PHOSPHOR THERMOMETRY TECHNIQUES FOR THE REALIZATION OF THERMAL STANDARDS

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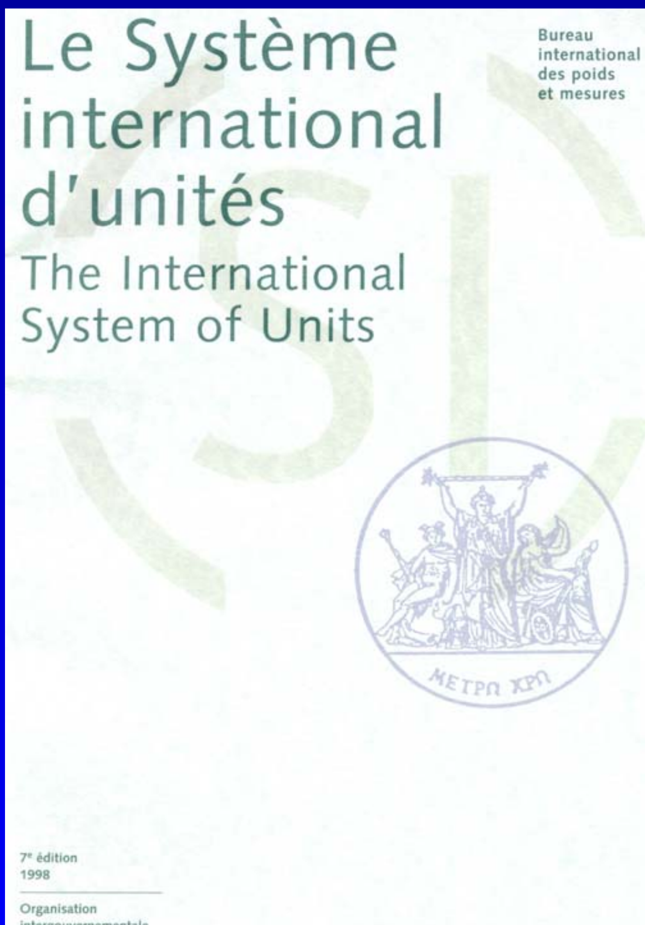
Acknowledgments to several colleagues at:

ORNL, Engineering Technology Division
Los Alamos National Laboratory, USAF, DOE
University of Tennessee, Department of Physics
U.Va., Department of Mechanical and Aerospace Engineering
The International Bureau of Weights and Measures
The U.S. National Institute of Standards and Technology

THE DEGREE KELVIN

A BASE UNIT OF THE SI



2.1.1.5 Unit of thermodynamic temperature (kelvin)

The definition of the unit of thermodynamic temperature was given in substance by the 10th CGPM (1954, Resolution 3; CR, 79) which selected the triple point of water as the fundamental fixed point and assigned to it the temperature 273.16 K so defining the unit. The 13th CGPM (1967-1968, Resolution 3; CR, 104 and *Metrologia*, 1968, **4**, 43) adopted the name *kelvin* (symbol K) instead of "degree Kelvin" (symbol °K) and defined the unit of thermodynamic temperature as follows (Resolution 4; CR, 104 and *Metrologia*, 1968, **4**, 43):

The kelvin, unit of thermodynamic temperature, is the fraction 1/273.16 of the thermodynamic temperature of the triple point of water.

Because of the way temperature scales used to be defined, it remains common practice to express a thermodynamic temperature, symbol T, in terms of its difference from the reference temperature $T_0 = 273.15$ K, the ice point. This temperature difference is called the Celsius temperature, symbol t, and is defined by the quantity equation

$$t = T - T_0.$$

The unit of Celsius temperature is the degree Celsius, symbol °C, which is by definition equal in magnitude to the kelvin. A difference or interval of temperature may be expressed in kelvins or in degrees Celsius (13th CGPM, 1967-1968, Resolution 3, mentioned above). The numerical value of a Celsius temperature t expressed in degrees Celsius is given by

$$t/°\mathrm{C} = T/\mathrm{K} - 273.15.$$

The kelvin and the degree Celsius are also the units of the International Temperature Scale of 1990 (ITS-90) adopted by the CIPM in 1989 in its Recommendation 5 (CI-1989) (PV, **57**, 115 and *Metrologia*, 1990, **27**, 13).

REALIZATION OF THE DEGREE KELVIN

Direct measurements of thermodynamic temperature: require "primary thermometers":

Constant-volume gas thermometer
Acoustic gas thermometer
Spectral and total radiation thermometers
Electronic noise thermometer

Uncertainties: $\lesssim$ 5 mK up to 373 K

Secondary thermometers: Platinum resistance thermometer

Easier to use
Reproducibility $\approx$ 10 times better

THE INTERNATIONAL TEMPERATURE SCALE OF 1990: (ITS-90)

"A temperature scale that is consistent with all the known laws of thermodynamics is termed a thermodynamic temperature scale. In practice, a well-understood thermodynamic system, such as an ideal gas, is prepared in the laboratory such that its thermodynamic temperature can be predicted from other known properties. Laboratory thermometers can then be calibrated at this thermodynamic temperature. The International Temperature Scale of 1990 is an approximation to the thermodynamic temperature scale."

Source: http://www.cstl.nist.gov/div836/836.05/thermometry/tempresearch/temperaturescale.htm

FEATURES AND USE OF THE ITS-90

Reference Points

Material	T_{90}/K	t_{90}/°C
e-H_2 (TP)	13.8033	–259.3467
e-H_2 (VP)	17	–256.15
e-H_2 (VP)	20.3	–252.85
Ne (TP)	24.5561	–248.5939
O_2 (TP)	54.3584	–218.7916
Ar (TP)	83.8058	–189.3442
Hg (TP)	234.3156	–38.8344
H_2O (TP)	273.16	0.01
Ga (MP)	302.9146	29.7646
In (FP)	429.7485	156.5985
Sn (FP)	505.078	231.928
Zn (FP)	692.677	419.527
Al (FP)	933.473	660.323
Ag (FP)	1234.93	961.78

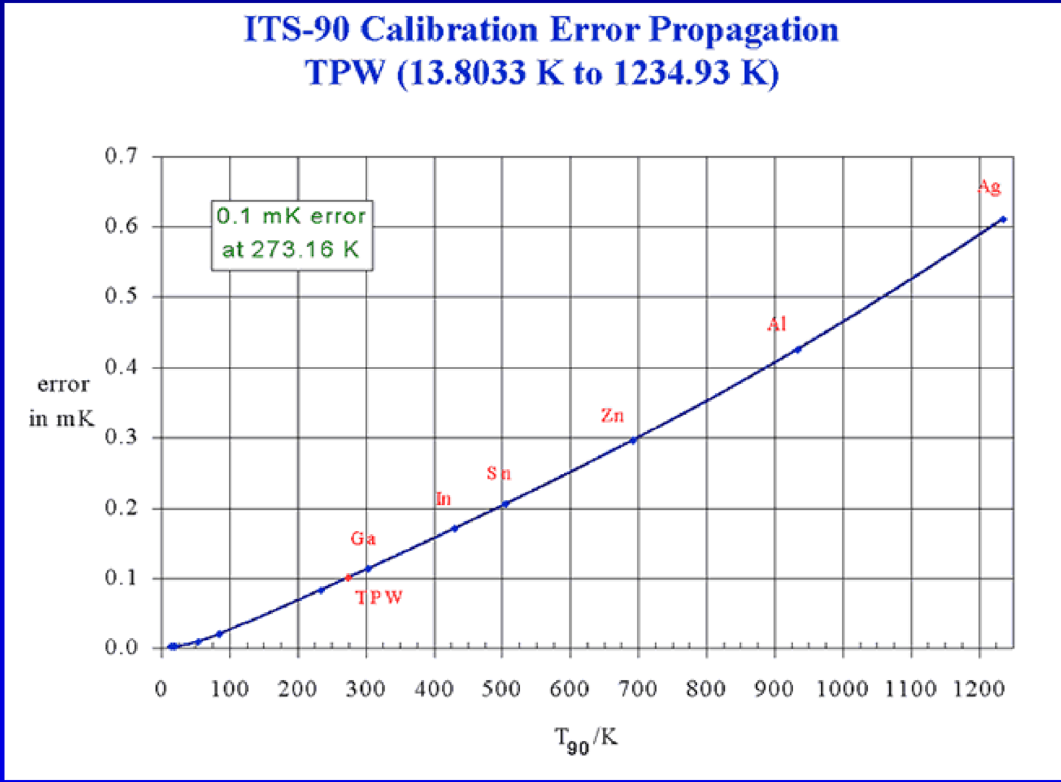
TP: triple point

MP: melting point

FP: freezing point

VP: vapor pressure point

Error Curve



Source: http://www.cstl.nist.gov/div836/836.05/thermometry/miscelaneous/faq.htm

The ITS-90 is:

- One of the most significant accomplishments in all of metrology
- Involves scientific input from all major national metrological laboratories around the world
- Constantly being improved and reviewed by the CCT, CIPM and the CGPM

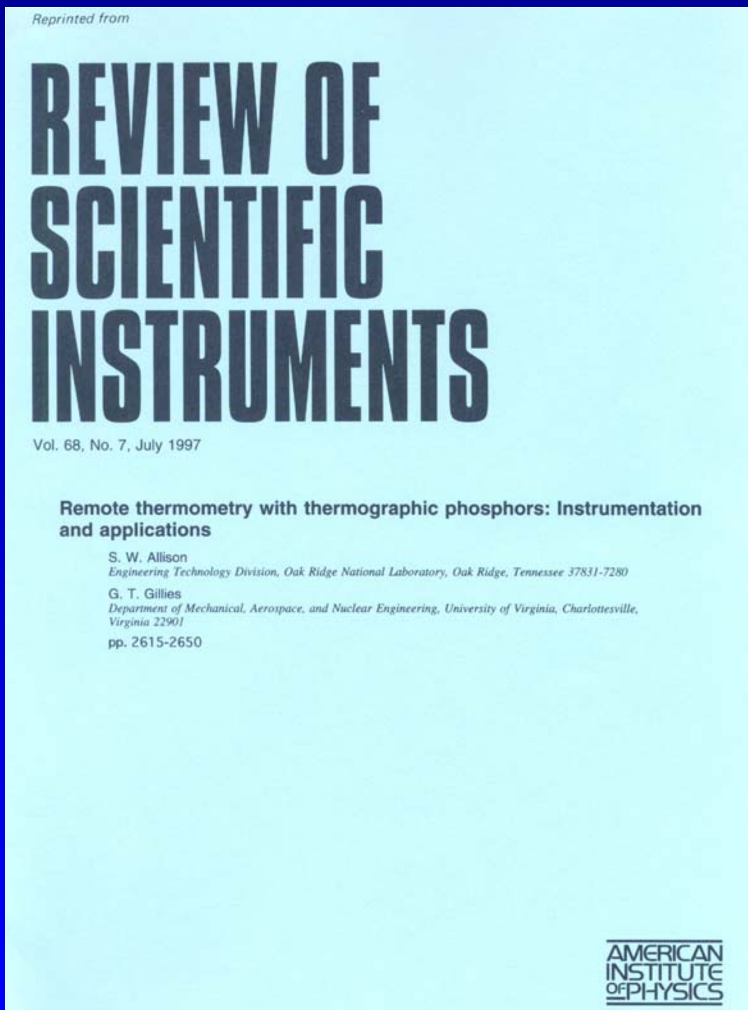
The ITS-90 is also:

- A discontinuous collection of thermodynamic fixed points (artefactual, not atomic standards)
- It therefore requires very broad interpolation over its entire range
- Unable to be realized by end users in industrial and other laboratories

FLUORESCENCE THERMOMETRY HAS THE POTENTIAL TO:

- Generate a continuous, uninterpolated scale from the cryogenic to the high temperature regimes
- Be founded on scientific “first principles” (quantum mechanics and statistical physics)
- Let the observables be atomic phenomena and processes (eg., quantized decay states)
- Tie all measurements to frequency and time standards
- Use doped single crystals of high stability ceramic oxides as the luminescent materials

LASER-INDUCED FLUORESCENCE OF THERMOGRAPHIC PHOSPHORS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Remote thermometry with thermographic phosphors: Instrumentation and applications

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pp. 2615-2650

AMERICAN INSTITUTE OF PHYSICS

- 50 years of research into the techniques
- Well understood quantum mechanical basis
- Measurement solutions for industrial, military problems
- Instrumentation systems are common to optical metrology

PHYSICAL BASIS FOR THE TECHNIQUE

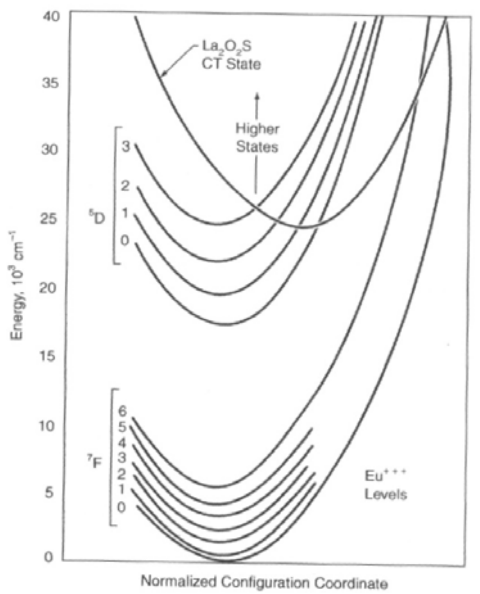


FIG. 2. The configuration coordinate diagram for La_2O_2S:Eu (after Ref. 49).

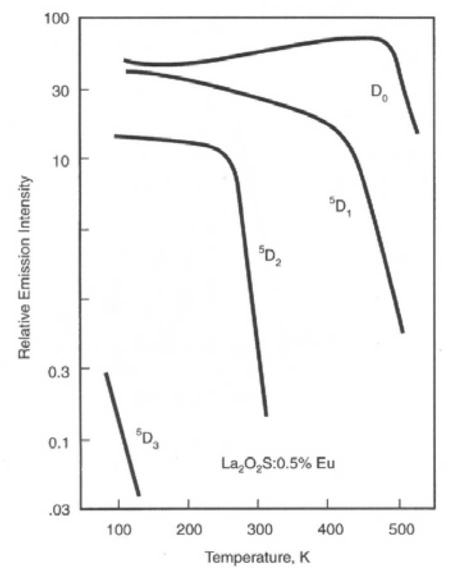


FIG. 7. Emission intensity vs temperature for La_2O_2S:Eu (after Ref. 49).

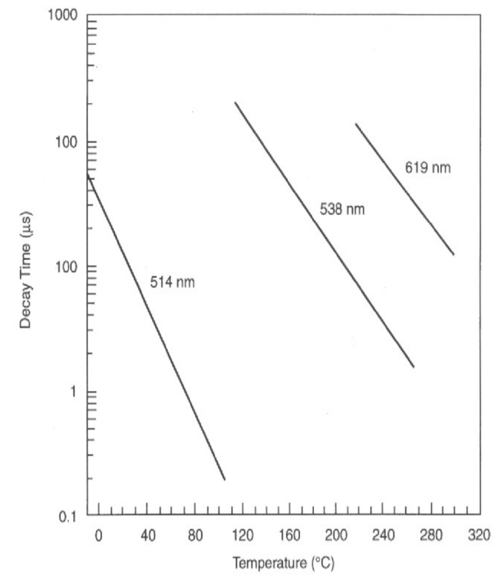


FIG. 9. Fluorescence decay time vs temperature for La_2O_2S:Eu.

Charge transfer states in rare-earth doped ceramic oxides and oxysulfides

Emission intensities vary with temperature of the host material

Decay lifetimes of excited states vary with temperature of host material

Decay-time constant is the key quantity

- Fonger and Struck model (1970)

$$\tau = [(1/\tau_0) + b \cdot e^{-(E/kT)}]^{-1}$$

- Ideally, τ_0, b, E are determined by atomic theory
- τ is measured relative to atomic clock time-base
- τ varies smoothly with temperature

EXPERIMENTAL ARRANGEMENT FOR REALIZING THE "FTS-89" AND THE DEGREE KELVIN

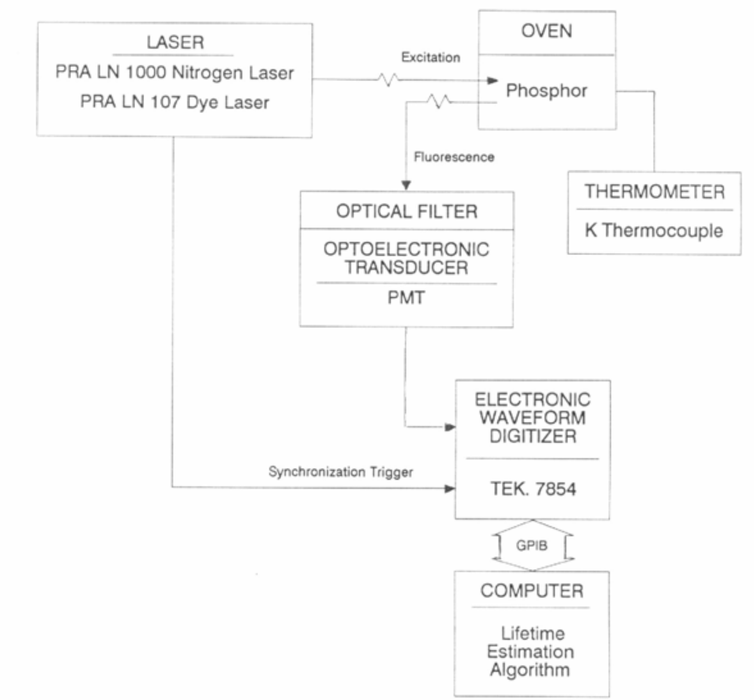
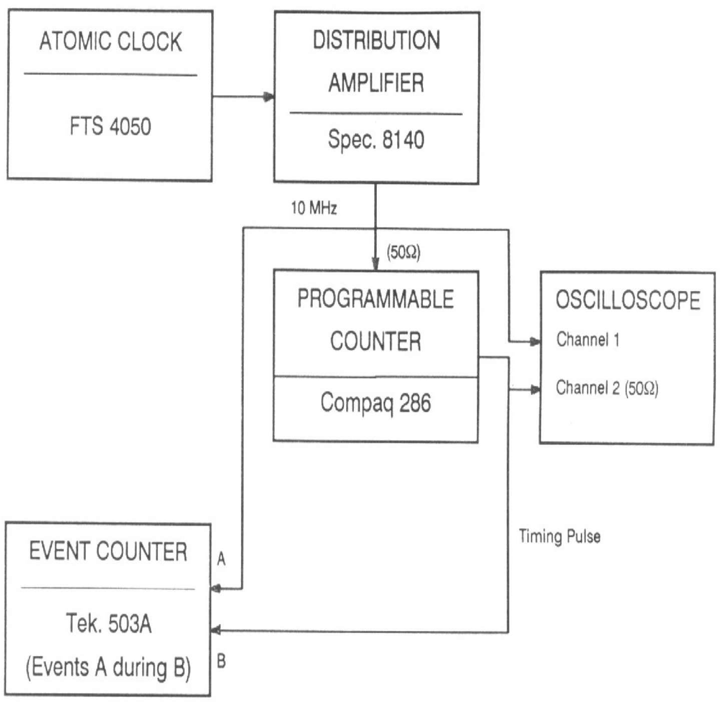


Figure 3-13. Functional block diagram of the fluorescence measurement system



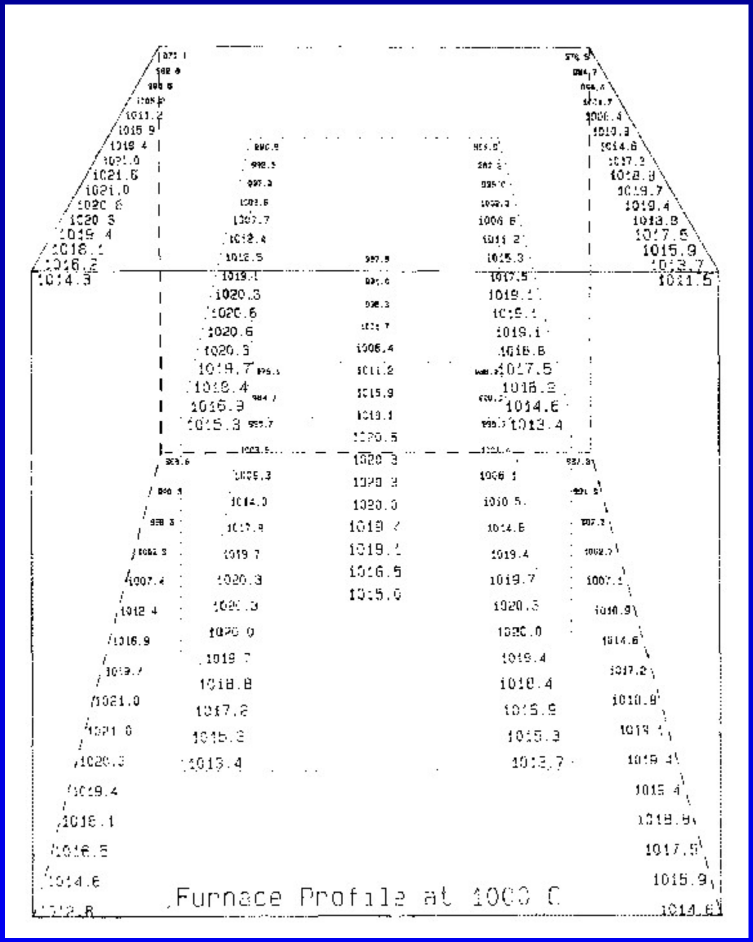
Source: L. J. Dowell, Ph.D. Dissertation, U.Va., 1989

CHARACTERIZING THE INSTRUMENTATION

- OPTICAL SYSTEM ALIGNMENT

Dowell, L. J., Gillies, G. T., and Allison, S. W., "Measurements of Lateral Offset Power Losses in Optical Fibers Scanning Point Sources," Optical Engineering, Vol. 26 (1987), pp. 547-552

· SAMPLE-POSITIONING REQUIREMENTS DUE TO THERMAL GRADIENTS IN OVEN

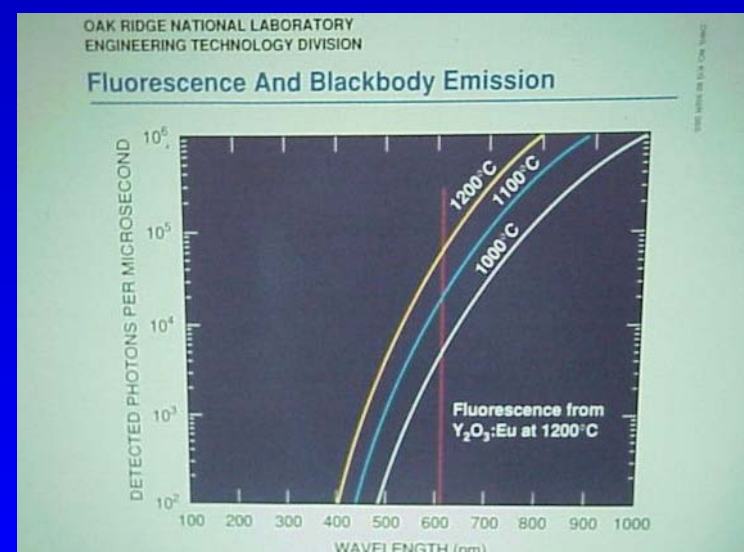


Lutz, W. N., Gillies, G. T., and Allison, S. W., "Computer-Aided Dated Acquisition System for Thermal Gradient Mapping and Calibrations of High-Temperature Cavities,“ Review of Scientific Instruments, Vol. 60 (1989), pp. 673-682.

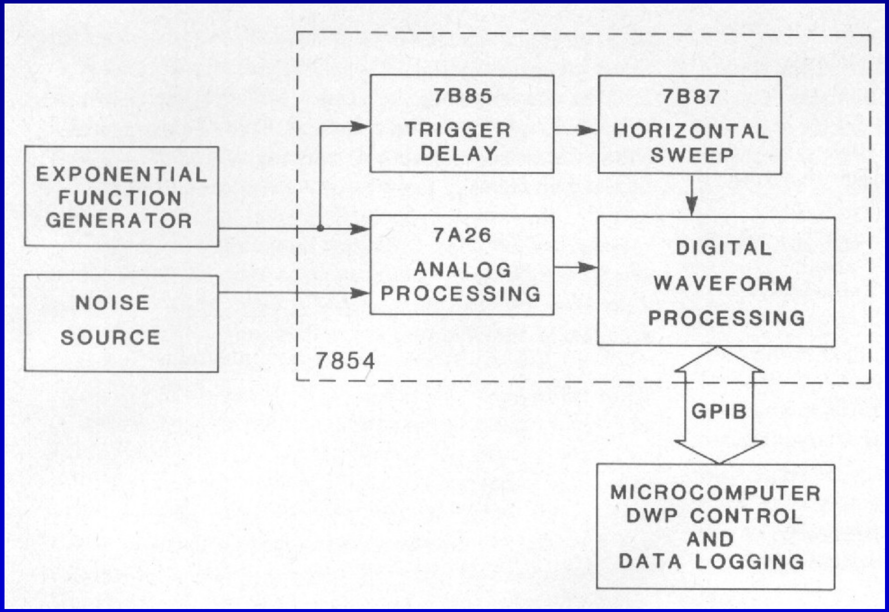
• BLACKBODY BACKGROUND IN FURNACE

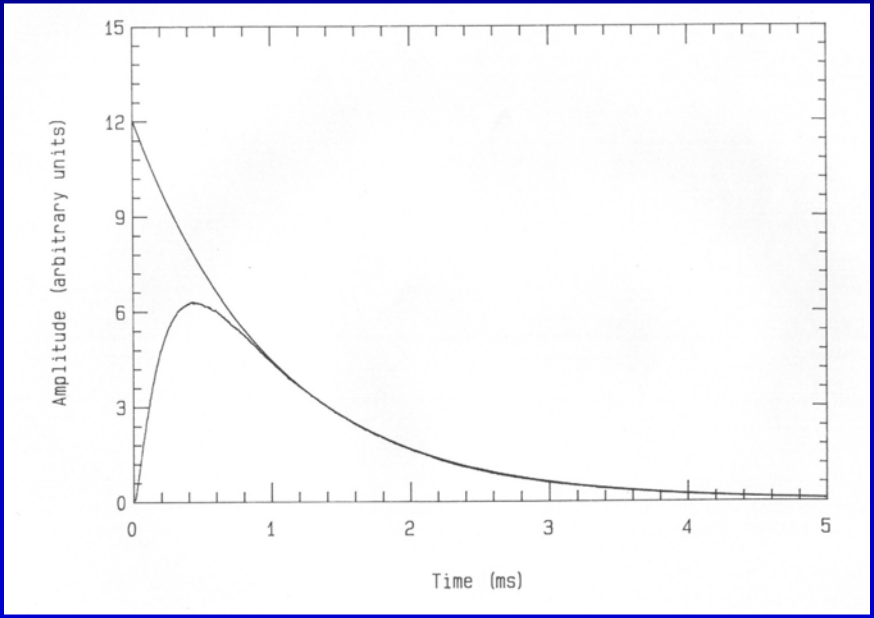
Almost an order of magnitude increase in the number of photons detected per 100 degree increase in temperature at 619 nm.

Careful optical bandwidth selection via filtering is needed to discriminate against the wideband background.



· ACCURACY OF WAVEFORM DIGITIZER





Dowell, L. J., Gillies, G. T., Cates, M. R., and Allison, S. W., "Precision Limits of Waveform Recovery and Analysis in a Signal Processing Oscilloscope," Review of Scientific Instruments, Vol. 58 (1987), pp. 1245-1250.

· ACCURACY OF TIME CONSTANT ANALYSIS

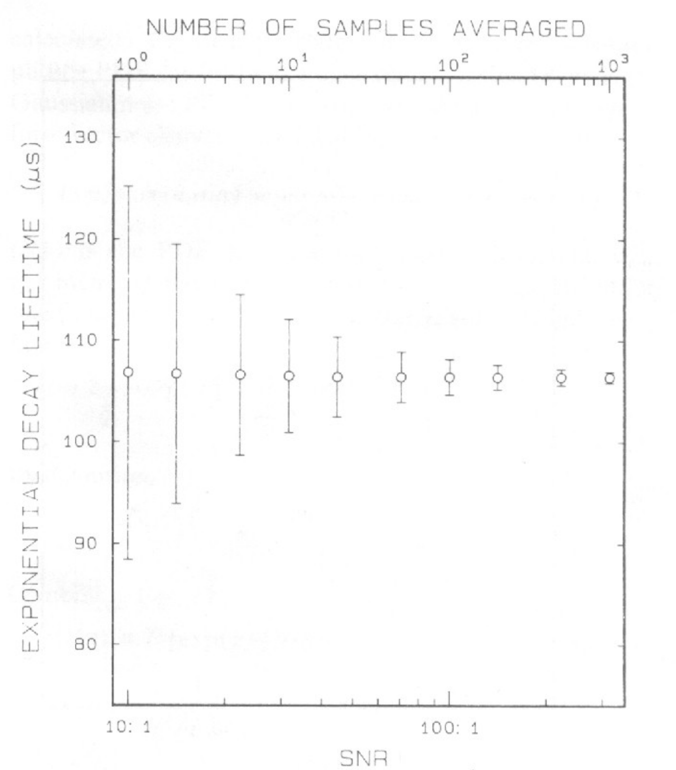


FIG. 3. Simulation results for the two data point estimation as a function of signal-to-noise ratio. Noise in a signal is reduced by averaging the signal measurements, and the SNR improves as the square root of the number of signal samples averaged. Here, the results simulate averaging a signal with an initial SNR of 10:1.

Dowell, L. J. and Gillies, G. T., "Precision Limits of Lifetime Estimation Algorithms as Determined by Monte Carlo Simulation: A Comparison of Theory and Experiment," Review of Scientific Instruments, Vol. 59 (1988), pp. 1310-1315.

Dowell, L. J. and Gillies, G. T., "Errors Caused by Baseline Offset and Noise in the Estimation of Exponential Lifetimes," Review of Scientific Instruments, Vol. 62 (1991), pp. 242-243.

• Y_2O_3:Eu SINGLE CRYSTAL PURITY

Impurity Element	YCl_3	Eu_2O_3
Al	<0.01	<0.005
Ca	<0.01	<0.005
Dy	0.006	-
Eu	-	-
Er	<0.005	-
Fe	<0.01	<0.005
Gd	<0.005	<0.01
Ho	<0.005	-
Lu	<0.005	-
Mg	<0.01	<0.005
Nd	<0.01	<0.01
Si	0.02	<0.005
Sm	<0.005	<0.01
Tb	<0.005	<0.01
Tm	<0.005	-
Y	-	<0.01
Yb	0.002	-
Zr	-	<0.005

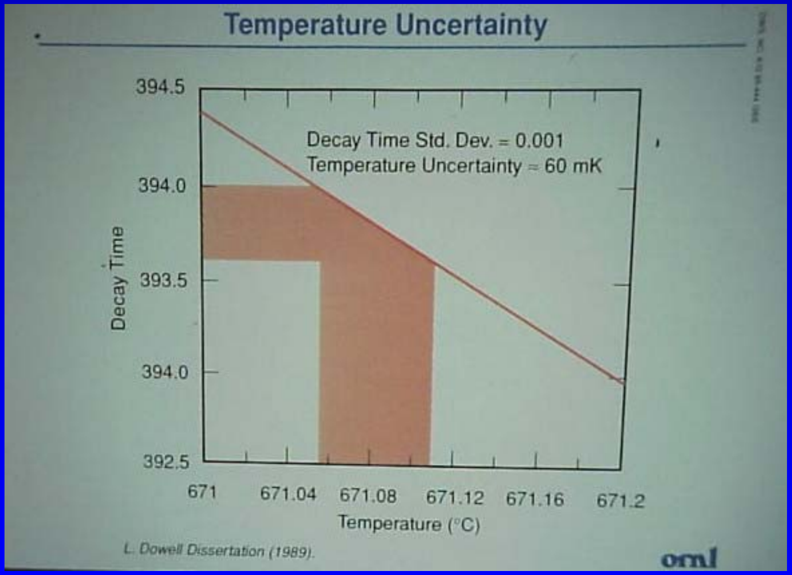
Table III-IV. Impurities in materials used to prepare Y_2O_3:Eu single crystals. The data are percent of composition for each impurity element. The data come from spectrographic analysis and were provided by Commercial Crystal Laboratories, Inc.

Also checked via neutron activation analysis at University of Virginia Reactor Facility.

RESULTS

Temperature (K)	SNR	β	τ (ms)
300	5690:1	2.693138±0.000247	0.930108±0.000140
666	4040:1	2.795084±0.000354	0.896184±0.000157
765	3780:1	2.848691±0.000382	0.879319±0.000158
865	6860:1	1.453592±0.000157	0.688964±0.000224
965	3110:1	0.930440±0.000306	0.270189±0.000187
1064	330:1	1.233660±0.003112	0.040672±0.000178

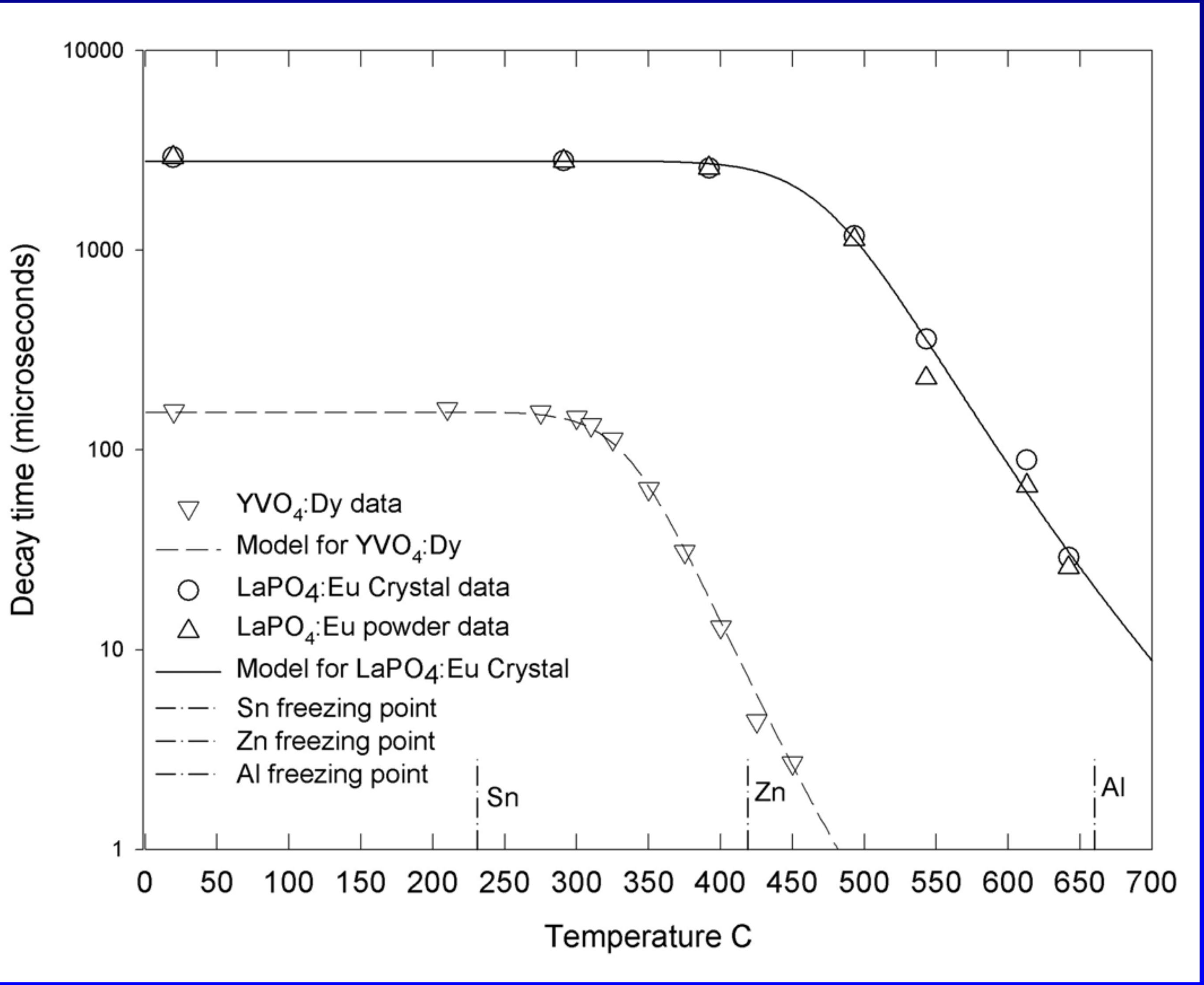
Table IV-IIIb. 1% Eu:Y_2O_3 611 nm lifetime with excitation near 466 nm.



L. J. Dowell, M.Sc. Thesis, U.Va. May 1987, 299 pp.

L. J. Dowell, Ph.D. Dissertation, U.Va., May 1989, 153 pp.

COMPARISON WITH THE ITS-90



OPEN QUESTIONS UNDER STUDY

- CAN THE UNCERTAINTIES MATCH ITS-90?
- IS THE DECAY TIME TRULY SINGLE-EXPONENTIAL?
- WHICH PHOSPHOR IS THE BEST?
- CAN MULTIPLE PHOSPHOR SYSTEMS SPAN THE RANGE FROM 0 K TO 2000+ K?
- WHAT EXCITATION SOURCE IS BEST? (BLUE LEDS?)

THE PHOSPHOR IS THE KEY

Source for SRM photo: http://www.cstl.nist.gov/div836/836.05/thermometry/srms/large_fps.htm

WORK IN PROGRESS

- SUMMARIZE WORK DONE TO DATE IN REVIEW ARTICLE FOR *METROLOGIA*
- CONTINUE DIALOGS WITH COLLEAGUES AT NIST, BIPM AND OTHER STANDARDS LABORATORIES
- CARRY OUT ADDITIONAL LABORATORY WORK ON LONG-TERM STABILITY OF EXPERIMENTAL SYSTEMS
- SEEK POSSIBLE USE WITHIN CONTEXT OF OTHER METROLOGICAL APPLICATIONS

OUR THANKS TO ISA FOR
THE OPPORTUNITY TO
PRESENT THIS PAPER.

A BRIEF PUBLISHED SUMMARY
OF THE WORK DONE TO DATE
IS IN THE PROCEEDINGS OF
THIS CONFERENCE.