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MONITORING SPACECRAFT ATMOSPHERE CONTAMINANTS
BY LASER ABSORPTION SPECTROSCOPY

Professor J. I. Steinfeld, Principal Investigator

B. D. Green, Research Assistant

Department of Chemistry, Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

The NASA Technical Officer for this grant is:

Phillip D. Quattrone
Environmental Control Research Branch
NASA Ames Research Center
Moffett Field, California

1. Since the last progress report, our aim has been to obtain data which will provide a test of the accuracy of the differential absorption method for trace contaminant detection in many-component gas mixtures. The necessary accurate absorption coefficient determinations were carried out for several more gases, namely, acetonitrile, 1,2-dichloroethane, Freon-113, furan, methyl ethyl ketone, and t-butyl alcohol. The absorption coefficients are displayed graphically in Figs. 1-6. This brings to fifteen the total number of gases for which we have catalyzed CO₂-laser line absorption coefficients to an accuracy of $\pm 1\%$.

2. We have tested an opto-acoustic method of measuring absorbance, similar to the system described by Dewey [Opt. Eng. 13, 483 (1974)]. However, since no improvement in sensitivity over a direct-absorption measurement was obtained, this method was not pursued.

3. A series of measurements have been carried out on known gas mixtures, in order to furnish data for testing calculational procedures. The runs for mixtures of trace gases were performed using the absorption method. The mixtures were chosen in such a way as to determine the effect of the following factors on the accuracy of the determination of contaminant concentrations:

- 1) The variation of the absorption for similar mixtures, i.e., mixtures with the same relative concentrations of the gases, but different total pressures of the contaminant mixture;
- 2) The presence of a relatively high concentration of a broadly absorbing gas;
- 3) The variation of the relative concentrations of two gases with very similar absorption spectra.

The following method was used in the preparation of the mixtures. The ratio of the volume of the absorption cell to the volume of a sidearm bulb was determined as accurately as possible ($\pm 0.5\%$). Each gas to be used in a mixture was first purified by the freeze-pump-thaw cycle, then fractionally distilled over to another cold finger for storage. All gas pressures were measured on a dibutyl phthalate manometer; all manometer readings were taken with a cathetometer. A predetermined amount of each gas was let into the manifold. After the pressure in the manifold reached equilibrium, the cell was closed off and the gas in the cell was frozen into the sidearm bulb. The whole system was then pumped on for a few minutes. After all the gases were stored in the bulb, it was brought to room temperature and the gases were allowed to expand into the absorption cell and mix overnight. (This was experimentally found to be sufficient mixing time.) The next day air was added to bring the mixture to atmospheric pressure.

The first few runs were mixtures of 6, 9, 11, and 12 gases. They will give an indication of the increasing inaccuracies in the results as the number of contaminants is increased. The concentrations used were sufficient for partial, but not total, absorption of the laser light. The pressures of some of the gases were varied, notably benzene and cyclohexane which have similar spectra, in order to see interference effects and the error in concentration as a function of concentration. The next run was with 12 gases all in weakly absorbing amounts. Nine gases were placed in the cell for the next run. They all had large absorption coefficients, and were present in moderate concentrations. During preparation, the sidearm bulb was closed off before admitting air to the cell. After the absorption measurements for this run were made,

the cell was evacuated and the contents of the sidearm bulb was again allowed to expand into the cell and mix overnight. Thus, the relative concentrations of the gases in these two runs should be the same, but the total pressure due to the trace contaminants is reduced by a factor of about 15. For the next two runs, a gas mixture with all gases present in strongly absorbing concentrations was made. An additional run was made on the mixture with the same relative concentrations, but the total pressure was reduced by a factor of 15. We also ran the same mixture further reduced in total pressure by the same factor with an amount of a broadly absorbing gas (isopropanol) added so that absorption values for the mixture were significant. The resultant spectrum should appear as the spectrum of the broadly absorbing gas with the absorption of the mixture added on top. It is thought that the presence of an absorber might improve sensitivity because small values of absorption have larger error limits associated with them.

A 15-component mixture was then prepared, where 12 of the gases were present in roughly the same absolute concentration as before, but once again an amount of isopropanol was added. A mixture was also prepared of 15 gases, all in concentrations which have moderate absorption of laser light. The measurements were repeated three times, $1\frac{1}{2}$ hours apart, to check the reproducibility of the data. The results are shown in the table below. No points were discarded in the standard deviation calculations.

4. A preliminary analysis of these data was carried out on the small PDP-8/L computer in our laboratory. Mr. Green is currently carrying out more extensive analysis at the computer facility at the NASA Ames Research Center. In the previous Progress Report, it was noted (for a three-gas mixture) that

I/I_0	Number of points	$\sigma = \left(\frac{1}{N-1} \sum_{i=1}^N \delta_i^2 \right)^{1/2}$	Typical A with 96% conf. limits for normal dist. (25)
0.5-0.3	27	0.013	2.00 ± 0.026 (1.3%)
0.15-0.11	33	0.013	4.00 ± 0.026 (0.7%)
0.07-0.04	72	0.03	6.00 ± 0.06 (1.0%)
0.025-0.007	13	0.03	9.00 ± 0.06 (0.7%)

using n wavelengths to determine the concentrations of n gases resulted in large errors due to errors in experimental values. Use of a least-squares fitting routine to use all experimental data to determine the concentrations was tried first. For a system with n different gases, λ different wavelength absorption measurements and c_j estimated concentrations ($j = 1, \dots, n$), the estimated absorption would be $y_i = \sum_{j=1}^n \epsilon_{ij} c_j$, where ϵ_{ij} is the absorption coefficient of the j^{th} gas at the i^{th} wavelength. The y_i values differ from the experimental absorptions A_i because the c_j are not the exact values and because of experimental measurement errors. Minimization of the sum of the squares of the residuals $\eta (= \sum_{i=1}^{\lambda} (y_i - A_i)^2)$ with respect to variation in concentration ($\partial \eta / \partial c_j = 0$ for all j) will give a set of simultaneous linear equations,

$$f_{j1}c_1 + f_{j2}c_2 + f_{j3}c_3 + \dots + f_{jn}c_n = d_j \quad \text{for each } j = 1, \dots, n$$

where $f_{jk} = \sum_{i=1}^{\lambda} \epsilon_{ij} \epsilon_{ik}$ and $d_j = \sum_{i=1}^{\lambda} \epsilon_{ij} (A_i - y_i)$

In matrix form, $\mathbb{F}\mathbb{C} = \mathbb{D}$, $\mathbb{C} = \mathbb{F}^{-1}\mathbb{D}$, where $\mathbb{F} = \xi^T \xi$, $\mathbb{D} = \xi^T (A - Y)$. The solutions c_j are functions of the errors in the input concentrations. They can be used

as correction values and added to the input c_j values. From these new c_j estimates a new value of η is found. The process is repeated until the residuals no longer decrease significantly.

The F matrix is a symmetric positive definite matrix. This allows elimination methods to be used which require non-vanishing positive pivots. In particular, the triangular decomposition method of Cholesky is compact, uses little memory space, and does not require inversion of the F matrix for solution. This method decomposes F into two triangular matrices (L, L^T) which are transpositions of one another; thus only one need be calculated. Solution is then by back substitution. Here $d_j = \sum_{i=1}^{\lambda} \epsilon_{ij} A_i$ and no initial estimates for the concentrations are required. Work is currently progressing at NASA Ames in evaluating the mixture absorption data by both methods in order to find the best method of solution. Various schemes of weighting absorption lines are being tried also. Here the equation becomes $\epsilon^T W \epsilon g = \epsilon^T W A$ or $(A-X)$, where W is the $\lambda \times \lambda$ weighting matrix.

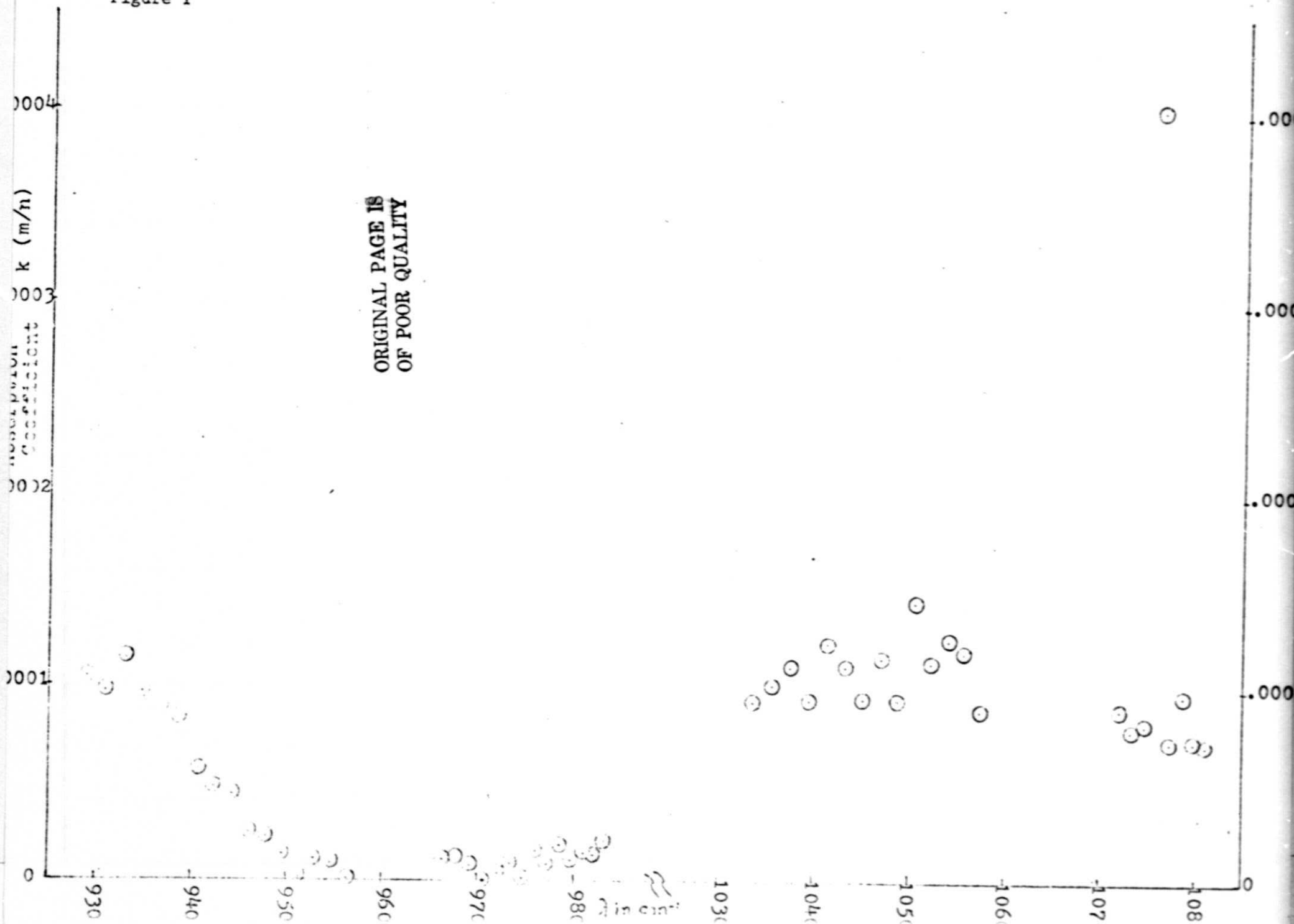
5. The absorption coefficients of vinyl chloride were measured in different pressures of air. Total pressures of the mixtures were 0.499, 0.748, 0.873, and 1.0 atmosphere, all with 4.1 Torr partial pressure of vinyl chloride. The absorption coefficients at some frequencies decreased slightly with increasing total pressure, at others it rose or remained constant. (For example, in the 10.6 μmP branch, absorbance at P(22) rose 5%, P(8) rose 20%, P(36) fell 15%, and P(30) fell less than 1%). Use of a tunable diode laser to observe these lineshapes as a function of pressure is planned. Stark tuning of the molecular levels with the resultant absorption spectrum changes monitored by the diode laser should allow identification of the molecular levels involved

and permit accurate calculation of the excited state dipole moment. These techniques will also be applied to other molecules which exhibit strong absorption in the 10-11 μm region.

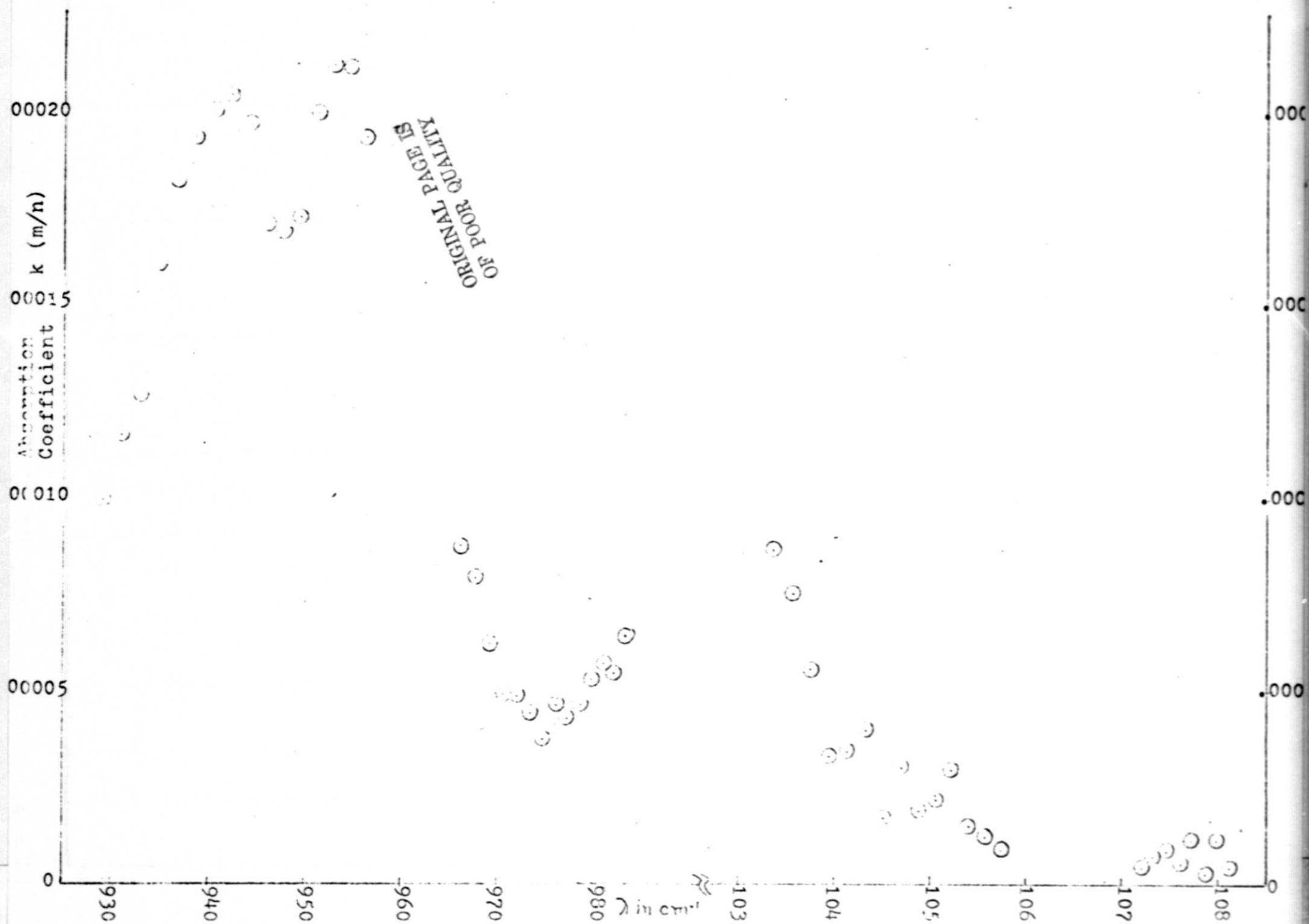
Acetonitrile

Figure 1

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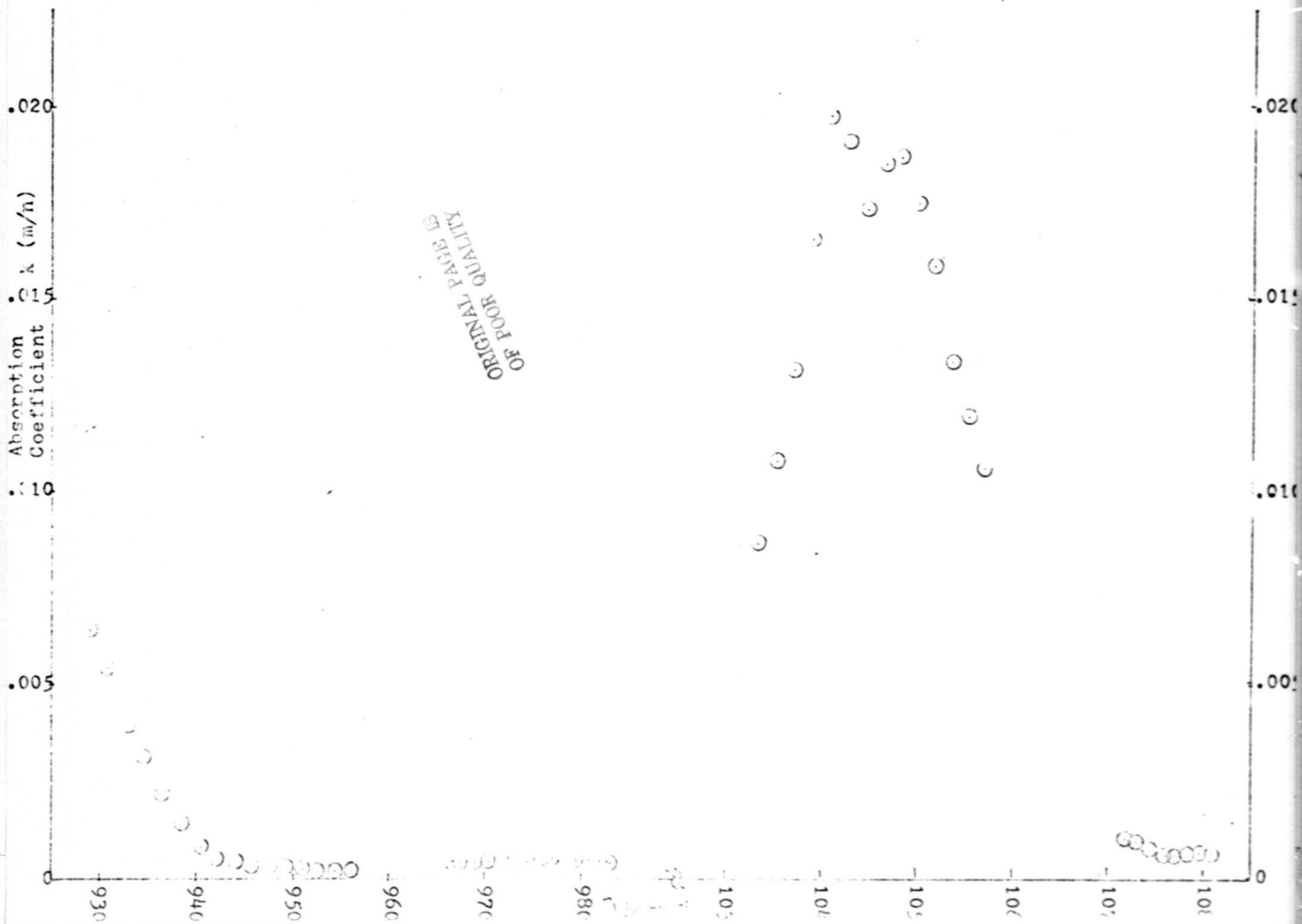


1,2 Dichloroethane
Figure 2



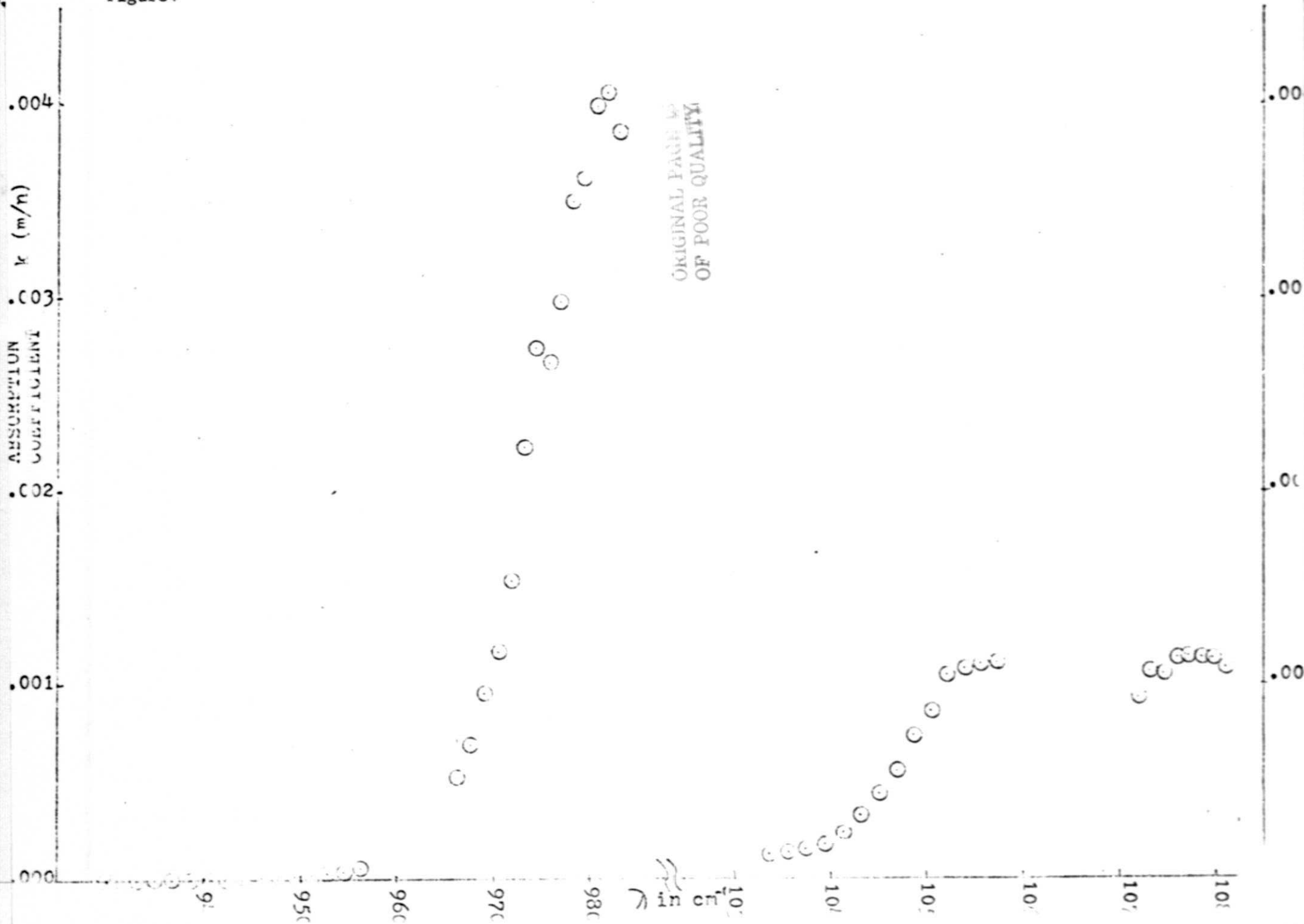
Freon 113

Figure 3



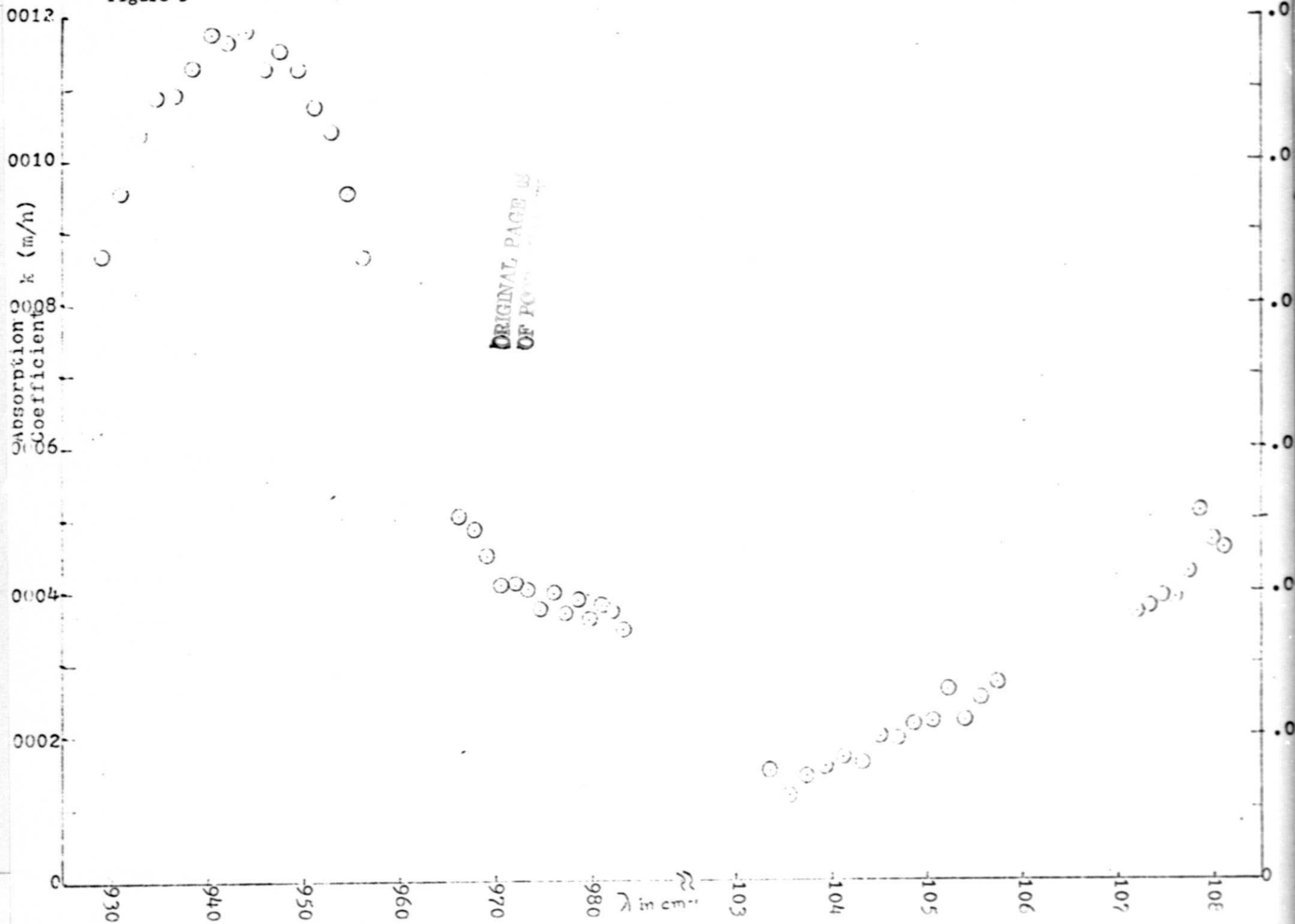
Furan

Figure 4



Methyl Ethyl Ketone

Figure 5



Tertiary Butyl Alcohol

Figure 6

