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DIRECT EMISSIVITY MEASUREMENTS ON LIQUIDS AND CORRECTIONS TO MULTI-COLOR PYROMETERS

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ABSTRACT

Optical pyrometry provides a means for non-contact temperature measurements whose accuracy depends on the accuracy with which specimen emittance is known. Two methods for obtaining the required emittance data are discussed here in which the emittance is determined from measurements of the wavelength or polarization dependence of light emitted by the specimen.

The spectral technique, multi-color pyrometry, yields apparent values for the specimen emittance and temperature from emitted intensity measurements at two or more wavelengths. An assumption about the functional relationship between emittance and wavelength is required by this method.

Emittance corrections cannot be eliminated by increasing the number of spectral intensity measurements required by an n-color pyrometer. Even if this were possible, the accuracy of temperature measurement by n-color pyrometry decreases with n such such that pyrometers that require four intensity measurements would be impractical. Analyses of emittance versus wavelength data for solids show that two- and three-color pyrometry may have large emittance corrections as does the one-color pyrometer. In contrast, emittance values and corrections for one-color pyrometers can be accurately measured by the polarized light technique.

The polarized light technique involves measurement of the degree of polarization for light emitted at an angle of 45° to the specimen normal. At this angle, the reflectivities (r) for light polarized parallel (p) and normal (n) to the plane of emission are related by $r_p = r_n^2$. This leads, for opaque materials, to a simple relation between the intensity ratio, I_p/I_n, for light emitted in the two polarization states and the emittance, i.e., $e_n = 2 - I_p/I_n$. The true specimen temperature is also obtained if absolute intensities are measured.

Development of the polarized light technique in combination with one-color optical pyrometry is recommended to achieve accurate non-contact temperature measurements on liquids. Liquids provide the smooth and specularly reflecting surfaces that the method requires. In this way, precise and accurate temperature control and measurement may be achieved in the containerless liquid phase processing and property investigations that are possible in the low gravity environment of space.

INTRODUCTION

This paper reviews concepts and practical results concerning two methods by which optical pyrometry can be used to achieve non-contact temperature measurements on incandescent objects. The discussion is particularly motivated by opportunities to advance containerless processing technology via experiments carried out in the low-gravity environment of space. Many of these processing applications involve the liquid state of materials that melt at high temperatures to form very corrosive liquids. New methods for non-contact property measurements are needed for process control and to make material property measurements in this environment.

The intensity of radiation emitted by a blackbody depends on temperature and wavelength of the radiation as given by Planck's law. The temperature of a blackbody can thus be accurately measured by a carefully calibrated one-color optical pyrometer. The method is simple, accurate, and has been used in a large fraction of high temperature materials property studies on solids or with solid containers that are reported in the literature. In these studies, blackbody radiation was collected from a sufficiently deep hole drilled in the container or solid material of interest.

The emittance of a material equals the intensity ratio for light emitted by its surface and from a blackbody at the same temperature. Material emittances differ significantly from unity and depend on temperature and composition as well as the wavelength and angle of emission. The apparent temperature measured by an optical pyrometer also varies with these properties. It is not practical to achieve blackbody holes in liquid specimens and new methods for emittance measurement are therefore needed to correct the apparent temperature measurements in containerless experiments.

The first method to be discussed involves the measurement of emitted intensities at two or more wavelengths. The apparent emittance and temperature are then calculated with the help of an assumed functional relation between emittance and wavelength.

The second method relies on measurements of the intensities and the degree of polarization of light emitted at a single wavelength by the specimen of interest. Light is collected at an angle of 45^o to the specimen normal. For opaque specular reflectors, the true specimen emittance and temperature can then be easily calculated.

The method of multi-color pyrometry is discussed with particular reference to papers by Coates[1] on the accuracy and precision of temperature measurement that may be achieved and by Nordine[2] on the corrections to multi-color pyrometers that actual emittance data require. Special use is made of three sets of emittance data[3-5] for solid tungsten. These are amoung the most accurate and precise material emittance values that have been measured. Emittance values for a wide variety of materials have been compiled by Touloukian and DeWitt.[6]

The discussion of emittance measurements by polarization techniques is based on work by Tingwalt and Magdeberg[7]. They report measurements of the emittance of solid tungsten that are in precise agreement with accepted values[3-5]. The accuracy of this technique has thus been established but it has not yet been applied for measurements on liquid specimens in containerless experiments.

In the following sections we first present a thermodynamic analysis[8] of the need for containerless methods in the processing of materials at very high temperatures. Then the methods of multi-color pyrometry and of emittance measurements by polarization techniques are discussed.

CONTAINER INTERACTIONS AT HIGH TEMPERATURES

The concept of a regular solution allows lower limits on the extent of container-specimen interactions to be related to estimates of the maximum endothermicity of solution for solvent-solute pairs. A regular solution is one for which the Gibbs Free Energy of mixing, ΔG_{mix} is given by

$$\Delta G_{mix} = -RT[x_c \ln(x_c) + x_s \ln(x_s)] + x_c x_s \omega \qquad (1)$$

where x_c and $x_s = 1 - x_c$ are the mole fractions of the container and specimen respectively. ω measures the departure from ideal solution behavior as the energy required to dissolve one mole of the container (solute) in the contained specimen (solvent). At equilibrium, $\Delta G_{mix} = 0$ and assuming $x_c << x_s$ we have

$$x_c = \exp(-\omega/RT) \qquad (2)$$

We take 20% of the enthalpy of vaporization (H_v^o) of the container as a physically reasonable estimate for the maximum value of ω, since it would surely take much less energy to dissolve the container in a vacuum (i.e., evaporate it) that to dissolve it in another condensed phase. The most refractory container that is available is tungsten for which $\Delta H_v^o = 860$ kJ/mol so that a reasonable limit on ω/R is

$$\omega/R < 20{,}700 \text{ K} \qquad (3)$$

Although the best container for a particular material of interest may not be tungsten, the chosen container will have an enthalpy of vaporization (per mol of atoms) less than that of tungsten and should satisfy Eq. (3). Values for the minimum solubility of containers in samples calculated from Eqs. (2) and (3) are given in Table 1.

Table 1

Estimate of Minimum Solubilities For Containers in Specimens[8]

Process Temperature, K	Solubility, mol fraction
1,000	1.0×10^{-9}
1,500	1.0×10^{-6}
2,000	3.2×10^{-5}
2,500	2.5×10^{-4}
3,000	1.0×10^{-3}
4,000	5.7×10^{-3}

The table is a numerical representation of a well known fact illustrated by temperature versus composition phase diagrams, that the solubility of sparingly soluble phases in each other always increases with temperature. Most systems would exhibit solubilities much greater than those given in the table, which estimates limiting values for the least soluble materials that might be found.

MULTI-COLOR PYROMETRY

The intensity, W, of radiation emitted by an object at a particular wavelength, λ, and temperature, T, as given by Wein's law

$$W(\lambda,T) = C \exp(-C_2/\lambda T)\ e \tag{4}$$

is within 0.2% of that given by Planck's law when $\lambda T < 0.2315$ cm·K, or at temperatures below 3562K at the common wavelength, 650 nm, of single-color optical pyrometers. We assume this relation holds in the following discussion. In Eq. (4) e is the spectral emittance of the specimen of interest and T is its true temperature. Apparent temperatures, T_a and emittances, e_a, appear in the equivalent expression that applies to an optical pyrometer:

$$W(\lambda,T_a) = C \exp(-C_2/\lambda T_a)\ e_a \tag{5}$$

The true and apparent temperatures are thus related by

$$C_2[1/T - 1/T_a] = \lambda \ln(e/e_a) \tag{6}$$

The temperature correction for a one-color pyrometer is easily derived by setting $e_a = 1$. For a two-color pyrometer, e_a is assumed independent of wavelength to obtain.

$$C_2[1/T - 1/T_a] = \lambda_1 \lambda_2/(\lambda_1 - \lambda_2)\ln(e_1/e_2) \tag{7}$$

The temperature corrections for three-color pyrometers are similarily derived, usually with the assumption that e_a or $\ln(e_a)$ is a linear function of wavelength.

Coates' analysis of n-color pyrometry[1] is based on an assumed emittance function of the form

$$\ln(e_a) = \sum_{i=0}^{n-2} A_i \lambda^i \tag{8}$$

Coates presents a general equation from which emittance corrections can be calculated for any value of n and n emittance measurements at different wavelengths. By numerical calculations with Eq. (8) as an approximation to model emittance data, Coates showed that the emittance correction becomes more sensitive to errors in the emittance function as such errors decrease with n. The net result is that the use of large values of n in Eq. (8) will not make a multi-color pyrometer accurate.

Nordine[2] explained the limits on the assumed emittance function in multi-color pyrometry in a slightly different way. He took Eq. (8) as a truncated Taylor series about a central wavelength, λ_0:

$$\ln(e_a) = \sum_{i=0}^{n-2} A_i [\lambda - \lambda_0]^i \tag{9}$$

This would be exact if $n = \infty$. The temperature correction for an n-color pyrometer is then easily shown to be:

$$C_2(1/T - 1/T_a) = (-1)^{n-1}/(n-1)!\, \lambda_0^n [d^{n-1} \ln(e)/d\lambda^{n-1}]_0 \tag{10}$$

Thus, the emittance correction remains, whatever the number of colors assumed. And as n increases, it becomes impossible to calculate the correction for an n color pyrometer because even the best emittance measurements are not sufficient for accurate calculation of $d^{n-1} \ln(e)/d\lambda^{n-1}$. For a similar reason, it becomes impossible to measure temperature accurately with an n-color pyrometer because the best intensity versus wavelength measurements will not give good precision in the derived high order derivitives of intensity with respect to wavelength.

Nordine also examined the precision that may be expected for two- and three-color pyrometry by analysis of emittance data for solid tungsten obtained by three different investigators[3-5]. These are probably the most accurate high temperature emittance data that exist. The values reported by the three investigators differ by less than ±1% at temperatures between 1600 - 3000K and wavelengths between 400 - 750 nm. The expected decrease in precision of apparent temperature measurement for two- and three-color pyrometers was illustrated. It was also shown that the emittance corrections for one-color pyrometers usually vary less with temperature than do corrections for two- and three-color pyrometers.

To be sure, the two- and three-color corrections for tungsten (and for molybdenum) are smaller than for the one-color pyrometer. But for many other materials, the one-color pyrometer gives the smaller temperature corrections. Tungsten and molybdenum are convenient test materials but provide misleading demonstrations of these instruments' accuracy.

The advantages of one-color pyrometry are three-fold, as applied to opaque metallic materials for which sufficient data are available to support the analysis.

- One-color pyrometers often exhibit emittance corrections that are smaller than the corresponding values for two- and three-color pyrometers.
- One-color pyrometers nearly always exhibit temperature coefficients for emittance corrections that are less than the corresponding values for two- and three-color pyrometers.
- One-color pyrometers always measure apparent temperature with a greater accuracy than two- or three-color pyrometers.

The greater temperature dependence of emittance corrections for two- than for one-color pyrometers derives from a general phenomenon exhibited by metallic substances wherein emittance versus wavelength curves obtained at different temperatures cross at a wavelength denoted as the "x-point". The emittance is independent of temperature at this point. Consequently it varies much less with temperature near the "x-point" than do the slopes of the curves on which two-color corrections depend. Two-color emittance corrections usually have a greater dependence on temperature than do one-color corrections because "x-points" usually occur in the visable to near-infrared spectral region used by optical pyrometers. It turns out that the same is true for three-color pyrometers. Four- or greater-color pyrometers are of little interest because they are not accurate and are inherently imprecise.

For these reasons, it is superior to calibrate one-color pyrometers at the known melting point of a material of interest and assume emittance corrections are independent of temperature than to do the same with two- or three-color pyrometers. It is worse yet to assume the emittance correction is zero for a two- or three-color pyrometer. However, the major disadvantage of large emittance corrections remains with one-color pyrometry, and the assumption of temperature independent corrections may also be insufficient for thermophysical property studies.

Since blackbody holes can be used to achieve unit emittance in work with solids, development of methods for accurate emittance measurements on liquids remains as an outstanding problem in high temperature materials science. The following section shows how this problem may be solved.

POLARIZED LIGHT TECHNIQUE FOR EMITTANCES OF LIQUIDS

In 1962 Tingwaldt and Magdeburg[7] published measurements of the emittance of polished tungsten at temperatures between 1630 - 2190K and at wavelengths between 466.5 - 698 nm that agreed within ±1% with the accepted values[3-5]. The method was to measure the intensity ratio for light emitted at 45° to the specimen normal and polarized normal (n) and parallel (p) to the emission plane.

The equations that describe the polarized reflectivities, r_n and r_p are:

$$r_n = [\sin(\theta - \phi)/\sin(\theta + \phi)]^2 \tag{11}$$

$$r_p = [\tan(\theta - \phi)/\tan(\theta + \phi)]^2 \tag{12}$$

where θ is the angle between the specimen normal and the incident light beam, N is the complex index of refraction, and

$$N \sin(\phi) = \sin(\theta) \tag{13}$$

It is easily demonstrated when $\theta = 45^\circ$ that

$$r_p = (r_n)^2 \tag{14}$$

For opaque materials, the sum of reflectivity and emissivity is unity:

$$r + e = 1 \tag{15}$$

This leads to

$$e_n = 2 - e_p/e_n \tag{16}$$

or

$$e_n = 2 - I_p/I_n \tag{17}$$

where I_p/I_n is the intensity ratio for emitted light in the two polarization states.

Tingwaldt and Magdeburg measured I_p/I_n for a polished tungsten filament that was oriented at 45° to the observation direction. The value of e_n was then derived from Eq. (17). Intensity measurements were also made in a direction normal to the surface. Normal spectral emittances were thus obtained which agreed well with the accepted values[3-5] to demonstrate the accuracy of this method.

The polarized light technique should be easily adapted for non-contact temperature and emittance measurements on liquid phases in containerless experiments. Liquids have the smooth and specularly reflecting surfaces that are required and will assume a spheroidal shape that, at some point on the surface, emits light at an angle of 45° to the specimen normal for any direction of observation. The emittance and temperature can then be accurately measured by an instrument that identifies the 45° point and measures the absolute intensities of the two components of polarized light emitted at this point.

An instrument that would implement this method for liquid temperature measurements is illustrated in Figure 1, whose caption describes the labeled parts. The device relys on reflection of a laser beam incident at an angle of 90° to the observation direction to find the 45° point. Since the liquid spheroid is a specular reflector, the instrument will collect reflected laser light only from a small region centered at the this point to which the instrument aperture may be adjusted. Simultaneous measurements by the two photodetecters will insure that the two intensities are measured at the same specimen temperature. Very accurate determination of relative detection sensitivities is possible by observing emission normal to the specimen surface where $I_n = I_p$. Manual positioning of the instrument would be possible if the suspended specimen has a stable position and shape. Alternatively, automatic alignment could be achieved via a quadrant detecter of the laser spot and oppropriate feed back to a positioning mechanism. If the specimen shape or position are not stable, electronic triggering of the intensity measurements could be used at moments when the reflected laser spot illuminates the instrument aperture.

CONCLUSIONS

Multi-color pyrometry cannot achieve accurate non-contact temperature measurements without information about specimen emittance. Emittance data for incandescent liquid specimens can be obtained by measuring the polarization properties of emitted light. Developement of a single instrument that combines this technique with one-color pyrometry is recommended for application to containerless materials processing in space experiments.

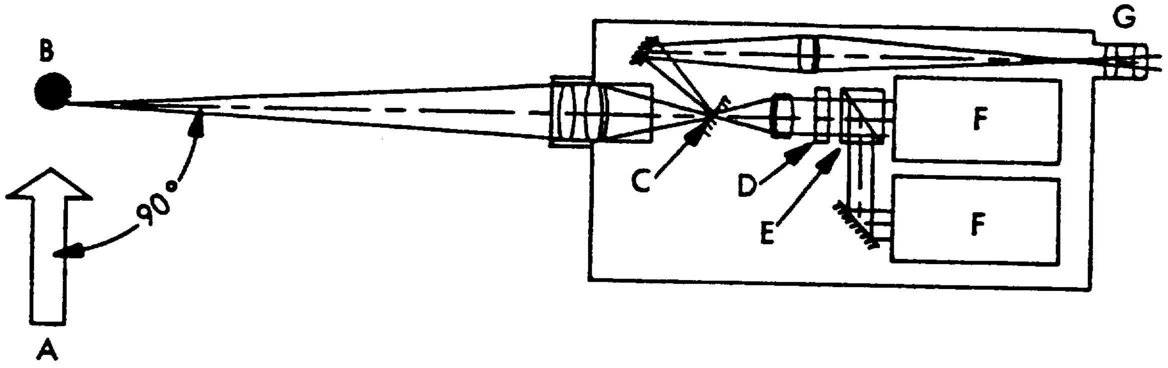

Figure 1. Instrument for Emittance and Temperature Measurement on Liquid Drops. A - HeNe laser beam; B - Liquid specimen; C - Instrument aperture; D - Color filter; E - Polarizing prism; F - Photodetectors; G - Alignment telescope.

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