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DEVELOPMENT OF A DRIFT-CORRECTION PROCEDURE FOR A DIRECT-READING SPECTROMETER

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16. Abstract
This procedure provides automatic correction for drifts in the radiometric sensitivity of each detector channel in a direct-reading emission spectrometer. Such drifts are customarily controlled by the regular analyses of standards, which provide corrections for changes in the excitational, optical, and electronic components of the instrument. This standardization procedure, however, corrects for the optical and electronic drifts. It is a step that must be taken if the time, effort, and cost of processing standards is to be minimized. This method of radiometric drift correction uses a 1000-W tungsten-halogen reference lamp to illuminate each detector through the same optical path as that traversed during sample analysis. The responses of the detector channels to this reference light are regularly compared with channel responses to the same light intensity at the time of analytical calibration in order to determine and correct for drift. Except for placing the lamp in position, the procedure is fully automated and compensates for changes in spectral intensity due to variations in lamp current. A discussion of the implementation of this drift-correction system is included.

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SUMMARY

Quantitative analyses with direct-reading spectrometers customarily rely on the use of standards to provide corrections for changes in the excitational, optical, and electronic components occurring subsequent to analytical calibration. This approach requires effort to prepare and to process the standards, and the effort contributes to the cost of the analysis. The analysis can be made more cost-efficient by developing a method of spectrochemical analysis which eliminates much of the effort required by the use of standards. A step in developing such a method was taken by devising a radiometric drift-correction procedure which eliminates the optical and electronic sources of systematic error.

A 1000-watt tungsten-halogen lamp with a frosted quartz envelope was used as a reference light source to illuminate the photoelectric detectors through an optical path identical with that traversed in sample analysis. The response of the optical-electronic system to the light emitted by this lamp was compared with the system response to the same light level at the time of analytical calibration. System drift factors for each detector channel of the spectrometer were computed from the comparison ratio

$$(\text{system drift factor})_i = \frac{(\text{initial response})_i}{(\text{present response})_i}$$

where the subscript i denotes the detector channel index. These factors were then used to correct for drifts which occurred subsequent to analytical calibration. The factors corrected for all drifts external to the spectroscopic excitation source, except for spectral line position shifts at the exit slits, with accuracy of about ±1 percent.

A discussion of problems encountered in implementing this system in a high-sample-volume environment is included. Problems such as precise relocation of the lamp, correcting the lamp current variations, and minimizing stray light inside the spectrometer were resolved in order to obtain system drift factors having the required accuracy.

INTRODUCTION

A general requirement in quantitative emission spectrochemical analysis is proper standardization. This is usually accomplished by using chemical calibration standards which are similar to the samples in both chemical composition and form. These standards serve three main purposes. The excitation of a series of standards provides (1) the functional relations between atomic emission intensities and element concentration, (2) compensation for systematic changes within the excitation source, and (3) compensation for systematic drifts in the optical and electronic components of the analytical system. Of these three purposes, only the first is completely accomplished in the initial calibration.

In some applications of emission spectrometry, the cost of maintaining control of instrument calibration can be comparable to that of processing unknown samples. In particular, the cost of maintaining calibration is high where the types of samples to be analyzed are nonrepetitive and standard samples are not available. A method of controlling or compensating for systematic drifts in the sensitivity of the instrumentation is needed in order to reduce the cost of maintaining calibration.

The requirements for an effective method applied to a multichannel spectrometer include a long-term repeatability of 1 percent or better, sensitivity to accumulated drifts in all optical and electronic components, effectiveness for wavelengths between 250 and 450 nanometers, and minimal operator time and effort.

Some alternative approaches include the use of a calibrating light source or use of a calibrating detector, as discussed in reference 1. The geometric arrangement of the calibration device in the spectrometer is critical to ensure sensitivity to the identical sources of drift that can affect analysis results. For example, the lamp and detector geometry suggested in reference 1 is not sensitive to certain parallax and scattering effects.

The best optical arrangement is one in which the radiation from the reference source traverses a path identical with that traversed by radiation from the analytical source; another acceptable arrangement is that of a calibrating detector receiving light according to the same criterion. In a multichannel spectrometer, this criterion can be more readily met with a constant light source because of the multiple positions of detectors on the focal curve.

In the system described in this report, the illumination from a tungsten-halogen standard lamp was selected as the reference. The long-term precision of this light source has been documented (ref. 2). It was chosen from several that were considered for this application, including a 40-watt deuterium lamp and an 80-ampere hydrogen arc. As shown in figure 1, the deuterium lamp does not have sufficient spectral intensity over the required wavelength region. Although the hydrogen arc has sufficient spectral intensity over the required wavelength region, its precision (ref. 3) and convenience of oper-

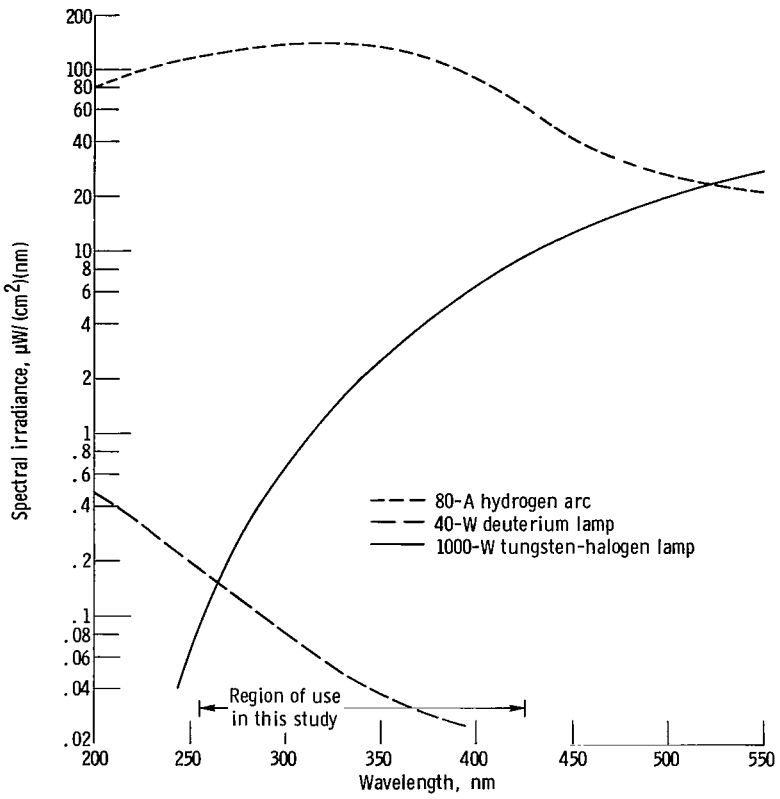

Figure 1. - Typical spectral irradiances of three standards of spectral radiance.

ation were not acceptable for this application.

The 1000-watt tungsten-halogen lamp has a spectral distribution which is sufficiently intense over most of the wavelength region where radiometric control is required. Lamps of this type, when powered by a highly regulated and stable current source, emit light which is reported to remain stable for over a period of at least 50 operating hours to within 0. 2 percent with respect to total irradiance and to within 1 to 2 percent with respect to spectral irradiance (ref. 2). These lamps are also reported to reproduce spectral intensity values which range within ±1 percent of their means. Although the uncertainties in the absolute values of the spectral irradiances are reported to be from 4 to 8 percent (ref. 2), this is of no consequence in this control application, because in this application the lamp was used only as a spectral irradiance reference source requiring long-term stability and precision rather than absolute accuracy.

This report describes the initiation and implementation of the radiometric control system in an automated emission spectrometer where it is presently under long-term evaluation. Because the illumination cycle data processing is automated and because the light intensity is inherently more precise than the emissions from analytical standards, the overall efficiency of the analytical system is improved.

APPARATUS AND PROCEDURE

Reference Light Source

Description. - A 1000-watt tungsten-halogen lamp with a frosted quartz envelope was chosen as the reference light source. It is a commercially available (General Electric Co., Cleveland, Ohio, Quartzline FBY, 120 V, 1000 W) high-intensity and stable spectral irradiance reference source rated at a current of 8.3 amperes. The lamp was used to illuminate the photoelectric detectors through an optical path identical with that traversed in sample analysis, and the responses to this illumination were used to correct for drifts in radiometric sensitivity. The spectral distribution of this lamp is plotted in figure 1 from calibration data supplied with the lamp. The ultraviolet wavelength region over which the lamp is used in this application is indicated along the abscissa. It is defined by the wavelength locations of the detectors used in the spectrochemical analysis program.

Location. - The lamp filament was located at the position where sample excitation takes place. The optical path traverses the same 22 optical surfaces from the lamp to the multiplier phototube detectors as traversed by atomic emissions during sample excitation. Figure 2 is a simplified representation of this arrangement. The lamp was

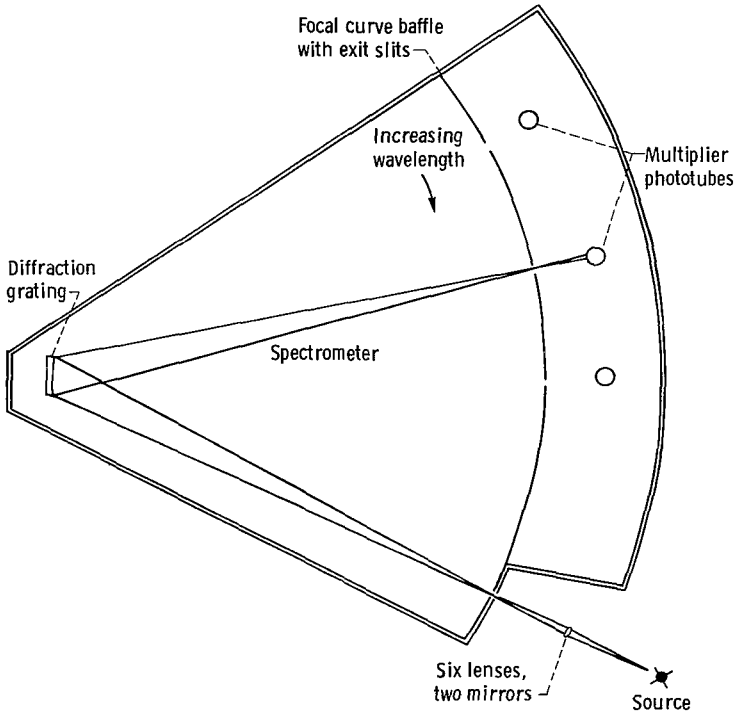

Figure 2. - Simplified diagram of spectrometer optics.

removed from position during sample excitation and reinstalled in precisely the same location for each lamp-standardizing illumination period. The relocation of the lamp was rather critical because of the small acceptance angle of the spectrometer at the analytical gap. It was required that the same region of the filament be placed inside this small angle of acceptance for each illumination period. This requirement was met by placing the lamp in a rigid holder which could be easily removed and reinstalled with the necessary precision by using self-locating screws. A brass holder, shown with the lamp in figure 3, provided both the rigidity and the electrical conductivity required.

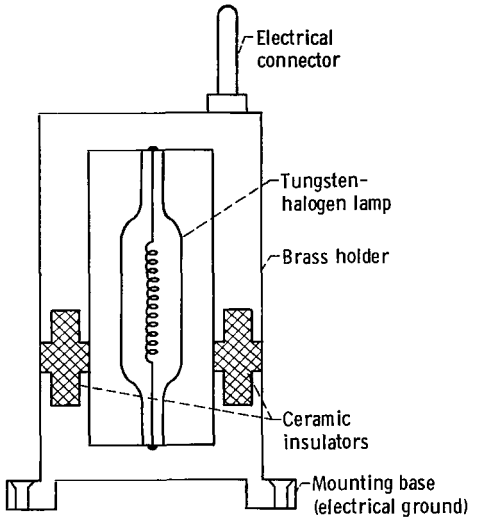

Figure 3. - Tungsten-halogen lamp in rigid holder.

Power Supply

A power supply is required which delivers 8.30 amperes, direct current, to the lamp filament with 0.1-percent regulation, if the best precision in spectral intensities is to be achieved. The current in this procedure, however, was supplied by the direct-current power supply used to excite the analytical samples. The current was monitored by measuring the potential drop across a precision 0.3-ohm series resistor. Although the power supply used for direct-current-arc spectroscopic excitation is convenient, it does not have the required current regulation for precise lamp operation. Consequently, to ensure that the reference lamp would provide the precision required, a procedure was devised which would compensate for the imprecise lamp current supply.

Compensation for Drifts in Lamp Current

Drifts in lamp current were compensated for by monitoring the lamp current and computing the initial lamp intensity that would have been obtained at the average lamp current measured at the time calibration was established. This required lamp calibration functions which provided the relations between detector responses and average lamp current. These functions were established by measuring the response of each detector to the spectral intensity of the lamp at 80 values of lamp current.

A current integrator was installed in the lamp circuit as shown in figure 4 to measure the time-averaged lamp current. The initial lamp calibration data were obtained by operating the lamp for a 5-second warmup period followed by a 17-second integration period at currents between 7.7 and 8.8 amperes. The responses from the detectors and the lamp current integrator were recorded. The warmup and integration times were the same as was used for sample excitation for convenience in automatic sequencing. The lamp and its holder were allowed to cool after each illumination to simulate the thermal conditions existing during routine operation. These data, initial detector responses as a function of the time-averaged lamp current, were fit to curves by computer to determine the lamp calibration functions for each detector. The curve fitting was done by the method of relative least squares with third-degree polynomial model equations.

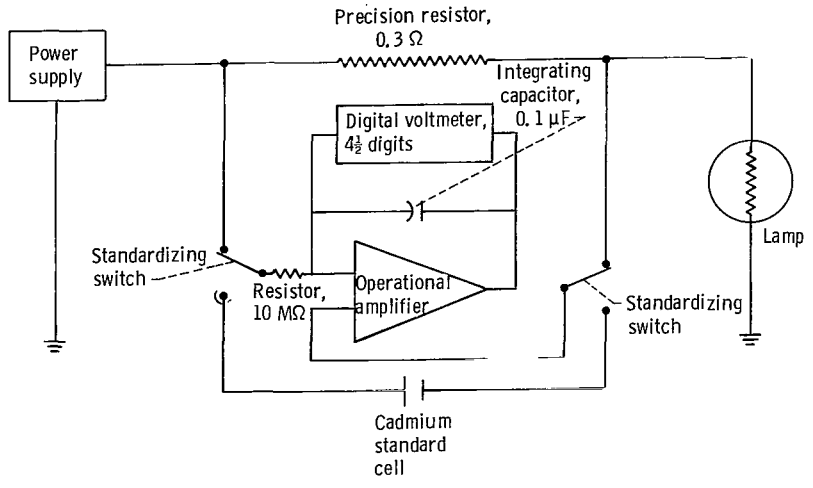

Figure 4. - Lamp circuit diagram.

These functions,

$$(\text{initial response})_i = f_i(\text{average lamp current}) \tag{1}$$

where the subscript i denotes the detector channel index (from 1 to 22), provide a means for computing the initial responses given by each detector at any time-averaged lamp current, within the domain over which the functions are defined. There is, therefore, no need to maintain a constant 8.30-ampere lamp current in order for the $(\text{initial response})_i$ values to be known. The functions used to generate these values are then stored in a computer program used to transform radiometric responses from excited samples into analytical results. There they are called upon regularly in computing the $(\text{initial response})_i$, which are required to determine drift-correction factors used to achieve radiometric control of the analytical system.

System Drift Factors

Method of computing. - In order to achieve the desired radiometric control of the analytical system, a system drift factor was computed for each detector channel of the spectrometer:

$$(\text{system drift factor})_i = \frac{(\text{initial response})_i}{(\text{present response})_i} \tag{2}$$

The $(\text{present response})_i$ are the responses of each detector channel to illumination from the lamp immediately before each series of 11 sample excitations. The $(\text{initial response})_i$ are computed by equations (1) from the time-averaged lamp current measured during this same illumination period. The system drift factors are wavelength-dependent. Evidence of this dependency and its effects on accuracy are presented in the section RESULTS AND DISCUSSION.

Method of applying. - These system drift factors are used in a spectrochemical analysis computer program. There radiometric analytical data from each detector channel are multiplied by the corresponding drift factors. These factors provide corrections for drifts in the radiometric sensitivity of the analytical system and hence the desired radiometric control.

Precision study. - The repeatability of this procedure for correcting systematic radiometric drifts was evaluated under conditions of actual use. The method of evaluation included all known sources of error in the procedure: the reference lamp, precision of removal and reinstallation of the lamp, the lamp calibration curve fits, and the

random radiometric errors of the spectrometer. The evaluation was accomplished by performing 10 illumination cycles within a time period of about 2 hours in which no significant changes in system drift factors were expected. The averages and coefficients of variation were computed for the 10 replicates for each detector channel. This precision study was conducted at lamp currents of 8.0 and 8.6 amperes.

Preliminary evaluation of responsiveness. - The degree to which this method of radiometric control provided the expected compensation was determined by introducing two systematic changes into the system. One was introduced by making a 1-percent change in the multiplier phototube dynode voltage. Another was introduced by cleaning 10 of the exposed optical surfaces. Both the increase in optical transmission and the change in dynode supply voltage were larger than could normally be expected over a typical time period of analytical operation.

Estimating fractions of stray light. - The degree to which stray light affects the accuracy of the system drift factors was estimated by obtaining estimates of the fractions of stray light and spectrally dispersed light coming from the reference lamp and illuminating each detector. Estimates of these fractions were made from spectral intensity ratios. Spectral intensities were measured with and without a colored glass filter, CS 7-54 (Corning Glass Works, Corning, N. Y.), in the optical path. The ratios of these intensities were compared, at each detector wavelength location, with the spectral transmittance of the filter. Each intensity ratio, the average for four precise replicates, was divided by the filter transmittance at the corresponding wavelength to obtain estimates of the maximum fraction of spectrally dispersed light or primary radiation P_i at each detector wavelength. The minimum fraction of stray light was estimated as $1 - P_i$ for each detector.

The experiment was repeated with another colored glass filter, Corning CS 7-50, to obtain better resolution of the intensity ratios and filter transmittance values for three detectors in the wavelength region between 400 and 430 nanometers. The principles of this method for estimating stray light are discussed in reference 4.

Provision for Lamp Replacement

Eventual replacement of the reference lamp was provided for by establishing the relation between the spectral irradiances of the reference lamp in service and of a spare lamp. The spare lamp was mounted in position and energized. The spectral intensities of the spare lamp were measured by each of the detectors. Immediately thereafter, the first lamp was put in position and energized at the same lamp current. Its spectral intensities were measured by each detector. The ratios were then used to compute a lamp factor for each detector channel:

$$(\text{lamp factor})_i = \frac{(\text{present response from second lamp})_i}{(\text{present response from first lamp})_i} \tag{3}$$

These $(\text{lamp factor})_i$ are then stored for use when the second lamp is used to determine the system drift factors. If the factors are assumed independent of lamp current over the 1-ampere operating range,

$$(\text{system drift factor})_i = \frac{(\text{initial response})_i}{(\text{present response})_i} (\text{lamp factor})_i \tag{4}$$

Here $(\text{initial response})_i$ are computed for the first lamp by using the current measured for the second lamp in equations (1). The $(\text{present response})_i$ are those measured for the second lamp.

These lamp factors are computed early in the lifetime of a lamp to establish a reference level for lamp performance. The lamp factors are redetermined at infrequent intervals to monitor the deterioration of the first lamp due to its regular use. When the lamp factors deviate by more than 2 percent from their original values, the first lamp is removed from service and replaced by the second. The lamp factors of another spare lamp are then determined, and it succeeds the previous lamp as a reference spare. This procedure allows for lamp replacement without complete recalibration of all elements in the spectrometer or of the new reference lamp.

Standardization of Lamp Current Integrator

The current integrator that measures the average lamp current is also itself an electronic device (ref. 5) which is subject to drift. It must be standardized at regular intervals to maintain its accuracy. This is accomplished by using a cadmium standard cell of the unsaturated type. It is referenceable to the National Bureau of Standards through a commercial supplier (Eppley Laboratory, Inc.; Newport, R. I.). These cells are well known and widely used as standard cells in potentiometers because of their accuracy and long-term stability. The cell was connected directly into the lamp current-measuring circuit as shown schematically in figure 4. The current drawn by this circuit was only about 0. 1 microampere for a period of 17 seconds, which was less than the current usually drawn from this type of cell in a potentiometer.

RESULTS AND DISCUSSION

Lamp Intensity Calibration Precision

The lamp, with the holder and power supply used in this procedure, yielded precise spectral intensity data, 70 percent of which lay within 1 percent of the lamp calibration curve fits, and 95 percent of which lay within 2 percent of the curve fits. A typical curve for one detector channel is shown in figure 5. The pooled relative standard deviations of these curve fits are listed in table I. These data show that the lamp calibration curve fits provide the required precision in computing the $(\text{initial response})_i$ values from equations (1). The pooled relative standard deviations ranged from a minimum of 0.6 percent for the detector at 283.3 nanometers (lead) to a maximum of 1.6 percent for the detector at 257.6 nanometers (manganese). The average was 0.9 percent for all detector channels.

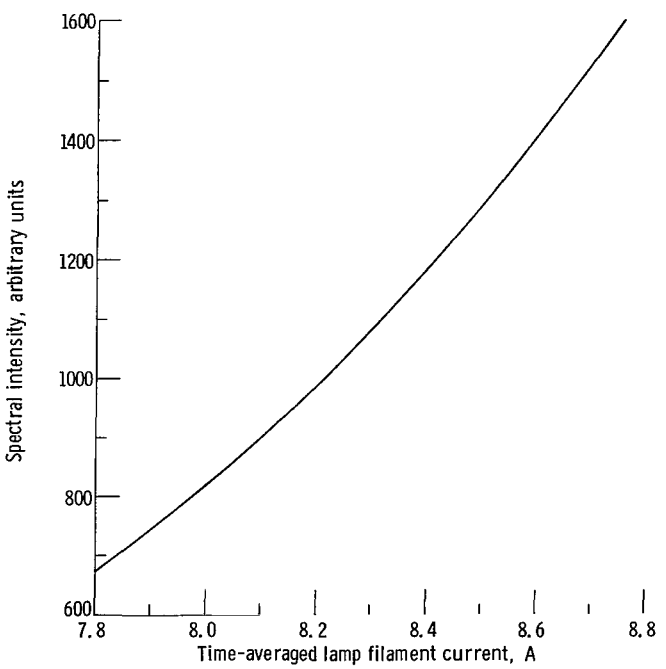

Figure 5. - Typical spectral intensity of 1000-watt halogen-filled tungsten-filament lamp at currents within 7 percent of lamp rating. Pooled relative standard deviation, 0.72.

TABLE I. - PRECISION OF RADIOMETRIC

DRIFT CONTROL PROCEDURE

Detector element	Detector wavelength, nm	Pooled rsd[a] of lamp calibration curve-fit, percent	Low-current region		High-current region	
			System drift factor[b]			
			Mean	rsd, percent	Mean	rsd, percent
Manganese	257.6	1.6	1.00	0.4	0.99	0.3
Lead	283.3	.6	.89	.9	.92	.5
Tantalum	296.5	.6	.92	.3	.94	1.2
Niobium	309.4	.9	.99	.5	.98	1.0
Vanadium	310.2	.8	.99	.4	.99	.3
Beryllium	313.1	1.5	.99	1.5	.99	1.5
Tin	317.5	.8	.99	.4	.99	.4
Copper	324.8	1.0	.94	.4	.95	.3
Titanium	334.9	.9	.96	.3	.96	.4
Zirconium	339.2	.7	.91	.5	.92	.7
Cobalt	345.4	.9	.90	.6	.90	.5
Cadmium	346.6	.6	.87	.3	.89	1.3
Nickel	356.6	.7	.92	.7	.93	.7
Yttrium	360.1	1.2	.94	.4	.95	.7
Iron	372.0	.7	.96	.3	.97	1.1
Molybdenum	386.4	.8	.94	.5	.94	.6
Aluminum	394.4	1.3	.95	.8	.98	.8
Tungsten	400.9	.8	.94	.6	.94	.7
Hafnium	409.3	.7	.96	.5	.97	.8
Chromium	425.4	.7	.88	.5	.89	.9
Zero order	-----	.5	.85	.3	.87	.8

[a]Relative standard deviation or coefficient of variation.

[b]Factors determined 11 weeks after calibration.

System Drift Factors

Radiometric drift-control precision. - The results of the system drift factor precision study are listed in table I and summarized in table II. The means and relative standard deviations of the system drift factors for each detector channel are tabulated for both low- and high-current regions of the lamp calibration curves. These relative standard deviations were obtained under the actual operating conditions of the complete radiometric drift-control procedure. With the fraction of stray light remaining constant, they include all sources of error that can be expected to affect the precision of that procedure. Generally, these precision values indicate that the method of compensating for variations in lamp filament current yields acceptable results. The results

TABLE II. - SUMMARY OF PRECISION OF RADIOMETRIC DRIFT CONTROL PROCEDURE

Relative standard deviation interval, percent	Number of detectors with precision in relative standard deviation interval for -		
	Lamp calibration	System drift factor	
		Low-current region	High-current region
0 to 0.5	[a]1	[a]13	7
0.5 to 1.0	16	7	[a]9
1.0 to 1.5	3	0	4
1.5 to 2.0	1	1	1

[a]Includes zero-order (total irradiance) detector.

are within the precision specifications for the lamp as stated by the supplier when it is used with a highly regulated current source, under controlled conditions including a 5-minute minimum warmup period. This period is 60 times longer than the warmup period used in this procedure. This method of compensation also eliminates the occasional readjustment or recalibration of the power supply generally required to maintain its accuracy.

Preliminary evaluation of responsiveness. - A preliminary evaluation of the effectiveness of this method of correcting radiometric drift in the analytical system gave results which indicated a reasonable and precise response of the system drift factors to systematic changes in the electronic and optical components.

A 1-percent decrease in voltage applied to the multiplier phototubes caused an average increase in system drift factors of 11.5 percent. These drift factors are plotted in figure 6. Their coefficient of variation is 0.8 percent. This value can be considered an acceptable variation for a population consisting of four different types of multiplier phototubes operating at voltages between about 650 and 1000 volts. This result is within the magnitude, direction, and variation expected.

System drift factors were also determined after 10 of the external optical surfaces were cleaned. This was done to evaluate the degree to which this method of radiometric drift control provided the expected compensation for normal optical fogging. The factors are plotted in figure 7 as ratios of the intensities after cleaning to those before. The wavelength dependencies of 19 of these 22 factors have a correlation coefficient of 0.95. This high degree of wavelength dependency is presumably due to the wavelength dependency of scattering from dirty lenses. It indicates the desirability of using light which traverses the same optical path during radiometric referencing as light from sample excitation. The factors for two other detectors are also plotted in figure 7.

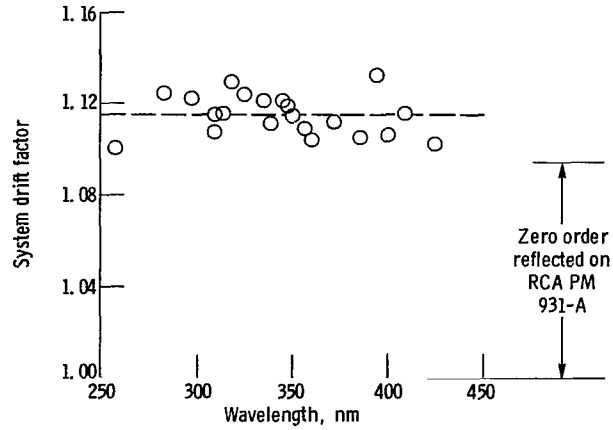

Figure 6. - Effect of 1-percent reduction in dynode voltage on system drift factors.

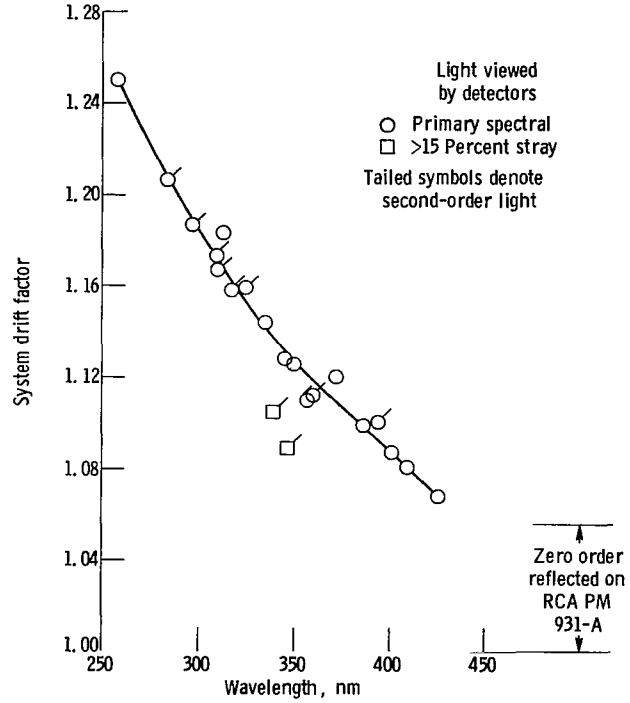

Figure 7. - Wavelength dependency of system drift factors for optics with dust accumulation which caused 5.6-percent decrease in total transmittance.

These factors approach the value of the factor determined for nonspectrally dispersed light reflected from the grating (zero order). This agreement suggests that these two detectors are viewing more stray light than spectrally dispersed primary radiation.

Effect of stray light. - The radiometric referencing procedure described in this report is based on the assumption that the variables upon which the sensitivity of each detector channel depends are the same during radiometric referencing as during analytical excitation. Erroneous system drift factors are produced whenever this is not the case. One such departure from the assumption occurs because the spectral intensity distribution of radiation from the tungsten-halogen reference lamp is quite different from that of the analytical arc source. As a result of this difference the fractions of stray light incident on each detector, and the spectral composition of the stray light, are different for the two sources. These differences can cause erroneous system drift factors to be determined for those detectors which view a significant fraction of stray light from the lamp. The erroneous drift factors occur because the optical contributions to the drift factors are wavelength-dependent. Therefore, factors determined for those detectors viewing a mixture of stray and primary radiation are not the correct factors to apply when the detector is viewing only the primary radiation to which it is assigned. Therefore, if valid system drift factors are to be provided, special consideration must be given to the errors originating from this inherent difference between the two light sources coupled with the wavelength dependency of the optical contributions to the system drift factors.

A quantitative estimate of these errors in system drift factors can be made. They are systematic errors which are the differences between the system drift factors computed from equations (2) by using reference lamp data and the factors that would be obtained if the analytical excitation source were used as the reference or if stray light from the reference lamp were identical to that from the analytical source. The latter condition prevails when the stray light reaching the detectors from both sources is nil. Therefore, the system drift factors that lie along the curve in figure 7 closely approximate the correct values for application to data from the analytical arc excitation source used in the authors' laboratory. This has been experimentally confirmed.

Estimates of these systematic errors due to stray light are computed for system drift factors, such as those plotted in figure 7, from

$$(ESE)_i = (SDF)_i - (SDF)_{\lambda, i} \tag{5}$$

where

$(ESE)_i$ estimate of systematic error due to stray light

$(SDF)_i$ system drift factors computed from eq. (2)

$(SDF)_{\lambda, i}$ system drift factors read from curve at wavelength λ corresponding to that viewed by detector channel i

An equation can be derived to compute $(ESE)_i$ from the fraction of stray light viewed by each detector i during radiometric referencing with the lamp. For this purpose, estimates of the fractions of stray light are required.

This need is met by estimating the fraction of stray light incident on each detector from the data plotted in figure 8. The apparent scatter of the data is not the result of random error. Each point is the mean of precise replicates. The scatter appears in the data because each detector views a different fraction of stray light. Deviations of the points from the filter curve are indicative of the presence of stray light at the respective detectors. Two channels are apparently viewing relatively large fractions of stray light. The ratios from the other 19 detectors are attenuated by the filter by about the amount predicted by the spectral transmittance of the filter. These are the same 19 detectors for which figure 7 shows a high correlation between the system drift factors and wavelength in the lens cleaning experiment. Again, the results indicate that the detectors are being illuminated mainly by spectrally dispersed light.

An estimate of the maximum fraction of spectrally dispersed primary radiation P from the lamp can be obtained for each detector by dividing the response ratios by the filter transmittance at the wavelength of the detector location. Such estimates are listed in table III. It can be seen that two elemental detectors, zirconium and cadmium,

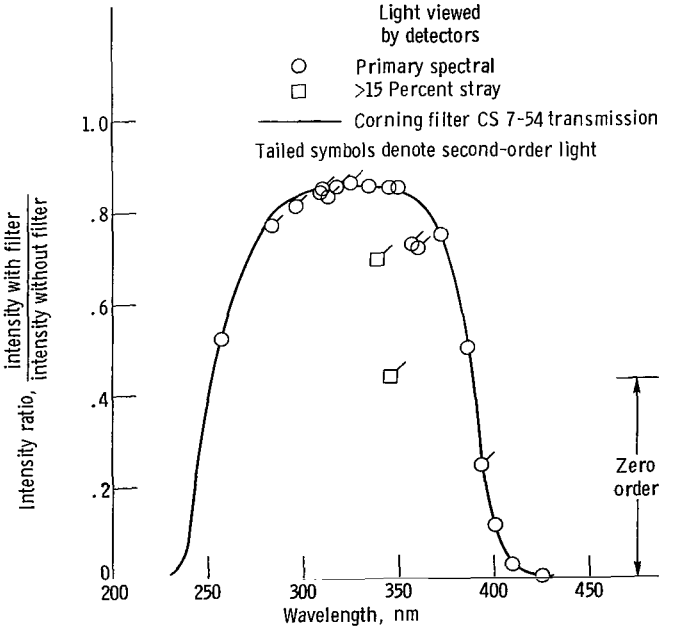

Figure 8. - Conformity of detector responses to spectral transmission from standard lamp through ultraviolet-band-pass filter.

TABLE III. - ESTIMATES OF MAXIMUM FRACTION OF PRIMARY SPECTRAL LIGHT TRANSMITTED TO EACH DETECTOR FROM STANDARD LAMP

Detector element	Detector location		Estimate of maximum spectral fraction, P
	Wavelength, nm	Order	
Zero	-----	0	0
Manganese	257.6	1	.98
Lead	283.3	2	.96
Tantalum	296.5	2	.98
Niobium	309.4	2	.99
Vanadium	310.2	1	1.00
Beryllium	313.1	2	.98
Tin	317.5	2	1.00
Copper	324.8	2	1.00
Titanium	334.9	1	1.00
Zirconium	339.2	2	.82
Cobalt	345.4	1	1.00
Cadmium	346.6	2	.52
Silver	350.2	1	1.00
Nickel	356.6	2	.87
Yttrium	360.1	2	.87
Iron	372.0	1	1.00
Molybdenum	386.4	1	.97
Aluminum	394.4	2	.96
Tungsten	400.9	1	.96
Hafnium	409.3	1	.97
Chromium	425.4	1	.95

are illuminated by less than 0.85 spectrally dispersed primary radiation. The values range from 0.52 to 1.00. Nineteen of the 22 values are above 0.85. When the experiment was repeated with a different colored glass filter to obtain better resolution of the intensity ratios and filter transmittance values in the wavelength region between 400 and 430 nanometers, the results confirmed those in table III.

The data presented in figures 7 and 8 were obtained over a short time period, so that drifts caused by effects other than changes in optical transmittance were minimal. The data in figure 7 were also obtained for what was intended to be an extreme change in optical transmittance. Thus, under these experimental conditions, data were provided for computing the maximum $(ESE)_i$ from

$$(\text{MESE})_i = P_i(\text{SDF})_{\lambda,i} + (1 - P_i)(\text{SDF})_0 - (\text{SDF})_{\lambda,i} \tag{6}$$

where

(MESE) maximum estimate of systematic error due to stray light

P maximum fraction of spectrally dispersed primary radiation

$(\text{SDF})_0$ system drift factor for zero-order detector channel

The values of $(\text{MESE})_i$ are valid estimates of maximum systematic errors as long as the optical drift contributions to $(\text{SDF})_{\lambda,i}$ and $(\text{SDF})_0$ used in equation (6) are greater than those occurring during routine operation. Also, P_i is expected to change as the internal optics of the instrument change; consequently, the $(\text{MESE})_i$ must be reevaluated as frequently as conditions warrant, if they are to be kept currently correct.

Equation (6) can be simplified to compute the relative (MESE), in percent, for each detector channel:

$$\text{relative } (\text{MESE})_i = \frac{[(\text{SDF})_{\lambda,i} - (\text{SDF})_0](P_i - 1)}{(\text{SDF})_{\lambda,i}} \times 100 \tag{7}$$

It can be seen from this expression that the relative $(\text{MESE})_i$ approaches zero as $(\text{SDF})_{\lambda,i}$ approaches $(\text{SDF})_0$, or as the stray light $(P_i - 1)$ approaches zero. The former condition occurs when there is no wavelength-dependent change in the sensitivity of the instrument (fig. 6). If either one or both of these conditions prevail, the factors determined with the reference lamp can be applied to the arc source within acceptable errors. An example of the magnitude of the errors is provided from an estimate of the relative $(\text{MESE})_i$ for a detector that views a significant fraction of stray light. Data from table III and figure 7 were used in equation (7) to estimate the error for the detector channel at 346.6 nanometers (cadmium). This estimate shows that, if the total optical transmittance were increased by 5.6 percent because of cleaning external lens surfaces, the system drift factor error for this worst-case detector would be about 3.1 percent. This example illustrates the importance of minimizing stray light and of routinely cleaning the lens surfaces. A related consideration is the probable wavelength dependency of the optical efficiencies of the grating and front-surface mirrors. However, the effect of the deterioration of the surfaces of these components was neither observed nor studied in this work.

Minimization of stray light. - The fractions of spectrally dispersed primary radiation illuminating each detector were maximized for each detector channel by improving the internal optics of the spectrometer used in this study. This was done by determin-

ing the causes of the stray light and eliminating or reducing them. Some causes of and cures for stray light are discussed in references 3 and 6.

One significant cause of stray light revealed in this study was first-order radiation, with wavelength 2λ, reaching second-order detectors assigned to wavelength λ. Evidence of this stray light due to lack of order selectivity can be seen in figure 8 and table III. They show that the fractions of stray light illuminating detectors in second-order positions are generally higher than those illuminating detectors in first-order positions. The increased stray light was traced to some first-order radiation which was transmitted through the filter-refractor plates located in front of the exit slits. This cause of stray light was virtually removed by installing glass filters with more suitable cutoff characteristics in the optical path of each detector channel where the need was indicated. This arrangement improved the selective passing of second-order light and reduced to acceptable levels stray light due to second-order radiation.

The search for sources of stray light led further to the detection of several other internal optical defects, such as a filter-refractor plate that was too short and small leaks in the exit-slit baffles that permitted radiation from the grating to reach several detectors without passing through their exit slits. Stray light from these causes was not significant with the arc source, but was a problem with the reference lamp source because of the higher total irradiance and spectral distribution of the lamp.

Another significant cause of stray light was specular reflections from exit-slit refractor plates. Some refractor plates were, by chance, normal to a ray from the grating through the exit slit. Refractor plates with this orientation acted as entrance slits, and radiation reflected from them was transmitted back to the grating and on to the focal curve. Photographic detection at the focal curve revealed dense, sharply defined, rectangular images at positions that were predictable by the grating equation. Some of these images fell at positions on the focal curve that were viewed by other detectors and thereby constituted a significant source of stray light. The problem was corrected by moving the slit body so that the orientation of the refractor plate was off normal to a ray from the grating through the exit slit.

Because the spectral distribution of the light from the lamp is much more intense at the higher wavelengths than at the lower wavelengths of the region of use, the problem of back reflection was manifested more significantly by the reflections from high- to low-wavelength positions than by the reverse. These observations and the methods used to reduce stray light were characteristic of the instrument used in this work (1. 5-m Atomcounter, Jarrell-Ash Div., Fisher Scientific Co., Waltham, Mass.), but might also apply in principle to other instruments.

CONCLUDING REMARKS

The effectiveness of this method of radiometric drift correction will ultimately be evaluated by the long-term quality of the analytical results. This evaluation is in process because the method is now being put to routine use in a spectrochemical analytical system. Meanwhile, it can be concluded that reasonably accurate radiometric control of the analytical system can be provided by this procedure when a precise light source, with long-term stability or predictable radiometric behavior, is energized at the same position where analytical samples are excited. The accuracy of the control provided also depends upon the stray light in the instrument.

A 1000-watt tungsten-halogen lamp has sufficient intensity and precision to be used as a reference light source. Although a high-regulation current supply is normally required for precise operation of the lamp, power supplies with considerably poorer regulation, including those used for direct-current arc excitation, are convenient and satisfactory if lamp intensity corrections are made to compensate for current drifts. The 1000-watt reference lamp can also be useful in the detection and subsequent reduction of stray light in the spectrometer.

A drift-correction procedure that provides the desired radiometric control is a step toward reducing the frequency of regular analytical calibration using reference samples. Because the lamp irradiance is referenceable to a standard irradiance (National Bureau of Standards), it can also be useful in experimental work concerned with absolute radiometric characterization of spectrometer components.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, January 6, 1977,
505-01.

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