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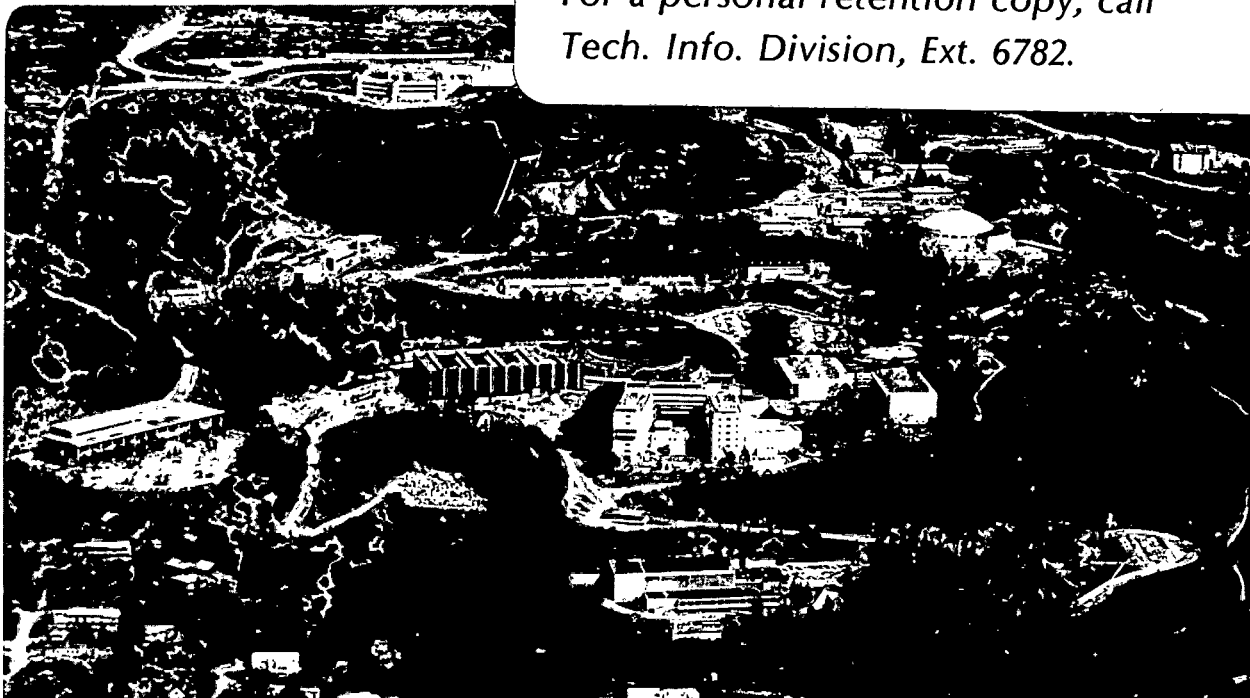
TUNABLE ATOMIC LINE MOLECULAR (TALM) SPECTROMETER

T. Hadeishi, H. Koizumi, R.D. McLaughlin,
and J.E. Millaud

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Tunable Atomic Line Molecular (TALM) Spectrometer

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ABSTRACT

A highly specific technique for real time monitoring of simple and complex molecules is described. This technique depends on using the Zeeman effect to tune an atomic emission line to coincide with a sharp molecular absorption feature and has been named TALMS (tunable atomic line molecular spectroscopy). Results are presented on the determination of di-atomic (NO), tri-atomic (NO_2 , SO_2), tetra-atomic (H_2CO) and more complex molecules. An explanation is offered for the ability of this technique to determine complex molecules which suggests that the method should be highly specific. It is concluded that work in this area will lead to instrumentation that will be valuable for process control or environmental monitoring.

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1. INTRODUCTION

One of the most difficult and perhaps most challenging problems in chemical analysis is the detection of both large and small molecules. In most cases when a sensor indicates the presence of a molecule, doubt still exists as to its precise identify. The thermal conductivity or electron capture detectors used for gas chromatography are examples of non-specific detectors. The identification and quantification of almost all organic compounds is presently accomplished using some type of chromatographic technique (e.g. GC, GC/MS, HPLC, TLC, etc.) These methods are time consuming, frequently not very selective, and, in the case of GC/MS, require expensive equipment and well trained scientific personnel.

The ideal analytical instrument would consist of a black box through which a sample is transported without coming in contact with surfaces that would cause alteration. The box would print out the levels of all species in a specified concentration range. Of course, no such instrument exists today. The properties of such an ideal instrument are:

- o No Interferences
- o High Sensitivity
- o No Matrix Effect
- o Inexpensive
- o Precise
- o Absolutely Accurate
- o Easy to Use

This paper deals with one of our attempts to to construct an instrument that approaches this ideal. This approach has been named TALM Spectroscopy. The instrument built to perform this analysis is referred to as TALMS (Tunable Atomic Line Molecular Spectrometer) The basic principle is high resolution molecular spectroscopy and it's characteristics are:

- o High Resolution (>500,000)
- o High Sensitivity
- o Unique Quantitative Analysis
- o Minimal Matrix Effect
- o Compact Instrument
- o Inexpensive to Construct
- o Easy to Use

TALM Spectroscopy consists of splitting a source atomic emission spectral line by means of a magnetic field (Zeeman Effect) and making a differential absorption measurement between one Zeeman component that has been magnetically tuned to match an analyte absorption line and an unmatched Zeeman reference component. The difference in polarization between Zeeman components permits the matching and nonmatching wavelengths to be alternately selected and the differential absorption measured very rapidly with an electrooptical device called a current controlled retardation (CCR) plate. [1] Since the wavelength separation between components is small, a signal will only be obtained if the analyte contains a sharp absorption feature. This process is illustrated in Fig. 1. The line with label $\Delta M = +1$ is tuned with

the magnetic field to exactly match the electronic-vibrational-rotational line of a specified molecule in the sample. The TALM spectrometer detects the difference between the $\Delta M = +1$ and $\Delta M = -1$ reference Zeeman components.

2. INSTRUMENTATION

The components of the TALMS system are pictured in Figure 2. A small diameter light source is fitted between the pole pieces one of which has a small hole drilled through it. This hole contains a collimating lens on the far side so as to minimize perturbation of the magnetic flux. The light is passed through the hole drilled in the magnetic core, then through an absorption cell, a variable phase retardation plate, a linear polarizer and finally focused on a small monochromator. Right and left circularly polarized light, hence the higher and lower Zeeman components, are selected by a CCR and a linear polarizer combination. The alteration (switching) between the right and left circularly polarized components can be accomplished at frequencies up to 250 Hz using the CCR. By the use of an acoustical resonance retardation plate the frequency can be increased to as much as 50 kHz. however, no significant advantage was found at higher frequencies. These components, that utilize features of the Zeeman effect, form the heart of the TALM spectrometer. This simple device is capable of a surprising resolving power (in excess of 500,000) with a large

acceptance angle. The resolving power ($R = f/\Delta f$) depends on the line width (Δf) of the atomic emission line. For a typical situation $\Delta f = 3$ GHz and $f = 1.5 \times 10^{15}$ (wavelength = 200 nm). Hence,

$$R = 1.5 \times 10^{15} / 3 \times 10^9 = 500,000$$

The function of the monochromator is simply to select the atomic emission line of interest and the final resolution achieved is not dependent on the resolution of this monochromator. To monitor a compound a phase sensitive detection method is used that detects the differential absorption between Zeeman components using the switching frequency of the CCR as a reference. To determine the shape of the absorption features a plot is made of the ratio of intensities (I/I_0) with the sample in and out of the optical path as a function of magnetic field.

3. RESULTS

Results will be given for a variety of molecules in order of increasing number of atoms in the molecule. Examples of di-atomic tri-atomic and tetra-atomic molecules will be presented followed by two very interesting examples of polyatomic molecules.

3.1. Nitric Oxide

The nitric oxide molecule has been extensively studied.

In fact this molecule has more or less assumed the same role in the study of other diatomic molecules as has the hydrogen atom in the study of other atoms. Measurements with the TALM spectrometer will be described with NO in the system. [2] In this case, there can be little doubt about the accuracy of the information on this molecule. Hence, it is a good molecule to use for the interpretation of the TALMS measurements.

Figure 3. pictures the low resolution band spectrum of NO (Y-band) and some atomic emission lines that fall within these electronic vibrational features. Each vibrational band consists of many rotational lines (of Doppler width $<1/2 kT$) most of which are resolvable. The electronic-vibrational-rotational line in the (1,0) band near the 214.2 nm line of Cd II is shown in Figure 4. It is apparent that the 214.4 nm line can be tuned by proper application of a magnetic field into exact coincidence with one of the rotational lines of NO. Fig. 5. shows the experimental result. In this case the Zeeman components of the Cd II 214.4 nm line are doublets (anomalous Zeeman effect). Hence, as the magnetic field is varied, first one then the other member of the doublet moves over the molecular absorption feature. This is the reason for the side band in the figure.

The 213.8 nm line of Zn can also be brought into coincidence with a NO rotational feature by magnetic scanning. This line exhibits a single Zeeman component. A similar

scan with this atomic line produced a single peak thus verifying that the TALM spectrometer is working as expected.

3.2 Nitrogen Dioxide

For molecules composed of more than two atoms the theory becomes very complicated and the experimental data are not quite adequate to pinpoint the location of sharp absorption features. However, reasonably intelligent guesses can be made. First, attention should be directed to wavelength regions where optical absorption takes place. Next, a region must be selected that has a large probability of containing sharp line features. This can be a difficult problem. One attractive region is that lying at wavelengths slightly below the molecular pre-dissociation limit.

Pre-dissociation occurs for nitrogen dioxide at wavelengths close to but shorter than 248.1 nm. [3] The B - X electronic transition occurs at longer wavelengths with features that are quite sharp. The 249.2 nm line of Cu I is intense and a good candidate for coincidence because it falls in the proper wavelength region. Fig. 6 shows the line absorption profile obtained when NO₂ was scanned with the Cu 249.2 nm line. For comparison this figure also contains a tracing of NO₂ in the same spectral region obtained by traditional high resolution spectrographic techniques. The equipment used all but masks off the sharp absorption that was recorded with the TALMS instrumentation.

3.3 Sulfur Dioxide

Similar sharp absorption features were observed for sulfur dioxide. [4] In this case a match was achieved with Cd 228.8 nm and Zn 213.8 nm which are reasonably close but at longer wavelengths than the predissociation limit at 195.0 nm. The 197.3 nm line from an arsenic lamp that has recently been developed would likely also give a signal, but there has not yet been an opportunity to try this.

3.4 Formaldehyde

The investigation of this molecule presented an excellent opportunity to compare the resolving power of the TALMS technique with a recent measurement made using Fabry-Perot Interferometry. [5] The interferometer was a pressure scanning type and was synchronized with a wavelength scanning grating. The 338.3 nm Ag line ($^2S_{1/2} - ^2P_{1/2}$ transition) is in near coincidence with the same formaldehyde lines that were investigated using the interferometric technique. Fig. 7 compares the TALMS scan with that made using the Fabry-Perot interferometer. These results were used to assign transitions in the formaldehyde molecule. [6] The higher resolving power of the TALMS technique is apparent. This additional resolving power revealed structure that was not obtained by Dieke and Kistiakowski [7] who used a spectrograph of 40 ft. focal length.

3.4 Larger Polyatomic Molecules

In a molecule whose moment of inertia is large (e.g. benzene) rotational energy levels, hence rotational transitions, are closely spaced. So closely spaced that there are, on the average, several rotational lines present in a typical rotational-vibrational- electronic transition. These lines cannot be resolved because their spacing is less than their Doppler line width. The logical conclusion is that the TALMS technique would not have application to such polyatomic molecules.

However, beginning in 1959, several high resolution studies of complex molecules like benzene revealed line-like structures in several absorption bands. The most reasonable theoretical explanation is based on the concept of rotational line coincidences proposed by HOLLAS [8] He adopted the quasi-symmetric top approximation to a number of large asymmetric molecules and found several ways in which strong lines could coincide to produce narrow, resolvable features. The existence of these sharp features led to the investigation and use of the TALMS technique for detection of complex molecules.

Experimental observations of line-like features in the high resolution spectra of a variety of molecules has recently been summarized by ROSS. [9] These high resolution absorption spectra clearly indicate the occurrence of line-like structures in certain isolated wavelength regions. Thus, once a near coincident atomic line is found, TALM

spectroscopic techniques would be capable of detecting such large molecules with a high degree of specificity (because rotational line coincidences are few) and high sensitivity. Figure 8 shows a line shape measurement of a sharp benzene feature that was obtained using the Hg 253.7 nm line. This measurement demonstrates that the line width of such large polyatomic molecules is not much different from that of di- and tri-atomic molecules. Figure 9 shows the line shape measurement of a feature in the spectra of chlorobenzene. In this case, the shape does not resemble a line at all. However, this very abrupt change in intensity over such a small wavelength interval allows a TALMS signal to be obtained which can be used to monitor this molecule. The very great difference in line shape between benzene and chlorobenzene is an example of an additional feature of the TALMS technique that is valuable for analytical purposes. If a TALMS signal is obtained, a line shape determination will serve to confirm the identity of the molecule. An exact mathematical treatment is not possible, but the probability of two molecules giving TALMS signals at the very same wavelength with the very same line shape seems very small indeed.

4. DISCUSSION

Tunable atomic line molecular spectroscopy is a new technique that is capable of monitoring molecules with high

sensitivity and high specificity. Although the tuning range of each atomic emission line is limited to about 60 GHz, there are a very large number of lines available from the vacuum ultra-violet to the far infra-red. Thus, it would seem that any molecule could be detected using this technique.

A practical analytical instrument can be constructed that is able to detect molecules with no chemical pre-treatment and that is interference free so that it should be simple for inexperienced people to operate. Reduction in size and weight of such an instrument should be possible as soon as near coincidence lines are found for the molecules to be determined. At this point the electro-magnet can be replaced with a much lighter permanent magnet and the TALMS instrument will be the size of a typical AA instrument. Background rejection will be automatically achieved in almost every case because in real monitoring situations the analyte molecule will be in the presence of other substances that show effective continuous absorption over the small region of interest. This is true because most molecular absorption results from rotational transitions whose spacing is small compared to the Doppler width. In this case the intensity change over a 60 GHz interval is negligible. Thus the background rejection for molecules will be comparable with the background rejection of the ZAA technique for atoms. Since the absorption coefficient for molecules is

smaller than that for atoms, the dynamic range will be larger. However, this does not necessarily mean that the sensitivity will be worse.

Unlike the atomic absorption situation, detection of molecules by this technique is non-destructive. Even though the oscillator strength of the molecule is smaller than the atom, this non-destructive feature can be used to greatly improve the signal to noise ratio. The sample is allowed to remain in the cell and electronic time averaging techniques are used to increase the signal to noise ratio and hence, the lower limit of detection. The most difficult problem with the measurement of small changes in absorption is the base line drift in the light source. However, if differences in absorption with sample in and sample out are monitored this base line drift is averaged out. The improvement in signal to noise ratio will be proportional to the square root of the number of runs with a light source that has a Gaussian noise distribution. If the sample size is limited, it can be re-circulated. If measurements of ambient air are required, the number of times the sample is introduced can be chosen to coincide with the averaging time of the particular monitoring problem.

5. CONCLUSIONS

The data presented demonstrate the versatility of the

TALMS technique. It can be used to perform high resolution molecular spectroscopy, it can be designed to monitor a particular molecule in the presence of many other absorption species and it seems that once constructed a TALMS instrument can be easily modified for a large number of different analytical applications. In this age, when chemical analysis is becoming of such great importance to the solution of so many problems, this technique can make an important contribution.

6. ACKNOWLEDGEMENTS

We would like to thank Dr. Donald Scott of the Environmental Protection Agency for many helpful discussions. Many of the light sources for these experiments were produced by Wilton Berlund. Without his contribution, many of these experiments would not have been possible.

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FIGURE CAPTIONS

Fig. 1: method of matching an atomic line to a molecular line using Zeeman effect.

Fig. 2: components of the tunable atomic line molecular spectroscopy system.

Fig. 3: coincidence between NO absorption and some useful atomic emission lines.

Fig. 4: rotational structure in absorption spectra of NO.

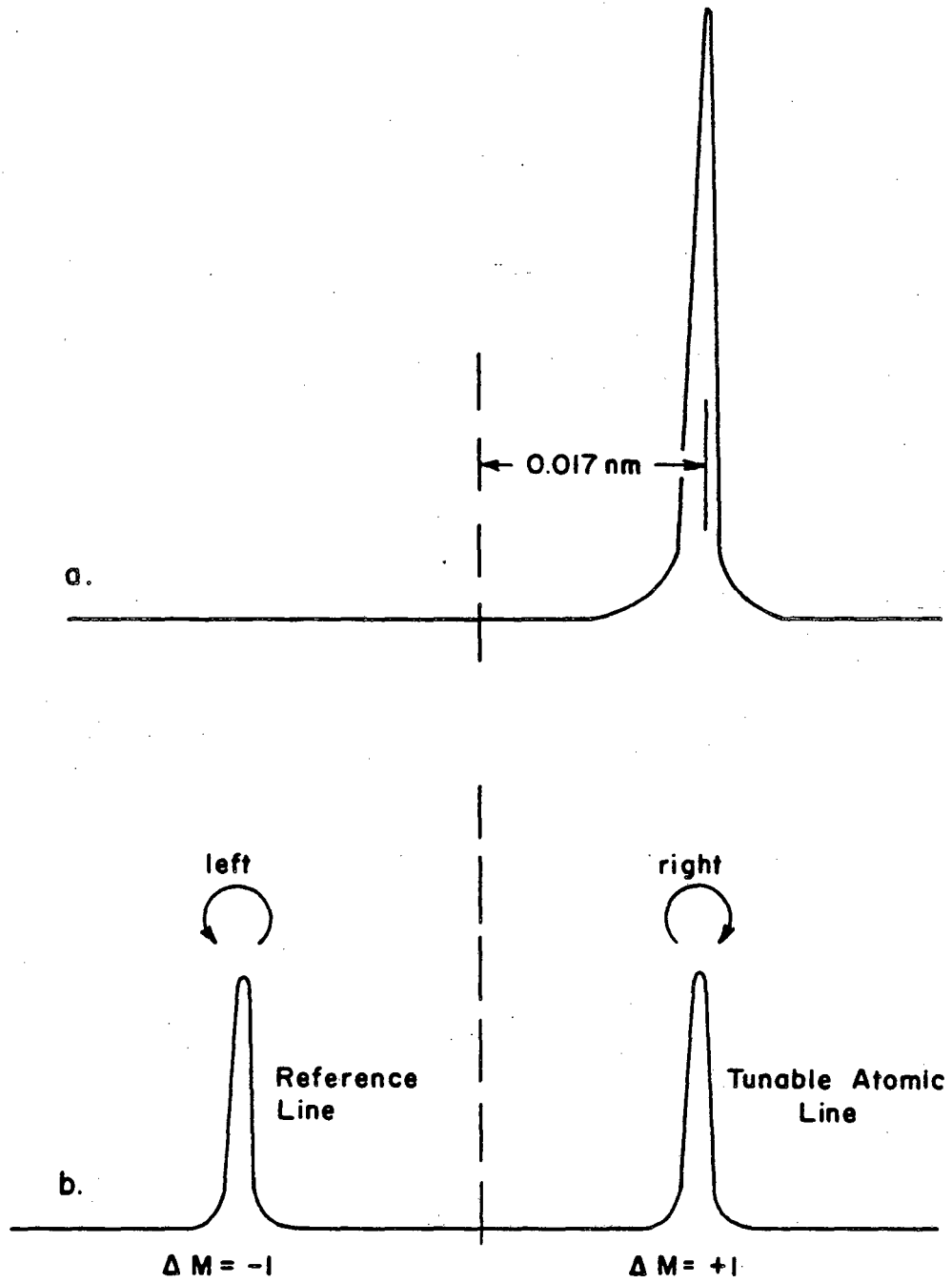
Fig. 5: high resolution absorption of NO obtained by TALMS measurement.

Fig. 6: high resolution absorption of NO₂ obtained by TALMS measurement.

Fig. 7: comparison of absorption spectrum of formaldehyde taken with instruments of different resolving power.

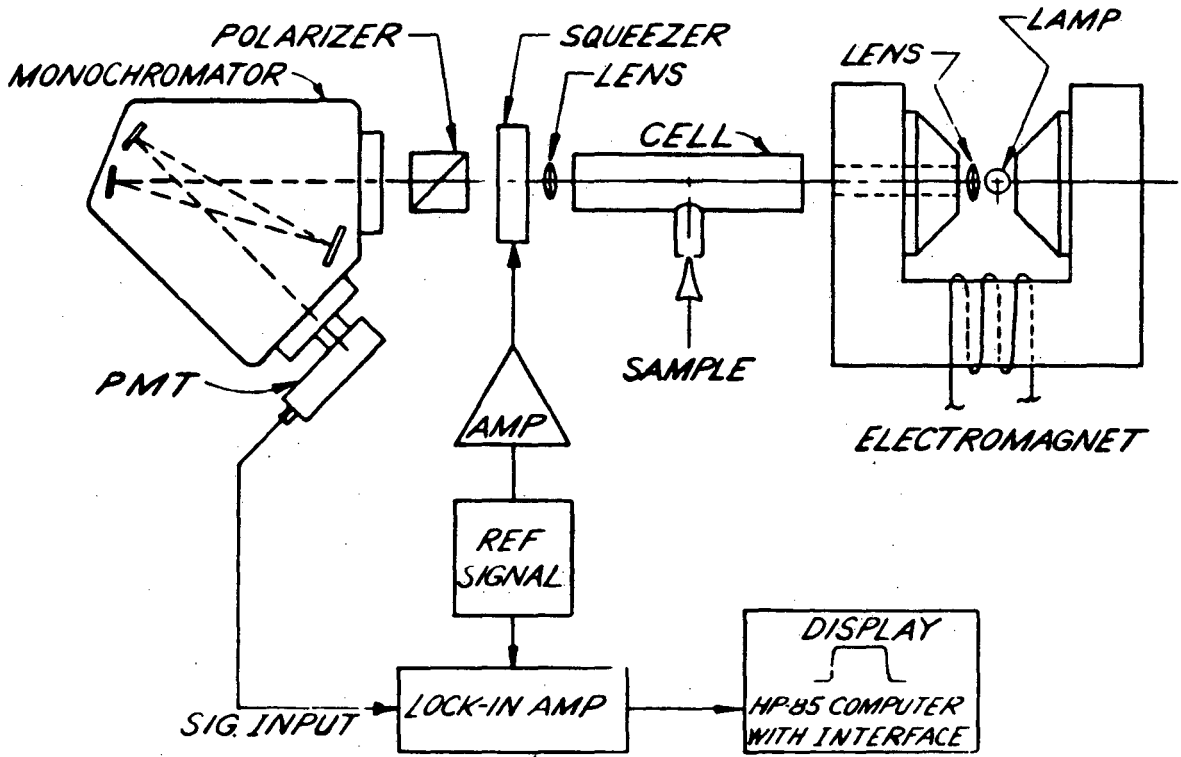
Fig. 8: sharp absorption feature in the spectrum of benzene.

Fig. 9: sharp absorption feature in the spectrum of chlorobenzene.



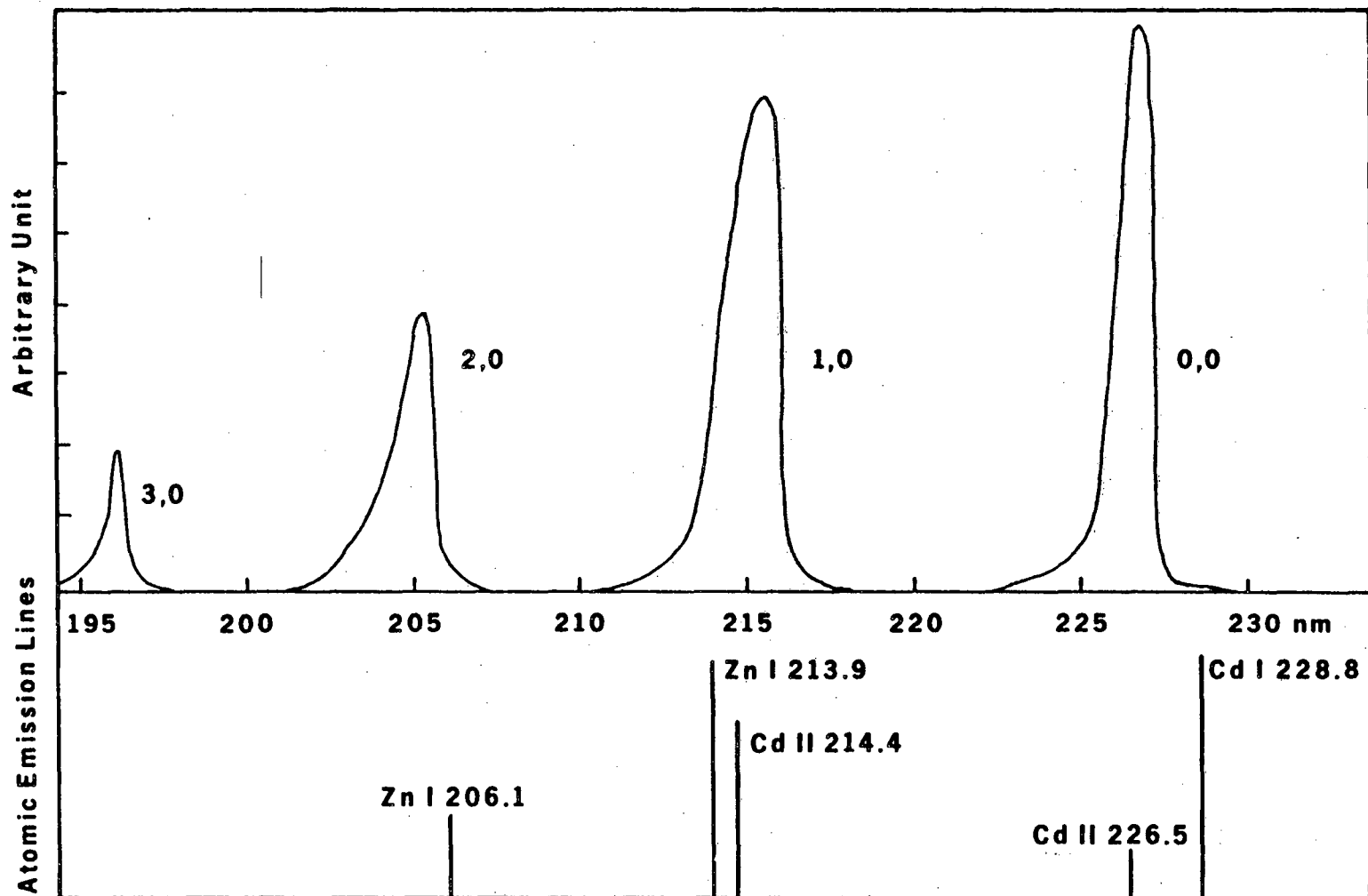
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Figure 1



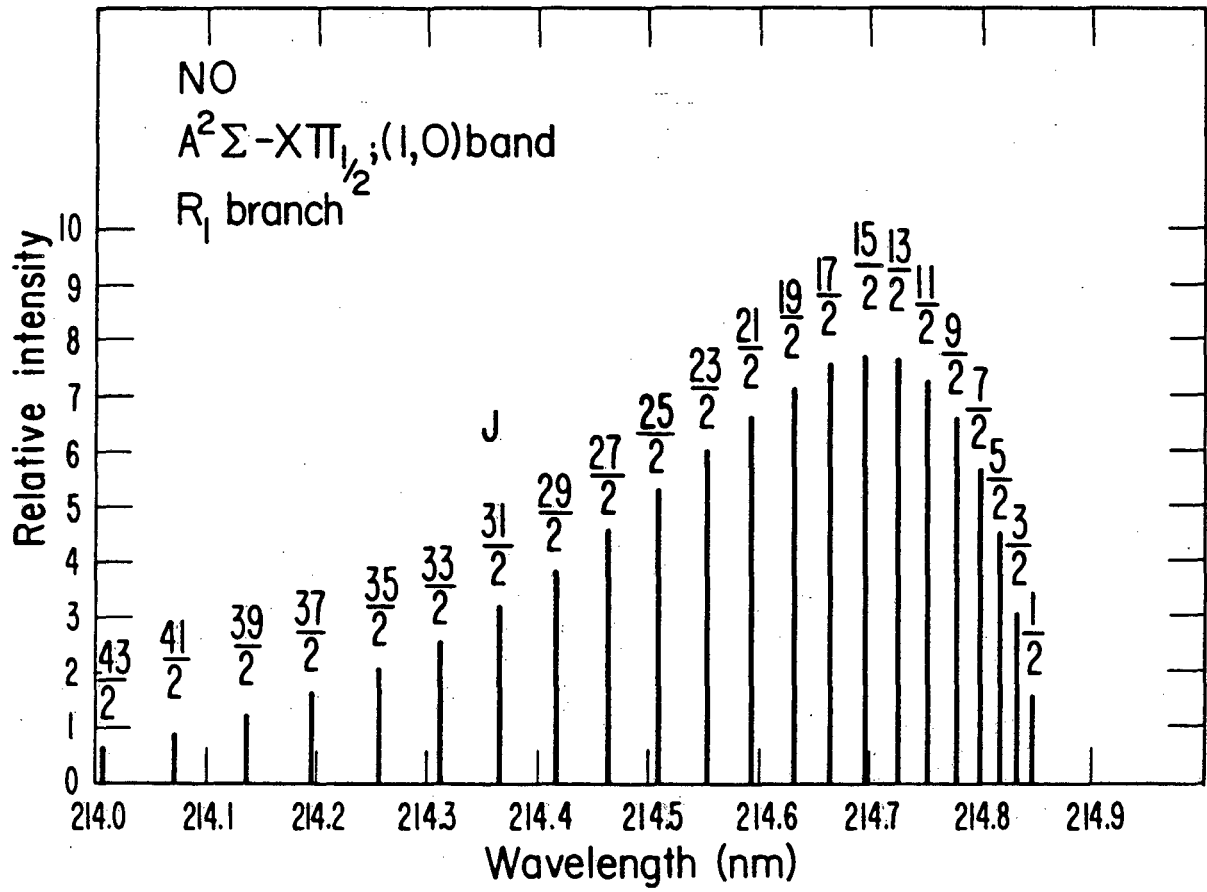
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Figure 2



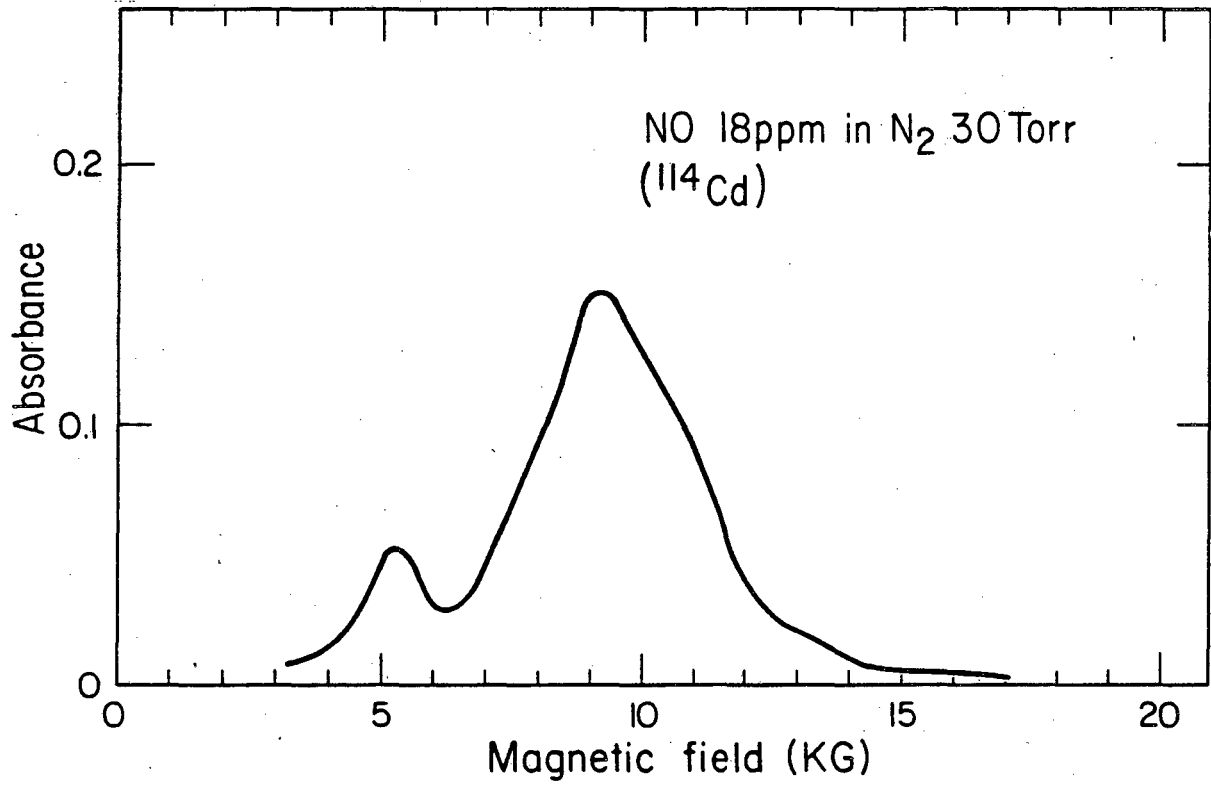
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Figure 3



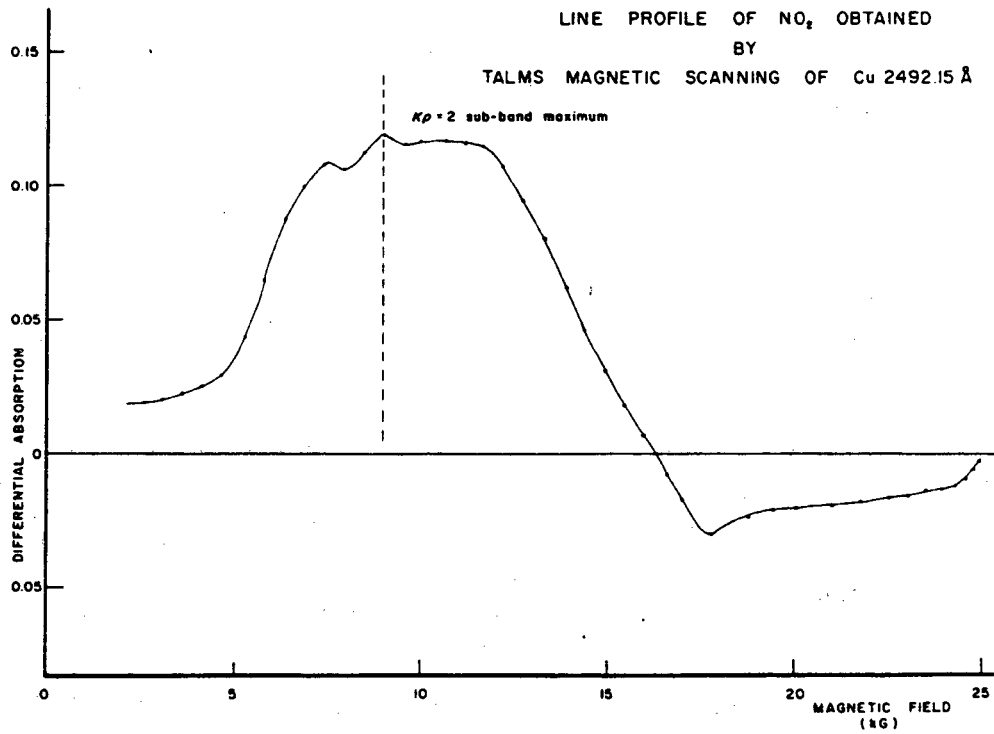
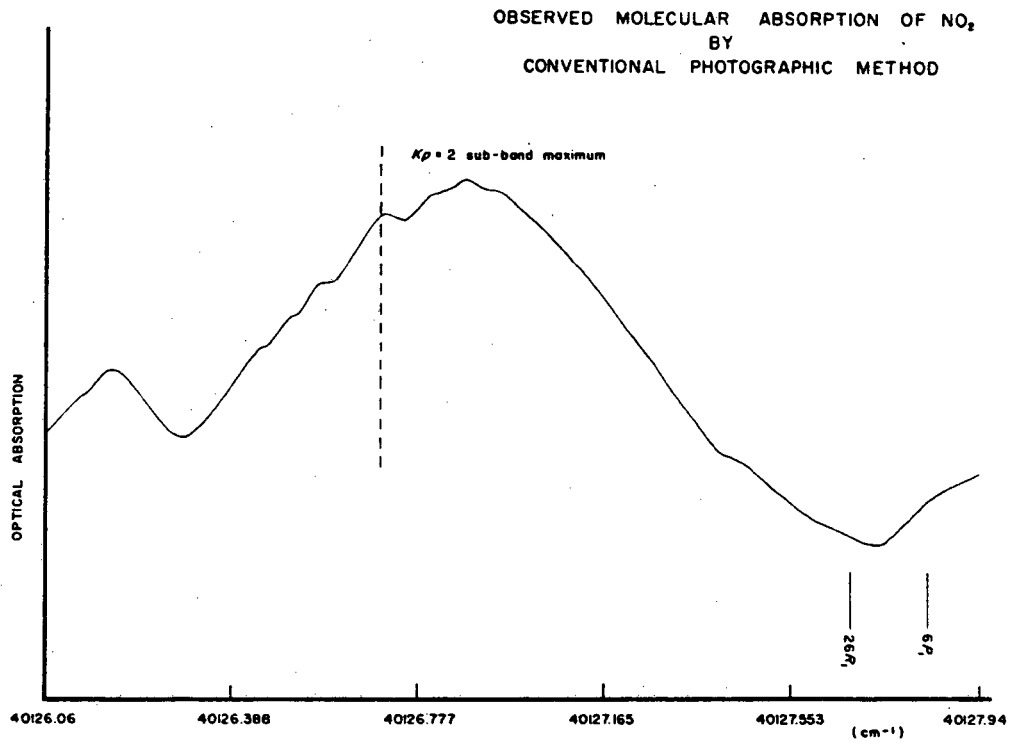
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Figure 4



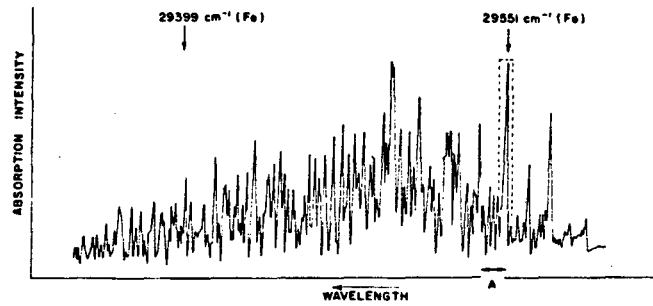
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Figure 5

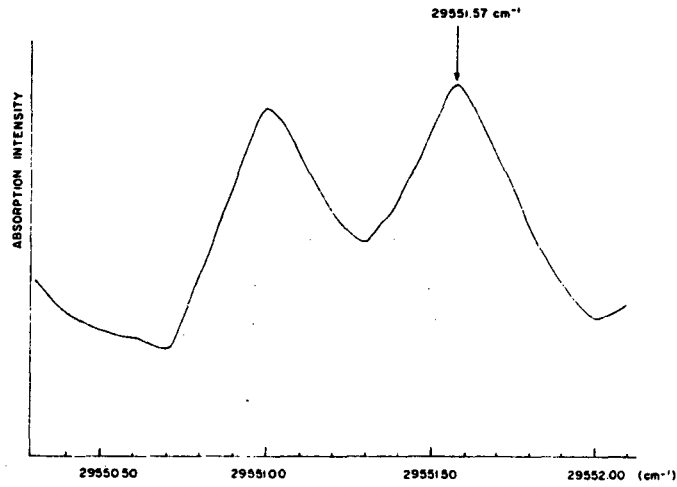


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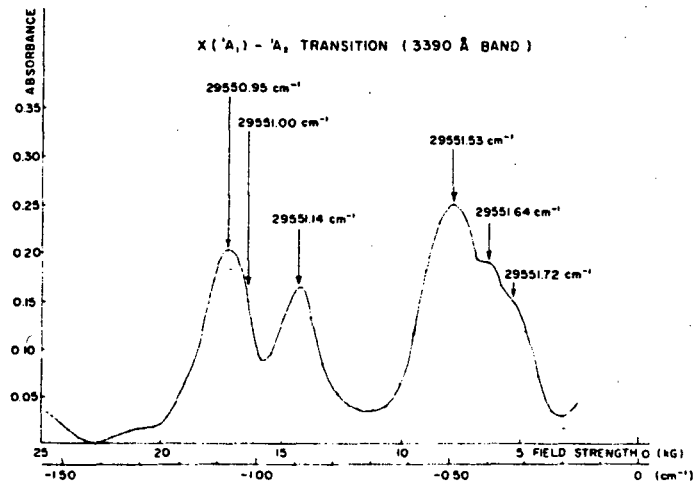
Figure 6



a. LOW RESOLUTION ABSORPTION SPECTRUM OF HCHO



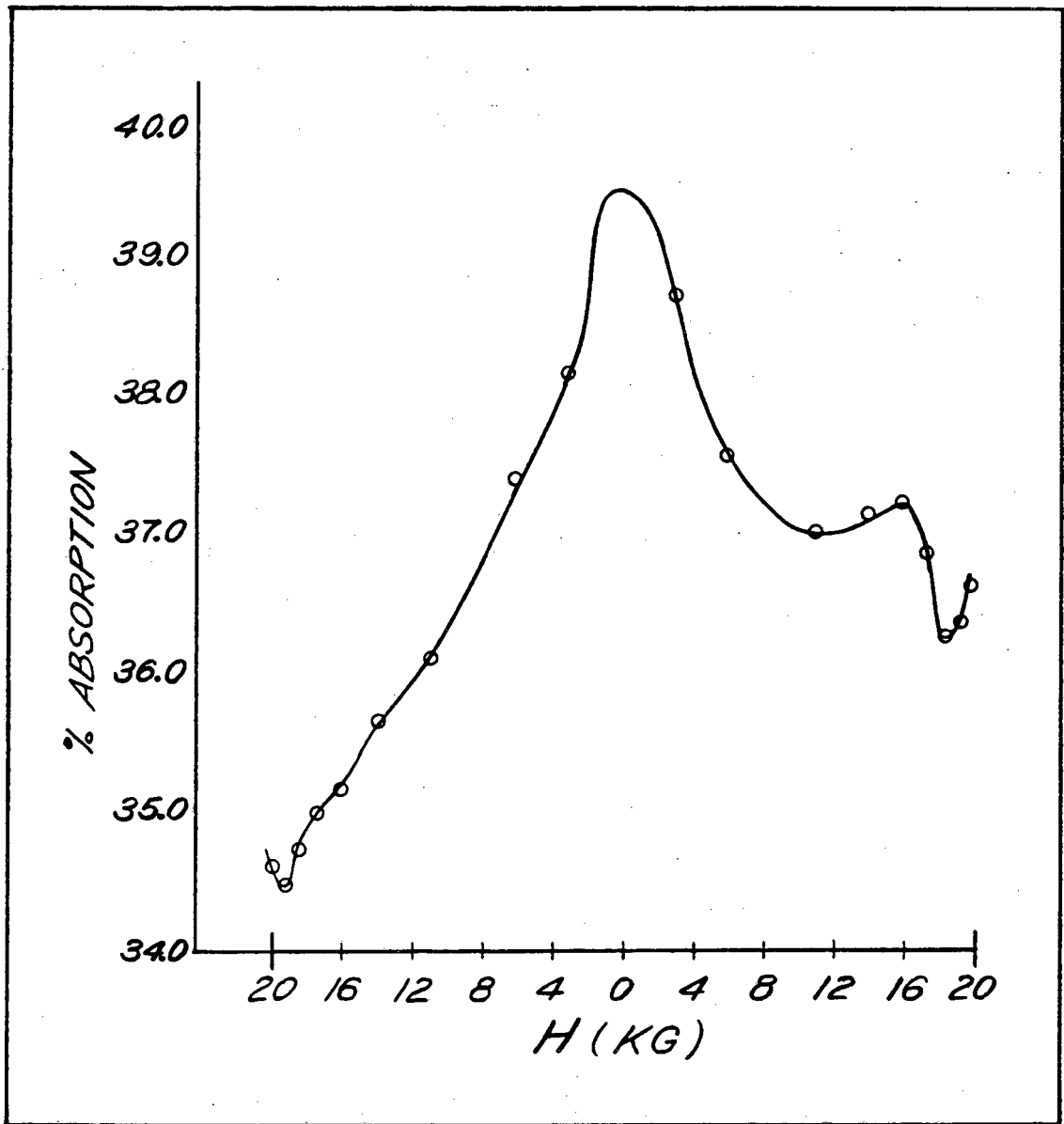
b. FABRY-PEROT INTERFEROMETRIC SCANNING OF SECTION "A" ABOVE



c. ZEEMAN SCANNING OF HCHO (Formaldehyde) BY Ag 3383 Å RESONANCE LINE

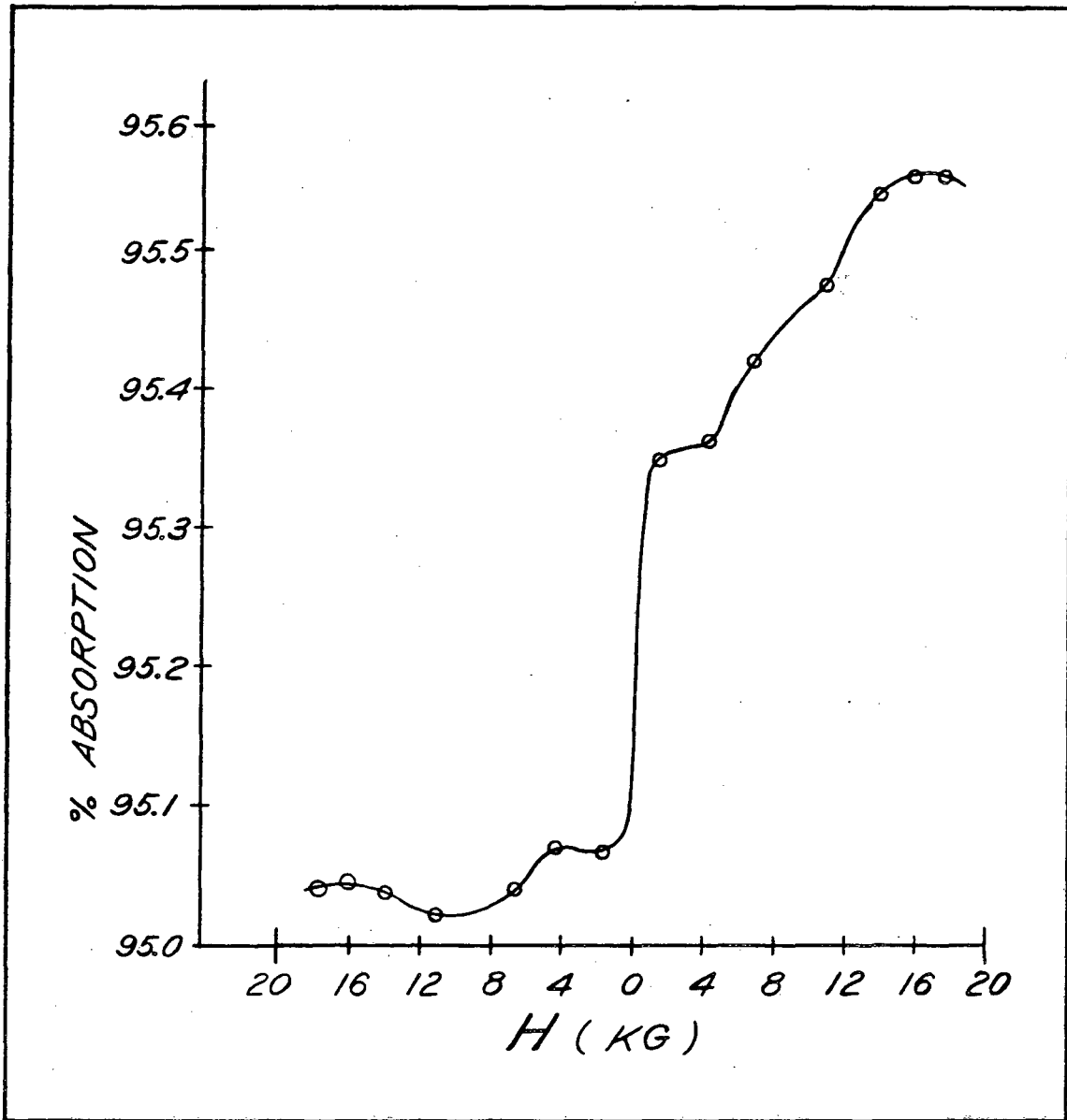
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Figure 7



XBL 817-10722

Figure 8



XBL 817-10723

Figure 9

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