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LOW COST SOLAR ARRAY PROJECT
Composition Measurements by Analytical Photon Catalysis

Final Report for October 1, 1978—September 30, 1979

By
David G. Sutton
Luis Galvan
James Melzer
Raymond F. Heidner, III

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The Ivan A. Getting Laboratories
The Aerospace Corporation
El Segundo, California

MASTER

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I. Summary

The object of this research is to assess the applicability of the photon catalysis technique for effecting composition analysis of silicon samples. In particular, our technique is to be evaluated as a detector for the impurities Al, Cr, Fe, Mn, Ti, V, Mo and Zr. During the first year we have detected Al, Cr, Fe, Mn, Ti and Si with the photon catalysis method. We have established the best fluorescence lines to monitor and determined initial sensitivities to each of these elements by atomic absorption calibration. In the course of these tests vapor pressure curves for these six pure substances have also been mapped.

We have also studied the detection of these impurities in silicon matrices. The evaporation process was shown to be congruent; thus, our spectral analysis of the vapor will yield the composition of the bulk sample. Qualitative analysis of metal impurities in silicon was demonstrated below the part per million level. Only one atomic spectral interference was noted, however, we determined that it is imperative to maintain a leak tight system due to chemical and spectral interferences caused by the presence of even minute amounts of oxygen in the active nitrogen afterglow.

A parametric study for the purpose of establishing optimal running conditions was completed. The parameters that we varied were temperature, nitrogen and argon pressures, pumping speed, and microwave power. The observable that was maximized in this study was signal to background. We will standardize our analysis technique on these parameters. Thus, when we establish the analytical curves all conditions except impurity level in the samples will remain fixed at their optimal values.

In addition, to these mainline tasks much ancillary information was obtained. The emission signatures were determined for several additional elements including As, Bi, B, Ca, Cu, Cr, Ga, Ge, Mg, Na, P and Pb. Ionic emission lines for Ca and Mg were determined to be useful for analysis. Many metal hydrides and alkyls were found to be detectable by our active nitrogen technique. We also examined pulsed sample introduction and determined that as little as 1 nanogram of lead is detectable in a single shot. As a result of these studies we have concluded that the photon catalysis technique is suitable for bulk analysis of solar grade silicon. The ancillary data also suggest that gaseous feedstocks in the form of metal hydrides can be analyzed by this technique and that pulsed sampling techniques are compatible. This last conclusion suggests the possibility of developing a surface analysis instrument by combining laser microprobe and photon catalysis technology.

II. Background

Work commenced during the week of September 11 with the assembly of our Analytical Photon Catalysis (MTES)¹ device into a configuration suitable for the study of silicon impurities. The resulting instrument and its function can best be explained with reference to Figure 1. It consists of a vertical section of quartz tubing 9 cm in diameter. An electrically heated metal vapor furnace is attached to

the bottom of the quartz tube, and a 60-l/sec pump, attached at the top of the quartz tube, provides the means to evacuate the system. Argon or nitrogen injected through the bottom of the furnace assembly entrains the flow of metal atoms from the furnace and carries it into the quartz observation section. In this section, the concentration of argon is much greater than the metal concentration. A thermocouple placed in contact with the metal in the furnace allows direct measurement of the metal atom source temperature, or an optical pyrometer may be employed by observing the heated metal down through the observation window.

A ring-shaped quartz gas injector is inserted into the apparatus at the junction of the furnace assembly and quartz flow tube. Through this injector, active nitrogen is introduced into the Ar-metal atom stream. The active nitrogen, consisting primarily of N atoms, $N_2(A^3\Sigma_u^+)$, and ground-state N_2 , was prepared upstream of the injector by passing N_2 gas through a 70-W microwave discharge. The region of the quartz flow tube approximately 5 cm above the active nitrogen injector is monitored photoelectrically with an uncooled RCA 1P28 phototube attached to a one meter monochromator. Apart from neutral density filters, which are used at higher metal concentrations to avoid high photomultiplier tube current, no other optics are used. Hollow-cathode lamps can be placed on the opposite side of the flow tube and at the same height as the monochromator entrance slits. They are used as a line source for the atomic absorption measurements to calibrate the fluorescence intensity measurements with respect to metal vapor concentration.

The Ar and N_2 flows were adjusted to give a total pressure of 2-4 Torr. With the microwave generator set to deliver 70 W to the N_2 flow, a pale straw-colored glow is observable downstream of the injector. The furnace is then set to a given temperature, and the resulting atomic line emission intensities are measured.

The most intense and spectroscopically isolated lines are chosen to be the best fluorescence lines to monitor for the purposes of analysis. The intensity is a direct measure of the concentration of the emitting species and can be calibrated at high source temperatures by the atomic absorption technique. If one plots the $\log I$ vs $10^4/T(K)$ a vapor pressure curve results.

III. Progress During Reporting Period

When aluminum is placed in the crucible and heated to 1000 Centigrade the fluorescence spectrum shown in Figure 2 is obtained. All four of the prominent lines are due to the presence of Al vapor in the active nitrogen stream. The two strongest lines at 309 nm and 396 nm were selected as the best for analysis and their intensities were measured as a function of the source temperature. The results for 309 nm are shown in Figure 3.

The results from two different runs are compared with Hultgren's² recommended vapor pressure curve. The slopes of both our curves are about 20% larger in magnitude than his, but the precision of our measurements is excellent. The most reasonable explanation for this discrepancy is a systematic error in our results due to the use of the pyrometer to measure temperature. In subsequent work a digital thermocouple was used to measure crucible temperature thus eliminating this source of error.

The important result is that we have easily measured the aluminum vapor concentration over more than four orders of magnitude. An attempt to calibrate our signal in order to obtain the absolute concentration of vapor in the observation zone was postponed because of the failure of our aluminum hollow cathode lamp.

In Figures 4 and 5 the MTES spectrum and the vapor pressure curves for chromium are shown. Cr, like aluminum, yields a simple line spectrum. The most intense emission lines have wavelengths of 359.4, 357.9 and 425.4 nm. Three additional lines at 360.5, 427.5 and 428.9 nm are also available for monitoring if spectroscopic interferences affect our first choices.

Figure 5 summarizes our temperature dependent measurements at two different wavelengths, 359.4 and 357.9 nm. The slope of the line through our data as determined by least squares fitting agrees within 5% with both Hultgren² and Nesmeyanov.³ Atomic absorption calibration using the 357.9 nm resonance line allows us to put the Cr concentration on an absolute scale as shown on the right side of Figure 5. Using this scale we see that the lowest concentration of Cr detected to date is 1.8×10^5 atoms per cm.³ However, these absolute calibrations cannot be determined with any great confidence, since the experimentally determined oscillator strengths⁴ upon which these determinations depend are not known to any great degree of certainty.

As expected when Fe is excited by active nitrogen a rich atomic emission spectrum results. See Figure 6. The best lines in terms of intensity occur at 344.1, 358.1 and 372.0 nm. Our temperature dependent studies give the vapor pressure curve shown in Figure 7. Our slope is substantially different from Hultgren's recommended curve. Significantly our slope would yield a lower heat of vaporization. If our sample were oxidized a higher value would be expected.

Our results for manganese are summarized in Figures 8 and 9. The manganese MTES spectrum is intermediate between Al and Fe in complexity. Fortunately, however, the intensity is concentrated in the triplet features near 280 and 403 nm. Either of these features could be monitored in its entirety with a wide bandpass detector. Maximum sensitivity could probably be achieved in this manner. However, with our monochromator only one line from each triplet could be monitored at a time. Figure 9 shows our system response to the lines at 279.5 nm and 403.1 nm as a function of the reciprocal of the source temperature. These two features are the most intense of their respective groups. Both sets of data give vapor pressure curves whose slopes come within 10% of Hultgren's² recommended value when fit with the least squares method to a straight line. The dynamic range of our detector extends over four orders of magnitude.

The data points on Figure 9 that are indicated with a circle were obtained with the atomic absorption technique. This data pegs our MTES measurements on the absolute scale given on the right side of Figure 9 and establishes a sensitivity of less than 10^5 cm.³ for Mn.

During the month of January we completed our testing of titanium. We show in Figures 11 and 12 the MTES spectrum and the vapor pressure curves for this element, respectively. The titanium spectrum consists of groups of triplets.

The most intense individual lines occur at 365.3, 398.2, 399.0 and 399.9 nanometers. The two aluminum peaks that appear are due to the presence of foil that serves as a reflector. Inadvertently it was placed too close to the heater element and some of it was vaporized. This problem has since been eliminated by redesigning the oven section and switching to Tantalum foil. Blank experiments done with empty crucibles now show only traces of sodium even at the highest temperatures. The sodium is presumably introduced as an impurity in the crucible. The signal due to this element rapidly diminishes on bake-out. An example of a blank experiment showing the spectrum obtained with an empty crucible is given in Figure 13.

Figure 12 summarizes our temperature dependent measurements at two different wavelengths, 365.3 and 399.8 nm. The data at both wavelengths are fit with straight lines calculated with a least squares fitting routine. The slopes of both lines are also determined in this process. They agree to within 3% and 7% with Hultgren's² recommended data. This excellent agreement is consistent with the high purity quoted for our titanium sample and verifies the accuracy of our calibration technique.

Attempts to calibrate Figure 12 using atomic absorption were unsuccessful. We can estimate the lowest concentrations observed with the rate of vaporization method outlined in Appendix I. The lowest temperature that still resulted in a measurable signal was 1285°K. At this temperature titanium sublimes⁶ at a rate of approximately 8×10^{-11} grams/cm²-sec. If we have identical sensitivities for Ti and Bi then our lowest signal for titanium corresponds to a Ti concentration of less than 10^4 atoms/cm³. The highest temperature our oven is capable of sustaining is 1590°K. The rate of vaporization method enables us to estimate our Ti concentration at this temperature to be between 10^6 and 10^7 atoms per cm³ in our observation region. These low values are consistent with the null signal we obtained in our atomic absorption experiments,³ since this method is normally insensitive to concentrations less than 10^8 per cm³.

During the month of February we attempted to detect vanadium vapor in our MTES apparatus. As anticipated the temperature obtainable from our oven was insufficient to yield a signal from vanadium. We can estimate a lower limit to the sensitivity for vanadium using the rate of evaporation technique discussed in Appendix I. This estimating procedure places the lower limit of detection for vanadium at 10^5 atoms per cm³ in the gas phase. No atomic absorption experiments were attempted, since such a low concentration is incompatible with detection by this classical method.

Since a null result was achieved with vanadium we attempted several preliminary experiments with Si. In particular, with NBS Standard Reference Material #57 (SRM57). The analysis supplied by NBS for this material is reproduced below.

SRM57
Chemical Composition (Weight Percent)

Mn	P	S	Si	Cu	Ni	Cr	Ti	Al	Zr	Ca	Mg	Fe
0.034	0.008	0.005	96.8	0.02	0.002	0.025	0.10	0.67	0.025	0.73	0.01	0.65

We can see that SRM57 is not particularly pure material. It does have the advantage, however, of containing a large number of the impurities that concern this investigation, and it is an NBS standard so that one may have confidence in the supplied analysis. Since this material contains over 3% impurities, we might expect some segregation and fractional distillation as the Si is melted and vaporized. This behavior would manifest itself in vapor pressure curves that would vary from the vapor pressure curve of the host matrix, silicon. This hypothesis was tested on SRM57 by measuring the vapor pressure curves of Si and as many impurities as practical simultaneously. If all the vapor pressure curves are identical, we have proof that the vaporization process is congruent and measurement of the vapor composition will reflect the composition of the silicon sample.

During March we analyzed the rich spectrum resulting from Si SRM57. Shown in Figure 14 is a portion of this MTES spectrum. In addition to the Si lines near 250 nm and 288 nm we can easily identify spectral lines from the following elements:

Element	Wavelength of Prominent Lines Observed from SRM57, nm
Si	251.6, 288.2
Al	308.2, 309.2
Cr	359.4, 425.4
Mn	279.5, 403.1
Fe	239.5 (?)
Mg	285.2
Cu	324.7, 515.3
Na	330.2 (background impurity)
Ca	422.7, 487.8

In order to prove that the vaporization process is occurring at a rate determined by the silicon matrix, we constructed apparent vaporization curves for most of these impurities, using SRM57 as the vapor source. Data is accumulated simultaneously on the intensities of the fluorescence lines due to impurities as well as the silicon 251.6 nm line. These data are plotted on semilog paper as a function of the inverse of the source temperature. These apparent vaporization curves are compared with the silicon curve and with the vapor pressure curves obtained by the previous work with pure metal sources.

An example of our analysis is shown in Figure 15. The solid lines on this plot connect data points obtained at 251.6, 422.7 and 309.2 nm and track Si, Ca, and Al, respectively. These three curves were established simultaneously using Si SRM57 as the source of the vapor. For comparison the vapor pressure curves obtained earlier for Al and Ca using the pure metal as a vapor source are plotted on the same graph as dashed lines. One easily discerns a trend for the apparent

vapor pressure curves of the impurities (Al, Ca) to parallel the curve of the host matrix (silicon). This is powerful evidence that the evaporation process is congruent, and thus, analysis of the vapor via MTES will reflect the composition of the original solid sample.

The significance of this milestone is perhaps best expressed mathematically. If the evaporation process is congruent, the composition of the vapor will be constant (i.e., the same as the source). Consequently, the ratio of MTES fluorescence intensities due to an impurity, i , and silicon will be constant

$$\frac{I_i}{I_s} = C \quad (1)$$

Take the log of both sides of (1) to get

$$\log I_i - \log I_s = \log C \quad (2)$$

For the host Si matrix the MTES vapor pressure curve is linear in inverse temperature.

$$\log I_s = \frac{a}{T} + b \quad (3)$$

Substituting (3) into (2) gives

$$\log I_i = \frac{a}{T} + b + \log C \quad (4)$$

By comparison of equations (3) and (4), we see that plots of $\log I_i$ and $\log I_s$ vs. $1/T$ would have the same slope, a . This behavior is observed in Figure 15 and is seen to be a direct consequence of congruent evaporation.

During April we extended these measurements by following the intensities of additional lines due to impurities as a function of the source temperature. These measurements included the Al (309.2), Ca (422.7), Cr(359.3), Cu(324.7), Mn(403.4) and Si(251.6) lines. The resulting curves were all well represented by straight lines. The slopes of each line was determined by least squares fitting and compared to the slope obtained from the silicon 251.6 line. This comparison and the comparison of the slope obtained from the vapor pressure curve measured over the pure material is compared in Figure 16. In this figure the relative slopes obtained from measurements over the pure material are plotted as circles and the vapor pressure data obtained from Si (SRM57) is plotted as squares.

It is immediately evident from the figure that the vaporization rate (as manifested by the slope of the apparent vapor pressure curves) of each of the impurities tends toward the host material. This is particularly evident in the case of calcium where the change in slope is more than a factor of three. This figure constitutes powerful evidence that the vaporization process is congruent, and that fractional distillation or segregation and independent evaporation is not the dominant mechanism of the evaporation process. This evidence becomes particularly convincing when we point out the range of melting points (Mg 650°C-Cr 1875°C) and the range of concentrations (Mg .01% - Al .67%) encompassed by the

five impurities studied. Thus we conclude that our analysis of the vapor will be equivalent to a bulk analysis of the solid sample.

Interferences encountered so far have mainly been of a spectral nature. The only chemical effect noticed was produced inadvertently. When pure manganese was being studied the crucible was overheated causing the deposition of manganese on our nitrogen injector and on walls of our quartz observation tube. We immediately noticed a drop in the intensity of the normal afterglow and a heating of the walls as well as loss of fluorescence signal.

The explanation is simple. Manganese promotes the heterogeneous recombination of nitrogen atoms. This occurs on the surfaces coated with manganese. The active nitrogen (normally produced by homogeneous, gas phase recombination of nitrogen atoms) is thereby quenched. The heat liberated by the heterogeneous process is absorbed locally on the wall. Careful cleaning eliminated the problem and restored the usual Lewis-Rayleigh afterglow and the MTES signal.

It is extremely unlikely that enough metal would be plated out under normal operating conditions to seriously affect the system performance. In addition, not all metals are as efficient as Mn in catalysing heterogeneous N atom recombination. However, after long hours of service at high temperature system performance may drop off. Simple cleaning will rectify the situation and this caveat should serve to alert potential users.

Spectral interferences are minimal in a leak tight system. The only overlap of atomic lines observed so far is between Na and Mg at 285.2 nm. Na is present as background. Baking out the crucible and insulation eliminates the sodium lines. In addition, there are usually ancillary lines available for each element if an unlikely overlap is encountered. Some of these lines were cataloged in the second quarterly report.

More serious in nature are the molecular bands due to N_2 and if leaks are present NO and N_2^+ . There will always be small signals due to the N_2 second positive emission. A sample background spectrum was shown in Figure 13 of the second quarterly report. This was taken with an empty beryllium oxide crucible heated to 1500°C. The Na feature in that figure at 330.2 nm will diminish with time. The band at 337.1 nm is excited by energy pooling between two excited metastable $N_2(A)$ molecules to form one $N_2(C)$ and a ground state molecule. The $N_2(C)$ species then radiates at 337.1 nm and to a lesser extent at 357.6 nm. The pooling reaction and subsequent emission mechanism has been studied by Setser and can be represented as follows:

Since $N_2(A)$ is responsible for our MTES signal as well, there is nothing we can do to eliminate this possible interference. Fortunately, however, the intensity from this transition is low and the bands are narrow.

Much more serious interferences are caused by leaks. NO is produced by the reaction

and is excited by collisions with $\text{N}_2(\text{A})$ molecules. The resultant emission from NO is normally confined to the gamma bands shown in Figure 17. Sometimes with large leaks the beta bands are also observed. See Figure 18. Worse still NO is known to catalyze the pink afterglow of nitrogen. The spectral signature of this glow is shown in Figure 19. The dominant emission is from the N_2 first negative systems. Unfortunately all of these emissions involve extensive, intense band systems in the useful spectral region for atomic emission spectrometry (200-500 nm). Fortunately the cure for this malady is simple. Fix the leaks.

May was devoted to the study of higher purity silicon. In particular, we examined SPEX Industries 5-9's grade. This powdered material is advertised to be greater than 99.999% pure. The sample we obtained was identified as lot number 12771. The following semiquantitative analysis was supplied with the material (See Figure 20).

Element	ppm
Cu	4-8
Al, Fe	0.5-2.0
Mg	0.1-0.5

Spex Industries representatives have explained to me that this analysis is obtained by spark photometry.

Our goals in examining this material are twofold. First we want to verify qualitatively that our analysis method is sensitive to metal impurities in a silicon matrix at the ppm level. Second, congruent evaporation needs to be demonstrated with high purity material in addition to the tests run with Si (NBS-SRM57) of 97% purity.

The results of the semiquantitative analysis were spectacular. The spectrum shown in Figure 20 displays most of the major spectral features used in our analysis. It was obtained when a sample of Spex 5-9's silicon was placed in one of our boron nitride crucibles, heated to 1500°C and the resulting vapor mixed with active nitrogen. The presence of all the elements, except Fe, identified as impurities by SPEX can be verified by two or more atomic emission lines. In addition, we can positively identify Cr and Ga by their omission signatures. These last two elements were not detected by SPEX's analysis technique.

The Na emission line at 330.2 nm is due to the background presence of this element in the crucible or the insulating material. The 330.2 nm line is present in the blank spectrum when we heat an empty crucible. See Figure 13 of the Second Quarterly Report (Jan.-March 1979). Unlike any of the other atomic lines shown in Figure 20, it slowly diminishes in intensity during the course of an experiment. We can therefore conclude that Na is not an integral impurity of the SPEX 5-9's silicon and that it is slowly being eliminated from the high temperature section of our

apparatus. In contrast, none of the other atomic line intensities change in intensity due to time alone. This fact is further evidence that the evaporation process is congruent. If selective evaporation were taking place, the composition of the sample would be constantly changing. This would manifest itself in time varying intensities for all or most of the impurity lines. Thus our failure to observe any time variations in the intensity of the impurity emission lines is further proof of our contention that the composition of the vapor is representative of the original sample.

Further proof of this hypothesis is contained in Figure 21. It compares the slopes of the vapor pressure curves obtained from the atomic emissions due to impurities to the slope of the VP curve obtained from the silicon line at 251.6 nm. Previously we showed mathematically that congruent evaporation would lead to parallel VP curves. Ideally this would manifest itself in a plot like Figure 21 where each point had an ordinate equal to one. In the April monthly report we included a plot, Figure 16, summarizing our VP slopes obtained with Si from NBS-SRM57. That Figure clearly showed the trend toward parallel VP curves. Figure 21 is an identical plot, but derives from data taken on SPEX 5-9's silicon.

The two Figures, 16 and 21, are almost identical. They both clearly show the trend toward parallel slopes; i.e., the approach toward congruent evaporation.

In June we obtained the MTES qualitative analysis of SPEX 6-9's silicon. This material is advertised to have less than one part per million total impurities. In fact their spectrographic analysis is incapable of detecting any impurities. In contrast we show in Figure 22 the MTES spectrum obtained with this material and a background spectrum taken with an empty crucible.

The background spectrum was recorded with one hundred times more sensitivity than the silicon spectrum. The only element that appears in the background is sodium. The intensity of these lines at 330.2 nm and 285.3 nm diminish slowly on bake-out. Thus, the 330.2 nm line does not appear in the silicon spectrum, since it was baked-out prior to adding the Spex 6-9's sample to the crucible. The Na line at 285.3 interferes with the 285.2 nm Mg line. We have noted only this one atomic interference to date.

The impurities Mg and Ca are clearly in evidence in our sample spectrum. Thus, if Spex's analysis is correct we have demonstrated sensitivity at less than one part per million. Interestingly, the ion lines from both these group IIA impurities have higher intensities than the neutral lines. Compare 279.6 nm with 285.2, for example. The Ca neutral line at 422.7 is weak and is not shown in the figure. This result belies our previous explanations of the excitation mechanism. We hypothesized that bimolecular collisions with $N_2(A^3\Sigma)$ was the source of excitation of the neutral atomic emission lines. Obviously this one step mechanism can not explain the excitation of ionic states at 9 to 12 eV (roughly twice the A state term value).

Nevertheless, we decided to empirically determine if the ion lines of Ca would be useful in an analysis of Si samples. Thus we determined the intensity of the 393.4 nm Ca II as a function of source temperature to see if the vapor pressure plot paralleled that of the silicon host. The results are shown in Figure 23. It is evident that the calcium ion line tracks the silicon intensities even more faithfully than the neutral Ca 422.7 nm line. We thus conclude that this line in particular will be useful for analysis.

We also conducted tests that support the same conclusion for Mg. In particular, monitoring the Mg II 279.6 nm line would yield a higher sensitivity than monitoring the Mg I 285.2 nm line. This is fortunate since the presence of sodium creates a spectral interference at 285.2 nm.

A parametric study for the purpose of establishing optimal running conditions was completed. We will standardize our analysis technique on these parameters. Thus, when we establish the analytical curves, all conditions except impurity level in the samples will remain fixed at their optimal values.

The parameters that we varied were temperature, nitrogen and argon pressures, pumping speed, and microwave power. The observable that was maximized in this study was signal to background. The signal was the measured intensity of one of many spectral lines due to impurities, and the monitored background was the nitrogen first negative band at 388.0 nm. An example of the results obtained when the nitrogen partial pressure was varied is shown in Figure 24. In this figure we have plotted the intensities measured for Si, Na and N_2 as a function of the nitrogen partial pressure in the observation zone. We see that the ratio of Si to 1N (nitrogen first negative) intensity is maximal at 0.6 Torr N_2 . The Na line is due to a background impurity. Its intensity has a peculiar oscillatory behavior with increasing nitrogen pressure. A minimum occurs near 0.6 Torr, however. Thus, we select 0.6 Torr N_2 as an optimal operating parameter. Temperature and argon flows have been selected in a similar manner. Blackbody radiation becomes a limitation at wavelengths longer than 450 nm at temperatures above 1700°C. Increased microwave power enhances most of the impurity signals, so we operate near our current maximum of 100 watts and will try higher powers under next year's contract. Pumping speeds above 10 cfm seem to reduce background signals.

During the course of the parameters study, we raised our crucible temperature above 1700°C. Apparently this was sufficient to drive off some free boron from the BN material, since we detected an emission doublet at 249.7 and 249.8 nm. These two lines are attributable to atomic boron. Detection of this emission indicates that we are sensitive to this element, although detailed tests would be necessary to establish the sensitivity.

IV. Ancillary Data

The gallium impurity in the SPEX 5-9's material was easily identified with reference to our earlier work (Aerospace Sponsored Research) on the detection of gaseous metal compounds. In particular, the same four gallium lines identified in

Figure 20 were observed when triethyl gallium was mixed with active nitrogen. In addition, we have observed that active nitrogen excites identical spectra from trimethyl bismuth and pure bismuth vapor. The same can be said for SiH_4 and silicon metal vapor. Thus, for the purposes of aiding potential users in identifying a wide variety of impurities we include here an auxiliary list of MTES lines. Most were obtained using metal alkyls and hydrides as sources. The ramifications of this earlier work with gaseous compounds might eventually lead to MTES analysis and monitoring of gaseous feedstocks and doping material used in the manufacture of solar grade silicon and in the fabrication of cells.

element	best MTES lines (nm)	ancillary lines nm
As	228.8, 235.0	193.7, 197.0
Bi	306.8	223.0, 289.8
Ga	403.3, 417.2	287.4, 294.3
Ge	265.1, 303.9	270.9, 275.4
Mg	285.2	279.1(II), 279.8(II)
P*	251.8	246.6, 260.5

*The wavelengths given for phosphorous are actually the band heads for the $\text{PN}(\text{A}^1\Pi - \text{X}^1\Sigma)$ transition.

Our company sponsored effort has also been directed at the detection of metals in liquids with the active nitrogen technique. We have recently demonstrated as a result of this project the detection of 1 ng of lead in 20 microliters of water (50 ppb). There are two lessons contained in these results that can be applied to the silicon analysis effort.

First, we have established the spectral signature of lead excited by active nitrogen. Second, these experiments were done in a pulsed mode; i.e., the lead was flashed off a metal boat by rapid ohmic heating. The resulting transitory lead fluorescence signal was integrated and found to be proportional to the metal content in the aqueous sample. The linear dynamic range was demonstrated to exceed four orders of magnitude in concentration. This intermittent mode of sample vapor introduction simulates the laser microprobe technique. Thus, we have demonstrated, in the course of our company funded project, the efficacy of the pulsed sample introduction and fluorescence detection technique that would be used in a laser microprobe with active nitrogen fluorescence detection.

V. Conclusions

Aluminum and chromium are both sensitively detected by the MTES technique. Their excitation spectra are simple line spectra with most of the fluorescence emanating from a few lines. Both elements give well defined vapor pressure curves with slopes comparable to the published values. This is direct evidence that the intensity of their fluorescence lines is a linear measure of the concentration of these materials in the vapor. The system sensitivity to aluminum was not directly calibrated, but it can be estimated from rate of vaporization data to be 3×10^5 atoms per cm^3 . The sensitivity to chromium was determined by atomic absorption to be 2×10^5 atoms per cm^3 . The spectral signatures for titanium and silicon have also been determined to be simple. The sensitivities to these elements are comparable to Al and Cr.

Iron and manganese give more complex spectra when excited by contact with active nitrogen. Each of these elements can be determined analytically by monitoring the most intense spectral features. The sensitivity to Fe can be estimated from rate of vaporization data (Appendix 1) to be 10^7 atoms per cm^3 . The atomic absorption method failed for iron due to a lack of sensitivity of this technique. With manganese most of the emission intensity is concentrated in six lines and the sensitivity is somewhat higher. As determined by atomic absorption calibration we have detected approximately 5×10^4 atoms per cm^3 of this element.

These results are summarized in the following table.

element	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Mn</u>	<u>Ti</u>	<u>V</u>	<u>Si</u>
best MTES lines (nm)	309.2, 396.1	359.4	344.1	279.5	399.8		251.6
ancillary lines (nm)	308.2, 394.4	347.9, 425.4	358.1, 372.0	403.1	365.3		288.3
sensitivity (cm^{-3})	3×10^5	2×10^5	10^7	5×10^4	10^4	$> 10^5$	
projected sensitivity in Si Matrix (ppb)	30	20	1000	5	1	> 10	

We can translate our quoted vapor phase sensitivities for these elements into detectivities for impurities in a silicon matrix. For this purpose one needs to understand that the sensitivities quoted in the table are our detection limits for the elemental vapor in a gas stream. We have also determined that our system saturates when the total metal vapor concentration in the active nitrogen stream reaches 10^{13} atoms per cm^3 . If we evaporate silicon from a sample into our active nitrogen stream and the evaporation process is congruent, then the composition of the vapor will be representative of the sample composition. If silicon saturates our system at 10^{13} atoms per cm^3 , then the minimum detectable level of impurity in a solid Silicon matrix by our technique is $(S/10^{13}) \times 10^9$ ppb, where S is our quoted sensitivity. Applying this formula to the third row of the above table gives the fourth row. Thus, we can currently expect to ultimately measure from 5 ppb Mn to 1000 ppb Fe in silicon with our technique. However, we expect to improve on this with a combination of improved light collecting efficiency and increased threshold for saturation.

A comparison with our observed MTES lines with the so called persistent lines of the elements is also instructive. One might expect little commonality between the two sets of lines due to the different modes of excitation, since the persistent lines refer to spark or arc excitation and MTES lines are excited by molecular energy transfer from a triplet species $\text{N}_2(\text{A}^3\Sigma^+)$. However, comparison of the above table with tabulated persistent lines⁵ yields the following results:

element	<u>Al</u>	<u>Cr</u>	<u>Fe</u>	<u>Mn</u>
MTES lines (nm)	309.2, 396.1	359.4, 357.9	344.1, 358.1	279.5, 403.1
persistent lines (nm)	309.2, 396.1	428.9, 425.4	302.1, 358.1	257.6, 403.1

One sees no discernable pattern. The Al MTES lines and persistent lines are identical. The Cr lines show no commonality. Fe and Mn are intermediate cases.

Our results with Si (SRM57) show that qualitative analysis is easily accomplished with MTES. In addition, the "best lines" established with use of the pure materials are seen to be invariant with matrix, suggesting that the excitation process occurs independently for each species present in the vapor. If this proves to be the case, then cooperative and matrix effects (interferences) will be minimal.

Analysis of the vapor pressure curves of the impurities in NBS silicon (SRM57) indicates that the vaporization is congruent. Successful qualitative analysis of the SPEX 5-9's material clearly demonstrates the sensitivity of our MTES technique to silicon impurities at the ppm level. Our detection of gallium and chromium shows that we have more sensitivity than the spark photometry method employed by SPEX. The high signal to noise level evident from Figure 20 portends well for our quest to achieve 10 ppb sensitivity.

The parallel vapor pressure curves and time independent intensity relations are antithetical to the occurrence of selective evaporation (fractional distillation of impurities). We conclude that the composition of the bulk solid can be determined by evaporation and subsequent analysis of the vapor.

The detection of Mg and Ca in the Spex 6-9's material indicates that MTES is sensitive to impurities present at less than a part per million. The Ca ion lines are more persistent than the MTES emission from the neutral atom and is useful for analysis by this technique.

Chemical interferences have not been encountered under normal operating conditions. Atomic spectral interferences are not frequently encountered and can be circumvented easily. N₂ second positive bands may cause spectral interferences occasionally. Atmospheric leaks must be scrupulously avoided in order to eliminate the extensive spectral interferences of the NO beta and gamma systems and the pink nitrogen afterglow.

VI. References

1. The term Metastable Transfer Emission Spectrometry, MTES, is somewhat more descriptive and is used synonymously with Analytical Photon Catalysis. See Rev. Sci. Instrum. 49, 1124 (1978).
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VII. Appendix 1

Estimation of Concentrations and Required Temperatures

From our experience with Bi and Pb we can estimate the concentrations of metal vapors produced in our apparatus at a given source temperature or conversely we can estimate the source temperature required to produce a given concentration of metal vapor. Both of these abilities are useful experimentally to bracket working temperatures, and they serve as consistency checks for the calibration data. This technique is best illustrated by the examples that follow.

Table 10.1 (S. Dushman, "Scientific Foundations of Vacuum Technique," Wiley 1966) shows rate of vaporization data for many metals. Selected data for Bi from this table is summarized in the first two columns below. The values in the fourth column are computed from the temperatures in the first column and used to determine the metal concentration from the MTES curve for bismuth (taken from Applied Physics Letters 30, 407 (1977)) shown in Figure 10.

	T(C)	Rate of Evaporation gr/cm ² -sec	Metal Concentration Determined by MTES cm ⁻³	10 ⁴ /T(K)
Bismuth	578	3 x 10 ⁻⁵	10 ⁹	11.75
	508	3 x 10 ⁻⁶	10 ⁸	12.8
	450	3 x 10 ⁻⁷	10 ⁷	13.83
		3 x 10 ^{-8*}	10 ⁶	14.8
		3 x 10 ^{-9*}	10 ⁵	15.8

If we assume that the concentrations of two different materials will be the same in the observation zone if their vaporization rates are the same, we can calculate the temperature required to produce a given concentration. For example, in Figure 10 the round data points were taken with the atomic absorption technique. This technique is limited to approximately 10⁹ atoms per cm³. For bismuth 10⁹ atoms per cm³ is produced in our apparatus at a source temperature of 850(K) or 580(C); we determine this from Figure 10 by observing that 10⁴/T(K) equals 11.75 when the Bi concentration equals 10⁹ per cm³. From the table given previously we see that a rate of vaporization of 3 x 10⁻⁵ gr/cm²-sec is responsible for this concentration. Using our assumption we can now estimate the temperature required to produce 10⁹ atoms per cm³ of any metal. Since atomic absorption is insensitive to concentrations much lower than this, our estimated temperature will have to be maintained in order to calibrate our apparatus by the AA method. Using table 10.1 we extract the following information on the metals of interest to our project.

*values obtained by extrapolation from table 10.1

Metal	T(C) required for rate of vaporization (3×10^{-5} gr/cm ² -sec) to sustain 10^5 atoms per cm ³
Al	1080
Cr	1300
Fe	1400
Mn	900
* Mo	2500
Si	1400
* Ti	1600
* V	1780
* Zr	2250

Since our apparatus is capable of sustaining a maximum temperature of 1600C, the materials marked with an asterisk cannot be calibrated with AA methods. Ti is a borderline case. In addition V, Zr and Mo have such low rates of vaporization at 1600C that more sophisticated sources will be required if we are to study the pure vapors of these materials.

We can also use our rate of vaporization technique to estimate concentrations at various temperatures. This was done for aluminum in the progress report for October and serves as an example here. Our lowest detectable MTES signal for Al (See Figure 3) was at $10^4/T(K)$ equal to 9.4 or T(C) equal to 790. From table 10.1 the extrapolated aluminum rate of vaporization at 790C is approximately 9×10^{-9} gr/cm²-sec. If we assume that Al and bismuth are detected with equivalent sensitivity by MTES, then we can use the bismuth table given above to estimate our aluminum detectivity at 5×10^5 atoms per cm³. When applied to chromium this method gives a sensitivity 3×10^5 atoms per cm³. The method of calibration by AA gives approximately 2×10^5 . This technique was also used to estimate the sensitivity to iron.

TABLE 10.1
Temperatures for Given Values of P_μ and Corresponding Rates of Evaporation

Metal	Ref.	Data Temp. Range (°C)	t (°C) and W	$P_\mu =$						t_m	P_μ	t_s
				10^{-8}	10^{-6}	1	10	100	1000			
Li	4	459-1080	t : 348 W : $6.17 \cdot 10^{-8}$	399 $5.93 \cdot 10^{-7}$	460 $5.68 \cdot 10^{-6}$	534 $5.41 \cdot 10^{-5}$	623 $5.13 \cdot 10^{-4}$	737 $4.84 \cdot 10^{-3}$	181			1331
Na	4	264-928	t : 158 W : $1.35 \cdot 10^{-7}$	195 $1.29 \cdot 10^{-6}$	238 $1.24 \cdot 10^{-5}$	290 $1.18 \cdot 10^{-4}$	355 $1.12 \cdot 10^{-3}$	437 $1.05 \cdot 10^{-2}$	98	10^{-4}		890
K	4	100-760	t : 91 W : $1.91 \cdot 10^{-7}$	123 $1.83 \cdot 10^{-6}$	162 $1.75 \cdot 10^{-5}$	208 $1.66 \cdot 10^{-4}$	266 $1.57 \cdot 10^{-3}$	341 $1.47 \cdot 10^{-2}$	64	$9 \cdot 10^{-4}$		766
Rb	4	...	t : 64 W : $2.94 \cdot 10^{-7}$	95 $2.81 \cdot 10^{-6}$	133 $2.68 \cdot 10^{-5}$	176 $2.55 \cdot 10^{-4}$	228 $2.41 \cdot 10^{-3}$	300 $2.22 \cdot 10^{-2}$	39	$2.6 \cdot 10^{-3}$		701
Cs	4	...	t : 46 W : $3.77 \cdot 10^{-7}$	75 $3.61 \cdot 10^{-6}$	110 $3.44 \cdot 10^{-5}$	152 $3.26 \cdot 10^{-4}$	206 $3.07 \cdot 10^{-3}$	277 $2.87 \cdot 10^{-2}$	30	$2.6 \cdot 10^{-3}$		685
Cu	4	969-1606	t : 942 W : $1.33 \cdot 10^{-7}$	1032 $1.29 \cdot 10^{-6}$	1142 $1.24 \cdot 10^{-5}$	1272 $1.18 \cdot 10^{-4}$	1427 $1.13 \cdot 10^{-3}$	1622 $1.07 \cdot 10^{-2}$	1084	0.26		2578
Ag	4	721-1000	t : 757 W : $1.89 \cdot 10^{-7}$	832 $1.82 \cdot 10^{-6}$	922 $1.75 \cdot 10^{-5}$	1032 $1.68 \cdot 10^{-4}$	1167 $1.60 \cdot 10^{-3}$	1337 $1.51 \cdot 10^{-2}$	961	2.5		2162
Au	4	727-987	t : 987 W : $2.31 \cdot 10^{-7}$	1082 $2.26 \cdot 10^{-6}$	1197 $2.14 \cdot 10^{-5}$	1332 $2.05 \cdot 10^{-4}$	1507 $1.94 \cdot 10^{-3}$	1707 $1.84 \cdot 10^{-2}$	1063	$5 \cdot 10^{-3}$		2709
Be	4	899-1279	t : 902 W : $5.11 \cdot 10^{-8}$	987 $4.93 \cdot 10^{-7}$	1092 $4.74 \cdot 10^{-6}$	1212 $4.55 \cdot 10^{-5}$	1367 $4.33 \cdot 10^{-4}$	1567 $4.08 \cdot 10^{-3}$	1283	28		2097
Mg	4	736-1020	t : 287 W : $1.22 \cdot 10^{-7}$	330 $1.17 \cdot 10^{-6}$	382 $1.12 \cdot 10^{-5}$	442 $1.08 \cdot 10^{-4}$	517 $1.02 \cdot 10^{-3}$	612 $0.97 \cdot 10^{-2}$	650	$2.5 \cdot 10^{-3}$		1104
Ca	4	527-647	t : 402 W : $1.42 \cdot 10^{-7}$	452 $1.37 \cdot 10^{-6}$	517 $1.31 \cdot 10^{-5}$	592 $1.26 \cdot 10^{-4}$	687 $1.19 \cdot 10^{-3}$	817 $1.12 \cdot 10^{-2}$	850	$1.9 \cdot 10^3$		1492
Sr	4	...	t : 342 W : $2.20 \cdot 10^{-7}$	394 $2.11 \cdot 10^{-6}$	456 $2.02 \cdot 10^{-5}$	531 $1.93 \cdot 10^{-4}$	623 $1.82 \cdot 10^{-3}$	742 $1.71 \cdot 10^{-2}$	770	$1.8 \cdot 10^3$		1367
Ba	4	1060-1138	t : 417 W : $2.60 \cdot 10^{-7}$	467 $2.51 \cdot 10^{-6}$	537 $2.40 \cdot 10^{-5}$	617 $2.28 \cdot 10^{-4}$	727 $2.16 \cdot 10^{-3}$	867 $2.03 \cdot 10^{-2}$	710	$7 \cdot 10$		1637
Zn	4	239-377	t : 208 W : $2.15 \cdot 10^{-7}$	246 $2.07 \cdot 10^{-6}$	290 $1.99 \cdot 10^{-5}$	342 $1.90 \cdot 10^{-4}$	405 $1.81 \cdot 10^{-3}$	485 $1.71 \cdot 10^{-2}$	420	$1.2 \cdot 10^3$		906
Cd	4	200-260	t : 149 W : $3.01 \cdot 10^{-7}$	182 $2.90 \cdot 10^{-6}$	221 $2.78 \cdot 10^{-5}$	267 $2.66 \cdot 10^{-4}$	321 $2.54 \cdot 10^{-3}$	392 $2.44 \cdot 10^{-2}$	321	10^3		765
Hg	4	...	t : -28 W : $5.28 \cdot 10^{-7}$	-8 $5.08 \cdot 10^{-6}$	16 $4.86 \cdot 10^{-5}$	45 $4.63 \cdot 10^{-4}$	81 $4.39 \cdot 10^{-3}$	125 $4.14 \cdot 10^{-2}$	-39	$2.6 \cdot 10^{-3}$		357
B	4	...	t : 1687 W : $4.33 \cdot 10^{-8}$	1827 $4.19 \cdot 10^{-7}$	1977 $4.05 \cdot 10^{-6}$	2157 $3.89 \cdot 10^{-5}$	2377 $3.73 \cdot 10^{-4}$	2657 $3.55 \cdot 10^{-3}$	2027	2		3927
Al	4	1137-1195	t : 882 W : $8.92 \cdot 10^{-8}$	972 $8.59 \cdot 10^{-7}$	1082 $8.23 \cdot 10^{-6}$	1207 $7.88 \cdot 10^{-5}$	1347 $7.53 \cdot 10^{-4}$	1547 $7.10 \cdot 10^{-3}$	659	...		2447
Sc	SD*	...	t : 1058 W : $1.56 \cdot 10^{-7}$	1161 $1.69 \cdot 10^{-6}$	1282 $1.62 \cdot 10^{-5}$	1423 $1.55 \cdot 10^{-4}$	1595 $1.48 \cdot 10^{-3}$	1804 $1.40 \cdot 10^{-2}$	1397	6.6		2400†
Y	SD*	...	t : 1249 W : $2.00 \cdot 10^{-7}$	1362 $1.92 \cdot 10^{-6}$	1494 $1.83 \cdot 10^{-5}$	1649 $1.74 \cdot 10^{-4}$	1833 $1.65 \cdot 10^{-3}$	2036 $1.55 \cdot 10^{-2}$	1477	0.76		3367
La	4	1327-1627	t : 1262 W : $1.56 \cdot 10^{-7}$	1377 $1.69 \cdot 10^{-6}$	1527 $1.62 \cdot 10^{-5}$	1697 $1.55 \cdot 10^{-4}$	1897 $1.48 \cdot 10^{-3}$	2147 $1.40 \cdot 10^{-2}$	920	...		3367
Ce	SD*	...	t : 1004 W : $2.00 \cdot 10^{-7}$	1091 $1.92 \cdot 10^{-6}$	1190 $1.83 \cdot 10^{-5}$	1305 $1.74 \cdot 10^{-4}$	1439 $1.65 \cdot 10^{-3}$	1599 $1.55 \cdot 10^{-2}$	785	$5.5 \cdot 10^{-3}$		1400†
Nd	4	899-1279	t : 957 W : $2.00 \cdot 10^{-7}$	1062 $1.92 \cdot 10^{-6}$	1192 $1.83 \cdot 10^{-5}$	1342 $1.74 \cdot 10^{-4}$	1537 $1.65 \cdot 10^{-3}$	1777 $1.55 \cdot 10^{-2}$	1024	$4.2 \cdot 10^{-3}$		3087
Ga	4	957-1245	t : 757 W : $1.52 \cdot 10^{-7}$	842 $1.46 \cdot 10^{-6}$	937 $1.40 \cdot 10^{-5}$	1057 $1.34 \cdot 10^{-4}$	127 $1.27 \cdot 10^{-3}$	1242 $1.22 \cdot 10^{-2}$	37	...		2237
In	4	727-1075	t : 670 W : $2.04 \cdot 10^{-7}$	747 $1.96 \cdot 10^{-6}$	837 $1.88 \cdot 10^{-5}$	947 $1.79 \cdot 10^{-4}$	1077 $1.70 \cdot 10^{-3}$	1242 $1.61 \cdot 10^{-2}$	156	...		2091
Tl	4	...	t : 412 W : $3.19 \cdot 10^{-7}$	468 $3.06 \cdot 10^{-6}$	535 $2.93 \cdot 10^{-5}$	615 $2.80 \cdot 10^{-4}$	713 $2.66 \cdot 10^{-3}$	837 $2.50 \cdot 10^{-2}$	304	$3 \cdot 10^{-3}$		1467
C	4	2084-2597	t : 1977 W : $4.27 \cdot 10^{-8}$	2107 $4.14 \cdot 10^{-7}$	2247 $4.03 \cdot 10^{-6}$	2427 $3.89 \cdot 10^{-5}$	2627 $3.76 \cdot 10^{-4}$	2867 $3.61 \cdot 10^{-3}$	...	...		(3927)
Si	4	...	t : 1177 W : $8.12 \cdot 10^{-8}$	1282 $7.84 \cdot 10^{-7}$	1357 $7.54 \cdot 10^{-6}$	1547 $7.24 \cdot 10^{-5}$	1717 $6.93 \cdot 10^{-4}$	1927 $6.59 \cdot 10^{-3}$	1415	1		2737
Ti	Morrison	1111-1323	t : 1321 W : $1.01 \cdot 10^{-7}$	1431 $0.98 \cdot 10^{-6}$	1558 $0.94 \cdot 10^{-5}$	1703 $0.90 \cdot 10^{-4}$	1877 $0.86 \cdot 10^{-3}$	2083 $0.82 \cdot 10^{-2}$	1800	...		>3000†
Zr	4	1676-1781	t : 1837 W : $1.21 \cdot 10^{-7}$	2002 $1.17 \cdot 10^{-6}$	2187 $1.12 \cdot 10^{-5}$	2397 $1.08 \cdot 10^{-4}$	2647 $1.03 \cdot 10^{-3}$	2977 $0.98 \cdot 10^{-2}$	1852	10^{-3}		4405
Th	SD*	...	t : 1686 W : $2.01 \cdot 10^{-7}$	1831 $1.94 \cdot 10^{-6}$	1999 $1.86 \cdot 10^{-5}$	2196 $1.79 \cdot 10^{-4}$	2431 $1.71 \cdot 10^{-3}$	2715 $1.63 \cdot 10^{-2}$	1827	$9.3 \cdot 10^{-3}$		4500†
Ge	4	1237-1612	t : 1037 W : $1.37 \cdot 10^{-7}$	1142 $1.32 \cdot 10^{-6}$	1262 $1.27 \cdot 10^{-5}$	1407 $1.21 \cdot 10^{-4}$	1582 $1.15 \cdot 10^{-3}$	1797 $1.09 \cdot 10^{-2}$	937	$7 \cdot 10^{-4}$		2827

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Vapor Pressures and Rates of Evaporation

Ch. 10

Sect. 10.2

Vapor-Pressure Data and Rates of Evaporation

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TABLE 10.1 (Continued)

Metal	Ref.	Data Temp. Range (°C)	t (°C) and W	$P_{\mu} =$						t_m	P_{μ}	t_B
				10^{-3}	10^{-1}	1	10	100	1000			
Sn	4	1151-1415	t : 882 W : $1.87 \cdot 10^{-7}$	977 $1.80 \cdot 10^{-6}$	1092 $1.72 \cdot 10^{-5}$	1227 $1.64 \cdot 10^{-4}$	1397 $1.56 \cdot 10^{-3}$	1612 $1.46 \cdot 10^{-2}$	232 ...	232	...	2679
Pb	4	...	t : 487 W : $3.05 \cdot 10^{-7}$	551 $2.93 \cdot 10^{-6}$	627 $2.80 \cdot 10^{-5}$	719 $2.67 \cdot 10^{-4}$	832 $2.53 \cdot 10^{-3}$	977 $2.38 \cdot 10^{-2}$	328 ...	328	...	1751
V	4	1389-1609	t : 1432 W : $1.01 \cdot 10^{-7}$	1551 $0.98 \cdot 10^{-6}$	1687 $0.94 \cdot 10^{-5}$	1847 $0.90 \cdot 10^{-4}$	2037 $0.87 \cdot 10^{-3}$	2287 $0.82 \cdot 10^{-2}$	1857 10	1857	10	3377
Cb	SD*	...	t : 2194 W : $1.16 \cdot 10^{-7}$	2355 $1.08 \cdot 10^{-6}$	2539 $1.06 \cdot 10^{-5}$	...	...	...	2500*	2500*	0.6	3700†
Ta	4	1727-2997	t : 2397 W : $1.52 \cdot 10^{-7}$	2587 $1.47 \cdot 10^{-6}$	2807 $1.41 \cdot 10^{-5}$	3067 $1.36 \cdot 10^{-4}$	3372 $1.30 \cdot 10^{-3}$	3737 $1.24 \cdot 10^{-2}$	2997 6	2997	6	5427
Pa	4	...	t : 107 W : $3.3 \cdot 10^{-7}$	130 $3.24 \cdot 10^{-6}$	157 $3.13 \cdot 10^{-5}$	187 $3.03 \cdot 10^{-4}$	222 $2.93 \cdot 10^{-3}$	262 $2.81 \cdot 10^{-2}$	597 ...	597	...	431
Sb ₃	4	...	t : 382 W : $2.52 \cdot 10^{-7}$	427 $2.43 \cdot 10^{-6}$	477 $2.35 \cdot 10^{-5}$	542 $2.26 \cdot 10^{-4}$	617 $2.16 \cdot 10^{-3}$	757 $2.01 \cdot 10^{-2}$	630 10 ³	630	10 ³	1637
Bi	4	409-497	t : 450 W : $3.14 \cdot 10^{-7}$	508 $3.02 \cdot 10^{-6}$	578 $2.89 \cdot 10^{-5}$	661 $2.76 \cdot 10^{-4}$	762 $2.62 \cdot 10^{-3}$	892 $2.47 \cdot 10^{-2}$	271 ...	271	...	1559
Cr	4	889-1288	t : 1062 W : $1.15 \cdot 10^{-7}$	1162 $1.11 \cdot 10^{-6}$	1267 $1.07 \cdot 10^{-5}$	1392 $1.03 \cdot 10^{-4}$	1557 $0.98 \cdot 10^{-3}$	1737 $0.94 \cdot 10^{-2}$	1903 $5.5 \cdot 10^{-3}$	1903	$5.5 \cdot 10^{-3}$	2665
Mo	4	1797-2231	t : 1987 W : $1.20 \cdot 10^{-7}$	2167 $1.16 \cdot 10^{-6}$	2377 $1.11 \cdot 10^{-5}$	2627 $1.06 \cdot 10^{-4}$	2927 $1.01 \cdot 10^{-3}$	3297 $0.95 \cdot 10^{-2}$	2577 8	2577	8	4827
W	4	...	t : 2547 W : $1.49 \cdot 10^{-7}$	2757 $1.44 \cdot 10^{-6}$	3007 $1.38 \cdot 10^{-5}$	3297 $1.32 \cdot 10^{-4}$	3647 $1.26 \cdot 10^{-3}$	...	3377 $2 \cdot 10$	3377	$2 \cdot 10$	5527
U	4	1357-1697	t : 1442 W : $2.17 \cdot 10^{-7}$	1582 $2.09 \cdot 10^{-6}$	1737 $2.01 \cdot 10^{-5}$	1927 $1.92 \cdot 10^{-4}$	2157 $1.83 \cdot 10^{-3}$	2447 $1.73 \cdot 10^{-2}$	1130 10^{-3}	1130	10^{-3}	3927

Se	4	...	t : 144 W : $2.54 \cdot 10^{-7}$	167 $2.47 \cdot 10^{-6}$	197 $2.39 \cdot 10^{-5}$	232 $2.31 \cdot 10^{-4}$	277 $2.21 \cdot 10^{-3}$	347 $2.08 \cdot 10^{-2}$	217 3.2	217	3.2	685
Te ₃	4	...	t : 261 W : $4.03 \cdot 10^{-7}$	296 $3.91 \cdot 10^{-6}$	336 $3.78 \cdot 10^{-5}$	383 $3.64 \cdot 10^{-4}$	438 $3.50 \cdot 10^{-3}$	520 $3.31 \cdot 10^{-2}$	450 $1.6 \cdot 10^{-1}$	450	$1.6 \cdot 10^{-1}$	987
Po	4	438-745	t : 187 W : $3.94 \cdot 10^{-7}$	220 $3.81 \cdot 10^{-6}$	263 $3.65 \cdot 10^{-5}$	314 $3.49 \cdot 10^{-4}$	382 $3.30 \cdot 10^{-3}$	472 $3.10 \cdot 10^{-2}$	254 $8 \cdot 10^{-1}$	254	$8 \cdot 10^{-1}$	962
Mn	4	...	t : 697 W : $1.39 \cdot 10^{-7}$	767 $1.34 \cdot 10^{-6}$	852 $1.29 \cdot 10^{-5}$	947 $1.24 \cdot 10^{-4}$	1067 $1.18 \cdot 10^{-3}$	1227 $1.12 \cdot 10^{-2}$	1244 $1.2 \cdot 10^{-3}$	1244	$1.2 \cdot 10^{-3}$	2051
Re	4	...	t : 2367 W : $1.55 \cdot 10^{-7}$	2557 $1.50 \cdot 10^{-6}$	2787 $1.44 \cdot 10^{-5}$	3057 $1.38 \cdot 10^{-4}$	3397 $1.31 \cdot 10^{-3}$	...	1539 30	1539	30	2857
Fe	4	1092-1246	t : 1107 W : $1.17 \cdot 10^{-7}$	1207 $1.13 \cdot 10^{-6}$	1322 $1.09 \cdot 10^{-5}$	1467 $1.05 \cdot 10^{-4}$	1637 $0.99 \cdot 10^{-3}$	1847 $0.95 \cdot 10^{-2}$	1495 67	1495	67	2877
Co	4	1090-1249	t : 1162 W : $1.18 \cdot 10^{-7}$	1262 $1.14 \cdot 10^{-6}$	1377 $1.10 \cdot 10^{-5}$	1517 $1.06 \cdot 10^{-4}$	1697 $1.01 \cdot 10^{-3}$	1907 $0.96 \cdot 10^{-2}$	1452 5	1452	5	2839
Ni	4	1034-1310	t : 1142 W : $1.19 \cdot 10^{-7}$	1247 $1.15 \cdot 10^{-6}$	1357 $1.11 \cdot 10^{-5}$	1497 $1.06 \cdot 10^{-4}$	1667 $1.01 \cdot 10^{-3}$	1877 $0.96 \cdot 10^{-2}$	2427 9.8	2427	9.8	...
Ru	SD*	...	t : 1913 W : $1.26 \cdot 10^{-7}$	2058 $1.22 \cdot 10^{-6}$	2230 $1.18 \cdot 10^{-5}$	2431 $1.13 \cdot 10^{-4}$	2666 $1.08 \cdot 10^{-3}$	2946 $1.04 \cdot 10^{-2}$	1966 5.5	1966	5.5	(3727)
Rh	4	...	t : 1587 W : $1.37 \cdot 10^{-7}$	1707 $1.33 \cdot 10^{-6}$	1857 $1.28 \cdot 10^{-5}$	2027 $1.23 \cdot 10^{-4}$	2247 $1.18 \cdot 10^{-3}$	2527 $1.12 \cdot 10^{-2}$	1550 11	1550	11	3127
Pd	4	...	t : 1157 W : $1.59 \cdot 10^{-7}$	1262 $1.54 \cdot 10^{-6}$	1387 $1.48 \cdot 10^{-5}$	1547 $1.41 \cdot 10^{-4}$	1727 $1.35 \cdot 10^{-3}$	1967 $1.27 \cdot 10^{-2}$	2697 ...	2697	...	>5300†
Os	SD	...	t : 2101 W : $1.65 \cdot 10^{-7}$	2264 $1.60 \cdot 10^{-6}$	2451 $1.54 \cdot 10^{-5}$	2667 $1.48 \cdot 10^{-4}$	2920 $1.42 \cdot 10^{-3}$	3221 $1.36 \cdot 10^{-2}$	2454 50	2454	50	(4127)
Ir	4	...	t : 1797 W : $1.78 \cdot 10^{-7}$	1947 $1.72 \cdot 10^{-6}$	2107 $1.66 \cdot 10^{-5}$	2307 $1.60 \cdot 10^{-4}$	2527 $1.53 \cdot 10^{-3}$	2827 $1.46 \cdot 10^{-2}$	1770 $1.7 \cdot 10^{-1}$	1770	$1.7 \cdot 10^{-1}$	3827
Pt	4	...	t : 1602 W : $1.88 \cdot 10^{-7}$	1742 $1.82 \cdot 10^{-6}$	1907 $1.75 \cdot 10^{-5}$	2077 $1.68 \cdot 10^{-4}$	2317 $1.60 \cdot 10^{-3}$	2587 $1.52 \cdot 10^{-2}$				

* SD = Dushman, 1st edition of this book.

† Handbook of Chemistry and Physics, 39th edition.

Figure 1: Schematic for MIES Apparatus

Figure 2: MTES Spectrum for Aluminum

Figure 3: MTES Vapor Pressure Curve for Aluminum at 309 nm

Figure 4: MTES Spectrum for Chromium

Figure 5: MTES Vapor Pressure Curve for Chromium

Figure 6: MTES Spectrum for Iron

Figure 7: MIES Vapor Pressure Curve for Iron at 344.1 nm

INTENSITY (arbitrary units)

Figure 8: MTES Spectrum for Manganese

Figure 9: MTES Vapor Pressure Curve for Manganese

Figure 10: MTES Vapor Pressure Curve for Bismuth at 307 nm

Figure 11: MTES Spectrum for Titanium

Figure 12: MTES Vapor Pressure Curve for Titanium

Figure 13: MTES Spectrum Obtained with Empty BeO Crucible

Figure 14: Partial MIES Spectrum for Si(NBS-SRM57)

Figure 15: MTES Vapor Pressure Curves for Si NBS-SRM #57

Figure 16: Evidence for Congruent Evaporation of Si SRM 57

Figure 17: NO Gamma Bands Excited by Active Nitrogen

Figure 18: NO Beta Bands Excited by Active Nitrogen

Figure 19: Spectrum of Pink Afterglow in Active Nitrogen

Figure 20: MTEs Spectrum for Si (SPEX 5-9's)

Figure 21: Evidence for Congruent Evaporation of Si (SPEX 5-9's)

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SLOPE OF VP CURVE RELATIVE TO SILICON

Figure 22: NIES Spectrum for Si (SPEX 6-9's)

Figure 24: Variation of Fluorescence Intensities with N₂ Pressure