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CRDEC-TR-399

CORRELATION FOR NON-LINEAR INFRARED CALIBRATION CURVES

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August 1992

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U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

399010 19pg.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
1992 August

3. REPORT TYPE AND DATES COVERED
Final, 89 Aug - 89 Nov

4. TITLE AND SUBTITLE
Correlation for Non-Linear Infrared
Calibration Curves

5. FUNDING NUMBERS
PR-1L161102A71A

6. AUTHOR(S)
Mahle, John J.; Buettner, Leonard C.; and
Tevault, David E.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
CDR, CRDEC, ATTN: SMCCR-RSC-A, APG, MD 21010-5423

8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-TR-399

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

An analytical expression has been identified which can be used to correlate absorbance versus concentration for gas phase infrared monitors. This expression can be used to correlate both positive and negative deviations from Beer's Law. Calibration data for several vapors has been measured. Correlation of this data provided a good fit over a wide range of concentration and absorbance.

14. SUBJECT TERMS
Correlation
Infrared analyzer
Beer's law deviations

15. NUMBER OF PAGES
21

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	**18. SECURITY CLASSIFICATION OF THIS PAGE**	**19. SECURITY CLASSIFICATION OF ABSTRACT**	**20. LIMITATION OF ABSTRACT**
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

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PREFACE

The work described in this report was authorized under Project No. 1L161102A71A. This work was started in August 1989 and completed in November 1989.

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CORRELATION FOR NON-LINEAR INFRARED CALIBRATION CURVES

1. INTRODUCTION

The development of portable, long pathlength infrared analyzers has allowed more accurate and dependable identification of chemical compounds in air samples. It is now possible to use these units for on-line monitoring of process streams with rapid analysis from remote locations. Most recently the introduction of miniature FT-IR systems has provided a versatile inexpensive analyzer that will greatly enhance the capabilities for non-destructive, on-line gas monitoring and the study of reactive gas mixtures. These analyzers are currently used in both industrial and laboratory settings.

One difficulty with any process analyzer is obtaining an accurate calibration curve which can be written as a simple analytical expression. Such a curve would minimize the need for calibration data and allow accurate interpolation. Also the availability of a simple analytical expression is often required in order to perform on-line data acquisition of process behavior.

A generalized calibration expression that relates infrared absorbance to concentration in the gas phase would be quite useful but to date has not been developed. Therefore an attempt has been made to develop an expression that could be used to correlate data for single or non-interfering multi-component vapors in air over a wide concentration range.

Any method to correlate absorbance data needs to incorporate the basic theory of absorption of radiation as described by Beer's law which states that absorbance is proportional to concentration as follows:

$$A = \ln(\frac{P_o}{P}) = \alpha cb \tag{1}$$

the absorbance, A, is defined relative to the incident radiant power, P_o , and the radiant power which reaches the detector, P. The molar absorptivity α is a proportionality constant which relates the absorbance to the concentration c and path length b. Beer's law can be used to accurately correlate data at low values of absorbance. However, as the absorbance values increase, deviations from Beer's law are often observed. Both positive and negative deviations from Beer's law have been reported where the slope of the concentration versus absorbance may either decrease or increase with absorbance. Both chemical and instrumental phenomena have been cited for these deviations from Beer's law[1,2]. Most often, the absorbance lags behind concentration due to instrumental resolution limitations. For example, an absorbance one-half the instrumental resolution(band pass) could only absorb 50% of the incident radiation at most. Therefore, such an absorption would approach a maximum of 50% T(0.301 absorbance) at high concentration. For this reason there has not been much success in developing a single expression to correlate all absorbance phenomena.

Attempts have been made to correlate concentration versus absorbance data by assuming a linear relationship and a non-zero intercept in order to correlate the deviations from Beer's law over a narrow absorbance range. However, this technique can introduce significant error when interpolating data. This approach naturally has problems at low concentrations. Potentially, there is room for improvement using more sophisticated modeling. Haaland[3] outlines a method to account for full spectra deviations from Beer's law in multicomponent systems. This approach is needlessly cumbersome for single component behavior. The presence of interferences would require some deconvolution algorithm. For many practical applications it is of interest to monitor for only a single species or to choose wavelengths where this is not any interference. In such cases the present method can be employed.

In order to resolve these problems, a new correlation for IR absorbance calibration has been developed which uses two parameters. The expression reduces to Beer's law at low values of absorbance, and approaches a zero intercept.
This calibration expression can be written as follows:

$$\ln(c) = K_0 + \ln(A) - K_1A^2 \qquad (2)$$

The terms K_0 and K_1 from equation(2) are empirical terms. It is convenient to write the expression with concentration as a function of absorbance because absorbance is the measured quantity. This makes calculation of concentration straightforward; numerical techniques are not required for the solution. In the limit as absorbance approaches zero the third term on the right becomes negligible so that the equation(2) assumes the form of Beer's law. This suggests that K_0 is proportional to the molar absorptivity, α. At higher absorbances the third term on the right of equation(2) becomes important providing the exponential relationship between absorbance and concentration. This expression can be used to correlate both positive and negative deviations from Beer's law where positive K_1 represents positive deviations and a negative K_1 represents negative deviations.

The data which has been correlated using equation(2) will be presented as well as an analysis of resulting parameter values.

2. EXPERIMENTATION

Calibration data has been obtained using five identical single beam spectrophotometers with variable pathlength 20 meter gas cells: the MIRAN-80 Computing Infrared Analyzer (Foxboro Inc.,Norwalk, CT). The analyzer was connected to a circulating pump (model MB-41, Metal Bellows Inc., Sharon, MA) in a closed-loop arrangement to measure calibration data as shown schematically in Figure 1. A four-way valve was used to operate the system in either purge or isolate mode. Attached to the outlet of the pump was a septum for injection of liquid or gas samples. Monitoring and control of the MIRAN was performed using a personal computer. The instrument had the capability to scan the 2.5-14.5 μm wavelength region of the infrared spectrum. A sample spectrum for 1,1,2-trichlorotriflouroethane is presented in Figure 2. The analytical wavelength λ_{max} for each instrument was chosen in order to optimize the optical response at a given pathlength and eliminate variability in instrument filter alignment. The reference wavelength was chosen from a null region of the spectrum. The total system volume was estimated by summing volumes of tubing and manufactures' specified cell and pump volumes. The total system volume was either 5.66 or 11.30 liters depending on whether one or two IR's were to be calibrated. The volume of the long path infrared cell was 5.60 liters.

In order to obtain the calibration curve the system was first purged with clean dry house air. The MIRAN was then zeroed to these conditions i.e., detector response in the absence of sample P_0 was measured and the values stored. Measured injections of the test chemical were made using a suitable gas-tight syringe(1000 Series, Hamilton Co.,Reno, NV). Absorbance values obtained from the MIRAN represented the difference between the absorbance at the analytical wavelength and the absorbance at the reference wavelength.

3. RESULTS

The IR calibration data has been correlated to equation(2) using a non-linear least squares regression based on Newton's method in order to minimize the variance. The variance was computed using the following relationship:

$$var = \frac{1}{N}\sum_{1}^{N}(\Delta c)^2 \tag{3}$$

N is the number of data points.

Some sample data is shown in Figures 3-5 with the corresponding parameters listed in Table 1 for: R-113(1,1,2-Trichloro-1,2,2-Trifluoromethane), R-22(Chlorodifluormethane). Each of these samples exhibited significant negative deviations from Beer's law resulting in negative values for the parameter K_1. Equation (2) provides a very good fit to the data for each compound as measured by the variance correlate this type of data over any previously proposed method. For data that did conform to Beer's law it would be trivial to apply equation(2) with $K_1 = 0$. The choice of the exponent 2 in equation(2) seemed to give better results than did values of 1 or 3, but obviously this could be chosen as a parameter to be fit if necessary.

Several other correlations were also examined. These included series expansions of the following form:

$$c = k_0 + k_1 A + k_2 A^2 + k_3 A^3 + \ldots \tag{4}$$

Cases where k_0 was non-zero were considered unacceptable because in the limit of low concentration this form does not converge to the correct physical limit and tends to overpredict concentration for a given absorbance value. For cases where k_0 was set equal to zero and a regression performed on the other parameters the following difficulty was noted. Close agreement could be obained between the non-linear correlation and the series expansion for calibration curves with ten or more data points and a third order dependence in absorbance. Second order dependencies were not able to represent the data well. This means that more parameters are needed in the series expansion correlation than are needed in equation(2). Also for cases where a limited data set is available such as three calibration points the series expansion will fit the data exactly while the non-linear model will introduce slightly more curvature. But if the calibration data has some scatter adding higher number of terms in the series model can lead to physically unrealistic fits as the slope the model changes sign in an attempt to fit every data point. The non-linear model(2) has an inherent smoothly capability.

The molar absorptivities, α, can be computed as follows:

$$\alpha = \frac{e^{-K_0}}{b} \tag{5}$$

Table 2 summarizes the results of this calculation for several samples. Figures 3 and 4 represent sample calibrations for R-113. Other results not presented here indicate that the computed absorptivities on different instruments are similar for R-113 at specified pathlengths. Figure 5 presents data for R-22 calibration again a good correlation is achieved over a wide range of concentration.

Equation (2) has been used to correlate the calibration curves of many chemicals covering a range of physical and spectral properties. This suggests that there might be a wide applicability for equation(2). One particular example is water vapor which has an absorbance spectra which is known to change with concentration due to the formation of clusters[4]. A good correlation has been computed for this and many other compounds over approximately two orders of magnitude in concentration.

4. CONCLUSIONS

A semi-empirical expression has been developed for calibration of absorbance versus concentration data taken from infrared spectrophotometers. This equation has been correlated to data over a wide concentration range using only a few well-spaced data points for systems exhibiting negative deviations from Beer's law. It is hoped that future efforts will be made to extend this work to a broad range of detectors, cell types and multicomponent vapor systems.

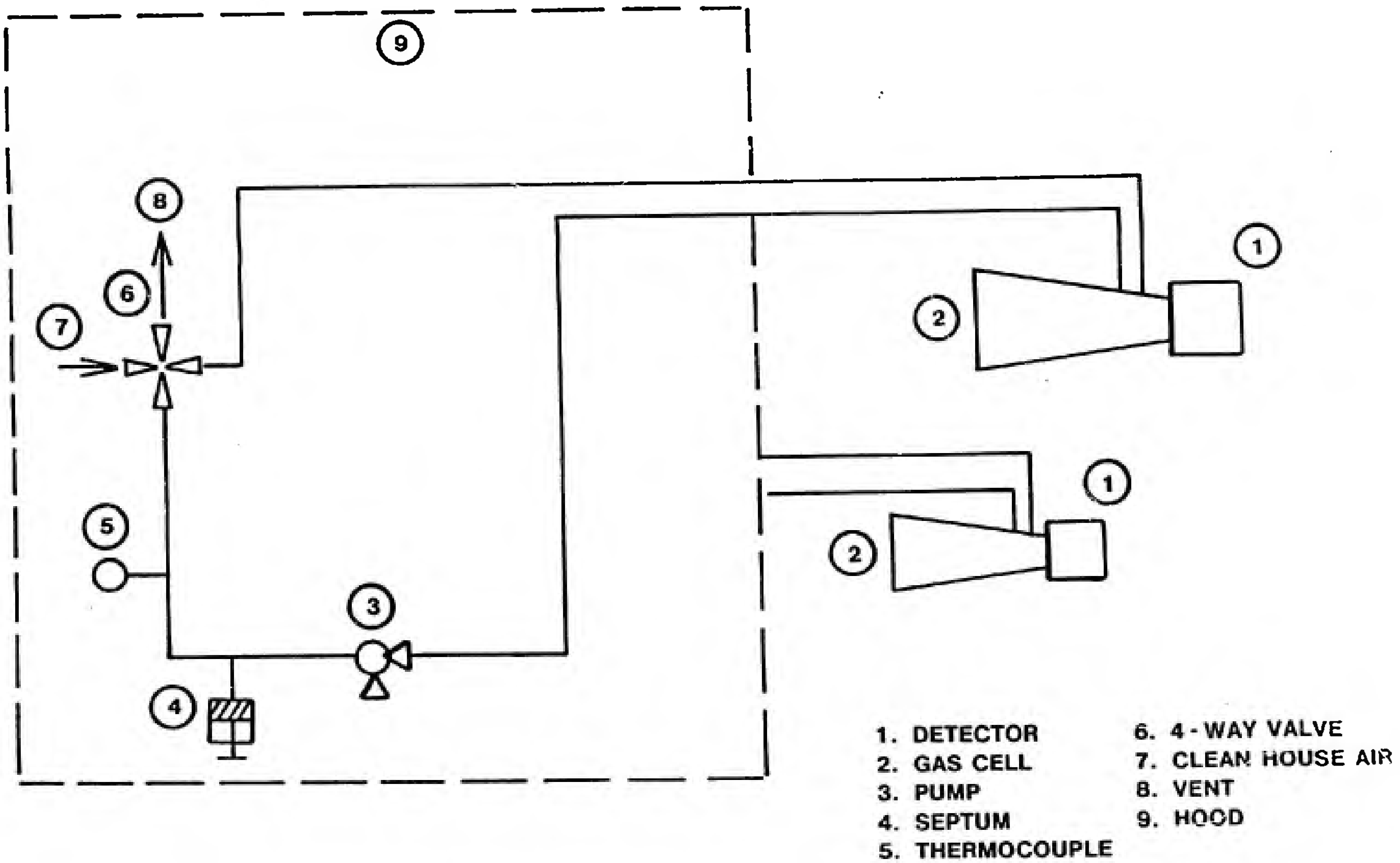

Figure 1. MIRAN Infrared Analyzer Calibration Loop

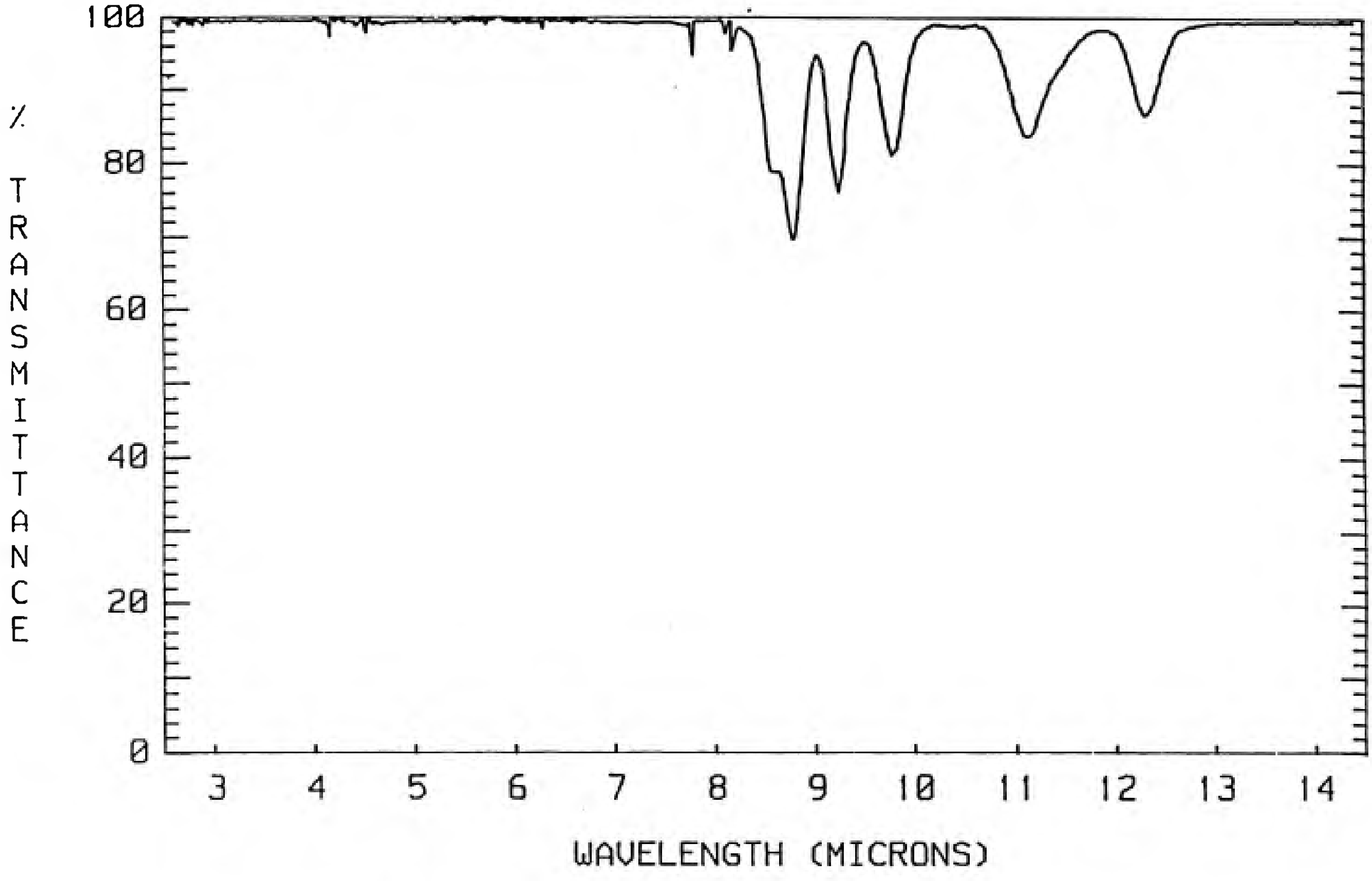

Figure 2. Difference Spectrum for R-113 with Background of Air on IR #3

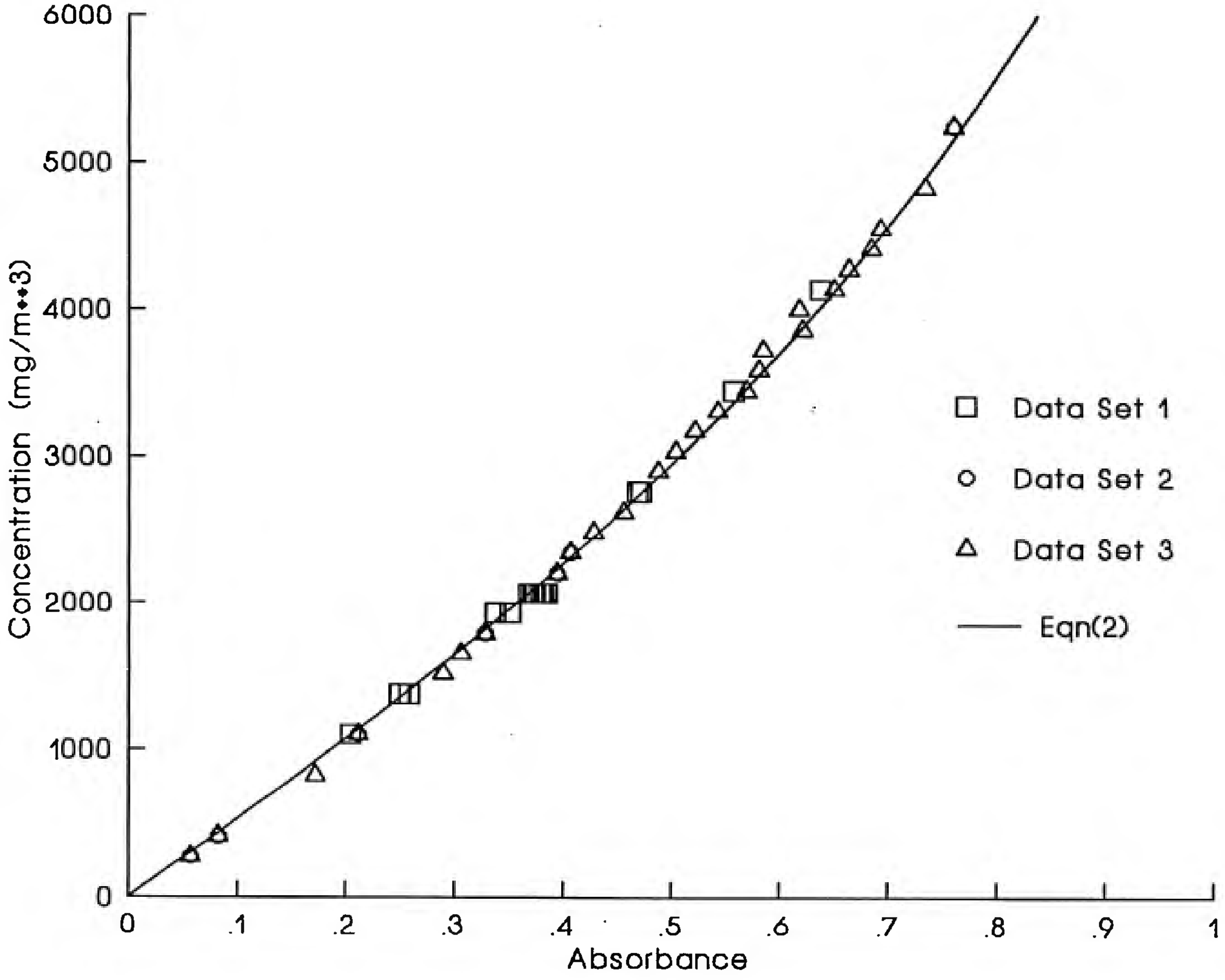

Figure 3. Calibration Curve for R-113 in IR #1

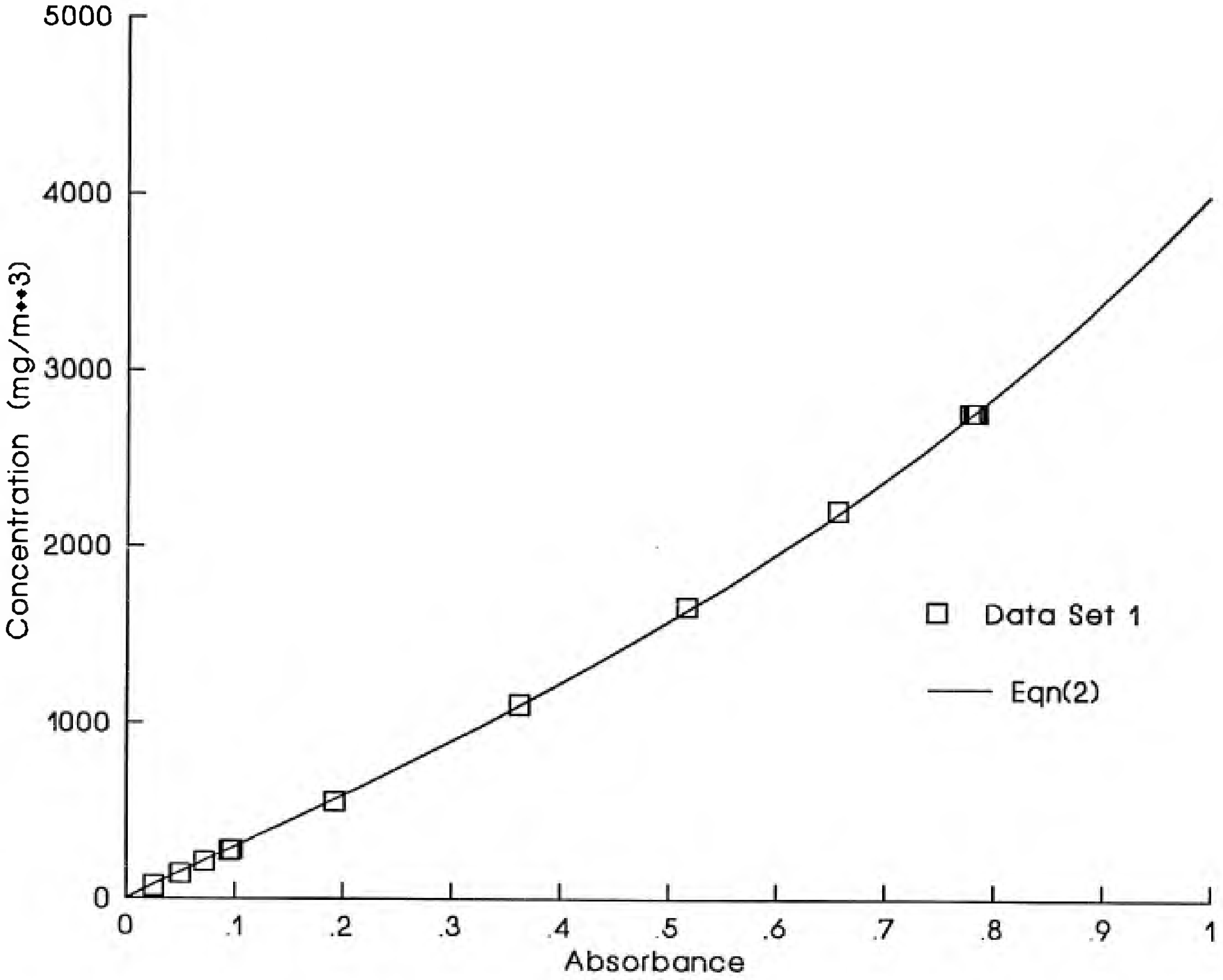

Figure 4. Calibration Curve for R-113 in IR #3

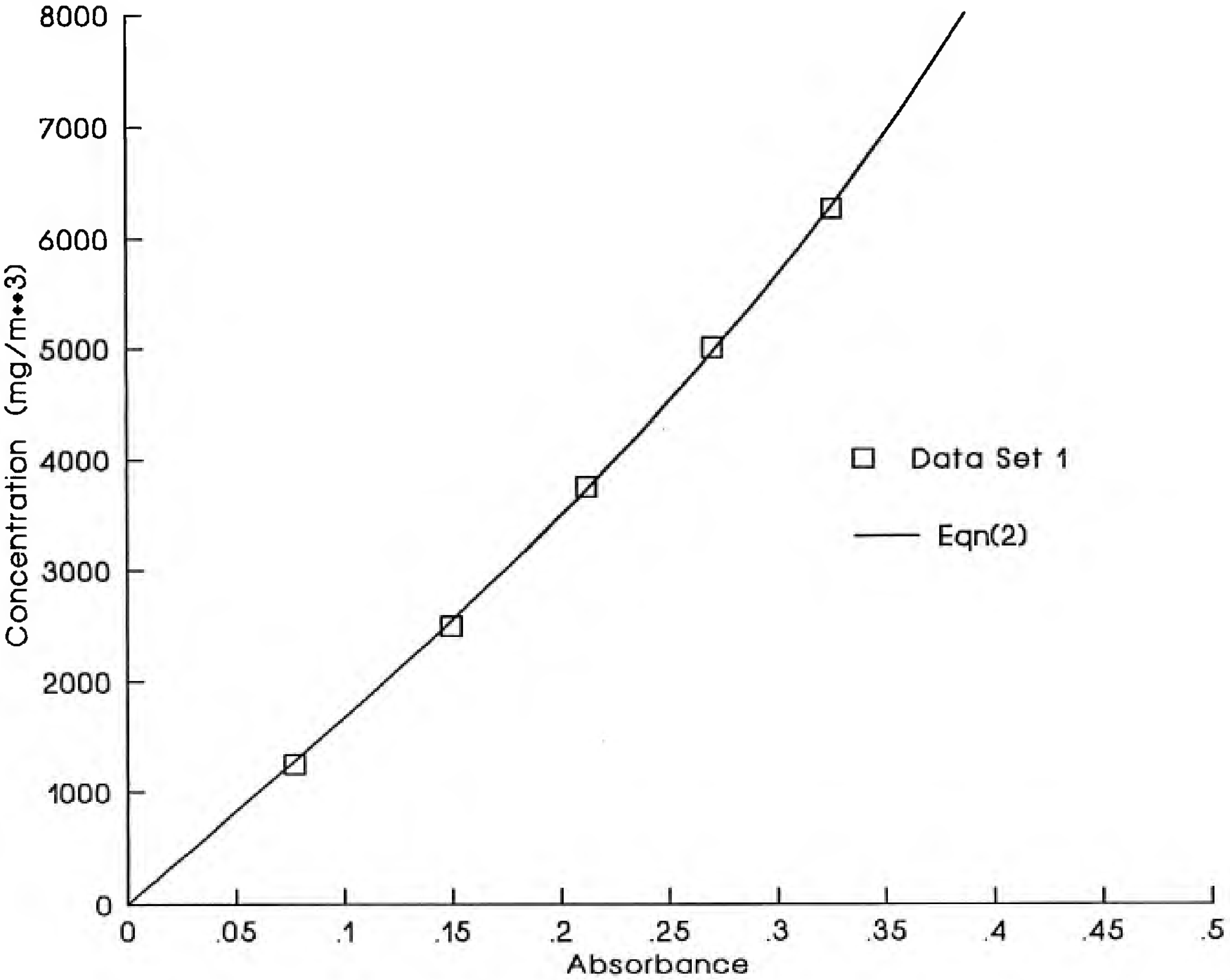

Figure 5. Calibration Curve for R-22 in IR #4

Table I. Correlation Parameters* For Equation (2)

Compound	std. dev.	K_0	K_1	Instrument
R-113	60	8.571	-0.4317	1
R-113	148	7.920	-1.093	2
R-113	47	7.975	-0.3173	3
R-22	36.34	9.708	-1.490	4

*Based on concentration in mg/m^3

Table II. Molar Absorptivity

Compound	$\lambda_{max}(\mu m)$	Path Length(m)	α $(l/mol\ cm)$	Instrument
R-113	8.328	9.75	36	1
R-113	8.689	3.75	181	2
R-113	8.759	3.75	171	3
R-22	7.410	0.75	7010	4

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GLOSSARY

A = Absorbance

b = Pathlength

c = Concentration

K_0, K_1 = Constant equation (2)

k_0, k_1, etc = Constant equation (4)

N = Number of observed points

P_0 = radiant power

P = Power reaching the detector

α = molar absorbtivity