Characterization of refractive properties of fluids for immersion photolithography

Simon G. Kaplan and John H. Burnett

Physics Laboratory
National Institute of Standards and Technology
Gaithersburg, Maryland USA

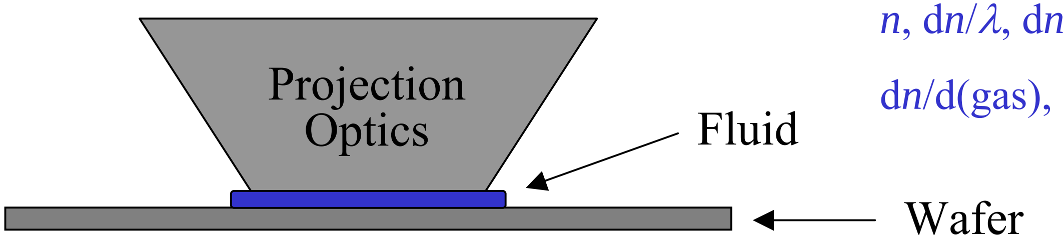
Xiaoping Gao and Peng Zhang
Air Products and Chemicals, Inc.
Allentown, Pennsylvania USA

Support from Office of Microelectronics Programs at NIST
and International SEMATECH

International Symposium on Immersion and 157 nm Lithography 8-3-2004

National Institute of Standards and Technology

NIST program for immersion fluid characterization



n, dn/λ, dn/T,dn/dP

dn/d(gas), dn/d(impurities)

Provide immersion fluid R & D community with facilities for measurements of fluid refractive properties:

- Construct and maintain apparatus for rapid survey of new classes of fluids. Transfer measurement methods to industry, e.g., cell design for Woollam, Inc. Minimum Deviation system.
- Use multiple methods to measure *n* to high accuracy for critical fluids (e. g., water at 193 nm), as well as sensitivity to key parameters.
- Perform our own survey of possible immersion fluids.

Facilities for refractive index measurement

(1) Classical minimum-deviation prism goniometer system, visible through DUV spectral range, can measure *n* to $\approx 5 \times 10^{-6}$ uncertainty.

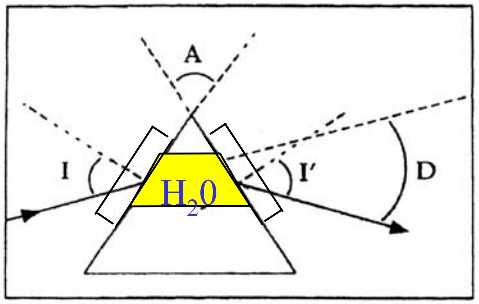
(2) Etalon fringe-counting method using sychrotron light source and Fourier-transform interferometer.

(3) New this year, a laser-based Hilger-Chance refractometer for quick measurements of *n* to 10^{-4} uncertainty and Δn (temperature, impurities, gas content, etc.) to $\approx 2 \times 10^{-6}$ uncertainty.

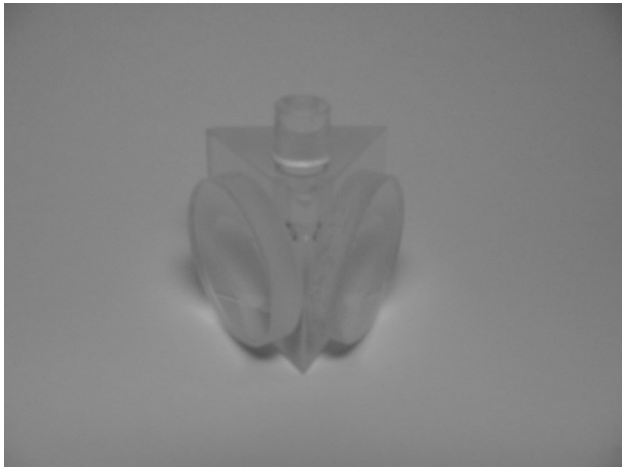
- All three systems: temperature control to ±0.01 °C, purge in N_2 with < ppm O_2.

<u>Under construction:</u> fully-automated replacement for (1) with 1×10^{-6} absolute uncertainty.

Prism- Goniometric Minimum Deviation Method



$$n(\lambda)=\frac{\sin\left(\frac{A+D(\lambda)}{2}\right)}{\sin\left(\frac{A}{2}\right)}\cdot n_{gas}(\lambda)$$



fused silica fluid cell

- Method similar to that we used for 193 nm[1] and 157 nm[2] index meas.
- Fluid prism made **entirely** from high-purity fused silica with optically-contacted windows ⇒ no impurities introduced!
- Measured HPLC water
- Control temp to $\Delta T = 0.01$ °C (corresponding to $\Delta n \approx 1 \times 10^{-6}$)
  ⇒ measurement of absolute index to $\approx 5 \times 10^{-6}$
  differential measurements to $\approx 1 \times 10^{-6}$

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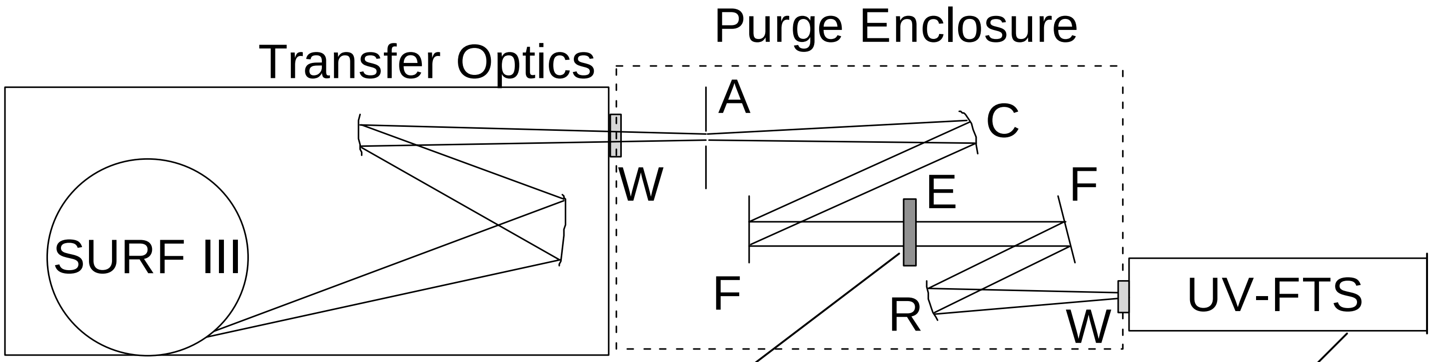
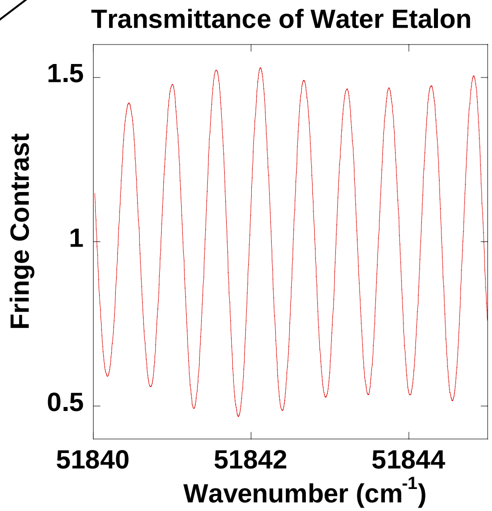
[1] R. Gupta, J. H. Burnett, U. Griesmann, and M. Walhout, Appl. Opt. **37**, 5964-5968 (1998).

[2] J. H. Burnett, R. Gupta, and U. Griesmann, Appl. Opt. **41**, 2508-2513 (2002).

Etalon fringe counting method: SURF III + FTS



Etalon Fluid Cell



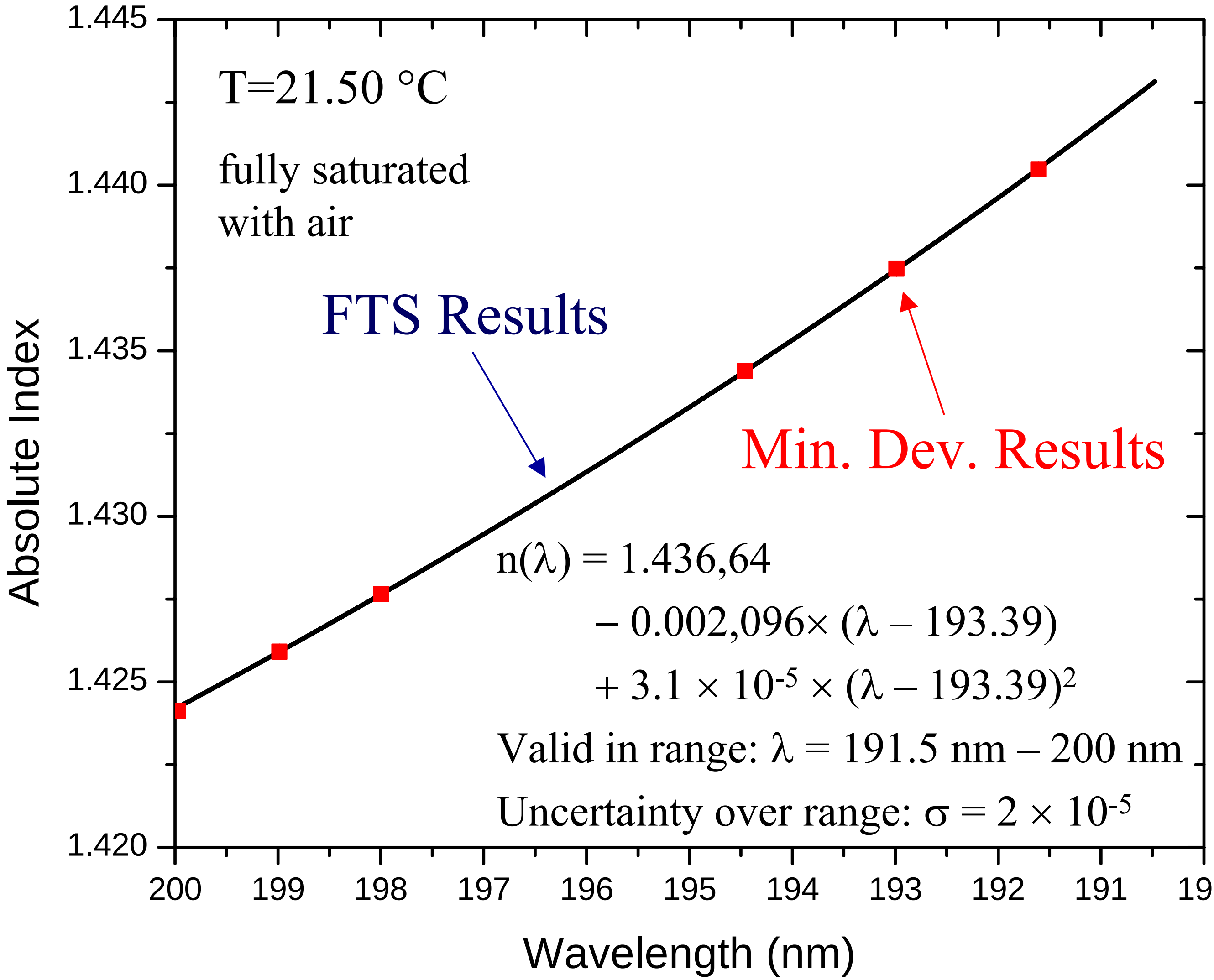
$$n(\nu_m) = \frac{m}{2 \cdot t \cdot \nu_m}$$

$m \approx 70{,}000$

$t \approx 0.5$ cm

- Fringe order *m* and etalon thickness *t* are determined from absolute visible refraction measurements at two wavenumbers.
- Synchrotron source and FTS yield continuous fringe spectrum 580 nm to 150 nm.

Absolute Index of HPLC Water Near 193 nm



T=21.50 °C

fully saturated
with air

FTS Results

Min. Dev. Results

$$n(\lambda) = 1.436{,}64 - 0.002{,}096 \times (\lambda - 193.39) + 3.1 \times 10^{-5} \times (\lambda - 193.39)^2$$

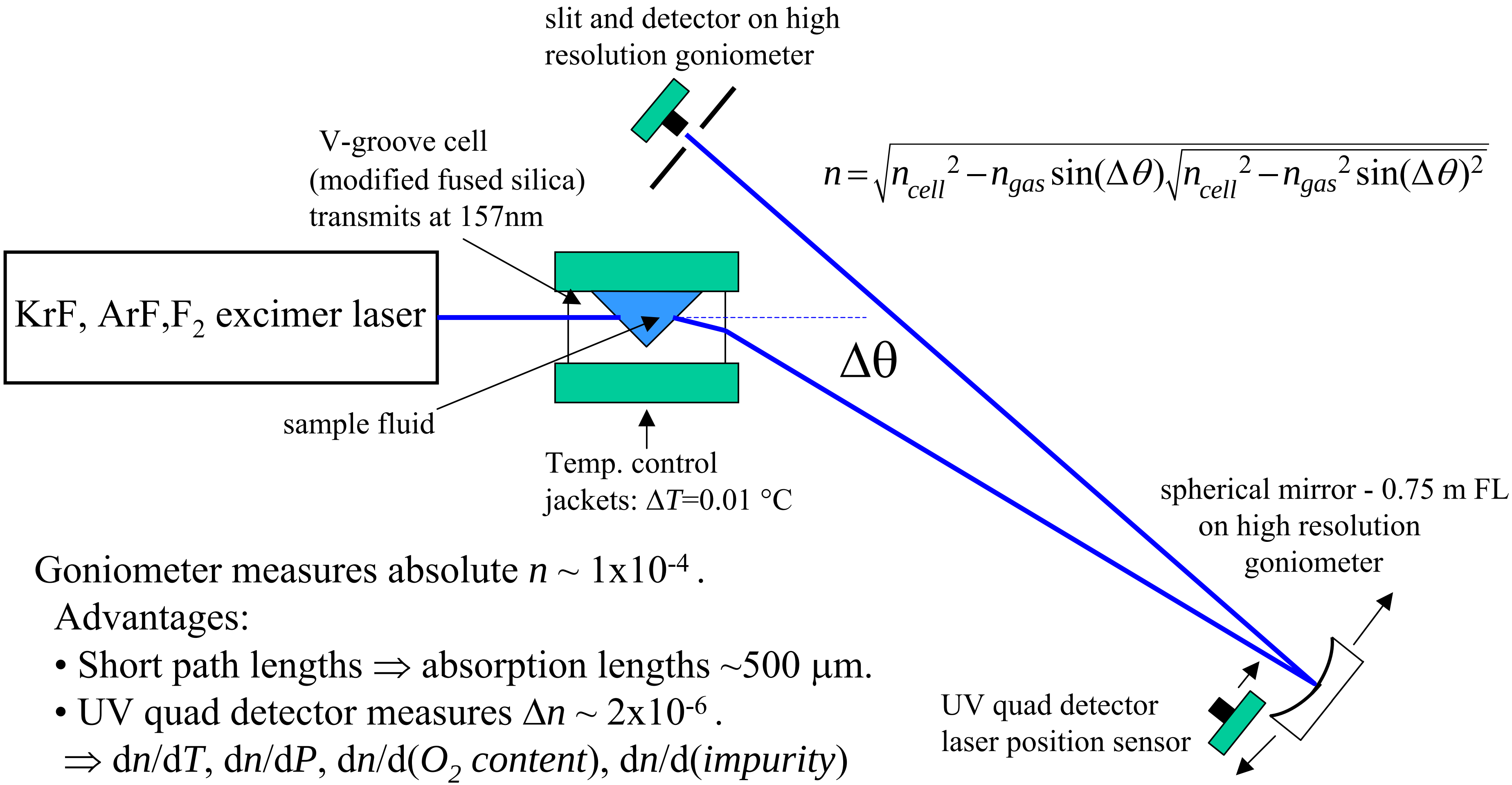
Valid in range: λ = 191.5 nm – 200 nm

Uncertainty over range: $\sigma = 2 \times 10^{-5}$

- Minimum Deviation and FTS methods agree to within 2×10^{-5}.
- Expect to achieve uncertainty of 5×10^{-6} shortly.

VUV Hilger-Chance Refractometer

For any fluid with absorption lengths ≥ 500µm at 193nm or 157nm:
quickly measures *n* with moderate accuracy, Δ*n* with high accuracy.



$$n=\sqrt{n_{cell}{}^2-n_{gas}\sin(\Delta\theta)\sqrt{n_{cell}{}^2-n_{gas}{}^2\sin(\Delta\theta)^2}}$$

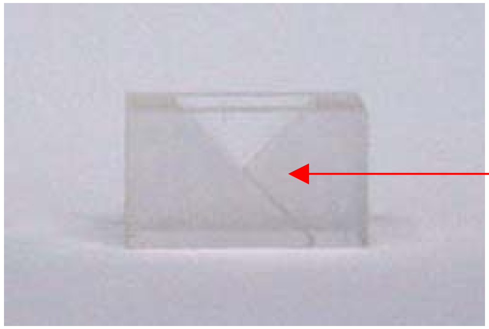
Goniometer measures absolute *n* ~ $1\text{x}10^{-4}$.

Advantages:

- Short path lengths ⇒ absorption lengths ~500 µm.
- UV quad detector measures Δ*n* ~ $2\text{x}10^{-6}$.
  ⇒ d*n*/d*T*, d*n*/d*P*, d*n*/d(*O$_2$ content*), d*n*/d(*impurity*)
- Remote loading, automation ⇒ rapid measurements.

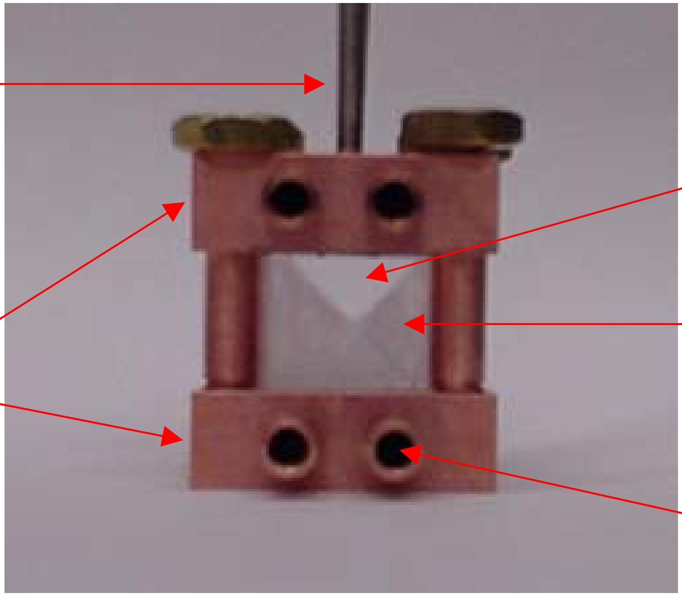
V-Groove Cell

Bare fused silica cell



Modified fused silica (transmits at 157nm)

Temperature-controlled cell sealed from atmosphere



Sealed ports for introducing fluid

Sample fluid

Fused silica cell

Water jackets for T control to 0.01 °C

Hose connections

Surveying fluids for immersion lithography

Desirable fluid properties: large *n*, low absorption, low d*n*/d*T*, inexpensive, chemically innocuous, stable, low viscosity (?)

Don't want: scattering, fluorescence, bubbles, deposits…

A convenient framework for thinking about possible fluids: the Lorentz-Lorenz formula for *n* of a condensed material

$$\frac{n^2-1}{n^2+2}=\frac{N_A}{3\varepsilon_0}\sum_i \rho_i(p,T)\cdot A_i(\lambda,p,T)$$

N_A = Avogadro's number
ε_0 = vacuum permittivity
ρ_i = molar density of constituent *i*.
A_i = molecular polarizability

Would like to increase *n* by increasing electron density and/or polarizability, but trade off against probably inevitable increase in absorption (Kramers-Kronig) and possible increase in d*n*/d*T*. Can we do better than water?

(1) Doping water with salts, acids, etc. (Bruce W. Smith *et al.*, preprint, and ISMT Immersion Workshop Jan. 2004.) Good candidates – H^+, Cs^+, K^+, Cl^-, SO_4^{2-}, PO_4^{2-}…

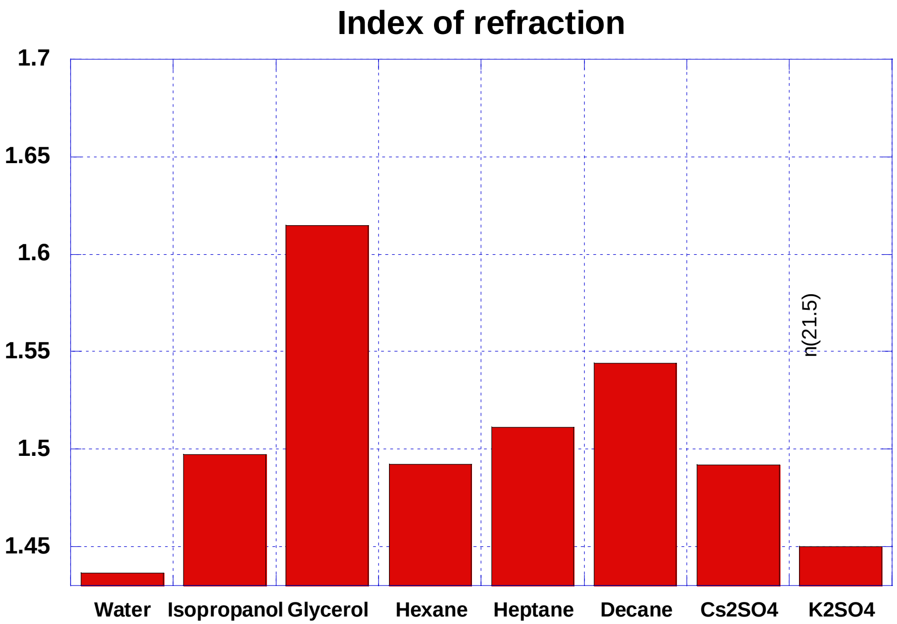
(2) Add to water molecule: C-H and O-H bonds probably OK for 193 nm, i. e., Water H[OH], Isopropanol $(CH_3)_2CH[OH]$, Glycerol $CH_2[OH]CH[OH]CH_2[OH]$, etc.

(3) Other organic liquids, e. g. simple hydrocarbons. Hexane C_6H_{14}, Heptane C_7H_{16}, Decane $C_{10}H_{22}$, etc.

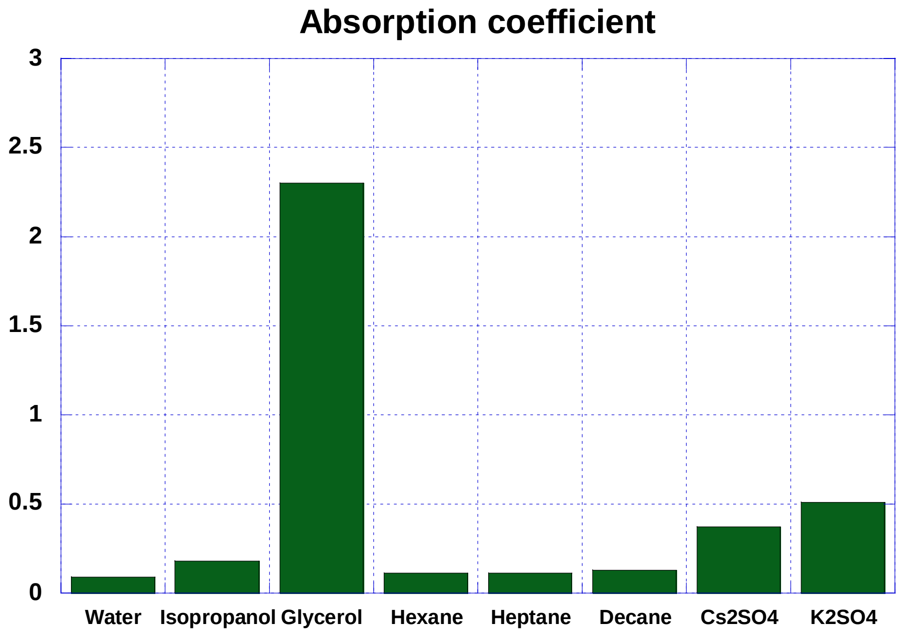
(4) Newly engineered molecules – especially for 157 nm.

Results for some 193 nm fluids

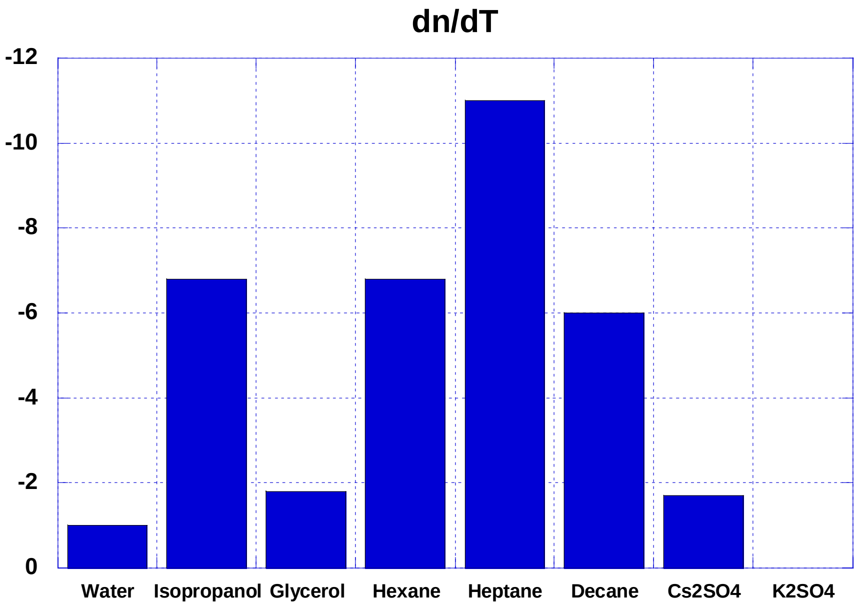
Air Products Samples	Sample ID	n at 21.5 C	dn/dT (10^-4/K)	α (/mm)
	1	1.4884	-1.6	
	2	1.5579	-6.2	
	3	1.6435	-5.7	
	4	1.5409	-3.6	
	5	1.4998	-2.4	
	6	1.5961	-3.1	
	7	1.5836	-3.9	
Our samples	Water	1.4366	-1.0	0.09
	Isopropanol	1.4973	-6.8	0.18
	Glycerol	1.6149	-1.8	2.3
	n-Hexane	1.4922	-6.8	0.11
	n-Heptane	1.5113	-11.0	0.11
	n-Decane	1.5440	-6.0	0.13
	4.2 % Cs2SO4	1.4919	-1.7	0.37
	1 % K2SO4	1.450		0.51
	5 % K2HPO4			>2.5



Index of refraction



Absorption coefficient



dn/dT

Conclusions

- Survey of higher index fluids for 193 nm and 248 nm is underway, both customer-supplied (proprietary) and other possibilities. Also measuring fluids for 157 nm (Dupont, Solvay-Solexis).
- Initial results show a few fluids with $n > 1.6$ @ 193 nm, with some increase in absorption, thermo-optic coefficient.
- New high-accuracy minimum deviation goniometer to be operational late 2004, with reduced-uncertainty results for water.
- More work to be done on impurity effects in water, especially from resist interaction.