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**ASSESSMENT OF ARGON ION LASER DISPERSIVE RAMAN  
SPECTROSCOPY FOR HOT CELL APPLICATIONS**

**WHC-SD-WM-RPT-098, REV.0**

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**July 29, 1994**

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**MASTER**

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## 1.0 INTRODUCTION

Characterization of high level waste (HLW) tank materials at Hanford is conducted to support safety assessments and waste treatment activities. Sample cores removed from these tanks come into hot cells as segments where they are extruded from sampling cylinders and subsampled for analysis. Approximately 150 tanks have been targeted for sampling in the next few years. Each of these tanks contains from one to more than twenty segments in a core sample depending on waste depth in the tank. Each segment may undergo homogenization, sample preparation and a number of analyses, depending on the needs of the customer.

Sample screening of the segment provides physical and chemical data which can assist in sampling and sample processing. Often the waste composition varies within each segment in a core. The waste may have the consistency of dry crystals, paste, dry crumbly solids and/or salt slurry. While the differences in these consistencies can be visually documented, the chemical composition remains unknown. Raman spectroscopy is expected to give chemical species information which may assist in defining layering in tank waste. Furthermore, the stratigraphy of each segment can be related to the total core to render a crude image of location of specific species within the tank. At the same time a rough indication of localized regions of high concentrations of particular species can be obtained which can further direct sampling of the segment. These regions may then be selectively subsampled and analyzed for the chemical species of concern. Additionally, samples which require homogenization may be processed and quickly checked for homogeneity during processing. A primary goal of this work was to provide operational parameters for Raman screening of core segments prior to detailed chemical analysis.

The present report describes the dispersive Raman system used in this year's investigation and the methodology used to collect and evaluate data taken on tank waste samples. Details of this work are furnished in the "Statement of Work for 1994 Activities" and the test plan, "Raman Program FY 94 Test" (Jewett, 1994 and Douglas, 1994). Spectra of expected tank constituents are shown. In addition, spectra and conventional laboratory results from archived tank waste are shown and discussed. Widely diverse tank waste matrices were investigated in order to test applicability to a representative range of tank materials.

The thrust of the HLW sampling and analysis effort is to acquire an overall composition of each tank. It is still important, from the safety assurance standpoint, that any large inhomogeneities within tanks are detected and recorded. Early knowledge of inhomogeneities in core samples can improve flow through the laboratory analysis process. Knowledge of layering within waste tanks can also improve waste retrieval and pretreatment efforts. Fiber optic Raman spectrometry has the potential to provide a quick and simple method of approximating sample composition and inhomogeneities which may be present.

## 2.0 BACKGROUND

Raman spectroscopy produces spectral information which may be used to identify molecules in solutions and solid materials. Like infrared molecular bonds. Unlike infrared spectra which results from direct absorption of infrared radiation, Raman shifts result from inelastic light scattering. This light scattering is dependent on the polarizability of molecular bonds. Therefore, nonpolar molecules, such as benzene and methane, provide strong Raman signals which are proportionately less intense in infrared spectroscopy. The similarities and differences between infrared and Raman spectroscopies make them complementary methods of analysis. For instance, Raman generally works better in aqueous mixtures because water is a strong infrared absorber. The water absorption masks analyte signals when conventional infrared absorption is used.

Raman speciation of major components expected to be found in Hanford HLW tanks was first attempted in 1992. The aim of this work was to define layering of materials in the waste tanks (Schlenoff, 1992). This work involved Florida State University. Westinghouse expanded the work to the characterization of simulants and real waste materials from tanks 241-BX-107, 241-BY-104, 241-T-111, and 241-T-107 during FY 1993. Oxyanions and ferrocyanide anions were successfully identified, (Crawford 1993a) generating optimism that the method could be extended to general molecular identification in tanks materials. The work described here extends the methods to analysis of several tanks matrices.

### 3.0 OBJECTIVE

The objectives of this work were to:

- obtain spectra of HLW samples using the Characterization Methods and Devices (CMD) developed dispersive Raman spectrometer.
- obtain spectra of pure materials expected to be found in HLW samples.
- analyze HLW spectra to determine what chemical composition information can be extracted.
- assess performance of the instrument and software in a radiologically controlled laboratory.

## 4.0 METHOD

Methods and system improvements have been pursued in order to provide spectral characterization of segments. Operation of the spectrometer system is outlined in the test plan (Douglas, 1994) and in the proposed procedure (Kunkel, 1994). These documents contain the collective methods describing the steps necessary for Raman data collection. The methods are a result of extensive system experience and collaboration between WHC and Florida State University.

The experimental conditions used to collect data from tank materials were as follows: the probe was immersed in the sample; the laser power was nominally 80 mW at the sample; the unfiltered Savannah River Laboratories (SRL) fiber optic probes (400  $\mu\text{m}$  for hood work and 600  $\mu\text{m}$  for hot cell work) were used; the connection for the spectrometer was a 400  $\mu\text{m}$  fiber optic; slit widths were set at 200  $\mu\text{m}$  with a 0.2 cm slit height; approximately 350 pixels were binned; detector temperature was maintained at  $-120\text{ }^{\circ}\text{C}$ ; total acquisition time was 1 minute. The only deviation from these parameters occurred while running the 241-B-202 tank sample. This sample was stored in a sealed vial and spectra were taken through the side of the vial; to avoid breaking the seal.

### 4.1 System Description

The system used for this work consists of three primary components and two software applications, which ran on a 486-PC computer. The spectrometer consists of: the laser source, the dispersive spectrometer, and the fiber optic cable that connects them to the sample (See figure 4-1). The fiber optics were constructed of high purity silica and were supplied by Savannah River Laboratories. The fiber optic probes consists of two 400- or 600-micrometer (core diameter) multi-mode fibers. The sample end is terminated with two chiseled fibers fitted with a quartz window. One fiber is the light delivery fiber; the other fiber receives backscattered light off of the sample surface, and transmits the light back to the spectrometer. The quartz window is placed at the position of greatest overlap between spot size and observation area (i.e., the coincidence plane).

The excitation source currently in use is an Omnicrome air-cooled argon-ion laser producing 200 mW of power at 514.5 nm, as measured at the laser head. The power delivered to the sample, through 15 feet of silica, fiber is estimated to be 80 mW with a divergent beam. The power estimation was based on rough measurements with a laser power meter.

Light collected in the returning fiber is fed through an optical train before entering the spectrometer. The optical train holds a collimating lens, a focusing lens and a notch filter. The notch filter is for rejection of the laser light (Rayleigh line).

The spectrometer is currently fitted with a 1200 groove/mm holographic grating, which creates a spectrum approximately 800 wavenumbers in width. The detector is a Princeton Instruments charge coupled device (CCD) chip with 1024 x 1024 detector elements. Approximately 150 to 400 pixels were "binned"

vertically to produce a single readout point on the spectrum. This configuration requires that the spectrometer be set to three different spectral windows to provide the data necessary for identifying oxyanion, ferrocyanide and organic species of interest. Setting the spectrometer to different spectral windows requires the supporting spectra (i.e., neon, tungsten lamp and probe response spectra) be recollected. The time involved in collecting the support spectra runs on the order of 10 to 15 minutes and severely limits this particular instrument's capabilities.

In order to facilitate data compatibility with Florida State University work, the spectrometer controller program used was the FSU RCAL (Raman Chemical Analysis Library) package. The RCAL package includes a spectrometer control program for data collection (CCF), a data treatment program (ACHEM), a calibration program (CLB), and a background removal program (BKG). Multiple versions of the RCAL package have been delivered to WHC, the 7/28/93 version was used for this work to maintain consistency in instrument operation. In addition, GRAMS/386 version 2.04B, a Graphical Relational Array Management System; marketed by Galactic Industries was used for data manipulation, comparison and graphics generation. Raw data was stored in binary, and ASCII formats using FSU's CCF software. All experimental parameters were documented within headers maintained with each file and in laboratory notebooks (Crawford, 1993b and Crawford, 1993c).

Raman shifts were calculated from pixel positions on the spectrometer with respect to laser frequency by calibration for linear dispersion. The result was calculated in ACHEM and transferred to GRAMS/386 for further processing. Raman shifts obtained in this way were corrected for wavenumber position on Galactic Industries' GRAMS/386 spectral processing software by recalibration from selected reference peaks. Within GRAMS/386 the wavenumber values were calculated by fitting a quadratic to pixel assignments for known neon emission lines. For the 580 nm window a cubic fit was used due to lack of neon emission lines.

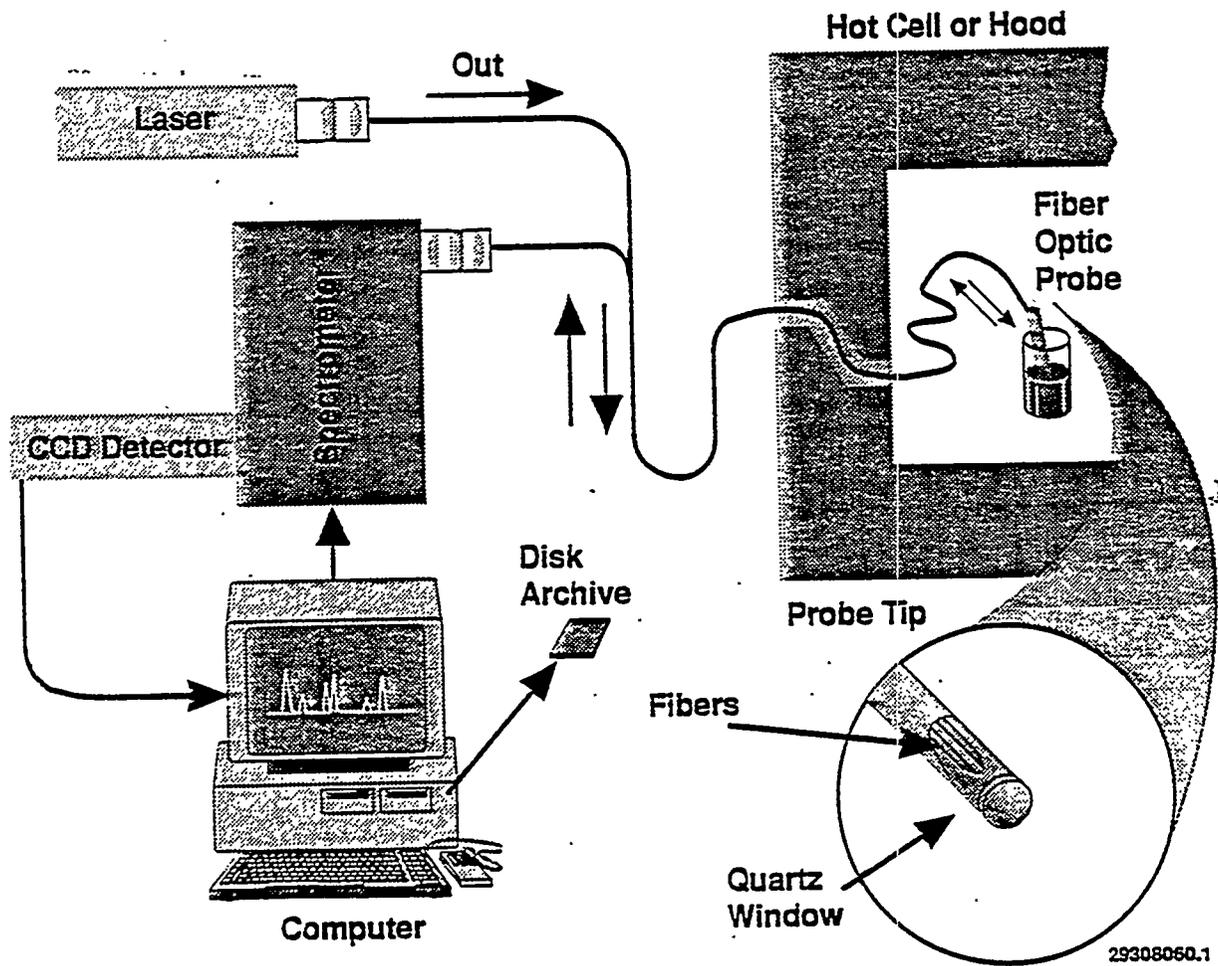
#### 4.2 Sample Presentation

Samples were presented to the probe by either immersing the probe directly into the sample or by spinning the sample at a fixed distance from the probe. Automated sample segment screening is under investigation for future work. This screening presentation will include stand off scanning along cores that are extruded in the hot cells.

The immersion technique was used to examine real tank waste samples in laboratory hoods and in hot cells where sample handling was difficult. Direct immersion of the probe required cleaning and contamination checks between analyses. Alternatively, probe cleanliness may be maintained by covering it with a polyethylene film. Regardless, probe cleanliness was checked by analysis of blanks between sample analyses.

Blank samples produce spectra containing distinctive silica peaks due to Raman scattering within the fiber optic, itself. When a probe cover is used

FIGURE 4-1 DIAGRAM - Dispersive Raman System



(i.e., in a hood as opposed to in the hot cell), polyethylene peaks are apparent in the  $2800\text{ cm}^{-1}$  region of the spectra. Raman peaks other than silica or polyethylene should not be apparent, however, on a clean probe.

The second sampling method uses a sampling jig which was developed at FSU. This jig spins the sample over the top of the probe window. Unlike immersion sampling, the probe is nominally 1 cm away from the sample. Sample rotation effectively averages out sample inhomogeneities (accounting for both composition and particle size). Therefore, this spinning method was usually the method of choice in most environments where the jig could be operated. This method was also used to obtain spectra for the spectral library to yield the highest quality spectra possible.

Eventually, samples will be rapidly scanned when they are extruded in the hot cells. In order to preserve sample integrity (i.e., control water loss) during spectroscopic sample screening, core segments must be scanned within one hour of extrusion. During this time the core must also be subsampled, and other data must be obtained. Therefore optical scanning must be accomplished in a timely manner with an optimal amount of information.

#### 4.3 Data Treatment

Comparison and familiarity with suspected tank constituents is necessary to quickly differentiate segments analytes. Table 4-1 lists compounds in pure form which are commonly found in tank waste samples. Peak positions provided in table 4-1 are taken from previous work (Crawford, 1993a) or have been obtained during library development on FSU AChem or GRAMS/386 software.

Table 4-1 - Common Tank Waste Analytes

Analyte	Observed Raman Shifts (cm <sup>-1</sup> )
Sodium ferrocyanide	2050, 2069, 2103
Sodium ferricyanide	2106
Potassium ferrocyanide	2128
Sodium nickel ferrocyanide	2106, 2143
cesium nickel ferrocyanide	2104, 2143
sodium sulfate	799, 994, 1124
sodium nitrate	774, 1068, 1384, 1664
sodium nitrite	831, 1239, 1336
sodium oxalate	887, 1358, 1458
sodium carbonate	1082
dimethylamine hydrochloride	976, 1384, 1631
cesium nickel ferrocyanide	2104, 2143
formamide	1115, 1140, 1325, 1405, 1605, 1687
methylamine hydrochloride	968, 1006, 1246, 1469, 1565

Because of particle size differences, sample surface drying, and other factors relating to presentation of solid samples to the fiber optic probe, the Raman spectra were not expected to be reproducible enough for direct analytical uses. However, analysis still might be obtained by rationing analyte peaks against those of an internal standard. Since nitrate is present in appreciable quantities in nearly all HLW, it could be used as such an internal standard. Furthermore, even if the nitrate concentration is not known for a sample, relative concentrations of the components could provide useful information about homogeneity and composition. In this way an estimation of the analyte concentration may be calculated. This estimate of concentration of a known analyte (X) in a sample is:

$$EST [X] = \{response X_{sample} / (response\ factor * response\ NO_3^-_{sample})\} * [NO_3^-]$$

where the response factor is a ratio of the response from pure analyte (X) divided by that of the pure NO<sub>3</sub><sup>-</sup>. In this way the response factor with respect to nitrate is based on a ratio which eliminates all other experimental parameters (i.e., matrix effects and sample/probe interface) and results in only Raman cross section differences.

## 5.0 DATA ACQUIRED

In accordance with the FY '94 test plan (Douglas, 1994), spectra were acquired for pure compounds. The pure compounds analyzed were those known from process history to have been put into tanks or those expected from hydrolysis of ferrocyanide compounds (Robuck, 1989). Some compounds (i.e. cyanate) show background fluorescence in the pure form. This fluorescence provides a basis for concern regarding the observation of fluorescence in real tank materials where the matrix is both unknown and highly complex.

Multiple measurements of archived waste samples from waste tanks were obtained. Tanks were selected which were expected to represent a wide gamut of waste types. The tanks chosen were: 241-T-107, 241-T-111, 241-B-202, 241-BX-107, 241-U-110, 241-SY-101, and 241-S-104. These include wastes of the following types: complex concentrate waste (SY-101), organic waste (B-202), bismuth phosphate process waste (U-110) and ferrocyanide waste (T-107). Waste tank samples were selected based on availability, concentration of target analytes and waste type.

### 5.1 Spectral Library Development

Spectra were obtained from eighteen pure compounds for purposes of comparison with spectra from real tank waste matrices. These spectra were obtained from expected ferrocyanide breakdown products, oxyanions and chelators, as well as organics such as tributyl phosphate (TBP). The list of reagents is provided in table 5-1, the spectra are contained in Appendix A.

All spectra were run under identical conditions. Each spectrum was acquired after a standard spectrum (i.e. sodium nitrate or sodium ferrocyanide) was obtained. Spectra obtained for pure sodium nitrate and sodium ferrocyanide produce clean spectra of comparable quality to those obtained by researchers at Florida State University (Schlenoff, 1992). Acquisition time per scan was 5 seconds with 10 scans co-added. This required slightly less than 1 minute total acquisition time. The center of the applicable spectral window is also provided in table 5-2. This window provides reasonable spectral results for the reagents listed.

The amounts of fluorescence background varied from nil to severe, depending on the compound. The spectrum of sodium cyanate indicates a sample which fluoresce (see Appendix A). Compounds used as the instrument performance standards (i.e., sodium ferrocyanide, and sodium nitrate) provide clean spectra without evidence of a fluorescence background. Other compounds which do not give background are tributyl phosphate, sodium carbonate, trimethylamine hydrochloride, and sodium nitrite.

### 5.2 Spectra of Actual Tank Waste

Results from Raman analyses of real tank waste samples are provided in appendix B. All spectra were run under identical conditions to those of the library compounds, with one minute total data acquisition time. The analyses

were performed on this time scale in order to examine the potential of the technique to provide reasonable spectra rapidly enough to preserve sample integrity without impacting processing.

#### Tank 241-B-202

The tank 241-B-202 sample shows strong bands which are attributable to polyethylene in the sheath used to cover the probe. These bands are located in the 2850 to 2890  $\text{cm}^{-1}$  region which is commonly recognized as the C-H stretch region in vibrational spectroscopy. The B-202 sample exhibits the strong silica background which is evident in most of the spectra obtained. In contrast, very little fluorescence background is evident in the spectrum. However, the silica contribution may be strong enough to mask the very weak band at 1060  $\text{cm}^{-1}$  which is common to the nitrate species.

#### Tank 241-S-104

There are no obvious peaks in the spectra obtained from 241-S-104 tank material. There is a possible band, however, which appears to be buried in noise in the spectral region where  $\text{NO}_3^-$  species are expected. The remaining spectral windows show gamma spikes but none of the resultant peaks could be attributed to Raman bands.

The presence of the weak nitrate band is surprising for this 241-S-104 sample considering the laboratory results. The analyzed concentration of nitrate for this tank is 18.0 weight percent. Other tanks such as 241-U-110 have lower analyzed concentration of nitrate but produce distinct peaks in the nitrate region. The absence of a stronger nitrate peak may be due to non-representative data or matrix effects.

#### Tank 241-U-110

The tank 241-U-110 sample produced similar results as the 241-S-104 sample. The concentration of nitrate was four times lower than that found in the 241-S-104 samples, however.

#### Tank 241-T-107

Spectra obtained from the tank 241-T-107 sample shows nitrate at 1066  $\text{cm}^{-1}$ . Other bands at 1822, 1882 and 2392  $\text{cm}^{-1}$  may be attributed to amines which are possible breakdown products of ferrocyanide hydrolysis in caustic media (Robuck, 1989). Amine bands have been observed in previous analyses (Crawford, 1993) of 241-T-107 tank materials.

#### Tank 241-T-111

Spectra obtained from tank 241-T-111 show significant residuals from silica subtraction. These residuals appear as slightly shifted bands under the more prominent silica bands (see Appendix B and the discussion in section 6.3 concerning silica response correction). There is a broad band in the 950 to 1100  $\text{cm}^{-1}$  region which is representative of the silica Raman response. This band totally obscures the nitrate region of interest.

Tank 241-SY-101

The spectra obtained from the 241-SY-101 composite sample provided a fairly clean nitrate band at  $1056\text{ cm}^{-1}$  on top of a fluorescence background. However, there was no apparent nitrite band which would be expected in this tank matrix. There is, however, a broad feature in the  $1300\text{ cm}^{-1}$  region where nitrite is expected to be found. This band is nearly buried in background noise. No other features are apparent in any of the spectral windows studied.

Tank 241-BX-107

Spectra obtained from tank 241-BX-107 samples are similar to those obtained in previous work (Crawford, 1993a). These spectra show pronounced fluorescence background after silica background has been removed. Interestingly, when  $\sim 830\text{ nm}$  excitation was used in previous work, spectral features were clearly apparent which showed the presence of nitrate in the sample (Crawford, 1993a). These spectra illustrate the effect of fluorescence at shorter wavelength.

Table 5-2 compares the Raman intensities with conventional laboratory analyses of tank constituents. The gross compositions of the waste samples are given with the spectral response of the Raman spectrometer. The first number given in each cell of the table is the anion concentration obtained by conventional laboratory means (ion chromatography). The number in brackets is the photon count rate obtained from the Raman peak during one minute of data acquisition. The reported result is corrected for background counts based on estimates of baseline count rate.

Background count results from all contributions (i.e., fluorescence, silica and nitrate) are provided in table 5-3. Silica background from the fiber optic provides the largest contribution to background. Samples from tank 241-T-111, 241-BX-107, 241-SY-101 and 241-S-104 produced fluorescence greater than the nitrate signal.

Table 5-1- Chemical Reagents for Spectral Library.

Reagent Name	Chemical Formula	Applicable Spectral Window(s) (in nm)
cesium nickel ferrocyanide	$\text{Cs}_2\text{NiFe}(\text{CN})_6$	575
dimethylamine hydrochloride	$(\text{CH}_3)_2\text{NH}\cdot\text{HCl}$	550, 600
formamide	$\text{HCONH}_2$	550, 600
methylamine hydrochloride	$\text{CH}_3\text{NH}_2\cdot\text{HCl}$	550, 600
sodium aluminate	$\text{Na}_3\text{AlO}_2$	no signal broad background
sodium carbonate	$\text{Na}_2\text{CO}_3$	550
sodium cyanate	$\text{NaOCN}$	575
sodium ferricyanide	$\text{Na}_3\text{Fe}(\text{CN})_6$	575
sodium ferrocyanide decahydrate	$\text{Na}_4\text{Fe}(\text{CN})_6\cdot 10\text{H}_2\text{O}$	575
sodium nickel ferrocyanide	$\text{Na}_2\text{NiFe}(\text{CN})_6$	575
sodium nitrate	$\text{NaNO}_3$	550
sodium nitrite	$\text{NaNO}_2$	550
sodium oxalate	$\text{Na}_2(\text{COO})_2$	550
sodium sulfate	$\text{Na}_2\text{SO}_4$	550
tetrasodium ethylene diamine tetraacetate dihydrate	$\text{Na}_4\text{EDTA}\cdot 2\text{H}_2\text{O}$	no spectra background
tributyl phosphate	$(\text{C}_4\text{H}_9\text{O})_3\text{PO}$	600
trimethylamine hydrochloride	$(\text{CH}_3)_3\text{N}\cdot\text{HCl}$	550, 600

Table 5-2 - Detectable Analytes in Tank Waste in weight percent

Analytes	Tank Identification							
	T-107 WT% Count	B-202 WT% Count	T-111 WT% Count	BX-107 WT% Count	U-110 WT% Count	SY-101 WT% Count	S-104 WT% Count	Expected LOD
Na <sub>2</sub> SO <sub>4</sub>	1.0 [ND]	0.17 [ND]	0.36 [ND]	1.4 [ND]	0.09 [ND]	0.21 [ND]	0.23 [ND]	1.4 [ND]
NaNO <sub>3</sub>	7.6 [191]	6.4 [15]	4.1 [252]	15.0 [ND]	3.6 [149]	11.4 [652]	18.0 [25]	N. K.
NaNO <sub>2</sub>	1.2 [ND]	0.11 [ND]	N.R. [ND]	0.9 [ND]	N.R. [ND]	10.8 [ND]	1.8 [ND]	1.1
Organic Carbon	0.17 [NA]	0.32 [NA]	0.29 [NA]	0.06 [NA]	0.28 [NA]	1.2 [NA]	0.17 [NA]	[NA]
Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.K.
Na <sub>2</sub> CO <sub>3</sub>	0.42 [ND]	0.26 [ND]	0.08 [ND]	0.12 [ND]	0.22 [ND]	0.38 [ND]	0.38 [ND]	N.K
EDTA	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.K.
Fe(CN) <sub>6</sub> <sup>n-</sup>	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	N.A. [ND]	0.3

LOD is limit of detection as determined by FSU (ref.5)

N. D. is not detected  
 N. K. is not known  
 N. A. is not applicable

### 5.3 Data Summary

The limit of detection for  $\text{NaNO}_2$  in solid  $\text{NaNO}_3$  as measured by FSU is 1.1 weight percent (Schlenoff, 1992). Tanks 241-T-107, 241-SY-101 and 241-S-104 exceed this concentration according to ion chromatography results (see table 5-2). In addition, sulfate peaks should be evident in tank 241-BX-107 and possibly tank 241-T-107 samples, as both samples are at or near the detection limit for  $\text{Na}_2\text{SO}_4$  in  $\text{NaNO}_3$ .

As indicated in table 5-3 all samples contain at least 1 weight percent nitrate, so they should produce nitrate bands in the  $1050$  to  $1075\text{ cm}^{-1}$  region. Results from this table, and from the spectra attached in appendix B, clearly illustrate the problem associated with subtraction of large signals to yield small numerical results. Furthermore, it is apparent from the count results that nitrate attributed counts are not related to the analyzed concentration from tank to tank. This may result from signal subtraction errors, fluorescence interference, matrix effects which vary between tanks, or non-representative sampling. For future work, it is important to consider that these tank to tank discrepancies should not effect comparison of nitrate and analyte results within an individual tank.

All of the waste tank spectra exhibit a great deal of silica background and fluorescence. Fluorescence yields a large broad background in which the smaller Raman peaks are embedded. The effect of this fluorescence, coupled with prominent Raman signals from the silica in the optical fibers, is to "bury" the desired Raman signals. Accordingly, only the relatively strong Raman signals due to nitrate have been observed in HLW samples with this system. Even these peaks can not be seen in some samples. This makes ratiometric results impossible to calculate (see Appendix B and table 5-3).

Due to fluorescence and silica background interferences the quality of data obtained from tank samples with this system (see appendix B) were not high enough to perform ratiometric comparisons with nitrate. In all of the tank material spectra the silica background completely, or nearly completely masked the analytical Raman peaks of interest. Subtraction of the silica "reference" spectrum yielded data of such low signal quality that only the strong nitrate peak (at  $\sim 1068\text{ cm}^{-1}$ ) was distinguishable. In most of the subtraction cases, the signal intensity was reduced by an order of magnitude or greater, making the noise a significant factor. Removal of the fluorescence background when present, through GRAMS/386 applications, yielded no detectable Raman peaks. A multi-point interactive background/baseline correction routine within GRAMS/386 was used.

Two methods are commonly employed to eliminate fluorescence interference in spectra: mathematical signal manipulation and/or selection of a longer wavelength laser for excitation (Measure, 1979). In this work, background fluorescence was eliminated by mathematical treatment. Fluorescence background removal was accomplished by tracing the background observed and defining its intensity. The resultant baseline is subtracted from the original spectrum.

Results are not consistent when several data manipulations are performed simultaneously, as in the mathematical treatise. The inconsistencies occur because of two problems: first of all, the fluorescence signal itself is noisy; second, methods for background subtraction are not reproducible. The presence of noise in the fluorescence signal creates a condition in which the spectra can not be reproduced from one spectrum to the next. This lack of reproducibility complicates the subtraction of background. Therefore, methods for background subtraction have not been established and the first problem must be solved in order to make the methods viable.

Perhaps the second option for eliminating fluorescence is more feasible. In work on another project, Fourier Transform Raman Spectra of sodium cyanate and tank 241-BY-104 tank simulants and solid wastes have been obtained using 1064 nm excitation. In stark contrast to results obtained with the dispersive instrument operated with 514.5 nm excitation, silica background and fluorescence is minimal in the FTRaman spectra (see figure 5-1).

FIGURE 5-1 - Cyanate spectra at 514.5 nm and 1064 nm

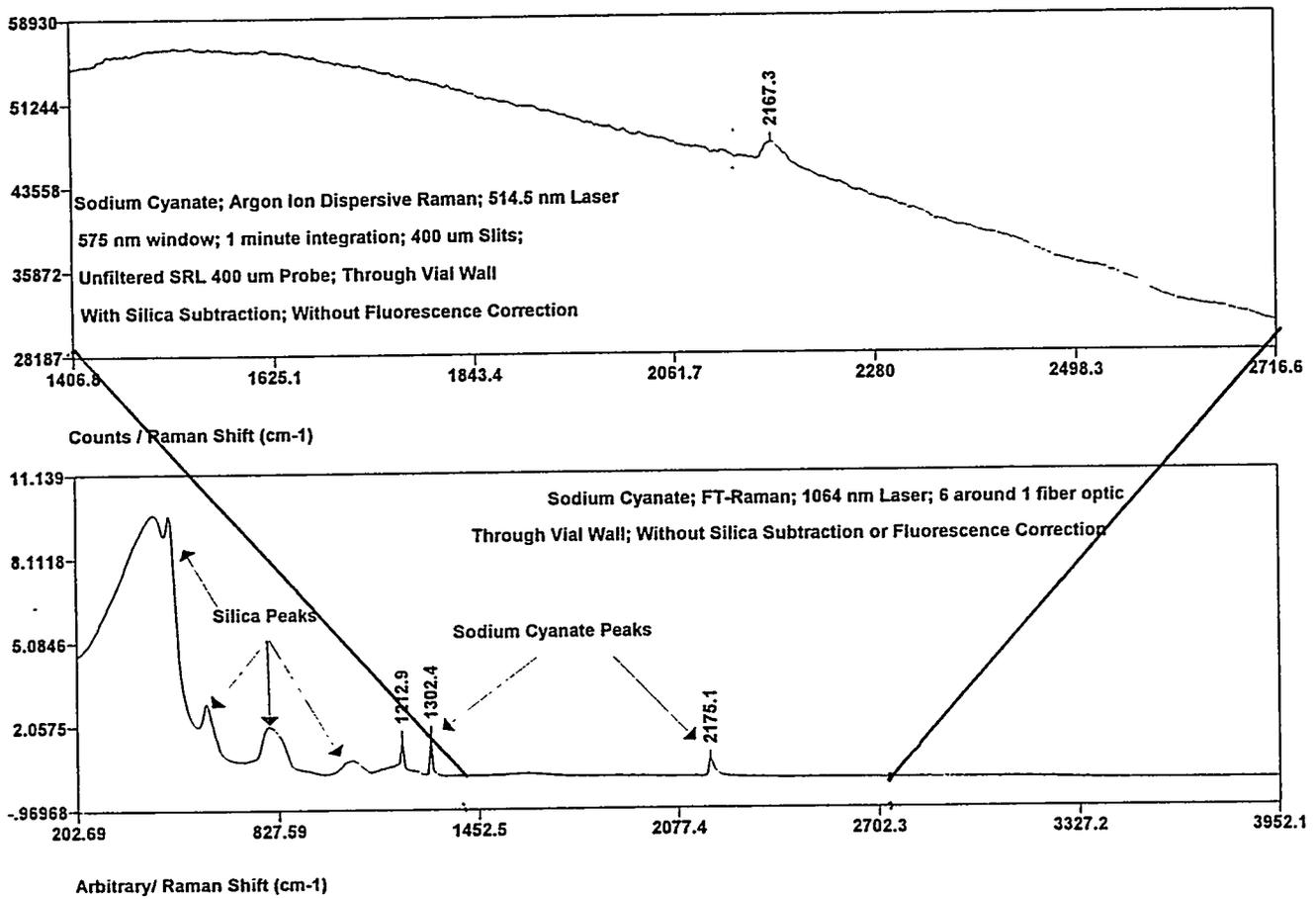


Table 5-3 - Fluorescence and Silica Background in counts per minute

Tank ID	conc. NaNO <sub>3</sub> (wt. %)	Fluorescence Background	Silica Background	NaNO <sub>3</sub> contribution
T-107	7.6	39	4562	191
B-202	6.4	8	1390	15
T-111	4.1	997	7404	250
BX-107	15.0	4176	12490	0
U-110	3.6	147	16950	149
SY-101	11.4	4357	11114	652
S-104	18.0	58	1502	25

## 6.0 SYSTEM ASSESSMENT AND IMPROVEMENTS

The assessment which follows includes a discussion of instrument modifications made during instrument development and how these changes affected data quality, instrument versatility, and ease of use. The instrument software and hardware were assessed to investigate how they affect the data obtained. These assessments were made before and after modifications were made to the instrument. Interferences and data treatment techniques are also discussed.

### 6.1 Instrumentation Improvements

Two major parts of the Raman system (i.e., the spectrometer, and fiber optic) were modified prior to data collection in attempts to improve the overall system performance. A third component, the laser source was changed in the previous year's work.

The laser source frequency was changed from 830 nm to 514.5 nm during last year's work (Crawford, 1993a). This modification was expected to improve signal intensity because the efficiency of Raman scatter increases as the fourth order of the excitation frequency. Unfortunately, two other major contributions occur at lower wavelength concurrently. Both the silica Raman response and the fluorescence in samples increases, making some sample analyses impossible.

The grating for the spectrometer was also changed in order to improve system light throughput. The grating originally in the spectrometer was blazed for use at 830 nm. The one currently being used is optimized for use at 514.5 nm. Upon change out, the total light throughput of the system was improved by a factor of two. Since all light throughput was equally effected this had little effect on the resultant Raman signal, however.

Finally, a series of filters were used with the fiber optic in attempts to eliminate silica background. A comparison of results obtained with the original unfiltered probes and those with silica rejection filters show signal-to-noise for unfiltered probes on solid sodium nitrate and sodium nitrate solution (see table 6-1 for results of the filter probe tests). Duplicate spectra were obtained from the original SRL probe and a new probe in which silica rejection filters were installed. The information provided in table 6-1 is with no filters installed (No Fltrs 1 and 2), with the original SRL unfiltered probe (Unfiltered 1 and 2), the silica rejection filter removed (Laser Fltr 1 and 2), and both filters in place (Both Fltrs 1 and 2). The raw data (CR) and the spectrometer response corrected data (DW) was analyzed. The Silica to Nitrate peak response was measured in addition to the signal-to-noise for the nitrate peak.

The results show that the silica-to-nitrate ratio for solid sodium nitrate is highest for the solid sample. The silica to nitrate ratio is highest in the original probe for solutions. This may be due to placement of the focal plane for the probe as designed. In other words, scattered light is not as easily collected through the depth of the sample (i.e., in solutions) when the focus is set for the sample surface as in the solid sample.

Regardless, the signal-to-noise measurements made on all probes for nitrate indicate that while the filtered probe may eliminate silica efficiently the nitrate signal is also compromised. The highest signal-to-noise ratio obtained for both samples was with the original probe. Therefore, based on these tests, the original probe was used for the tests reported here.

Table 6-1 - Filter tests for Fiber Optic

Filtered Probe Evaluation:

Solid Sodium Nitrate - NaNO <sub>3</sub> (s) Signal to Noise Ratios								
	Unfiltered 1	Unfiltered 2	Both Ftrs 1	Both Ftrs 2	Laser Ftr 1	Laser Ftr 2	No Ftrs 1	No Ftrs 2
bckgrd avg.	693.968	587.597	88.0365	-310.007	635.582	541.258	831.458	558.425
std. dev.	29.811	20.0547	23.5665	25.9027	24.2674	108.842	63.8701	38.04
variance	894.669	402.191	555.378	670.948	588.906	11846.6	4078.39	1298.68
I (@1068)	72090	71954	82362	30688	46760	47716	22126	25108
S/N	2380.28	3558.59	1370.33	1196.71	1900.67	433.42	333.40	681.18

Solid Sodium Nitrate - NaNO <sub>3</sub> (s) Peak Ratios								
	Unfiltered 1	Unfiltered 2	Both Ftrs 1	Both Ftrs 2	Laser Ftr 1	Laser Ftr 2	No Ftrs 1	No Ftrs 2
SI (@~796) CR	31914	31812	8901	8430	35958	34228	27749	29319
SI (@~796) DW	66260	66024	17580	16590	74931	71218	57473	60825
I (@~1068) CR	48381	48438	21853	20750	37940	37619	21515	23738
I (@~1068) DW	94779	94892	42046	39868	74079	73358	41640	45850
S/I CRD	0.6598	0.6586	0.4073	0.4063	0.9478	0.9099	1.2895	1.2351
S/I DWT	0.6991	0.6958	0.4184	0.4161	1.0115	0.9708	1.3836	1.3237

Saturated Sodium Nitrate Solution - NO <sub>3</sub> <sup>-</sup> (aq) Signal to Noise Ratios								
	Unfiltered 1	Unfiltered 2	Both Ftrs 1	Both Ftrs 2	Laser Ftr 1	Laser Ftr 2	No Ftrs 1	No Ftrs 2
bckgrd avg.	146.574	90.688	-430.755	-480.57	-10.7552	-122.756	932.28	820.534
std. dev.	7.69314	10.9749	22.0026	22.605	29.8122	24.4272	138.09	183.323
variance	59.1843	120.448	484.115	520.07	876.883	596.687	19069	18133.4
I (@1050)	10896	11167	4982	4960	7200	7053	10062	10121
S/N	1397.63	1009.24	246.01	237.69	243.51	293.76	68.11	88.51

Saturated Sodium Nitrate Solution - NO <sub>3</sub> <sup>-</sup> (aq) Peak Ratios								
	Unfiltered 1	Unfiltered 2	Both Ftrs 1	Both Ftrs 2	Laser Ftr 1	Laser Ftr 2	No Ftrs 1	No Ftrs 2
SI (@~796) CR	1491	1453	4817	4595	18682	18638	39721	39767
SI (@~796) DW	1931	1854	8539	8497	38373	38231	82830	82984
I (@~1051) CR	6343	6478	5493	5462	11855	11295	19977	20008
I (@~1051) DW	11501	11783	8816	9793	21487	21845	38659	38713
S/I CRD	0.2351	0.2243	0.8405	0.8382	1.6453	1.6501	1.9883	1.9878
S/I DWT	0.1878	0.1573	0.8689	0.8677	1.7859	1.7911	2.1426	2.1431

## 6.2 Software

While it is desired to provide a turn-key system for routine application to waste characterization, the state of our knowledge about Raman spectroscopy of these inhomogeneous solids demands that the system have great versatility, so that operating parameters may be changed quickly. The dispersive Raman software, supplied by FSU, is not designed with versatility in mind, so it is difficult to operate in a developmental mode. The CCF software used for data acquisition has redundant steps. One step includes log-in each time the operator exits before the last menu. In addition, each time the spectrometer is operated whether the grating is moved or the slits are adjusted, the same four condition questions are asked before the system begins to collect data. Several situations have occurred in the past where the system randomly rebooted even during data acquisition. In general, the system has been set up to run with multiple screens and requires specialized expertise. Furthermore, the entire RCAL package has not undergone verification or validation.

Problems noted with the CCF program focus primarily around an unfriendly user interface. CCF requires multiple key strokes and multiple menu selections to accomplish tasks. For example, to change the spectrometer's wavelength value in CCF, one must traverse through 4 screens to enter the new value. Furthermore, CCF displays three separate verification screens before a spectrum can be collected and saved, with each screen requiring a <yes> or <no> answer. Extensive expertise is required to perform functions in CCF efficiently. In the RCAL package, data treatment calls for the use of the separate programs, ACHEM, BKG and CLB. This situation requires the user to continually switch from program to program to perform routine tasks.

Another problem experienced with the CCF controller software was outright program failure. Originally, this effect was attributed to the use of Windows<sup>®</sup> 3.1 with the program, but experience does not corroborate this theory. If meticulously operated, the software will function normally; if a few inadvertent keystrokes are made, however, the software will fail to work, and may completely reboot the computer (i.e., the software is not stable with respect to normal keyboarding errors). This situation, when added to the complexities of operation mentioned above, creates a difficult and unreliable operating software program for the user.

No fatal program errors have been encountered with operating the ACHEM or CLB programs. As in the case of the CCF package, however, these programs are intricate and difficult to operate without experience. These user prompts do not provide adequate cues even for people with the data processing concepts.

The BKG program offers a single background removal feature, consisting of a line fitting function to replicate the background. The user defines the order of the function and the points which define the line, BKG then calculates the simulated background and allows for its subtraction from the original data.

In order to expedite data treatment processes, a commercial software package was purchased. GRAMS/386, from Galactic Industries, was chosen due to its power, flexibility, and ease of use. The GRAMS/386 program allows the user to do as much or more than the RCAL package, within a commercially tested product. An example of GRAMS/386's flexibility is the variety of fluorescence background removal routines available. As opposed to RCAL, GRAMS/386 gives the user a choice between six types of background removal, including the method used by RCAL/BKG. The spectra contained in Appendix B were all produced using the GRAMS/386 program, after collection of the Raman data via RCAL/CCF. In addition, GRAMS/386 imports multiple types of spectroscopic data and allows for the integration of instruments operating under different software packages.

### 6.3 Spectral Interferences and Data Quality

As mentioned in section 3.3, the quality of the data obtained and the limits at which analytes are detected is severely affected by the background observed in each of the spectra. The background contribution due to Raman signal from the silica fiber is devastating. Also, certain components of the waste fluoresce when excited at 514.5 nm. When many of the compounds are present in a sample the background can be significant.

By far, the most troublesome spectral interference encountered was the Raman response from the silica fiber optics. The greatest effect of the silica interference is observed in the 550 nm region, where nitrate and the other oxyanions produce Raman peaks; the silica Raman peaks are much broader than the analytical Raman peaks due to the amorphous structure of silica. In fact, the sodium nitrate peak normally found at  $1068\text{ cm}^{-1}$  lies on the shoulder of a silica peak at approximately  $1056\text{ cm}^{-1}$ . This proximity creates a serious problem in tank material spectra. The typically strong nitrate peak is almost completely hidden by the silica interference. Simply put, the silica response hides most or all of the analytical Raman peaks in samples that give weak signals, like tank materials.

Subtraction of the silica fiber optic response is possible, though not always successful. Spectra of pure materials show strong analytical Raman peaks, but even after subtracting, unsubtracted or incorrectly subtracted silica peaks may remain in the spectrum. With the very weak signals obtained from tank materials, subtraction of the silica response is difficult and provides questionable results.

Some thought has been given to why the silica response does not properly subtract out. One possibility may be due to spectral shifts caused by temperature differences between runs. A second hypothesis focuses on changes in the fiber optic. Indeed, the silica response changes depending on the physical state (i.e., bends, twists, or turns) of the fiber optic, as noted by SRL researchers during the November 1993 technical exchange. Finally, the tanks do contain varying amount of siliceous material which may contribute to the signal.

The silica response in the 580 (or 575) nm and 600 nm windows does not initially appear as a major problem; the silica peaks in these regions are less prominent than the peaks in the 550 nm window. Upon subtraction of the silica response, it is apparent that the signal intensity is greatly reduced. The silica spectrum is normally taken at exposure times twice as long as the sample spectra, and yet the noise left after subtraction is substantial. In many cases the signal of an analyte peak may be an order of magnitude lower than in the original spectrum.

A higher laser wavelength would reduce the extremely strong silica Raman peaks noted. Past research has shown that the argon ion laser wavelength is in a high attenuation region for the silica fibers. Hence, the Raman response in silica at this wavelength is high (Greenwell, 1992). The same study indicated that lasers in the 780 to 1064 nm range produce lower silica response. An indication of this advantage was illustrated in FY '93 work when the diode laser, operating at 840 nm, produced less silica response. Investigations using a 780 nm laser and a dispersive Raman system, or a Fourier transform Raman system should be undertaken to avoid the noted silica interference with this argon-ion laser based instrument.

As stated earlier, fluorescence background may also contribute to subtraction errors which effect data quality. Complex mixtures such as waste tank samples, which have a potential to contain many fluorescing species, are almost certain to fluoresce. The background caused by fluorescence is much broader than the Raman peaks. It is most pronounced at higher energies (i.e., lower wavelengths). The argon-ion laser used for this work stimulated fluorescence in most tank materials and in some of the library samples examined. The most prudent option for reducing the occurrence of fluorescence also appears to be the use of a longer wavelength excitation source.

## 7.0 CONCLUSION

The work completed this year and last year clearly show that collection of useful Raman spectra from tank materials is possible under the correct conditions. Continued development of remote Raman techniques for hot cell screening is recommended, though modifications to the current direction of development need to be made. The current argon-ion Raman system is not suitable for screening of tank cores. The primary factors which hinder the current system are the silica interference, the fluorescence interferences and the extensive time required to collect and treat the data.

At the outset of this work, it was assumed that tank waste samples could be readily analyzed using the dispersive CCD-based Raman Spectrometer. This assumption was founded on the ability to analyze single components many of which are free from background interferences. Fluorescence creates a complex problem when applied to real tank waste, however, since many of the components in the waste are potentially fluorescent, and a combination of them may overwhelm the weaker Raman signals.

Silica background presents an even greater interference, due to the low wavelength of the laser light. Attempts to eliminate the silica background with filters have not completely eliminated all spectral features due to silica, as shown in spectra in Appendix B. In addition, spectral anomalies resulting from background oversubtraction are common. The source of these anomalies may be related to bending of the fiber optic, silica from the samples themselves or a combination of the two. The origin of this interference is not entirely understood.

Based on observations in this work, it is apparent that further developmental work is required to provide a turn-key spectrometer that can be used for direct analysis without complex data manipulation routines. In order to incorporate and test these changes the instrument should be tested in a "non-application" environment. It is therefore recommended, that further testing on radioactive samples be delayed until successful demonstrations have been completed on complex synthetic mixtures. The "successful" instrument would show improvement in both operational utility and data acquisition methods.

The following options should be pursued to provide the laboratory with a usable remote Raman screening system. The laser source must be changed to reduce silica and fluorescence interferences and improve quality data. The use of Fourier transform Raman spectroscopy should be investigated based on promising results to date. More efficient filtered fiber optics should be developed for use with the argon-ion laser excitation, if it is pursued further. Non-contact methods should be explored in order to mitigate the silica interference and probe contamination concerns. Focused work on developing a Raman system for hot cell applications should result in success, if the proper direction is followed in the future.

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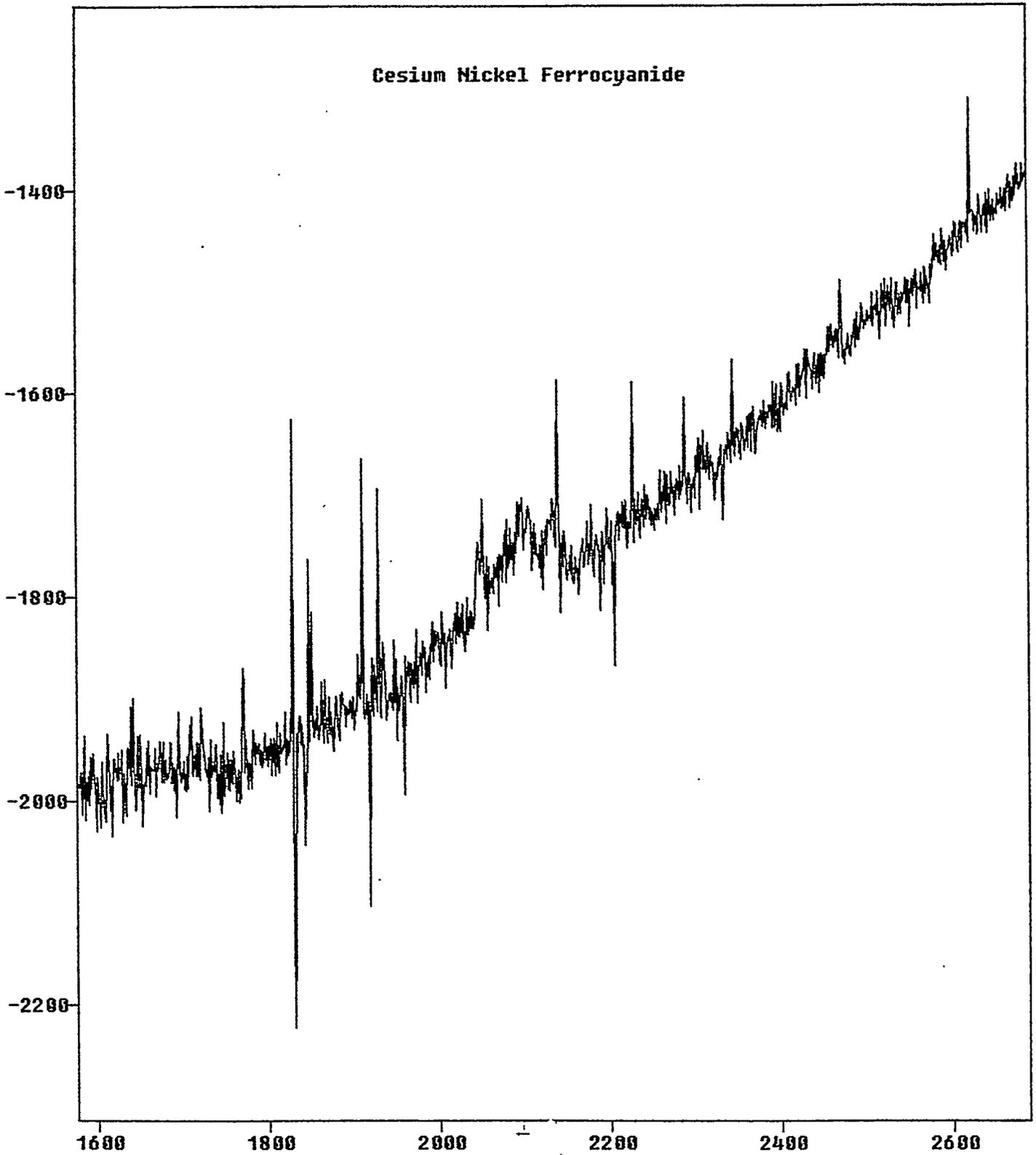
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**Appendix A**  
**Reagent Spectra**

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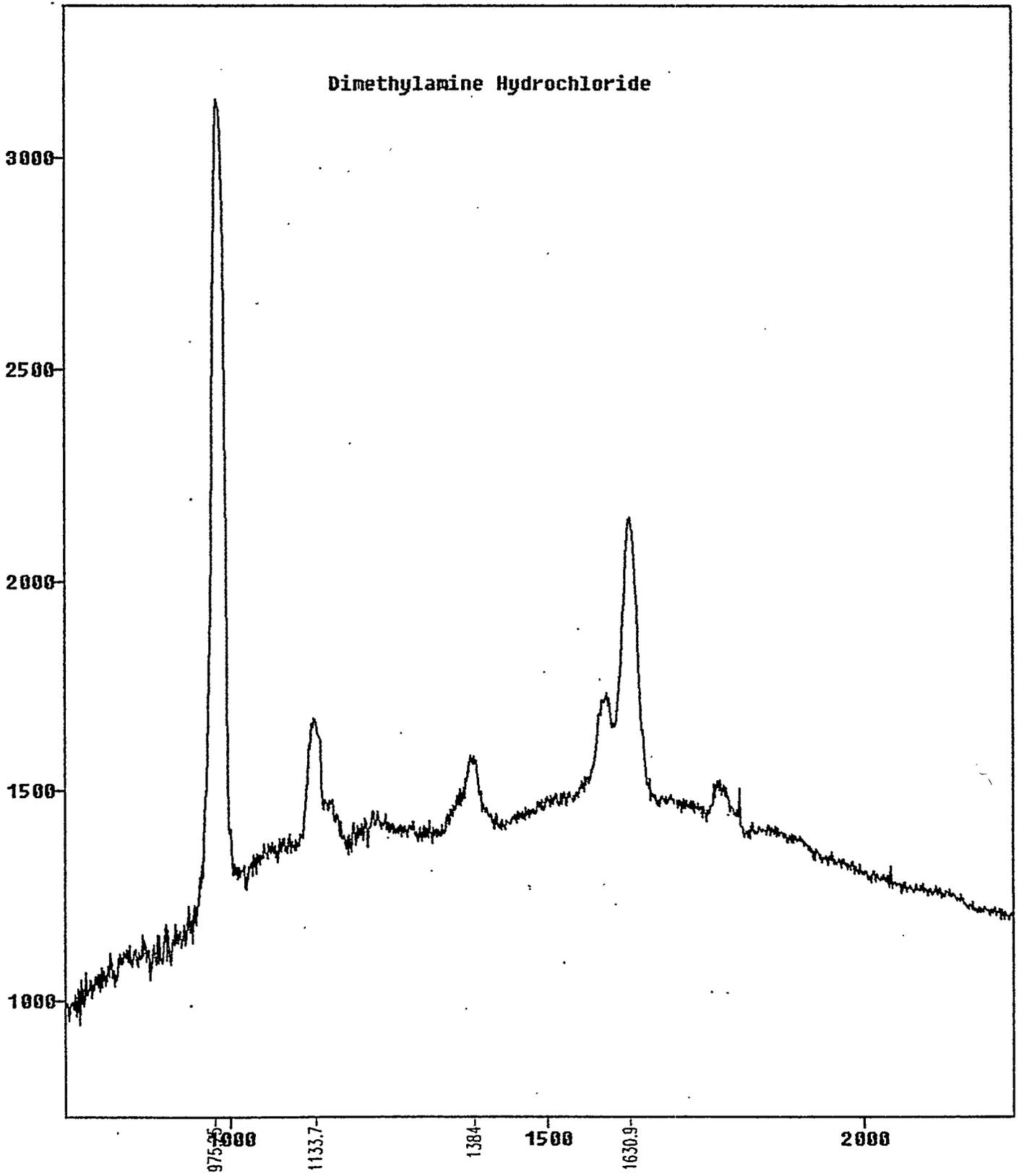
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A-3

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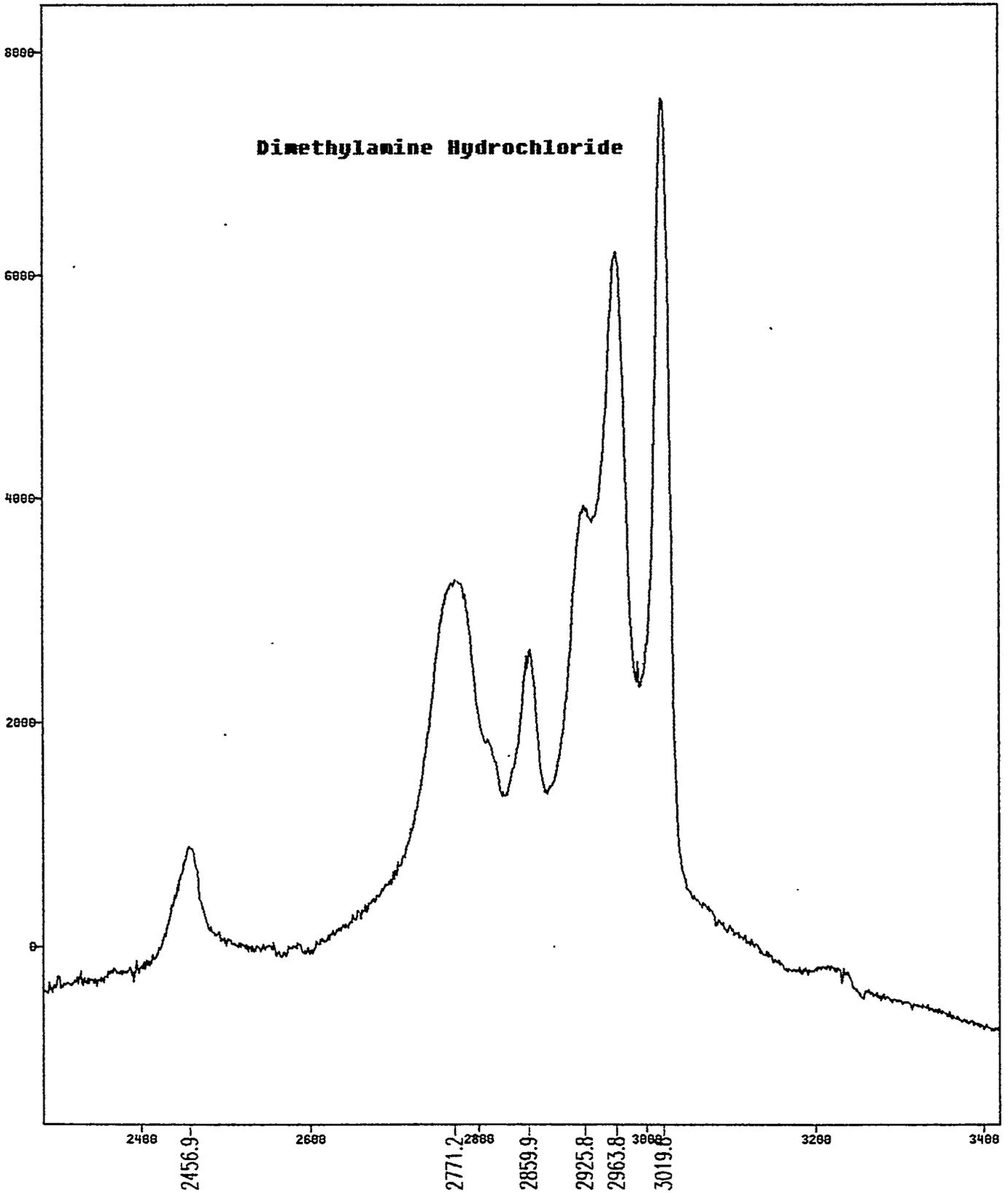
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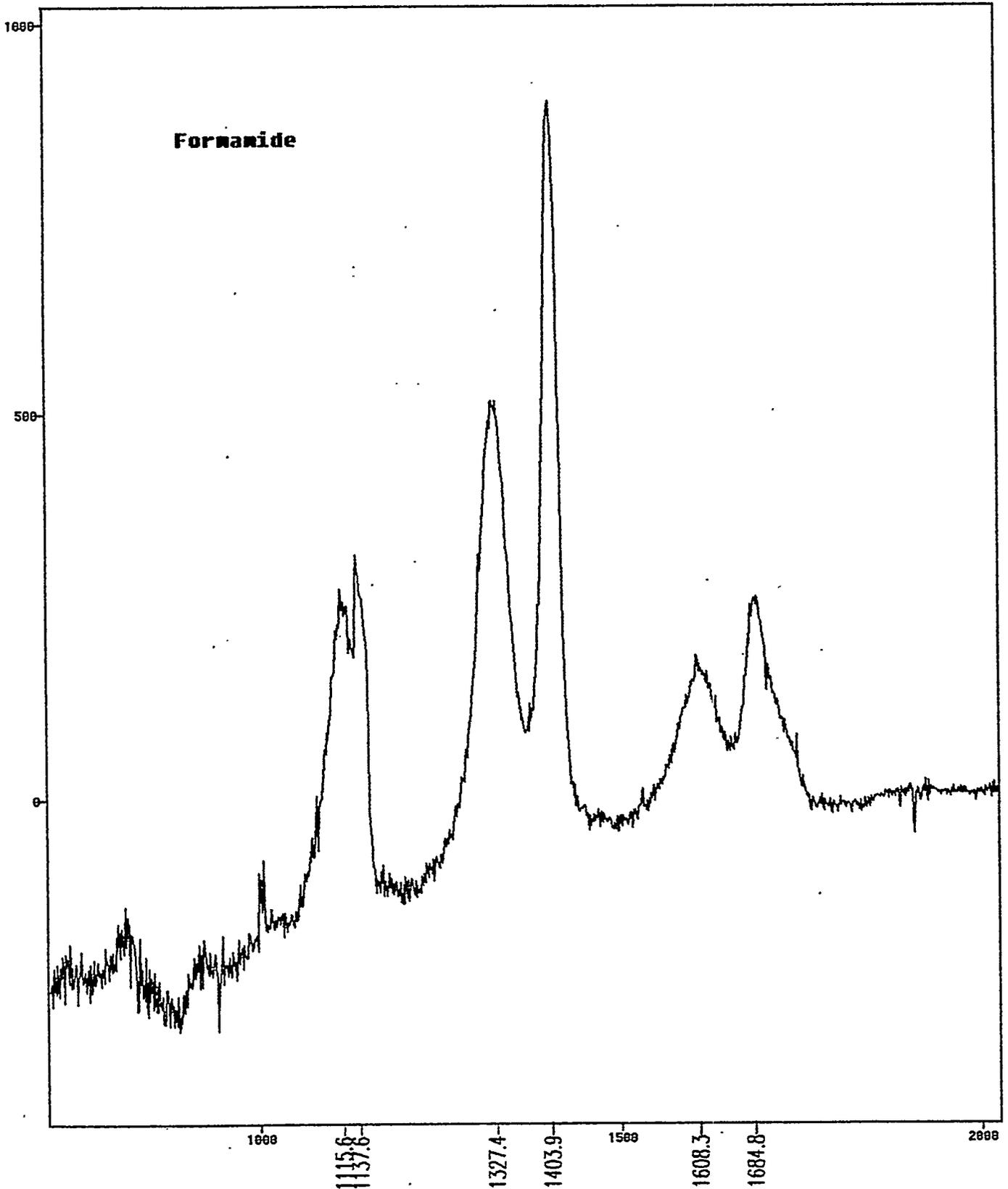
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A-5

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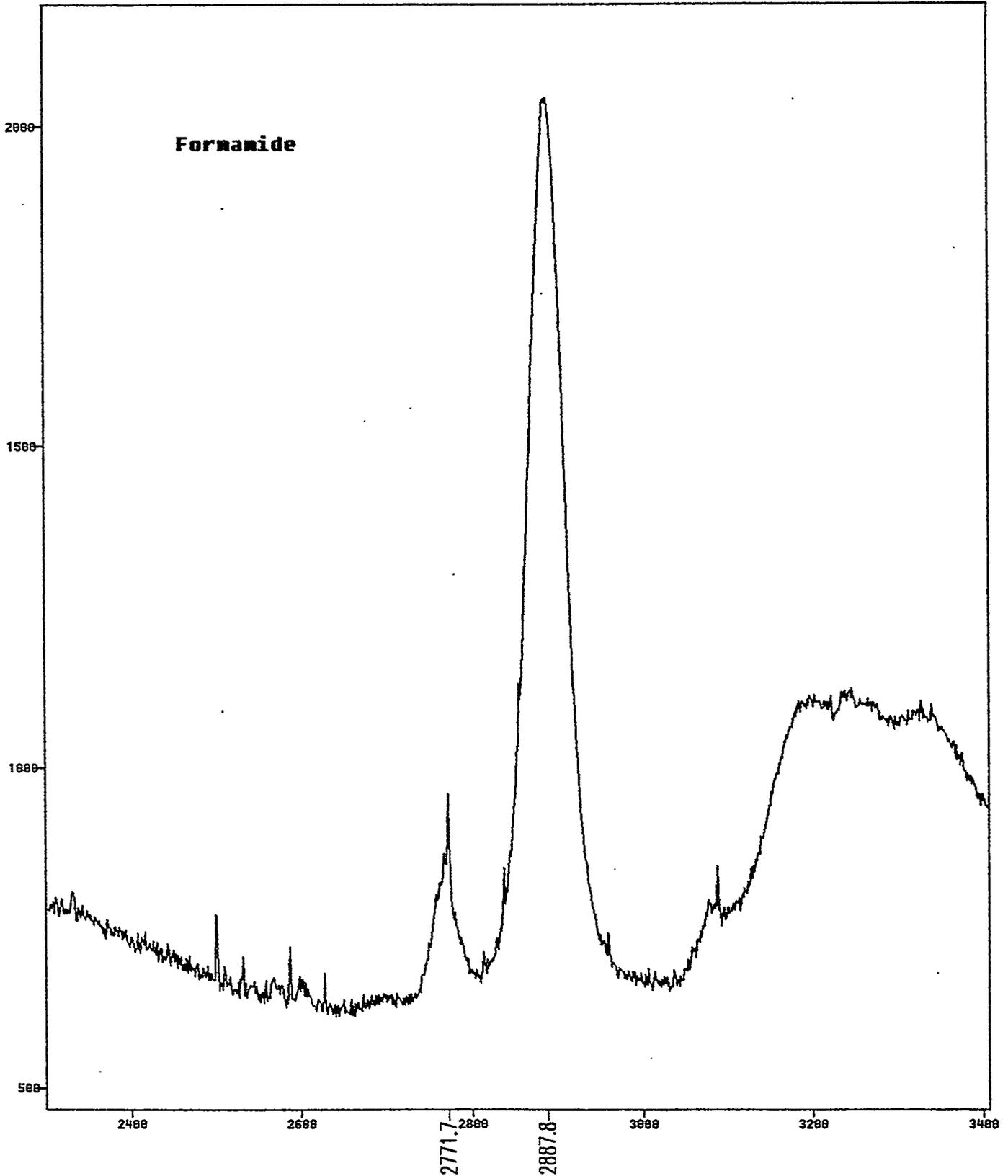
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A-6

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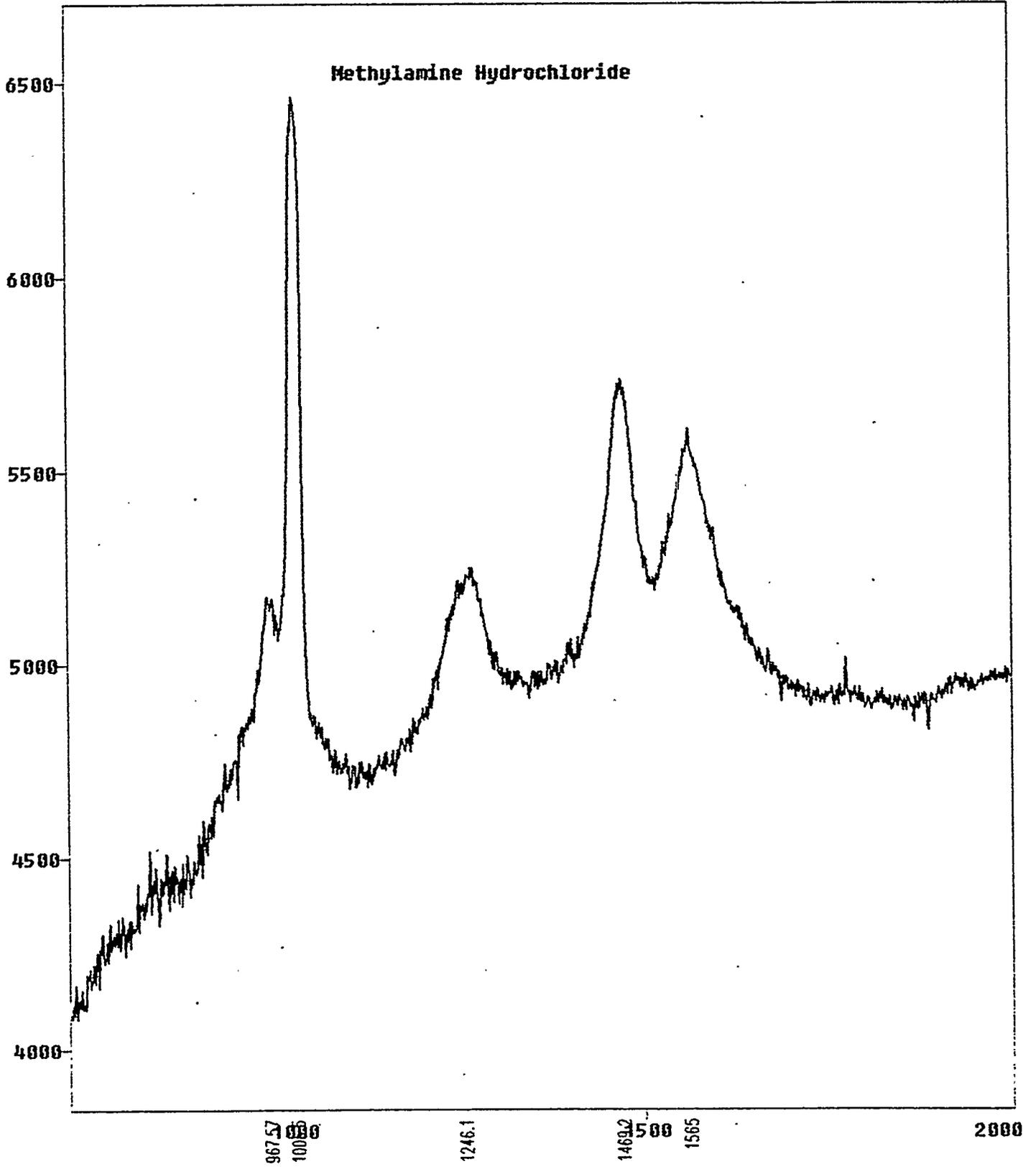
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A-7

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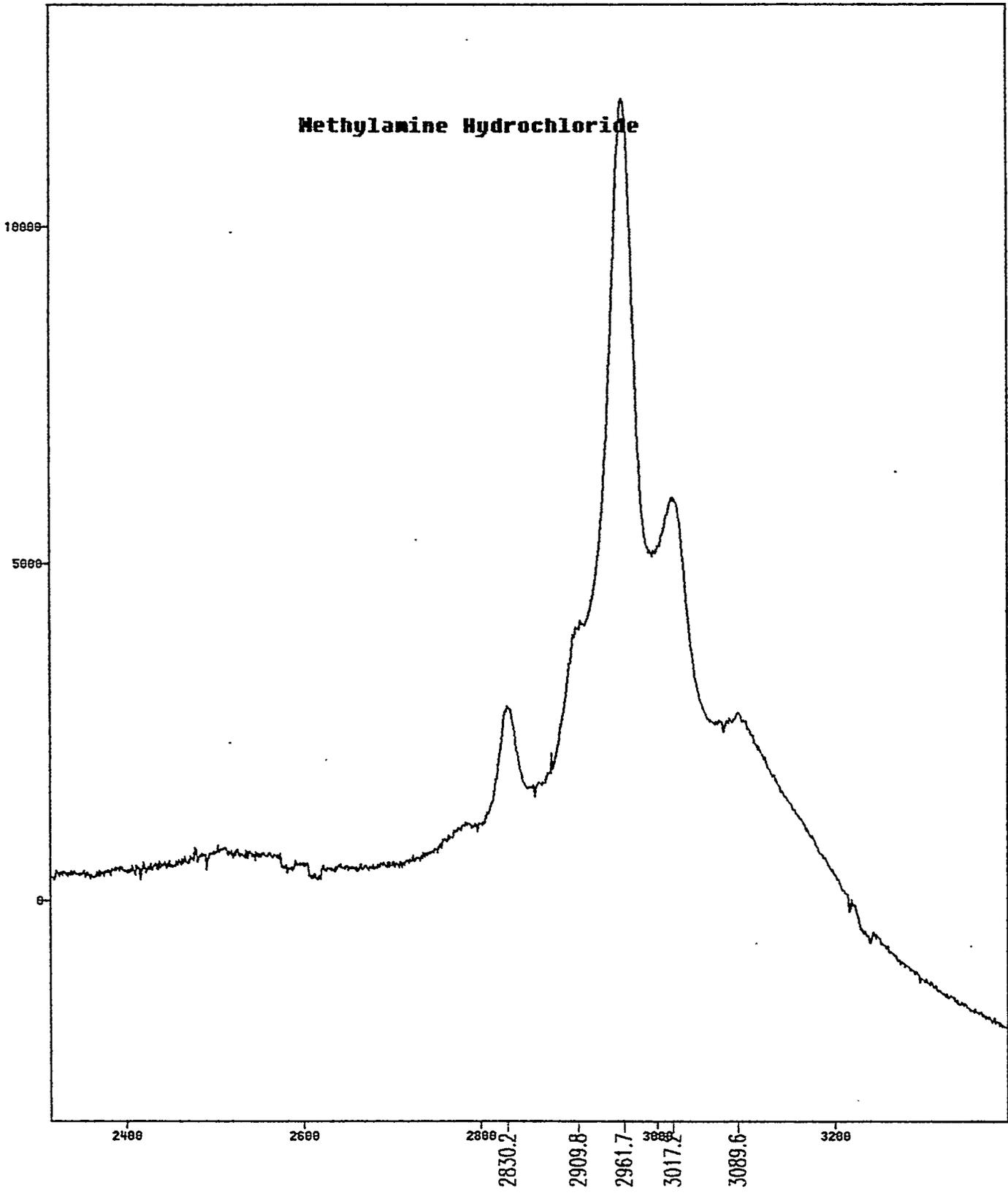
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A-8

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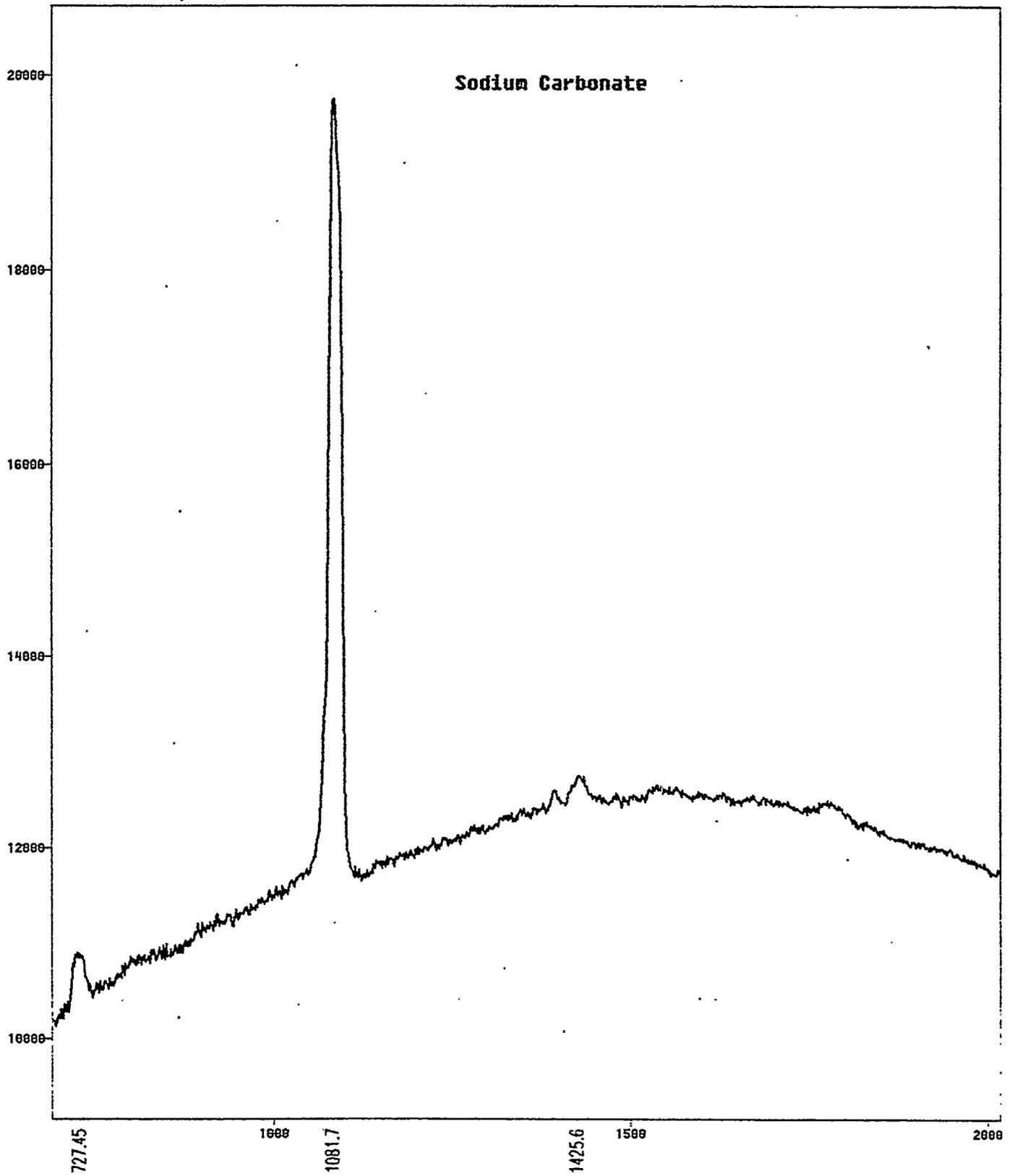
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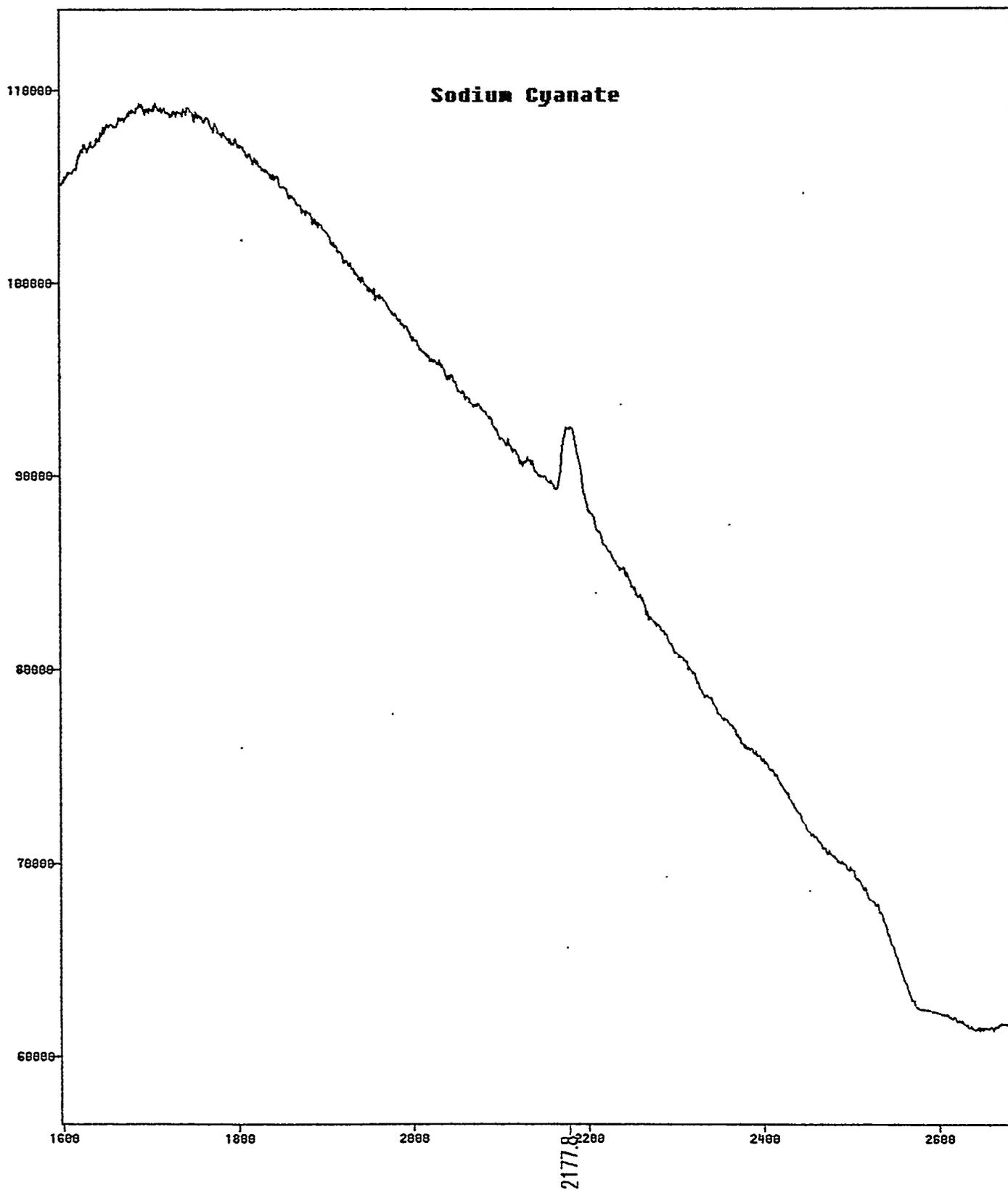
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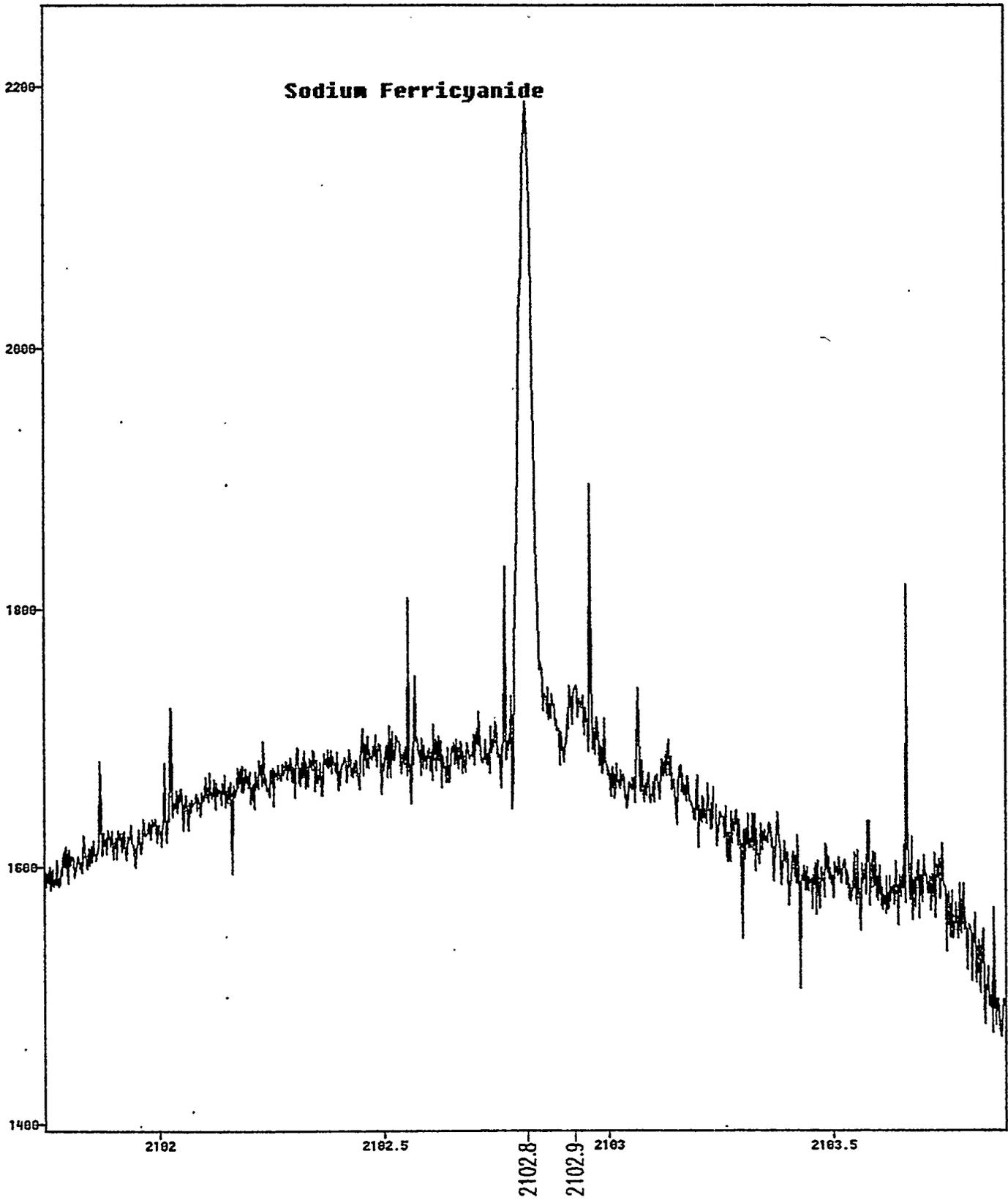
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A-11

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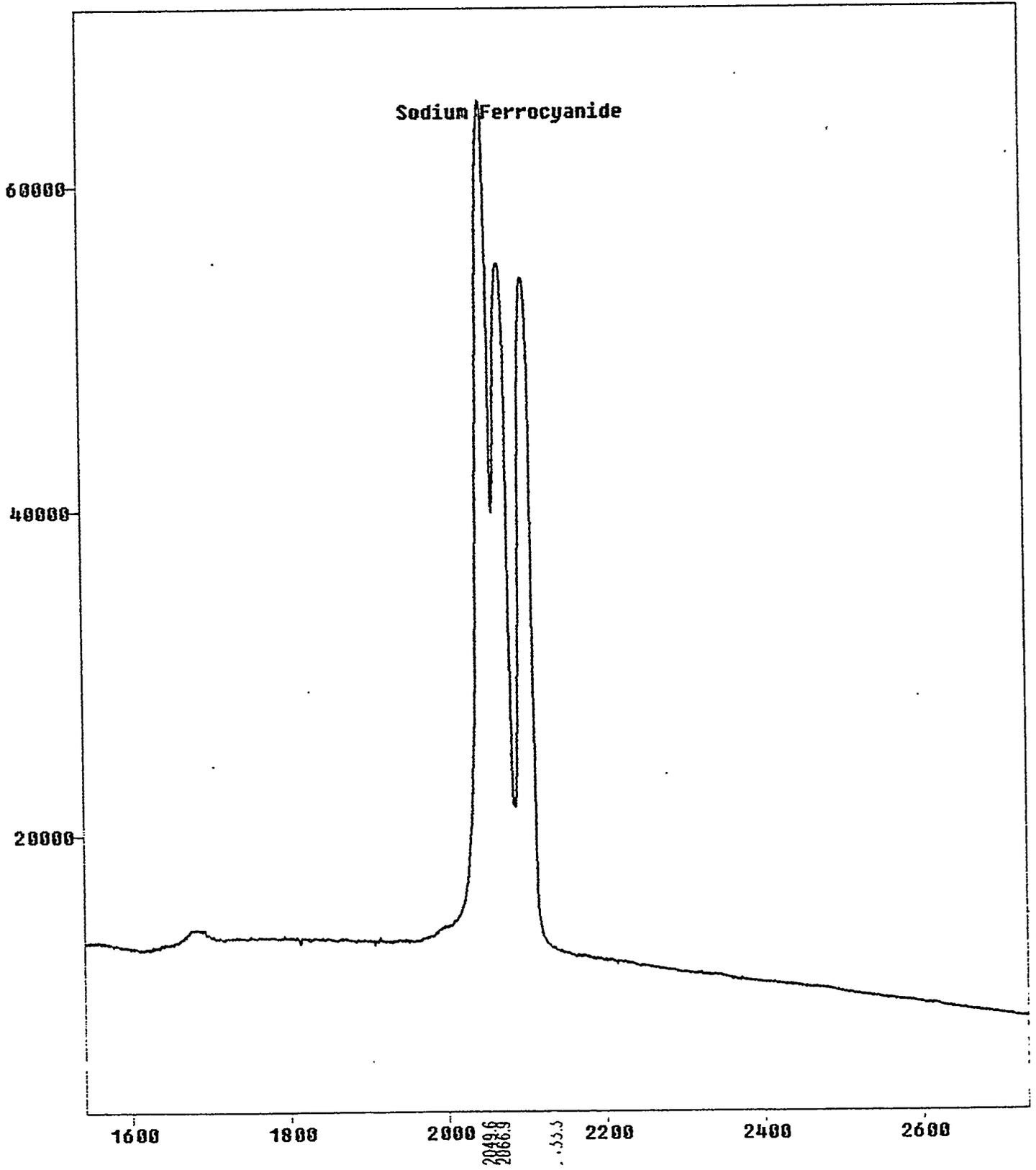
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A-12

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A-13

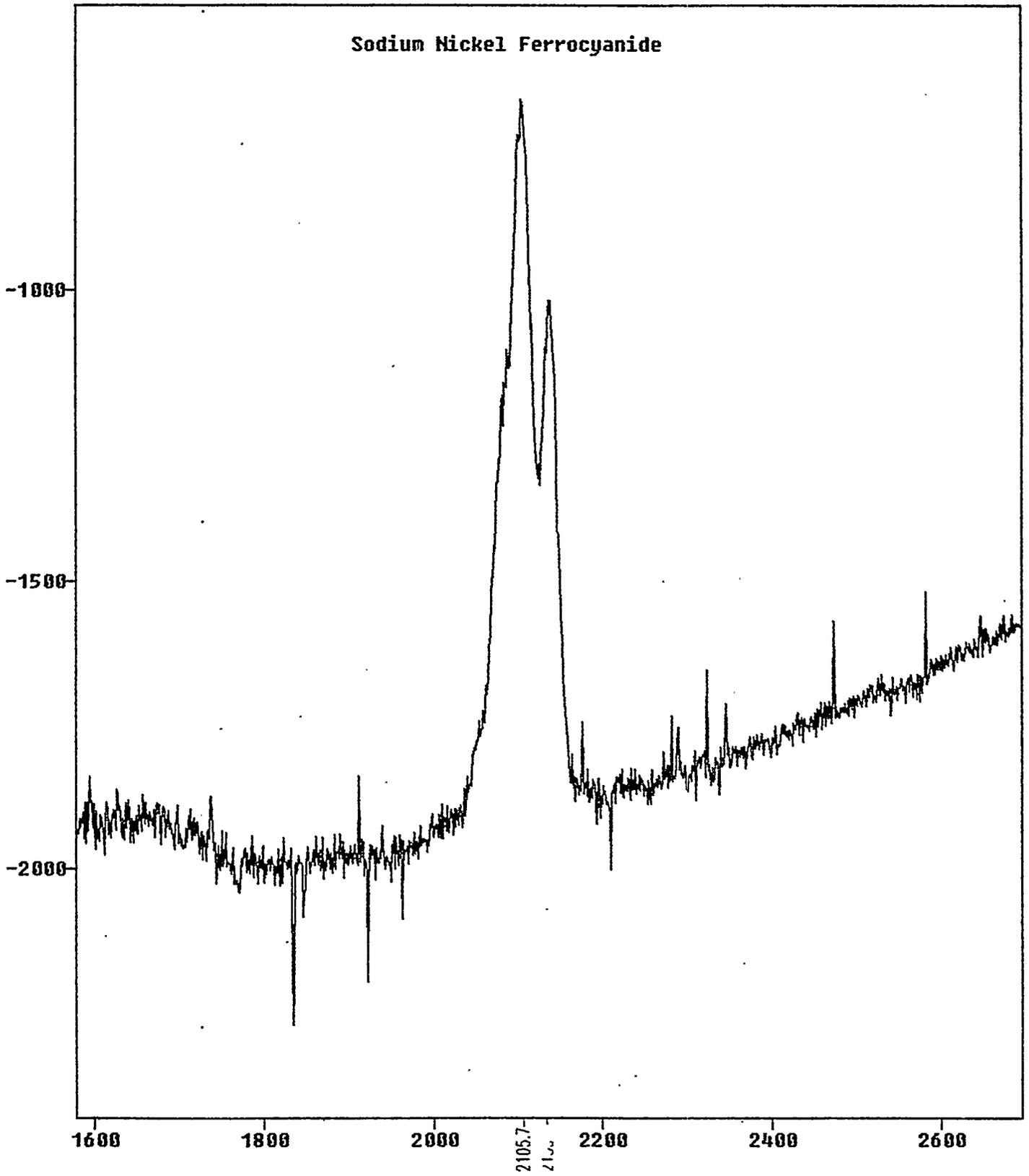
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Paged Y-Zoom CURSOR

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Sodium Nickel Ferrocyanide



Arbitrary Y / Wavenumber (cm-1)

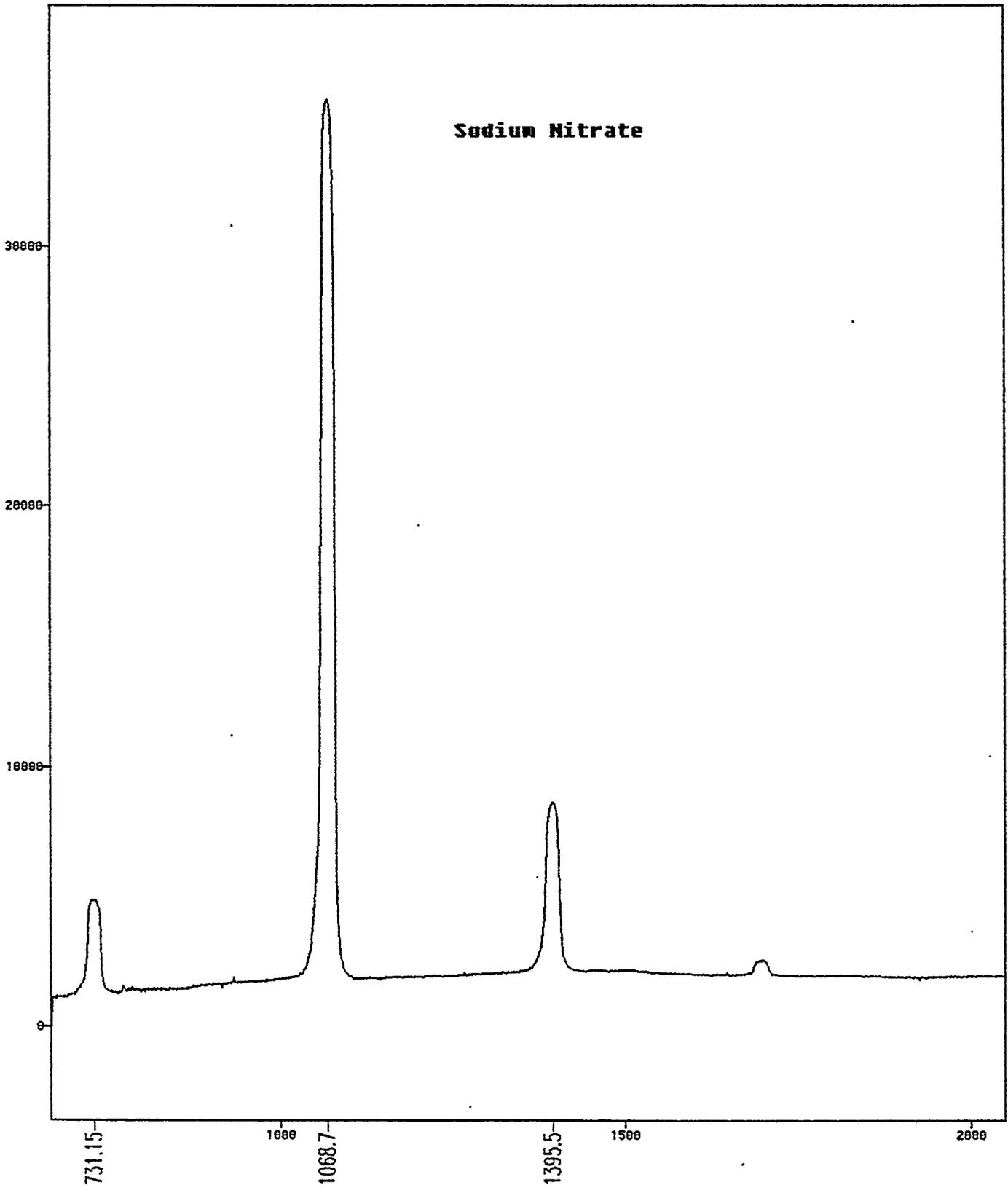
A-14

Paged Y-Zoom CURSOR

File # 1 : NANIFEA

Res=None

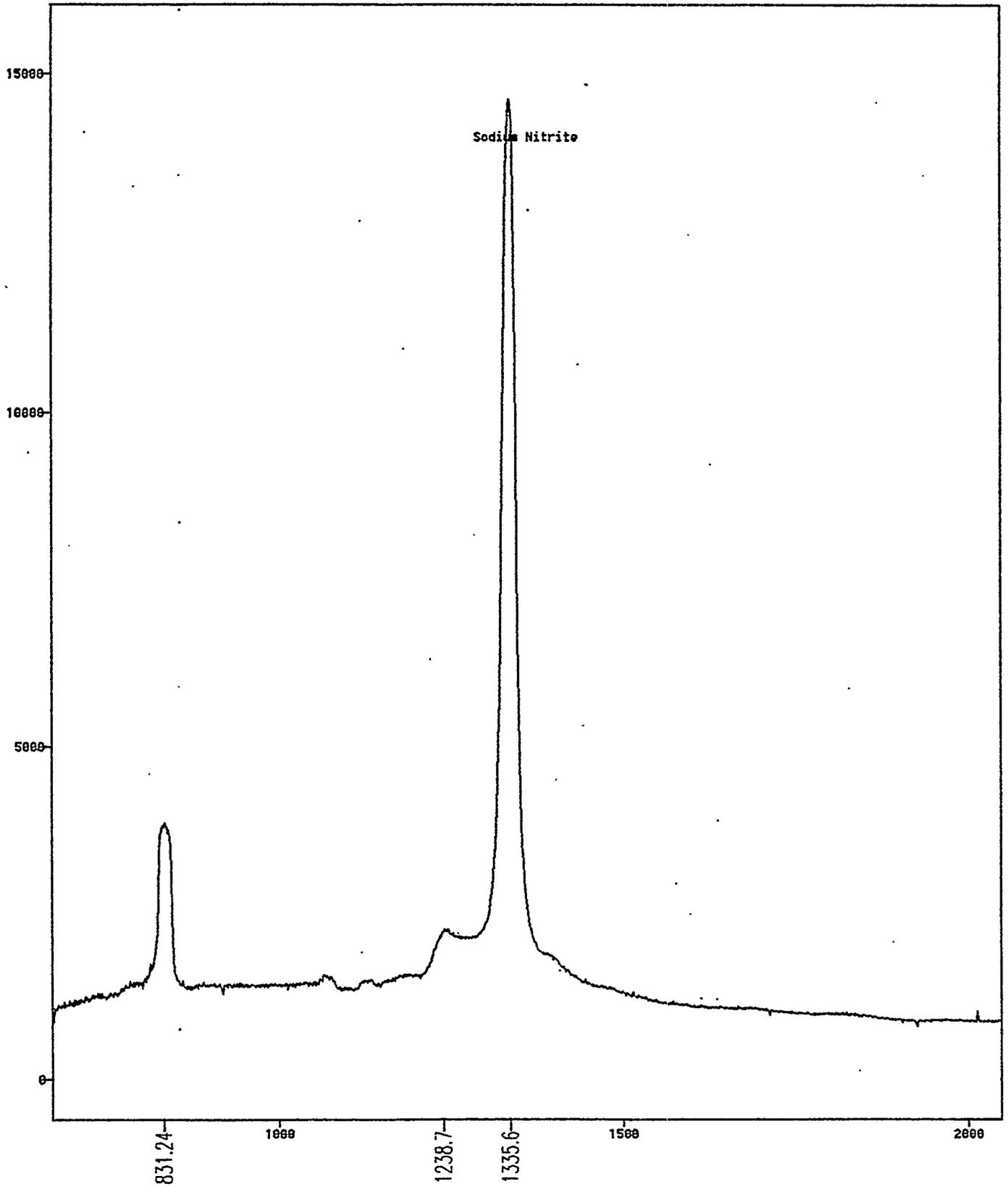
**Sodium Nitrate**



Arbitrary Y / Wavenumber (cm-1)

A-15

Paged Y-Zoom CURSOR



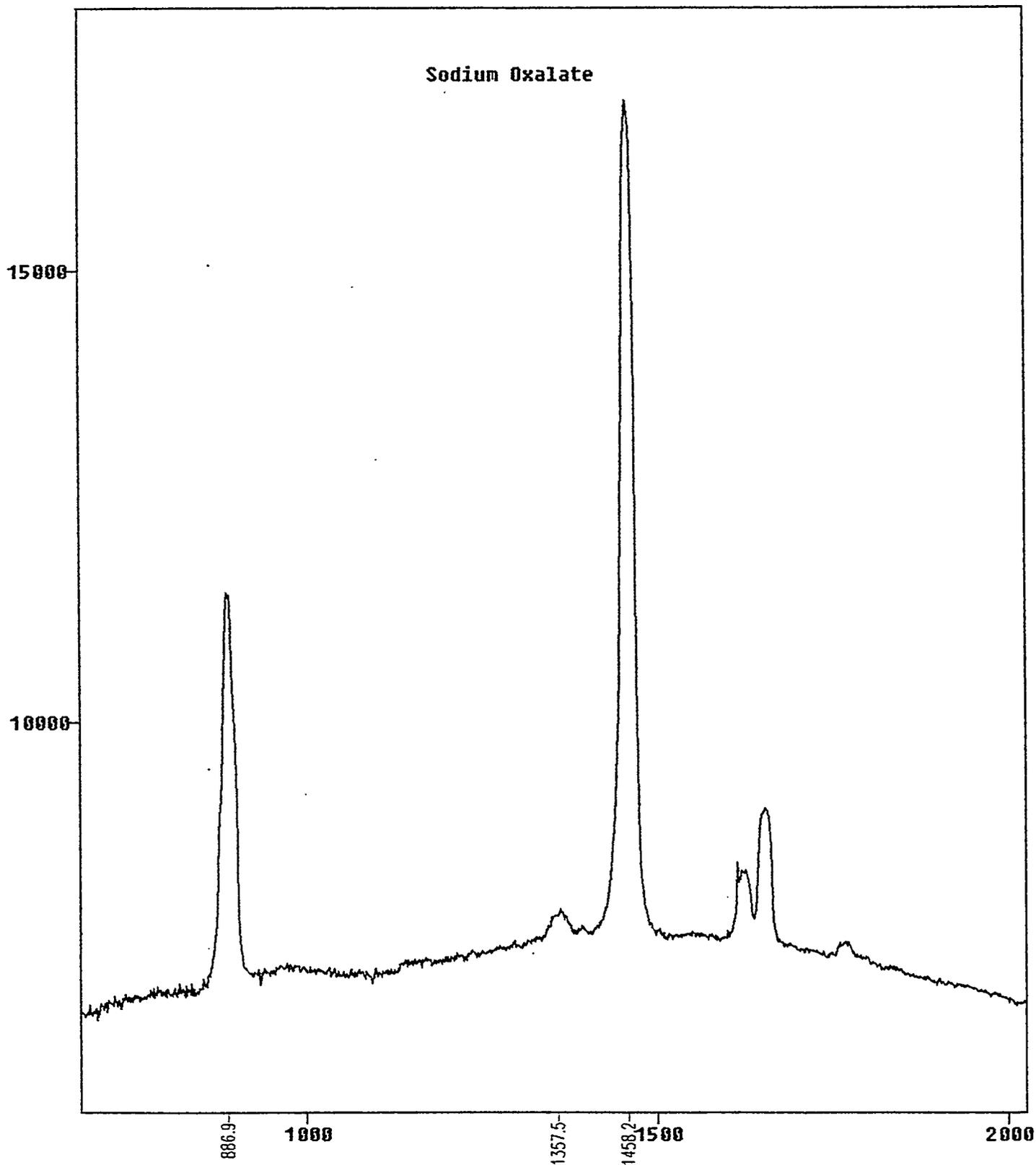
Arbitrary Y / Wavenumber [cm-1]

A-16

Paged Y-Zoom CURSOR

File # 1 : NANO2\_1A

Res=None



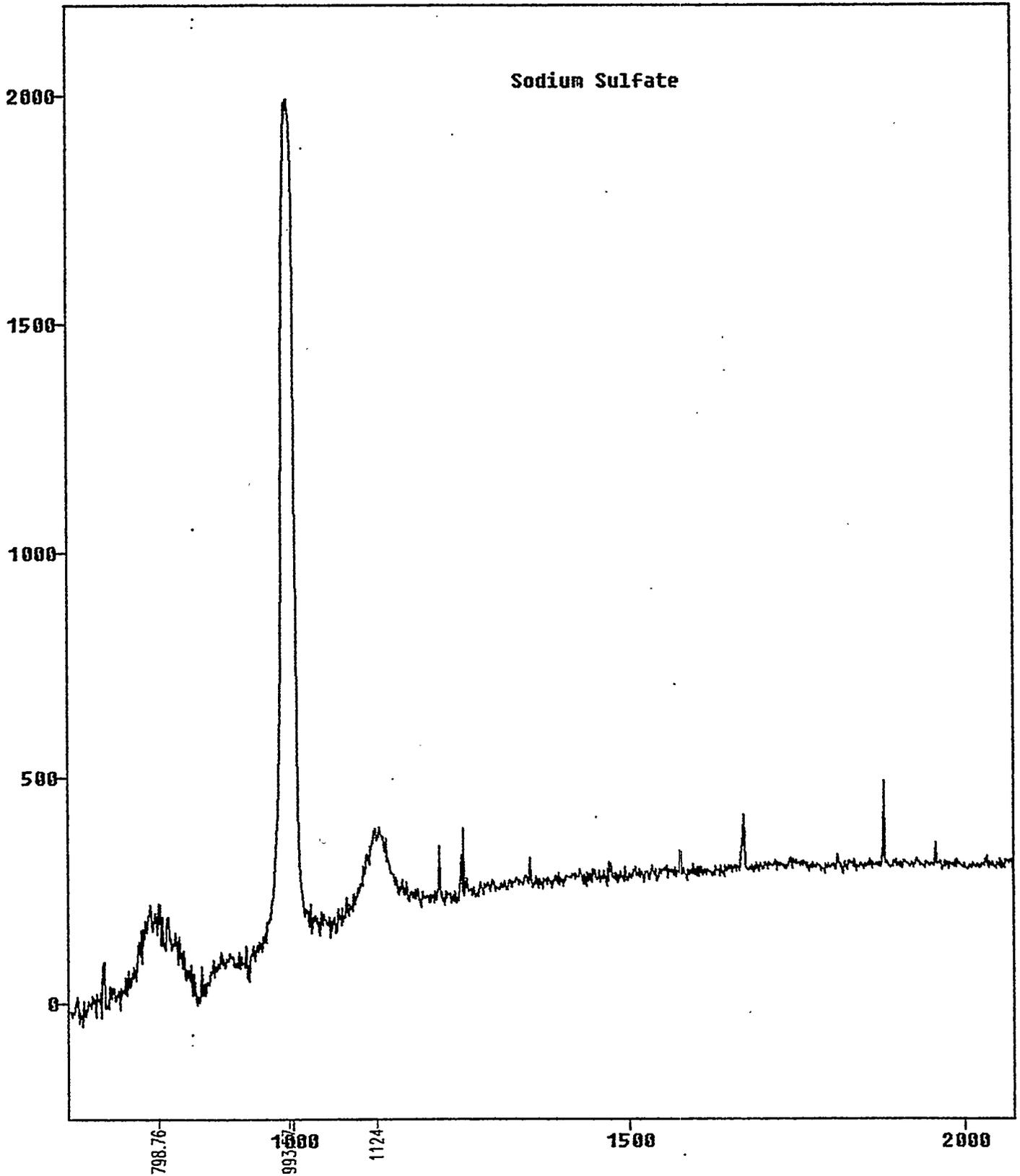
Arbitrary Y / Wavenumber (cm-1)

A-17

Paged Y-Zoom CURSOR

File # 1 : NA2C2O4A

Res=None



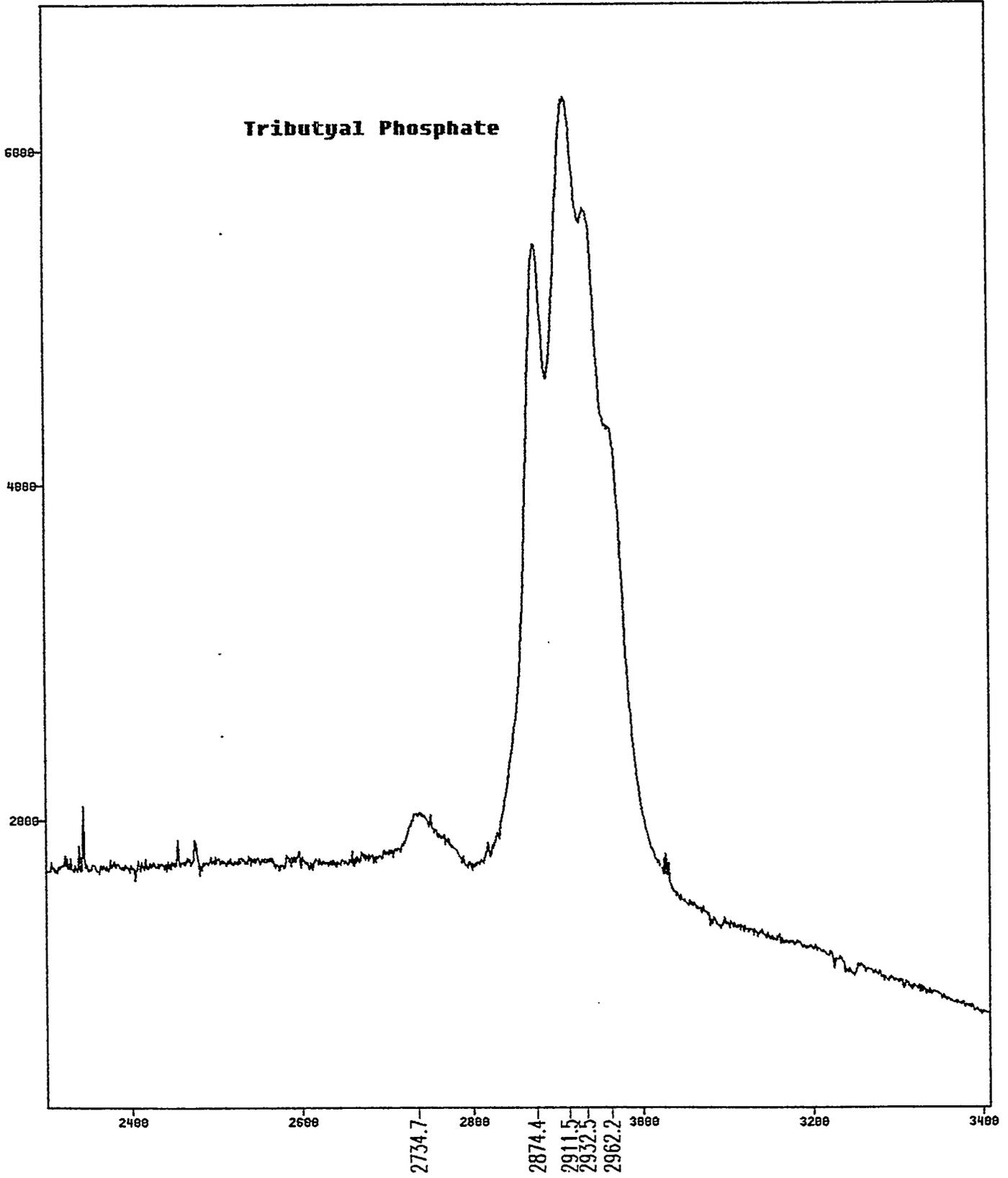
Arbitrary Y / Wavenumber (cm-1)

A-18

Paged Y-Zoom CURSOR

File # 1 : NA2SO4A

Res=None



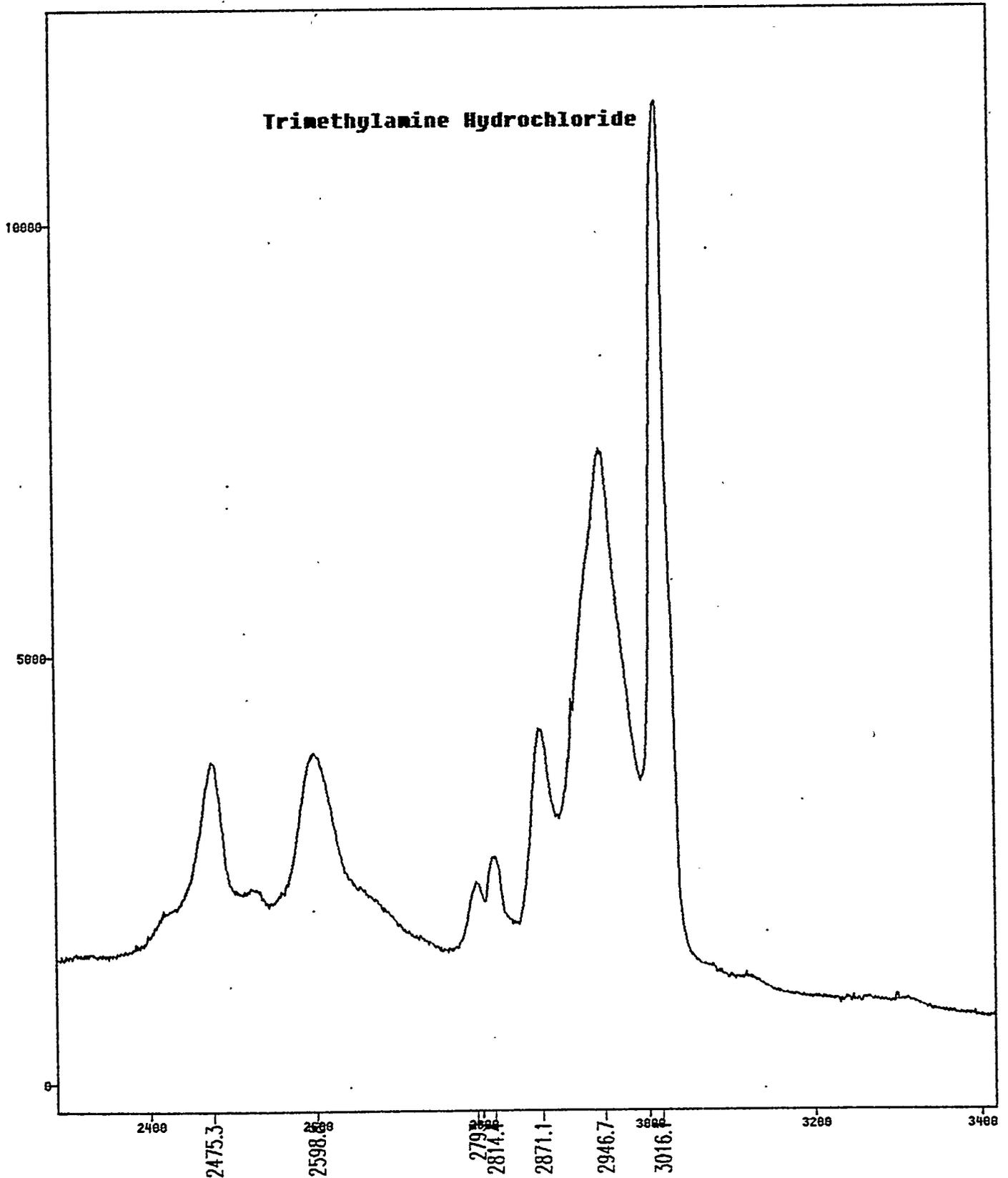
Arbitrary Y / Wavenumber [cm-1]

A-19

Paged Y-Zoom CURSOR

File # 1 : TBPA

Res=None



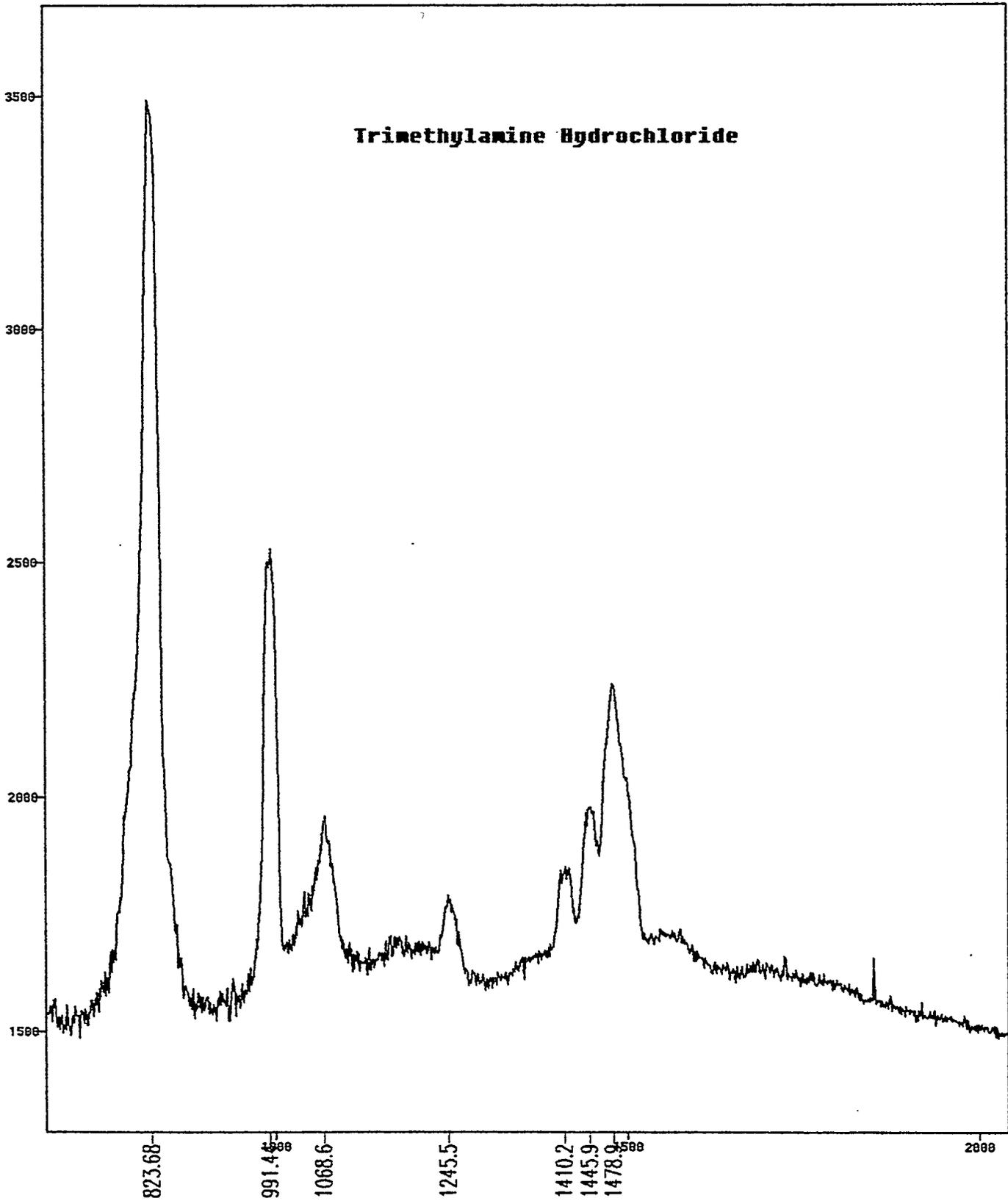
Arbitrary Y / Wavenumber (cm-1)

A-20

Paged Y-Zoom CURSOR

File # 1 : TRIMETHA

Res=None



Arbitrary Y / Wavenumber [cm-1]

A-21

Paged Y-Zoom CURSOR

File # 1 : TRIMETA

Res=None

**APPENDIX B**  
**ARCHIVED WASTE SAMPLE SPECTRA**

APPENDIX B  
ARCHIVE WASTE TANK SPECTRA

Tank B-202

Core 24/Composite 1

550 nm Window; With and Without Silica Subtraction.....B-4  
 580 nm Window; With and Without Silica Subtraction.....B-5  
 580 nm Window; Corrected and Uncorrected Background.....B-6  
 600 nm Window; With and Without Silica Subtraction.....B-7

Tank S-104

Archive Sample #F2019

550 nm Window; With and Without Silica Subtraction.....B-8  
 580 nm Window; With and Without Silica Subtraction.....B-9  
 580 nm Window; Corrected and Uncorrected Background.....B-10  
 580 nm Window; With and Without Silica Subtraction.....B-11  
 580 nm Window; Corrected and Uncorrected Background.....B-12  
 600 nm Window; With and Without Silica Subtraction.....B-13  
 600 nm Window; Corrected and Uncorrected Background.....B-14

Tank U-110

Core 14/Segment 2

550 nm Window; With and Without Silica Subtraction.....B-15  
 550 nm Window; With and Without Silica Subtraction.....B-16  
 550 nm Window; Corrected and Uncorrected Background.....B-17  
 580 nm Window; With and Without Silica Subtraction.....B-18  
 580 nm Window; Corrected and Uncorrected Background.....B-19  
 600 nm Window; With and Without Silica Subtraction.....B-20  
 600 nm Window; Corrected and Uncorrected Background.....B-21

Tank T-107

Core 51/Segment 2

550 nm Window; With and Without Silica Subtraction.....B-22  
 580 nm Window; With and Without Silica Subtraction.....B-23  
 600 nm Window; With and Without Silica Subtraction.....B-24  
 600 nm Window; Corrected and Uncorrected Background.....B-25

Tank T-111

Core 33/Segment 1

550 nm Window; With and Without Silica Subtraction.....B-26

Core 33/Segment 5

550 nm Window; With and Without Silica Subtraction.....B-27

Core 33/Segment 9

550 nm Window; With and Without Silica Subtraction.....B-28

Core 31/Segment 3

575 nm Window; With and Without Silica Subtraction.....B-29

575 nm Window; Corrected and Uncorrected Background.....B-30

600 nm Window; With and Without Silica Subtraction.....B-31

Tank 101-SY

Composite Sample #1386

550 nm Window; With and Without Silica Subtraction.....B-32

550 nm Window; Corrected and Uncorrected Background.....B-33  
580 nm Window; With and Without Silica Subtraction.....B-34  
580 nm Window; Corrected and Uncorrected Background.....B-35  
600 nm Window; With and Without Silica Subtraction.....B-36  
600 nm Window; Corrected and Uncorrected Background.....B-37

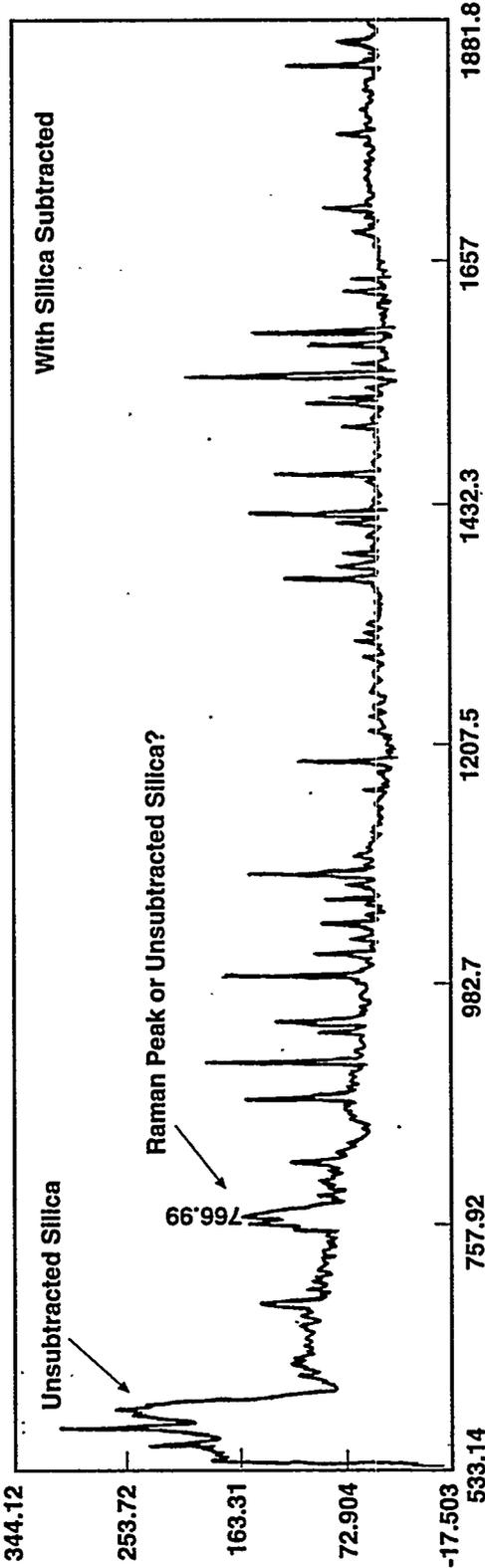
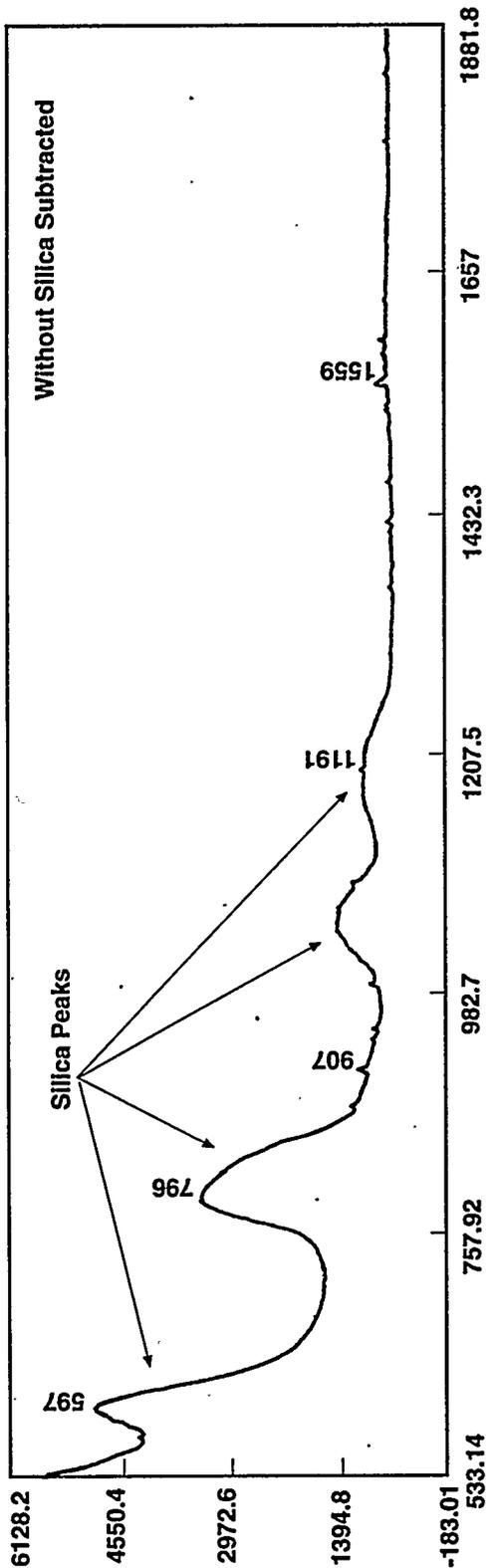
Tank BX-107

Core 41/Segment 3

546.5 nm Window; With and Without Silica Subtraction.....B-38  
546.5 nm Window; With and Without Silica Subtraction.....B-39  
575 nm Window; With and Without Silica Subtraction.....B-40  
575 nm Window; Corrected and Uncorrected Background.....B-41  
600 nm Window; With and Without Silica Subtraction.....B-42  
600 nm Window; Corrected and Uncorrected Background.....B-43

Core 41/Segment 6

600 nm Window; With and Without Silica Subtraction.....B-44  
600 nm Window; Corrected and Uncorrected Background.....B-45



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