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Report of the Results of SIM.QM-P6: UV/Visible Spectrophotometry Wavelength Standard Interlaboratory Comparison

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Abstract

A study was designed to compare wavelength axis measurements in ultraviolet and visible (uv/vis) spectrometry at several laboratories of the Interamerican Metrology System (Sistema Interamericano de Metrologia, or SIM) using holmium oxide solution Certified Reference Materials (CRMs). The goals of the study were to demonstrate comparability of wavelength measurements among the participants, to demonstrate the comparability between National Institute of Standards and Technology (NIST) and Centro Nacional de Metrologia (CENAM) versions of holmium oxide in perchloric acid solution CRMs, to acquire holmium oxide solution spectral data from a variety of spectrometers for use in a NIST study of wavelength assignment algorithms, and to provide a basis for a possible reassessment of the NIST-certified wavelength values. The goals were generally met, with widespread agreement of the measurements, evidence that sample origin is irrelevant, and support for re-assignment of the NIST-certified wavelength values for absorption band positions in SRM 2034.

Keywords

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1. INTRODUCTION

This study of holmium oxide solution wavelength Certified Reference Materials (CRMs) was designed to compare wavelength axis measurements in ultraviolet and visible (uv/vis) spectrometry at several laboratories of the Interamerican Metrology System (Sistema Interamericano de Metrologia, or SIM). The goals of the study were to demonstrate the degree of comparability of wavelength measurements among the participants, to demonstrate the comparability between National Institute of Standards and Technology (NIST) and Centro Nacional de Metrologia (CENAM) versions of holmium oxide in perchloric acid solution CRMs, to acquire holmium oxide solution spectral data from a variety of spectrometers for use in a NIST study of wavelength assignment algorithms, and to provide a basis for a possible reassessment of the NIST-certified wavelength values. This study was not intended to be a comparison of national wavelength scales.

2. METHODS AND MATERIALS

2.1 Participation

This SIM study was conducted from April 2000 through June 2002, involving eleven organizations in seven nations. The study evolved from a comparison [1] performed by five organizational units in three national laboratories within the North American Cooperation in Metrology (NORAMET), a subregion of SIM. Table 1 lists the organizations and the individuals involved in the SIM study. Table 2 lists the instruments and operating parameters used to acquire the data sets. Since two data sets were provided by one participant using the same instrument but at widely different times and operating conditions, the complete study consists of twelve data sets.

Three of the participants in the original NORAMET comparison were associated with the discipline of radiometric physics while two were primarily associated with chemistry. All five of these participants used comparable, modern instruments of a "conventional" double-beam scanning monochromator design. These instruments had variable, software-controlled slits that enabled spectral acquisition at nominal spectral slit width (SSW) settings of 0.1 nm, 1.0 nm, and 3.0 nm.

The SIM invitation was only to laboratories associated with the discipline of chemistry. The majority of organizations expressing an interest in participation proposed use of instruments that were unable to acquire spectra at all three of the desired SSWs and/or were of "inverted" design (wavelength dispersion following the sample, with array detection) with fixed SSW. Since such instruments represent the majority of applications of chemical spectrophotometry, the original protocol was modified to enable participation by all interested organizations.

2.2 Samples

The sample kit contained four sealed, fused-silica cuvettes each filled with holmium oxide in perchloric acid: two samples each of the CENAM DMR 41e (2000) [2] and the NIST SRM 2034 (1999) [3] reference materials. Each sample was marked with a colored dot on the bottom of the cuvette to permit easy identification of a particular sample. The kit also contained a copy of the NIST SRM certificate for SRM 2034, NIST SP 260-102 "Holmium Oxide Solution Wavelength Standard From 240 to 640 nm – SRM 2034," [4] and ASTM Standard E958-93 (1999) "Standard Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers," [5] and the Materials Safety Data Sheet for holmium oxide in perchloric acid solution.

2.3 Measurement Protocol

Participants were requested to acquire transmittance spectra for each of the samples from 230.0 nm to 679.9 nm with a data interval of 0.1 nm at SSWs of 0.1 nm, 1.0 nm, and 3.0 nm. Spectra were to be

collected in constant SSW (fixed-slit) mode using an airpath reference. Participants using instruments of limited SSW range were requested to provide spectra at whatever subset of these three SSWs could be achieved. Participants using instruments of fixed SSW were requested to provide whatever spectra could be acquired, at the suggested data density or the highest data density possible. Participants were requested to acquire spectra for each sample in the same specified order at each SSW evaluated. To enable assessment of short- and intermediate-term variance components, participants were requested to acquire two complete sets of data in separate sessions at least one day apart. Each participant was thus requested to acquire 8 spectra (4 samples × 2 sessions) for each SSW evaluated.

Where practical, each instrument's wavelength axis was to be bias-corrected by substituting appropriate atomic pen lamps for a continuum lamp and fitting a low order polynomial to the bias vs. indicated wavelength data. If the requested pen lamp calibration could not be performed, participants were requested to report any wavelength calibration measures taken. Participants were likewise requested to, where possible, verify actual spectral slit width values using the method described in ASTM 958-93 [5].

Participants were requested to report the temperature of the sample at the time of measurements. Some of the participants reported the ambient temperature of the room in which the spectrometer was housed rather than the temperature within the instrument's sample chamber.

Participants were asked to report evaluated band locations and associated uncertainties for the 14 bands identified in Figure 1 (the bands certified for location in NIST SRM 2034), along with a description of the band location method or algorithm used. Unmodified spectra in text or spreadsheet format were also requested so that the same polynomial interpolation location algorithm could be applied to all spectra. One participant ("d") provided spectra in a proprietary format that could not be decoded.

2.4 Band Location
Band locations for all spectra furnished in a readable format were determined at NIST's Chemical Science and Technology Laboratory (CSTL) using both the data minimum and cubic interpolation methods described in Ref. [1]. Calibration corrections were applied if furnished by the participant. The calibrated locations determined by the CSTL algorithms were compared to those furnished by the participant. With the exception a few bands in one set of spectra having atypically high photometric noise/signal, the two location estimates agreed within ±0.01 nm. The location of the bands having the least optical depth (especially band 8) in the "noisy" spectra were more repeatably located by the participant than by the data minimum or the CSTL interpolation algorithm.

To reflect participant measurement systems while using the most consistent and most appropriate band location measurements, the following discussion is based upon the analysis of: 1) participant-provided interpolated band locations, 2) CSTL-interpolated locations when participants provided spectra but not interpolated locations, and 3) participant-provided data minima when neither interpolated locations nor readable spectra were provided. Table 2 lists the band locations algorithms used for each data set.

3. RESULTS AND DISCUSSION

3.1 Measured Positions of Certified Bands and Inter-laboratory Variability
Tables 3 – 6 summarize the band location results for all participants, band positions, and SSW values. Tables 3 – 5 are for nominal SSW values of 0.1 nm, 1.0 nm, and 3.0 nm, respectively; Table 6 reports results for instruments of nominal SSW 1.6 nm and 2.2 nm. The NIST SRM 2034(01) certified band locations and associated uncertainties for the appropriate SSW of the 14 bands is given to the left of each table. Each value in the remaining columns represents the difference between the average of eight

determinations (4 samples × 2 replicate measurements) by a given participant and the certified value, along with the standard deviation of the eight determinations. For Table 6, the reference values and uncertainties are interpolated from the certified values.

None of the reported band locations for the 0.1 nm, 1.0 nm, and 3.0 nm SSW spectra are outside of the certified value range specified in Reference [3]. Several band locations for the 2.2 nm SSW spectra are outside of the expected range (italicized values in Table 6). Since there are both positive and negative differences, it is unclear whether these excursions are attributable to the particular spectra, the intrinsic performance of the instrument, or to the interpolation process used to establish the reference location and uncertainty values for this SSW. Both of the 1.6 nm SSW instruments appear to provide locations that are systematically higher than expected, although generally within the 0.5 nm data granularity set by the instrument's 1.0 nm data spacing.

Figures 2 – 4 display the differences between each average band position and the certified value as functions of the nominal wavelength for all participants providing data at 0.1 nm, 1.0 nm, or 3.0 nm SSW. Individual participant uncertainties are omitted for clarity, as uncertainty issues are separately discussed below. The bars span ±twice the among-participant standard deviations (*i.e.*, the expanded uncertainties using a coverage factor of k = 2) about each average. Figure 5 similarly displays the differences for three fixed-slit instruments of 1.6 nm or 2.2 nm SSW, with insufficient data to compute among-participant expanded uncertainties.

3.2 Central Values for Band Positions

Figures 2 – 4 clearly support the need to reassign the certified values for some bands of SRM 2034 in addition to re-evaluating the uncertainties. The clearest example is band 13 at 1.0 nm (Figure 3), for which all SIM participants found lower values than certified. Figure 3 also implicates bands 6, 7, and, 12, with apparently high certified values. Figure 2 illustrates the potential problems with bands 12, 13 and 14 at 0.1 nm SSW. Figure 4 shows a curious "drift" of the data to high values with decreasing wavelength at 3.0 nm SSW. This could represent a skew in the nominally triangular slit function in the original certifying instrument, resulting from non-uniform illumination of the wide entrance slit. The effect of such a skew would be magnified in the UV, due to the lower relative width of the bands there when displayed in constant wavelength increments.

A multi-center exercise of similar protocol to the one reported here is currently underway to address the need to re-assign the band positions. Calibrated SIM data will be used in this re-assignment of the band positions and uncertainties for SRM 2034.

3.3 Uncertainties in Band Position Assignment

The lower segment of each of Figures 6 – 19 displays all band locations (relative to their average value) reported for a given band by all participants for all SSW values. The individual measurements are alphabet- and color-coded to correspond to the four samples marked as Red and Blue (NIST SRM 2034) and Green and Yellow (CENAM DMR 41e). The symbols are in lower case for measurements on the first day and upper case for the second day. Light dotted lines at ±0.05 nm represent the bias that might result from the granularity of the 0.1 nm data spacing if one were to employ the simplest band location algorithm of all – the location of the minimum data point.

The "scatter" along the ordinate in these plots is representative of the "within instrument" variance component, including possible effects due to sample differences and measurement repeatability (discussed below). By visual comparison of the "within instrument" scatter in Figures 6 – 19 and the "among instrument" scatter in Figures 2 – 5, it is clear that instrument to instrument differences are the largest component of band location uncertainty. For 0.1 nm and 1.0 nm SSW values, the "within instrument" scatter of Figures 6 – 19 is consistent with the claim of many laboratories to be able to

calibrate instruments to an accuracy of ±0.1 nm, the overall uncertainty quoted for SRM 2034 for all bands and SSW values prior to Series 2002. However, the legitimacy of this claim to accuracy is called into question by the differences among instruments calibrated to atomic wavelength standards by qualified operators.

For this reason, the findings from the NORAMET study were used to recalculate the overall uncertainties for the certified bands for the Series 2002 certificate for NIST SRM 2034, shown as $\pm U_{95}$ in the tables. These uncertainties were constructed to allow for the variance components identified in the study in addition to a component added linearly to account for the bias between the certified value and the average of the values determined by all of the NORAMET instruments.

Recertification of the band positions will remove the "bias" component of the uncertainty, but it is clear that the uncertainties will average closer to ±0.2 nm than to the prior value of ±0.1 nm, and that individual uncertainties for each band and SSW are called for by the varying band shapes encountered.

3.4 Sample-to-sample and Replication Variability
Holmium oxide solution made according to a well-defined composition and procedure could be declared an "intrinsic standard" if it can be shown that the band positions are robust with respect to a reasonable variation in sample preparation parameters. The present study addresses that issue through the presence of reference materials separately prepared by NIST and CENAM.

The uppermost plots in Figures 6 – 19 represent the standard uncertainty component which may be assigned to differences among the samples ("heterogeneity", closed circles) and that which represents replication on separate days with removal and replacement of the sample ("repeatability", open circles). Variability among the samples would cause the component due to sample difference to routinely exceed that resulting from simple replication, whereas the opposite is observed. The fundamental conclusion is that the four samples can not be distinguished on the basis of band location.

Since replication was on separate days, there may be some question of the importance of a "day" effect as opposed to a simple replication effect. Examination of the lower case (Day 1) and upper case (Day 2) data of the lower plots suggests that replication with removal and replacement of the sample is the source of the variability rather than a "day" effect.

4. CONCLUSIONS

1) All the band locations measured by participants at 0.1 nm, 1.0 nm, and 3.0 nm SSW were consistent with the certified values for NIST SRM 2034 at a level appropriate to the 95% confidence limit uncertainties given in the Series 02 certificate for that material.

2) Sample pairs produced by NIST and CENAM were indistinguishable within and across production laboratories.

3) Instrument-to-instrument variability exceeded the estimated wavelength uncertainty of most participants by nearly two-fold. Individual instruments seem to exhibit minor variations about a "smooth" calibration curve due to characteristics of individual gratings, sine-bar drives, and so forth.

4) It is recommended that multiple instruments be involved in the assignment of wavelength values and uncertainties to spectral features for use as absorptive wavelength standards. Calibrated SIM results will be combined with others from a wider international participation to re-assign certified values for NIST SRM 2034.

REFERENCES

1   J.C. Travis, J.C. Zwinkels, F. Mercader, A. Ruiz, E.A. Early, M.V. Smith, M. Noel, M. Maley, G.W. Kramer, K.L. Eckerle, and D.L. Duewer, "An International Evaluation of Holmium Oxide Solution Reference Materials for Wavelength Calibration in Molecular Absorption Spectrophotometry," Anal. Chem. 74, 3408 (2002).

2   Reference Material DMR 41e, Centro Nacional de Metrología, 76900 Querétaro, México. http://www.cenam.mx/sitio/MaterialesMetalicos.htm

3   Standard Reference Material SRM 2034, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA. http://srmcatalog.nist.gov/

4   V.R. Weidner, R. Mavrodineanu, K.D. Mielenz, R.A. Velapoldi, K.L. Eckerle, and B. Adams, Holmium Oxide Solution Wavelength Standard from 240 to 640 nm – SRM 2034, NBS Special Publication 260-102, U.S. Government Printing Office, Washington DC, USA (1986). http://ts.nist.gov/ts/htdocs/230/232/splist/splist.htm

5   ASTM E 958-93 "Standard Practice for Measuring Practical Spectral Bandwidth of Ultraviolet-Visible Spectrophotometers", Annual Book of ASTM Standards, Vol. 03.06, ASTM, West Conshohochen PA, USA (2000).

Table 1
Participants in SIM.QM-P6

Country	Organization	Coordinators/Analysts
Argentina	Instituto Nacional de Tecnología Industrial (INTI) Centro de Investigación en Tecnología e Industrialización de Alimentos (CEIAL) Parque Tecnológico Miguelete San Martín (1650) Buenos Aires	Celia Puglisi
Argentina	Instituto Nacional de Tecnología Industrial (INTI) Misiones 1156 (1876) Bernal Buenos Aires	Celia Puglisi
Brazil	Institute for Technological Research of São Paulo State Optical Laboratory Mechanical and Electrical Engineering Division Av. Prof. Almeida Prado, 532 - Cid. Universitária CEP: 05508-901 Butantã São Paulo SP	Tsai Soi Mui Lee Oswaldo Luiz Bueno Martins Antonio Francisco Gentil Ferreira Jr.
Canada	Institute of National Measurement Standards National Research Council Canada Ottawa, Ontario K1A 0R6	Joanne Zwinkels, Mario Noel
Costa Rica	Laboratorio de Metrología Escuela de Química Universidad de Costa Rica	Sandra Marcela Rodríguez Zúñiga Jorge Chacon
Mexico	Metals Division Centro Nacional de Metrología 76900 Querétaro	Flora Mercader
Mexico	Optical and Radiometric Division Centro Nacional de Metrología 76900 Querétaro	Arquimedes Ruiz
Trinidad & Tobago	Trinidad & Tobago Bureau of Standards PO Box 467 Port of Spain	Anne Marie Sirju, Seema Gonowrie Debbie Dindial
Trinidad & Tobago	Ministry of Health Drug Lab, Chemistry Food and Drugs Division 115 Frederick Street Port of Spain	Rosemary James Debbie Dindial (TTBS/coord.)
USA	Chemical Science and Technology Laboratory National Institute of Standards and Technology Gaithersburg, MD 20899-8394	John Travis, Melody Smith Marissa Maley, David Duewer, Gary Kramer
USA	Physics Laboratory National Institute of Standards and Technology Gaithersburg, MD 20899-8441	Edward Early, Kenneth Eckerle

Table 2
Instruments for SIM.QM-P6

Code	Instrument	Nominal SSW nm	Data Spacing nm	Temperature °C	Location Algorithm	Notes
a	Hitachi U 3000	0.1, 1.0	0.1	26.8 to 29.2	Participant interpolation	Wavelength and SSW calibration furnished.
b	Varian Cary 5e	0.1, 1.0, 3.0	0.1	?	CSTL interpolation	
c	PE Lambda 19	0.1, 1.0, 3.0	0.1	?	CSTL interpolation	Wavelength calibration furnished
d	Varian Cary 4	0.1, 1.0, 3.0	0.1	20.7 to 21.6	Data minimum	
e	PE Lambda 900	0.1, 1.0, 3.0	0.1	22 to 24	Participant interpolation	Wavelength and SSW calibration furnished
f	PE Lambda 900	0.1, 1.0, 3.0	0.1	22 to 24	Participant interpolation	Wavelength and SSW calibration furnished.
g	PE Lambda 19	0.1, 1.0, 3.0	0.1	26 to 27	Participant interpolation	Wavelength and SSW calibration furnished.
h	Varian Cary 5e	0.1, 1.0, 3.0	0.1	?	CSTL interpolation	Wavelength axis verified to within 0.1 nm
i	Varian Cary 100	1.0, 3.0	0.1	23.0 to 23.5	CSTL interpolation	
j	HP 8453	1.6	1.0	20.2 to 27.7	CSTL interpolation	Wavelength and SSW calibration furnished
k	HP 8453	1.6	1.0	20.5	CSTL interpolation	
l	Metrolab M1700	2.2	0.1	?	CSTL interpolation	Wavelength and SSW calibration furnished.

Table 3
Differences from SRM 2034 Certified Values for 0.1 nm SSW Measurements

Δ = (Measurement - SRM 2034 Certified), nm

$\overline{\Delta}$ = Average Difference, nm; S = Standard Deviation of Differences, nm

Band	SRM 2034 Cert	±U_{95}	Participant Codes a $\overline{\Delta}$	a S	b $\overline{\Delta}$	b S	c $\overline{\Delta}$	c S	d $\overline{\Delta}$	d S	e $\overline{\Delta}$	e S	f $\overline{\Delta}$	f S	g $\overline{\Delta}$	g S	h $\overline{\Delta}$	h S
1	240.99	0.23	-0.06	0.01	0.03	0.02	-0.18	0.04	0.01	0.00	0.12	0.00	-0.02	0.00	-0.02	0.01	0.00	0.01
2	249.83	0.30	-0.04	0.03	-0.02	0.02	-0.22	0.02	-0.03	0.00	0.15	0.03	-0.05	0.01	-0.07	0.01	-0.01	0.02
3	278.15	0.23	-0.02	0.01	0.04	0.01	-0.15	0.03	0.05	0.00	0.15	0.01	0.02	0.00	0.03	0.01	0.01	0.01
4	287.01	0.22	0.01	0.01	0.07	0.01	-0.14	0.03	0.00	0.04	0.14	0.01	-0.01	0.01	0.01	0.00	0.04	0.01
5	333.47	0.21	0.00	0.03	0.06	0.02	-0.13	0.04	0.04	0.04	0.12	0.02	0.00	0.02	0.00	0.02	0.07	0.02
6	345.55	0.36	0.03	0.03	0.00	0.09	-0.21	0.05	-0.01	0.12	0.16	0.05	-0.07	0.06	-0.07	0.03	0.03	0.06
7	361.36	0.25	0.07	0.04	0.01	0.02	-0.20	0.04	0.00	0.05	0.00	0.02	-0.10	0.01	-0.09	0.01	-0.02	0.01
8	385.45	0.25	0.18	0.05	-0.03	0.04	-0.15	0.07	-0.02	0.05	-0.01	0.07	-0.13	0.06	-0.12	0.04	-0.06	0.03
9	416.07	0.22	0.06	0.02	0.05	0.01	-0.13	0.03	0.03	0.00	0.06	0.01	-0.06	0.01	-0.10	0.02	0.01	0.01
10*																		
11	467.82	0.19	0.05	0.03	-0.01	0.02	-0.13	0.03	-0.02	0.00	-0.01	0.02	-0.08	0.01	-0.11	0.01	0.01	0.02
12	485.28	0.25	0.03	0.02	-0.03	0.01	-0.16	0.03	-0.03	0.05	0.00	0.01	-0.11	0.01	-0.16	0.01	-0.03	0.01
13	536.54	0.28	0.03	0.01	-0.06	0.02	-0.21	0.03	-0.05	0.04	-0.04	0.01	-0.14	0.01	-0.17	0.03	-0.06	0.01
14	640.51	0.27	0.05	0.02	-0.05	0.03	-0.17	0.03	-0.01	0.00	0.01	0.03	-0.08	0.04	-0.17	0.03	-0.02	0.01
Average($\overline{\Delta}$)			0.03		0.00		-0.17		0.00		0.07		-0.06		-0.08		0.00	
S($\overline{\Delta}$)			0.06		0.04		0.03		0.03		0.07		0.05		0.07		0.04	

* The location of Band 10 at 0.1 nm SSW for SRM 2034 is not certified.

Table 4

Differences from SRM 2034 Certified Values for 1.0 nm SSW Measurements

$$\Delta = (\text{Measurement - SRM 2034 Certified}), \text{nm}$$

$$\bar{\Delta} = \text{Average Difference, nm; } S = \text{Standard Deviation of Differences, nm}$$

Participant Codes

Band	SRM 2034 Cert	±U$_{95}$	a $\bar{\Delta}$	a S	b $\bar{\Delta}$	b S	c $\bar{\Delta}$	c S	d $\bar{\Delta}$	d S	e $\bar{\Delta}$	e S	f $\bar{\Delta}$	f S	g $\bar{\Delta}$	g S	h $\bar{\Delta}$	h S	i $\bar{\Delta}$	i S
1	241.13	0.21	-0.01	0.04	0.08	0.01	-0.18	0.03	0.07	0.00	0.10	0.00	-0.02	0.01	-0.02	0.00	0.06	0.01	-0.12	0.04
2	249.87	0.21	0.00	0.04	0.08	0.01	-0.17	0.03	0.06	0.05	0.10	0.06	-0.01	0.01	-0.01	0.01	0.02	0.02	-0.09	0.04
3	278.10	0.20	0.01	0.04	0.08	0.00	-0.12	0.03	0.10	0.00	0.11	0.01	0.02	0.00	0.04	0.01	0.07	0.01	-0.06	0.04
4	287.18	0.27	0.03	0.04	0.13	0.01	-0.13	0.03	0.11	0.04	0.15	0.01	0.00	0.01	0.01	0.01	0.12	0.01	-0.05	0.04
5	333.44	0.21	0.08	0.03	0.08	0.02	-0.08	0.03	0.11	0.05	0.10	0.05	0.01	0.00	0.01	0.01	0.15	0.02	-0.05	0.04
6	345.47	0.20	0.06	0.05	-0.05	0.03	-0.18	0.03	0.00	0.07	-0.04	0.03	-0.09	0.01	-0.10	0.01	-0.03	0.01	-0.15	0.07
7	361.31	0.18	0.03	0.04	0.02	0.01	-0.15	0.04	0.00	0.04	-0.04	0.01	-0.08	0.00	-0.08	0.01	0.00	0.02	-0.17	0.04
8	385.66	0.20	0.03	0.03	0.03	0.05	-0.14	0.04	0.04	0.05	-0.01	0.05	-0.04	0.01	-0.11	0.01	0.06	0.04	-0.13	0.05
9	416.28	0.21	0.01	0.03	0.07	0.01	-0.14	0.03	0.02	0.00	0.02	0.01	-0.06	0.01	-0.12	0.01	0.07	0.01	-0.11	0.02
10	451.30	0.31	-0.13	0.02	0.14	0.17	0.11	0.05	0.08	0.09	0.07	0.04	0.07	0.04	0.20	0.01	0.12	0.03	0.02	0.04
11	467.83	0.16	0.02	0.04	0.03	0.01	-0.11	0.03	0.02	0.05	-0.02	0.03	-0.05	0.01	-0.07	0.01	0.06	0.02	-0.11	0.02
12	485.29	0.21	0.01	0.03	-0.03	0.01	-0.14	0.03	0.01	0.00	-0.03	0.02	-0.10	0.00	-0.15	0.01	0.00	0.01	-0.14	0.03
13	536.64	0.24	-0.02	0.02	-0.04	0.01	-0.18	0.03	-0.03	0.04	-0.04	0.01	-0.10	0.01	-0.18	0.01	-0.01	0.01	-0.16	0.05
14	640.52	0.20	0.01	0.03	0.00	0.02	-0.12	0.03	0.02	0.05	0.03	0.02	-0.06	0.00	-0.14	0.01	0.06	0.02	-0.10	0.04
Average($\bar{\Delta}$)			0.01		0.05		-0.12		0.04		0.03		-0.04		-0.05		0.05		-0.10	
S($\bar{\Delta}$)			0.05		0.06		0.07		0.04		0.07		0.05		0.10		0.05		0.05	

Table 5
Differences from SRM 2034 Certified Values for 3.0 nm SSW Measurements

Δ = (Measurement - SRM 2034 Certified), nm

$\bar{\Delta}$ = Average Difference, nm; S = Standard Deviation of Differences, nm

Band	SRM 2034 Cert	±U$_{95}$	Participant Codes b $\bar{\Delta}$	b S	c $\bar{\Delta}$	c S	d $\bar{\Delta}$	d S	e $\bar{\Delta}$	e S	f $\bar{\Delta}$	f S	g $\bar{\Delta}$	g S	h $\bar{\Delta}$	h S	i $\bar{\Delta}$	i S
1	240.90	0.33	0.21	0.01	-0.01	0.03	0.26	0.05	0.11	0.07	0.10	0.01	0.23	0.01	0.17	0.05	0.23	0.02
2	249.92	0.45	0.18	0.04	0.00	0.04	0.33	0.16	0.29	0.24	0.05	0.03	0.17	0.03	0.32	0.18	0.27	0.06
3	278.03	0.23	0.08	0.02	-0.11	0.03	0.19	0.07	0.07	0.07	-0.03	0.01	0.13	0.01	0.08	0.03	0.15	0.03
4	287.47	0.40	0.22	0.01	-0.02	0.03	0.33	0.05	0.22	0.06	0.04	0.01	0.20	0.01	0.25	0.07	0.27	0.04
5	333.32	0.34	0.04	0.07	0.13	0.03	0.27	0.08	0.11	0.11	0.10	0.01	0.22	0.01	0.28	0.10	0.29	0.04
6	345.49	0.21	-0.11	0.07	0.01	0.04	0.15	0.14	-0.01	0.10	-0.01	0.02	0.08	0.01	0.12	0.10	0.18	0.06
7	361.04	0.22	0.02	0.02	0.10	0.04	0.11	0.05	-0.01	0.03	0.01	0.01	0.15	0.01	0.12	0.03	-0.09	0.05
8	386.01	0.24	-0.05	0.07	-0.02	0.06	0.00	0.10	0.05	0.14	-0.08	0.06	-0.04	0.02	0.15	0.07	-0.10	0.12
9	416.84	0.17	0.02	0.02	0.02	0.03	0.07	0.04	0.03	0.03	-0.01	0.00	0.02	0.01	0.15	0.02	0.03	0.03
10	451.24	0.17	0.02	0.02	0.07	0.03	0.15	0.04	-0.06	0.01	-0.04	0.01	0.03	0.02	0.11	0.02	0.05	0.03
11	468.07	0.18	0.01	0.07	-0.04	0.03	0.13	0.08	0.06	0.11	-0.02	0.01	0.02	0.01	0.14	0.07	-0.02	0.07
12	485.21	0.23	-0.08	0.05	0.04	0.03	0.04	0.05	-0.12	0.08	-0.10	0.01	-0.03	0.01	0.06	0.01	-0.01	0.04
13	537.19	0.19	0.00	0.01	-0.03	0.03	0.11	0.00	0.08	0.01	-0.02	0.00	-0.07	0.02	0.14	0.01	-0.01	0.03
14	641.05	0.28	0.03	0.03	-0.01	0.03	0.15	0.00	0.14	0.05	0.01	0.01	-0.11	0.01	0.19	0.03	0.05	0.02
Average($\bar{\Delta}$)			0.04		0.01		0.16		0.07		0.00		0.07		0.16		0.09	
S($\bar{\Delta}$)			0.10		0.06		0.10		0.11		0.06		0.11		0.07		0.14	

Table 6

Differences from SRM 2034 Certified Values for 1.6 & 2.2 nm SSW Measurements

Δ = (Measurement - SRM 2034 Certified), nm

$\overline{\Delta}$ = Average Difference, nm; S = Standard Deviation of Differences, nm

	1.6 nm SSW						2.2 nm SSW			
	SRM 2034		Participant Codes				SRM 2034		Code	
			j		k				l	
Band	Cert*	±U95†	$\overline{\Delta}$	S	$\overline{\Delta}$	S	Cert*	±U95†	$\overline{\Delta}$	S
1	241.06	0.25	0.12	0.11	0.40	0.01	240.99	0.31	0.12	0.11
2	249.89	0.30	0.26	0.03	0.51	0.01	249.90	0.41	-0.08	0.11
3	278.08	0.21	0.02	0.08	0.45	0.01	278.06	0.23	0.26	0.09
4	287.27	0.31	0.42	0.07	0.97	0.02	287.35	0.38	0.39	0.11
5	333.40	0.26	0.16	0.06	0.75	0.02	333.37	0.32	0.44	0.12
6	345.48	0.20	0.05	0.05	0.40	0.02	345.48	0.21	0.07	0.12
7	361.23	0.20	0.15	0.05	0.50	0.02	361.15	0.21	0.24	0.09
8	385.77	0.21	0.12	0.10	0.95	0.01	385.87	0.23	0.21	0.12
9	416.45	0.20	0.34	0.09	0.74	0.01	416.62	0.18	-0.42	0.05
10	451.28	0.27	0.05	0.03	0.60	0.01	451.26	0.20	-0.03	0.05
11	467.90	0.16	0.13	0.15	0.73	0.01	467.97	0.18	-0.32	0.06
12	485.27	0.21	0.18	0.01	0.38	0.04	485.24	0.23	0.30	0.02
13	536.81	0.23	0.36	0.11	0.57	0.01	536.97	0.20	0.18	0.03
14	640.68	0.23	0.22	0.16	0.44	0.01	640.84	0.27	0.11	0.07
Average($\overline{\Delta}$)			0.18		0.59				0.10	
S($\overline{\Delta}$)			0.12		0.20				0.25	

* Interpolated from the SRM 2034 1.0 nm and 3.0 nm SSW certified values.

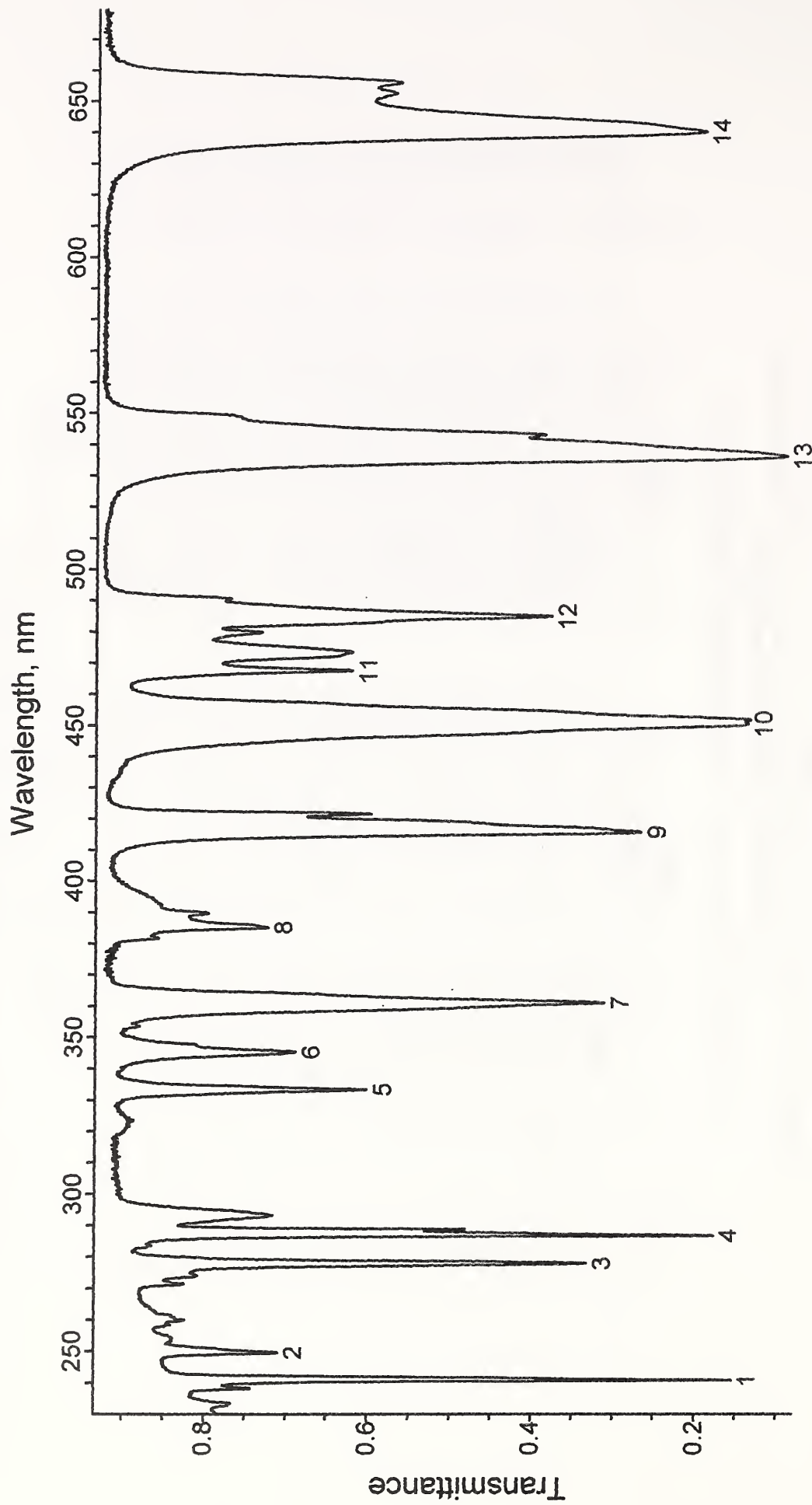† Interpolated from the SRM 2034 1.0 nm and 3.0 nm SSW U_{95} uncertainties.

Figure 1: Typical 0.1 nm SSW Spectrum of Ho$_2$O$_3$ in Dilute Perchloric Acid.
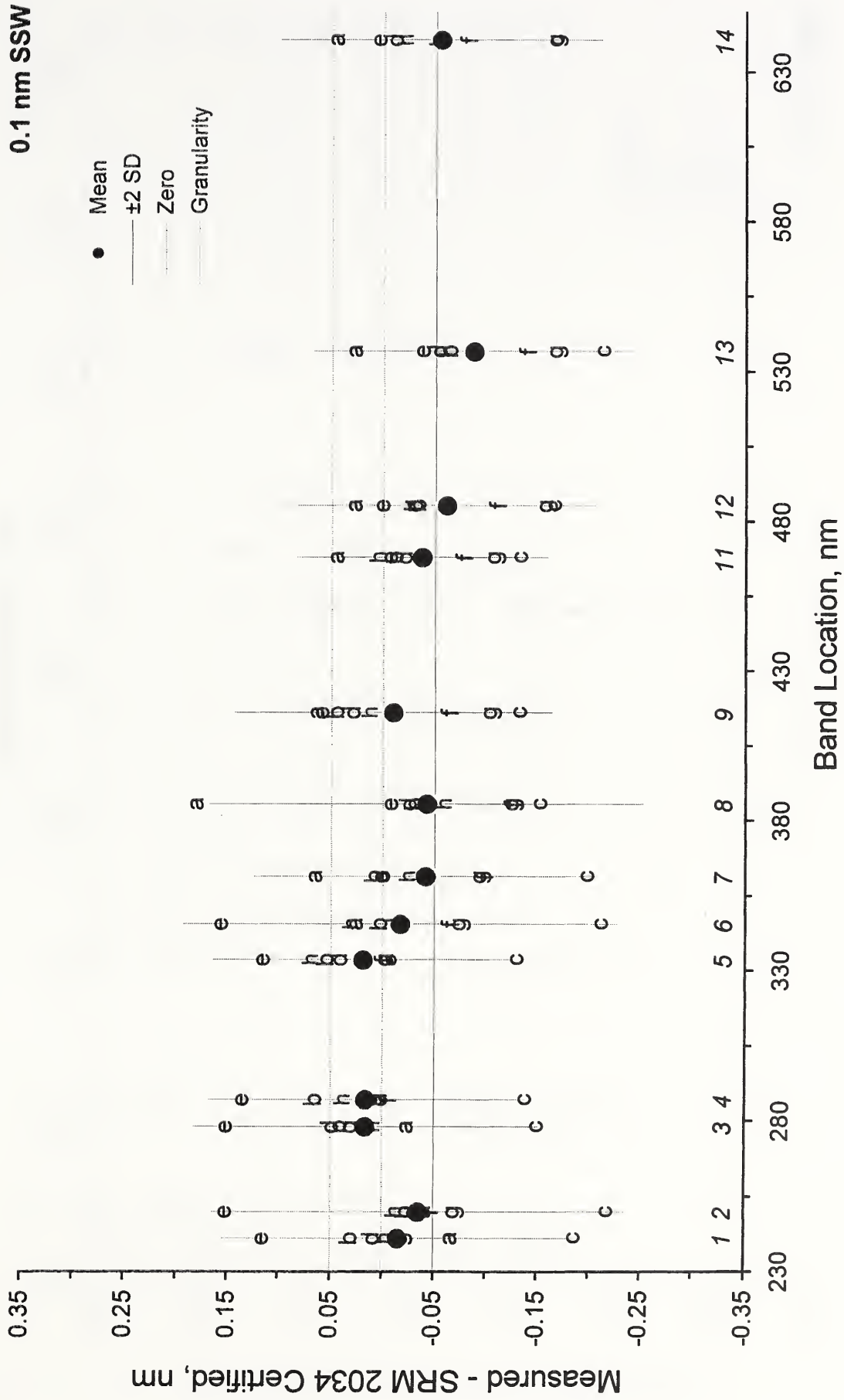Band labels are as assigned in Reference [3]

Figure 2: Differences from SRM 2034 Certified Values for 0.1 nm SSW Measurements
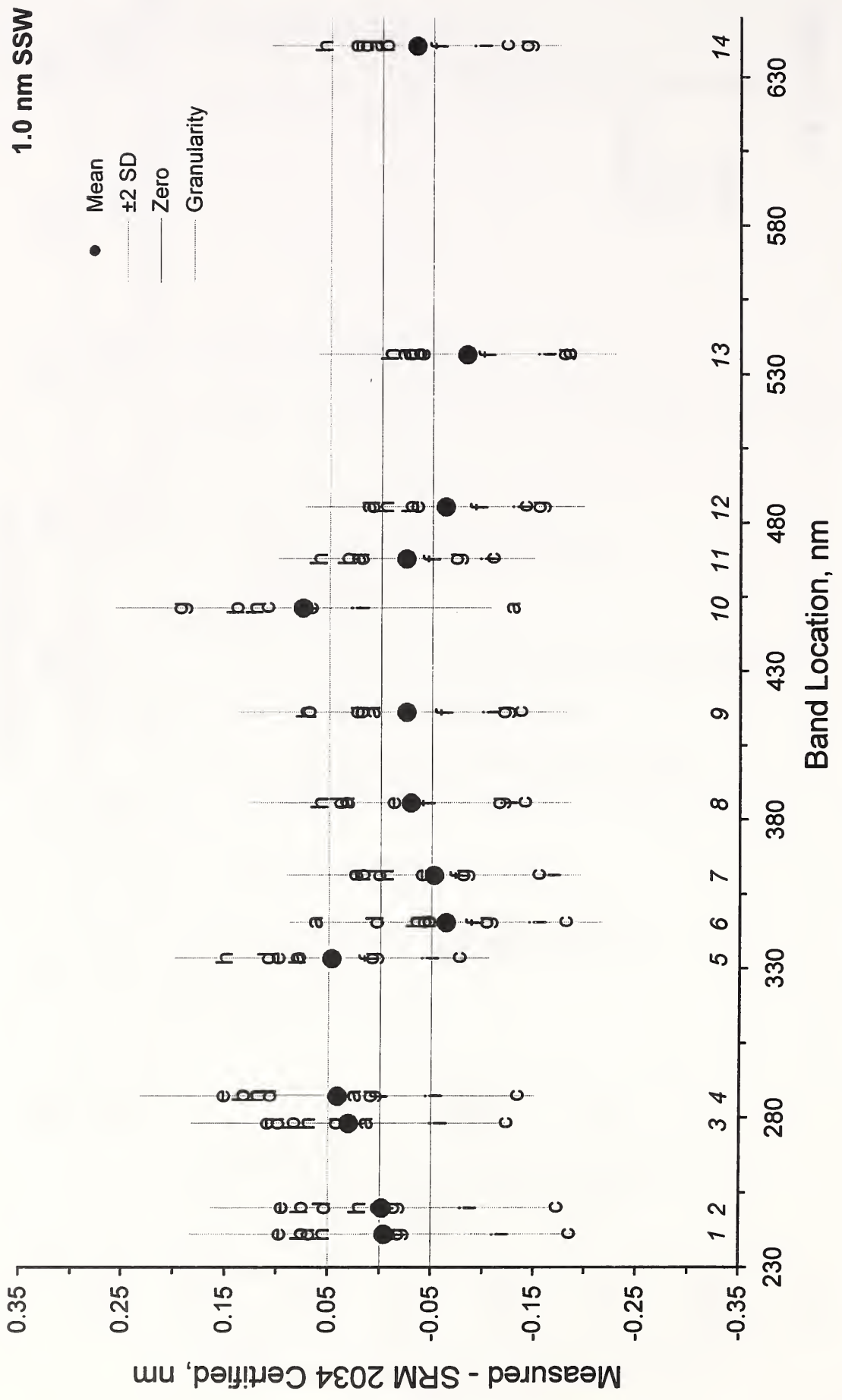
Figure 3: Differences from SRM 2034 Certified Values for 1.0 nm SSW Measurements
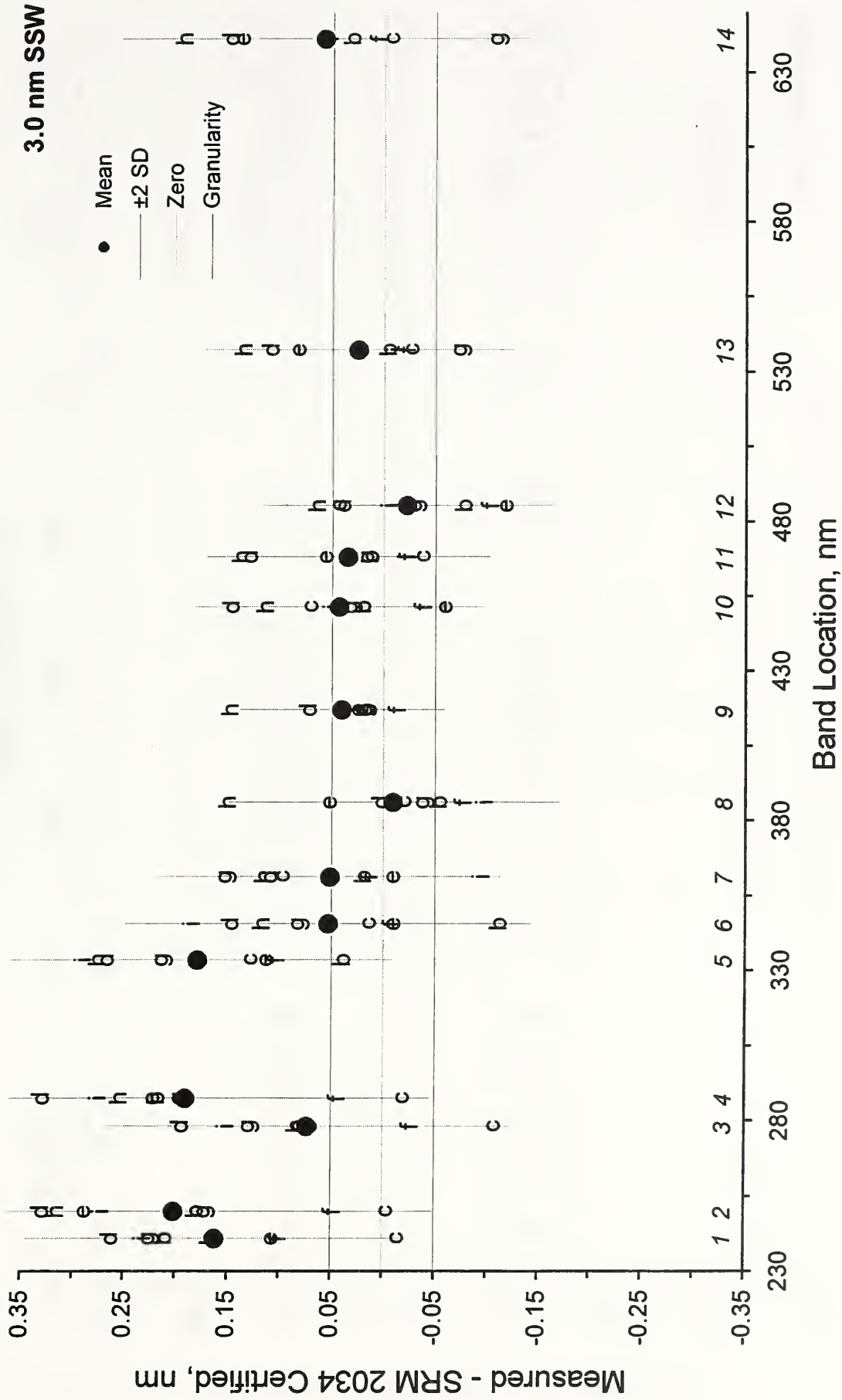
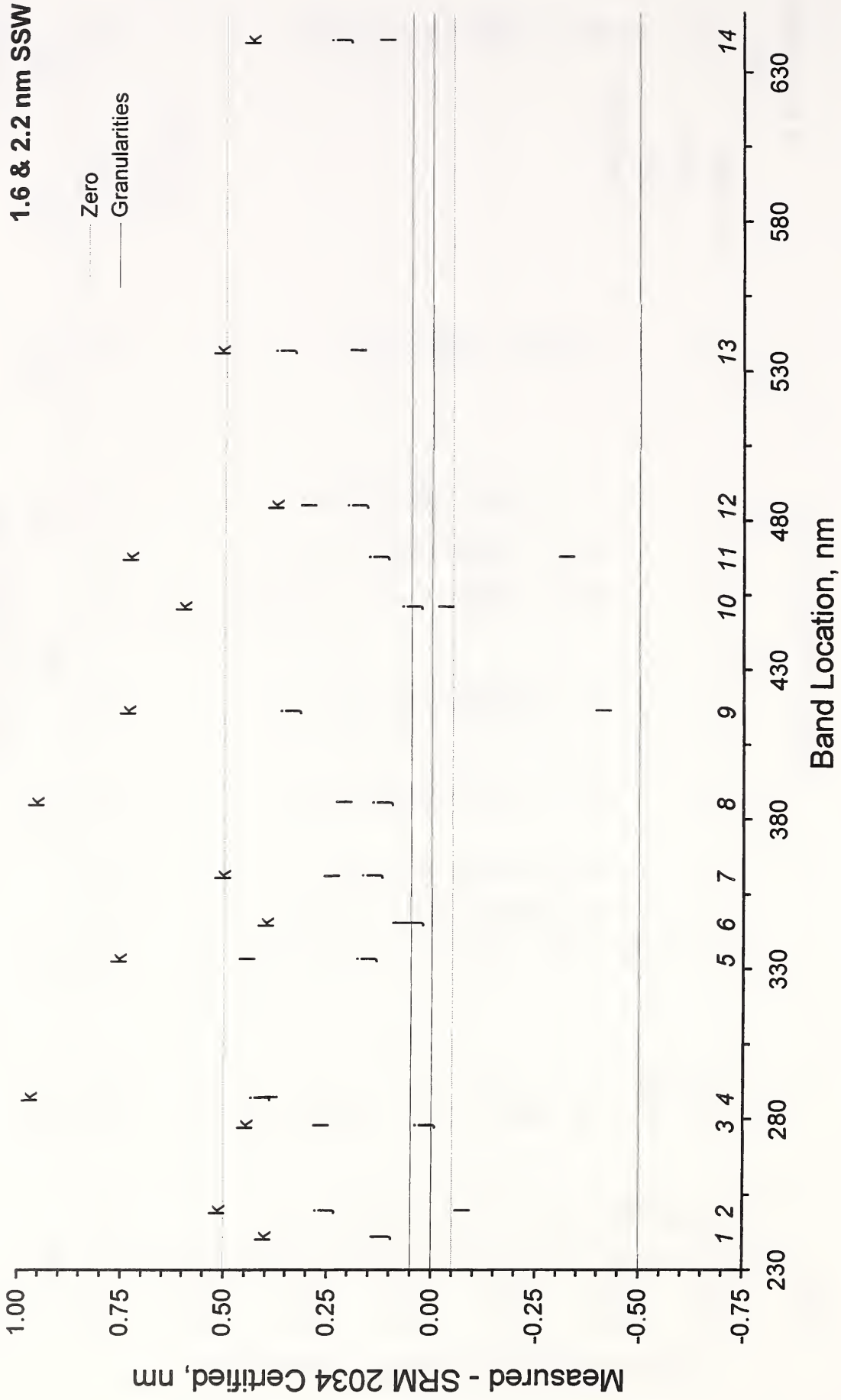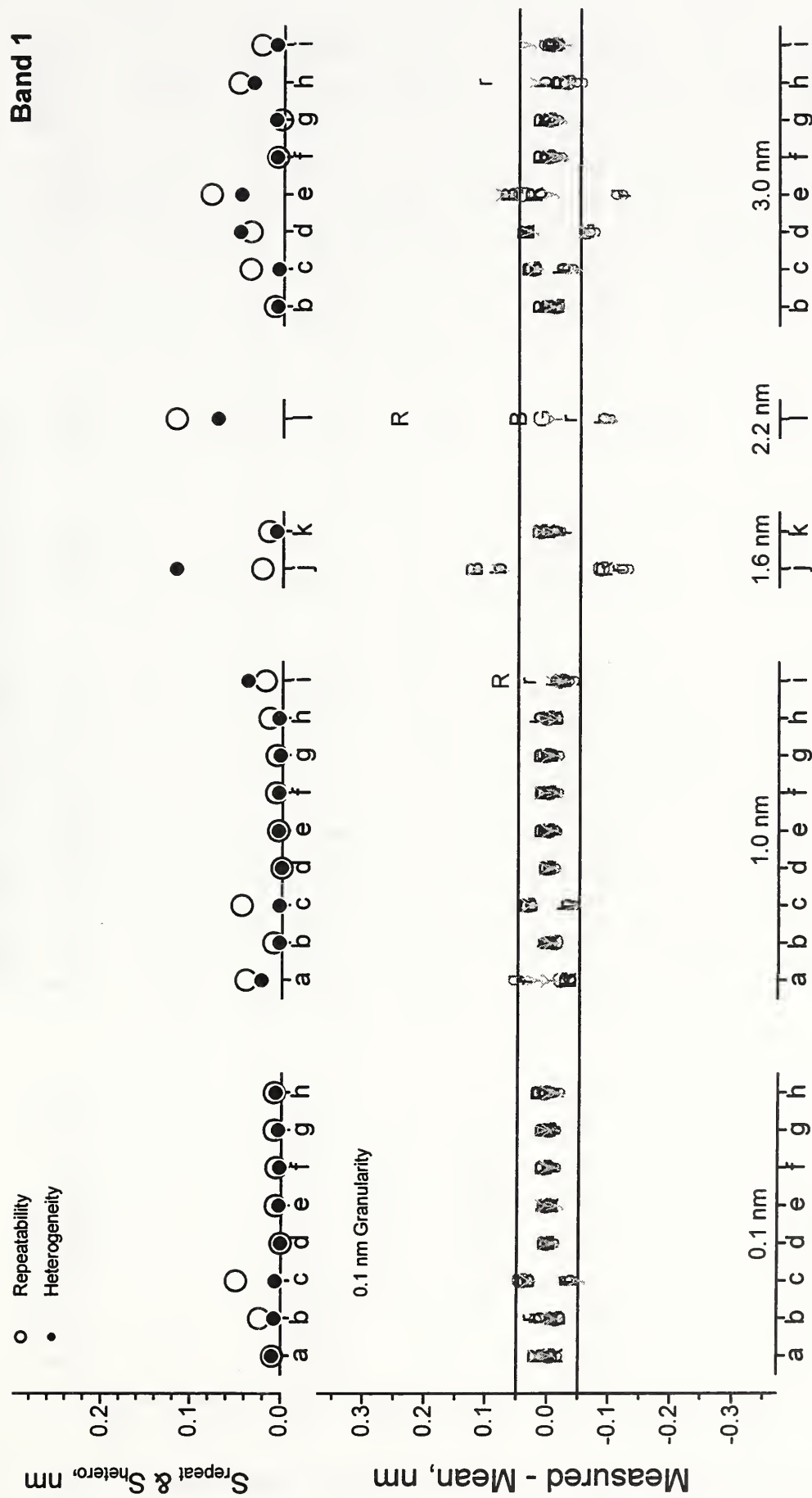Figure 4: Differences from SRM 2034 Certified Values for 3.0 nm SSW Measurements

Figure 5: Differences from SRM 2034 Certified Values for 1.6 and 2.2 nm SSW Measurements

Band 1

Figure 6: Relative Measurements and Components of Variance for Band 1
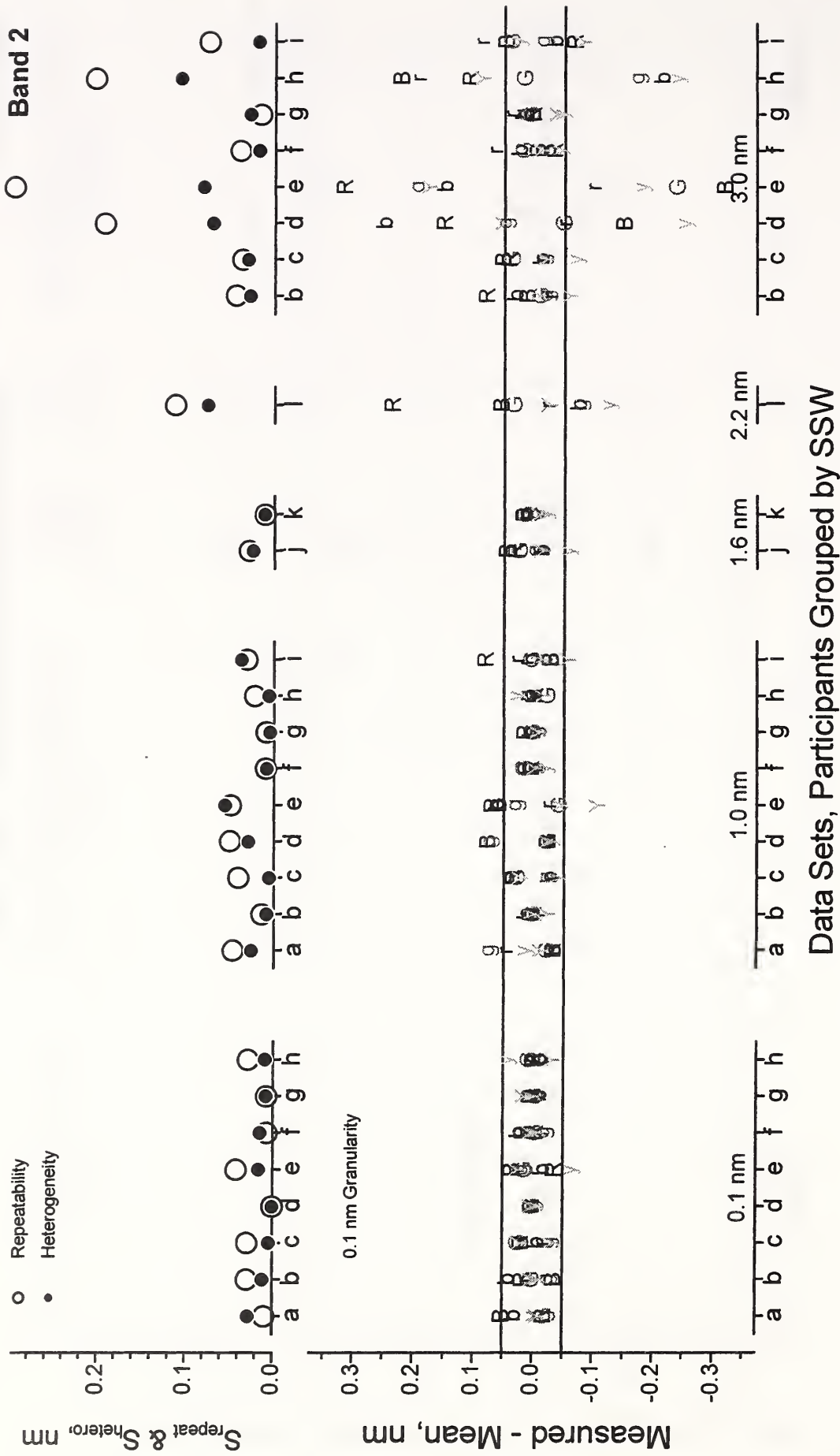
Figure 7: Relative Measurements and Components of Variance for Band 2
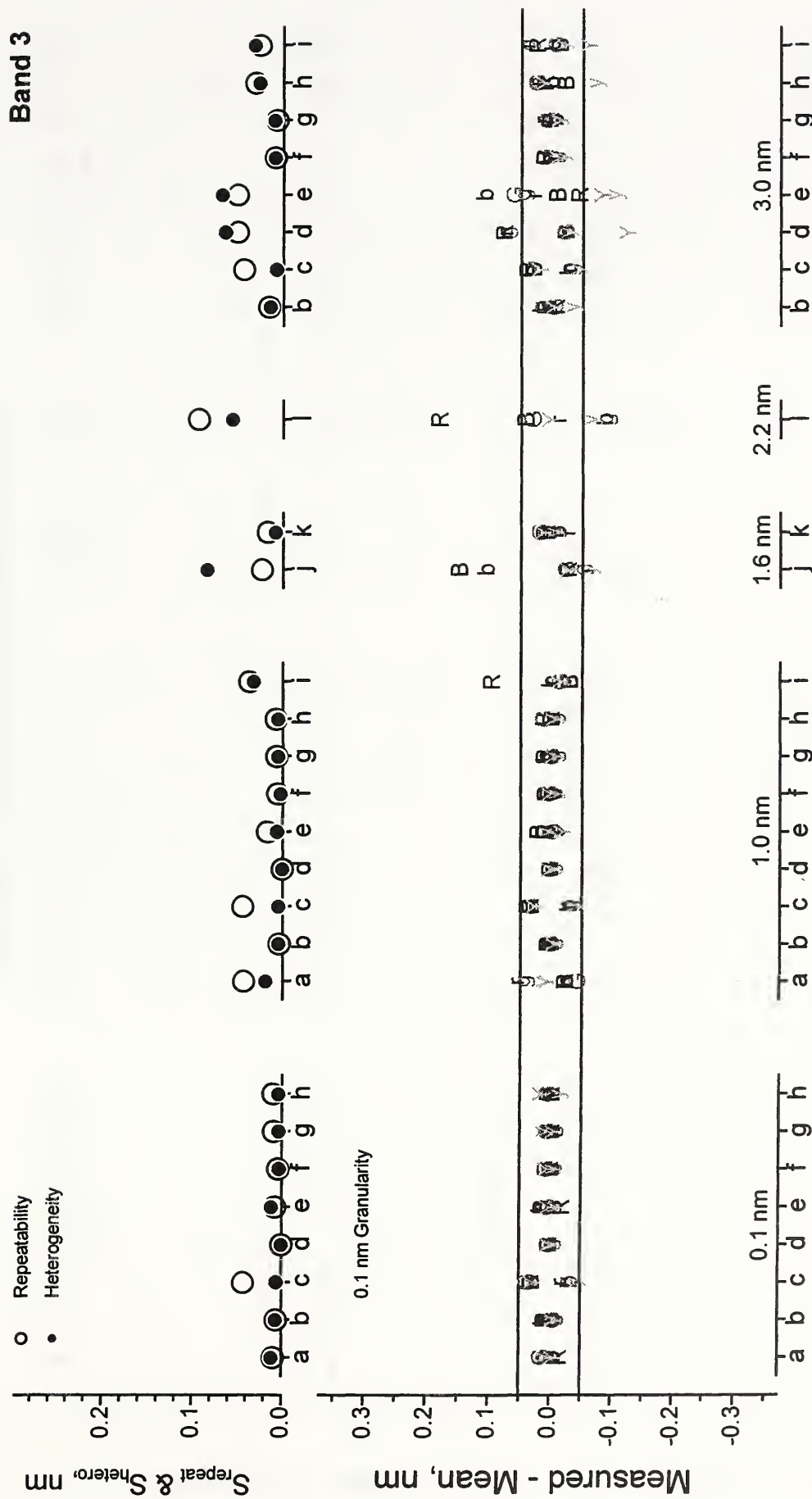
Figure 8: Relative Measurements and Components of Variance for Band 3
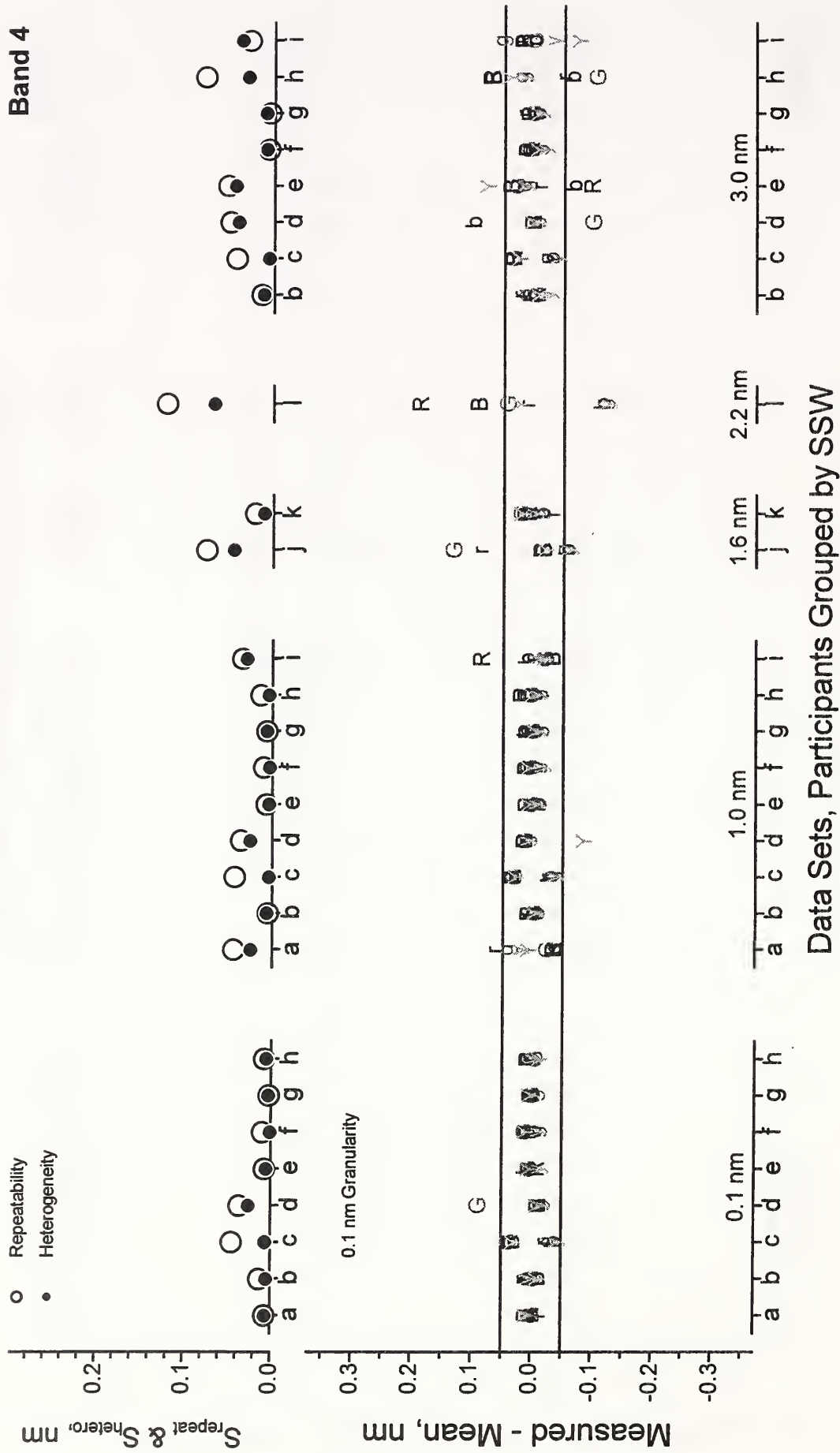
Figure 9: Relative Measurements and Components of Variance for Band 4
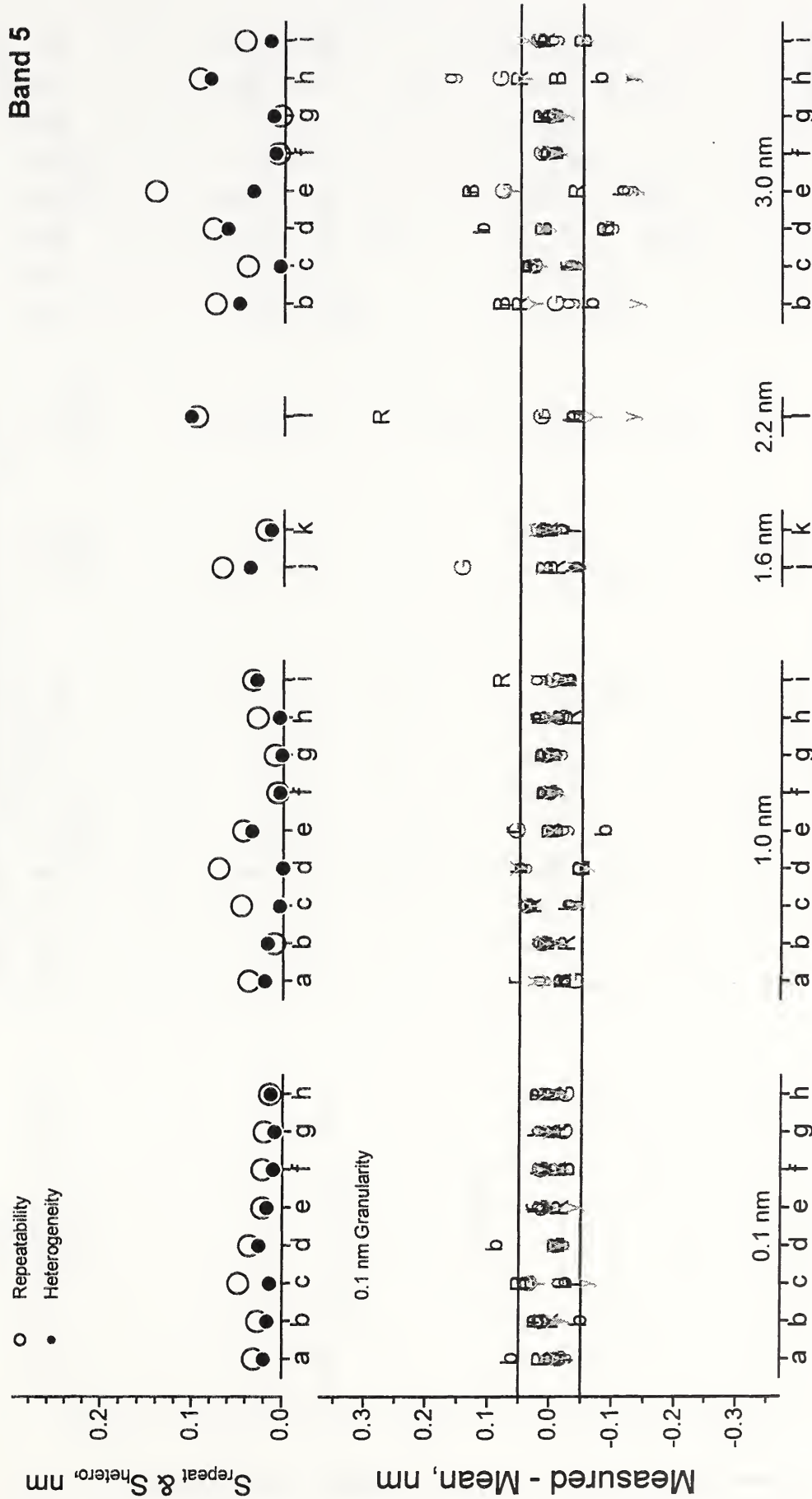
Figure 10: Relative Measurements and Components of Variance for Band 5
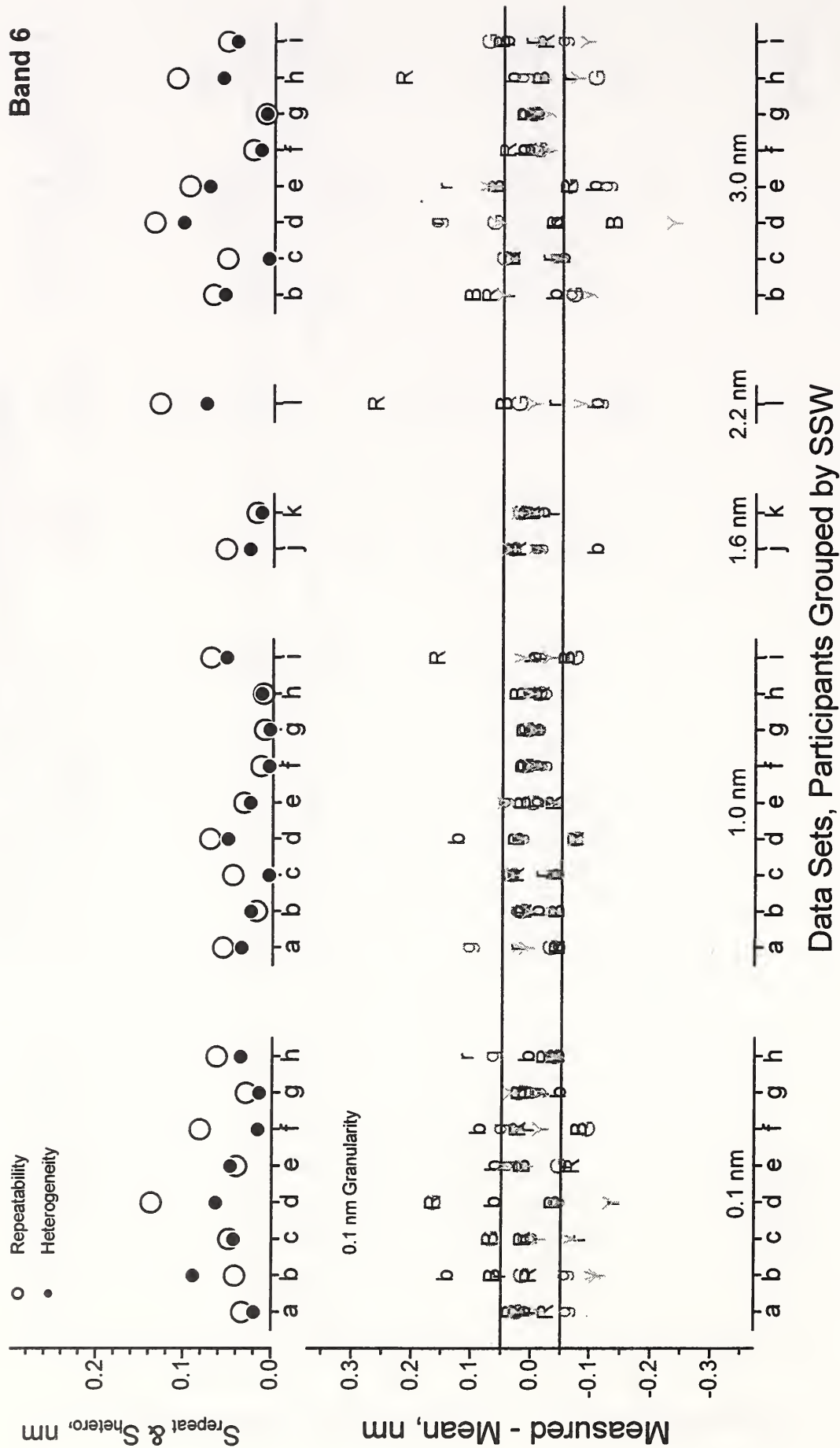
Figure 11: Relative Measurements and Components of Variance for Band 6
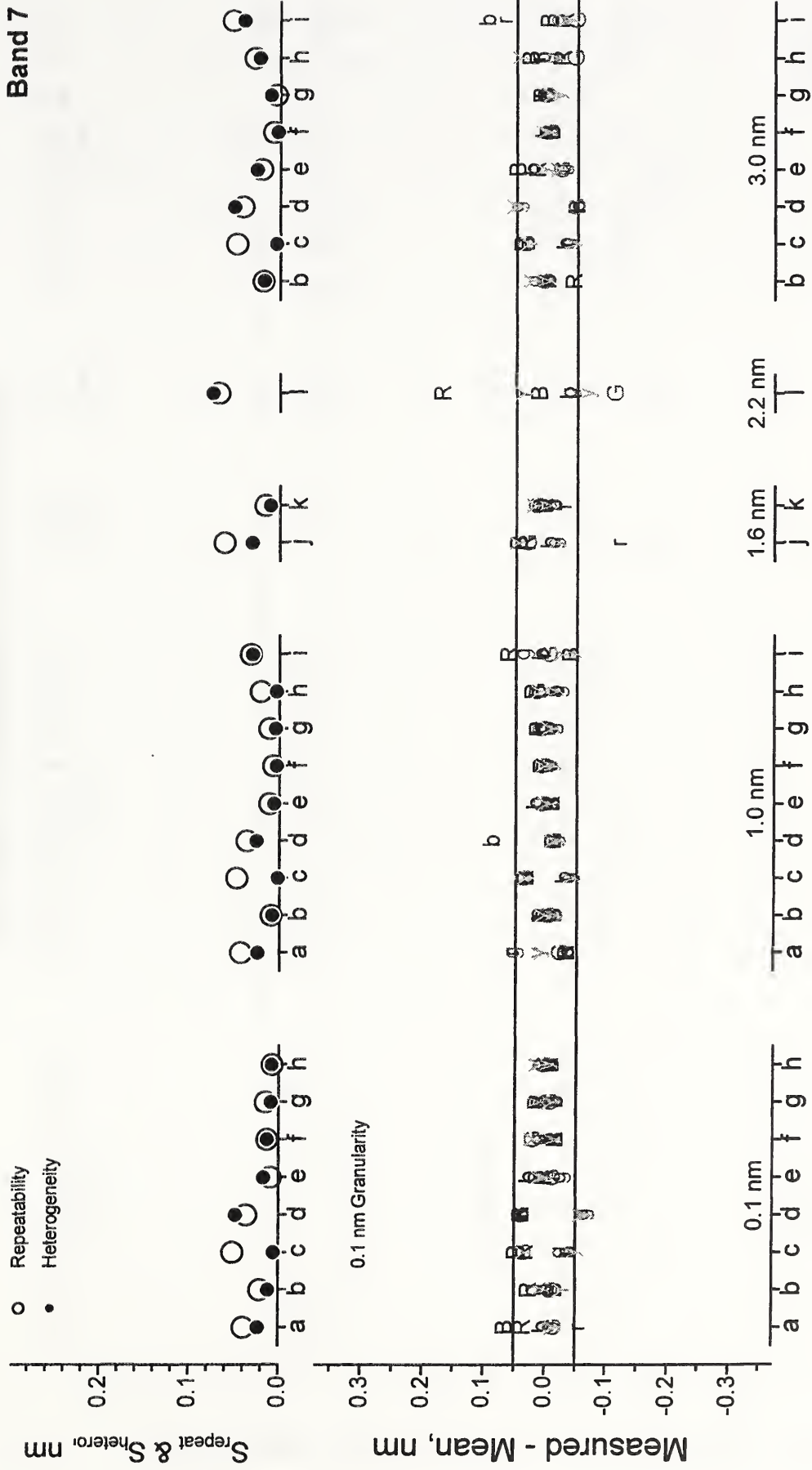
Figure 12: Relative Measurements and Components of Variance for Band 7
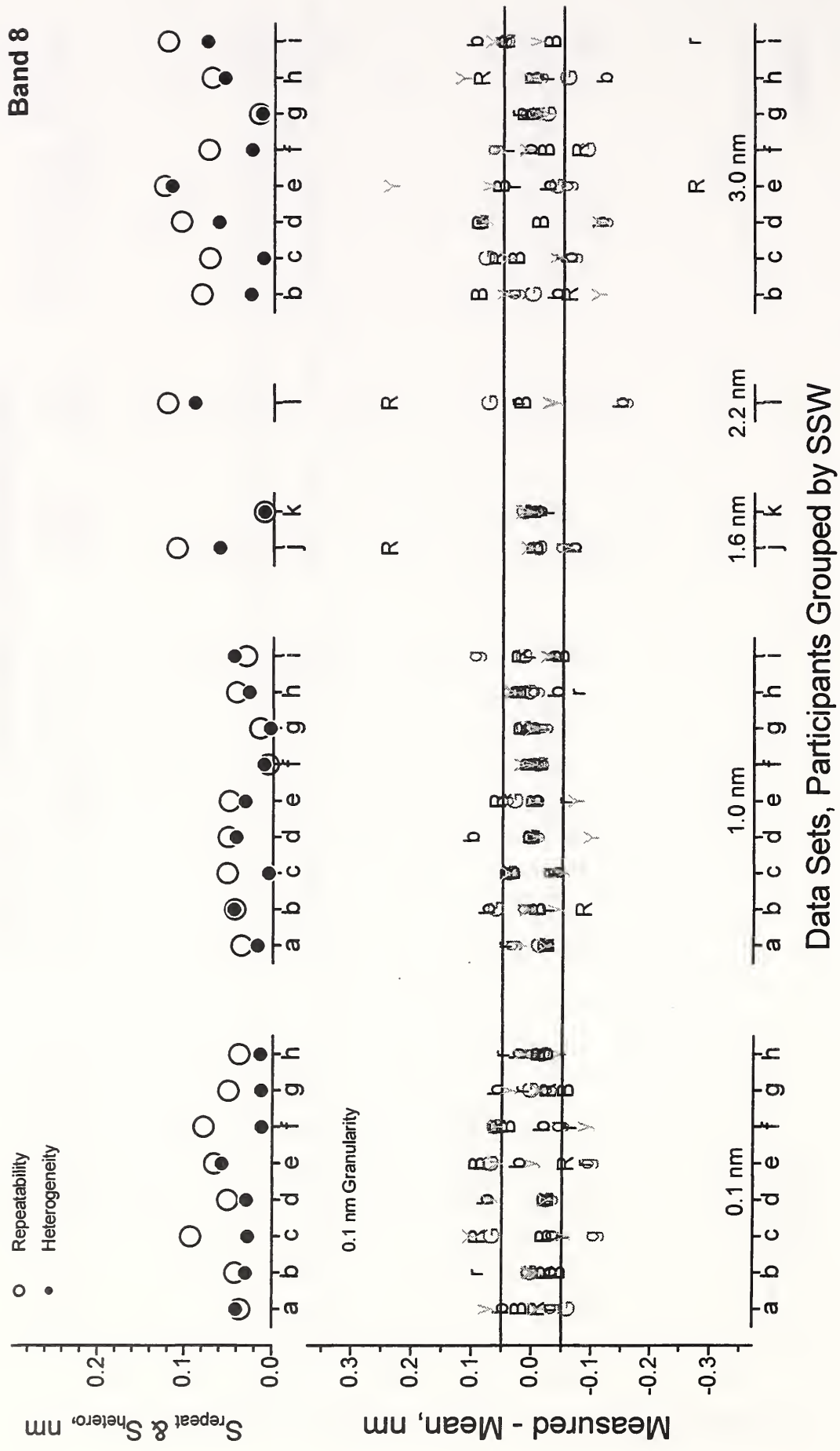
Figure 13: Relative Measurements and Components of Variance for Band 8
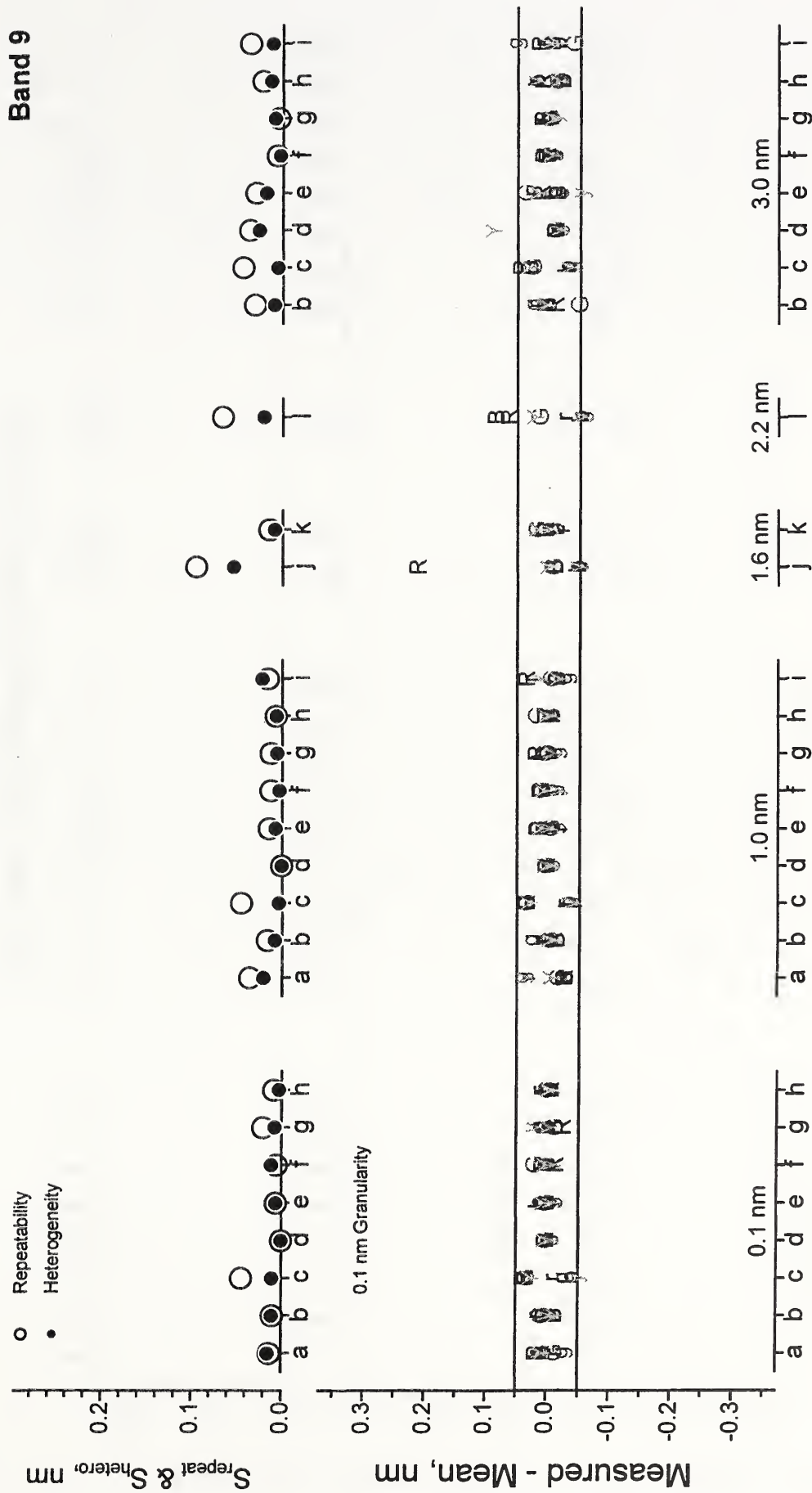
Figure 14: Relative Measurements and Components of Variance for Band 9
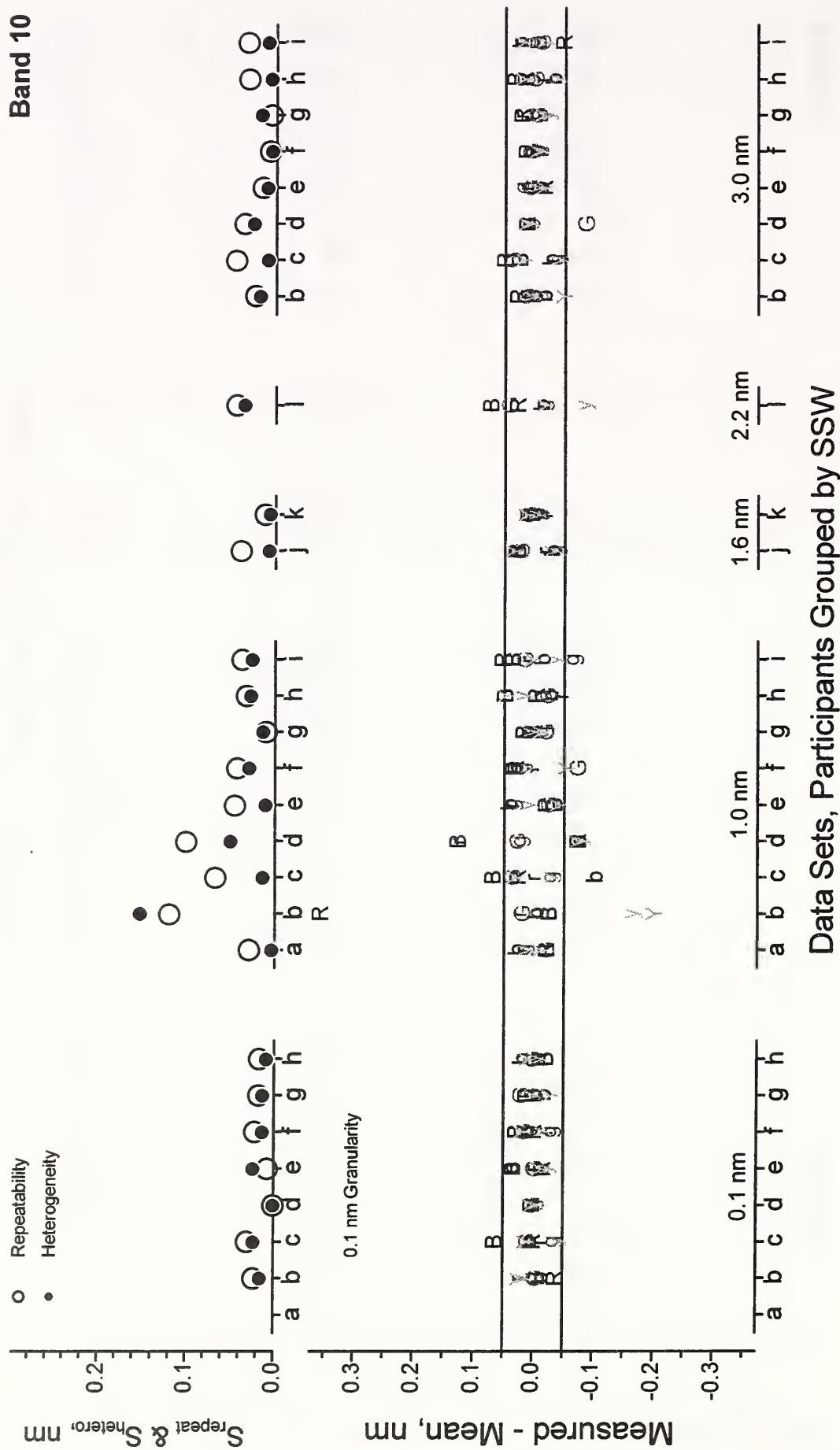
Figure 15: Relative Measurements and Components of Variance for Band 10
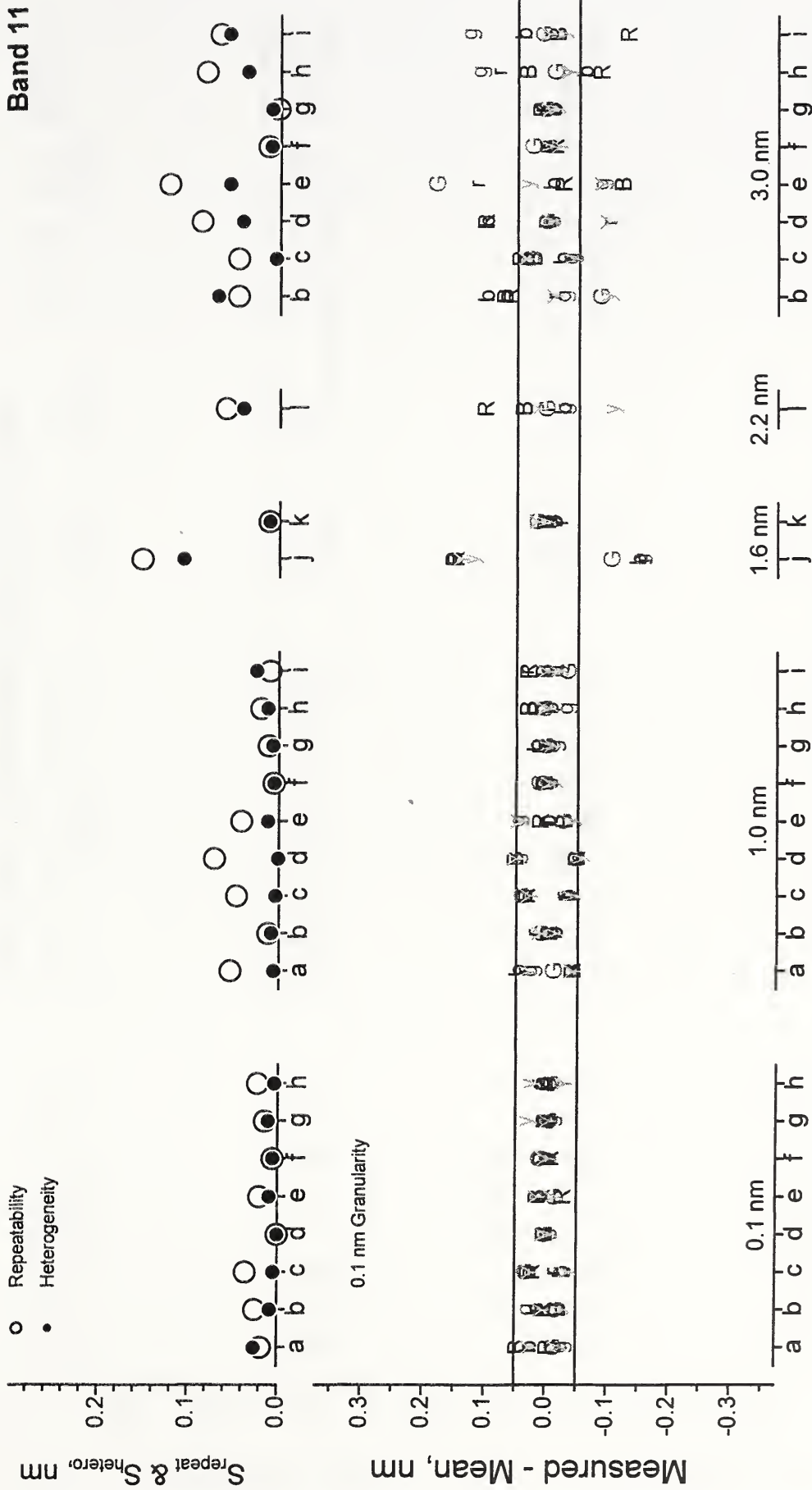
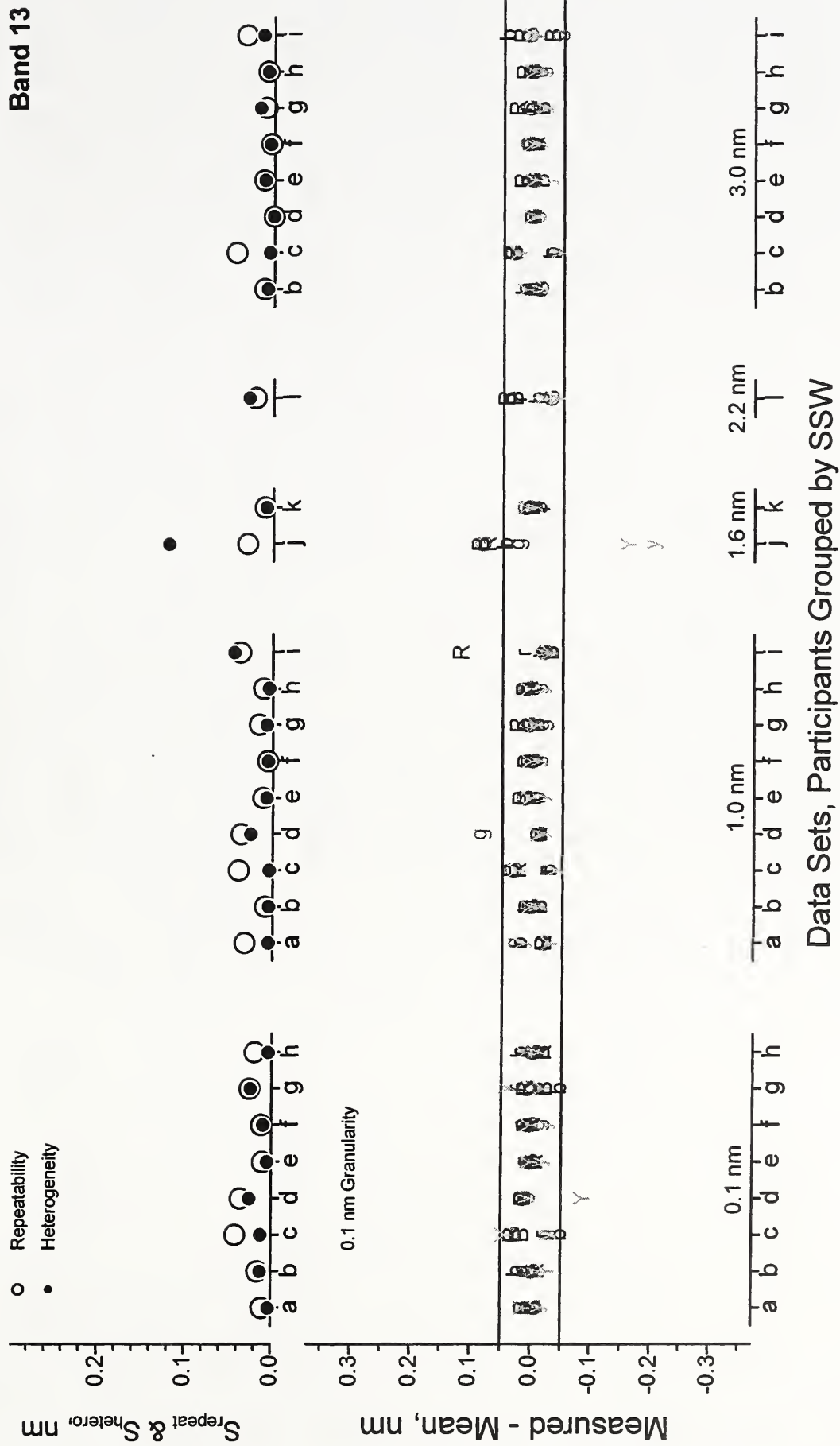Figure 16: Relative Measurements and Components of Variance for Band 11
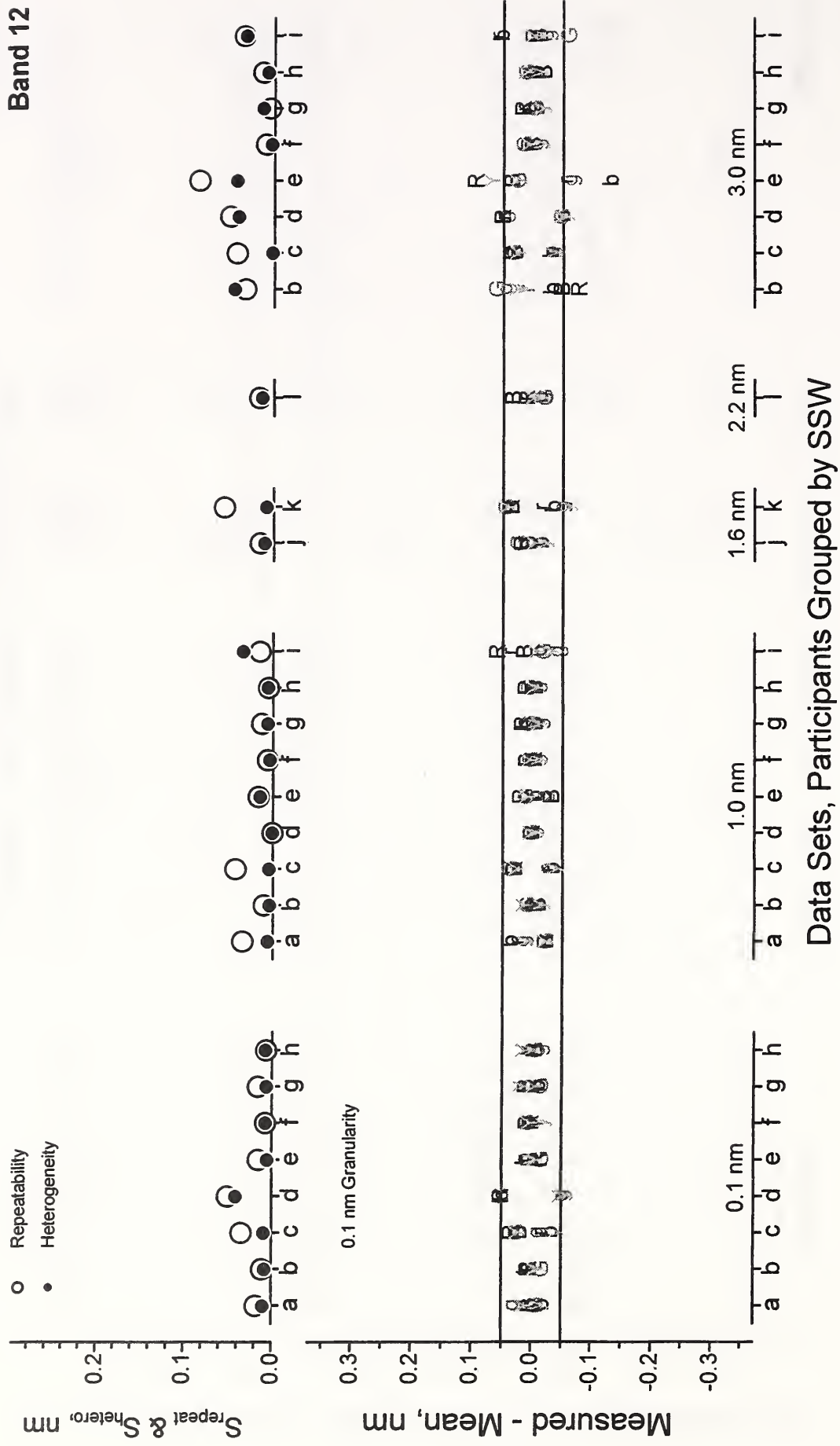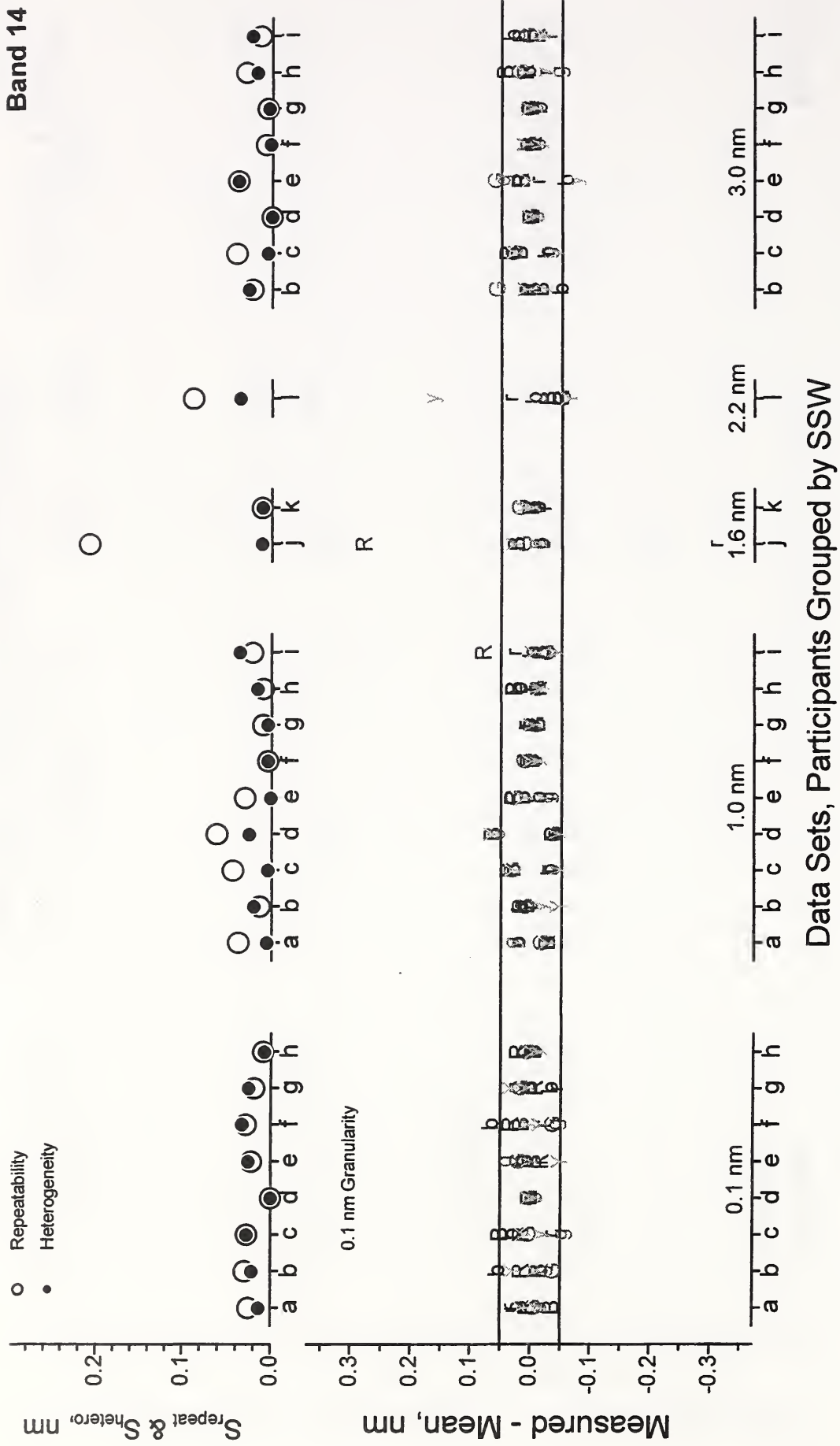
Figure 17: Relative Measurements and Components of Variance for Band 12

Figure 18: Relative Measurements and Components of Variance for Band 13

Figure 19: Measurements Relative to Participant Averages and Components of Variance for Band 14