a reprint from Applied Optics

Wavelengths of spectral lines in mercury pencil lamps

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The wavelengths of 19 spectral lines in the region 253-579 nm emitted by Hg pencil-type lamps were measured by Fourier-transform spectroscopy. Precise calibration of the spectra was obtained with wavelengths of ^{198}Hg as external standards. Our recommended values should be useful as wavelength calibration standards for moderate-resolution spectrometers at an uncertainty level of 0. 000 1 nm.

Key words: Mercury pencil lamp, wavelengths, Fourier-transform spectroscopy, spectral lines.

1. Introduction

Hg pencil-type discharge lamps are widely used for alignment and calibration of instruments in analytical spectroscopy laboratories. Their wide availability, easy operation, and simple spectrum make them an attractive source for wavelength calibration; however, no precise measurements of the Hg lines as emitted by these lamps have previously been published. As one component of a Cooperative Research and Development Agreement between the National Institute of Standards and Technology and Oriel Instruments, we have observed several Hg pencil lamps with a high-resolution Fourier-transform spectrometer (FTS) and have evaluated their suitability as a source of wavelength standards. The lamps have also been evaluated for their usefulness as radiometric standards. Results of the radiometric measurements are presented in an accompanying paper.[1]

2. Experiment

All samples of the Hg pencil lamp used in this work were supplied by Oriel Instruments.[2] The lamp (Oriel Model 6035) consists of a quartz tube with U-shaped capillary filled with Ar at a low pressure and a few milligrams of metallic Hg of natural isotopic composition (Fig. 1). The lamp operates as a low-current discharge with either ac or dc excitation. For our measurements the power supply (Oriel Model 6060) was used in dc mode with a discharge current of 15.00 ± 0.01 mA as the standard operating condition. The lamp was mounted unshielded in a vertical orientation with the base down and operated in ambient air at a temperature of approximately 23°C. The air surrounding the lamp was not subject to drafts. The lamp was rotated about a vertical axis so that the optical axis of the FTS passed through both legs of the U-shaped capillary.

All measurements were made with a Chelsea FT-500 Fourier-transform spectrometer.[2,3] This instrument is optimized for response in the near-ultraviolet region and is capable of operation from approximately 180 to 900 nm. Each Hg lamp was observed in two overlapping wavelength regions: 230-460 and 375-600 nm. The spectral bandpass for each region was limited by optical filters and by the responses of the photomultiplier tubes used as detectors. All our spectra were recorded at a resolution of 0.03 cm^{-1} (0.0002 nm at 250 nm to 0.0010 nm at 580 nm), which is the maximum resolution of the instrument. The FTS was operated in a dual channel mode, recording as the interferogram the difference of the two detector signals. For most of our spectra three to five interferograms were co-added to improve the signal-to-noise ratio. Typical values of the signal-to-noise ratio ranged from ~10^4 for the 435.8-nm line to ~40 for the weak line at 434.7 nm.

To obtain absolute calibration of the pencil-lamp spectra, precisely known lines of ^{198}Hg were used as external wavelength standards. Each observation of a natural-Hg pencil was preceded and followed by the observation of ^{198}Hg lamp made under identical conditions. ^{198}Hg was excited in an electrodeless discharge lamp containing Ar at a pressure of 33 Pa (0.25 Torr). The lamp was operated with ~70 W of microwave power over an open-cup antenna and was cooled with a gentle stream of air from a fan. Values for the standard wavelengths were taken from Kaufman.[4]

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Received 14 April 1995; revised manuscript received 7 August 1995.

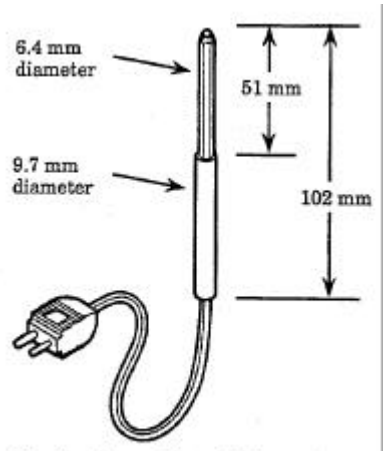

Fig. 1. Hg pencil-type discharge lamp.

To obtain an accurate calibration of Fourier spectra with an external standard source, it is necessary that the unknown and the standard sources illuminate the instrument in the same way. This problem has been discussed in some detail by Learner and Thorne.[5] Our ^{198}Hg discharge was contained in a quartz capillary of approximately the same diameter as the pencil lamp. Both sources were placed directly in front of the aperture of the FTS, with no external optics, at a distance chosen so that the source just filled the collimating mirror of the instrument. We aligned the sources on the axis of the instrument by opening the input aperture to its maximum size, observing the source through one of the detector apertures of the FTS, and visually centering the source in the aperture. The reproducibility of the results obtained when the ^{198}Hg source was removed and realigned demonstrate that this was a satisfactory alignment procedure at our desired level of accuracy.

For comparison with the pencil lamps, and as a general test of the accuracy of our measurement methods, we also made a single observation of the spectrum of natural Hg excited in an electrodeless discharge lamp. The lamp consisted of a quartz tube of 10-mm inner diameter containing a small quantity of natural Hg and Ar at a pressure of 400 Pa 3 Torr). It was operated with ~60 W of microwave power over an open-cup antenna with gentle air cooling.

3. Analysis

Because natural Hg contains six isotopes in substantial abundance, two of which have a magnetic hyperfine structure, all the Hg lines show complex line profiles at high resolution, as illustrated in Fig. 2. For most lines, the transitions of the four even number isotopes are unresolved in a strong asymmetric feature near the center of the line profile. Components of the odd-number isotopes, which are more widely split by hyperfine structure, appear as partially and fully resolved satellites. The detailed appearance of each line and the wavelength of the maximum-intensity point in the profile are critically

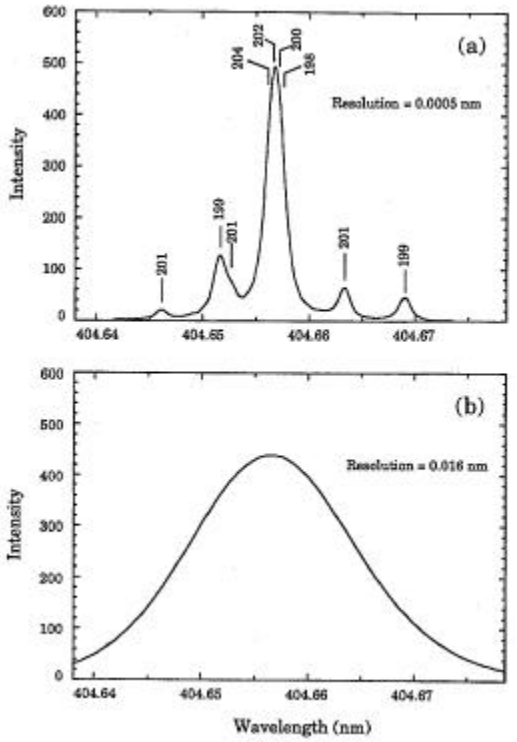

Fig. 2. (a) Spectrum of the 404.6-nm line of natural Hg from a pencil-type lamp at an instrumental resolution of 0.03 cm-1 (0.0005nm). (b) The same spectrum with the resolution degraded to 1.0 cm-1 (0.016 nm) by convolution with a Gaussian instrumental function.

dependent on the resolution of the spectrometer with which the line is observed. Because setting on the point of maximum intensity is the most convenient and commonly used method for determining the position of a spectral line, the structures of the Hg lines are an important consideration when they are to be used as wavelength standards.

We tested the effect of instrument resolution on the usefulness of these complex lines as wavelength standards by convolving the observed high-resolution spectra with Gaussian profiles of varying widths. From these tests we determined that all observed lines appear as simple symmetric profiles if the resolution is degraded to 1.0 cm^{-1} (from 0.0063 nm at 250 nm to 0.034 nm at 580 nm). Any further reduction in resolution broadens but does not shift the lines. The results we present apply to the case in which the resolution is low enough that the structure is entirely unresolved. For this case the position of the line is the same whether it is determined as the center of gravity or as the point of maximum intensity. At higher resolutions all lines eventually become asymmetric and display shifts in the position of the intensity peak with changing

resolutions. For this reason use of our present results should be limited to wavelength calibration of spectrometers with resolving powers of less than ~ 17 000.

Although our data were recorded and transformed to produce a resolution of 0.03 cm^{-1}, both the pencil lamp and the ^{198}Hg spectra were convolved with a 1.0-cm^{-1} Gaussian profile to degrade the resolution before any wavelength determinations were made. The line positions were then determined by use of a quadratically smoothed, first-derivative algorithm to locate the intensity peak of the profile. Tests showed that this rapid, simple procedure produced results that differed negligibly from a more time consuming procedure in which the entire line profile was fitted. The measured values for the lines of ^{198}Hg were compared with the literature values[4] to determine the multiplicative correction factor to be applied to the wave numbers. Typically the correction factor for a single ^{198}Hg spectrum was defined to better than one part in 10^7, with results for individual lines scattering about the average by a few parts in 10^7. Correction factors before and after the pencil-lamp spectrum typically agreed to ~5 parts in 10^8, with a maximum difference of 8 parts in 10^8. There was a high degree of consistency in the correction factors for all spectra acquired on a single day. Variations from day to day were larger. For each pencil-lamp spectrum we used as the correction factor the average of the factors determined from the ^{198}Hg spectra taken immediately before and after.

4. Results

Results of our measurements are listed in Table 1. Because these lamps are used as a source for wavelength-calibration standards, we display the results of all individual measurements to show the reproducibility obtained. Detailed analysis of the results shows that the standard deviation for repeated measurements in the same lamp is ~0.00004 nm, whereas in lamp-to-lamp comparisons it is 0.00007nm. Only the weak line at 434.7 nm showed a significant lamp-to-lamp variation. Its wavelength was -0.0005 nm longer in lamp 3 than in the other lamps.

In Table 2 we present our recommended values for the wavelengths and wave numbers of the strongest Hg lines emitted by the pencil-type lamps. All results correspond to the operating conditions described above. We estimate the uncertainty of the average wavelengths, calculated as 2 times the standard error, to be ~0.0001 nm. The primary measures of the uncertainty are the statistical scatter in measurements made with the same lamp (0.00004 nm) and the statistical scatter in lamp-to-lamp comparisons (0.00007 nm). The precision of the correction factors determined from the ^{198}Hg external-standard spectra (approximately 3 parts in 10^8) is reflected in these statistical variations.

By using the results from our high-resolution spectrum of a natural-Hg electrodeless discharge lamp, it is possible to test the general accuracy of our wavelength-calibration methods for a few strong Hg lines. In the high-resolution spectrum, fully resolved hyperfine-structure components of ^{199}Hg can be measured. By combining these measurements with the precisely measured intervals between the various hyperfine-structure and isotope lines reported by Blaise and Chantrel,[6] we can calculate values for the wavelengths of ^{198}Hg in the natural lamp. These are compared with the results of Kaufman[4] in Table 3. The average deviation of only -0.000019 nm provides additional evidence of the accuracy of the external-standard calibration method used for all of our spectra.

Table 1. Results of the Individual Measurements for Hg Pencil-Type Lamps

	Lamp 1		Lamp 2				Lamp 3		
Line (nm)	Measure-ment 1	Measure-ment 2	Measure-ment 1	Measure-ment 2	Measure-ment 3	Measure-ment 4	Measure-ment 1	Measure-ment2	Measure-ment 3
253	.6523		.6520	.6522					.6520
289	.3600		.3601	.3600					.3603
296	.7282		.7283	.7283					.7283
302	.1503		.1505	.1505					.1504
312	.5674		.5674	.5674					.5674
313	.1555		.1554	.1554					.1554
313	.1844		.1844	.1844					.1844
334	.1485		.1482	.1484					.1484
365	.0158		.0159	.0159					.0158
365	.4842		.4842	.4843					.4842
366	.2886		.2888	.2888					.2888
366	.3284		.3285	.3284					.3283
404	.6564	.6565	.6565	.6565	.6565	.6565	.6565	.6565	.6565
407	.7837	.7837	.7837	.7837	.7836	.7837	.7836	.7837	.7836
434		.7505			.7505	.7504	.7510	.7510	
435	.8334	.8334	.8335	.8335	.8334	.8335	.8334	.8335	.8334
546		.0749			.0750	.0750	.0750	.0750	
576		.9610			.9610	.9611	.9609	.9609	
579		.0670			.0670	.0671	.0671	.0670	

Table 2. Recommended Wavelengths (Air) and Wave Numbers (Vacuum) for Selected Hg Spectral Lines Emitted by Pencil-Type Lamps

Intensity[a]	Wavelength[b] (nm)	Wave Number (cm^{-1})
300,000	253.6521	39412.236
160	289.3601	34548.888
2600	296.7283	33691.025
280	302.1504	33086.464
2800	312.5674	31983.828
1900	313.1555	31923.765
2800	313.1844	31920.819
160	334.1484	29918.220
5300	365.0158	27388.271
970	365.4842	27353.171
110	366.2887	27293.096
650	366.3284	27290.138
4400	404.6565	24705.339
270	407.7837	24515.883
34	434.7506[b]	22995.229
10,000	435.8335	22938.095
10,000	546.0750	18307.415
1100	576.9610	17327.389
1200	579.0670	17264.372

[a]Intensities are relative values based on irradiance values from Ref. 1 with the intensity of 436 nm set arbitrarily to 10,000.

[b]The wavelength uncertainty is 0.0001 nm, with the exception of that of the 434.7506-nm line (see text).

5. Discussion

Precise wavelength measurements for natural Hg have previously been reported by Burns *et al.*[7] Comparison of our results with the earlier values shows significant deviations. All lines from the pencil lamps are shifted to the red by an average of 0.00068(32) nm with respect to the Fabry-Perot measurements by Burns *et al.*[7] It is not clear whether this shift represents a real difference between the pencil lamps and the positive column source used in Ref. 7 or whether it is a result of measurement of weakly exposed, partially resolved line profiles by Burns *et al.*[7]

We have also compared the pencil-lamp results with our measurements of the Hg lines in the natural-Hg electrodeless discharge lamp. For this comparison the high-resolution spectrum of the electrodeless lamp was degraded to a resolution of 1.0 cm-1 by convolution with a Gaussian as was done for the pencil lamps. Again the pencil-lamp wavelengths were found to be consistently shifted to the red, in this case by an average of 0.00054(25) nm. On the basis of the pressure shifts measured by Kaufman,[4] a shift of this size is too large to be explained by the Ar pressure in the pencil lamps. The shift may be attributable to a higher pressure of Hg in the pencil lamps, which operate at a significantly higher temperature than the electrodeless lamp. In any event, our present results represent the Hg wavelengths as emitted by the pencil lamps and should not be applied to other types of low pressure Hg lamps if an accuracy higher than 0.001 nm is required.

We note that wavelengths emitted by the pencil lamps at different discharge currents or with ac excitation may differ slightly from those obtained in this work. We thus recommend that, if these lamps are used in applications for which accuracies of better than 0.0005 nm are required, our experimental conditions should be carefully reproduced.

Table 3. Comparison of 198Hg Wavelengths Derived from Our High-Resolution Fourier-Transform Spectrum of a Natural-Mg Electrodeless Lamp with the Results Obtained by Kaufman[a]

Vacuum Wavelength (nm)		Deviation
This Study[b]	Kaufman[c]	(nm)
546.227060	546.227063	-0.000003
407.898902	407.898940	-0.000038
404.771464	404.771469	-0.000005
435.975227	435.975257	-0.000030

[a]Ref. 4.

[b]Derived from the fully resolved, hyperfine-structure components of ^{199}Hg by use of intervals measured by Blaise and Chantrel.[6]

[c]Calculated from the optimized energy levels for ^{198}Hg in a lamp with a pressure of 400 Pa (3 Torr) Ar.[4]

6. Conclusion

In summary, we have made precise measurements of the Hg lines emitted from three Hg-Ar pencil lamps. With the exception of the 434.7-nm line, the wavelengths are consistent for the three lamps observed, and the values we present should be useful as wavelength standards at the level of 0.0001 nm for instruments with resolving powers of less than 17 000.

We thank Bruce Pulliam for making available his spectrum-measuring and spectrum-analysis software, for modifying it to better meet the needs of our ongoing Hg observations, and for coming to the National Institute of Standards and Technology to install and test it on our computers.

References and Notes

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