
2
2.2
2.4
2.6
2.8
3


υ_1 (NO_3^-)
υ_4 (HA^+)
$Ca(NO_3)_2$
1:1
HAN
RELATIVE INTENSITY
0
20
40
60
80
100
940
980
1020
1060
1100
1140
WAVENUMBER (cm^{-1})


υ_4 (NO_3^-)
Ca(NO_3)$_2$
1:1
HAN
RELATIVE INTENSITY
WAVENUMBER (cm^{-1})
0
20
40
60
80
100
640
660
680
700
720
740
760
780
800


100
80
60
40
20
0
RELATIVE INTENSITY
υ_1 (NO_3^-)
υ_4 (HA^+)
120° C
90° C
70° C
23° C
940
980
1020
1060
1100
1140
WAVENUMBER (cm^{-1})

CONCLUSIONS

Designed cell capable of examining concentrated aqueous salt solutions at high temperatures and high pressures

Increased concentration of "bound" species as temperature is raised

Increased cation–anion interaction with an increase in temperature

Very difficult to develop a general description of the behavior of inorganic nitrate salts in concentrated aqueous solutions at elevated temperatures and pressures

CONCLUSIONS

1) Little previous work on concentrated salt solutions at elevated temperatures and pressures

2) More molecular HAN as temperature is increased and pressure is applied

3) Mixtures of metals and HAN solutions behave additively

US ARMY
LABORATORY COMMAND

BALLISTIC RESEARCH LABORATORY

THERMAL CHARACTERISTICS OF CONCENTRATED HYDROXYLAMMONIUM NITRATE SOLUTIONS

RONALD SASSE'

BRL-MR-3561, MARCH 1988

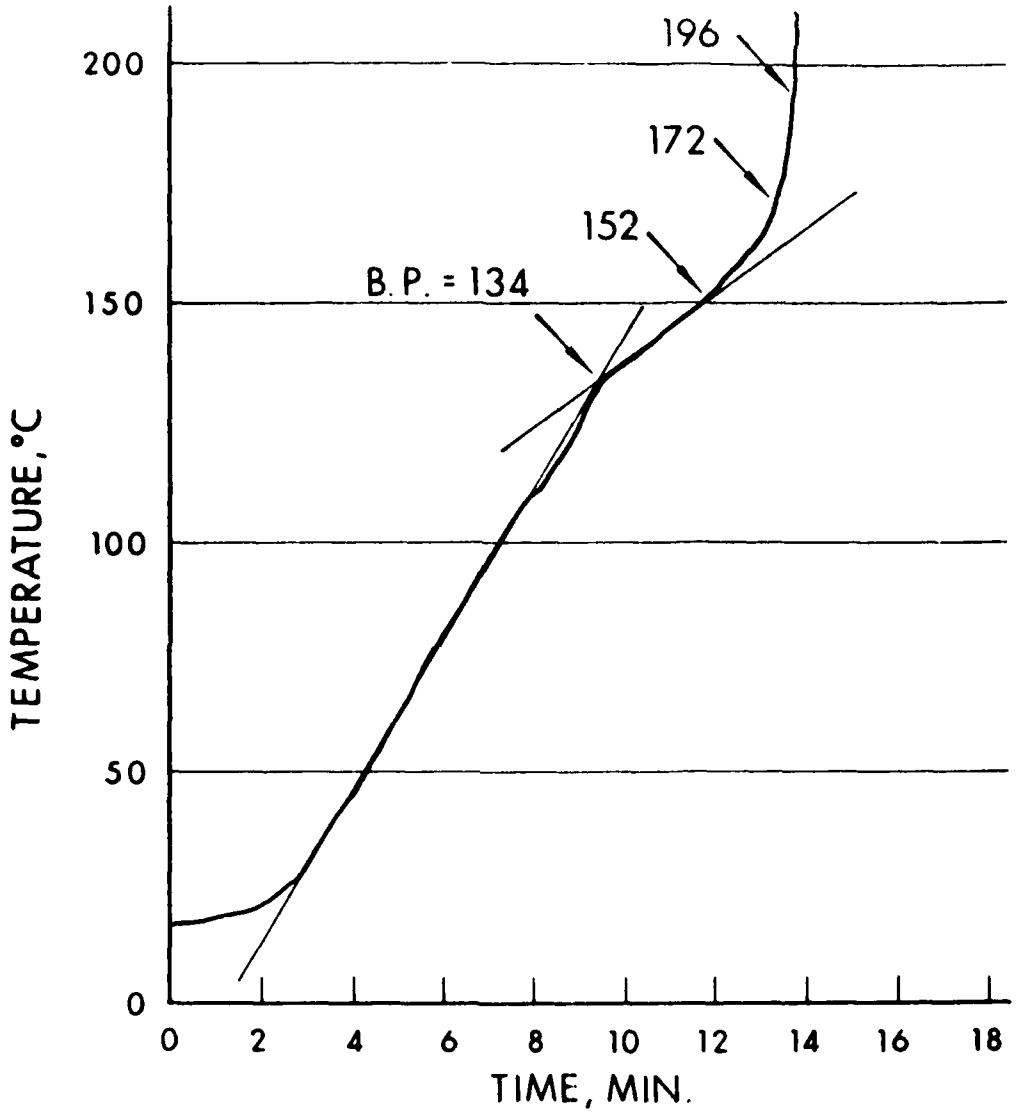


Figure 3. Temperature History of 13.0M HAN Heated in an Open Vessel

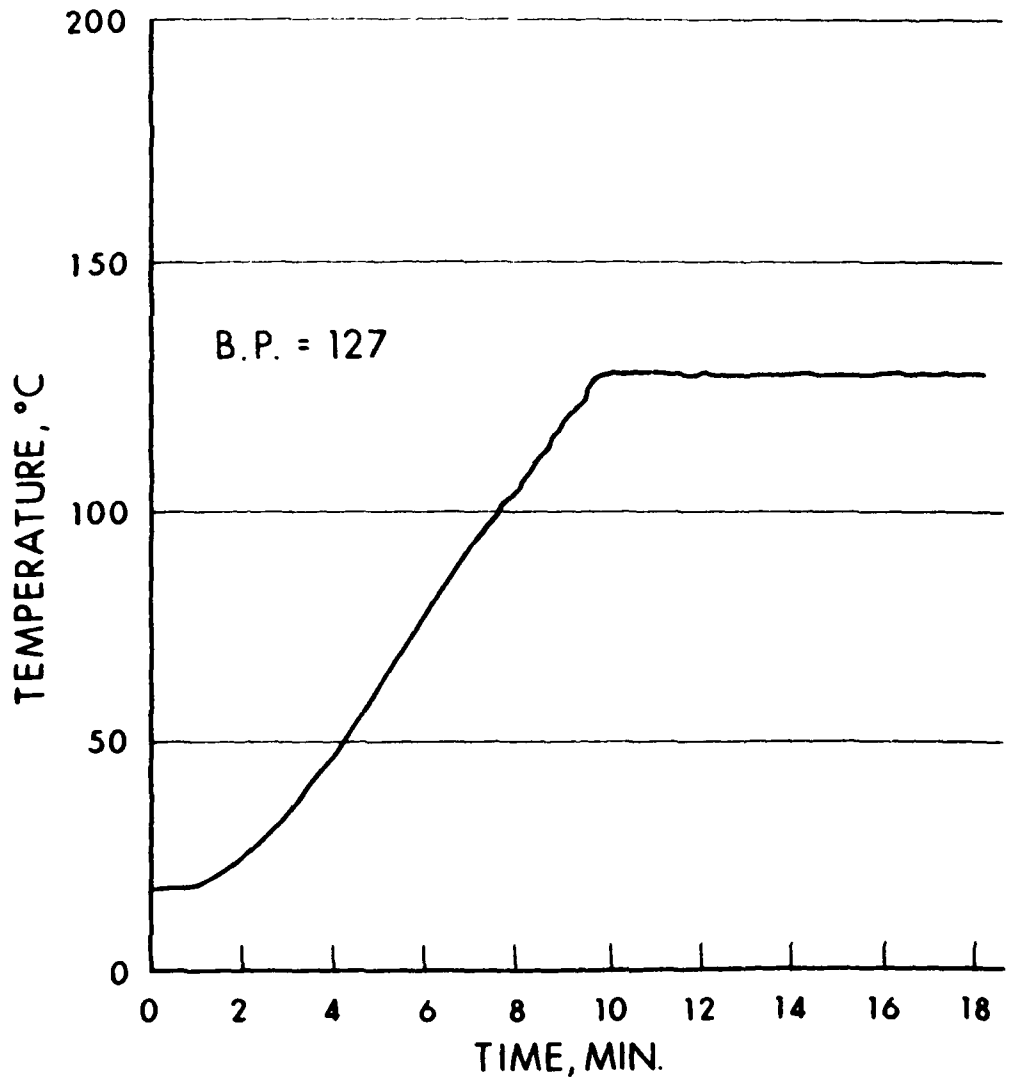


Figure 1. Temperature History of 12.48M HAN Using a Reflux Condenser

Table 1. Thermal Decomposition of 12.48 M HAN Solution

Sample Description	Weight in Grams		
	Total	HAN	Water
Before Reflux	12.4043	9.6188	2.4317
		9.7938	2.4412
After Reflux	11.6286	9.1030	2.5697
		9.0773	2.5596
Weight Change	-0.7757	-0.6161	+0.1417

Table 2. Boiling Points for Different HAN Concentrations

HAN M	Water M	Boiling Point °C	HAN Mole Fraction
0.0	55.56	100	0.0000
4.0	43.72	107	0.1547
9.0	28.99	115	0.3831
12.0	20.16	127	0.5435
12.48	16.72	132	0.5848
13.0	17.21	129	0.6017
13.0	17.21	134	0.6017
15.8	8.97	145	0.7789

$$-\ln X_A = -\ln (1-X_B) = -\ln \left[1 - \frac{2n_2}{2n_2+n_1}\right] = \frac{\Delta H_{vap}}{R} \cdot \frac{T_2-T_1}{T_2T_1} \qquad (1)$$

where: T_1 is the boiling point of pure water and T_2 is boiling point of the solution in degrees K, R is the gas constant; 1.987 cal mole^{-1} degree^{-1}, and the accepted value for the heat of vaporization for water, ΔH_{vap} is 9720 cal mole^{-1} degree^{-1}. n_2 is the HAN molar concentration and n_1 is the molar concentration of water.

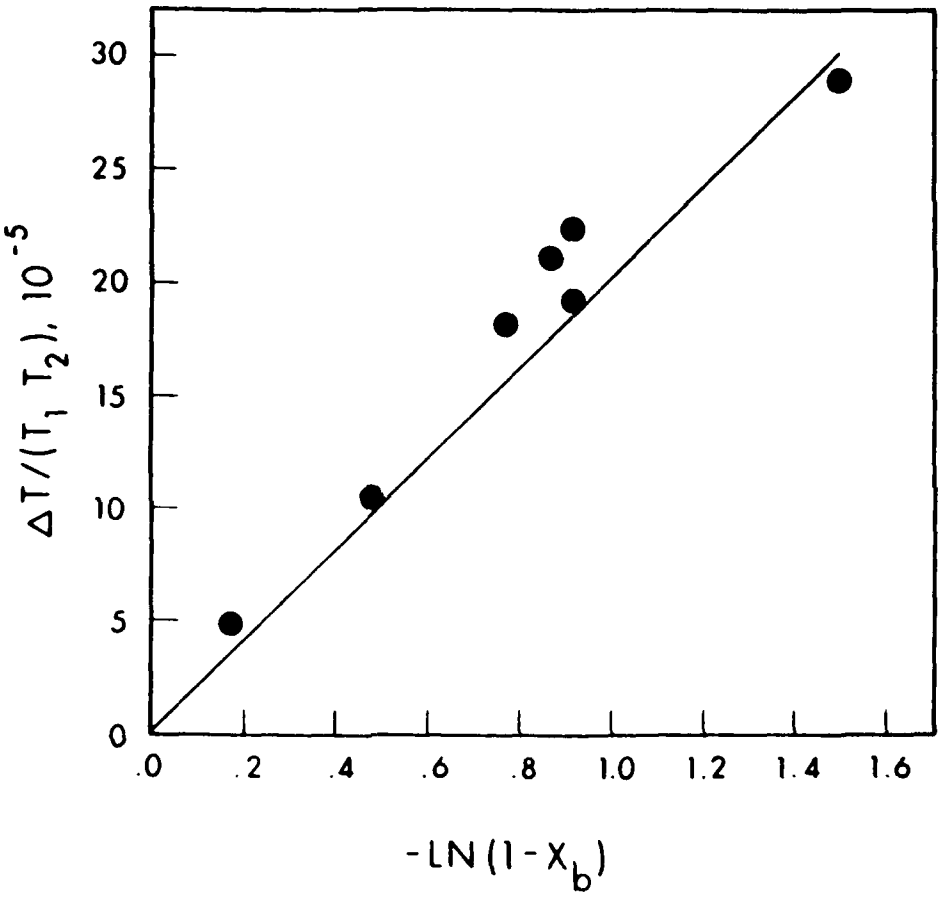


Figure 4. Evaluation of Boiling Points of Different Concentrations of HAN

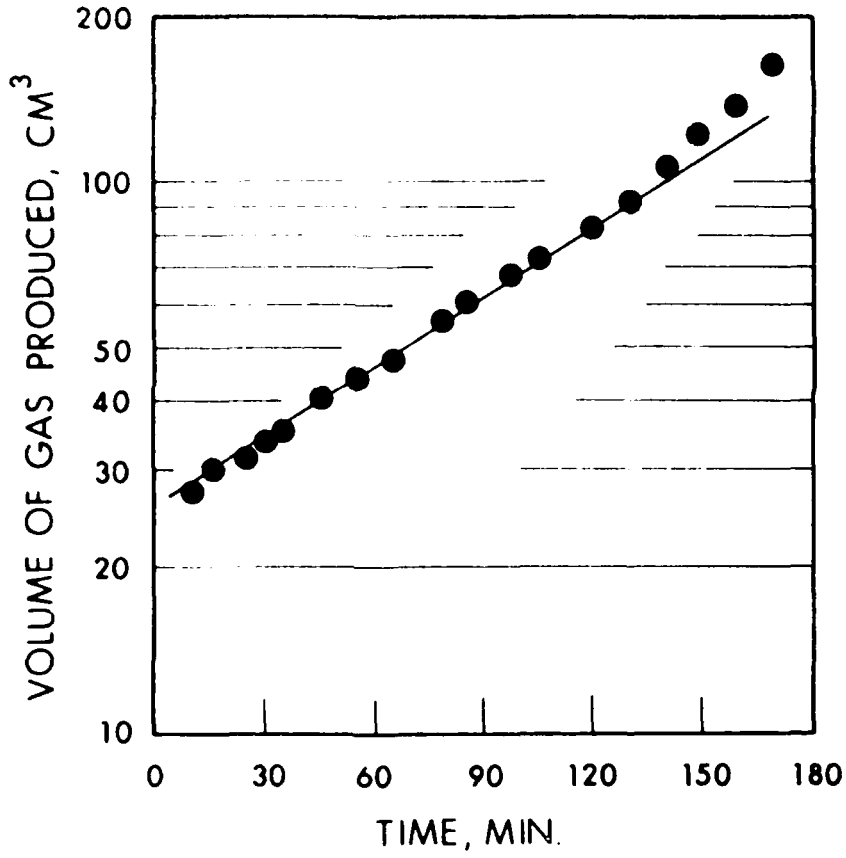


Figure 5. First Order Presentation of Gas Product Yield

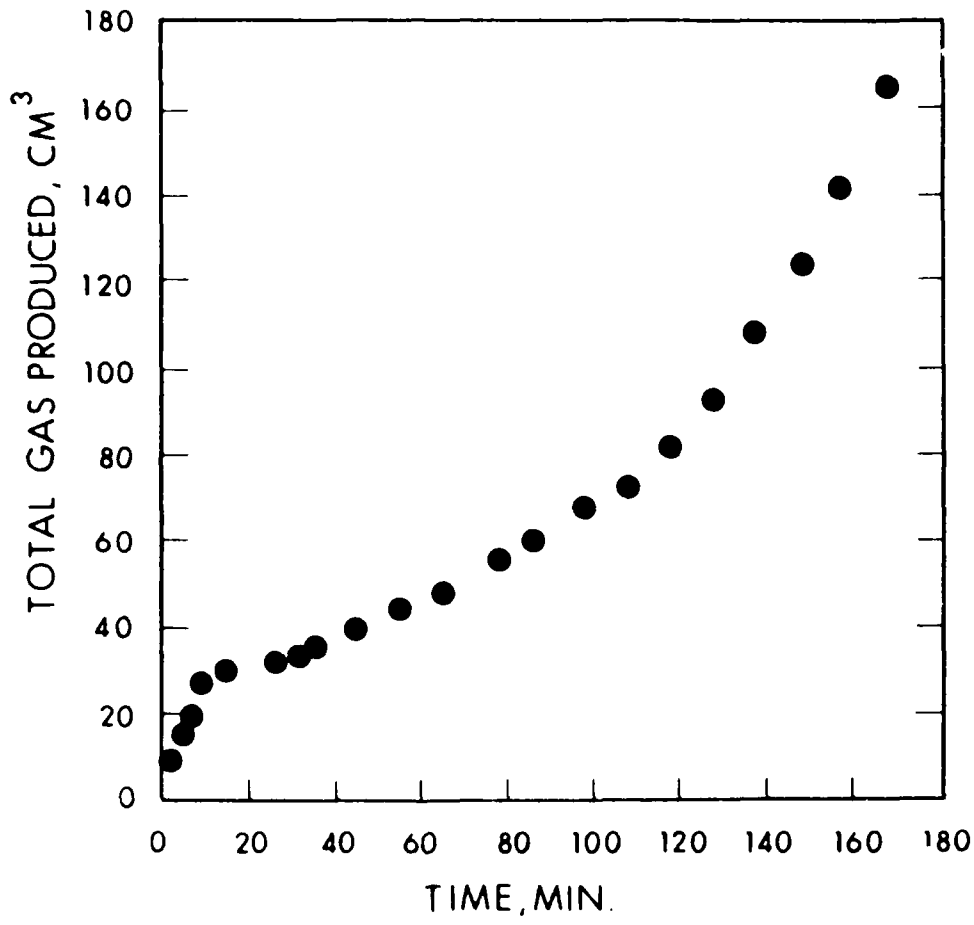


Figure 2. Total Gas Produced While Refluxing 12.48M HAN

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STRUCTURE AND PROPERTIES
US ARMY BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MD
30 AUG - 1 SEP 88

Title of Paper: Electrosynthesis of High-Purity Hydroxylammonium Nitrate by Electrolytic Reduction of Nitric Acid
Presentation Time Request: 30 minutes
Type of Paper: State of Art
Speaker's Name: Dr. James A. Leistra **Phone Number:** (203) 789-5242
Affiliation/Address: OLIN Chemicals
24 Science Park
New Haven, CT 06511
Co-author(s) name(s): Dr. Ronald L. Dotson, James H. Barnatt

ABSTRACT:

Olin developed a continuous electrolytic process to produce high purity 2.8 molar hydroxylammonium nitrate (HAN) meeting propellant specifications. Olin exceeded contract deliverables by producing 2.85 molar HAN at production rates of 3.35 kg HAN/day. An electrolytic reactor was designed and operated at up to 30 times the amperage of previous work. Olin obtained 92% yield of HAN from nitric acid and 77% current efficiency at a 1.5 kA/m^2 current density. The HAN product contained less than 2.5 ppm transition metals and 0.5 wt% ammonium nitrate, which were superior to the specifications required in the contract. Contract deliverables included 2.8 molar HAN, 1 kg HAN/day, less than 5 ppm transition metals, and less than 1 wt% total impurities.

A statistically designed experimental program was utilized to evaluate the effect of operating variables on cell performance. The critical variables for electrolytic production of HAN were demonstrated to be catholyte nitric acid concentration and mercury temperature. At high catholyte nitric acid concentrations, excess nitric acid oxidizes HAN to nitrogen oxides resulting in a current efficiency loss. At low catholyte nitric acid concentrations, HAN reduces to ammonium nitrate. The control and importance of this parameter was demonstrated in the laboratory. Mercury temperature was important to overall cell performance; mercury temperatures below 25°C appeared to yield maximum current efficiency.

The laboratory cell was continuously and successfully operated under controlled conditions at current densities of 1.5 kA/m^2. This current density was limited only by the equipment used; current densities greater than 1.5 kA/m^2 may be achievable.

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HAN ELECTROSYNTHESIS

OBJECTIVE

DEVELOP AND CHARACTERIZE A CONTINUOUS LABORATORY SCALE (100 AMP) ELECTROLYTIC REACTOR WHICH PRODUCES HIGH PURITY SOLUTIONS OF HYDROXYLAMMONIUM NITRATE FROM NITRIC ACID

CONTRACT DELIVERABLES

HAN PRODUCTION RATE:	1 KG HAN/day
HAN PRODUCT SPECIFICATIONS:	2.8 M HAN < 5 PPM TRANSITION METALS < 1 WT% TOTAL IMPURITIES < 0.1 WT% NITRIC ACID

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HAN ELECTROSYNTHESIS

PROCESS CHEMISTRY

ANODE: $3\,H_2O \rightarrow 3/2\,O_2 + 6\,H^+ + 6\,e^-$

CATHODE: $HNO_3 + 6\,H^+ + 6\,e^- \rightarrow NH_2OH + 2\,H_2O$

$HNO_3 + NH_2OH \rightarrow (NH_3OH)NO_3$

OVERALL: $2\,HNO_3 + H_2O \rightarrow 3/2\,O_2 + (NH_3OH)NO_3$

HAN ELECTROSYNTHESIS

SIDE REACTIONS

LOW $[HNO_3]$: $NH_3OH^+ \rightarrow NH_4OH$

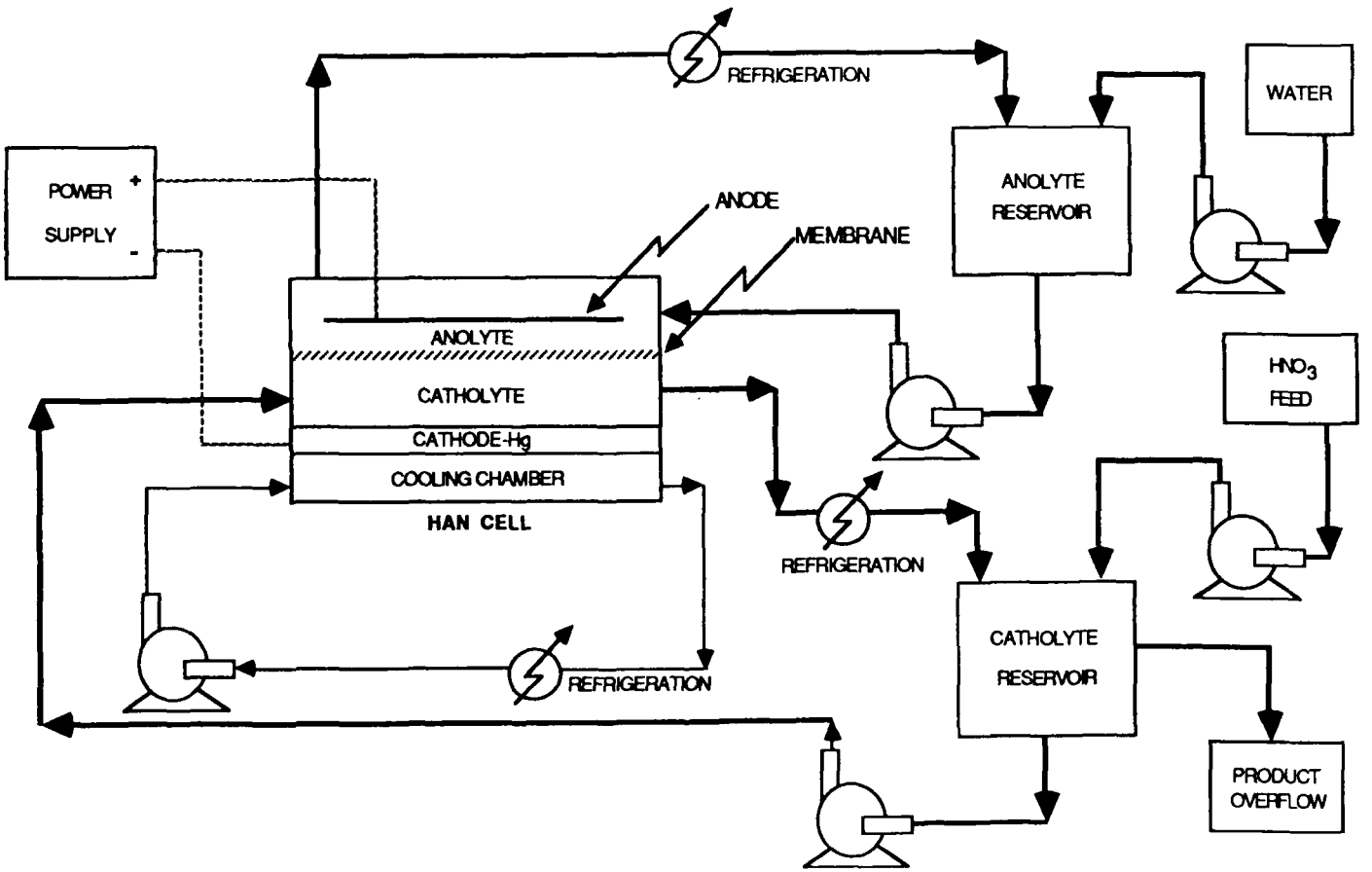
HIGH $[HNO_3]$: $(NH_3OH)NO_3 \rightarrow NO_x$

IMPURE Hg OR CATHOLYTE :

$$2\,H^+ + 2\,e^- \rightarrow H_2\,(gas)$$

HAN ELECTROSYNTHESIS

100 AMP PROCESS FLOW DIAGRAM



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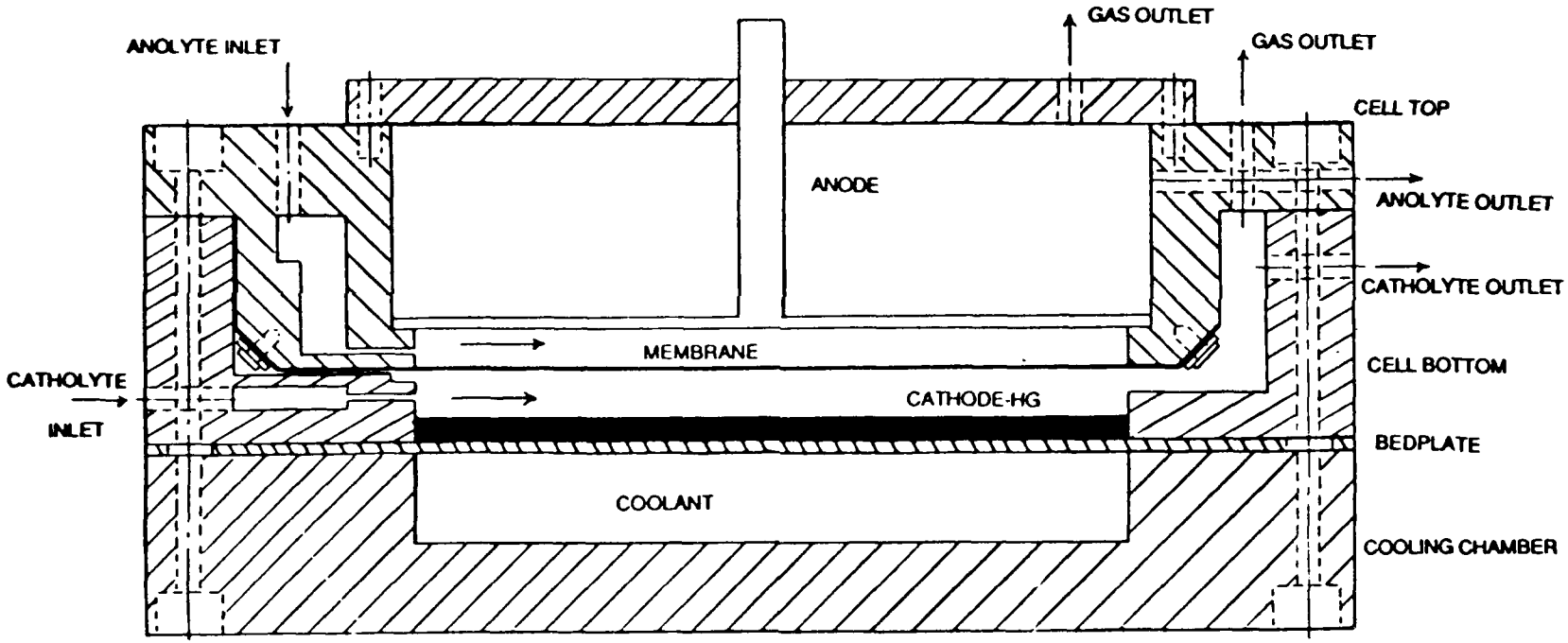
HAN ELECTROSYNTHESIS

100 AMP CELL : CROSS SECTION



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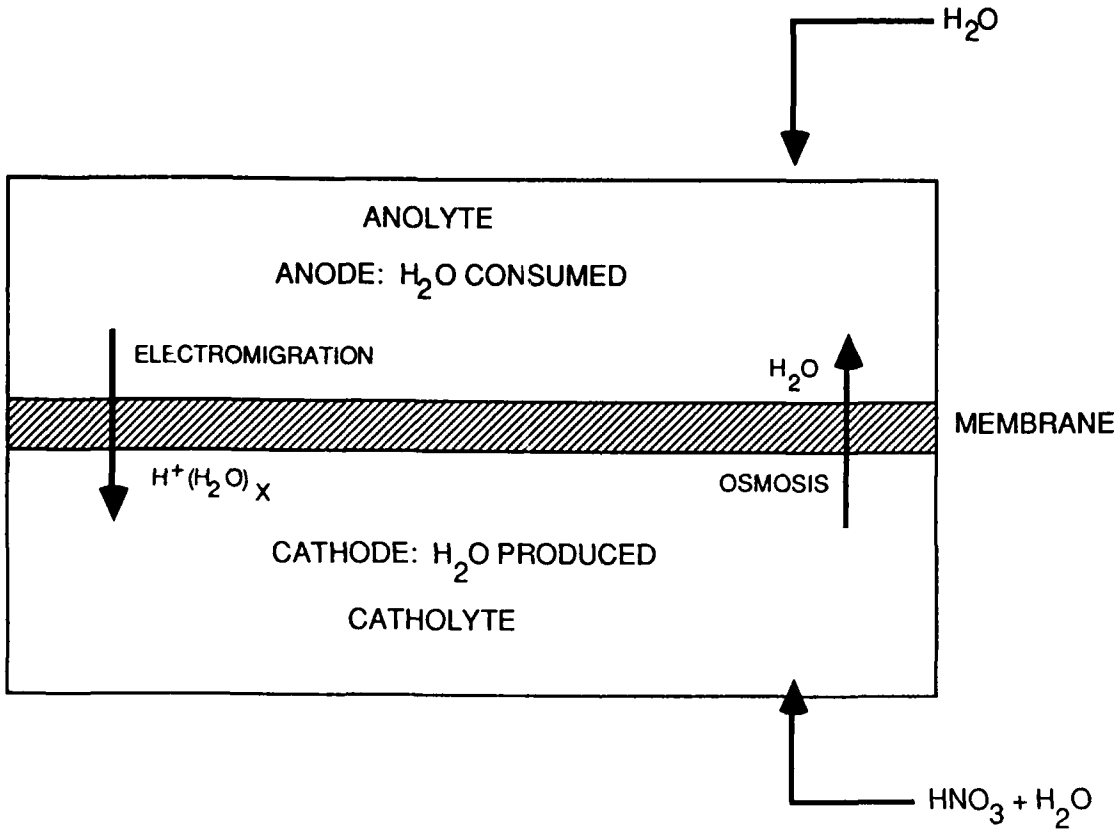
HAN ELECTROSYNTHESIS

HAN RUN #003 : CATHODE VOLUME INCREASE vs $[HNO_3]_a$

$[HNO_3]_c$	$[HNO_3]_a$	ΔVOL_c
1 M	1 M	10.0 ml/hr
1	3.3	6.2
0.5	3.3	5.4
0.5	5.8	1.0
0.35	5.8	1.8

HAN ELECTROSYNTHESIS

WATER BALANCE IN OPERATING CELL



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HAN ELECTROSYNTHESIS

100 AMP EXPERIMENTAL APPROACH

STATISTICALLY BASED

PERFORMANCE VARIABLE

- Current Efficiency (CE)

INDEPENDENT OPERATING VARIABLES

1. $[HNO_3]_c$
2. $[HNO_3]_a$
3. Catholyte Recycle Rate
4. Anolyte Recycle Rate
5. Mercury Temperature
6. Catholyte Temperature
7. Anolyte Temperature
8. Current Density
9. Membrane Material
10. Anode Material
11. Electrolyte Impurity
12. Mercury Impurity

HAN ELECTROSYNTHESIS

100 AMP SCREENING MATRIX : EXPERIMENTAL RESULTS

EXPERIMENTAL CONDITION	[HNO3]c	CATHOLYTE RECYCLE	TEMP Hg	[HNO3]a	CURRENT EFFICIENCY
1	0.2 M	2000 ml/min	10 C	3.0 M	0%
2	0.6	2000	10	5	61
3	0.2	5500	10	5	11
4	0.6	5500	10	3	69
5	0.2	2000	30	5	NP*
6	0.6	2000	30	3	56
7	0.2	5500	30	3	18
8	0.6	5500	30	5	NP*
	VARIABLE 1	VARIABLE 2	VARIABLE 3	VARIABLE 4	

*NP = NO PRODUCT OBTAINED. EVALUATED AS 0% CURRENT EFFICIENCY.

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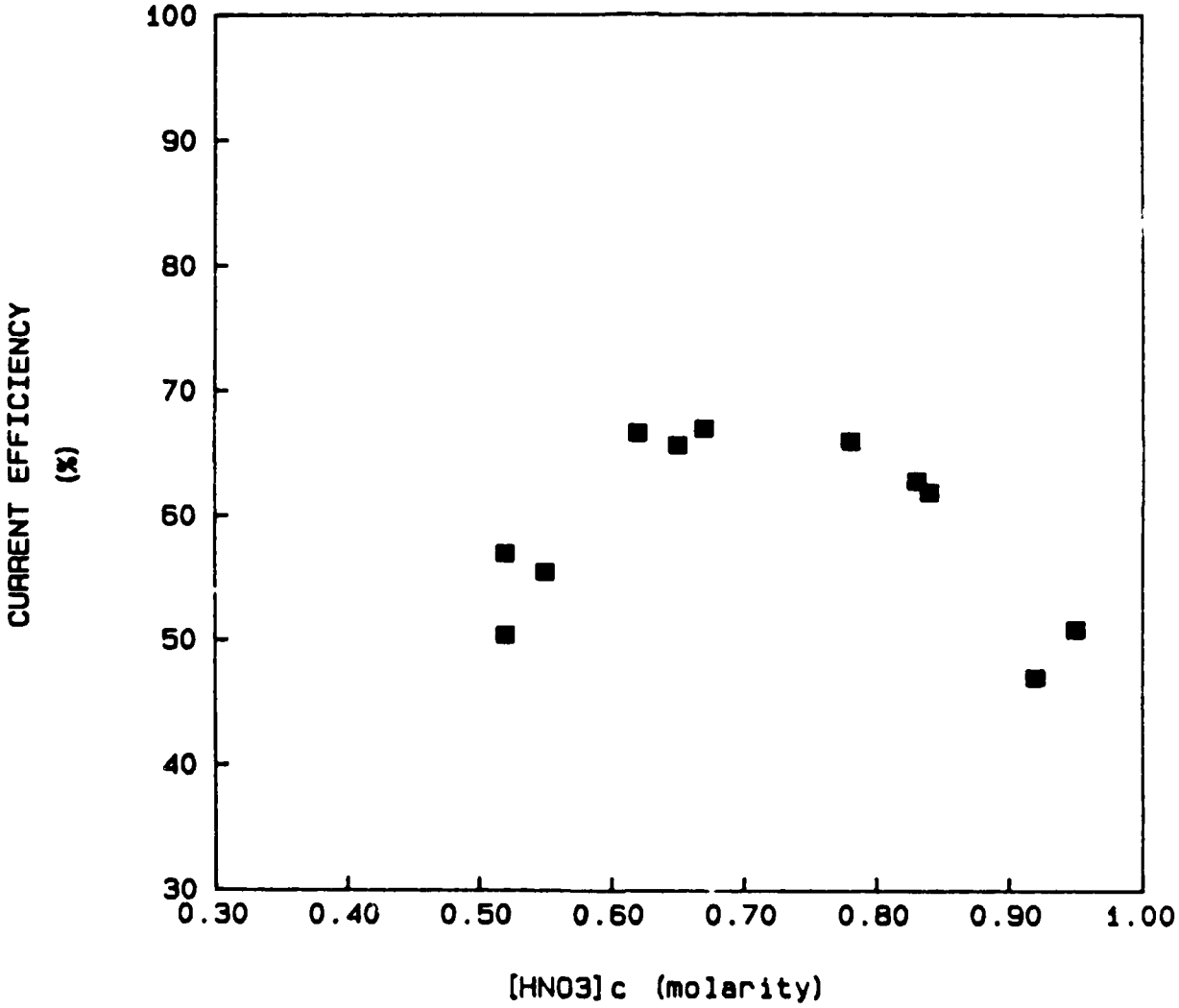
HAN ELECTROSYNTHESIS

RUN #103 : CURRENT EFFICIENCY vs $[HNO_3]_c$

1.5 kA/m^2, 36 ^oC



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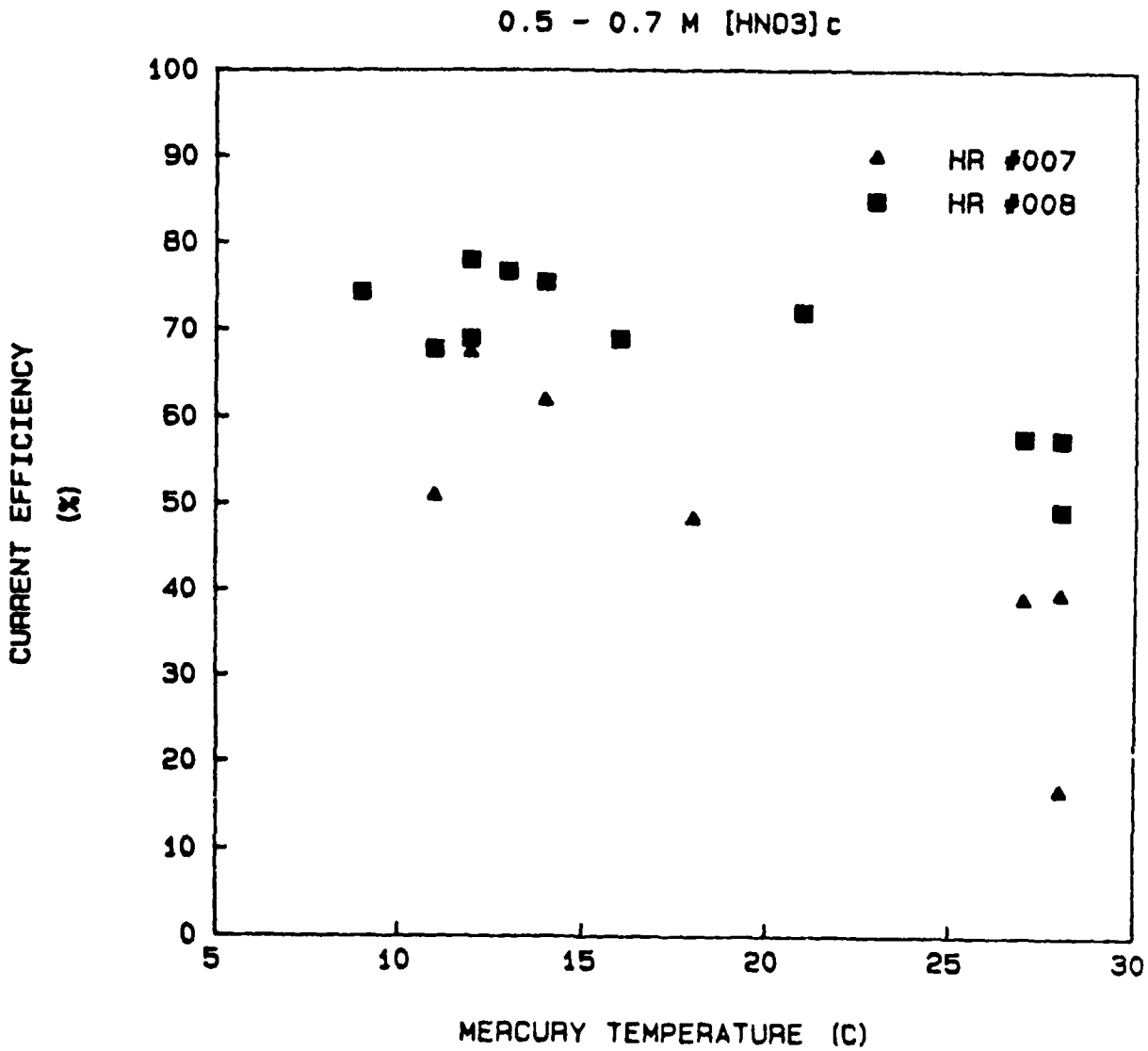
HAN ELECTROSYNTHESIS

CURRENT EFFICIENCY vs MERCURY TEMPERATURE



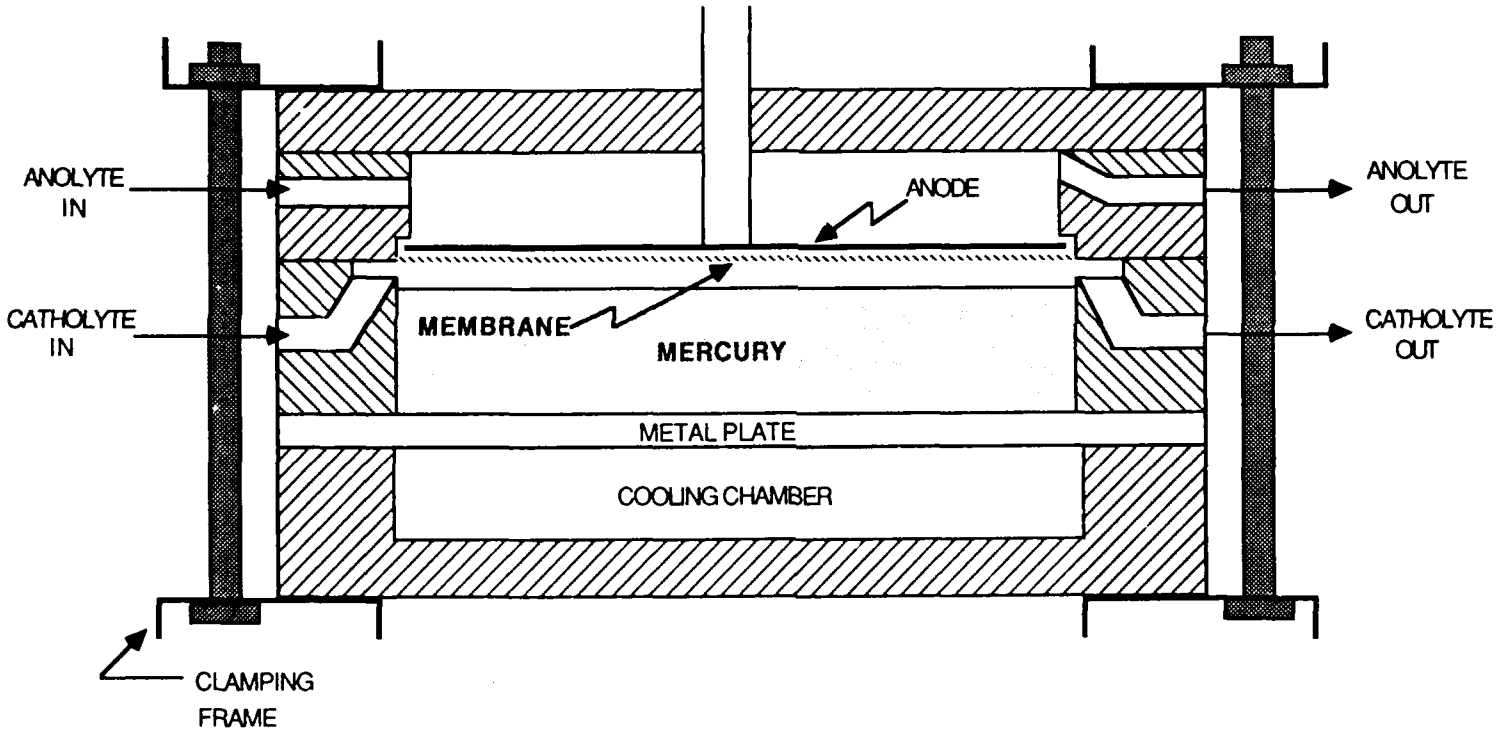
HAN ELECTROSYNTHESIS

CONCERNS WITH 100 AMP CELL DESIGN

- Possible leakage at corners between membrane and cell top
- 70 bolts holding membrane to cell top (70 holes)
- Membrane sag
- Leakage at glue joints
- Machining time (approximately 20 pieces)

HAN ELECTROSYNTHESIS

REVISED 100 AMP CELL DESIGN



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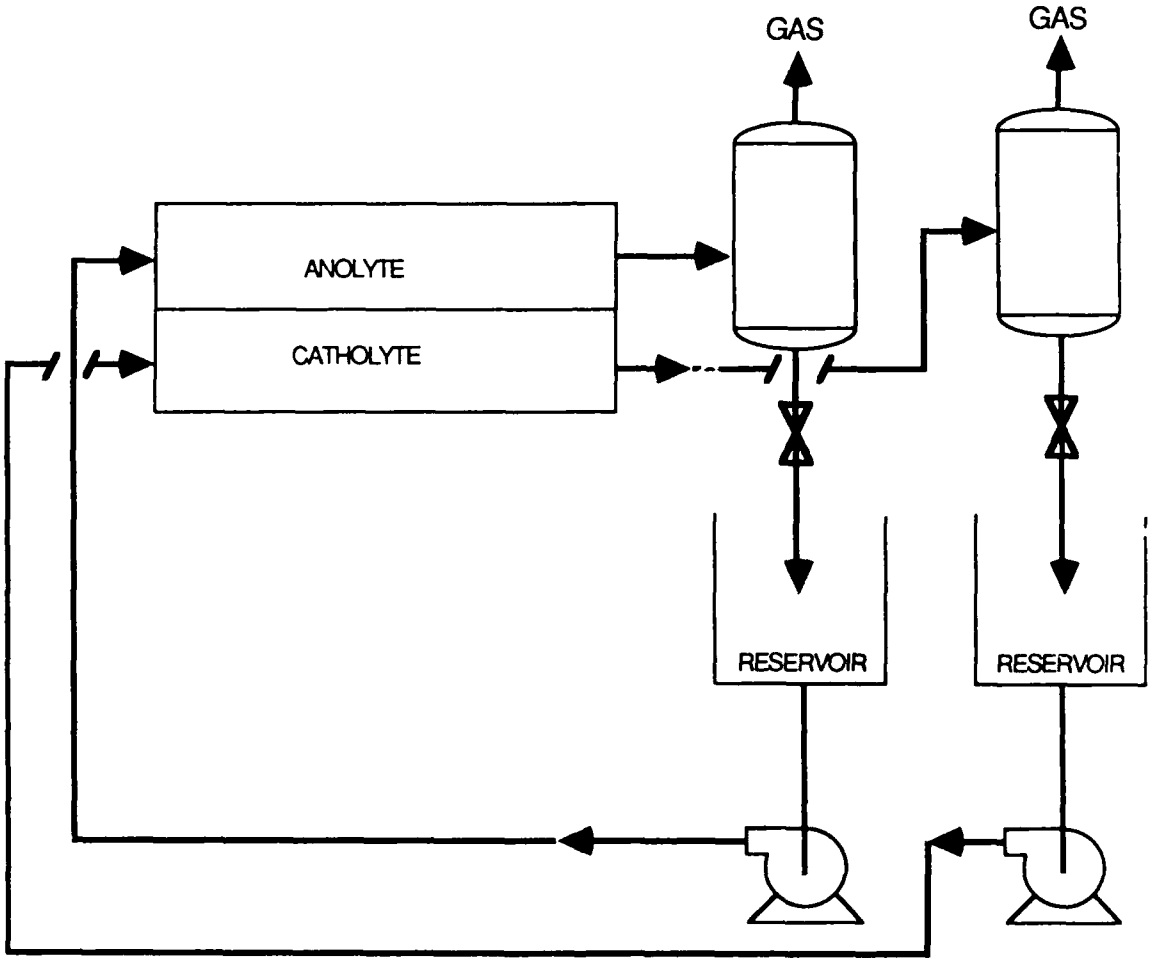
HAN ELECTROSYNTHESIS

100 AMP GAS-LIQUID SEPARATORS



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HAN ELECTROSYNTHESIS

REVISED 100 AMP CELL DESIGN

IMPROVEMENTS	ADVANTAGES
• Membrane Seal	• Leak Detection
• Reduced Anode/Cathode Gap	• Lower Energy Costs
• No Membrane Sag	• Better Flow Patterns
• Less Machining	• Less Construction Time/Cost
• No Glue Joints	• Eliminate Leak Potential
• Multiple Inlet/Outlet Ports	• Flexibilty
• Closer To Full Scale Design	• Scale-Up Ease
• External Gas/Liquid Separators	• Measure Off-Gas For Material Balances

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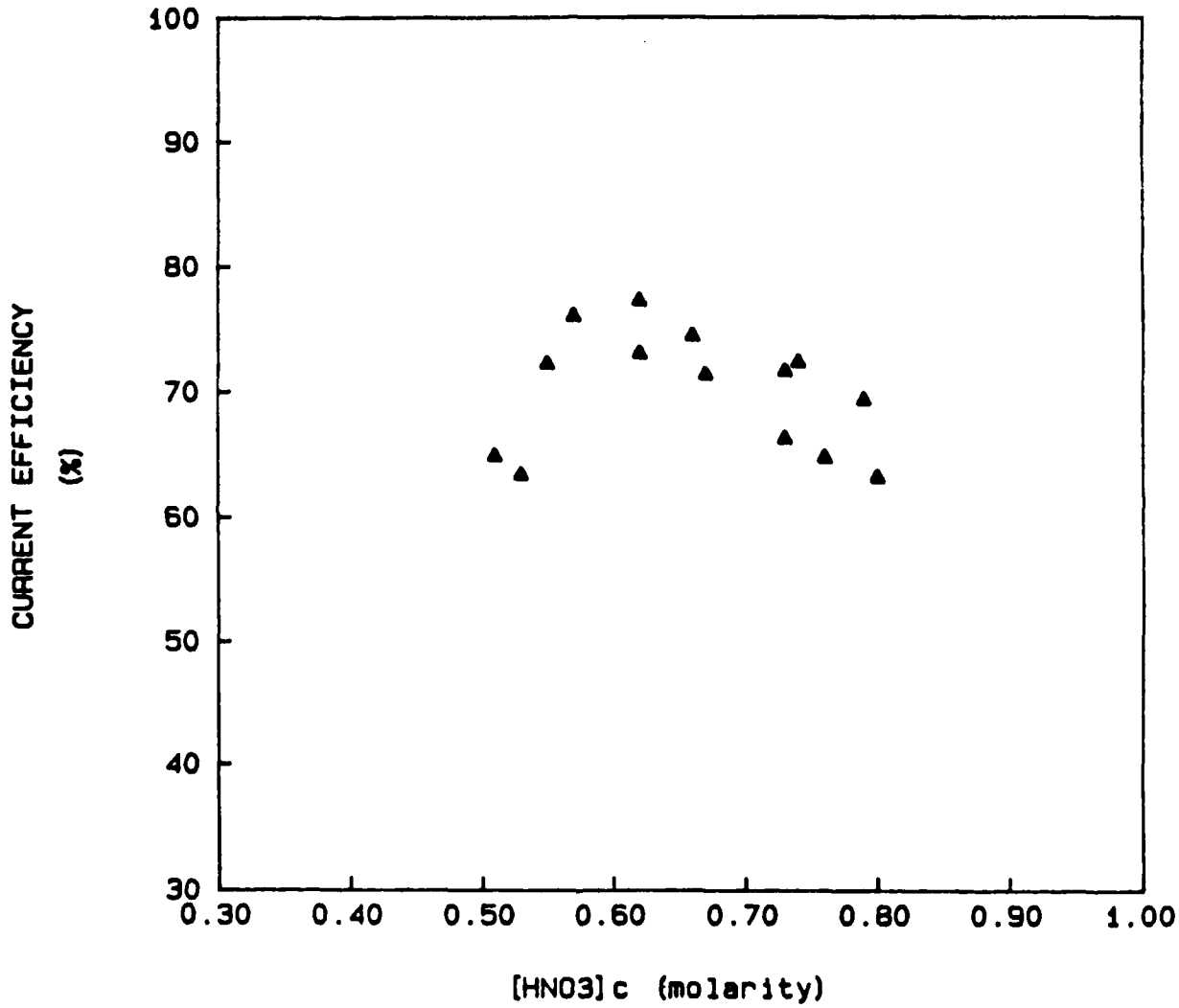
HAN ELECTROSYNTHESIS

HAN RUN #106 : CURRENT EFFICIENCY vs $[HNO_3]_c$
1.5 kA/m^2, 27 ^oC



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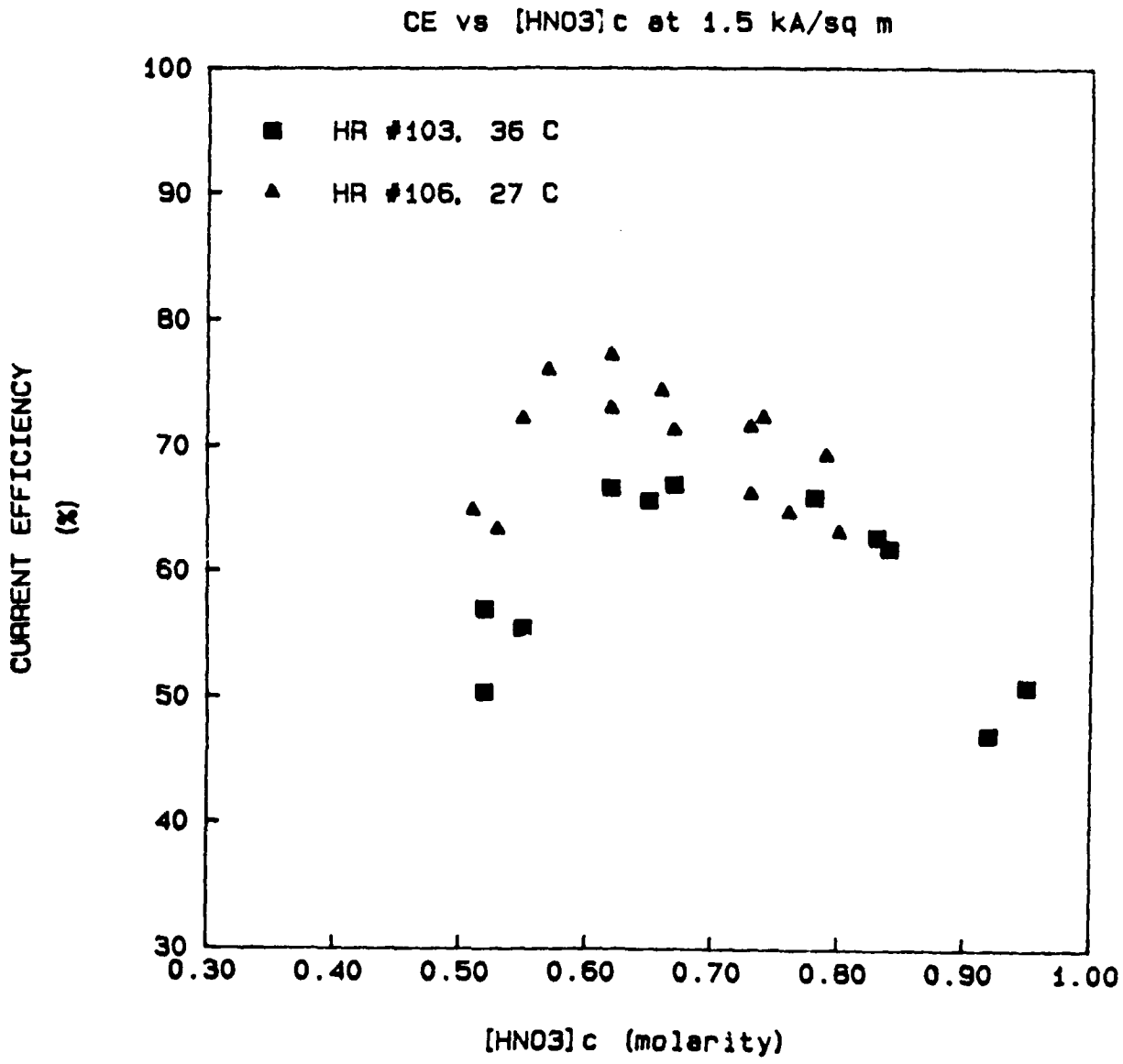
HAN ELECTROSYNTHESIS

COMPARISON : HAN RUN #106 vs HAN RUN #103



HAN ELECTROSYNTHESIS

HAN RUN #106 : TRACE METALS ANALYSIS

COMPOUND	CATHOLYTE @ 82,000 A-HRS	ANOLYTE @ 82,000 A-HRS	MERCURY @ 82,000 A-HRS
NICKEL	<0.2 ppm	<0.05 ppm	<1 ppm
IRON	<0.03	0.03	<0.3
COPPER	<0.05	<0.02	<1
CALCIUM	0.06	0.02	<0.2
SODIUM	<0.3	<0.1	<2
CHROMIUM	0.06	<0.02	<0.4
SILVER	<0.06	<0.03	<0.4
PLATINUM	<0.3	2.6	<2
NIOBIUM	<0.6	<0.25	<4
TITANIUM	<0.03	<0.02	<0.25
RUTHENIUM	<0.3	<0.1	<2
PALLADIUM	<0.4	<0.2	<3
MERCURY	<0.07	1.2	-
IRIDIUM	<0.2	<0.1	<2
ALUMINUM	<0.2	<0.1	<2
TOTAL TRANSITION METALS	<2.50 ppm		

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HAN ELECTROSYNTHESIS

COMPARATIVE PERFORMANCE CHARACTERIZATION

(current density = 1.5 kA/m^2)

	ORIGINAL CELL	REVISED CELL
CURRENT EFFICIENCY	67%	77%
YIELD OF HAN FROM NITRIC ACID	72%	92%
HAN PRODUCTION RATE	2.87 kg HAN/day	3.35 kg HAN/day
MERCURY TEMPERATURE	36 ^{o}C	27 ^{o}C

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HAN ELECTROSYNTHESIS

ACHIEVEMENTS

CONTRACT SPECIFICATION	ACHIEVED
• 1 ELECTROLYTIC CELL	• 2 ELECTROLYTIC CELLS
• 2.8 MOLAR CONCENTRATION	• ~3.0 MOLAR CONCENTRATION
• 1 KG HAN/DAY (70% CE AT 0.5 KA/M^2)	• 3.35 KG HAN/DAY (77% CE AT 1.5 KA/M^2)
• < 1 WT% IMPURITIES	• < 0.5 WT% IMPURITIES
• < 5 PPM TRANSITION METALS	• < 2.5 PPM TRANSITION METALS
• < 0.1 WT% HNO_3	• ~ 3.3 WT% HNO_3 (DESIGNED NEUTRALIZATION PROCESS)

NEUTRALIZATION AND REMOVAL OF FREE NITRIC ACID IN HYDROXYLAMMONIUM NITRATE

Ronald L. Dotson

Olin Corporation

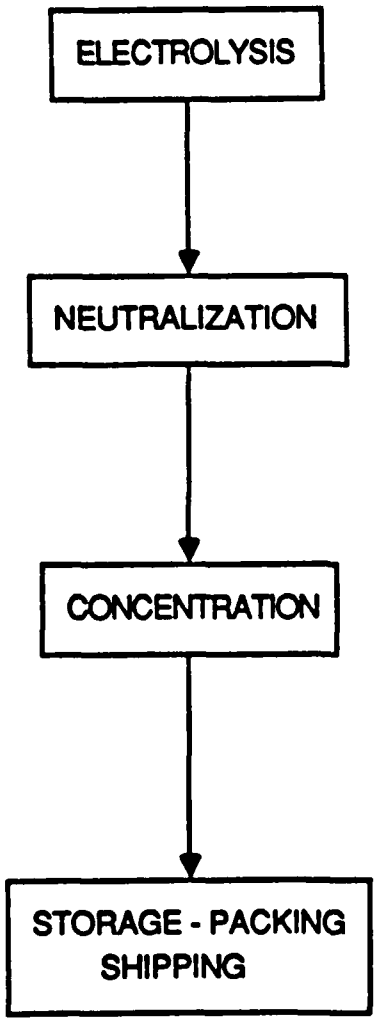
4th ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT
STRUCTURE AND PROPERTIES
US ARMY BALLISTIC RESEARCH LABORATORY
ABERDEEN PROVING GROUND, MD
30 AUG - 1 SEP 88

Title of Paper: Neutralization of High-Purity Hydroxylammonium Nitrate
Presentation Time Request: 30 minutes
Type of Paper: State of Art
Speaker's Name: Dr. Ronald L. Dotson **Phone Number:** (203) 789-5284
Affiliation/Address: OLIN Chemicals
24 Science Park
New Haven, CT 06511
Co-author(s) name(s): Dr. James A. Leistra, James H. Barnatt

ABSTRACT:

Olin developed and demonstrated a process to remove free nitric acid from the HAN product produced in the electrolytic cell. The neutralization step involves a single unit operation: weak-base ion exchange. Weak-base resins remove free nitric acid without decomposing HAN. Several resins were tested and evaluated in an extensive laboratory program. HAN product, meeting the contract specification of less than 0.1 wt% HNO_3, was obtained by controlling the pH of the neutralized product.

HAN PROCESSING UNIT OPERATIONS



DECOMPOSITION REACTIONS OF HYDROXYLAMMONIUM NITRATE

BASIC CONDITIONS:

$$4NH_2OH \longrightarrow N_2O + 2NH_3 + 3H_2O$$

ACIDIC CONDITIONS:

$$3NH_2OH \longrightarrow N_2 + NH_3 + 3H_2O$$

NEUTRALIZATION OF FREE NITRIC ACID IN HYDROXYLAMMONIUM NITRATE

REACTIONS:

OPERATION:

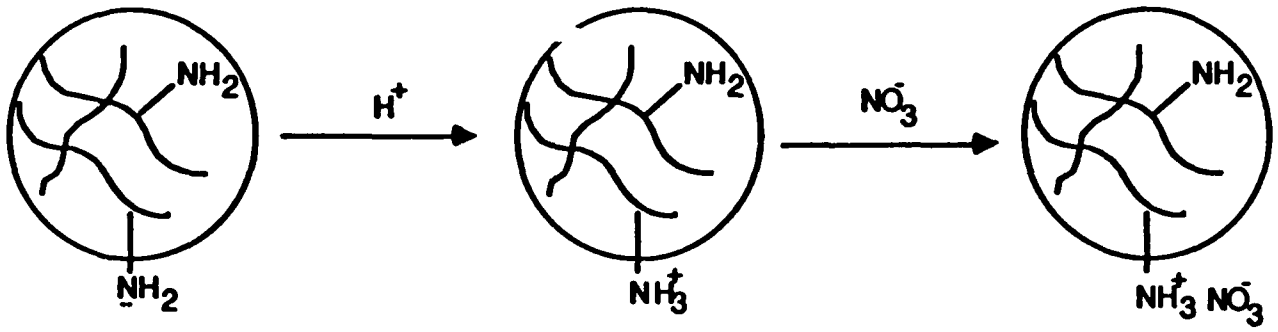
$$\sim CH_2 - C_6H_3(NH_2)_2 + 2HNO_3 \longrightarrow \sim CH_2 - C_6H_3(NH_3)_2\ 2NO_3$$

REGENERATION:

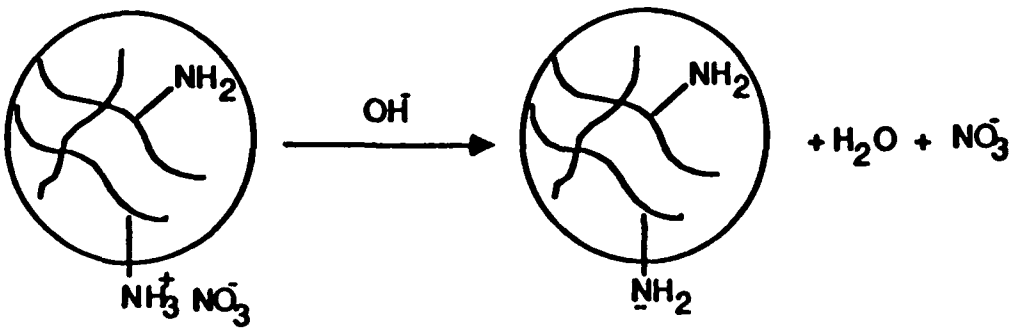
$$\sim CH_2 - C_6H_3(NH_3)_2\ 2NO_3 + 2NH_4OH \longrightarrow \sim CH_2 - C_6H_3(NH_2)_2 + 2NH_4NO_3 + 2H_2O$$

REMOVAL OF NITRIC ACID FROM HAN

OPERATION:

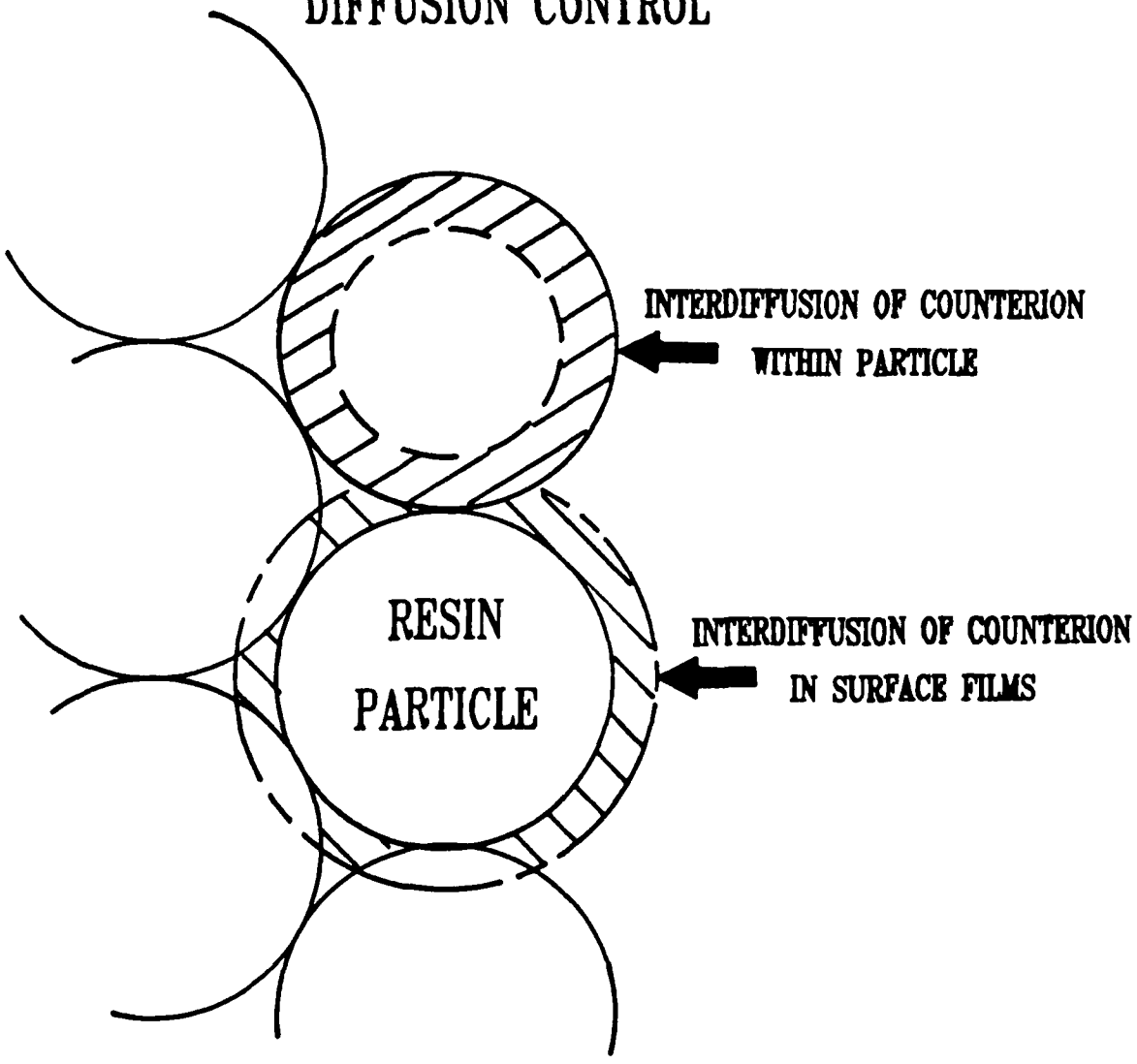


REGENERATION:



KINETICS OF ION EXCHANGE

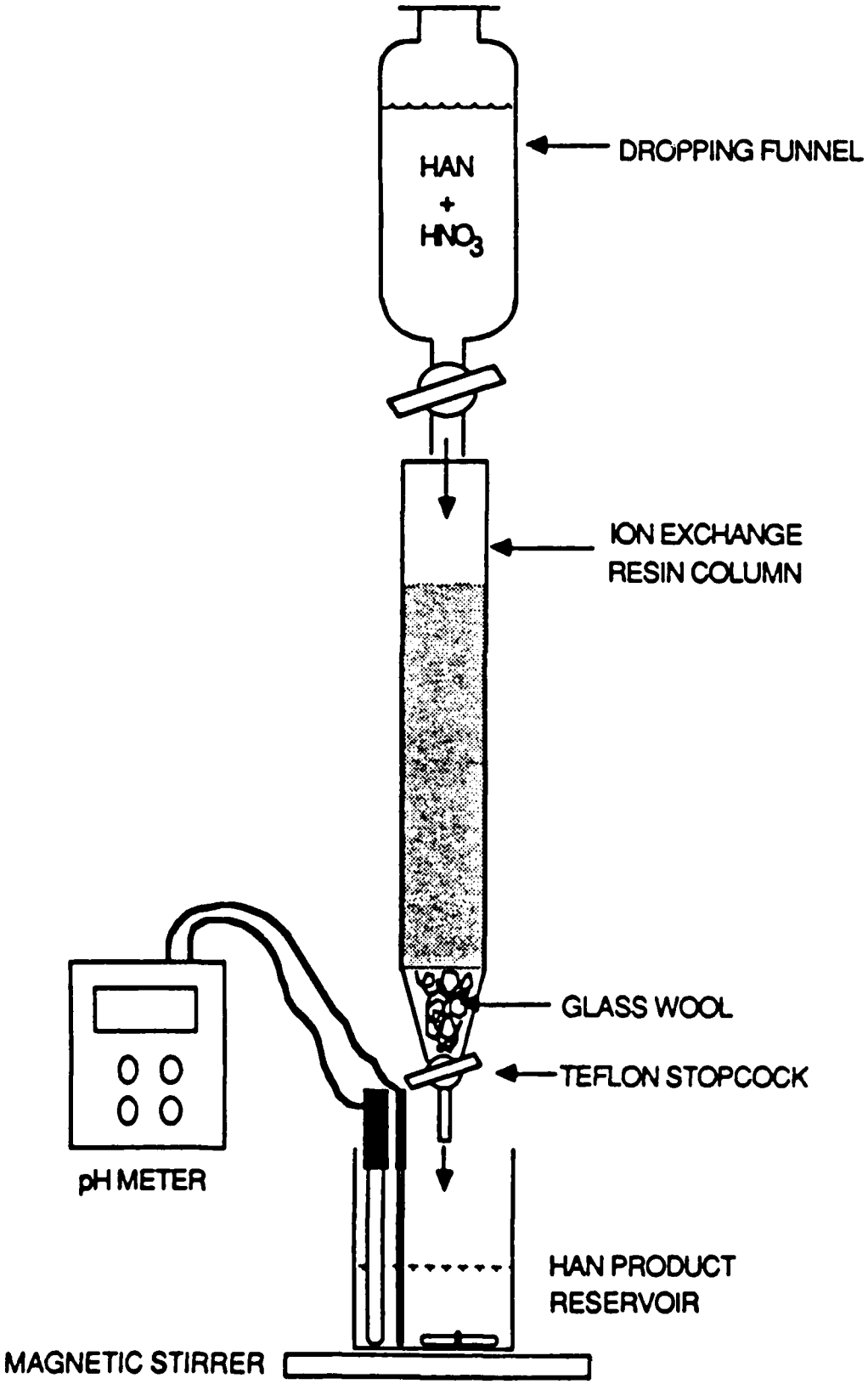
DEPENDS ON FILM AND/OR PARTICLE DIFFUSION CONTROL



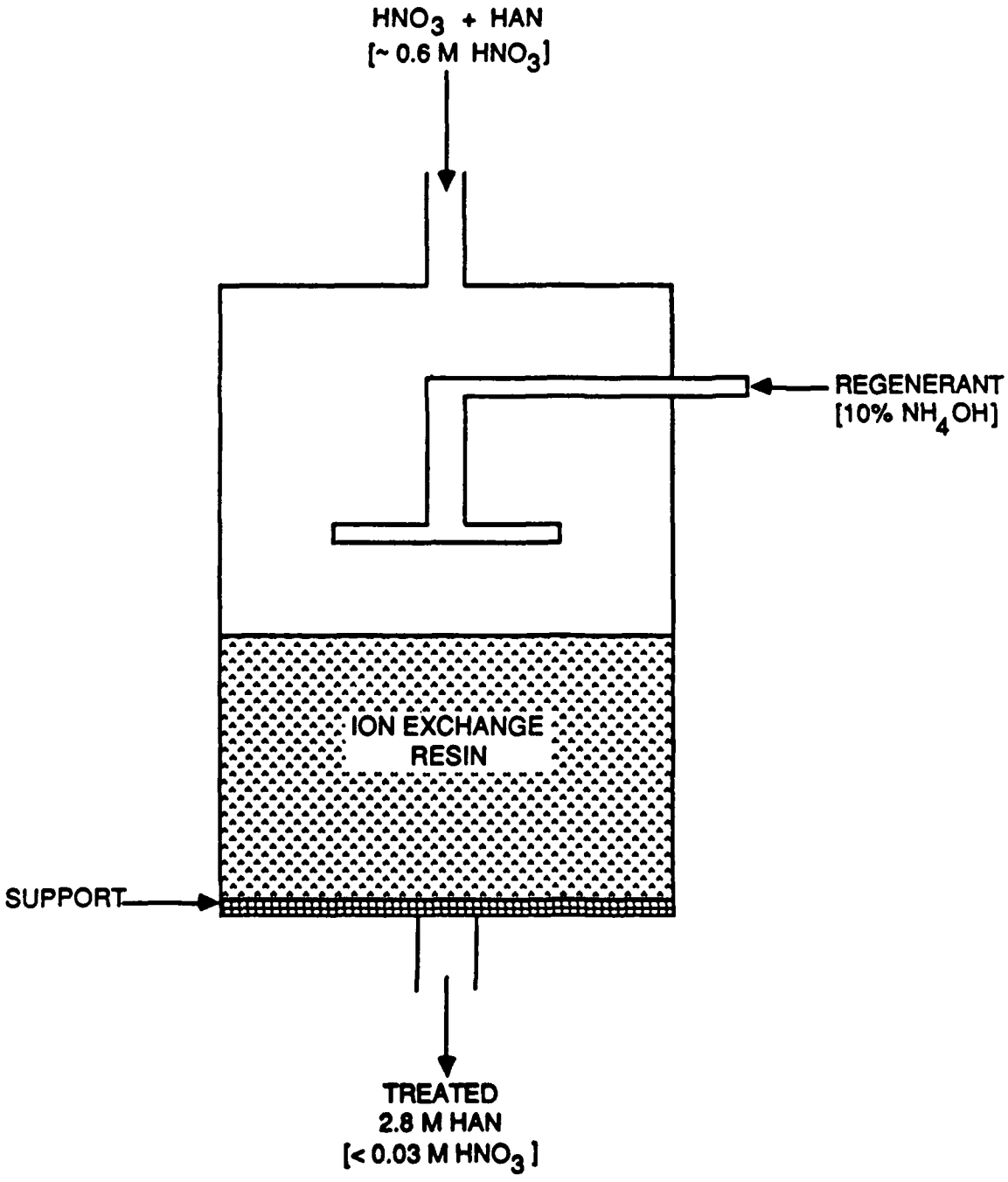
OPERATION AND REGENERATION OF ION EXCHANGE RESINS REQUIRES:

* Backwash
* Regeneration
* Push out
* Rinse
* Load

NEUTRALIZATION OF FREE NITRIC ACID EXPERIMENTAL APPARATUS

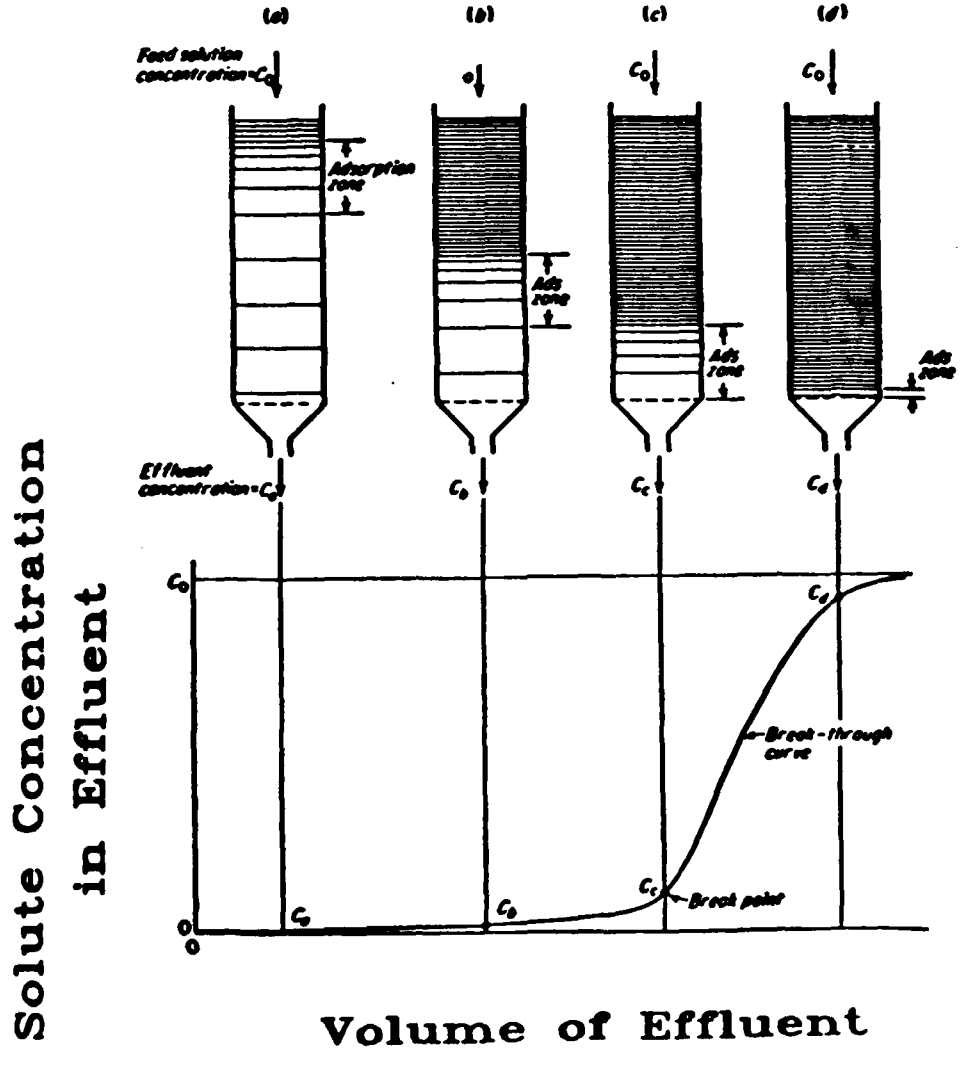


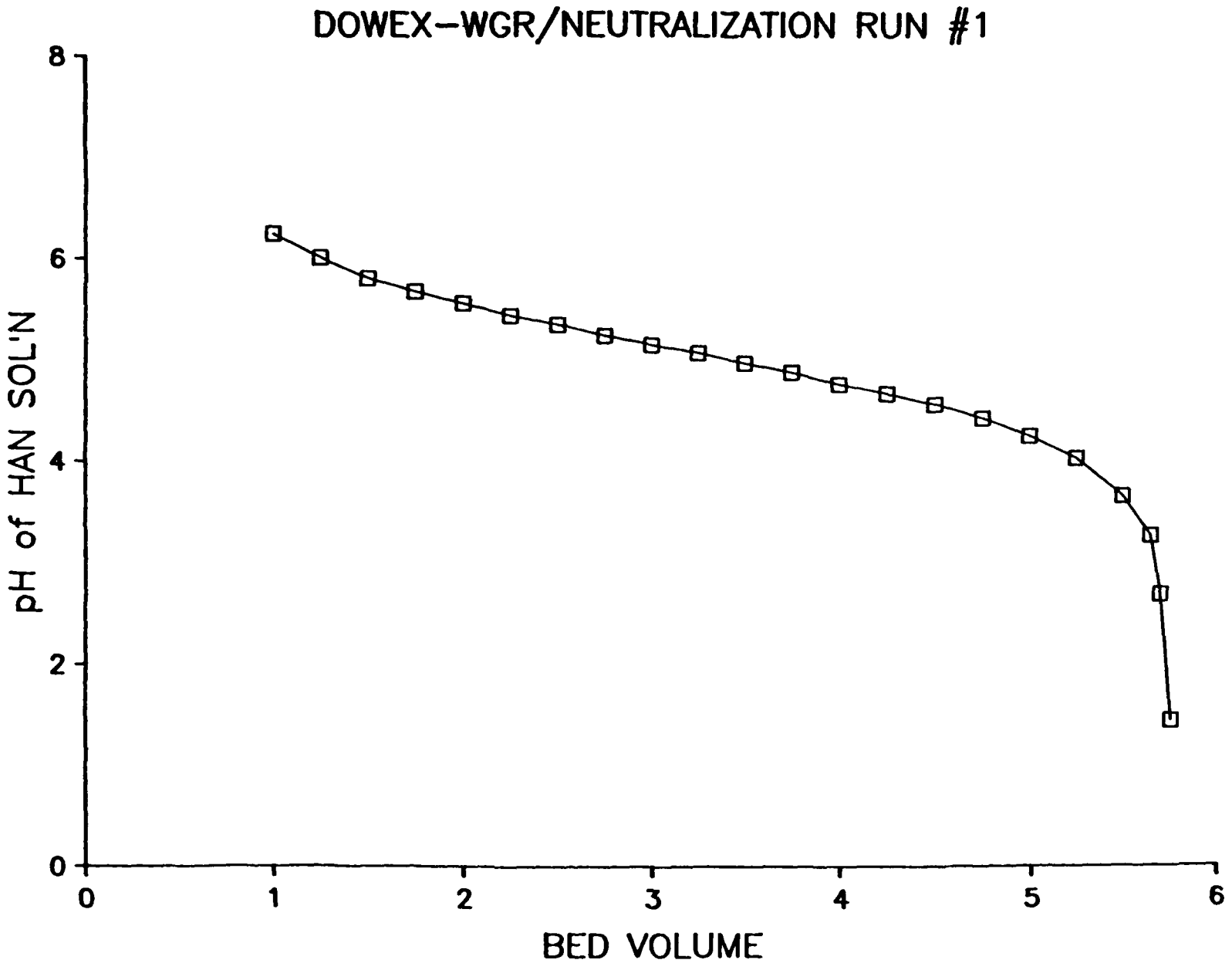
EQUIPMENT FOR ION EXCHANGE RESIN

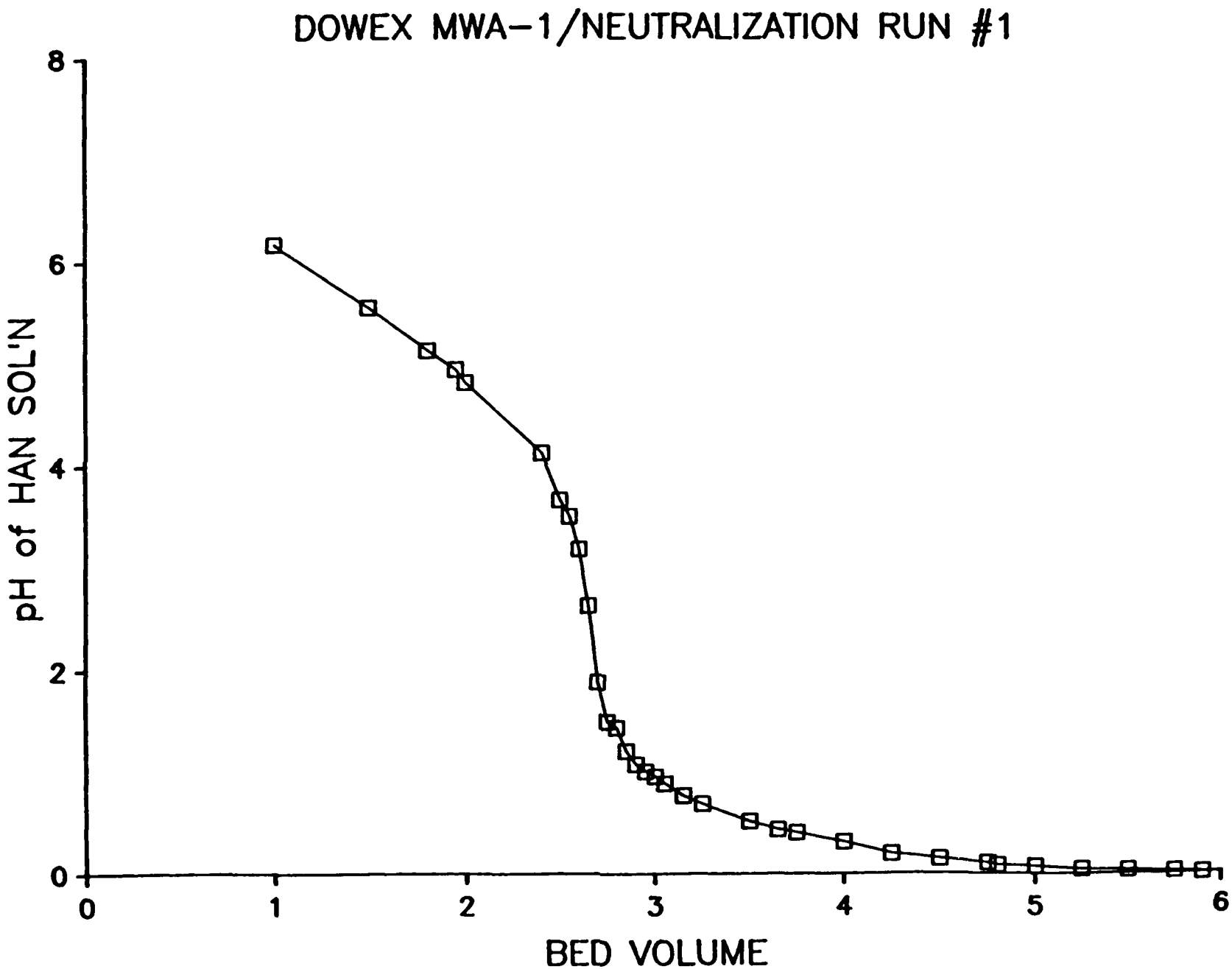


Operating ion exchange resins requires precise determination of the *breakthrough capacity* as a function of operating life, from the *adsorption wave.*

THE ADSORPTION WAVE




DOWEX-WGR/NEUTRALIZATION RUN #1
pH of HAN SOL'N
BED VOLUME
0
2
4
6
8
0
1
2
3
4
5
6


DOWEX MWA-1/NEUTRALIZATION RUN #1
pH of HAN SOL'N
BED VOLUME
0
2
4
6
8
0
1
2
3
4
5
6

BED VOLUMES PASSED THROUGH COLUMN

RESIN	BED VOLUMES (VOL. HAN / VOL. RESIN)
DOWEX MWA 1	3.2
DOWEX M 44	2.7
DOWEX M 43	3.5
AMBERLITE IRA 68	3.7
DOWEX WGR	5.8
DUOLITE A 7	3.9

NEUTRALIZATION RESULTS

		HAN NEUTRALIZED WITH RESINS						
COMPOUND	HAN UNNEUTRALIZED	IRA-68 RUN #2	M-43 RUN #1	M-43 RUN #2	M-44 RUN #2	MWA-1 RUN #2	WGR RUN #1-35	WGR RUN #2
TOC	<50 ppm	<50 ppm	<50 ppm	<50 ppm	<50 ppm	<50 ppm	<50 ppm	<50 ppm
NICKEL	<0.2	<0.2	<0.3	<0.3	<0.3	<0.3	<0.2	<0.2
IRON	0.06	0.13	0.23	0.1	0.3	0.09	0.22	0..09
COPPER	<0.05	<0.05	<0.1	<0.1	0.1	<0.1	<0.05	<0.05
CALCIUM	0.6	0.75	0.8	0.7	0.9	3.2	0.7	0.7
SODIUM	0.4	0.4	0.35	0.53	1.1	4.6	0.46	0.4
CHROMIUM	<0.05	<0.05	<0.10	<0.1	<0.1	<0.1	<0.05	<0.05
SILVER	<0.06	<0.08	<0.1	<0.1	<0.1	<0.1	<0.06	<0.06
PLATINUM	<0.3	<0.3	<0.5	<0.5	<0.5	<0.5	<0.3	<0.3
NIOBIUM	<0.6	<0.6	<1.5	<1.5	<1.5	<1.5	<0.6	<0.6
TITANIUM	0.19	0.18	0.2	0.2	0.2	0.18	0.2	0.19
RUTHENIUM	<0.3	<0.3	<0.5	<0.5	<0.5	<0.5	<0.3	<0.3
PALLADIUM	<0.4	<0.4	<0.8	<0.8	<0.8	<0.8	<0.4	<0.4
MERCURY	<0.07	<0.07	-	-	<0.065	-	0.4	<0.07
IRIDIUM	<0.2	<0.2	<0.5	<0.5	<0.5	<0.5	<0.2	<0.2
ALUMINUM	0.3	0.3	-	-	-	-	0.5	0.3
EXCESS HNO3	0.6 M	0.03	0.03	0.03	0.03	0.03	0.03	0.03

SUMMARY AND CONCLUSIONS

- OLIN'S WEAK BASE RESIN PROCESS IS VERY EFFECTIVE IN REMOVING EXCESS FREE NITRIC ACID FROM HAN.

- SIX RESINS HAVE BEEN TESTED AND OTHER COMMERCIAL RESINS EVALUATED.

- FUTURE WORK WILL FOCUS ON APPLIED ENGINEERING AND PROCESS DEVELOPMENT.

ABSTRACT OF PRESENTATION TO 4TH ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT STRUCTURE AND PROPERTIES

BRL/APG

August 30 - September 1, 1988

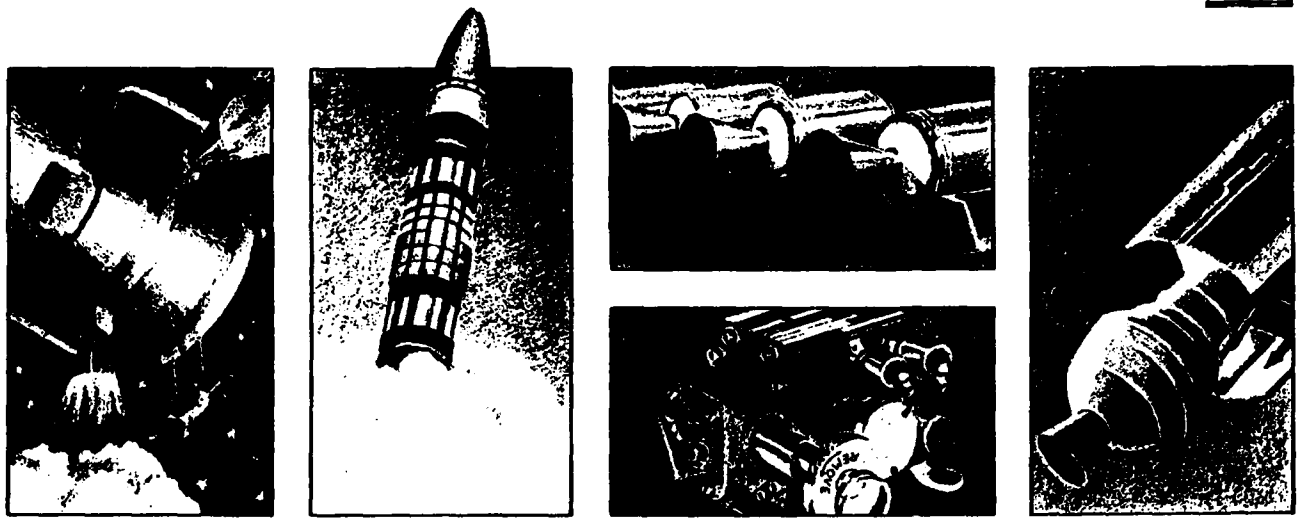
R. A. Biddle

PRODUCING HAN-BASED LIQUID GUN PROPELLANTS

Since 1978, a number of liquid gun propellants (LGP) have been produced at the Elkton Division of Morton Thiokol, Inc. These have included NOS365, LGP1776, LGP1845 and LGP1846 which have been prepared in batch process on various scales from nominal 1 to 2000 kg levels. The process involves concentration of an aqueous hydroxylammonium nitrate (HAN) solution and synthesis of the appropriate alkyl ammonium nitrate (AAN) salt. Handling of these materials and blending them together in all glass or inert plastic systems has allowed adequate control of trace metal contamination. Typical examples of this process will be discussed along with results of various analyses used for both in-process materials and the product LGP.

MORTON THIOKOL, INC.

Elkton Division



PRODUCING HAN-BASED LIQUID GUN PROPELLANTS

R. A. BIDDLE
MORTON THIOKOL, INC.
ELKTON DIVISION
ELKTON, MD

Morton Thiokol Inc., Elkton Division P.O. Box 241, Elkton, Maryland 21921-0241 (301) 398-3000

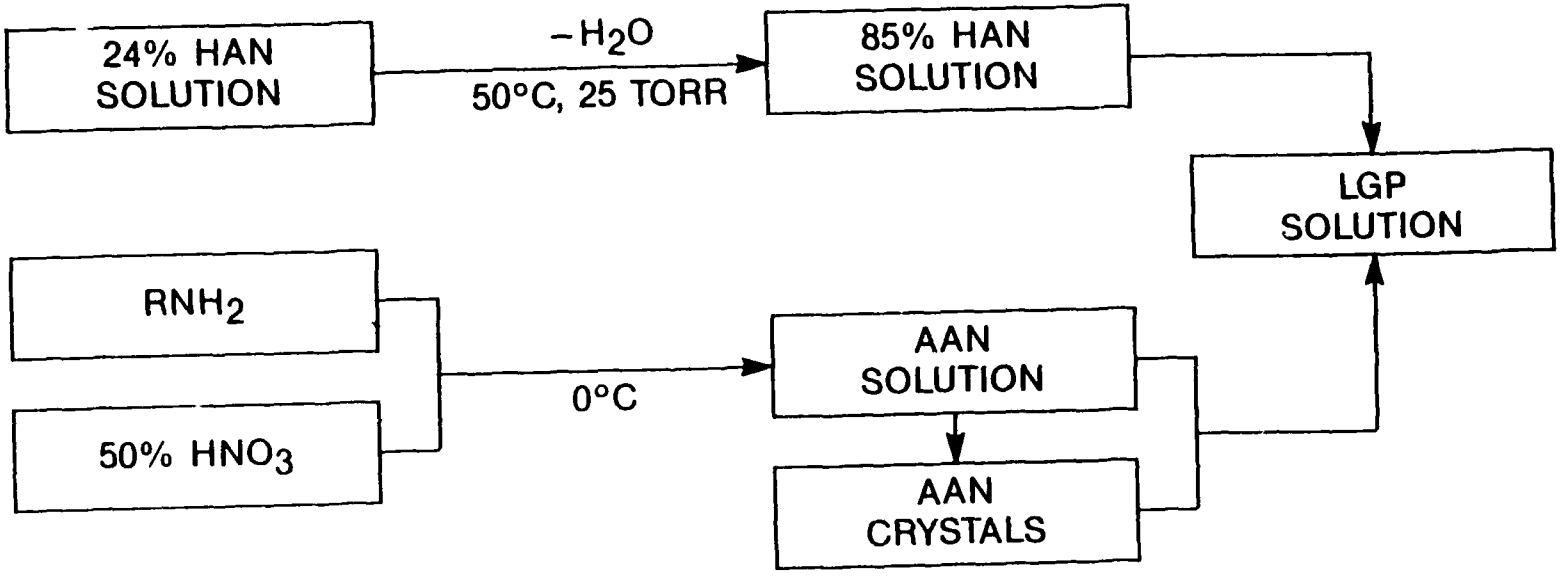
LIQUID GUN PROPELLANT COMPOSITIONS PRODUCED

NOS 365	500 kg
LGP 1776	20 kg
LGP 1845	2200 kg
LGP 1846	6000 kg

LAB SCALE TO PILOT PLANT

- 5-liter evaporator / 2-liter resin flask
- 20-liter evaporator / 50-liter glass reactor
- 50-gal glass-lined reactor / 50-liter glass reactor
- 500-gal glass-lined reactor / 50-gal glass-lined reactor

GENERAL PROCESS SCHEME



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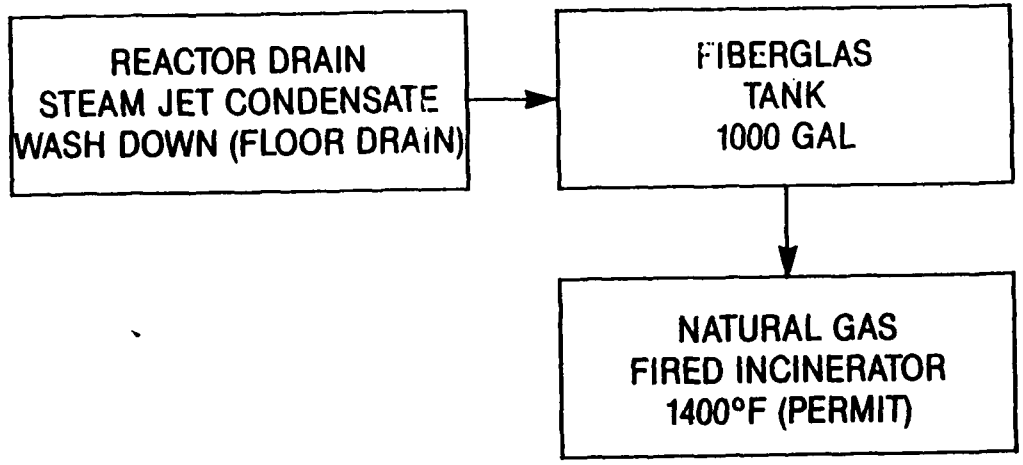
Elkton Division

SA24646

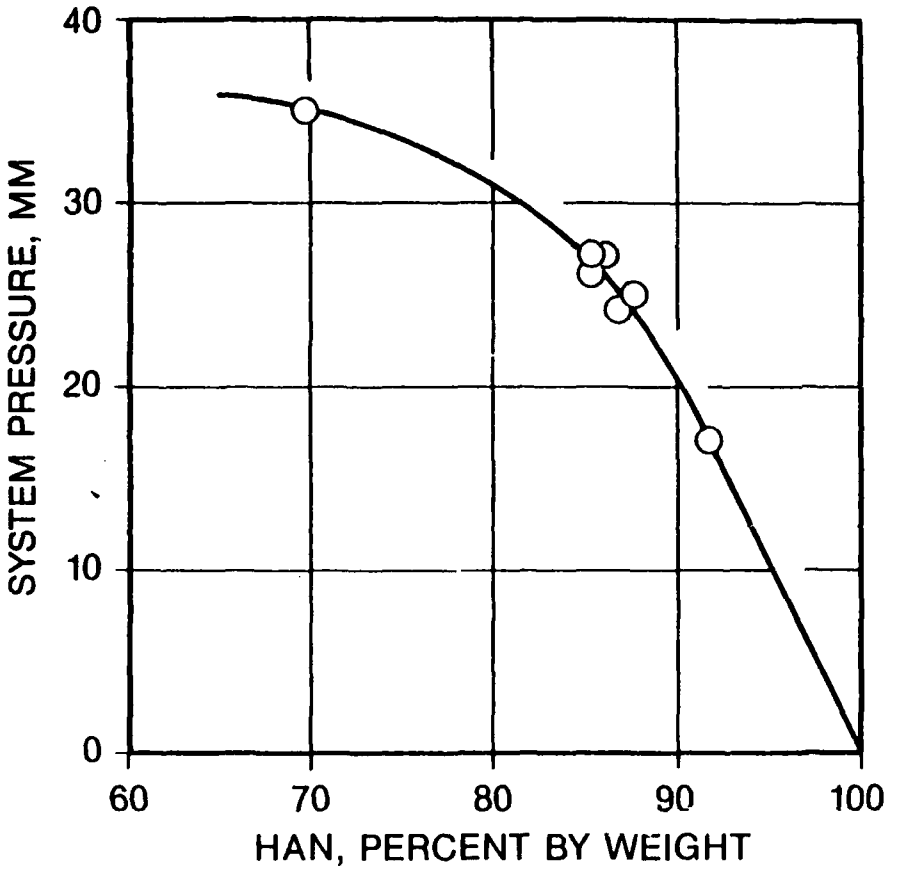
WASTE CONTROL



CONCENTRATION OF HAN SOLUTION

- Source: Southwestern Analytical Chemicals
- Method:
  - Vacuum evaporation at ~50°C
  - Glass-lined reaction vessel
  - Teflon / PVC / ABS components
- Concentration:
  - Upper limit ~95% (saturated solution at ambient temperature)
  - Usual concentration 80-85%

HAN CONCENTRATIONS



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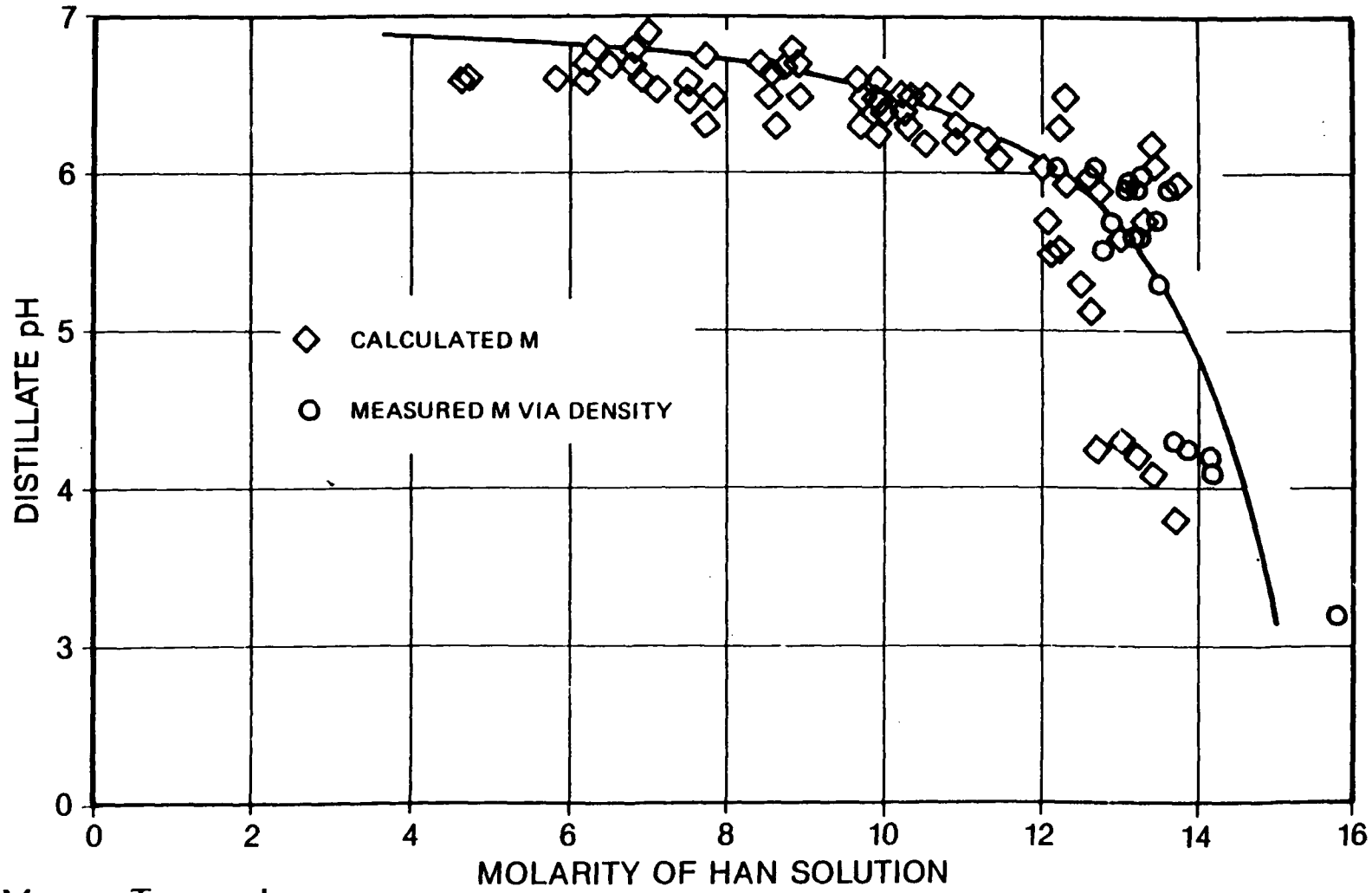
SA5376A

EFFECT OF HAN CONCENTRATION ON DISTILLATE pH



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Elkton Division

SA15736A

STABILITY OF HAN SOLUTION

NOMINAL CONCENTRATION (M)	THERMAL STABILITY DTA (0.3G, 10°C/MIN) SELF HEATING		DETONATION SUSCEPTIBILITY 43 CC SAMPLE (NO. 8 CAP + 5G TETYL BOOSTER) INDENTATION OF Al PLATE, IN.
	ENDOTHERM, °C	EXOTHERM, °C	
2.8	92	~198	0.01
5	96	196	0.02
9	98	192	0.01
13	97	187	0.02
15	100	168	0.01

CONCENTRATION OF HAN SOLUTION IN THE 50-GALLON REACTOR

BATCH	WT, LB	BEFORE NO_3^- AS % HAN	EXCESS ACID	Fe, PPM	WT, LB	AFTER NO_3^- AS % HAN	EXCESS ACID	Fe, PPM
3	358	23.5	0.003	0.02	102	84.9	0.014	0.08
4	371	23.4	0.007	0.19	116	74.1	0.013	0.19
5	393	24.7	0.013	0.17	102	85.1	0.004	0.25
6	425	26.2	0.005	0.10	72	86.0	0.027	0.03
7	364	23.6	0.004	0.18	96	78.3	0.003	0.12
8	370	24.0	0.003	0.16	63	75.3	0.005	0.08

RECENT EXPERIENCE IN HAN CONCENTRATION

- 500-gal Pfaudler Glasteel reactor
- Two-stage Schutte & Koerting steam jet vacuum system

Lot No.	Batch Size, drums	Final Concentration, % HAN	Contamination Level	
			Free Acid, M	Fe, ppm
87-500-001	9	86.6	0.02	4.3
-002	9	81.2	0.02	1.2
-003	9	82.5	0.03	0.9
-004	9	82.6	0.03	1.0
-005	10	84.7	0.02	1.1
88-500-001	10	81.0	0.02	1.2
-002	9	81.0	—	0.7
-003	10	86.1	0.02	1.4
-004	10	86.1	0.03	3.0

SYNTHESIS OF AAN SALTS

$$RNH_2 + HNO_3 \xrightarrow{H_2O} RNH_3^{\oplus}\ NO_3^{\ominus}$$

RNH_2 = IPA (L), TMA (G), TEA (L)

$$\text{IPA (L)} \xrightarrow[H_2O]{HNO_3\ 1:1} \text{IPAN} \xrightarrow[\text{STIR}]{\text{CHILL}} \text{IPAN (S)}$$

RXN POT $_t$ < 43°C

$$\text{TMA (G)} \xrightarrow[H_2O]{HNO_3\ 1:1} \text{TMAN} \xrightarrow[0^oC]{\text{CHILL TO}} \text{TMAN (S)}$$

RXN POT$_t$ < 40°C

$$\text{TEA (L)} \xrightarrow{HNO_3\ 2:1} \text{TEAN} \xrightarrow[\text{STIR}]{\text{CHILL}} \text{TEAN (S)}$$

RXN POT $_t$ < 25°C

ANALYSES USED FOR CONTROL

Density	hydrometer
NO_3^- content	UV (302 nm)
Water content	Karl Fischer
Amine content	Acid titration Oxime titration
Metal contamination	Atomic absorption

COMPARISON OF LGP 1846 LOTS

Lot No.	-01	-02	-03	-04
Density, g/cc	1.441	1.430	1.440	1.430
H_2O (via KF), %	19.8	20.3	19.7	20.2
Total NO_3^-, moles/100g	0.7270	0.7258	0.7275	0.7234
Acid/oxime, moles/100g	0.7279	0.7301	0.7279	0.7272
HAN, %	60.3	61.1	61.0	61.1
TEAN, %	21.0	19.1	19.6	19.4
Fe, ppm	3	1	0.8	0.7

TYPICAL ANALYTICAL RESULTS

	UV (NO_3^-)	Titration		Karl-Fisher % H_2O
		Acid (without acetone)	Oxime (with acetone)	
HAN Lot 88-500-004 Drum 3	85.75 ±0.15%	85.64 ±0.21%	85.63 ±0.09%	14.3 ±0.1
TEAN Lot 88-50-008/010	79.64 ±0.00%	79.69 ±0.17%	79.71 ±0.10%	20.0 ±0.5

ANALYSES OF LGP 1845 SAMPLE

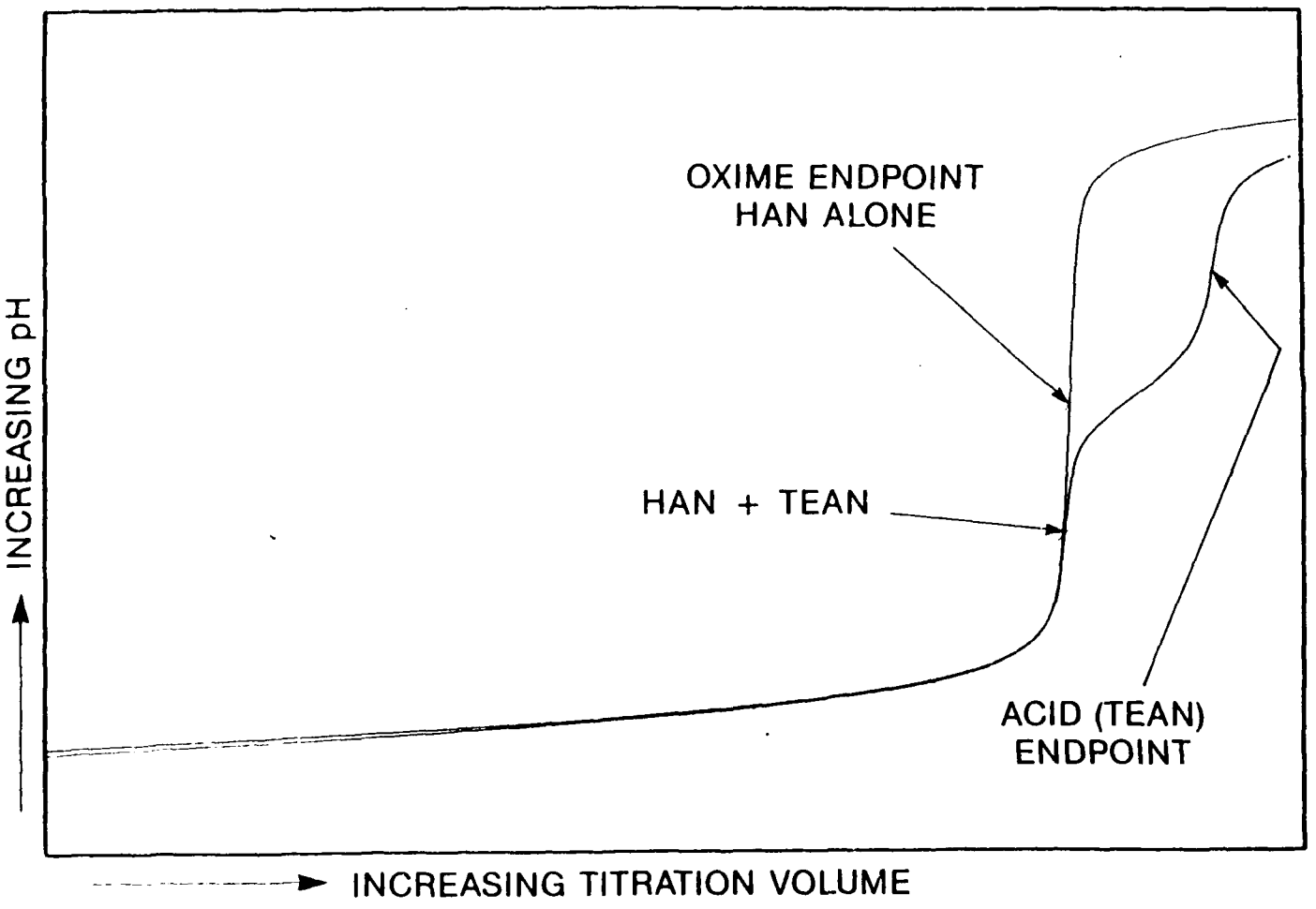
	UV (NO_3^-) (moles / 100g)	Titration		K-F (% H_2O)
		(% HAN)	(% TEAN)	
Target	0.7525	63.2	20.0	16.8
Theoretical	0.7511	63.08	20.02	16.9
Experimental	0.7589	62.74	21.38	17.3
1σ	±0.0006	±0.09	±0.06	±0.1

ANALYSIS OF HAN-TEAN MIXTURES

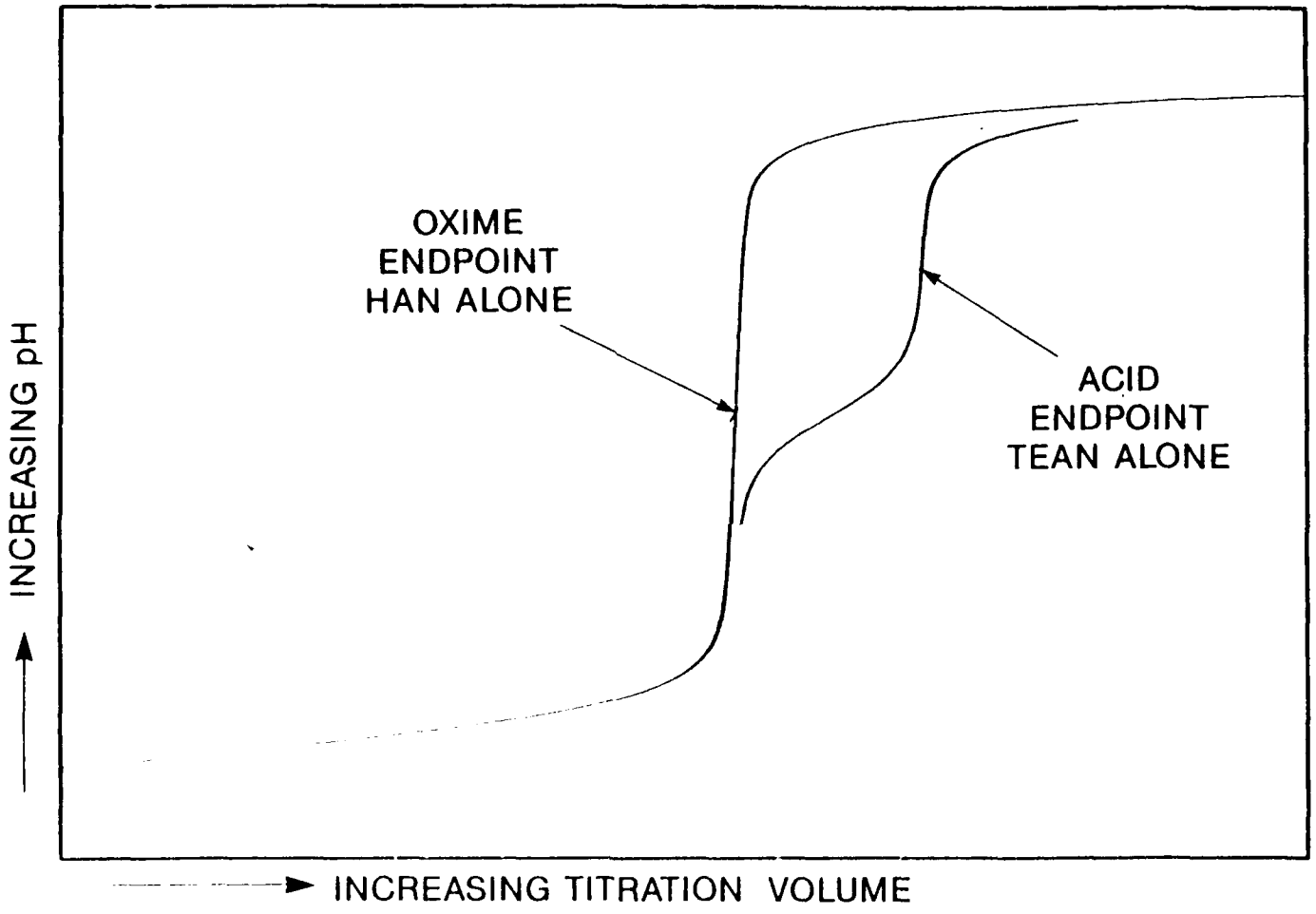
Volume of Solutions		Percent Found	
85% HAN	27% TEAN	HAN	TEAN
1	0	100.10	—
		99.98	—
1	1	99.28	107.5
		99.40	106.0
1	2	99.33	105.7
		99.50	105.7
1	2*	100.2	101.9
		100.1	103.1

*Titrated separately from oxime break

COMBINED ACID / OXIME TITRATION CURVES



SEPARATE ACID / OXIME TITRATION CURVES



MORTON THIOKOL, INC.
Elkton Division

SA24694

REVERSIBILITY OF OCULAR IRRITATION OF LP1846

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Division of Toxicology
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ABSTRACT

LP1846 is a liquid propellant under development by the U.S. Army. The purpose of this study was to determine whether LP1846 is an ocular irritant, and if so, whether flushing the eye with water 10 seconds or 30 seconds after exposure will reduce the ocular toxicity. The compound was tested in the laboratory rabbit.

The results of this study indicate that LP1846 is an ocular irritant. Observations included conjunctival redness, chemosis, iritis, corneal opacities, and neovascularization of the cornea. All lesions were reversible except for the neovascularization. Washing the eye at 30 seconds alleviated the conjunctival and iritic symptoms and prevented the development of corneal lesions. Immediate washing at 10 seconds was even more successful at alleviating the symptoms. However, even after washing, the ocular irritation potential of LP1846 was sufficient to produce a positive response.

OBJECTIVE

The objective of this study was to determine the ocular irritation potential of LP1846 both with and without washing. The results would demonstrate the effectiveness of washing in preventing ocular injury after accidental occupational exposure.

ANIMALS

- New Zealand White Rabbits
- Hazleton Research Products
- Weighed 2.6 kg to 3.4 kg on dosing day

LP1846

- Lot # 50-4
- Requested from:

US Army Biomedical Research and Development Laboratory
Fort Detrick, Frederick, Maryland

- 60.8% Hydroxylammonium Nitrate (HAN)
- 19.2% Triethanol Ammonium Nitrate (TEAN)
- 20% Water

GROUP ASSIGNMENT

- No-Wash Group
- Wash-at-30-Seconds Group
- Wash-at-10-Seconds Group

EXPOSURE CONDITIONS

- One tenth millileter (145.3 mg)
- Instilled into conjunctival cul-de-sac
- Eyelid gently held closed for 1-2 seconds

TEST PROCEDURES

- Eyes were examined a day before dosing
- Untreated eye served as the control
- Washing was accomplished by gently squirting room temperature water onto the eye
- Wash period was for 60 seconds
- Wash volume was approximately 80 milliliters
- Observations were conducted at 1, 4, 24, 48, and 72 hours and 7, 14, and 21 days

GRADES FOR OCULAR LESIONS

CONJUNCTIVA

Chemosis: lids and/or nictitating membranes

No swelling 0

Any swelling above normal including nictitating membranes 1

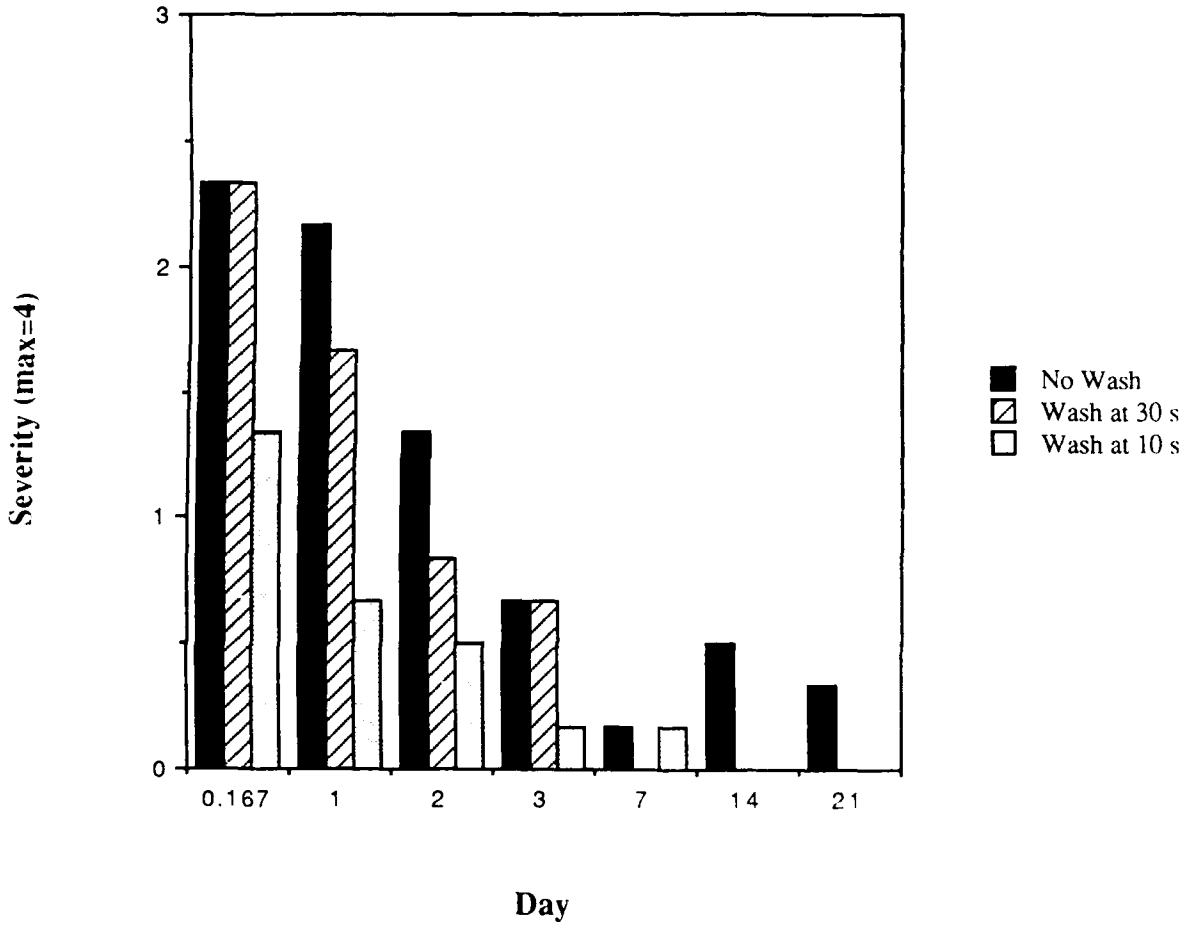
Obvious swelling with partial eversion of lids . . . . . 2 *

Swelling with lids about half-closed 3

Swelling with lids more than half-closed 4

* Indicates minimum level for a positive response

CHEMOSIS


3
2
1
0
Severity (max=4)
0.167
1
2
3
7
14
21
Day
No Wash
Wash at 30 s
Wash at 10 s

GRADES FOR OCULAR LESIONS

CONJUNCTIVA

Redness: (refers to palpebral and bulbar conjunctiva, excluding cornea and iris)

Blood vessels normal 0

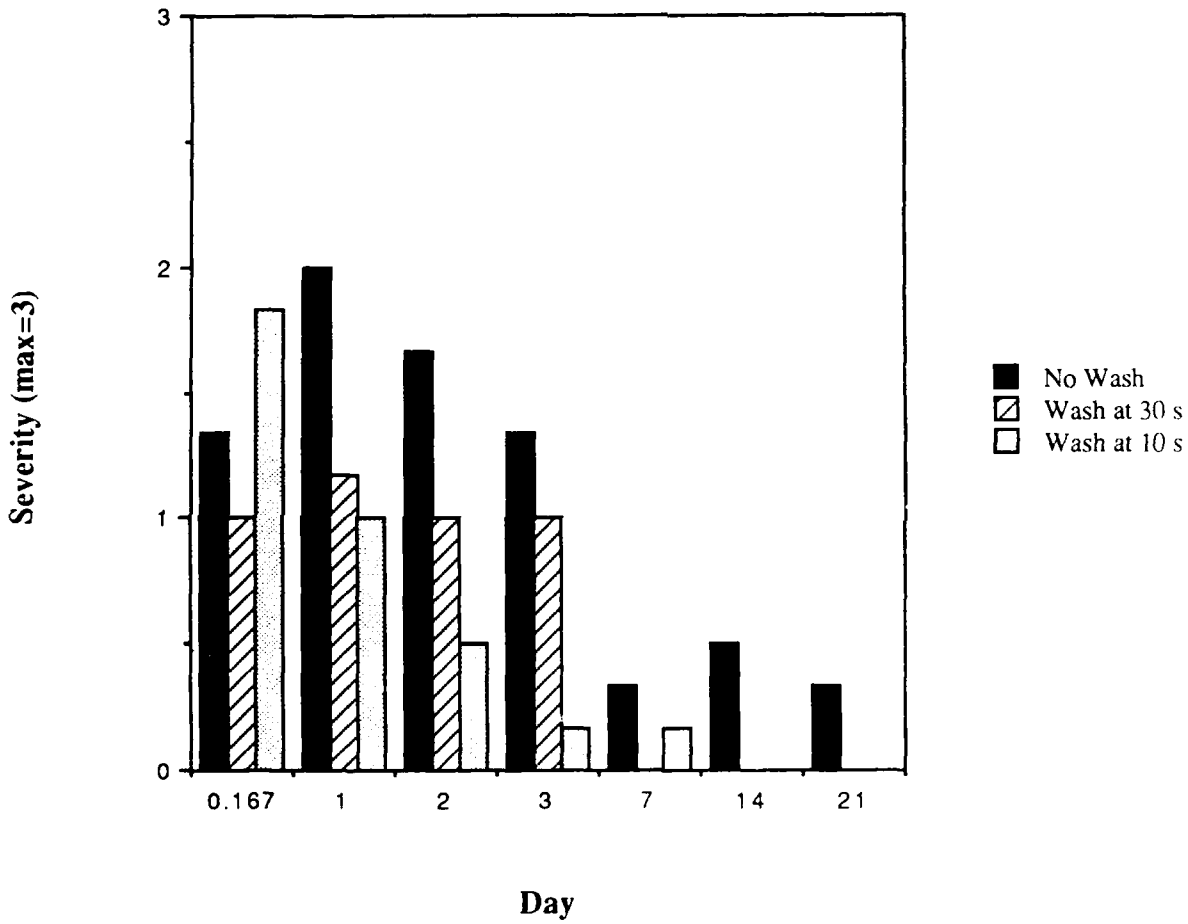
Some blood vessels definitely hyperemic (injected) . 1

Diffuse, crimson color, individual vessels not easily discenible . . . . . 2 *

Diffuse, beefy red 3

* Indicates minimum level for a positive response

CONJUNCTIVAL REDNESS



GRADES FOR OCULAR LESIONS

IRIS

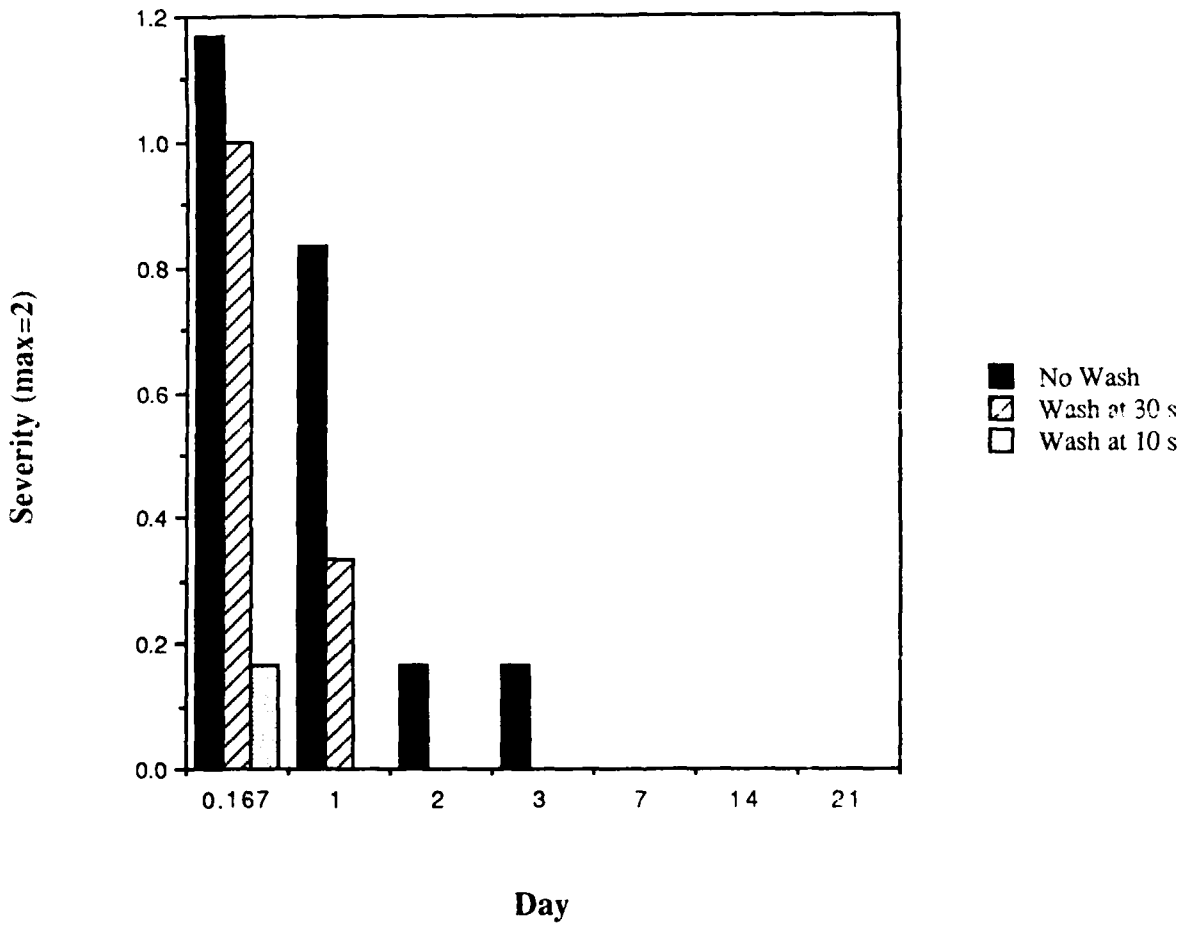
Normal 0

Markedly deepened rugae, congestion, swelling, moderate circumiridial hyperemia or injection, any of these or any combination thereof, iris still reacting to light (sluggish reaction is positive) . . . . . 1 *

No reaction to light, hemorrhage, gross destruction (any or all of these) 2

* Indicates minimum level for a positive response

IRIDIC CHANGES



GRADES FOR OCULAR LESIONS

CORNEA

Opacity: degree of density (area of greatest density taken for reading)

No ulceration or opacity 0

Scattered or diffuse areas of opacity (other than slight dulling of normal luster)details of iris clearly visible. . . 1 *

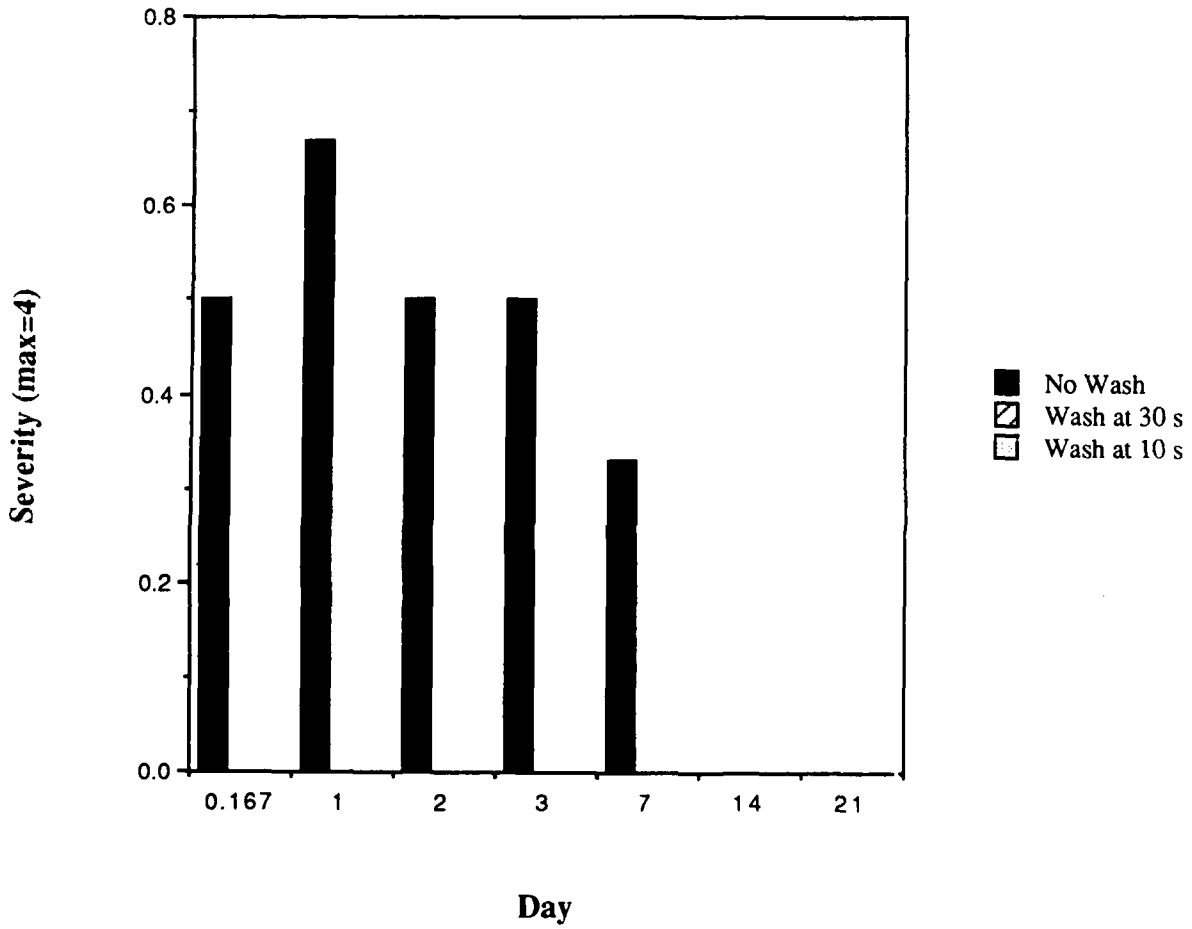
Easily discernible translucent areas, details of iris slightly obscured 2

Nacreous areas, no details of iris visible, size of pupil barely discernible. 3

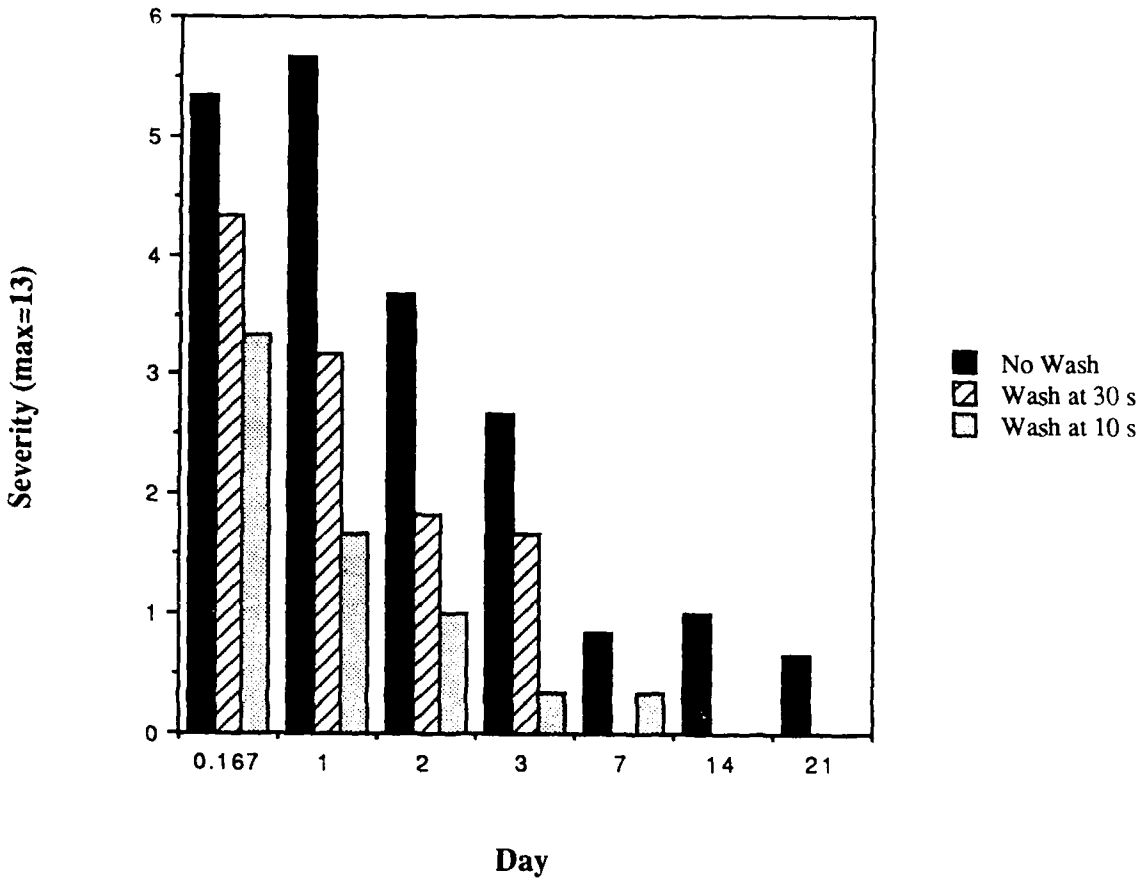
Opaque cornea, iris not discernible through opacity. 4

* Indicates minimum level for a positive response

CORNEAL CHANGES



OCULAR IRRITATION INDEX



CONCLUSIONS

- LP1846 is an ocular irritant
- Washing the eye at 30 seconds after exposure:
  - ◊ alleviated conjunctival symptoms
  - ◊ alleviated iritic symptoms
  - ◊ prevented development of corneal lesions
- Washing the eye at 10 seconds after exposure:
  - ◊ was even more successful at alleviating the conjunctival and iritic symptoms
  - ◊ prevented development of corneal lesions

CIRCULATORY AND HEMATOLOGICAL EFFECTS OF LP1846 FOLLOWING ORAL ADMINISTRATION TO RATS

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Letterman Army Institute of Research
Presidio of San Francisco, CA 94129-6800
(415) 561-2963

ABSTRACT

Hydroxylammonium nitrate (HAN), a major component of the liquid propellant 1846 (LP1846), has been reported to produce methemoglobinemia, Heinz body formation, and hypotension in rats. This study was conducted to define the relative sensitivity and reversibility of the methemoglobinemia, hypotension, and Heinz body formation following oral administration of LP1846 to male rats. The left carotid artery of each Sprague-Dawley rat was surgically implanted with customized polyurethane catheters. After a 3- to 5-day recovery period, the animals were assigned to one of three groups and were administered a single dose of either sterile water (control) or LP1846 (equivalent to 50 or 100 mg/kg of HAN) by oral gavage. Blood pressure was monitored before dosing and for 60 minutes following dosing. Blood samples for determining the presence of methemoglobin and identifying Heinz bodies were obtained at -1, 5, 15, 30, 60, 120, 180, 240, 300, and 360 minutes after dosing, and then at 24-hour intervals until methemoglobin values returned to normal. LP1846 had no effect on mean arterial pressure at a dose of 50 mg(HAN)/kg, but a dose of 100 mg(HAN)/kg produced a significant decrease of 14% at five minutes. LP1846 produced a dose-related increase of 5.2% and 10.6% in methemoglobin values for the 50 and 100 mg(HAN)/kg groups, respectively. The half-times for methemoglobin reduction were 113.0 hrs for the 50 mg(HAN)/kg and 93.2 hrs for the 100 mg(HAN)/kg groups. The times to the maximum methemoglobin concentration were 1.27 hrs for the 50 mg(HAN)/kg and 2.63 hrs for the 100 mg(HAN)/kg groups. Heinz bodies were present in all treated animals; the time of first observance being significantly shorter in the high-dose group. These data suggest that the presence of elevated methemoglobin levels and/or Heinz bodies would be useful indices of occupational exposure to LP1846.

METHODS

TIME COURSE OF METHEMOGLOBINEMIA, HEINZ BODY FORMATION, AND HYPOTENSIVE RESPONSES TO LP1846 ADMINISTRATION

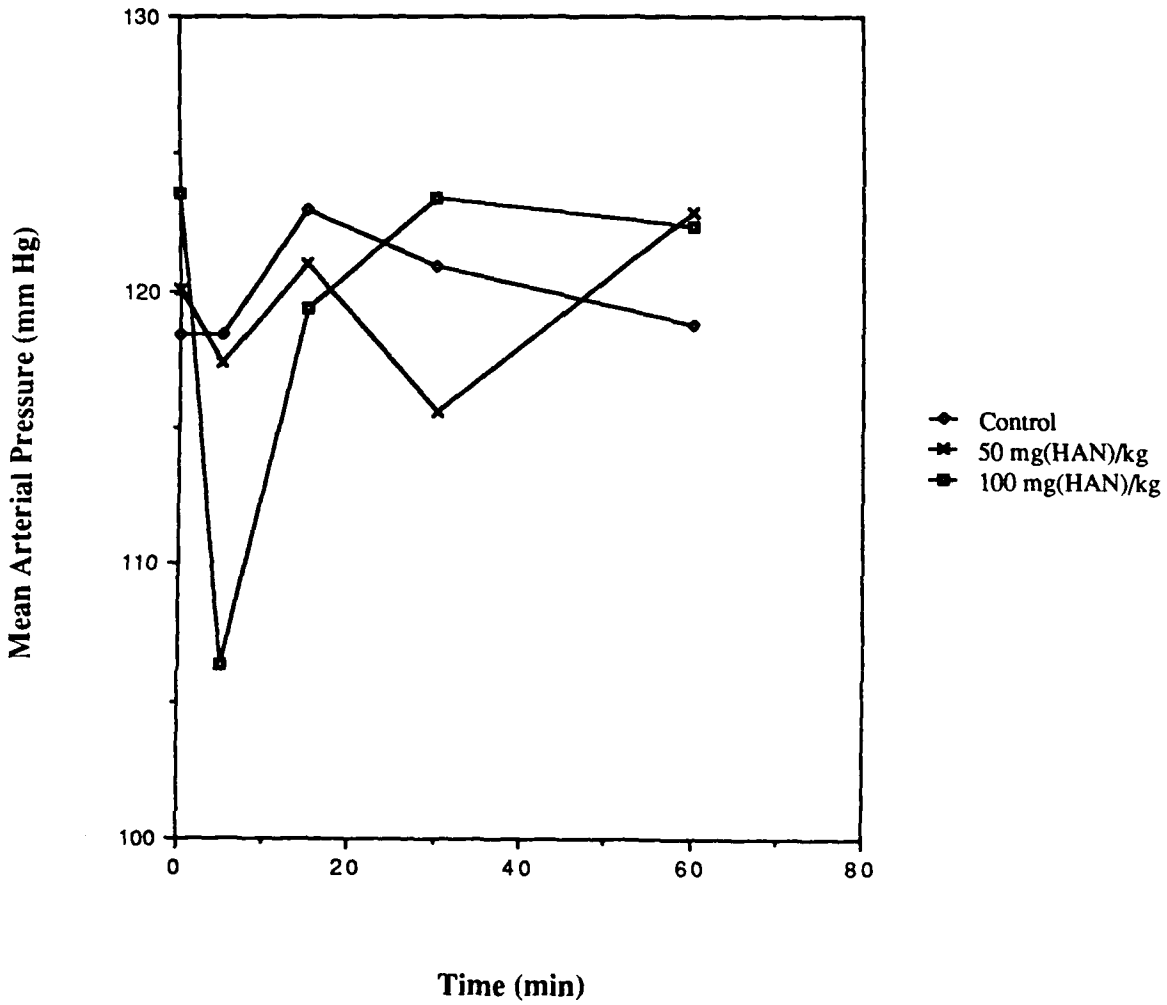
1. Male rats 227-380 g. are chronically catheterized intra-arterially in the carotid artery under Innovar-Vet anesthesia.

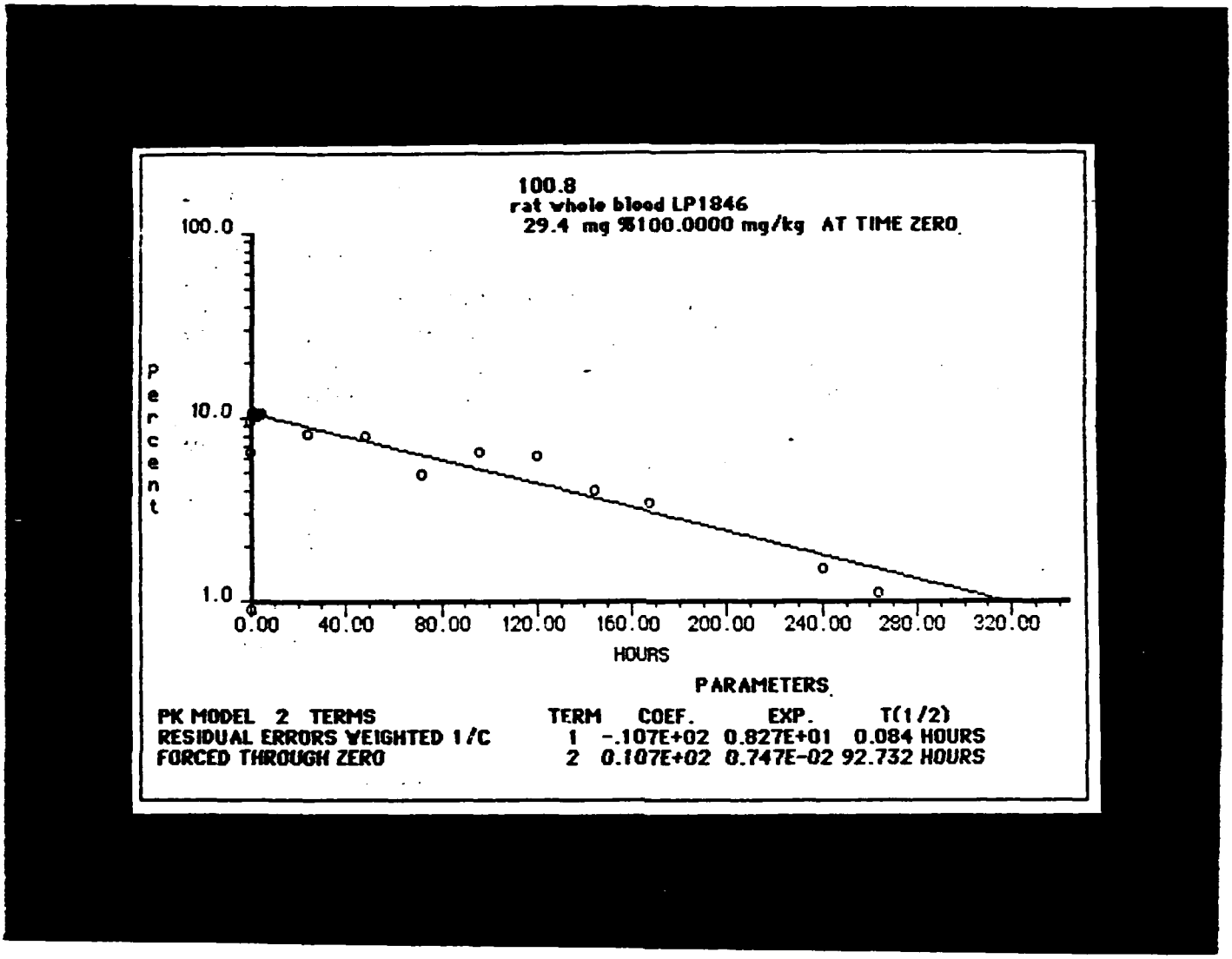
2. Rats are allowed to recover for 3-5 days.

3. LP1846, 50 mg(HAN)/kg or 100 mg(HAN)/kg or sterile water (vehicle) is given by oral intubation after baseline blood pressure and blood samples are obtained.

4. Blood pressure is monitored during first 60 minutes. Blood samples are obtained at 5, 15, 30, 60, 120, 180, 240, 300, and 360 minutes and then at 24 hour intervals until methemoglobin values return to baseline.

EFFECT OF LP1846 ON MEAN ARTERIAL PRESSURE





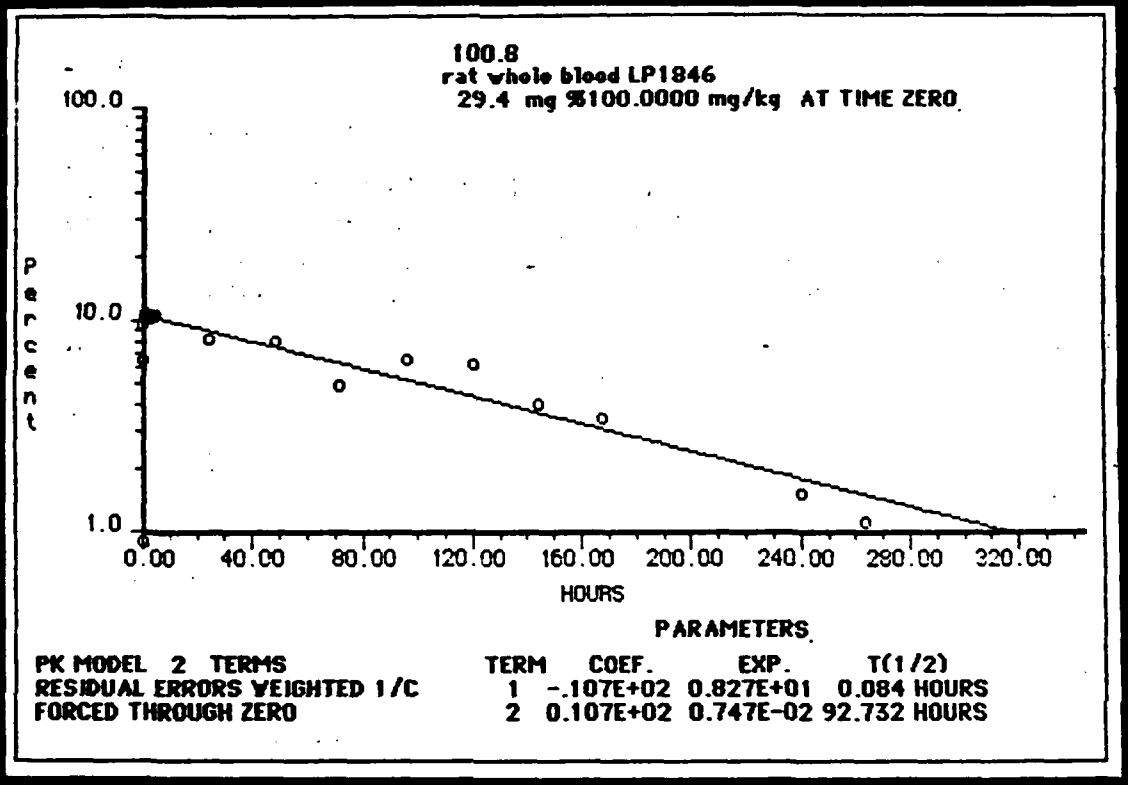
Representative concentration vs time curve for methemoglobin concentration in 100 mg(HAN)/kg dose group.

Methemoglobin Kinetics Following Oral Administration of LP1846 to the Conscious Rat[a,b]

Group[c]	T-1/2 Red (hrs)	AUC (% hrs)	T-max (hrs)	C-max (%)
50 mg(HAN)/kg (n=8)	113.1 ±9.4	848.3 ±87.3	1.27 ±0.15	5.2 ±0.5
100 mg(HAN)/kg (n=8)	93.2 ±12.4	1358.0[d] ±100.9	2.63 ±1.22	10.6[d] ±1.1

a. Abbreviations: T-1/2 Red: half-time for methemoglobin reduction
AUC: area under the curve described by the methemoglobin vs time plot
T-Max: time to maximum methemoglobin concentration
C-Max: maximum methemoglobin concentration

b. Values are mean ± standard error of the mean.
c. Control Methemoglobin values did not change from baseline. No kinetic analysis was attempted.
d. Significantly different from 50 mg(HAN)/kg: Student's t-test, $p \leq 0.05$.



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(n=8)	±9.4	±87.3	±0.15	±0.5
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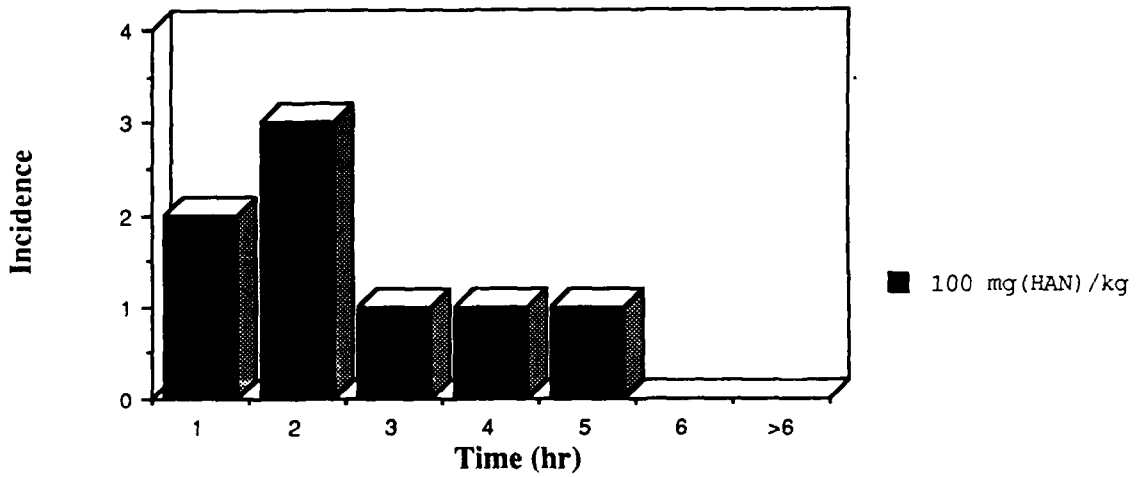
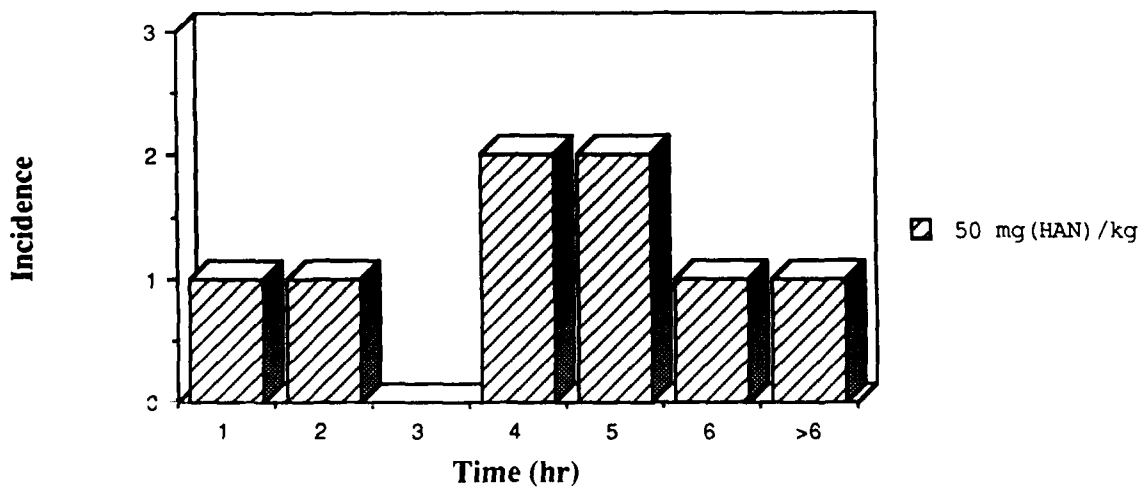
(n=8)	±12.4	±100.9	±1.22	±1.1

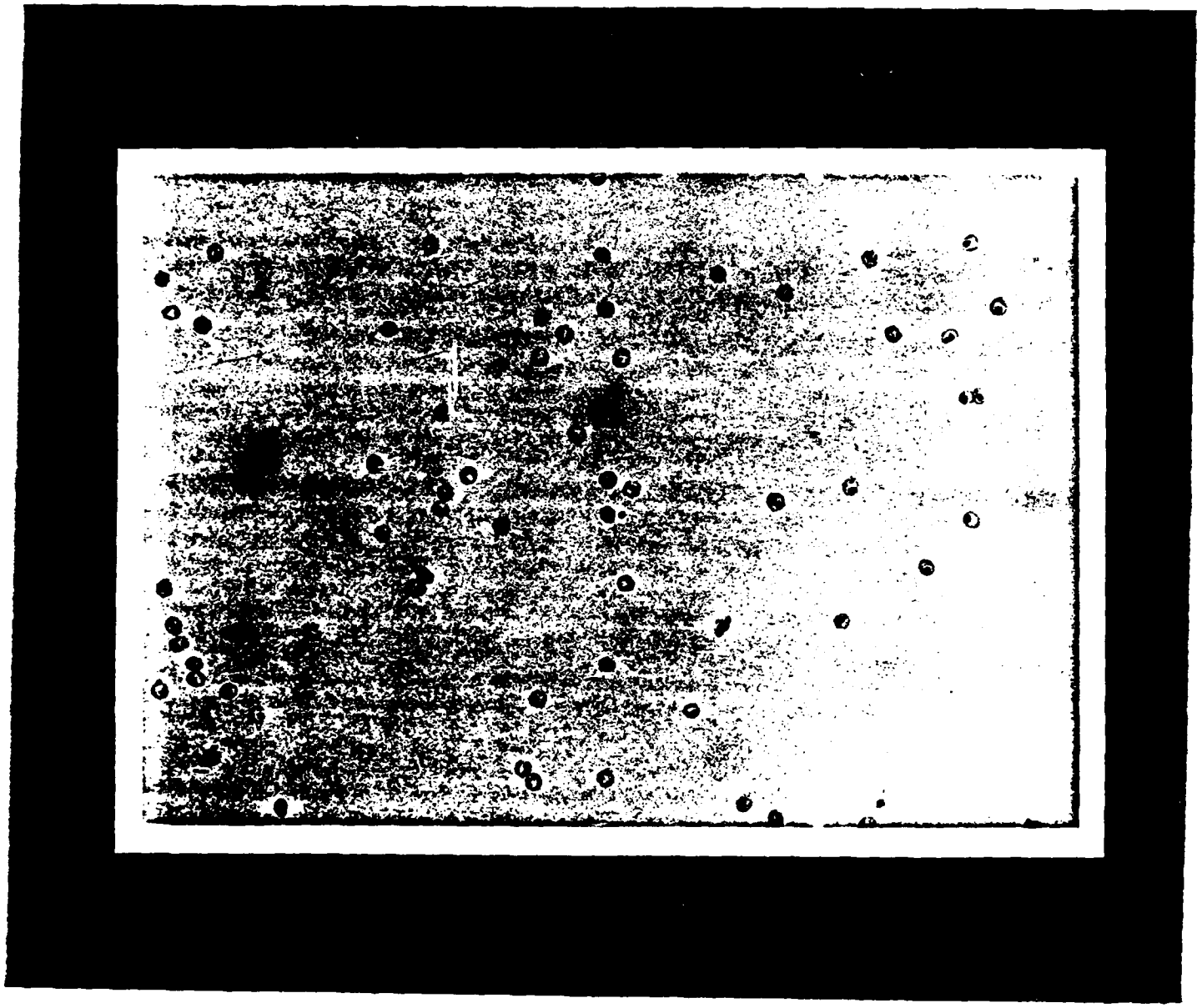
a. Abbreviations: T-1/2 Red: half-time for methemoglobin reduction
AUC: area under the curve described by the methemoglobin vs time plot
T-Max: time to maximum methemoglobin concentration
C-Max: maximum methemoglobin concentration

b. Values are mean ± standard error of the mean.
c. Control Methemoglobin values did not change from baseline. No kinetic analysis was attempted.
d. Significantly different from 50 mg(HAN)/kg: Student's t-test, $p \leq 0.05$.

TIME TO HEINZ BODY FORMATION







Photomicrograph of Heinz body-containing erythrocytes from the blood sample of a 100 mg(HAN)/kg animal.

CONCLUSIONS

1. This study confirms earlier reports that HAN-containing liquid propellants produce hypotension, methemoglobinemia, and Heinz body formation.

2. All variables measured responded in a dose-related fashion to LP1846 administration.

3. LP1846 was more potent in producing methemoglobinemia and in promoting Heinz body formation than in producing hypotension.

4. At dose levels used in this study, the hypotensive response was transient; however, higher doses used in a pilot study produced prolonged periods of hypotension.

5. The relatively long half-life of four days for methemoglobin reduction in the rat following administration of LP1846 suggests that LP1846 (or its active component) may have a long half-life of elimination.

6. Either determination of methemoglobin titres or the presence of Heinz bodies would be sensitive indicators of occupational exposure to LP1846.

REVIEW OF THE FOURTH LIQUID PROPELLANT CONFERENCE*

Eli Freedman**

INTRODUCTION

"Instant analysis", as practiced by TV commentators, has increasingly come into disrepute. Nevertheless, it is possible for an outside observer with a background in LP technology, but without any official or contractual connections to the BRL, to comment on the conference. In an effort to maintain objectivity, especially in the case of a few adverse observations, conference authors' names have been omitted throughout.

TRENDS

With 26 papers compared to last year's 20, this conference continues to show a healthy growth. It continued a trend that started last year, the active participation of LP investigators from abroad. The increasing participation of workers from industry is another welcome event.

Another encouraging trend is the general acceptance of "1845" and "1846" as the designations of the two principal formulations for HAN-based LPs. These designations are of course purely arbitrary--any other set would do as well. What is important is that having a generally-accepted nomenclature makes it much easier to carry on technical discussions without the need to spend time repeating the same material over and over.

DUPLICATION

Intentional duplication is desirable, particularly when it comes to difficult questions like stability, lifetimes, and related kinetic questions. But unintentional duplication rarely accomplishes anything other than wasting time and money. In my judgment there is entirely too much unintentional duplication, particularly in studies of stability and compatibility. This is especially the case when considering projects underway in different countries.

---

* The evening before the final session, the chairman of that session, Dr Nathan Klein, invited this author to present his personal comments on the Conference the next day after the last scheduled paper. The present paper is based on those remarks In a few places, some additional comments or discussion have been inserted All of the opinions expressed are the author's own

** Eli Freedman & Associates, 2411 Diana Road, Baltimore, MD 21209

Further discussion of this point quickly brings up political questions that are altogether outside the scope of this meeting; however, there does exist a political forum in which dialogues about these matters would be quite appropriate, namely, the existing Data Exchange Agreements.

Earlier in this meeting, Professor Koski, referring to the increasing reliance on automated literature searches, commented that no one seems to read any literature written before 1965. Alas, the situation is even more distressing than that. While listening to the talks, it became apparent that some earlier reports from BRL or by BRL authors have been overlooked, leading to additional unplanned duplication.

Table 1 contains a short list of these reports, all of them unclassified. It contains titles and the BRL report number, but authors' names have been deliberately omitted. The Defense Technical Information Center (DTIC) numbers have been included to make it easier to obtain copies. There are also several classified reports which, however, may not be listed here; qualified persons should not have much difficulty in learning their titles and obtaining copies.

Table 2 lists two papers that were presented at the well-known ICT Conferences.

PHYSICAL PROPERTIES

Progress continues in the determination of the physical properties of HAN-based LPs, although one discordant note was sounded. The pressure-volume-temperature properties of some LPs have now been determined in two different ways: by direct volumetric measurement, and by measurement of ultrasonic velocity as a function of pressure and temperature. The latest direct volumetric measurements, just reported here, disagree with the ultrasonic measurements first reported at last year's conference. There are earlier volumetric measurements done at Lawrence Livermore National Laboratory which perhaps can help point to the better values.

The apparent freezing of LP1845 at -14°C and 24 kpsi definitely needs to be reinvestigated. The importance of this matter more than justifies considerable intentional duplication. In fact, one would hope that some proposed modelling work might be set aside until this issue is settled. This is not to disparage the importance of modelling; however, for solutions as complex as a typical HAN-based LP, the real importance of modelling will be the development of guides for interpolating or extrapolating properties between compositions and conditions, rather than the derivation of meaningful molecular models from first principles.

STABILITY AND COMPATIBILITY STUDIES

This meeting showed a large increase in the number of papers concerned with various aspects of the stability or compatibility of HAN-based LPs. This is indeed a proper emphasis on one of the most important aspects of any propellant system. However, previous comments about unwitting duplication apply particularly to these studies.

Another unfortunate aspect of these studies is that various investigators reported their results in different ways, making direct comparison difficult if not impossible. The most popular experiment is measuring the amount of gas produced either as a function of time or after a fixed time has elapsed. Some investigators reported this quantity in cubic centimeters at standard temperature and pressure; others reported pressure instead of volume; and still others reported only the total pressure produced after a fixed time.

While measuring the rate of gas evolution is a well-established and often-useful technique for kinetic studies, it has drawbacks. It cannot detect changes in mechanism, and accordingly, it must assume a fixed stoichiometry. A change in mechanism is indicated by the change in the ratio of N_2 to N_2O reported in one of the papers presented here.

A more direct, if more difficult, method is to measure the change in concentration of the reactant (HAN, in the present case). Some investigators who did directly measure the concentration of HAN chose to report the results as time required to reach a fixed percentage decomposition, which also makes intercomparison difficult.

Similarly, reporting percentage compositions as a function of time is uninformative. For example, consider the following synthetic data:

Time (days)	HAN (%)	TEAN (%)
0	60.0	20.0
30	30.0	25.0

Certainly HAN decomposed, but what happened to the TEAN? One cannot decide from these data alone whether TEAN also decomposed, but its concentration certainly did not increase.

The temperature coefficient of the rate of decomposition is the second most important kinetic parameter after the room temperature rate itself. There is presently no requirement for knowing this coefficient with great precision, a situation that will soon change. Until then, rate measurements at two temperatures are sufficient. Room temperature is the obvious choice for the lower one; the higher one should be as far away as feasible. Since US Army stability requirements specify 65°C as the upper required limit, this temperature seems to be a good choice. The 95°C used by some investigators is too high, and tends to obscure some important factors, such as the efficacy of proposed heavy-metal complexing agents.

SENSITIVITY, VULNERABILITY, SCALING, AND MODELLING

"Sensitivity" is a difficult concept to define, which explains why it is also difficult to measure. Traditionally, sensitivity has been evaluated on the basis of results obtained from simple apparatuses, such as the familiar drop-weight tester. The discussion at this conference on aspects of drop weight testers gave some idea of the complications attendant on their use. Experiments of this type are easy to perform but hard to interpret.

Raymond Rogers (Los Alamos National Laboratory) suggested some time ago that sensitivity can be better evaluated by performing difficult experiments that are easy to interpret. His own choice was a form of reaction calorimetry with well-defined boundary conditions that permitted the application of Frank-Kamenetskii's theory. Whether this is or is not a good choice can be debated, but his basic idea is a good one that ought to be pursued more vigorously.

Hazard evaluation and vulnerability are difficult but important parts of propellant development. Some of its aspects are necessarily political and are outside the scope of the conference. Future conferences will undoubtedly have many more reports on these subjects. Such studies may be premature now in view of the current state of the art; another deterrent is the expense of performing the needed experiments, especially the cost of the large quantity of material required.

Laboratory scale experiments are needed that will give a good indication of the results of much larger scale experiments. Some years ago, F. Weinberg (Imperial College, UK) suggested an experiment in which a laser would be used to deposit a large amount of energy in a point inside a small quantity of an energetic liquid; another laser would then monitor the progress of the reaction wave thus generated. His insight here was that the "scale" of this experiment would be determined by the ratio of a dimension of the container to the diameter of the hot spot, a large number, even though the actual scale of the experiment was quite small.

A paper at this conference established that the apparent inverse-power dependence of the rate of decomposition of HAN solutions is an artifact, not a physical fact. But why do HAN solutions show this artifact, while other liquids (e.g., aliphatic nitrates, mixtures of hydroxylammonium perchlorate with propyl nitrate) do not? Modellers ought to be attracted by this result.

Another question that I would like modellers to address is the relation (or lack of it) between kinetics and gun performance.

Table 1: Some Worthwhile BRL Reports on Liquid Propellants

Title	Date	Report Number*	DTIC Number**
Titrimetric Analysis of HAN-Based Liquid Propellants	Mar/88	TR-2907	A 196 225
An Infrared Investigation of HAN-Based Liquid Propellants	Nov/87	TR-2850	A 187 226
HAN-Based Liquid Gun Propellants: Physical Properties	Nov/87	TR-2864	A 195 246

* In all cases, the letters ARBRL- are to be prefixed to these numbers.

** In all cases, the letters AD- are to be prefixed to these numbers.

Table 2: Two Significant Papers Presented at ICT Conferences

Title	Reference
Methods for Product Analysis in Production of HAN Propellants	Internationale Jahrestagung ICT **1977**, p. 325.
Liquid Propellant Stability Studies	Internationale Jahrestagung ICT **1984**, p. 167.

APPENDIX A

LP

4TH ANNUAL CONFERENCE ON HAN-BASED LIQUID PROPELLANT STRUCTURE AND PROPERTIES

August 30, 31 and September 1, 1988

Sponsered By

Ballistic Research Laboratory

Aberdeen Proving Ground, MD 21005-5066

4th Annual Conference on HAN-Based Liquid Propellant
Structure and Properties

All sessions will be held in Bldg 330.

Walter F. Morrison . . . . General Chairman

Sponsered by: LP Materials Team
Advanced Ballistic Concepts Branch
Interior Ballistics Division

Conference Room Phone	301-278-6842 AV 298-6842
Information	301-278-6188 AV 298-6188

Tuesday, Aug 30

0800 Registration and Coffee

0830 Welcome, Walter F. Morrison, Program Manager, LP Program

0845 Arrangements, J. Wojciechowski, ABCB, BRL

SESSION I

Chairman: Charles S. Leveritt, BRL

0850 "Liquid Propellant Fail-Safe Criteria Program" by S. Griff and G. Doyle, Geo-Centers, Wharton, NJ

0910 "An Overview of the Thermal Reactivity of Substituted Ammonium Nitrates" by Dr. V. R. Pai Verneker, Martin Marietta Laboratories, Baltimore, MD and S. C. Deevi and C. K. Law, University of California, Davis, CA

0940 "Impact Sensitivity of HAN-Based Liquid Monopropellants" by I. C. Stobie, B. D. Bensinger and J. D. Knapton, BRL, Aberdeen Proving Ground, MD

1000 Break

1020 "Quantitative Analysis of HAN-Based Liquid Propellants" by Dr. H. J. de Greiff, ICT, Pfinztal, FRG

1040 "An Overview of the UK Approach to the Characterization and Classification of the HAN-Based Liquid Propellant LP101" by S. Westlake, RARDE, Waltham Abbey, UK

1105 "Possible Test Methods To Study the Thermal Stability of HAN-Based Liquid Gun Propellants" by P. Bunyan and S. Westlake, RARDE, Waltham Abbey, UK

1130 Lunch

Tuesday, Aug 30

SESSION II

Chairman: Sally Westlake, RARDE

1300 "Hydrodynamic Theory of Liquid Propellant Dynamics" by J. W. Haus and F. C. Yau, Rensselaer Polytechnic Institute, Troy, NY

1320 "Ionic Aspects of the Decomposition of HAN Solution" by W. S. Koski, The Johns Hopkins University, Baltimore, MD

1340 "Reaction Kinetics of HAN, TEAN and Water Mixtures Using a Personal Computer" by A. K. Macpherson, Lehigh University, Bethlehem, PA and A. J. Bracuti, ARDEC, Dover, NJ

1400 "Electrical Ignition of HAN-Based Liquid Gun Propellants" by H. Rockstroh and G. Klingenberg, Ernst-Mach Institut, Weil am Rhein, FRG and H. J. Frieske, Dynamit Noble, Cologne, FRG

1420 Break

1450 "The Burning Rate of HAN-Based Liquid Propellants: The Effect of HAN Concentration on Burning Rates" by S. R. Vosen, Sandia National Laboratories, Livermore, CA

1510 "Study of Thermal Diffusive-Reactive Instability in Liquid Propellants: The Effects of Surface Tension and Gravity" by R. C. Armstrong and S. B. Margolis, Sandia National Laboratories, Livermore, CA

1530 "The Response of an LP to Heating at High Pressure" by R. A. Beyer, BRL, Aberdeen Proving Ground, MD

1600 Close

Wednesday, Aug 31

0800 Coffee

SESSION III

Chairman: Anthony J. Beardell, ARDEC

0830 "Equations of State and Thermodynamic Properties of a Series of Aqueous Mixtures of HAN and Aqueous Mixtures of TEAN From Ultrasonics" by J. Frankel, W. Scholz and J. F. Cox, Watervliet Arsenal, Watervliet, NY

0850 "Physical Properties of Liquid Propellants: Measurements of Shear Viscosity, Volume Viscosity and Density" by J. Schroeder, C. S. Choi, Y. T. Lee, Rensselaer Polytechnic Institute, Troy, NY and J. Frankel, Watervliet Arsenal, Watervliet, NY

0910 "The Solubility of Gases Under Pressure in Liquid Propellants" by S. Murad and P. Ravi, University of Illinois at Chicago, Chicago, IL

0940 Break

1010 "Compatibility of Elastomeric Materials With HAN-Based Liquid Propellant 1846" by G. Rodriguez, H. Feuer and A. Teets, Ft. Belvoir RD&E Center, Ft. Belvoir, VA

1030 "Influence of Metal Ions on the Chemical Stability of HAN-Based Liquid Propellants" by Dr. R. Hansen, ICT, Pfinztal, FRG

1050 "Selection Criteria for Metals and Plastics as Construction Materials for Long Term Pressure-Testing Apparatus on Liquid Propellants (LPs)" by Dr. E. Backof, ICT, Pfinztal, FRG

1110 "Compatibility Study with 60 % HAN Solution" by O. Briles, Sundstrand Aviation, Rockford, IL

1130 Lunch

Wednesday, Aug 31

SESSION IV

Chairman: Walter S. Koski, JHU

1300 "Diamond Anvil-FTIR Studies of Aqueous HAN and dHAN to 40 Kbar" by R. A. Fifer and M. A. Davies, BRL, Aberdeen Proving Ground, MD

1320 "Infrared Spectroscopy of Acoustically Levitated Droplets" by T. B. Brill and J. T. Cronin, University of Delaware, Newark, DE

1350 "Laser-Induced Shape Distortion and Breakdown in Single NH_4NO_3 Water Droplets" by R. K. Chang, D. H. Leach, J. Zheng and J. Z. Zhang, Yale University, New Haven, CT

1420 Break

1450 "Droplet Combustion and Thermal Decomposition Behavior of Liquid Propellants" by C. K. Law, S. C. Deevi, D. L. Zhu and C. Call, University of California, Davis, CA

1520 "Raman Spectroscopy of Nitrate Salt Solutions Up to 500° C and 35 MPa" by T. B. Brill and P. D. Spohn, University of Delaware, Newark, DE

1550 "Thermal Characteristics of Concentrated Hydroxylammonium Nitrate Solutions" by R. A. Sasse', BRL, Aberdeen Proving Ground, MD

1610 Close

Thursday, Sep 1

0800 Coffee

SESSION V

Chairman: Nathan Klein, BRL

0830 "Electrosynthesis of High-Purity Hydroxylammonium Nitrate by Electrolytic Reduction of Nitric Acid" by Dr. J. A. Leistra, Dr. R. L. Dotson and J. H. Barnatt, Olin Chemicals, New Haven, CT

0900 "Neutralization of High-Purity Hydroxylammonium Nitrate" by Dr. R. L. Dotson, Dr. J. A. Leistra and J. H. Barnatt, Olin Chemicals, New Haven, CT

0930 "Producing HAN-Based Liquid Propellants" by R. Biddle, Morton-Thiokol, Elkton, MD

0950 Break

1020 "Reversibility of Occular Irritation of LP 1846" by MAJ Korte, LAIR, Livermore, CA

1040 "Circulatory and Hemotological Effects of LP 1846 Administration" by MAJ Korte, LAIR, Livermore, CA

1100 Open Discussion

1200 Close

APPENDIX B

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