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M. Koga, T. Hadeishi, and R.D. McLaughlin

May 1984

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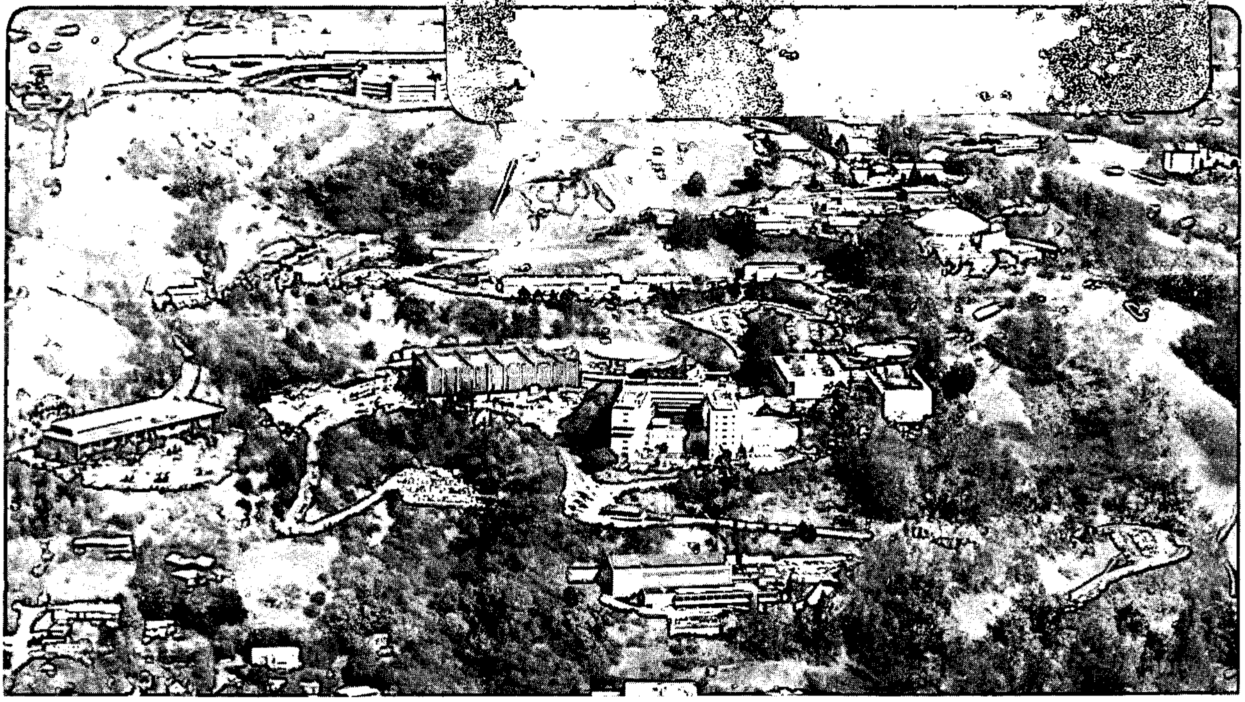

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Atomic Line Molecular Analysis for Multicomponent Determinations in the Gas Phase

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May 1984

This work was supported by the Directors Office of Energy Research, Office of Fossil Programs, U.S. Department of Energy, Morgantown Energy Technology Center, under Contract No. DE-AC03-76SF00098.

Atomic Line Molecular Analysis for Multicomponent Determinations in the Gas Phase*

Masataka Koga, Tetsuo Hadeishi, and Ralph D. McLaughlin

ABSTRACT

A method to continuously monitor several molecules in the gas phase by measuring absorption in the ultraviolet and vacuum ultraviolet spectral regions is described. This approach is capable of almost simultanous monitoring even when the spectra overlap. Molecules characterized by highly structured absorption spectra, diffuse absorption spectra, or mixtures of both can be determined. Good agreement between experimental measurements and samples of known concentration was obtained. Special light sources that emit strong atomic and ionic lines in this wavelength region were constructed and are important in achieving the high sensitivities that were observed. A method of checking for the presence of interferents and improving specificity by using measurements at several wavelengths for one molecule is described. This technique can easily be applied to on-line process control and provides almost real time analysis.

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*This work was supported by the Directors Office of Energy Research, Office of Fossil Programs, U.S. Department of Energy, Morgantown Energy Technology Center, under Contract No. DE-AC03-76SF00098.

INTRODUCTION

A new technique for highly specific detection of molecules in the the gaseous state has recently been described [1-3]. This technique depends upon finding sharp molecular absorption features that coincide with atomic lines and monitoring the intensity between Zeeman components that fall on and off the peak of the molecular absorption. High specificity results because of the low probability that other absorption will occur that shows differences in intensity over the small wavelength internal separating the Zeeman components. The technique is called tunable atomic line molecular spectroscopy (TALMS) because Zeeman components are tuned, by adjusting the magnetic field, to optimum position with respect to the absorption feature.

The sensitivity of this technique is better when the intensity difference of the absorption feature at the wavelengths of the Zeeman components is greater. In general, the sensitivity increases as the distance between Zeeman components increase. The tunable range of Zeeman scanning is about 30 GHz; which corresponds to .004 nm at 200 nm. If the molecular absorption consists of broad, diffuse absorption features or the sample is contained at high temperature or high pressure (conditions that contribute to diffuse absorption spectra), the TALMS technique is not effective because there is little change of absorption in spectral regions only .004 nm apart.

A similar approach is described to determine molecules that do not contain sharp absorption features. In this case, it can no longer be assumed that background absorption does not affect the measurement.

Instead, additional lines are used to determine the background (scattering by particulates or absorption by other molecules) and the appropriate corrections are applied to the absorbance of the analyte molecules. This approach is referred to as atomic line molecular spectroscopy (ALMS). By choosing atomic lines that coincide with regions of intense absorption by the molecule to be monitored, the method can be extremely sensitive. A knowledge of the specific monitoring problem (e.g. the absorption spectrum of the molecule to be determined, other molecules in the sample and their absorption spectrum, and the wavelength of atomic lines that overlap the region of absorption) will allow the optimum choice of monitoring parameters. This paper describes application of this technique to molecules that display sharp absorption features as well as to those that have only broad diffuse spectra.

Every molecule has highly sensitive absorption bands in the ultraviolet and vacuum ultraviolet spectral regions because of strong electronic transitions. There are many references to spectroscopic properties in these regions including those of the molecules NO, SO_2, AsH_3 and PH_3; which were constituents of the sample gas chosen to demonstrate the detection technique to be described [4-10]. In the past, little analytical use has been made of ultraviolet and vacuum ultraviolet molecular absorption spectroscopy. Syty, et al. detected sulphite, sulphide, ammonium ion, iodide, and bromide in liquid samples by converting these ions to the gaseous species SO_2, H_2S, NH_3, I_2 and Br_2 and measuring the ultraviolet or visible molecular absorption [11-18]. Fuwa and Vallee detected SO_2 using flame absorption at 207 nm [19]. Saturday measured UF_6 and PuF_6 using fiber optics [20]. These workers achieved sensitive detection but had to develop methods to confirm that the analyte gas was the only species absorbing at the wavelength used for the analysis. Chemical treatment of the samples was used to eliminate interference by absorbing molecules. Such chemical separations may not be necessary if the ALMS technique is utilized.

Measurement of multi-component samples by molecular absorption of solutions using several wavelengths has been described by Bareman [21] and Sterns [22]. These workers use one wavelength (isolated with a spectrophotometer) for each component in the sample. The concentration of each component can be determined by solving the appropriate matrices.

If a sample contains n molecules, the relationship between the absorbances, the extinction coefficients, and the concentrations is given by:

$$\vec{A} = \vec{B}\,\vec{C}$$

where

$$\vec{A} = \begin{bmatrix} a_1 \\ a_2 \\ | \\ a_i \\ | \\ a_n \end{bmatrix} \qquad \vec{B} = \begin{bmatrix} b_{1,1} & b_{1,2} & - - & b_{1,j} & - - & b_{i,n} \\ b_{2,1} & b_{2,2} & - - & b_{2,j} & - - & b_{2,n} \\ | & | & & | & & | \\ b_{i,1} & b_{i,2} & - - & b_{i,j} & - - & b_{i,n} \\ | & | & & | & & | \\ b_{n,1} & b_{n,2} & - - & b_{n,j} & - - & b_{n,m} \end{bmatrix}$$

and

$$\vec{C} = \begin{bmatrix} c_1 \\ c_2 \\ | \\ c_j \\ | \\ c_n \end{bmatrix}$$

a_i = absorbance at wavelength λ_i

b_{ij} = extinction coefficient of molecule M_j at wavelength λ_i

c_j = concentration of molecule M_j

The values of b_{ij} can be measured using a known concentration of a known gas in a cell of known path length. Then equation (1) can be solved using Cramer's relationship in the following form:

$$\vec{C}_j = \frac{\begin{vmatrix} b_{1,1} & \cdots & b_{1,j-1} & a_1 & b_{1,j+1} & \cdots & b_{i,n} \\ b_{2,1} & \cdots & b_{2,j-1} & a_2 & b_{2,j+1} & \cdots & b_{2,n} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ b_{i,1} & \cdots & b_{i,j-1} & a_i & b_{i,j+1} & \cdots & b_{i,n} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ b_{n,1} & \cdots & b_{n,j-1} & a_n & b_{n,j+1} & \cdots & b_{n,m} \end{vmatrix}}{\begin{vmatrix} b_{1,1} & \cdots & b_{1,j-1} & b_{1,j} & b_{1,j+1} & \cdots & b_{i,n} \\ b_{2,1} & \cdots & b_{2,j-1} & b_{2,j} & b_{2,j+1} & \cdots & b_{2,n} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ b_{i,1} & \cdots & b_{i,j-1} & b_{i,j} & b_{i,j+1} & \cdots & b_{i,n} \\ \vdots & & \vdots & \vdots & \vdots & & \vdots \\ b_{n,1} & \cdots & b_{n,j-1} & b_{n,j} & b_{n,j+1} & \cdots & b_{n,m} \end{vmatrix}}$$

A multi-component method of gas sample analysis was developed that depends upon these relationships. Absorption is measured at various wavelengths using atomic and ionic lines that are easily available in the ultraviolet and vacuum ultraviolet wavelength regions. A molecule with sharp absorption spectrum, could be detected with higher sensitivity and specificity than was obtained with a continuous light source. The analysis of gas mixtures of NO and SO_2 in N_2 is reported to illustrate results obtained when one molecule of a mixture has sharp absorption features and the others has broad features. A mixture of AsH_3 and PH_3 in Ar is reported as an example of the results obtained when both spectra are diffuse and quite similar. (Maximum absorption for these two molecules occur at 183 nm and 180 nm respectively.) The first mixture represents pollutant molecules that should be monitored and kept under control in energy producing processes. Examples are, the combustion of coal and oil to produce energy and emissions from coal gasification systems. It is important to monitor these species both on-line and in real time. In coal gasification systems the sample gases may be at temperatures of 600°C and pressures of 100 atmospheres; which would be expected to broaden the spectra. The AsH_3 PH_3 mixture represents this situation. The use of this method to indicate the presence of interferents that would cause the result to be suspect is also discussed.

EXPERIMENTAL APPARATUS

A block diagram of the ALMS system is shown in Figure 1. Experimental conditions and parameters are listed in Table 1. The light source is one of the most important parts of the system. A hollow cathode lamp that emitts atomic and ionic lines of Cd, Zn, and Cu was designed and constructed in this laboratory for the determination of NO and SO_2. Figure 2 is a block diagram of this lamp. It is capable of operation in a strong magnetic field [23] (as was necessary for TALMS experiments) but was operated without a field in this experiment. For determinations of AsH_3 and PH_3, sealed off quartz light sources in the shape of a U were prepared [23]. Both light sources were operated by the same power supply and produced stable and high intensities of not only atomic resonance lines, but also non-resonance lines and ionic lines. The discharge was modulated at 100% amplitude with 50% duty cycle at a frequency of 10 kHz. In each cycle the discharge was started with a spark discharge and maintained by a glow discharge after breakdown.

The light path in the monochromator was about one meter and was purged with Ar to prevent absorption by O_2 molecules in the vacuum ultraviolet region. With high purity quartz lenses and windows it was possible to extend the usable region to 165 nm by gas purging. In these experiments the wavelengths were selected manually, but this function will eventually be under computer control.

After passing through the monochromator, the light is divided into two beams (see Figure 1). One (the sample beam) passes through the cell and is stopped by the photomultiplier tube (PMT 1). The other (the reference beam is intercepted by (PMT 2). The gases used for calibration were diluted and mixed through a series of connections of flowmeters to obtain a wide range of concentrations (as much as 300 times dilution) before introduction into the sample cell. The gas flow rate was kept constant at either 0.4 or 1.6 L/min. One or two minutes were required to complete gas exchange in the cell when concentrations were changed. The electronics consisted of amplifiers, band pass filters, and logarithmic conversion devices. The band pass filters were designed to pass only the modulation frequency of the light source.

RESULTS AND DISCUSSION

Figures 3(a) and 3(b) show the calibration curves obtained for mixtures of NO and SO_2 in N_2 at atmospheric pressure using the Cd II 214.438 nm and Zn I 213.856 nm lines. The near coincidence between a rotational line of the NO γ system and the Cd II 214.438 line has already been reported [3]. This rotational line is included in the transition between the $A^2\Sigma^+$ and $X^2\Pi$ electronic states and the 1 and 0 vibrational states. It is one of the two sharp lines located in the double band head at 215.49 nm and 214.9 nm. This vibrational band contains a number of narrow rotational lines. Even without Zeeman scanning the Cd II 214.438 nm line overlaps one of the rotational lines and can be used to monitor NO with high sensitivity. But the Zn I 213.856 nm line (only 0.6 nm from the Cd II line) only slightly overlaps a NO absorption feature which results in the low sensitivity shown in 3(b).

Below 228 nm SO_2 displays both continuous and discrete absorption spectra [23]. The Zn I 213.856 nm line overlaps a strong absorption feature and the Cd II 214.438 nm line overlaps a somewhat weaker one which explains the results shown in Figures 3(a) and 3(b). From these figures the following values for the matrix elements of B in equation (1) were obtained:

$$B = \begin{pmatrix} 6.99 & 7.71 \\ 0.287 & 19.0 \end{pmatrix} \times 10^2 \text{ cm}^{-1}(\text{mole/L})^{-1}$$

where,

$b_{1,1}$ is the molar extinction coefficient of NO in one atmosphere of N_2 at 214.438 nm (the Cd II line)

$b_{1,2}$ is the molar extinction coefficient of SO_2 in one atmosphere of N_2 at 214.438 nm (the Cd II line)

$b_{2,1}$ is the molar extinction coefficient of NO in one atmosphere of N_2 at 213.856 nm (the Zn I line)

$b_{2,2}$ is the molar extinction coefficient of SO_2 in one atmosphere of N_2 at 213.856 nm (the Zn I line)

These values correspond to the slopes of the calibration curves. To solve equation (1) it is necessary to avoid wavelengths that cause the determinant $\vec{B}$ to equal 0; that is $(b_{1,1})/(b_{2,1})$ must not equal $(b_{1,2})/(b_{2,2})$. Severals mixtures of NO and SO_2 were prepared, and the absorbance was measured at 214.438 nm (the Cd II line) and at 213.856

(the Zn I line). Solving equation (1) the calculated concentrations of NO and SO_2 agreed with the prepared values within an experimental error of 1%. The major error occurred during the gas diluting and mixing procedures.

Figures 4(a) and 4(b) show the calibration curves of AsH_3 and PH_3 using the Hg I 184.950 nm line and the As I 200.334 nm line. The following values of the matrix elements of B were obtained:

$$B = \begin{pmatrix} 10.04 & 2.84 \\ 7.39 & 1.17 \end{pmatrix} \times 10^3 \text{ cm}^{-1}(\text{mol/L})^{-1}$$

where $b_{1,1}$ is the molar extinction coefficient of AsH_3 in one atmosphere of Ar at Hg I 184.950 nm, $b_{1,2}$ is that of PH_3 under the same conditions, $b_{2,1}$ is that of AsH_3 at 200.334 nm (the As I line), and $b_{2,2}$ is that of PH_3 at the same wavelength. Known concentrations of AsH_3 and PH_3 in mixed samples were easily and precisely obtained using this relationship; which proves that even with diffuse absorption spectra, mixtures of gases can be monitored by selecting the proper combination of wavelengths.

A big advantage of the ALMS technique is its applicability to nonintrusive monitoring of plant gas streams. When a sample gas is somewhat transparent it is easy to install windows so that the ALMS technique may be used for continuous, on-line monitoring.

Chemical and physical properties of the molecules in the sample may be used to increase the value of the ALMS technique. Analysis of mixtures of PH_3 and AsH_3 is a good example of the use of temperature dependent characteristics. PH_3 undergoes thermal decomposition at around 375°C whereas ASH_3 starts to decompose at 300°C. Hence, it might be possible to measure low concentrations of PH_3 in very high concentrations of AsH_3 by holding the sample cell at high enough temperatures to decompose AsH_3 but not PH_3. In semiconductor manufacturing processes AsH_3 is a very important gas and is used quite often. Knowledge of the presence of impurities in AsH_3 is important for quality control.

Background absorption by other molecules or scattering by small particles will interfere with the ALMS technique. The best way to avoid this problem is to monitor all molecules that might be in the sample that absorb at the wavelengths used for measurement. Correction for scattering by small particles or darkened windows would not be difficult. Generally this kind of absorption will be constant over the spectral region used and a measurement at one wavelength will provide the information needed to make the correction. Two wavelengths would be used if the absorption is not constant but approximately linear.

When the sample contains unknown molecules having different extinction coefficients at the measuring wavelengths, it may be necessary to use many lines and subject the results to mathematical analysis. To illustrate, Table 2 lists the molar extinction coefficients of SO_2 and NO obtained at several wavelengths using 11 atomic and ionic lines of Cd, Cu, Zn, and Ar. Since NO has a very structured absorption spectrum, only a few lines are available to detect this molecule. Because of its broad absorption, SO_2 has several highly sensitive lines. Figure 5 displays the extinction coefficients graphically using the first 5 lines of Table 2. Using these lines, we can obtain four independent matrix equations of (λ_1, λ_5), (λ_2, λ_5), (λ_3, λ_5), (λ_4, λ_5) and four values of the concentration for each species. If other molecules are not absorbing, the four answers will show good agreement. This statement was verified experimentally using the lines in Table 1. If other molecules are present that absorb in this region, each matrix equation would have provided a different answer; indicating the presence of interfering substances. Increasing the number of wavelengths leads to higher specificity because each molecule has its specific absorption spectrum. Hence, by monitoring at several wavelengths and determining the standard deviation of the results, it is possible to validate the analysis.

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Table 1. Experimental Apparatus and Parameters

Light Sources

1. Hollow cathode lamp with a brass cathode containing Zn and CdO powder operated with Ar carrier gas at a pressure of 1.1 torr.
2. Gas discharge Hg lamp and As lamp (available from Grun Optik, Wetzlar, Federal Republic of Germany)

Lamp Power Supply

Both types of lamps are powered by a 10 kHz amplitude modulated supply:

Discharge current: 0 to 100 mA

Discharge voltage: up to 10 kV

Monochromator

GCA/McPherson Instrument Model 218

Dispersion - 2.6 nm/mm

Entrance and exit slits were set at 100 μm which provides a 0.26 nm bandwidth

Sample Cell

Quartz cell with high purity quartz windows, 180 mm long

Photomultiplier

Hamamatsu Photonics, R928

Band Pass Filter

Double pole active filter

Attenuation 3 of dB at 4 kHz and 20 kHz

Log Conversion Electronics

Analog Devices, 755P

Strip Chart Recorder

Linear Instruments Corp., Model 285

Gases

Matheson Gas Product Co.

Pure N_2

1000 ppm NO in N_2

1100 ppm SO_2 in N_2

Pure Ar

1.02 % AsH_3 in Ar

1112 ppm PH_3 in Ar

Table 2. Molar Extinction Coefficients of SO_2 and NO

Wavelength [nm]		Molar Extinction Coefficient [$\times 10^3$ $cm^{-1}(mol/L)^{-1}$]	
		SO_2	NO
Zn II	202.548	2.92	0.012
Zn II	206.200	1.09	0.012
Zn II	209.994	2.41	0
Zn I	213.856	1.90	0.029
Cd II	214.441	0.771	0.699
Cu I	216.509	0.496	0
Cu I	217.849	0.421	0
Cu II	224.700	0.264	0.006
Cd II	226.502	0.106	0.120
Cd I	228.802	0.275	0
Ar II	294.289	0.415	0

FIGURE CAPTIONS

Figure 1. A block diagram of the experimental apparatus. Lenses are designated L1, L2, L3, and L4.

Figure 2. This hollow cathode lamp used to excite the spectra of Cd, Zn, and Cu. The lamp container is connected to a vacuum pump and Ar allowed to leak in at a rate that maintains a pressure of 1.1 torr.

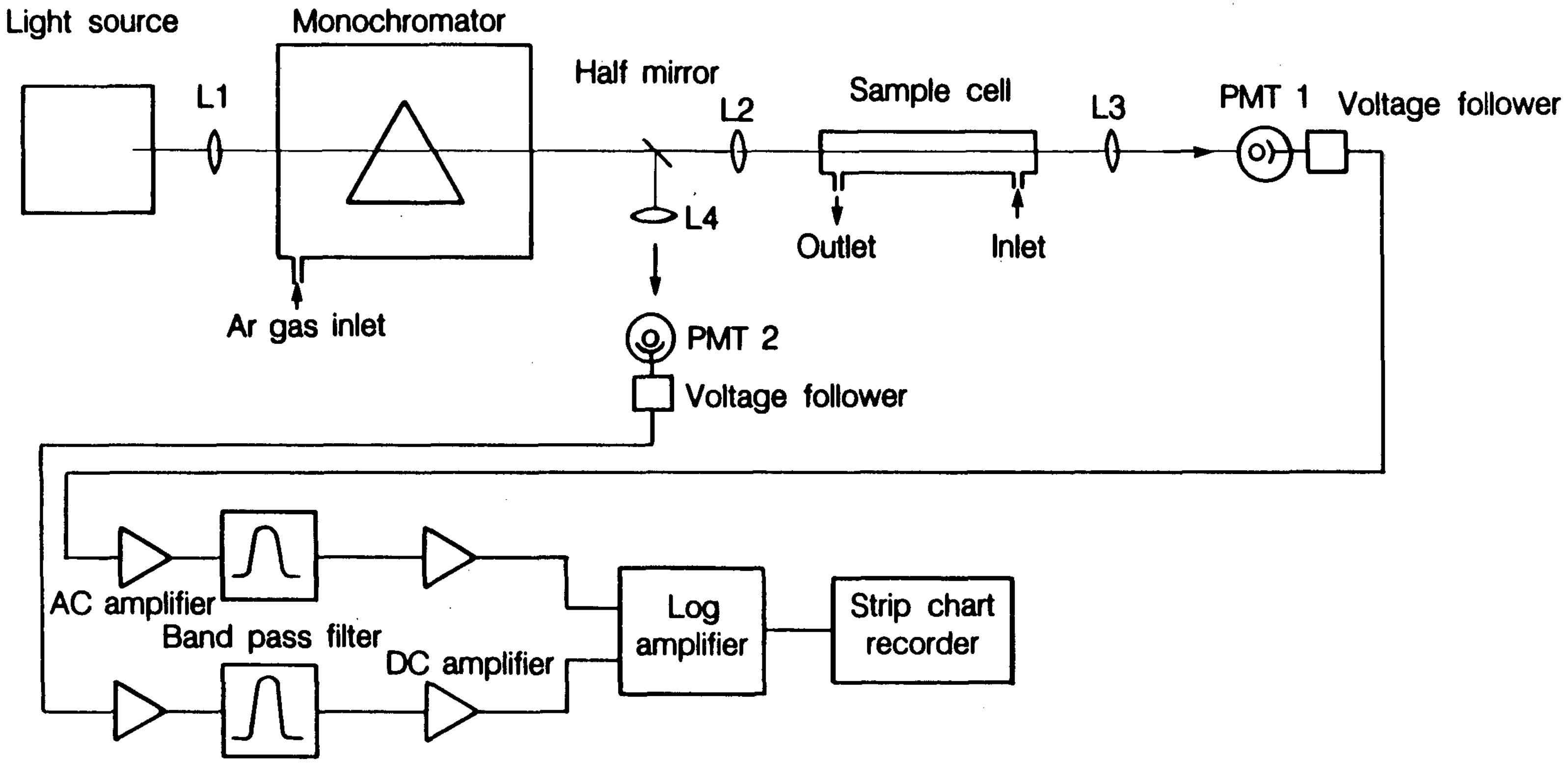
Figure 3(a). Calibration curves for SO_2 and NO using the Cd II 214.4 nm line.

Figure 3(b). Calibration curves for SO_2 and NO using the Zn I 213.9 nm line.

Figure 4(a). Calibration curves for AsH_3 and PH_3 using the Hg I 184.9 nm line.

Figure 4(b). Calibration curves for AsH_3 and PH_3 using the As 200.3 nm line.

Figure 5. Extinction coefficients of first five lines from Table 2 for SO_2 and NO.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Monochromator
Half mirror
L1
L2
Sample cell
L3
PMT 1
Voltage follower
L4
Outlet
Inlet
Ar gas inlet
PMT 2
Voltage follower
AC amplifier
Band pass filter
DC amplifier
Log amplifier
Strip chart recorder

Fig. 1

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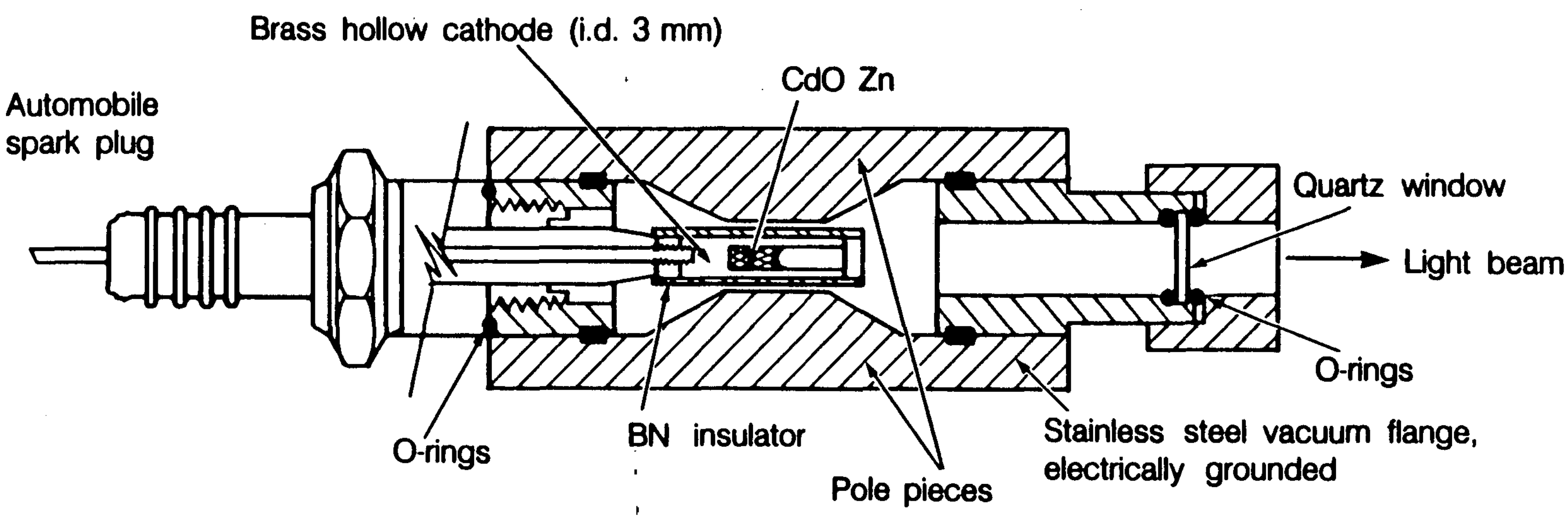
Brass hollow cathode (i.d. 3 mm)
CdO Zn
Automobile spark plug
Quartz window
Light beam
O-rings
O-rings
BN insulator
Pole pieces
Stainless steel vacuum flange, electrically grounded

XBL 844-9316

Fig. 2

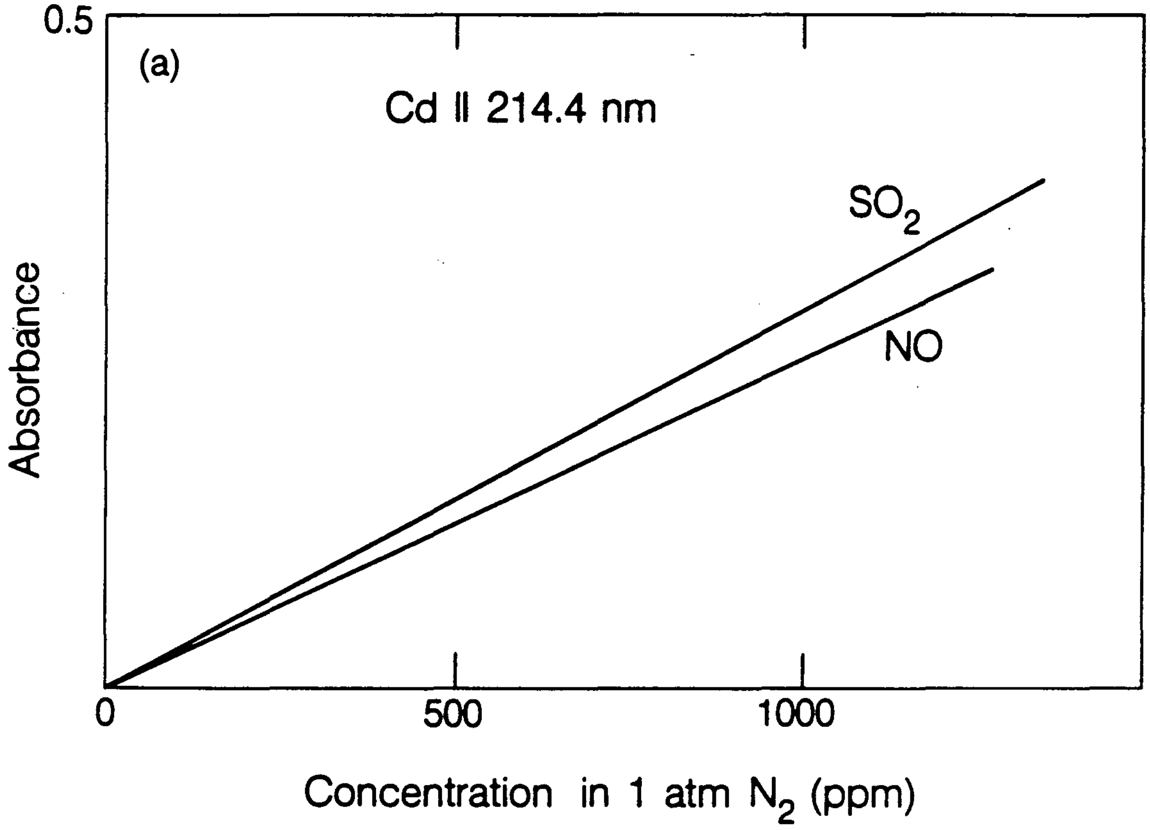

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Fig. 3a

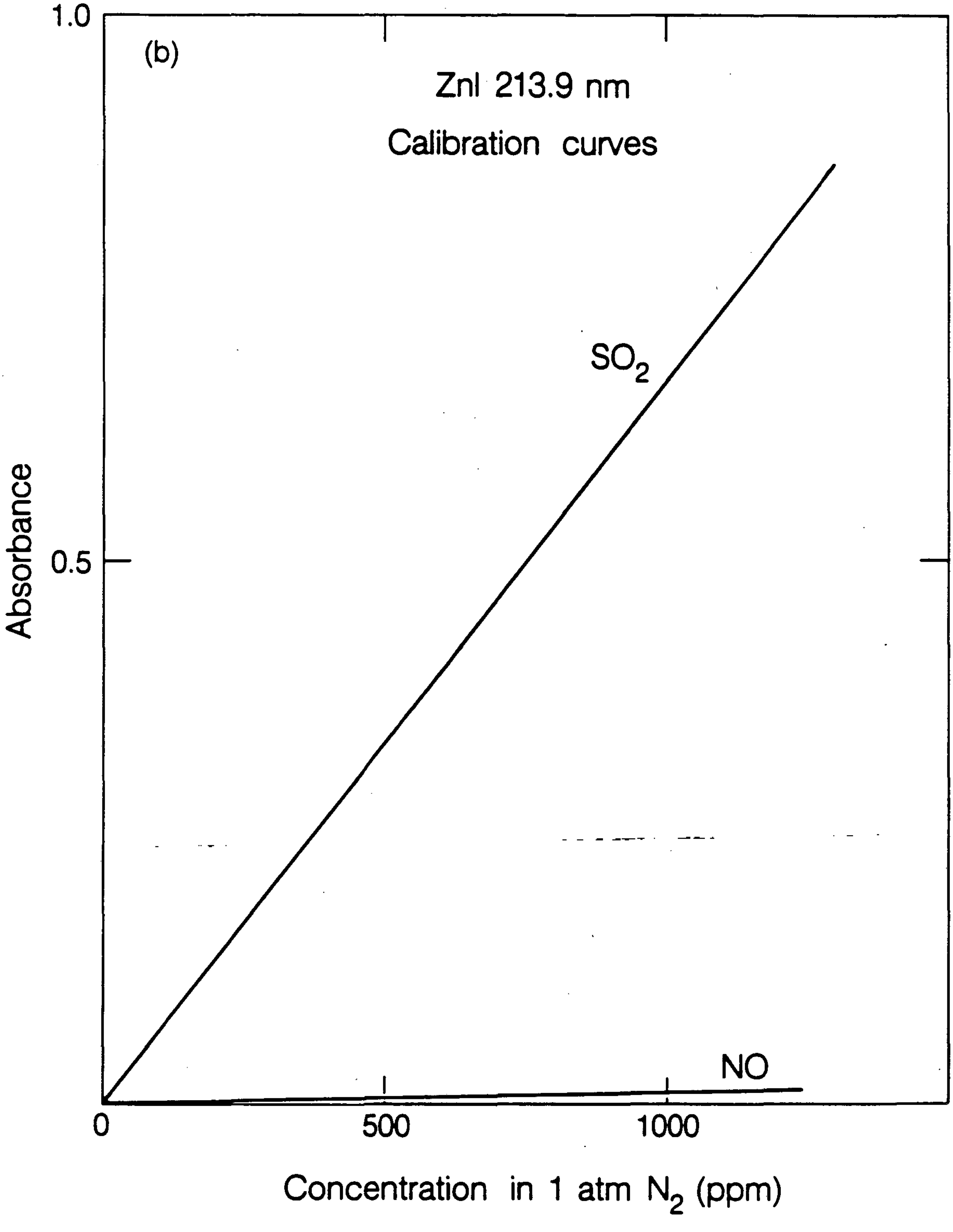

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Fig. 3b

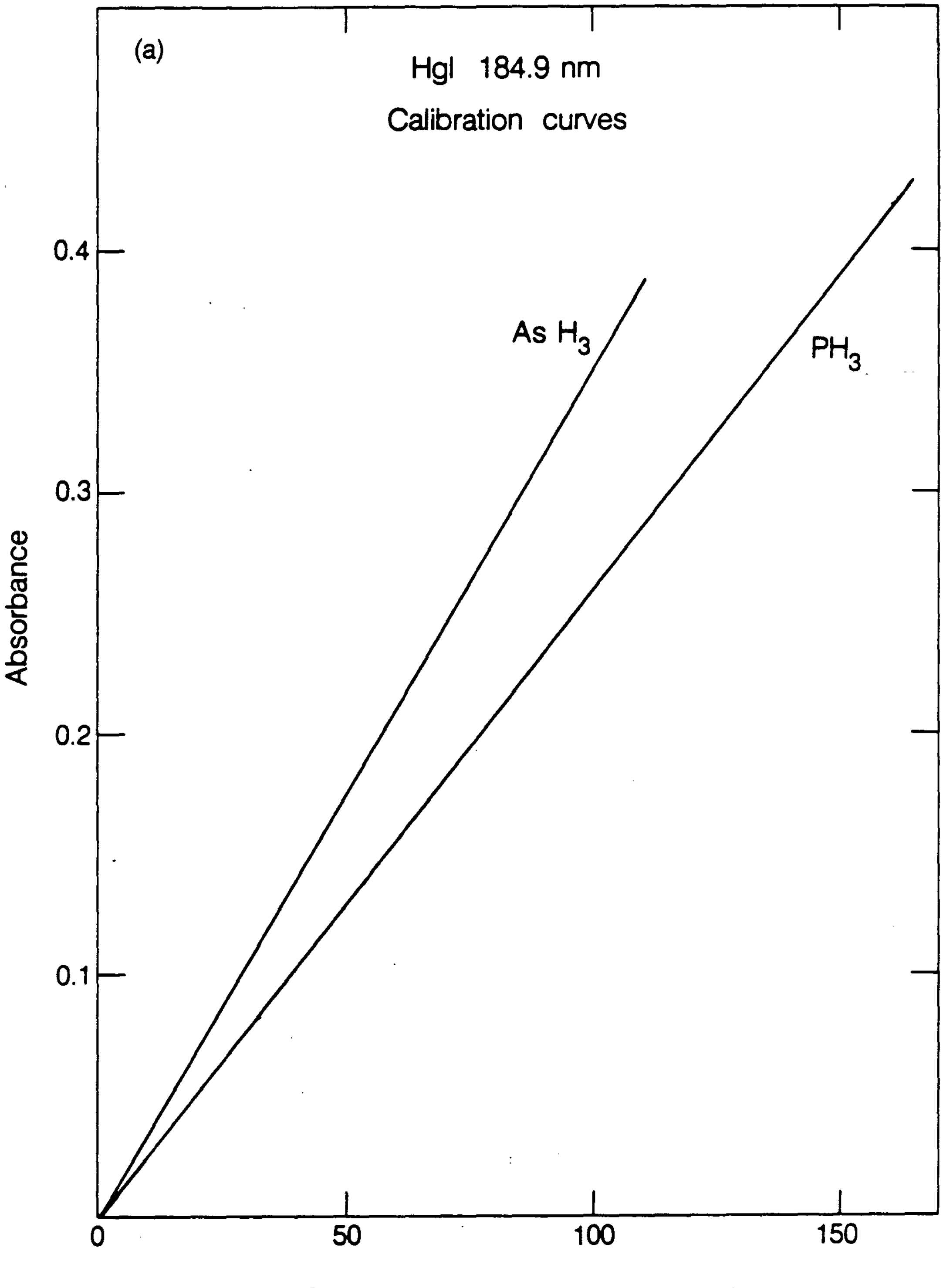

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Fig. 4a

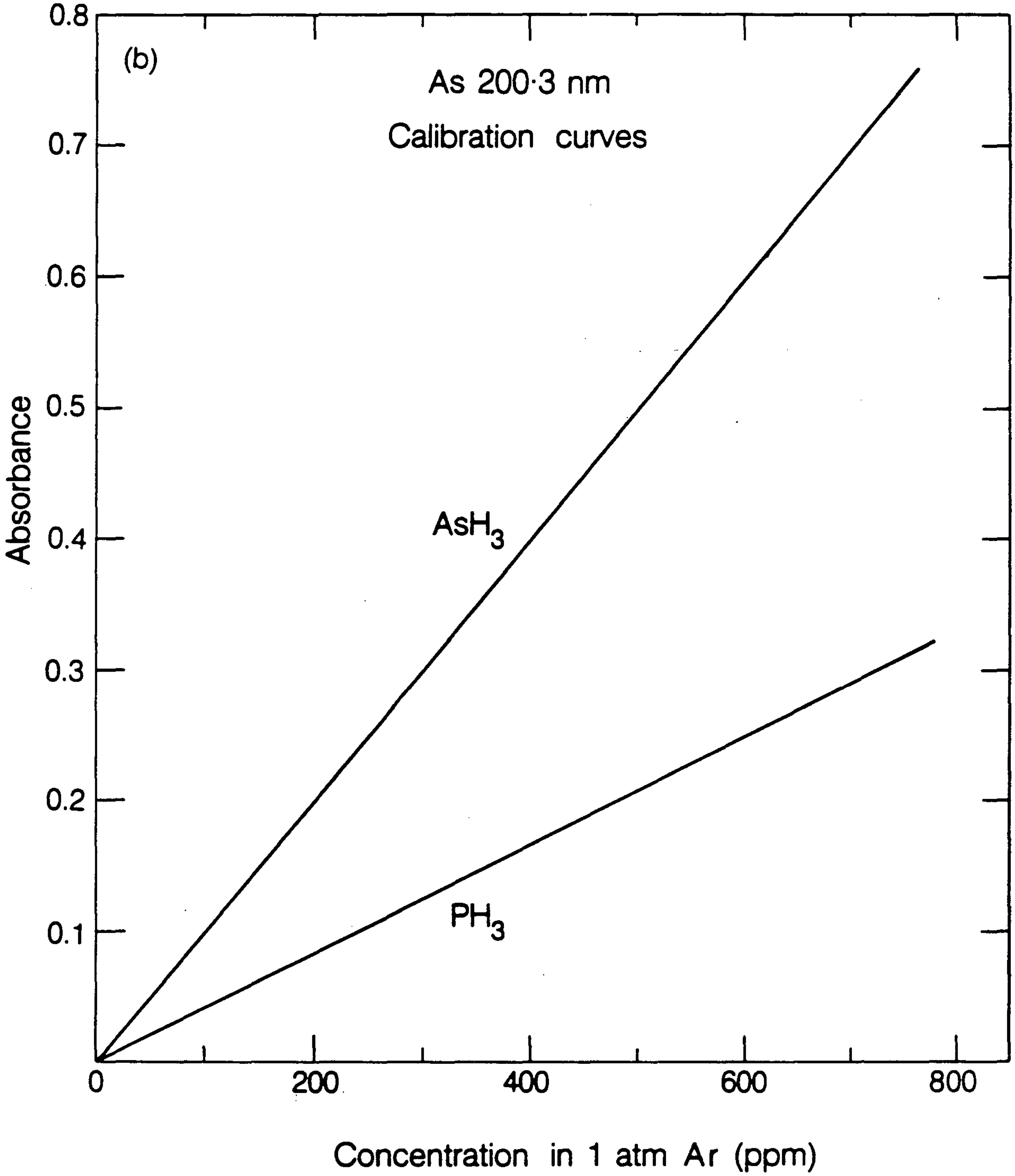

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Fig. 4b

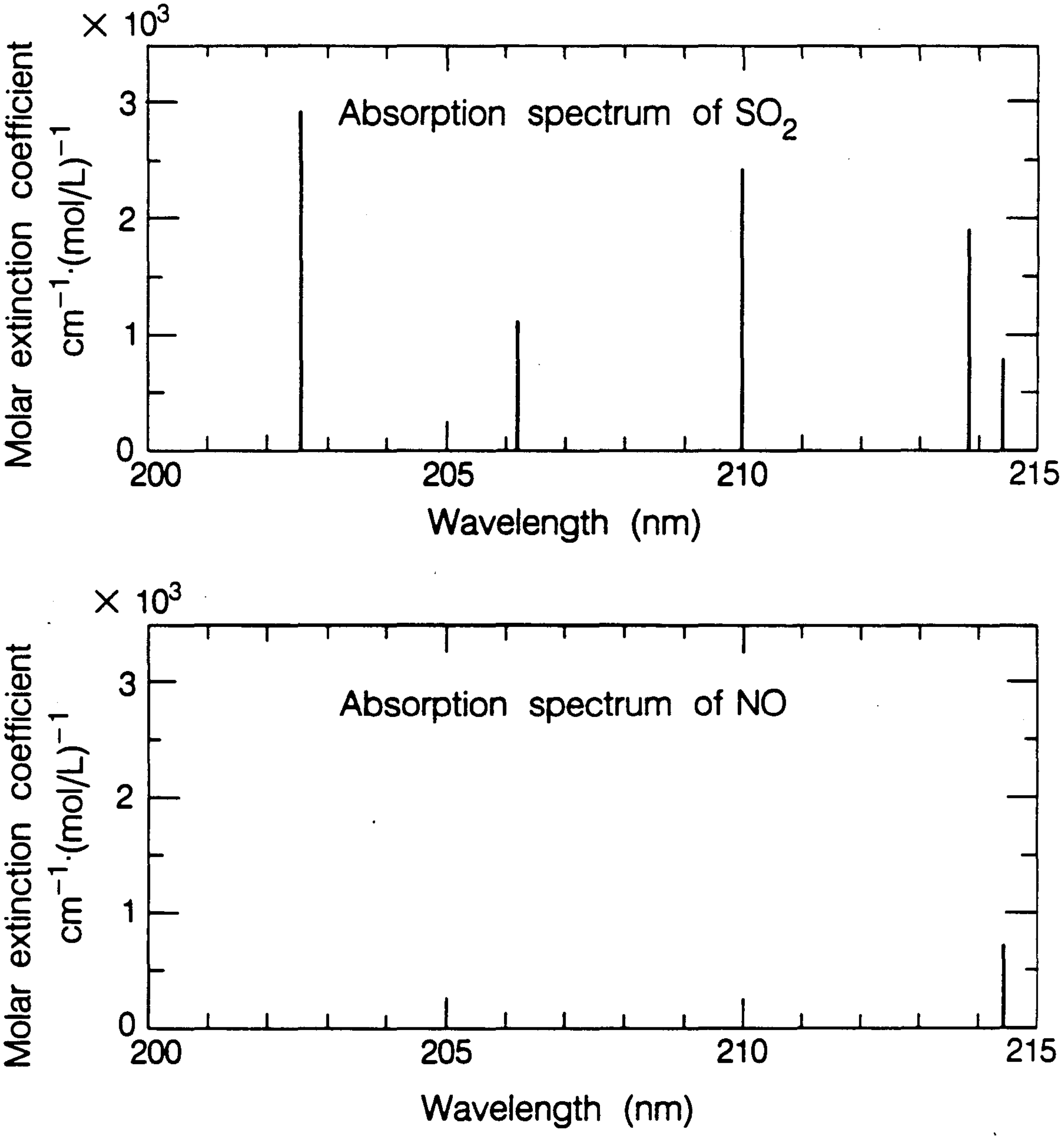

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Fig. 5

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